



HAL
open science

A fast, single column extraction chromatography method for the isolation of neodymium from iron-rich materials prior to radiogenic isotope ratio measurements

Abdelmouhcine Gannoun, Krzysztof Suchorski, Christian Pin

► To cite this version:

Abdelmouhcine Gannoun, Krzysztof Suchorski, Christian Pin. A fast, single column extraction chromatography method for the isolation of neodymium from iron-rich materials prior to radiogenic isotope ratio measurements. *Journal of Analytical Atomic Spectrometry*, 2022, 37 (1), pp.165-171. 10.1039/d1ja00397f. hal-03516508

HAL Id: hal-03516508

<https://uca.hal.science/hal-03516508v1>

Submitted on 7 Jan 2022

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.

J A A S

Journal of Analytical Atomic Spectrometry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. GANNOUN, K. SUCHORSK and C. Pin, *J. Anal. At. Spectrom.*, 2022, DOI: 10.1039/D1JA00397F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

1
2
3
4 1 **A fast, single column extraction chromatography method**
5
6 2 **for the isolation of Neodymium from iron-rich materials**
7
8
9 3 **prior to radiogenic isotope ratio measurements**
10
11 4
12
13
14 5
15
16 6

View Article Online
DOI: 10.1039/D1JA00397F

17 6 **Abdelmouhcine Gannoun^a, Krzysztof Suchorski^a and Christian Pin^b**
18
19
20 8

21
22
23 9 ^aCNRS, IRD, OPGC, Laboratoire Magmas et Volcans, UMR 6524, Université Clermont Auvergne, F-63000,
24 10 Clermont-Ferrand, France. *E-mail:* mouhcine.gannoun@uca.fr

25 11 ^bLaboratoire de Géochimie Isotopique environnementale (GIS), Université de Nîmes, 150 rue Georges Besse,
26 12 30035 NIMES CEDEX 1, France

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

16 A novel separation method is described for the separation of Nd from Fe-rich, silicate samples
17 in view of isotopic analyses. The procedure is based on the synergistic enhancement of the
18 extraction of the REE from HCl media by the diglycolamide ligand in the presence of large
19 amounts of Fe (III). Following sample decomposition with a mixture of HF and HCl, the
20 resulting, ca. 4M HCl solution is immediately loaded on a column of DGA resin, without
21 evaporation of HF and volatilization of silicon. Both Fe(III) and the REE are extracted by the
22 resin while most other elements pass through the column. Then, iron is stripped from the
23 column with 3M HNO₃. Finally, the LREE are eluted sequentially by means of HCl of decreasing
24 strength, thereby providing a Nd fraction suitable for isotope ratio measurements by MC-ICP-
25 MS. Because it does not require evaporation steps, this method offers a robust,
26 straightforward alternative to more complicated schemes when samples unusually rich in iron
27 are to be analysed. The potential of this protocol is demonstrated by several replicate analyses
28 of two Fe-rich international SRMs, namely the banded iron IF-G (56 wt% Fe₂O₃) and the bauxite
29 BX-N (23% Fe₂O₃).

31 Introduction

View Article Online
DOI: 10.1039/D1JA00397F

32 The overall composition of magmatic silicate rocks primary constitutive of the continental and
33 oceanic crusts and of the underlying upper mantle involves some ten, so-called major
34 elements (Si, Al, Na, K, Ca, Mg, Fe, Ti, Mn), whose relative proportions span a relatively narrow
35 range reflecting the rather limited fractionation of these elements during igneous processes.

36 In contrast with these lithologies formed at high temperatures, some sedimentary rocks offer
37 much more extreme compositions, characterized by the overwhelming proportion of a few
38 elements only.

39 This is the case of two peculiar classes of sedimentary rocks that are highly enriched in iron,
40 namely banded iron ores, formed via selective chemical precipitation of silica and iron
41 hydroxides in the oceans, on the one hand, and laterites, left as residues of severe continental
42 alteration processes, on the other.

43 (i) Banded iron ores, or banded iron formations (BIF), are chemical deposits generally
44 formed in relatively deep-water settings, consisting of alternating layers of chert (amorphous
45 silica) and iron oxides (magnetite and hematite).¹ These peculiar sediments, mostly restricted
46 to the end of Archaean times (2800-2400 Ma), form the main deposits of iron worldwide.
47 Besides their economic interest, they receive much academic attention because they are
48 interpreted to reflect the precipitation of Fe(III), insoluble at near neutral pH value in the
49 presence of even traces of dissolved oxygen, from Fe(II) dissolved in the ocean waters ² (and
50 refs therein). Accordingly, they provide an important piece of information on the redox state
51 of the ocean and atmosphere, as suggested by the observation that the peak of their
52 deposition shortly preceded the first rise in atmospheric oxygen, the so-called « Great
53 Oxidation Event », ca. 2.4 Ga ago.³

54 (ii) Laterites are brick-like rocks, passively enriched in those major elements forming
55 insoluble hydroxides, Fe and Al, through severe leaching of all accompanying, soluble
56 constituents, under hot and wet tropical climates (e.g., ⁴ and references therein). Laterites can
57 be the products of advanced chemical weathering of a wide range of parent rocks, and these
58 residual lithologies occupy about one third of the surface of the continents.⁵ Their Al₂O₃-rich
59 end-member, bauxites, are of great economic importance as the major source of aluminum.

60 Likewise, some 70% of land-based nickel resources are contained in laterites developed from
61 ultramafic source rocks.⁶

62 Just as Fe(III) and Al, the trivalent lanthanide form insoluble hydroxides in natural waters under
63 most circumstances, and they can be used to study the petrogenetic processes involved in the
64 formation of iron-rich sediments. Among them, Nd is of special importance because its
65 radiogenic isotope composition can be used as a proxy for tracing the provenance of Fe and,
66 for example in the case of BIFs, discriminating models advocating a continental source against
67 those favouring an origin at hydrothermal vents of mid-ocean ridges. It is thus interesting to
68 develop straightforward separation schemes enabling the analyst to recover the REE from
69 such chemically distinct matrices. In this scope, it was decided to develop a method exploiting
70 a unique synergistic effect discovered by Horwitz and coworkers,⁷ namely, the strong
71 enhancement in the uptake of trivalent REE from chloride media by a diglycolamide-based
72 extraction chromatography resin in the presence of high levels of ferric ion.

