



HAL
open science

Miniaturized, rapid separation of neodymium from ultramafic and chondritic samples prior to high precision measurements of $^{142,143}\text{Nd}/^{144}\text{Nd}$ isotope ratios by TIMS

Christian Pin, Abdelmouhcine Gannoun

► To cite this version:

Christian Pin, Abdelmouhcine Gannoun. Miniaturized, rapid separation of neodymium from ultramafic and chondritic samples prior to high precision measurements of $^{142,143}\text{Nd}/^{144}\text{Nd}$ isotope ratios by TIMS. *Journal of Analytical Atomic Spectrometry*, 2019, 34 (10), pp.2136-2146. 10.1039/c9ja00272c . hal-02305663

HAL Id: hal-02305663

<https://uca.hal.science/hal-02305663>

Submitted on 10 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1
2
3 **Miniaturized, rapid separation of Neodymium from ultramafic**
4 **and chondritic samples prior to high precision measurements of**
5
6 **$^{142,143}\text{Nd}/^{144}\text{Nd}$ isotope ratios by TIMS**
7
8
9

10
11
12
13 **Christian Pin^a and Abdelmouhcine Gannoun^b**
14
15

16
17
18 **Abstract**
19

20
21 An improved method is described for isolating Nd from challenging silicate materials. After a
22 short dissolution with hydrofluoric acid, the 1-2 gram sample is subjected to a protracted
23 treatment with nitric and hydrochloric acid at mild temperature. Then, the sample is taken up
24 in 15-20 ml of 1M HNO₃. Residual fluorides are isolated by centrifugation, and decomposed
25 with boric acid. Ascorbic acid is added to reduce Fe(III) to Fe(II) and the solution is loaded
26 onto a small column containing 1.5 ml of TRU extraction chromatography (EXC) resin, to
27 extract the REE + Th and U. The LREE are stripped by using 3M HCl and directly loaded
28 onto the next, on-line column filled with 1 ml of DGA EXC resin which achieves the
29 separation of Nd from Sm, and from the bulk of Ce and Pr. Neodymium is stripped with
30 0.006M HCl onto a 1 ml column of LN2 EXC resin for further purification from residual Ce
31 and Pr. By virtue of small EXC columns and reagents permitting direct cross-over from a
32 column to the next one, this scheme does not involve evaporation steps, and can be performed
33 in about 12 hours, with good Nd yields and negligible blanks. The method is validated by the
34 analysis of depleted basic and ultra-basic rocks, and a sample of the Allende carbonaceous
35 chondrite. Compared with previous methods used to process difficult samples, this protocol is
36 drastically down-scaled, relatively simple to implement, and much less demanding in terms of
37 analyst time, reagent volumes, and costs.
38
39
40
41
42
43
44
45
46
47
48
49
50
51

52
53 ^a Géologie, CNRS & Université Clermont-Auvergne, Campus des Cézeaux, 6 avenue Blaise
54 Pascal, 63 178 Aubière Cedex, France
55
56

57
58 ^b Laboratoire Magmas et Volcans, Université Clermont Auvergne, CNRS UMR 6524, OPGC-
59 IRD, F-63000, Clermont-Ferrand, France
60

1 Introduction

The determination of neodymium isotope ratios in LREE-poor samples of ultramafic bulk composition is a challenging task. This is particularly true when $^{142}\text{Nd}/^{144}\text{Nd}$ ratios are to be measured. In this case indeed, counting statistics constraints necessitate obtaining 0.5-1 μg of Nd in a highly purified form to achieve the degree of precision required to detect isotopic anomalies at the few ppm level.¹ In order to fulfill this requirement, large samples, one gram or more, need to be processed, while keeping Nd chemical yield as elevated as possible. This puts stringent constraints on both the sample dissolution procedure and the separation scheme which needs to accommodate a large volume of starting solution.

Different strategies have been proposed in an attempt to circumvent the potentially poor chemical recovery caused by the formation of insoluble, Mg-rich, complex fluorides which may sequester large amounts of LREE.^{2,3} These include the removal, prior to dissolution with hydrofluoric acid, of as much as possible magnesium by leaching the sample powder with HCl at elevated temperature^{4,5}, and the treatment of sparingly soluble compounds formed during the hydrofluoric acid dissolution step with boric acid or a solution of an Al salt.^{2,5}

Cation-exchange chromatography is most often used to perform the isolation of the REE from matrix elements, but the inherent lack of selectivity of such technique requires using columns commensurate to the amount of sample processed. This is made by up-scaling the size of the cation-exchange columns, filled with 20 ml⁶ or more of resin. Alternatively, the sample solution is split into several aliquots, each corresponding to 150-200 mg of sample, which are passed through as many conventional columns (which typically contain 10 ml of cation-exchange resin each), and then combining the LREE-bearing fractions in order to process a single sample. Repeated passes through a small column have also been used.⁷ These approaches are time-consuming (e.g., some 10 hours)⁸ and they necessitate copious amounts of relatively strong acid, first for getting rid of the unwanted elements (e.g., 95 mL of 2.5M HCl⁹), and then for stripping the REE from the columns (e.g., 60 mL of 4N HCl). Before the subsequent separation of Nd from accompanying trace elements, it is therefore necessary to evaporate to dryness large volumes of strong acid, a procedure which is lengthy and far from being friendly with the environment.

Prior to the cation-exchange separation step, it is possible to reduce the amount of magnesium through precipitation, in slightly basic medium, of iron and aluminum as their hydroxides, which act as carriers for tri- and tetravalent trace elements, while Mg and Ca should remain in

1
2
3 solution. Then, the hydroxide precipitate is isolated by filtration or centrifugation, and
4 dissolved with HCl in view of the subsequent separation of the REE by cation-exchange.^{10,11}
5 In some cases, iron is removed by using solvent extraction with di-ethyl ether prior to cation-
6 exchange.⁵ These procedures based on hydroxide precipitation involve ammonia as an
7 additional reagent, are cumbersome if batches of several samples are to be processed, and
8 require highly skilled analysts to achieve a clean separation from Mg, because the bulky
9 hydroxide precipitate tends to include droplets of solution containing many of those elements
10 which partitioned into the supernatant.
11

12 In this paper, we describe how to perform the isolation of LREE from large volumes of (ultra-
13) mafic sample solutions by taking advantage of suitable extracting agents offering a far better
14 selectivity than cation-exchange resins. A small (1.5 ml) column of an extraction
15 chromatography resin is used to isolate the LREE (+ Th and U) from the major elements,
16 especially Mg, and unwanted trace elements, which all pass through the column during the
17 loading and early rinsing steps. Then, the LREE are stripped with a small volume of acid and
18 processed on-line, without intervening evaporation, through a tandem column extraction
19 chromatography scheme modified from our previous work.¹² In this way, a Nd fraction
20 purified from any Ce and Sm interfering isotopes, and suitable for high precision TIMS
21 measurements of $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios is obtained from notoriously
22 difficult matrices, at a strongly reduced cost in terms of time, analyst labour, and reagent
23 volumes.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41

42 **2 Experimental**

43 **2.1. Chemicals, labware, extraction chromatographic materials, and instrumentation**

44
45
46
47 All the chemicals (H_2O , HF, HNO_3 , HCl, H_3BO_3 , ascorbic acid), the labware, the three
48 commercially available extraction chromatography resins (TRU resin, DGA resin, and LN2
49 resin, supplied by Triskem International, Bruz, France), and the ICP- and thermal ionisation-
50 mass spectrometers used in this study were identical to those employed in our earlier work¹².
51 The only difference was the use of zone-refined Re ribbon (99.999%) instead of regular grade
52
53
54
55
56
57
58
59
60

1
2
3 Re filament (H. Cross Co, Moonachie, N.J., USA). Isotope ratio measurements were made
4 with a Triton TI thermal ionization mass spectrometer operated in the static multi-collection
5 mode following methods described elsewhere.¹² Twenty-seven blocks of data, each consisting
6 of 20 cycles of 8 seconds, were collected, with baseline measurements before each block
7 during 30 integrations of 1 second, after deflection of the ion beam in the ion source. Between
8 each block, the “amplifier rotation” function was used to interchange, by means of a relay
9 matrix, the connections between the 9 collectors and the 9 amplifiers in order to cancel
10 relative differences of amplifier gains. After correction for any residual isobaric interference
11 of ¹⁴²Ce on ¹⁴²Nd and ¹⁴⁴Sm on ¹⁴⁴Nd, the raw isotope ratios were corrected for mass
12 fractionation by using the empirical exponential “law” and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 as the
13 reference ratio.
14
15
16
17
18
19
20
21
22
23
24

25 **2.2. Chromatographic columns**

26 Aliquots of 500 mg of TRU resin were slurried in 0.05M HNO₃ and poured into *ca.* 7.5 mm i.d.
27 polystyrene columns fitted with a 15-45 μm polyethylene filter at the bottom (5-inch
28 chromatography columns, Caplugs Evergreen, Buffalo, N.Y., U.S.A.), thereby making a *ca.* 32
29 mm high resin bed. This is the first EXC column, used for the initial separation of the LREE from
30 major and most trace elements. The further separation steps aiming to isolate and further purify
31 the Nd fraction involved the same EXC columns as those (based on LN2 and DGA resins,
32 respectively) used in our previous work.¹² Both columns consist of disposable polyethylene
33 pipettes (Bio-Rad DPTP Style E,) *ca.* 4 mm i.d. and *ca.* 80 mm length, filled with 350 mg of
34 LN2 and DGA resins, respectively with polyethylene frits at the bottom and on top of the resin
35 bed. However, in this case, they were configured in a reverse order, that is, the DGA column
36 ahead from the LN2 column.
37
38
39
40
41
42
43
44
45
46
47