73 The aim of this paper is to describe a new protocol based on this effect, and document its
74 potential for the Nd isotope analyses of this peculiar class of geological samples.

75

76 **Experimental**

77 **Chemicals, labware, extraction chromatographic materials, and instrumentation**

78 All chemical handlings were made under Class 10 vertical laminar flow hoods in a laboratory
79 supplied with an overpressure of filtered air, at a temperature of 20°C.

80 Water was deionized with conventional ion-exchange resins and further purified to a resistivity of
81 18.20 MOhm cm with an Aqua System Distribution (Bondoufle, France) device. Reagent grade
82 hydrofluoric, hydrochloric, and nitric acids (Fluka, Seelze, Germany) were purified by subboiling
83 distillation in PFA DST-100 systems (Savillex, Eden Prairie, MN, USA). Ammonium thiocyanate
84 (Honeywell Fluka) was used as a colorimetric agent to monitor the behaviour of iron during the
85 separation and check that it was reduced to negligible level before starting the elution of the
86 lanthanides.

1
2
3 87 Screw cap PFA vessels with a rounded bottom (15 ml capacity, Savillex, Minnetonka, USA) were
4 used to decompose the samples on a hot plate.
5
6

7
8 89 The DGA resin was obtained from Triskem International (Bruz, France). A quadrupole-base ICP-
9 MS (Model 7500, Agilent Technologies, Massy, France) was used in the semi-quantitative mode
10 90 to set up the separation protocol, and for measuring the concentrations of the Rare Earth
11 91 Elements in the studied samples, while a Neptune Plus multi-collector ICP-MS (Thermo
12 92 Instruments, Bremen, Germany) was used for the measurements of Nd isotope ratios.
13
14
15 93
16
17
18 94
19
20 95

96 **Chromatographic columns**

97 Aliquots of 500 mg of DGA resin were slurried in 0.05M HNO₃ and poured into *ca.* 7.5 mm i.d.
98 polystyrene columns fitted with a 15-45 μm polyethylene filter at the bottom (5-inch
99 chromatography columns, Caplugs Evergreen, Buffalo, N.Y., U.S.A.), giving a *ca.* 31 mm high resin
100 bed. An additional frit was placed on top of the resin to ensure a flat upper surface of the resin
101 bed.
102

103 **Chemical procedure**

104 *Sample digestion (for 100-200 mg)*

105 About 100- mg of iron-rich, BIF or lateritic sample is weighted on a piece of weighting paper,
106 and gently poured into a 15 ml screw cap PFA vessel containing 4 ml of 6M HCl. The mixture
107 is thoroughly mixed 15 minutes in an ultrasonic bath. Then, 2 ml of 48% HF is added, and the
108 closed vessel placed on a the hot plate at ~110°C overnight. The next day, the still warm sample
109 solution is transferred to a centrifuge tube with an additional fraction of 1 ml 4M HCl to rinse
110 the PFA dissolution vessel, and centrifuged 5 minutes at 4000 rpm. Because such samples do
111 not contain appreciable amount of Ca and Mg, a clear HF-HCl solution should be obtained at
112 this stage, without precipitate of sparingly soluble fluorides of alkali earth elements. In case a
113 solid residue of refractory minerals (e.g. zircon) is observed, this should be isolated,
114

1
2
3 114 transferred to a steel jacketed, Teflon high pressure vessel for being decomposed with HF at Article Online
DOI: 10.1039/D1JA00397F
4
5 115 elevated temperature, and the resulting liquid added to the main sample solution.
6
7

8 116

9
10 117 *Separation chemistry:*
11

12
13 118 The column of DGA resin is first preconditioned with one column reservoir (ca. 6 ml) of 4M
14
15 119 HCl. Then, the centrifuged HF-HCl sample solution, roughly 4M in HCl, is loaded onto the resin,
16
17 120 which takes a brown colour and is rather soon saturated in Fe(III), as indicated by the bright
18
19 121 yellow colour of the effluent. The REE are extracted at that stage. Following loading, the
20
21 122 column is rinsed with 2 x 1 ml of 4M HCl to get rid of the interstitial sample solution. Then, the
22
23 123 eluant is switched to nitric acid in order to strip iron while leaving the REE strongly held by the
24
25 124 column. The decrease of Fe (III) to a negligible level is verified using an ammonium thiocyanate
26
27 125 colorimetric test carried out on a few μl of each successive fraction, until the dark red colour
28
29 126 gives way to a very pale pink. Four fractions of 1 ml of 3M HNO_3 are usually sufficient to get
30
31 127 rid of iron, but a twice larger volume can be passed through the column without causing any
32
33 128 breakthrough of the light lanthanides. Then, the eluant is switched back to the hydrochloric
34
35 129 medium to start the sequential elution of the REE. After 1 ml of 3M HCl to effect the acid
36
37 130 transition, a pre-Nd fraction containing essentially all La and Ce, and a large part of Pr is eluted
38
39 131 with 5 ml of 2M HCl. Then, a Nd cut suitable for MC-ICP-MS isotope ratio analyses is obtained
40
41 132 with 4 ml of 1.25M HCl. If required, Sm can be recovered in a further fraction of 5 ml of 0.70
42
43 133 M HCl. Next, the heavier lanthanides (from Eu to Lu) are stripped as a group with one column
44
45 134 reservoir (~6 ml) of very dilute, 0.05M HCl. Finally, the column is washed with one reservoir of
46
47 135 0.1M HCl-0.29M HF followed by one further reservoir of 0.05M HCl. This protocol is outlined
48
49 136 in Table 1 and displayed in Figure 1. The total duration of the separation process is about 5
50
51 137 hours.
52

53 138

54 139 *Mass spectrometry*

55 140 After evaporation to dryness to get rid of HCl, the Nd fraction was dissolved in an appropriate
56
57 141 volume of 0.05M HNO_3 prior to isotope ratios analysis by MC-ICP-MS. The operating
58
59 142 parameters of the Neptune Plus instrument are detailed in Table 2.
60