48 **2.3. Chemical procedure**

49
50 *2.3.1. Sample digestion:* Carbonaceous chondrites, such as the sample of the Allende
51 meteorite analysed in this work, contain copious amounts of organic molecules which are not
52 fully decomposed during the acid dissolution of the mineral components. The resulting
53 organic residue is rather intractable, and not easy to isolate from the rest of the sample. This
54 results in “dirty” solutions which are not ideal for chemical separation work. In order to
55 alleviate this problem, it was decided to destroy the organic matter physically, prior to sample
56
57
58
59
60

1
2
3 dissolution. The powdered sample of Allende was placed in a loosely covered porcelain
4 crucible and ignited at 550 °C during two hours in a muffle furnace. After this treatment, the
5 solution left after the acid dissolution was free of blackish material. The other sample powders
6 were used as received. One gram to 1.5 g of powder is weighted in a 60 mL PFA jar, wetted
7 with 10 mL of 7M HNO₃ followed by 10 mL of 29M HF. The PFA vessel is closed and
8 heated on a hot plate at 100°C during 20 minutes. Then, the jar is opened, and the fluoride
9 slurry left after the reaction with HF is diluted with 10 mL of 7M HNO₃ and gently
10 evaporated to near dryness (50°C). Ten mL of 6M HCl are added to the moist residue, and
11 again slowly evaporated to near dryness at 50°C. This treatment is repeated with 10 mL of
12 7M HNO₃, before the final salt residue is taken up with 12 to 20 mL of 1M HNO₃, and
13 centrifuged in order to isolate the resulting solution from sparingly soluble fluorides which
14 survived the previous treatments. These are broken down with up to 5 mL of a 1M HNO₃
15 solution saturated in boric acid in an ultrasonic bath heated at 80°C, and the resulting solution
16 is centrifuged to get rid of insoluble grains of Cr-spinel and recover the supernatant that is
17 combined with the bulk sample solution.
18
19
20
21
22
23
24
25
26
27
28
29
30

31 2.3.2. Column separation

32 Before separation, ascorbic acid (100 to 600 mg, depending on the concentration of iron in the
33 sample) is added as a reducing agent¹³ until a test for Fe (III) with a 1 M aqueous solution of
34 ammonium thiocyanate gives a faint rose colour. Then, the solution is loaded portion-wise
35 (e.g., 5 mL per 5 mL) onto the TRU column, before a final rinse of the PFA jar and the
36 column reservoir with twice 1 mL of fresh 1M HNO₃. Following this loading step, during
37 which matrix elements are essentially not extracted, the unwanted residual elements and
38 mildly retained HREE are removed from the column with the following succession of more
39 and more dilute nitric acid solutions: 1M HNO₃ (2 mL), 0.5M HNO₃ (2 mL), 0.25 M HNO₃
40 (1.5 mL), and finally 0.125M HNO₃ (2.5 mL).
41
42
43
44
45
46
47
48

49 Then, the eluting solution is switched to 3M HCl, in order to strip the LREE from the TRU
50 column and concomitantly load them onto the next, on-line DGA column. The first 0.75 mL,
51 containing the interstitial 0.125M nitric acid left from the previous step are discarded. At this
52 point, the TRU column is put on top of the DGA column (previously conditioned with 0.5 mL
53 of 3M HCl), and the LREE are eluted from the TRU column with 4 x 0.5 mL of 3M HCl and
54 simultaneously sorbed onto the DGA column (1st tandem configuration of Fig. 1 and Table 1).
55
56
57
58
59
60

1
2
3 Following this combined TRU stripping / DGA loading step, the columns are decoupled, and
4 the procedure continues on the DGA column, in order to separate Nd from most of the
5 accompanying LREE (La, Ce, and Pr on the one hand, Sm, Eu and Gd on the other). First, the
6 DGA reservoir is rinsed with 0.5 mL of 0.1M HNO₃. Then, La-Ce-Pr are eluted with 3 mL of
7 0.05M HNO₃ followed by 3.5 mL of 0.03M HNO₃, 2 mL of 0.025M HNO₃ and finally 0.5
8 mL of 0.025M HNO₃.

9
10
11 At this stage, the LN2 column is pre-conditioned with 0.5 mL of 0.006M HCl and positioned
12 below the tip of the DGA column (2nd tandem of Fig. 1 and Table 1) in order to strip Nd from
13 the DGA column and immediately collect it on top of the LN2 column. This is made by
14 means of 2 mL of 0.006M HCl.

15
16
17 The DGA and LN2 columns are decoupled, and processed as follows: If Sm is needed, it can
18 be eluted from the DGA column with 1 mL of 0.1M HCl, before the column cleaning
19 procedure is started, in preparation of further uses, such as an optional, final clean-up of the
20 Nd fraction (see hereafter).

21
22
23 After rinsing its reservoir with 0.1 mL of 0.05M HNO₃ the LN2 column is used to purify the
24 Nd eluted from the DGA column from accompanying traces of Ce and Pr left from the tail of
25 their respective elution peaks. This is made by passing through the column 2.6 mL of 0.08M
26 HNO₃, then 0.1 mL of 0.10M HNO₃, before Nd is stripped with 3 mL of 0.15M HNO₃. In
27 case of measurements by MC-ICP-MS, this solution could be used directly. In this work, it
28 was evaporated to dryness in preparation to isotope analyses by TIMS.

29
30
31 Optionally, the Nd separated in this way can be further purified on-line by means of a second,
32 on-line pass through the DGA column preconditioned with 1 mL of 0.2M HNO₃. Following
33 the loading step with 3 ml 0.15M HNO₃, 3.5 ml of 2M HCl are passed through the column to
34 get rid of unwanted residual elements, before a purified Nd cut is obtained with 3 mL of the
35 same acid (Table 1).

32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 **3 Results**

53 54 55 **3.1. Samples**

56
57
58 Two international references materials representative of highly depleted oceanic basalts (BIR-
59 1, prepared and distributed by the U.S. Geological Survey, Reston, Va) and ultramafic rock
60

(UB-N, prepared by A.N.R.T. and obtained from S.A.R.M.-CR.P.G., Nancy, France) were analysed. In addition, two samples of komatiitic basalt from the Barberton (Rep. of South Africa) and the Abitibi (Québec, Canada) greenstone belts kindly donated by Prof. H. Martin and Prof. C. Nicollet (both from Clermont), respectively, were processed to evaluate the separation protocol for processing samples very rich Mg and/or Fe. Finally, a sample taken from the Allende carbonaceous meteorite, kindly supplied by Prof. K.W. Burton (Durham University) was analysed in order to demonstrate the applicability of the method to extra-terrestrial samples in which ^{142}Nd isotope anomalies are most prominent. Selected major and trace element data corresponding to these samples are given in Table 2.

3.2. Isotope ratios measurements

The full Nd isotope compositions measured by TIMS in the static multi-collection mode are listed in Table 3. These include $^{142}\text{Nd}/^{144}\text{Nd}$ ratios, potentially affected by the extinct decay of the short-lived ^{146}Sm (half-life ~ 68 Ma)¹⁴ into ^{142}Nd , and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, reflecting the time-integrated in-growth of ^{143}Nd produced by the alpha decay of ^{147}Sm (half-life = 106 Ga), while the rest of the isotope ratios are constant in nature. It can be seen that within-run precisions, ranging from 3 to 9 ppm and from 2 to 8 ppm (2 RSD) were achieved for $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, respectively. These are within a factor of two, or better, of those obtained for the chemically pure international standard JNdi-1 and our shelf standard AMES. External precisions expressed by the RSDs of 3 or 4 replicate analyses are in general within a factor of 2 of the within-run precisions, documenting the good overall reproducibility of the whole procedure. Further, the accuracy can be judged from the fair agreement of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured in this work for BIR-1 with the range of values reported in the literature for this SRM.¹⁵ There is no compiled value of $^{143}\text{Nd}/^{144}\text{Nd}$ for UB-N, the other international SRM analysed in this work, but our results are in excellent agreement with two published TIMS values of 0.512926 ± 6 and 0.512925 ± 6 , respectively.¹⁶ Moreover, our data plot within the range of values reported most recently for these two SRMs.¹⁷ The interferences of ^{142}Ce on ^{142}Nd and ^{144}Sm on ^{144}Nd are reduced to the 1-4 ppm and <0.2 ppm levels, respectively, similar to those measured in the JNdi-1 and AMES high purity Nd standards. In all but one terrestrial rocks, no significant ^{142}Nd anomaly is found, while a faint negative anomaly ($\mu^{142}\text{Nd} = -7.2 \pm 3.1$) is suggested for the *ca.* 3.5 Ga old komatiite of the Barberton greenstone belt. Our sample of the Allende meteorite displays a strongly negative $\mu^{142}\text{Nd}$ of -62 ± 10 , further extending towards the non radiogenic side the range of values measured so far for this carbonaceous chondrite.¹⁸ The other isotope ratios involving non radiogenic

isotopes, $^{145}\text{Nd}/^{144}\text{Nd}$, $^{148}\text{Nd}/^{144}\text{Nd}$, and $^{150}\text{Nd}/^{144}\text{Nd}$ are very consistent, and identical within errors to those measured in the Nd standards, further demonstrating that the degree of purity achieved by the separation protocol is suitable for high precision isotope ratio measurements.