143 Results

View Article Online
DOI: 10.1039/D1JA00397F

144 Two international SRMs, representative of the iron-rich matrices for which the separation
145 procedure was developed, have been used to demonstrate its applicability, namely, IF-G, an
146 Archaean (ca. 3.8 Ga) banded iron from Isua (Greenland), and BX-N, a Cretaceous (ca. 100 Ma)
147 bauxite (Al-rich laterite) from Brignoles (France). Both geostandards were prepared by, and
148 are available from SARM-CRPG (Nancy, France). Their recommended major element
149 composition and Nd concentration are given in Table 3, along with abundances measured in
150 this work. Interestingly, these two SRMs have highly contrasting REE abundances, with Nd
151 contents differing by two orders of magnitude, viz. $1.7 \mu\text{g g}^{-1}$ in the chemical precipitate IF-G
152 against $163 \mu\text{g g}^{-1}$ in the Al-rich laterite (leaching residue) BX-N. This contrast provides a good
153 means to assess the potential of our separation method on a wide range of Nd/matrix ratios.

154

155 $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ isotope ratios

156 The results of multiple replicate analyses of Nd separated from the two Fe-rich SRMs are listed
157 in Table S1, together with measurements of the Nd isotope standard JNdi-1.¹⁴ The raw
158 $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for the isobaric interference of ^{144}Sm on
159 ^{144}Nd and also for instrumental mass bias by normalization to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ by using
160 an exponential function. It can be seen that the within-run (or internal) precisions of the
161 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured for the two rock samples ($6 \times 10^{-6} < 2\text{SE} < 10^{-5}$ for IF-G ; $4 \times 10^{-6} <$
162 $2\text{SE} < 7 \times 10^{-6}$ for BX-N) do not differ significantly from those achieved for the chemically pure
163 JNdi-1 standard ($5 \times 10^{-6} < 2\text{SE} < 10^{-5}$), thereby demonstrating the efficiency of our single
164 column separation procedure. Likewise, the uncertainty of the grand mean of the replicate
165 analyses is only marginally larger than those of individual measurements, and not much
166 different from that obtained on the pure Nd standard. The efficiency of the separation
167 protocol and the robustness of the correction for the effect of the ^{144}Sm interference were
168 further checked by preparing several aliquots of the JNdi-1 isotopic standard spiked with
169 variable amounts of Sm in order to encompass the range of Sm/Nd ratio found in natural
170 samples. Half of these aliquots were processed through the DGA column in order to separate
171 Nd from Sm prior to MC-ICP-MS measurements, while the rest of the Sm-Nd mixtures were
172 analysed without further treatment. The $^{143}\text{Nd}/^{144}\text{Nd}$ were compared with repeat analyses of

1
2
3 173 the Sm-free JNdi-1 solution as reference. The results listed in table S2 and depicted in Fig. S1
4 show that, whatever the Sm/Nd ratios of the mixtures, the Sm abundance in the Nd separate
5 174 is reduced by at least a factor of 10^3 . Also, it can be seen that, within analytical precision, the
6 175 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured on the separated mixtures (0.512089 , $2\text{SD} = 5 \times 10^{-6}$, $N=5$) do not
7 176 differ from those measured on the pure JNdi-1 solution (0.512087 , $2\text{SD} = 7 \times 10^{-6}$, $N=6$) thereby
8 177 demonstrating the overall adequacy of the interference correction procedure. Finally, the
9 178 results obtained on mixed Sm-Nd solutions analysed without any mutual separation show that
10 179 accurate $^{143}\text{Nd}/^{144}\text{Nd}$ data still can be obtained (0.512091 , $2\text{SD} = 9 \times 10^{-6}$, $N=4$). This further
11 180 demonstrates that the interference correction of ^{144}Sm during MC-ICP-MS analyses is
12 181 extremely robust, a feature already well established, both by in situ laser ablation
13 182 measurements of accessory minerals (e.g.,¹⁶⁻¹⁷) and by analyses of bulk LREE fractions
14 183 separated from matrix elements (e.g.,¹⁸). The accuracy of our data can be assessed by the good
15 184 agreement of the values of $^{145}\text{Nd}/^{144}\text{Nd}$ (constant) measured on the two SRMs and JNdi-1 and,
16 185 for the radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, by a comparison with published values on IFG (Fig. 2). As
17 186 far as we know, there is no Nd isotope data available for BX-N. Overall, these results highlight
18 187 the good external reproducibility and accuracy of the method, thereby demonstrating its
19 188 capacity to provide, in a very straightforward way, Nd fractions suitable for MC-ICP-MS isotope
20 189 ratios determinations.
21 190

191

192

193 **Chemical yields**

194 Due to the small difference of their distribution ratios, the short column used in this work does
195 not allow to resolve the elution peaks of Pr and Nd, thus requiring making a trade-off between
196 the chemical yield of Nd and its purity with regard to this element. However, the Fig. 1 show
197 that about 80-90% of Nd can be recovered in a fraction containing <15 % of Pr and <1% Ce.
198 Although an overwhelming proportion of the REE were extracted by the DGA column under
199 these conditions, the data of Table S3 show that minor amounts (in the 2-10% range) were
200 found in the loading fractions. It is not clear at present whether these determinations are
201 significant or have been biased to spuriously high values due to polyatomic interferences
202 based on the relatively heavy elements Fe and Cl present in large amounts in these fractions.