3.3 Chemical yield and procedural blanks

Overall Nd recoveries were estimated by comparing the amounts of Nd obtained in the final cut to those anticipated from consensus values (geostandards BIR-1 and UB-N) or values measured at SARM-CRPG (Nancy, France) by using standard methods based on LiBO_2 fusion and ICP-QMS measurement,¹⁹ or our published values for Allende.¹⁸ These ranged from 70% to nearly quantitative (Table 4). It is noteworthy that the lowest yields were obtained for the two komatiitic basalt samples, which were processed *before* their major and trace element composition was available. These rocks, and especially the Abitibi sample, proved to be much richer in Nd than anticipated, resulting in a gross overloading of the columns. It is inferred that this inadvertent overload caused severe peak broadening on the DGA and LN2 columns, thereby causing a strong decrease of the Nd recovery. Total procedural blanks lower than 50 pg were achieved (Table 5), quite negligible with respect to the amount of Nd processed.

4 Discussion

4.1. Sample dissolution

In order to cope with mafic and ultramafic samples which contain much more Mg than common silicate rocks, the standard HF-HNO₃ procedure was slightly modified, in an attempt to limit the formation of insoluble fluorides which are likely to sequester a significant proportion of the small amounts of LREE present in these incompatible element depleted rock-types, thus leading to poor Nd yield. Firstly, the duration of the initial dissolution at elevated temperature was reduced to 20 minutes only, in order to prevent the growth of “old and strong” fluorides which would be more difficult to break-down during the subsequent treatments with nitric and hydrochloric acid, which are known to be poorly efficient for that purpose.² Indeed, the use of much better accompanying acids with high boiling temperatures such as perchloric or sulfuric acid was not possible in our laboratory. It was found that this short dissolution at 100°C was quite sufficient to “open-out” the mineral assemblages of the samples analysed (as indicated by the discoloration of the sample powder to a whitish fluff). Secondly, the slurry of sparingly soluble fluorides left in the excess HF-HNO₃ mixture after

1
2
3 the dissolution was immediately diluted to a large volume with nitric acid, and with
4 hydrochloric acid in a subsequent stage, in order to reduce the concentration of the fluoride
5 ion in the solution during a protracted evaporation at mild (50°C) temperature, while avoiding
6 to bring the sample salts to complete dryness. Albeit quite tedious, this treatment enabled us
7 to keep to a relatively small volume the precipitate obtained when the final 1M HNO₃ solution
8 was centrifuged prior to the chromatographic column procedure. The precipitate was
9 dissolved by the action of a few ml of 1M HNO₃ saturated in boric acid in an ultrasonic bath,
10 isolated from any insoluble Cr-spinels by centrifugation, and combined with the bulk solution.
11
12
13
14
15
16
17
18
19

20 **4.2. Extraction chromatography**

21 *4.2.1 First separation of the LREE from matrix elements*

22
23
24
25 Extraction chromatography (EXC) is much better suited than conventional cation-exchange
26 (CE) for isolating trace elements from large amounts of matrix elements. This is because, with
27 a proper choice of the active extracting agent, only a few trace elements (ideally, only the
28 target element, in so far as a highly specific molecule is identified and can be used to prepare
29 an EXC material) are extracted while the rest of the elements pass through the column without
30 any interaction with the EXC resin (Fig. S1). This is the case for Al, Ca, and particularly Mg
31 with the TRU resin, in obvious contrast with CE resins which adsorb, to a variable degree, *all*
32 the cations contained in the sample solution, thereby necessitating the use of larger and larger
33 amounts of resin as the sample size is increased. This is especially obvious when very large
34 samples are to be processed to palliate their very low concentration of the trace element of
35 interest. With EXC, instead, the amount of specific resin required needs to be commensurate
36 to the quantity of trace element of interest. As a matter of fact, the only practical limitation to
37 this tremendous advantage is the necessity to handle the large volume of acid required to
38 bring in solution the large sized sample. Indeed, it is necessary to use columns with relatively
39 high flow rates in order to keep loading times of such large volumes to reasonable durations.
40 This precludes the use of the narrow bore columns which are routinely used when the sample
41 solution does not exceed a few milliliters. Extraction resins embedded within flat filters might
42 offer an elegant alternative to columns in this case²⁰, but as far as we are aware, no such
43 material is commercially available for a selective extraction of the Lanthanides. Accordingly,
44 an up-scaled version of the well established TRU resin was used.²¹⁻²³ Specifically,
45 commercially available, disposable polystyrene columns with *ca.* 7.5 mm i.d. were used
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 instead of the 4 mm i.d. columns used in our previous works. This allowed 15 ml to be loaded
4 within some 45 minutes. Besides this simple column up-scaling, the elution protocol was
5 largely modified. First, instead of using 1M HNO₃ throughout the column washing step, a
6 sequence of nitric acid of decreasing strength (from 1M to 0.125M) was passed through the
7 column, in order to improve the stripping of unwanted residual major elements and heavy
8 REE. Secondly, the LREE were stripped from the column by using 3M HCl instead of very
9 dilute (0.05M) nitric acid as used in previous studies. This is a significant change, which
10 provides a sharper elution peak compared to the usual 0.05M HNO₃ strip, which shows rather
11 significant tailing. Importantly, this change of stripping medium of the first column requires a
12 major modification, in fact, an overturn, of the subsequent separation protocol, namely, using
13 the DGA resin for the early separation of Nd, instead of the LN2 resin as done in our previous
14 method. This is because the LN2 resin (and the classical LN resin as well) acts as a cation
15 exchanger, able to extract the LREE only from very dilute HNO₃ or HCl solutions.
16 Accordingly, the LN2 column cannot be used in tandem with a TRU column in this case.
17 However, the DGA resin is able to strongly extract the Lanthanides, not only from nitric acid
18 solutions of almost any strength, but also from relatively strong HCl.²⁴ For this reason, it can
19 be used in the second on-line column, downstream from the TRU column, when this is
20 stripped from the LREE with 3M HCl. An additional benefit of this new TRU-DGA tandem
21 elution step is an improved removal of the last traces of Fe and Ti. Iron (III) and titanium are
22 indeed the only major elements which are extracted to a limited, but not entirely negligible
23 extent by the TRU resin from 1M HNO₃ medium²⁵ (D = 5 and 7, respectively). Both elements
24 accompany the LREE during their stripping with 0.05M HNO₃, and would be extracted on,
25 and subsequently “leak” from the next, on-line LN2 column. In contrast, any Fe(III)
26 remaining on the TRU column will still be held by the resin if the LREE are stripped by using
27 3M HCl.²⁵ Residual Ti (IV) is eluted along with the LREE, but this element is not extracted
28 by the forthcoming DGA resin from both HCl and HNO₃ media (D < 3 for all
29 concentrations).²⁴ This allows a better purification of Nd to be achieved from those two major
30 elements which are potentially problematic for the TRU column.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50

51 52 4.2.2 *Isolation and further purification of neodymium* 53

54 The gross separation of Nd from the adjacent LREE is achieved by using the DGA resin
55 which, just as the LN or LN2 resins, has an increasing affinity for individual Ln (III) elements
56 as their atomic number increases. Accordingly, for both resins, the REE are eluted from the
57 light to the heavy ones, either in HCl or HNO₃ media^{24,26}, with broadly similar separation
58
59
60

1
2
3 factors between Ce and Nd, and Pr from Nd, respectively.²⁷ However, in contrast with LN
4 resins, more and more dilute, instead of stronger and stronger acid, is required to strip Ln's of
5 increasing atomic number, with the practical limitation that the HREE still have very high D's
6 even in extremely dilute nitric acid²⁴ (e.g., $D > 500$ in 0.05M HNO₃). In this respect, it is
7 beneficial that the TRU column permits to get rid of the HREE before coupling with the DGA
8 column. An excellent separation of Nd ahead from Sm is easily achieved with the DGA
9 column (Fig. S2), but some unavoidable tailing of the Ce and Pr peaks occurs and lends to
10 significant contamination of the Nd cut, therefore necessitating a further purification step in
11 case ¹⁴²Nd/¹⁴⁴Nd ratios are to be measured. This is accomplished without intervening
12 evaporation by means of a second, DGA-LN2 column tandem, permitted by the very dilute
13 acid (0.006M HCl) used to strip Nd from the DGA resin, which is compatible with its
14 forthcoming extraction by the LN2 resin.

15
16
17 Although Nd isolated in this straightforward way (total duration of the separation: about 12
18 hours, to be compared with the 3-4 days typically needed by previous methods⁸) gave
19 satisfactory thermal ionization mass spectrometric runs (Table 3), a further on-line clean-up
20 can easily be implemented by immediately recycling the Nd fraction through the
21 reconditioned DGA column to perform an additional purification stage (Table 1). In this way,
22 the ¹⁴²Ce contribution to the ¹⁴²Nd signal was further reduced by a factor of three, and perhaps
23 more interestingly, more intense ion beams were obtained in most cases (Fig. 2), suggesting a
24 significant improvement of the overall purity of Nd from those foreign elements which have
25 an adverse effect on the production of thermal ions.

26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

5 Summary and Conclusion

This work elaborates on a recently published¹² triple tandem separation scheme entirely based on extraction chromatography, enabling the analyst to isolate Nd in a form sufficiently pure to be used to determine ¹⁴³Nd/¹⁴⁴Nd and ¹⁴²Nd/¹⁴⁴Nd isotope ratios by Thermal Ionisation Mass Spectrometry. This previous procedure was designed for processing ~100 mg-sized samples of common silicate rocks. Here, the method has been modified in order to make it possible to analyse much larger and challenging samples, namely, chondritic materials and ultramafic, LREE-depleted, Mg-rich rocks. Specifically, the acid dissolution protocol has been modified to a "soft" version, with strongly shortened HF dissolution duration, and mild subsequent treatments, in order to limit the formation of those fluoride compounds which cause poor

1
2
3 chemical recoveries. More significantly, the separation scheme has been largely reworked, by
4 using an up-scaled column (albeit still at least an order of magnitude smaller than commonly
5 used counterparts based on cation-exchange) filled with 1.5 ml TRU EXC resin to get rid of
6 matrix and unwanted trace elements by using a new elution protocol. After column rinsing
7 with dilute nitric acid of decreasing strength, the LREE are stripped with 3M hydrochloric
8 acid instead of 0.05M nitric acid, and directly loaded on a column of DGA EXC resin which
9 performs the separation of Nd from adjacent LREE. Nd is then eluted onto the next column of
10 LN2 EXC resin, providing Nd sufficiently purified from Ce and Sm for high precision
11 $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ isotope ratio measurements. In so far as the DGA and LN2
12 columns are not overloaded, Nd recoveries in the 90% range are achieved. The whole
13 separation procedure can be performed in a single, albeit long (12 hours) working day. For an
14 even better purity, the Nd fraction can be further cleaned-up on-line by means of a second
15 pass through the DGA column. Evaporation steps are totally eliminated throughout the
16 separation, by virtue of the systematic use of columns arranged in tandems, considerably
17 reducing the overall duration of the separation process. Compared with conventional methods
18 based on large columns of cation-exchange resin for removing matrix elements, and involving
19 the oxidation of Ce to the +4 state for making its separation from Nd easier, this triple
20 extraction chromatographic protocol is drastically down-scaled, relatively simple to
21 implement, and much less demanding in terms of analyst time, reagent volumes, and costs.
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38

39 **Conflicts of interest**

40
41
42 There are no conflicts to declare
43
44
45
46

47 **Acknowledgements**

48
49 We are very grateful to Dr Aude Bombard (Triskem International) for kindly donating
50 samples of LN2 resin. We also thank Jean-Luc Piro and Delphine Auclair for maintaining in a
51 very good condition the Agilent 7500 ICP-QMS and the Triton TIMS, respectively, Chantal
52 Bosq for preparing high purity acids and Krzysztof Suchorski for monitoring reagent blanks.
53 We thank the Geological Survey of Japan for providing the isotopic standard JNdi-1. The
54 manuscript benefited from the reports of two anonymous referees, and particularly from a
55
56
57
58
59
60

1
2
3 perceptive adjudicative review by Ryan Ickert (Purdue University) which are gratefully
4 acknowledged. We thank Matthew Bown for editorial handling. C.P. thanks the ClerVolc
5 "Laboratoire d'Excellence" for a conditional, albeit modest, grant. This is Laboratory of
6 Excellence ClerVolc contribution number XXX.
7
8
9

10 11 12 13 **References**

- 14 1 R.W. Carlson, Chapter 15.18, 337-354. in: *Treatise on Geochemistry*, 2nd edition, 2014,
15 Elsevier.
- 16 2. Sulcek, Z. & Povondra, P. (1989) *Methods of Decomposition in Inorganic analysis*. CRC
17 Press: Boca Raton (Florida), 325 pp.
- 18 3 R.H. Boer, G.J. Beukes, F.M. Meyer and C.B. Smith, *Chem. Geol.*, 1993, **104**, 93-98
- 19 4 T. Shibata and M. Yoshikawa, *J. Mass Spectrom. Soc. Japan*, 2004, **52**, 317-324.
- 20 5 C. Frisby, M. Bizimis and S. Mallick, *Chem. Geol.*, 2016, **440**, 40-72.
- 21 6 N.S. Saji, D. Wielandt, C. Paton and M. Bizzarro, *J. Anal. Atom. Spectrom.*, 2016, **31**, 1490-
22 1504.
- 23 7 S. Kagami and T. Yokoyama, *Anal. Chim. Acta*, 2016, **937**, 151-159.
- 24 8 M. Garçon, M. Boyet, R.W. Carlson, M.F. Horan, D. Auclair and T.D. Mock, *Chem. Geol.*,
25 2018, **476**, 493-514.
- 26 9 M. Boyet and R.W. Carlson, *Science*, 2005, **214**, 427-442.
- 27 10 M. Sharma, G.J. Wasserburg, D.A. Papanastassiou, J.E. Quick, E.V. Sharkov and E.E.
28 Laz'ko, *Earth Planet. Sci. Lett.*, 1995, **135**, 101-114.
- 29 11 M. Sharma and G.J. Wasserburg, *Geochim. Cosmochim. Acta*, 1996, **60**, 4537-4550.
- 30 12 C. Pin and A. Gannoun, *J. Anal. Atom. Spectrom.*, 2019, **34**, 310-318.
- 31 13 G.G. Rao and V.N. Rao, *Fres. Z. anal. Chemie*, 1955, **147**, 338-347.
- 32 14 M. Kinoshita and 18 others, *Science*, 2012, **335**, 1614-1617.
- 33 15 GeoReM Data Base; <http://georem.mpch-mainz.gwdg.de>
- 34 16 C. Pin and J.F. Santos Zalduegui, *Anal. Chim. Acta*, 1997, 339, 79-89
- 35 17 Z. Chu, M. Wang, C. Li, Y. Yang, J. Xue, W. Wang and J. Guo, *J. Anal. Atom. Spectrom.*,
36 2019, DOI: 10.1039/C9JA00200F
- 37 18 A. Gannoun, M. Boyet, H. Rizo and A. El Goresy, *Proc. Nat. Acad. Sci*, 2011, **108**, 7693-
38 7697.
- 39 19 J. Carignan, P. Hild, G. Mevelle, J. Morel, and D. Yeghicheyan, 2001, *Geostandards*
40 *Newlett.*, **25**, 187-198.

- 1
2
3 20 S. Joannon and C. Pin, *J. Anal. Atom. Spectrom.*, 2001, **16**, 32-37.
4
5 21 E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond and D.M. Nelson, *Anal. Chim. Acta*,
6
7 1993, **281**, 361-372.
8
9 22 C. Pin, D. Briot, C. Bassin and F. Poitrasson, *Anal. Chim. Acta*, 1994, **298**, 209-217.
10
11 23 C. Pin and J.F. Santos Zalduegui, *Anal. Chim. Acta*, 1997, **339**, 79-89.
12
13 24 E.P. Horwitz, D.R. McAlister, A.H. Bond and R.E. Barrans Jr, *Solvent Extr. Ion Exch.*,
14 2005, **23**, 319-344.
15
16 25 E.A. Huff and D.R. Huff, 34th ORNL/DOE Conf. on Anal. Chem. in Energy Technol.,
17 Gatlinburg, TN, 1993.
18
19 26 D.R. McAlister and E.P. Horwitz, *Solvent Extr. Ion Exch.*, 2007, **25**, 757-769.
20
21 27 D.R. McAlister and E.P. Horwitz, 2011, *Radiobioassay & Radiochem. Measurements*
22 *Conf.*, Sandestin, Florida.
23
24 28 K. Govindaraju, *Geostandards Newsletter*, 1994, **18**, 1-158.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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 DGA column; (3) elution of La, Ce, and Pr from the DGA column; (4) second tandem step: on-line elution of Nd from the DGA column to the next, LN2 column; (5) elution of residual Ce and Pr; (6) final stripping of the purified Nd fraction

Fig. 2: Effect of the additional purification stage on Nd extracted from the komatiitic basalt sample from Abitibi. Purified samples (pink circles) display (a) reduced ^{142}Ce contribution and (b) increased ^{142}Nd signal by a factor up to three compared to the samples processed through DGA-LN2 tandem only (blue circles), suggesting a significant improvement of the overall purity of Nd from those foreign elements which have an adverse effect on the production of thermal ions. Corrected $^{142}\text{Nd}/^{144}\text{Nd}$ (c) and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (d) remain unchanged.

Fig. 3: $^{142}\text{Nd}/^{144}\text{Nd}$ ratios in reference materials and other various samples 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. Our sample of the Allende meteorite displays a strongly negative $\mu^{142}\text{Nd}$ of -62 ± 10 , further extending towards the non radiogenic side the range of values measured so far for this carbonaceous chondrite.¹⁸

Table 1 Outline of the separation scheme enabling the isolation of highly purified Nd in (ultra-) mafic samples by extraction chromatography

	Reagents	Volume (mL)
<u>Column pre-cleaning and pre-conditioning</u>		
TRU Spec (500 mg)	1 M HNO ₃	1
DGA (350 mg)	3 M HCl	1
LN2 (350 mg)	0.1 M HCl 0.006M HCl	0.5 1
TRU Spec alone		
Sample loading	1 M HNO₃-C₆H₈O₆	4 × 5
Matrix elution	1 M HNO ₃ 0.5 M HNO ₃ 0.25 M HNO ₃ 0.125M HNO ₃ 0.125M HNO ₃	2 × 1 2 × 1 1.5 2 × 1 0.5
Pre-LREE cut	3M HCl	3 × 0.25
<u>TRU spec and DGA columns in tandem</u>		
Elution of LREE	3M HCl	4 × 0.5
<u>Columns decoupling and further elution</u>		
<u>DGA alone</u>		
Rinse	0.1M HNO ₃	0.5
Rinse	0.05M HNO ₃	3
Elution of Ce	0.03 M HNO ₃	3
Elution of Pr	0.025M HNO ₃	2.5
<u>DGA and LN2 columns in tandem</u>		
Online elution of Nd	0.006M HCl	2
<u>Columns decoupling and further elution</u>		
<u>LN2 alone</u>		
Rinse	0.05 M HNO ₃ 0.08M HNO ₃	0.1 2.6
Elution of Nd[§]	0.15 M HNO₃	3
<u>DGA alone</u>		
(Elution of Sm, optional)	0.1M HCl	1
<u>Cleaning before storage</u>		
LN2	3 M HNO ₃ 0.05 M HNO ₃	2 2
DGA	1 M HCl 0.01 M HCl	2 2
TRU Spec	0.1 M HCl - 0.29 M HF 0.05 M HNO ₃ 3 M HCl 0.05 M HNO ₃	4 4 4 4
<u>Optional step for further clean up of Nd fraction if needed</u>		
DGA column		
Pre-conditioning	0.2M HNO ₃	1
Sample loading (fraction eluted in [§])	0.15M HNO₃	3
Rinse	2M HCl	3.5
Elution of Nd	2M HCl	3

Table 2 Major and some trace element abundances in the samples investigated during this study determined by ICP-AES and ICP-QMS, respectively.