1
2
3 203 However, the data probably document a real leak of REE during the loading steps. In this case
4 the lost fraction would reflect the presence of non extractable species, likely fluorides. Further
5 204 work showed that reducing the amount of HF by a factor of two while leaving the sample
6 205 weight unchanged (100 mg) allows reducing the early loss of REE to less than 10% bringing a
7 206 positive consequence on the Nd recovery (i.e. 90 – 95 %).
8 207

13 208 **Procedural blanks**

15 209 Nd concentrations measured in the three acids used in the sample dissolution and Nd
16 210 separation step are given in Table 4, along with column and total procedural blanks. It can be
17 211 concluded that the contamination associated to the method is negligible with respect to the
18 212 amount of Nd (typically in the 0.2 – 15 µg range) processed.
19 213

21 214 **Discussion**

23 215 **Sample decomposition**

25 216 From an analytical point of view, a critical feature of the iron-rich, silicate sediments object of
26 217 this study is the near absence of alkali earths from their bulk composition. For this reason, a
27 218 major problem inherent in any dissolution with hydrofluoric acid is avoided, namely the
28 219 formation of poorly soluble fluorides of Ca and Mg, and more complex species based on these
29 220 elements.¹⁹ These precipitates sequester significant amounts of many trace elements of
30 221 interest, including the REE, and they must be destroyed before subsequent analytical steps,
31 222 by means of lengthy treatments with other acids, the most efficient of which (H₂SO₄ and
32 223 HClO₄) are not welcome.

33 224 No such problem arises with banded iron ores and laterites, essentially composed of silica,
34 225 and iron oxides, +/- alumina, all soluble in HF-HCl mixtures. As a result, clear sample solutions
35 226 are achieved, and they could be used without further treatment for isolating the REE from
36 227 unwanted matrix elements, in so far as a separation procedure operating in HF-HCl mixture is
37 228 made available.

39 229 **Chemical separation**

1
2
3 230 By virtue of their greatly improved selectivity, chemical separation methods based on
4 extraction chromatography have largely superseded those using cation exchange.²⁰ One of
5 231 these methods, based on the ligand tetra-n-octyldiglycolamide (TODGA, hereafter
6 232 abbreviated to DGA) is particularly attractive in the present case, for several reasons. First,
7 233 and in contrast with the other widely used EXC resins TRU and RE Spec, operated in nitric
8 234 media, the DGA resin is able to extract the REE in both HCl and HNO₃. The LN resin, based on
9 235 the classical HDEHP extractant can also be used in hydrochloric medium, but the distribution
10 236 ratios of the light lanthanides are relatively small, and decrease drastically with increasing acid
11 237 strength. Moreover, its selectivity against other several tri- and tetravalent elements,
12 238 including iron, is relatively poor. On the contrary, the distribution ratios of the REE on the DGA
13 239 resin increase as a function of increasing acid strength, and as the function of atomic number
14 240 along the lanthanide series. When the resin is used in nitric acid medium, the extraction of
15 241 calcium is fairly important, and it is necessary to use concentrated acid to get rid of that
16 242 element.²¹ Although Ca is not a source of concern in the specific samples investigated in this
17 243 work, available distribution data indicate that it is more weakly extracted from HCl medium.²²
18 244
19 245 However, there is another, much more decisive reason to choose the DGA resin to separate
20 246 the REE from iron-rich matrices. Indeed, the presence of macro amounts of Fe is not a source
21 247 of concern but instead actually enhances the extraction. This synergistic effect was discovered
22 248 by Horwitz et al.⁷ who found that the uptake of lanthanides and trivalent actinides increases
23 249 by several orders of magnitude when the extractions takes place from HCl containing mg/L
24 250 quantities of anionic chlorides, including ferric iron. Horwitz et al.⁷ further noticed that the
25 251 synergistic effect persists, even when the amount of metal chloride exceeds the capacity of
26 252 the resin. Based on these observations, it was decided to develop a separation scheme
27 253 specifically adapted to iron-rich silicate rocks.

28 254 The elution behaviour of a large spectrum of unwanted major and trace elements is shown in
29 255 Table S2. It can be seen that ≥ 98 % of the amount of most of them are found in the loading
30 256 fractions plus initial 4M HCl column rinse. This indicates that these elements (Be, V, Cr, Mn,
31 257 Co, Ni, Cu, As, Rb, Sr, Zr, Cd, Sn, Cs, Ba, Hf, Pb, Bi and Th), are not extracted by the resin from
32 258 the HF-HCl mixed medium. Likewise, 92 to 98% of several further trace elements (Na, Mg, Al,
33 259 Ca, Sc, Ti, Zn, Ge, Nb, Mo, Sb and U) are recovered in the loading fraction, documenting an
34 260

260 essentially passive behavior, while few elements such as Ga and Tl are significantly retained
261 (ca. $\geq 70\%$).

262 The behaviour of iron is particularly noteworthy. As observed visually during the experiment,
263 and can be checked from the results of the four successive loading fractions, iron was
264 extracted, but the column was soon saturated, since about 80% of Fe (III) occur in the three
265 last ml of sample loading. Nevertheless, some 90% of the REE were extracted by the resin.
266 Therefore, the observation of Horwitz et al. that the synergistic effect persists even when the
267 amount of iron chloride exceeds the capacity of the resin is confirmed. It was noticed that Ga
268 and Tl, two other elements forming very stable chloride complexes, are also significantly
269 retained. Following the mechanism proposed by Horwitz et al, this is interpreted to reflect the
270 strong co-extraction of their tetrachloro-complexes, in replacement of the Cl⁻ counter ion
271 required for charge neutrality in the Ln-DGA complex. As Fe, these elements were readily
272 released from the resin when the column was rinsed with nitric acid.

273 It is further observed that, even in the presence of a fairly high concentration of HF, the DGA
274 resin is still able to extract most of the lanthanides from ca. 4M HCl containing large amounts
275 of Fe(III). However, it is most likely that fluoride complexing was responsible for the early loss
276 of some 10-20% of the lanthanides during the column loading step. Whether this lost
277 component reflects extremely fine-grained insoluble compounds (not removed by
278 centrifugation in the absence of alkaline earth-based carriers) or soluble molecular species,
279 not extractable by the diglycolamide ligand, or both, is not clear at present. However,
280 additional experiments show that a twofold decrease of the amount of HF used for dissolution
281 (that is, 1 ml for 0.1 g sample) permits to reduce the early loss of lanthanides to less than 10%.
282 Thus, provided a too large excess of HF is not used for dissolving the samples, the important
283 saving of time inherent in the direct loading of the column with the HCl-HF mixture has a rather
284 limited cost in terms of chemical yield. The next fractions of nitric acid achieve a rapid stripping
285 of the ca. 30 % of iron that were initially extracted, while the REE are still strongly held by
286 virtue of the relatively high (3M) acid strength. At this stage, almost all matrix elements have
287 been removed. For the subsequent steps, hydrochloric acid is used again, because it allows
288 the sequential elution of the LREE to be achieved,²³⁻²⁵ as depicted in Fig. 1. The lanthanides
289 heavier than Nd are still retained on the column, and need more and more dilute HCl to be
290 stripped from the DGA resin. This can be made by using 0.7M HCl for Sm, and then 0.05M HCl

1
2
3 291 in order to elute as a group the M- and HREE. Finally, washing the column with a dilute HCl-HF mixture strips the rest of the few elements still present on the column, mainly Th. The
4
5 292 comparison of the elution profiles (Fig. 1) obtained for the two studied international SRMs,
6
7 293 and an additional BIF sample from the Eastern Indian Craton, even richer in iron (BIF-2, 59.3
8
9 294 wt% Fe₂O₃), shows that the position of the elution peaks of the individual LREE is quite stable,
10
11 295 thereby demonstrating the robustness of the method in the 20-60 wt% range of total iron as
12
13 296 Fe₂O₃. It is further noticed that, in all cases, the Nd peak is well resolved from those of Sm and
14
15 297 Ce, while the overlap by the tail of the Pr peak can be reduced to < 10% without important
16
17 298 loss of Nd. This is a noteworthy achievement for a single column chromatographic separation.
18
19 299

20
21 300 Using a single column of DGA resin for separating Nd is not new²³⁻²⁵ but, as far as we are aware,
22
23 301 our protocol is the first to load the sample onto the column in hydrochloric acid medium, an
24
25 302 approach particularly well suited for high-Fe samples. Moreover, in so far as the samples are
26
27 303 sufficiently poor in alkaline earth elements, such as the rocks targeted by this study, the HF-
28
29 304 HCl solution resulting from the sample decomposition can be directly loaded onto the column,
30
31 305 without any further treatment. This feature of our protocol alleviates the need for time-
32
33 306 consuming evaporation to dryness of the dissolved sample and repeated treatments of the
34
35 307 residue with nitric acid, thereby making the whole procedure extremely straightforward.

36
37 308 Indeed, following sample weighing and the addition of HCl and HF acids (taking a few minutes
38
39 309 per sample), dissolution is made overnight. After centrifugation of the resulting solution (some
40
41 310 10 minutes), the column separation procedures takes less than 5 hours only. Thus, starting
42
43 311 from the sample powder, 6 to 12 neodymium fractions ready for MC-ICP-MS can be obtained
44
45 312 in less than 24 hours with relatively little analyst time and effort.

46 313

47 48 49 314 **Conclusion**

50
51 315 The aim of this work was to develop a new procedure based on the unique properties of the
52
53 316 diglycolamide-based EXC resin (DGA) in hydrochloric acid medium containing large amounts
54
55 317 of ferric ion⁷ and evaluate its potential for geochemical applications, specifically, ¹⁴³Nd/¹⁴⁴Nd
56
57 318 isotope ratio analyses. The resulting protocol enables the analyst to separate in a very
58
59 319 straightforward way the lanthanides from iron-rich silicate materials such as Banded Iron ores
60

1
2
3 320 or lateritic samples, and to isolate in a single step a Nd fraction suitable for isotope ratio
4 measurements by MC-ICP-MS. The method is extremely rapid, by virtue of two major
5 321 features : (i) the solution obtained after sample dissolution with an HF-HCl mixture is directed
6 322 to the DGA EXC column for separation without any intervening step, thereby circumventing
7 323 the time-consuming evaporation and conversion steps inherent in conventional methods; and
8 324 (ii) the separation is performed by using a single, relatively short column allowing fast, gravity
9 325 driven flow rates. Besides its obvious interest in terms of analyst labor, the method is very
10 326 simple, as it involves only three most common minerals acids and does not require a fume
11 327 hood or any sophisticated piece of equipment. In addition, it is believed that it might be
12 328 extended rather easily to other radiogenic isotopic systems involving lanthanide elements.
13 329 Indeed, La and Ce might be recovered ahead of Nd and further purified from each other by
14 330 using conventional HDEHP or DGA resins, or a combination thereof. Likewise, after
15 331 evaporation to dryness to remove silicon, the loading + rinse fraction containing Fe (III) and
16 332 most of the accompanying elements might be used to separate other elements of radiogenic
17 333 isotope interest by EXC, as described elsewhere.²⁶ Finally, it is suggested that the procedure
18 334 outlined in this paper might deserve further work to evaluate its potential for processing iron-
19 335 rich meteorites (siderites, pallasites).
20 336

337 **Conflicts of interest**

338 There are no conflicts to declare

340 **Acknowledgements**

341 We thank Chantal Bosq for preparing high purity acids and Jordan Wright for providing The
342 BIF-2 sample used during the setup of our procedure. We also thank Mhammed Benbakkar for
343 major element analysis on the ICP-AES. We thank three anonymous referees for their
344 perceptive reviews which led to significant improvements of the manuscript and Ziva
345 Whitelock for editorial handling. We thank the Geological Survey of Japan for providing the
346 isotopic standard JNdi-1. This research was financed by the French Government Laboratory of
347 Excellence Initiative n°ANR-10-LABX-0006, the Région Auvergne and the European Regional
348 Development Fund. This is Laboratory of Excellence ClerVolc contribution N° 514.

349 Author contributions

350 A.G. and C.P. designed the analytical procedure, carried out the early tests and isotopic
351 measurements on the standard reference materials. K.S. prepared and analysed the trace
352 element data. A.G. and C.P. wrote the main paper. All authors discussed the results and
353 commented on the manuscript at all stages.