	CaO (wt. %)	MgO (wt. %)	Al ₂ O ₃ (wt. %)	Fe ₂ O _{3(т)} (wt. %)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)
Komatiitic basalt Abitibi	12.3	8.07	7.54	19.1	12.9	29.5	17.2	3.86
Komatiitic basalt Barberton	9.10	12.2	8.74	10.9	1.34	3.60	2.77	0.97
Allende [§]	2.59	24.6	3.29	27.2	0.49	1.15	0.94	0.30
BIR-1 [£]	13.2	9.68	15.4	11.3	0.62	1.95	2.50	1.10
UB-N [£]	1.20	35.2	2.90	8.34	0.35	0.83	0.62	0.23

[§] Data from ref. 18. Note that the samples analysed in this study are not from the same batch of this meteorite

[£] Data from ref. 28

Table 3 Nd isotope ratios measured by static multi-collection TIMS for the isotopic standard JNdi-1 and AMES and five natural samples including international reference materials BIR-1 and UBN. The numbers refer to single dissolution for each measurement processed through the separation scheme reported in this study. Additional letters refer to aliquots from the same dissolution. The individual ratios are listed with their individual within-run precision (expressed as 2 standard errors), while the average values (in bold italic) are quoted with their external reproducibility (expressed as 2 standard deviations)