354

355 References

- 356 1 A. Trendall, in *Encyclopedia of geology*, ed. R. Selley, R. Cocks and I. Plimer, Elsevier,
357 Academic Press, 2005, 37-42.
- 358
- 359 2 A. Bekker, N.J. Planavsky, B. Krapez, B. Rasmussen, A. Hofmann, J.F. Slack, O.J. Rouxel, K.O.
360 Konhauser, in *Treatise on Geochemistry*, ed. H. Holland and K. Turekian, Elsevier, Netherlands,
361 2014, **9**, 561-628.
- 362
- 363 3 P. Cloud, *Economic Geology.*, 1973, **68**, 1135–1143.
- 364
- 365 4 G.J.J. Aleva, *Laterite, Concepts, Geology, Morphology, and Chemistry*, ISRIC, Netherlands,
366 1994.
- 367
- 368 5 Y. Tardy, *Petrology of laterites and tropical soils*, Taylor and Francis group, Netherlands,
369 1997.
- 370
- 371 6 A.D. Dalvi, W.G. Bacon and R.C. Osborne, *The past and the future of nickel laterites*. PDAC
372 International Convention, Trade Show and Investors Exchange, March 2004, 1-27.
- 373
- 374 7 E.P. Horwitz, D.R. McAlister and A.H. Thakkar, *Solvent Extr. Ion Exch.*, 2008, **26**, 12-14.
- 375
- 376 8 K. Govindaraju, *Geostand. Newsletter*, 1995, **19**, 55-96.
- 377
- 378 9 K. Govindaraju, and I. Roelandts, *Geostand. Newsletter*, 1989, **13**, 5-67.
- 379
- 380 10 B.W. Alexander, M. Bau and P. Andersson, *Earth Planet. Sci. Lett.*, 2009, **283**, 144-155.
- 381
- 382 11 S. Viehmann, M. Bau, B. Bühn, E.L. Dantas, F.R.D. Andrade and D.H.G. Walde, *Precambrian*
383 *Research*, 2016, **282**, 74-96.
- 384
- 385 12 G. Caro, P. Morino, S.J. Mojzsis, N.L. Cates and W. Bleeker, *Earth Planet. Sci. Lett.*, 2017,
386 **457**, 23–37.
- 387
- 388 13 P. Morino, PhD thesis, University of Lorraine, 2017.
- 389

- 1
2
3 390 14 T. Tanaka, S. Togashi, H. Kamioka, H. Amakawa, H. Kagami and 14 others, *Chem. Geol.*,
4 391 2000, **168**, 279–281. Article Online
DOI: 10.1059/D13A00397F
- 5 392
6 393 15 *GeoReM Data Base*, <http://georem.mpch-mainz.gwdg.de>.
7 394
- 8 395 16 C.R.M. McFarlane and M.T. McCulloch, *Chem. Geol.*, 2007, **245**, 45-60.
9 396
- 10 397 17 C. Fisher, C.R.M. McFarlane, J.M. Hanchar, M.D. Schmitz, P.J. Sylvester, R. Lam and H.P.
11 398 Longerich, *Chem. Geol.*, 2011, **284**, 1-20.
12 399
- 13 400 18 M.E. Sánchez-Lorda, S. García de Madinabeitia, C. Pin and J.I. Gil Ibarguchia, *Int. J. Mass*
14 401 *Spectrom.*, 2013, **333**, 34-43.
15 402
- 16 403 19 Z. Šulcek and P. Povondra, *Methods of decomposition in inorganic analysis*. CRC Press, Boca
17 404 Raton, FL, USA, 1989.
18 405
- 19 406 20 C. Pin and J. Rodriguez, in *Treatise on Geochemistry*, ed. H. Holland and K. Turekian, Elsevier,
20 407 Netherlands, 2014, **15**, 147-170.
21 408
- 22 409 21 A. Pourmand and N. Dauphas, *Talanta*, 2010, **81**, 741-753.
23 410
24 411
- 25 412 22 E.P. Horwitz, D.R. McAlister, A.H. Bond and R.E. Barrans Jr, *Solvent Extr. Ion Exch.*, 2005, **23**,
26 413 319-344.
27 414
- 28 415 23 Y. Wang, X. Huang, Y. Sun, S. Zhao and Y. Yue, *Anal. Methods*, 2017, **9**, 3531-3540.
29 416
- 30 417 24 A. Retzmann, T. Zimmermann, D. Pröfrock, T. Prohaska and J. Irrgeher, *Anal. Bioanal.*
31 418 *Chem.*, 2017, **409**, 5463-5480.
32 419
- 33 420 25 Z.-Y. Chu, M.-J. Wang, C.-F. Li, Y.-H. Yang, J.-J. Xu, W. Wang and J.-H. Guo, *J. Anal. At.*
34 421 *Spectrom.*, 2019, **34**, 2053-2060.
35 422
- 36 423 26 C. Pin and A. Gannoun, *Anal. Chem.*, 2017, **89**, 2411-2417.
37 424
38 425
39 426
40 427
41 428
42 429
43 430
44 431
45 432
46 433
47 434
48 435
49 436
50
51
52
53
54
55
56
57
58
59
60

1
2
3 437
4 438
5 439
6 440

Figure captions

8
9 441

11 442 **Fig. 1:** Elution curves on DGA single column performed for three natural samples. The first two
12 443 are international standard reference materials of bauxite (BX-N) and Banded Iron Formation
14 444 (IF-G). The third is a BIF sample from Eastern Indian Craton (BIF-2). Despite the chemically
16 445 distinct matrices between these samples, the recovery of REE is reproducible within the given
18 446 step.

19 447

21 448 **Fig. 2:** Nd Isotope composition for each individual digestion of the international reference
23 449 material IF-G and BX-N processed through the protocol described in this study. Single
25 450 measurements are plotted with their standard errors (± 2 S.E) while the average values are
27 451 plotted with their external reproducibility (± 2 S.D). Literature data for IF-G standard are also
29 452 reported.

31 453

Downloaded on 12/10/2021 16:59 AM.
Published on 09 December 2021.

454

View Article Online
DOI: 10.1039/D1JA00397F

455 **Table 1** Outline of the separation scheme enabling the isolation of purified Nd from
 456 iron-rich samples by single column extraction chromatography.