	¹⁴⁰ Ce	¹⁴⁷ Sm	¹⁴² Nd	¹⁴⁴ Nd	¹⁴² Ce/ ¹⁴² Nd	¹⁴⁴ Sm/ ¹⁴⁴ Nd	¹⁴² Nd/ ¹⁴⁴ Nd	μ ¹⁴² Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁶ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴⁶ Nd/ ¹⁴⁴ Nd
	(V)	(V)	(V)	(V)	(ppm)	(ppm)	(ppm)	(ppm)					
BIR-1													
BIR-1 #1	3.3E-4	2.8E-6	6.4	5.6	6.4	0.1	1.141835 ± 5	-1.3 ± 4.3	0.513081 ± 2	0.348404 ± 1	0.241581 ± 1	0.236452 ± 2	0.721492
BIR-1 #2	5.5E-5	3.3E-6	5.0	4.4	1.4	0.2	1.141831 ± 7	-4.9 ± 6.3	0.513081 ± 3	0.348406 ± 1	0.241585 ± 2	0.236454 ± 3	0.722629
BIR-1 #3	7.8E-5	2.8E-6	2.8	2.5	3.5	0.2	1.141838 ± 7	2.0 ± 6.4	0.513082 ± 3	0.348403 ± 2	0.241581 ± 2	0.236453 ± 3	0.721823
Average					3.7	0.2	1.141835 ± 8	-1.4 ± 6.9	0.513082 ± 1	0.348405 ± 3	0.241582 ± 4	0.236453 ± 2	
K-B ABI[†]													
K-B ABI #1a	2.4E-4	4.2E-6	10.6	9.2	2.8	0.1	1.141833 ± 4	-3.1 ± 3.5	0.511642 ± 2	0.348405 ± 1	0.241580 ± 1	0.236448 ± 1	0.721066
K-B ABI #1b	6.7E-5	1.7E-6	6.0	5.2	1.4	0.1	1.141832 ± 5	-3.7 ± 4.3	0.511641 ± 2	0.348405 ± 1	0.241580 ± 1	0.236450 ± 2	0.719679
K-B ABI #2a [§]	5.3E-5	3.3E-6	10.8	9.4	0.6	0.1	1.141837 ± 4	1.1 ± 3.3	0.511643 ± 1	0.348404 ± 1	0.241580 ± 1	0.236451 ± 1	0.721281
K-B ABI #2b [§]	2.3E-5	4.5E-7	4.1	3.6	0.7	0.0	1.141840 ± 6	3.8 ± 5.3	0.511645 ± 2	0.348406 ± 1	0.241581 ± 2	0.236449 ± 2	0.721711
K-B ABI #3a [§]	5.0E-5	5.4E-6	14.8	12.9	0.4	0.1	1.141831 ± 4	-4.6 ± 3.6	0.511648 ± 2	0.348404 ± 1	0.241580 ± 1	0.236448 ± 2	0.720696
K-B ABI #3b [§]	3.2E-5	5.1E-6	15.2	13.3	0.3	0.1	1.141839 ± 4	2.8 ± 3.3	0.511649 ± 1	0.348404 ± 1	0.241579 ± 1	0.236446 ± 1	0.721446
K-B ABI #4a	1.2E-4	1.4E-6	9.1	7.9	1.7	0.0	1.141839 ± 6	2.6 ± 4.9	0.511650 ± 2	0.348404 ± 1	0.241580 ± 2	0.236448 ± 2	0.719581
K-B ABI #4b	8.8E-5	1.7E-5	5.7	5.0	1.9	0.7	1.141829 ± 5	-6.2 ± 4.7	0.511645 ± 3	0.348406 ± 1	0.241578 ± 1	0.236449 ± 2	0.721663
K-B ABI #5a	8.3E-5	2.4E-6	4.8	4.2	2.2	0.1	1.141830 ± 6	-5.5 ± 5.0	0.511650 ± 2	0.348405 ± 1	0.241581 ± 2	0.236448 ± 2	0.719657
K-B ABI #5b	1.0E-4	2.7E-6	6.9	6.0	1.8	0.1	1.141833 ± 6	-2.6 ± 5.0	0.511650 ± 2	0.348404 ± 1	0.241581 ± 2	0.236449 ± 2	0.719876
K-B ABI #6a [§]	5.9E-5	6.5E-6	8.9	7.8	0.8	0.2	1.141837 ± 5	1.1 ± 4.1	0.511651 ± 2	0.348405 ± 1	0.241580 ± 1	0.236448 ± 2	0.720921
K-B ABI #6b [§]	1.3E-4	3.9E-6	13.0	11.3	1.2	0.1	1.141834 ± 4	-2.1 ± 3.8	0.511652 ± 2	0.348404 ± 1	0.241580 ± 1	0.236448 ± 2	0.719349
K-B ABI #7a [§]	5.9E-5	3.2E-6	12.8	11.2	0.6	0.1	1.141831 ± 3	-4.9 ± 3.0	0.511650 ± 1	0.348404 ± 1	0.241580 ± 1	0.236447 ± 1	0.719916
K-B ABI #7b [§]	3.8E-5	3.8E-6	13.1	11.4	0.4	0.1	1.141832 ± 4	-3.6 ± 3.6	0.511650 ± 1	0.348404 ± 1	0.241579 ± 1	0.236449 ± 1	0.719607
Average					1.2	0.1	1.141834 ± 8	-1.8 ± 6.8	0.511648 ± 7	0.348404 ± 1	0.241580 ± 2	0.236448 ± 2	
K-B BAR[§]													
K-B BAR #1	3.1E-5	4.5E-6	8.9	7.8	0.4	0.1	1.141829 ± 5	-6.4 ± 4.6	0.512863 ± 2	0.348403 ± 1	0.241581 ± 1	0.236448 ± 2	0.721263
K-B BAR #2	9.5E-5	2.0E-6	10.9	9.5	1.1	0.0	1.141828 ± 4	-7.0 ± 3.4	0.512864 ± 1	0.348406 ± 1	0.241580 ± 1	0.236447 ± 1	0.719849
K-B BAR #3	3.9E-5	-6.8E-7	5.8	5.1	0.9	0.0	1.141825 ± 6	-9.4 ± 5.4	0.512860 ± 2	0.348404 ± 1	0.241580 ± 2	0.236449 ± 2	0.722123
K-B BAR #4	2.0E-5	4.2E-6	6.3	5.5	0.4	0.2	1.141830 ± 5	-5.8 ± 4.6	0.512864 ± 2	0.348405 ± 1	0.241582 ± 1	0.236451 ± 2	0.722277
Average					0.7	0.1	1.141828 ± 4	-7.2 ± 3.1	0.512863 ± 4	0.348404 ± 2	0.241581 ± 2	0.236449 ± 3	
UBN													
UBN #1	1.7E-5	1.7E-6	2.2	1.9	1.0	0.2	1.141829 ± 10	-5.9 ± 9.1	0.512932 ± 4	0.348403 ± 3	0.241584 ± 3	0.236451 ± 4	0.723606
UBN #2	1.4E-4	4.4E-6	8.7	7.6	2.1	0.1	1.141833 ± 4	-2.9 ± 3.5	0.512929 ± 2	0.348405 ± 1	0.241581 ± 1	0.236451 ± 2	0.722491
UBN #3	3.6E-5	3.7E-6	4.4	3.9	1.0	0.2	1.141830 ± 8	-5.2 ± 7.3	0.512927 ± 3	0.348405 ± 2	0.241581 ± 2	0.236452 ± 3	0.723635
UBN #4	2.0E-4	4.1E-6	7.5	6.6	3.4	0.1	1.141842 ± 5	5.4 ± 4.2	0.512927 ± 2	0.348404 ± 1	0.241582 ± 1	0.236454 ± 2	0.723688
Average					1.9	0.2	1.141834 ± 12	-2.1 ± 10.4	0.512929 ± 5	0.348404 ± 1	0.241582 ± 3	0.236452 ± 3	
Allende													
Allende #1	9.2E-5	4.9E-6	5.5	4.8	2.1	0.2	1.141765 ± 5	-62 ± 5	0.512077 ± 2	0.348403 ± 1	0.241582 ± 2	0.236448 ± 2	0.720348
Allende #2	1.5E-5	1.1E-5	8.3	7.3	0.2	0.3	1.141766 ± 4	-62 ± 4	0.512077 ± 2	0.348404 ± 1	0.241578 ± 1	0.236444 ± 2	0.723900
Allende #3	4.1E-5	3.5E-7	4.9	4.3	1.1	0.0	1.141773 ± 5	-56 ± 5	0.512076 ± 2	0.348403 ± 1	0.241584 ± 2	0.236451 ± 2	0.723113
Allende #4	7.7E-5	1.9E-6	7.7	6.8	1.3	0.1	1.141760 ± 8	-67 ± 7	0.512066 ± 3	0.348404 ± 2	0.241584 ± 4	0.236453 ± 3	0.723122
Average					1.2	0.1	1.141766 ± 11	-62 ± 10	0.512074 ± 10	0.348403 ± 1	0.241582 ± 5	0.236449 ± 7	
JNdi-1													
JNdi-1 #1	8.0E-5	3.2E-6	3.6	3.2	2.8	0.2	1.1418369 ± 8	0.7 ± 6.7	0.512106 ± 3	0.348401 ± 2	0.241581 ± 2	0.236452 ± 3	0.719772
JNdi-1 #2	2.8E-5	8.4E-6	4.9	4.3	0.7	0.4	1.1418369 ± 7	0.7 ± 6.4	0.512104 ± 3	0.348403 ± 2	0.241579 ± 2	0.236449 ± 2	0.720947
JNdi-1 #3	4.9E-5	7.3E-6	4.4	3.9	1.4	0.4	1.1418339 ± 7	-1.9 ± 6.0	0.512104 ± 3	0.348403 ± 2	0.241583 ± 2	0.236454 ± 3	0.720216
JNdi-1 #4	1.4E-4	8.8E-6	6.8	5.9	2.6	0.3	1.1418396 ± 6	3.1 ± 5.0	0.512105 ± 2	0.348403 ± 1	0.241581 ± 2	0.236450 ± 2	0.719938
JNdi-1 #5	8.3E-5	1.3E-5	7.6	6.7	1.4	0.4	1.1418322 ± 5	-3.5 ± 4.6	0.512102 ± 2	0.348403 ± 1	0.241581 ± 2	0.236451 ± 2	0.720721
JNdi-1 #6	1.3E-4	1.5E-5	7.8	6.8	2.1	0.4	1.1418351 ± 5	-0.9 ± 4.3	0.512103 ± 2	0.348404 ± 1	0.241581 ± 2	0.236451 ± 2	0.720918
JNdi-1 #7	3.2E-5	1.1E-5	5.1	4.4	0.8	0.5	1.1418309 ± 7	-4.5 ± 5.7	0.512102 ± 3	0.348403 ± 1	0.241578 ± 2	0.236448 ± 2	0.720819
JNdi-1 #8	1.2E-4	1.4E-5	9.6	8.4	1.6	0.3	1.1418358 ± 4	-0.3 ± 3.5	0.512105 ± 1	0.348403 ± 1	0.241582 ± 1	0.236452 ± 1	0.719966
JNdi-1 #9	1.8E-4	1.9E-5	10.0	8.8	2.2	0.5	1.1418332 ± 4	-2.5 ± 3.6	0.512104 ± 2	0.348404 ± 1	0.241582 ± 1	0.236453 ± 1	0.720608
JNdi-1 #10	1.1E-4	2.3E-5	11.3	9.9	1.2	0.5	1.1418417 ± 4	4.9 ± 3.4	0.512106 ± 1	0.348404 ± 1	0.241582 ± 1	0.236454 ± 1	0.720969
JNdi-1 #11	1.6E-4	1.9E-5	10.6	9.3	1.9	0.4	1.1418425 ± 5	5.6 ± 4.1	0.512107 ± 2	0.348404 ± 1	0.241582 ± 1	0.236452 ± 2	0.720190
JNdi-1 #12	1.6E-4	1.7E-5	11.1	9.7	1.8	0.4	1.1418402 ± 4	3.6 ± 3.3	0.512106 ± 1	0.348405 ± 1	0.241582 ± 1	0.236452 ± 1	0.720005
JNdi-1 #13	5.8E-5	8.1E-6	5.6	4.9	1.3	0.3	1.1418329 ± 5	-2.8 ± 4.6	0.512105 ± 2	0.348405 ± 1	0.241583 ± 1	0.236452 ± 2	0.719533
JNdi-1 #14	9.1E-5	1.2E-5	6.8	5.9	1.7	0.4	1.1418373 ± 5	1.0 ± 4.3	0.512105 ± 2	0.348405 ± 1	0.241582 ± 1	0.236453 ± 2	0.720486
JNdi-1 #15	1.1E-4	9.5E-6	6.7	5.8	2.1	0.3	1.1418324 ± 5	-3.3 ± 4.1	0.512103 ± 2	0.348404 ± 1	0.241579 ± 1	0.236449 ± 2	0.719539
Average					1.7	0.4	1.141836 ± 7	0.0 ± 6.4	0.512104 ± 3	0.348404 ± 2	0.241581 ± 3	0.236451 ± 4	
AMES													
AMES #1	2.3E-5	8.0E-6	14.8	13.0	0.2	0.1	1.1418407 ± 3	4.0 ± 2.9	0.512155 ± 1	0.348405 ± 1	0.241581 ± 1	0.236451 ± 1	0.720678
AMES #2	2.4E-5	5.1E-6	5.7	5.0	0.5	0.2	1.1418404 ± 5	3.8 ± 4.6	0.512155 ± 2	0.348405 ± 1	0.241581 ± 1	0.236451 ± 2	0.721026
AMES #3	9.0E-5	6.3E-6	11.3	9.9	1.0	0.1	1.1418407 ± 4	4.0 ± 3.2	0.512155 ± 1	0.348405 ± 1	0.241583 ± 1	0.236451 ± 1	0.720800
AMES #4	6.5E-5	2.1E-6	11.6	10.2	0.7	0.0	1.1418413 ± 4	4.5 ± 3.2	0.512154 ± 1	0.348404 ± 1	0.241580 ± 1	0.236452 ± 1	0.721089
AMES #5	5.2E-5	5.0E-6	12.8	11.2	0.5	0.1	1.1418399 ± 3	3.3 ± 3.0	0.512154 ± 1	0.348405 ± 1	0.241581 ± 1	0.236452 ± 1	0.721100
AMES #6	3.5E-5	1.7E-5	10.0	8.8	0.4	0.4	1.1418347 ± 7	-1.2 ± 6.0	0.512152 ± 3	0.348405 ± 2	0.241584 ± 2	0.236455 ± 3	0.720805
AMES #7	3.8E-5	1.6E-6	7.3	6.4	0.7	0.1	1.1418379 ± 7	1.6 ± 6.4	0.512152 ± 3	0.348404 ± 1	0.241579 ± 3	0.236449 ± 5	0.720463
AMES #8	5.4E-5	4.8E-6	15.2	13.3	0.4	0.1	1.1418388 ± 3	2.4 ± 2.9	0.512153 ± 1	0.348404 ± 1	0.241578 ± 1	0.236449 ± 1	0.720736
Average					0.6	0.1	1.141839 ± 4	2.8 ± 3.8	0.512154 ± 2	0.348405 ± 1	0.241581 ± 4	0.236451 ± 4	

[†] komatiitic basalt from ~ 2.7 Ga Abitibi greenstone belt (Canada)

[§] komatiitic basalt from ~3.5 Ga Barberton greenstone belt (South Africa)

[‡] for these samples, separated Nd was further purified on-line by means of a second, on-line pass through the DGA