	Reagents	Volume (mL)
DGA (500 mg)		
Pre-conditioning	4 M HCl	6
Sample loading	4 M HCl	2 × 3.5
Column rinse	4 M HCl	2 × 1
Iron stripping	3 M HNO ₃	4 × 1
Elution of LREE	3 M HCl	1
	2 M HCl	5 × 1
Elution of Nd (Elution of Sm, optional)	1.25 M HCl	4 × 1
	0.70 M HCl	5 × 1
Elution of HREE	0.05 M HCl	5 × 1
Cleaning before storage	0.1 M HCl - 0.29 M HF	6
	0.05 M HCl	6

457

458

459

460
461**Table 2** Instrument settings and data acquisition parameters for isotope ratio measurements of Nd by MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific)

Analysis	Nd isotopes						
Laboratory	Magmas et Volcans						
MC-ICP-MS model	Thermo Neptune Plus						
Plasma condition	Wet (cyclonic spray chamber)						
RF power	1200 W						
Resistors	10 ¹¹ Ohms						
Resolution	Low (M/ΔM ~ 400)						
Cool gas flow (Ar)	15 L.min ⁻¹						
Auxiliary gas (Ar)	0.7 - 0.8 L.min ⁻¹ (optimised daily)						
Sample gas (Ar)	0.9 - 1.1 L.min ⁻¹ (optimised daily)						
Sample uptake	100 μL.min ⁻¹						
Sample cone	Standard						
Skimmer cone	H						
Scanning mode	Static multi-collection						
Integration time	8.4 s						
Number of cycles	60						
Number of blocks	1						
Cup configuration	L2	L1	C	H1	H2	H3	H4
Mass collected	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁸ Nd	¹⁵⁰ Nd

462

463

464 **Table 3** Major and some REE trace element abundances in the standard reference materials investigated during this
 465 study (IF-G and BX-N) by ICP-AES and ICP-QMS, respectively

View Article Online
 DOI: 10.1039/D1JA00397F

(Wt.%)	IF-G (Iron Formation)				BX-N (Bauxite)			
	This study	Number	Ref. ⁸	Number	This study	Number	Ref. ⁹	Number
SiO ₂	40.15 ± 0.05	3	41.20 ± 0.67	81	7.11 ± 0.06	3	7.40 ± 0.46	37
Al ₂ O ₃	0.34 ± 0.03	3	0.15 ± 0.09	76	53.38 ± 0.02	3	54.21 ± 1.16	34
Fe ₂ O _{3T}	54.98 ± 0.17	3	55.85 ± 0.99	79	23.22 ± 0.08	3	23.2 ± 1.0	11
MgO	2.23 ± 0.02	3	1.89 ± 0.16	84	0.28 ± 0.01	3	0.11 ± 0.08	29
CaO	1.47 ± 0.03	3	1.55 ± 0.15	83	0.04 ± 0.02	3	0.17 ± 0.14	34
(ppm)								
La	2.66 ± 0.86	5	2.8 ± 0.6	24	353 ± 2	5	355 ± 76	12
Ce	3.9 ± 1.1	5	4.0 ± 0.8	16	544 ± 12	5	520 ± 43	13
Nd	1.7 ± 0.2	5	1.8 ± 0.2	15	163 ± 2	5	163 ± 31	7
Sm	0.38 ± 0.01	5	0.4 ± 0.1	19	22.1 ± 0.2	5	22.0 ± 3.4	8
Yb	0.58 ± 0.01	5	0.6 ± 0.3	22	11.0 ± 0.1	5	11.6 ± 2.1	8

466

467

Downloaded on 12/10/2021 16:59 AM.
 Published on 09 December 2021. Downloaded from www.rsc.org on 12/10/2021 16:59 AM.

Journal of Analytical Atomic Spectrometry Accepted Manuscript

468 **Table 4** Reagent, column and total procedural Nd blanks measured by ICP-QMSView Article Online
DOI: 10.1039/D1JA00397F

	Reagent blanks (pg.mL ⁻¹)				Used column blank	Total procedural blank
	29M HF	6M HCl	14M HNO ₃	H ₂ O (18.2 MΩ cm)	(pg)	(pg)
Range	0.3 - 0.7	0.2 - 0.4	0.4 - 0.9	0.01 - 0.04	5 - 12	17 - 32
Mean ± 1SD	0.4 ± 0.2	0.3 ± 0.1	0.6 ± 0.2	0.02 ± 0.02	9 ± 3	25 ± 6
Number	3	2	3	4	5	7

469

470

471

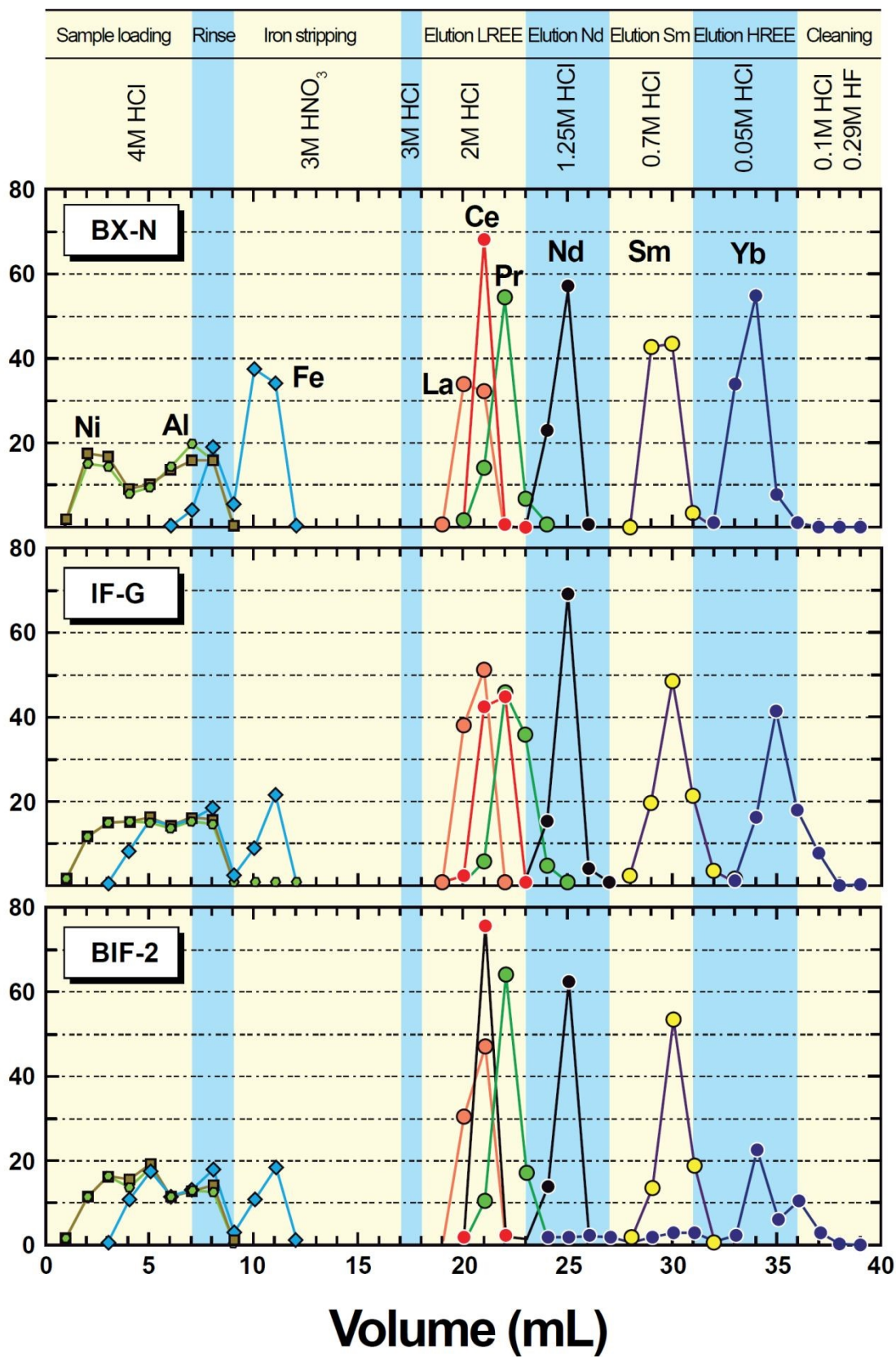


Figure 1

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

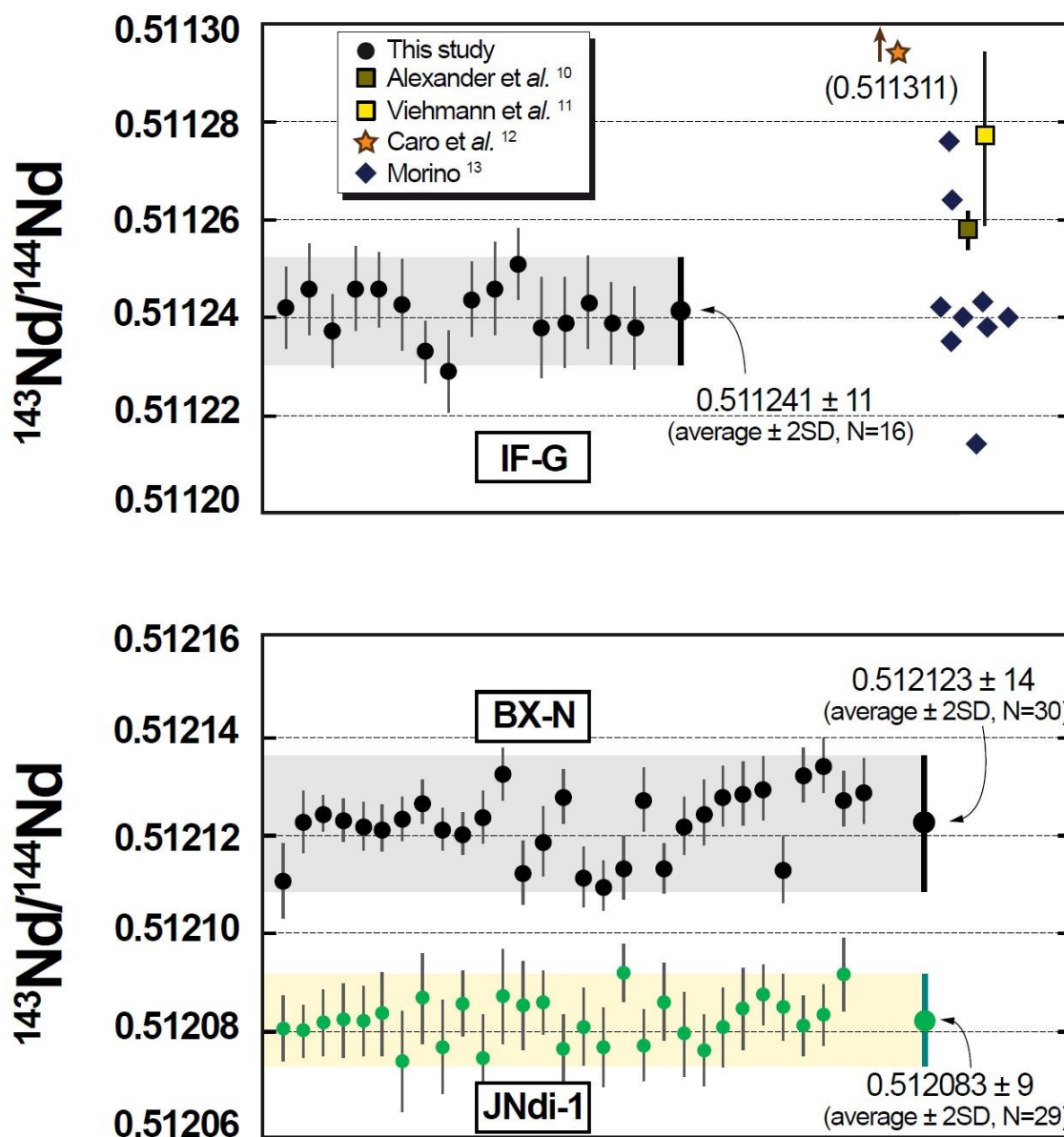


Figure 2