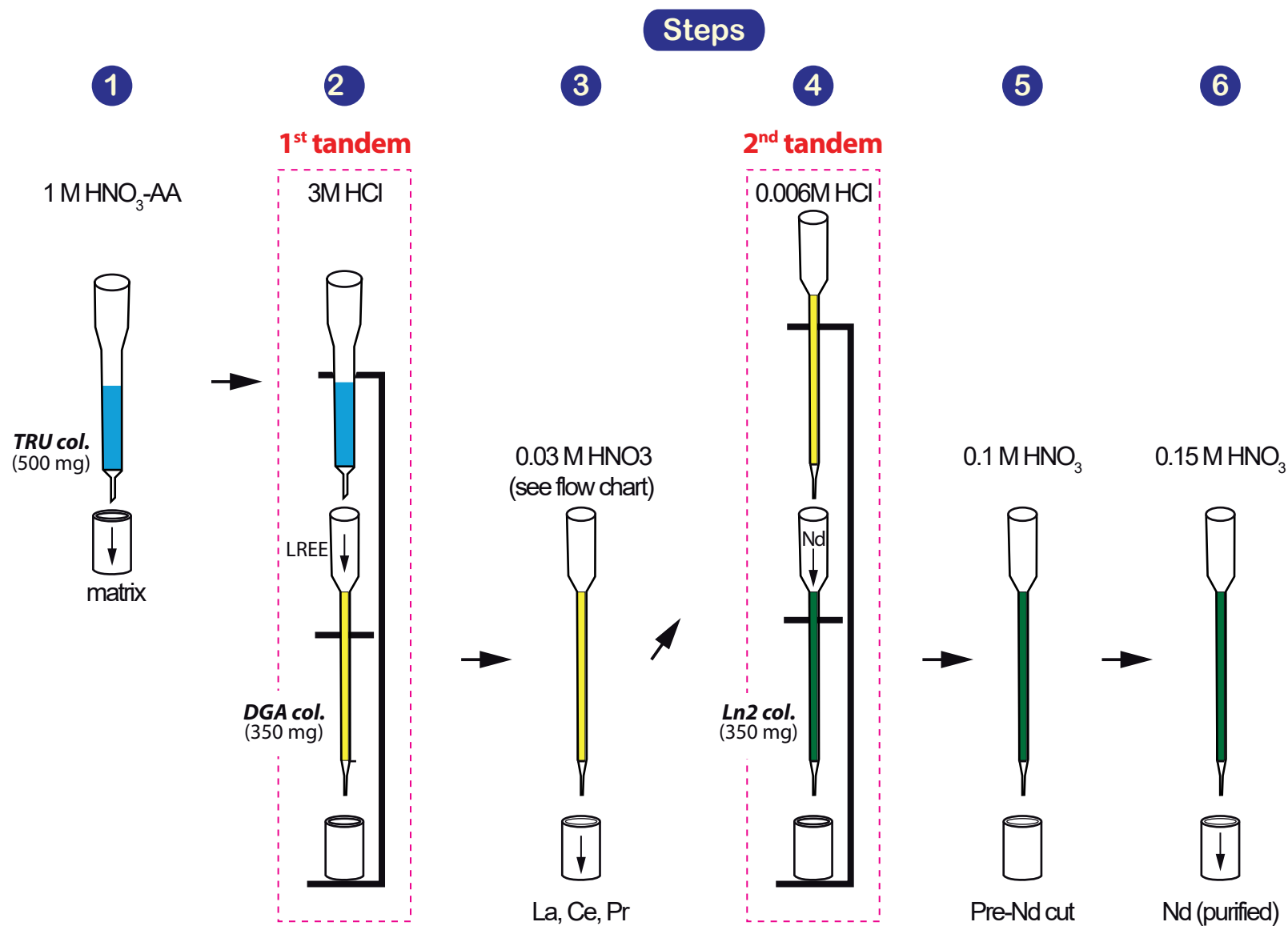
Table 4 Chemical recoveries (%) achieved during the separation of Nd

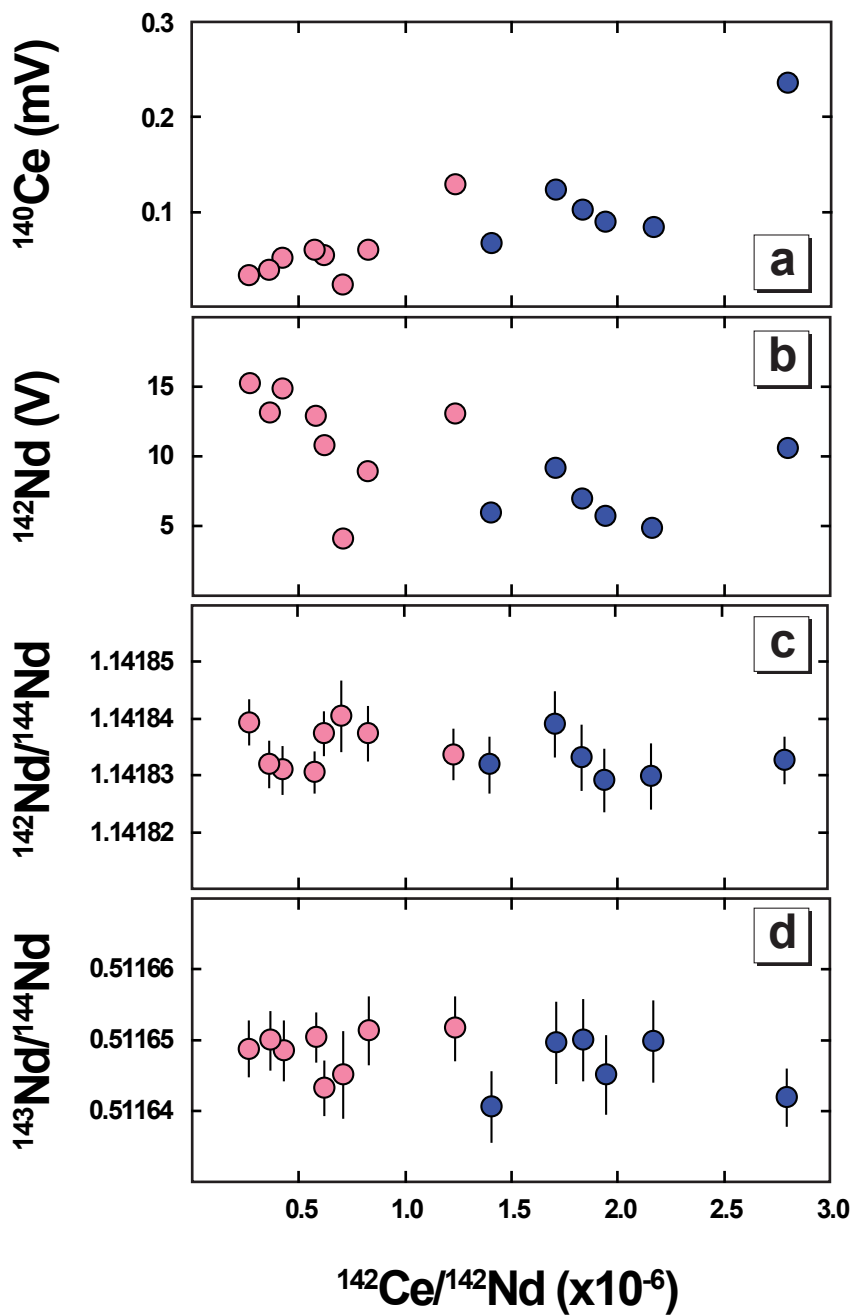
	N	Min (%)	Max (%)	Average (%)
Komatiitic basalt Abitibi	7	71	80	76
Komatiitic basalt Barbetron	4	81	92	87
Allende	4	91	99	95
BIR-1	3	90	98	95
UBN	4	94	97	95

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 5 Reagent, column and total procedural Nd blanks measured by ICP-QMS

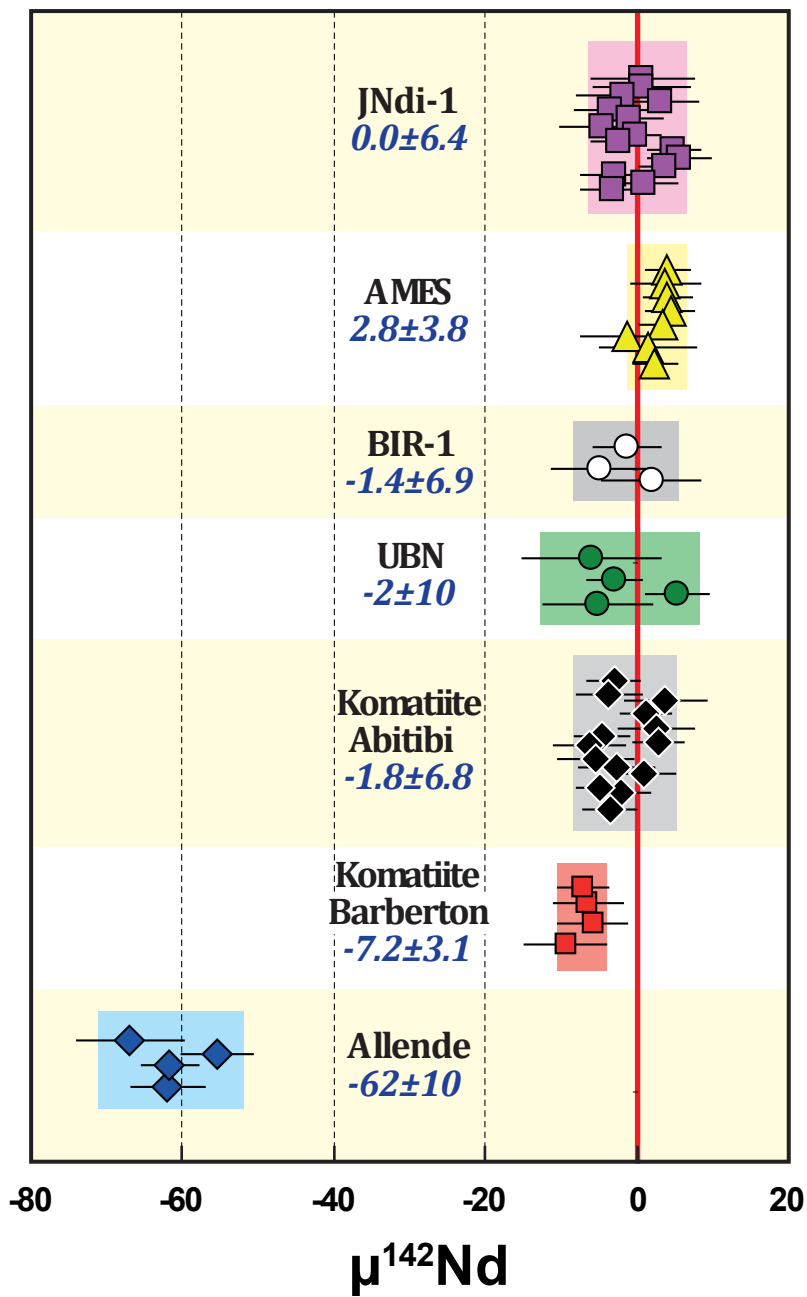
	Reagent blanks (pg.mL ⁻¹)			Reagent blanks (pg.g ⁻¹)		Column blank	Total procedural blank
	29M HF	6M HCl	14M HNO ₃	Ascorbic acid	Boric acid	(pg)	(pg)
Range	0.4 - 0.9	0.2 - 0.6	0.3 - 0.8	< 5	< 5	7 - 15	21 - 45
Mean ± 1SD	0.5 ± 0.3	0.4 ± 0.2	0.5 ± 0.2			11 ± 3	32 ± 9
Number	4	4	4	1	1	6	6





1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figure 3



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

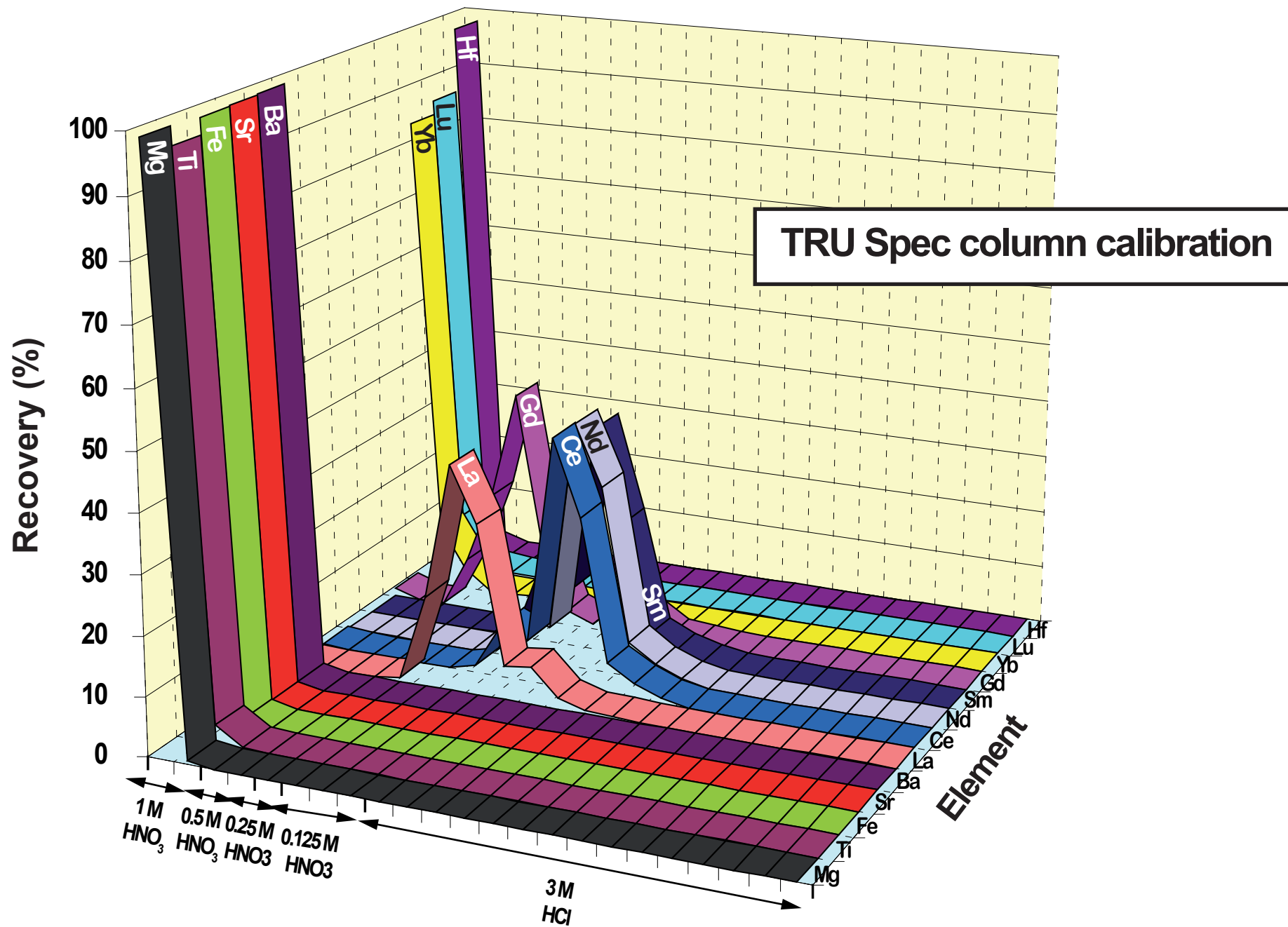


Fig. S1

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46

TRU/DGA tandem column calibration

Recovery (%)

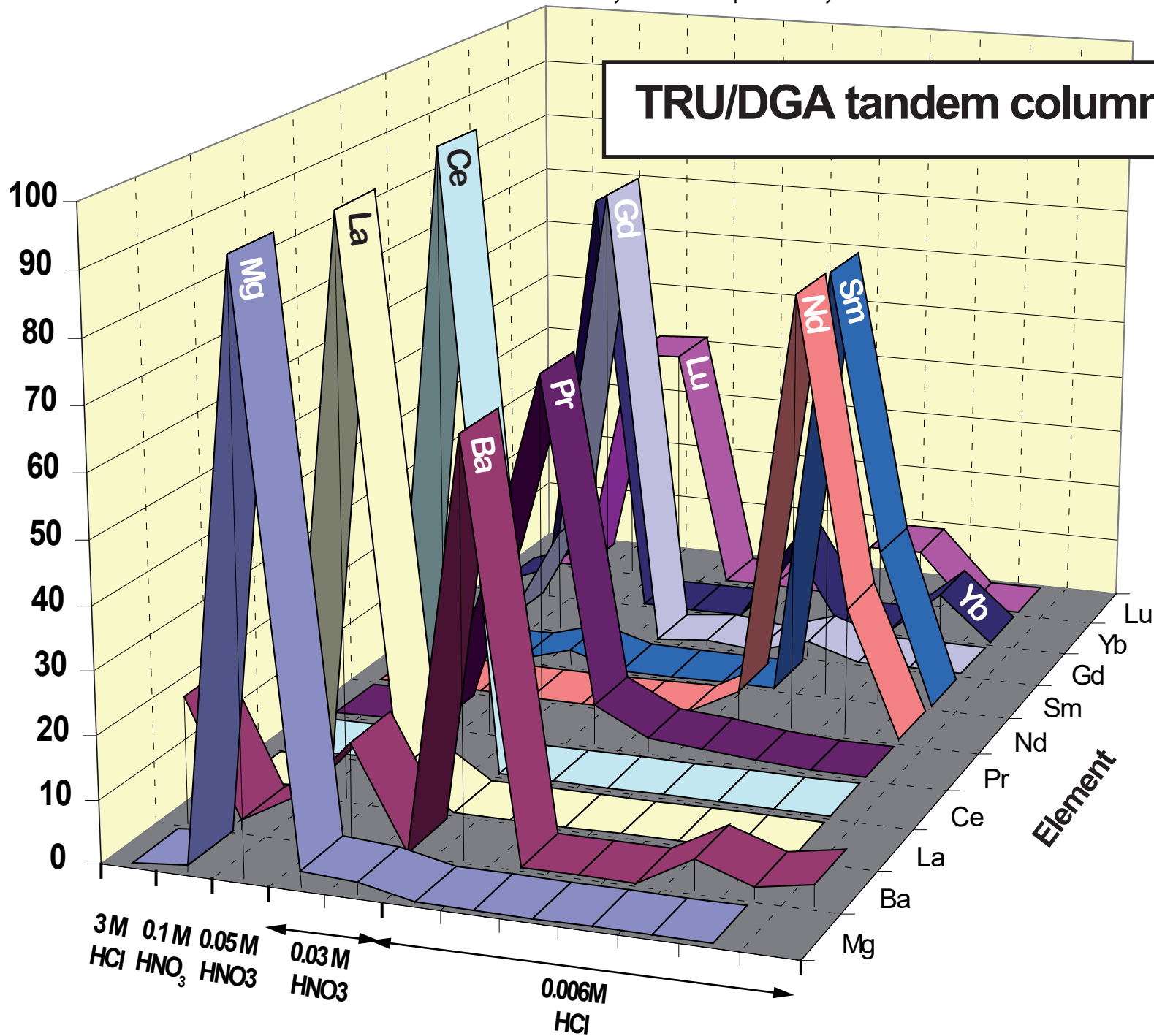


Fig. S2