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## A new chemical separation procedure for the determination of rare earth elements and yttrium abundances in carbonates by ICP-MS

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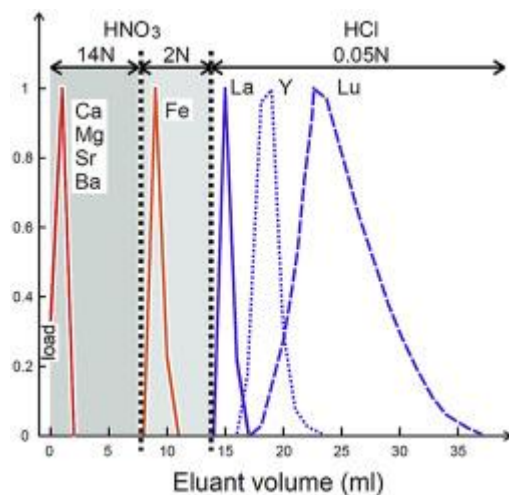
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### Abstract :

The determination of rare earth elements (REEs) and Y in carbonates can be complicated by low REE abundances and the presence of significant amounts of Ba resulting in problematic interferences when analyzed by ICP-MS. We describe here a novel ion-exchange method using the DGA resin (TODGA), combined with addition of a Tm spike, which allows the separation of the REEs+Y as a whole prior to analysis using an Element XR ICP-MS. This method was validated with results obtained on three different reference carbonate materials (CAL-S, JLS-1 and BEAN, an in-house standard), yielding reproducibility levels better than 3% (RSD) in most cases. This new separation scheme is particularly well suited for carbonate samples having very low REE contents, but could be equally applied to various rock types and organic-rich sample matrices whenever quantitative Ba removal is required.

## Graphical abstract



## Highlights

- ▶ A novel cation exchange method was developed for the analysis of REE+Y in carbonates by ICP-MS.
- ▶ Measurements of REEs were free of Ba interferences.
- ▶ Low blanks and high enrichment-factor for REEs+Y are achieved, and allow the analysis of ultradepleted samples.
- ▶ Precision better than 3 % RSD was achieved for most elements analyzed.

**Keywords** : Rare Earth Elements, DGA resin, carbonate, ICP-MS, CAL-S, JLs-1

## 48 **1. Introduction**

49

50           The lanthanides and other rare earth elements (REEs) are amongst the most studied  
51 chemical elements in geochemistry, being of prime importance for addressing a wide range of  
52 issues in earth and planetary sciences, such as e.g. the condensation of the first solids in the  
53 Solar System, the formation of magmas, the reconstruction of present and past ocean  
54 circulation patterns [e.g., 1]. The usefulness of REE as unique tracers of geochemical  
55 processes comes first from their overall very consistent behavior in nature, which enables the  
56 modelling of their abundance in geochemical reservoirs. Most REEs are trivalent and, as a  
57 consequence, cannot be easily fractionated from each other during petrogenetic processes.  
58 However, two REEs, Ce and Eu, can also exist in different valence states ( $\text{Ce}^{4+}$  and  $\text{Eu}^{2+}$ ,

59 respectively), which implies that they can be decoupled from the other REEs, resulting in  
60 quantifiable abundance anomalies, which, in turn, can be used to provide constraints on rock  
61 formation processes and other redox-sensitive bio-geochemical reactions. Another important  
62 field of application of REE geochemistry is based on the use of particular radioactive and  
63 radiogenic isotopes for geochronological purposes (i.e. the La/Ce, Sm/Nd, and Lu/Hf isotope  
64 systematics).

65 Over the recent years, an increasing interest has been placed in the application of  
66 REEs to both biogenic and chemical carbonates, as chemical tracers of the composition of  
67 seawater and other natural waters. For instance, the abundances of REEs in various carbonate  
68 material (e.g. stromatolites, shells, corals, stalagmites, methane-derived carbonates,  
69 hydrothermal carbonates) can provide unique constraints on the chemistry of oceans [e.g., 2-  
70 4], to characterize the fluids from which these mineral phases were precipitated [e.g., 5], to  
71 reconstruct past climatic changes [e.g., 6], or to track pollution linked to medical or industrial  
72 uses [7-9].

73 Since the 1990s, ICP-MS has become the method of choice for determining trace  
74 element concentrations in rocks, minerals and waters. A multitude of protocols have been  
75 described to date, and successfully applied to a wide range of materials [e.g., 10-17]. The very  
76 high sensitivity of ICP-MS instruments makes it possible to determine very low trace element  
77 abundances in solution, with dilution factors (=solution weight/sample weight) up to several  
78 tens of thousands. Compared to previous state-of-the-art techniques, such as isotope dilution-  
79 thermo-ionization mass spectrometry (ID-TIMS) or instrumental neutron activation analyses  
80 (INAA), the use of ICP-MS allows high sample throughput at comparatively low analytical  
81 costs. The dissolution of biogenic and chemical carbonate samples is generally relatively  
82 straightforward, so that high quality trace element data can be obtained in the vast majority of  
83 case studies [e.g., 2, 4, 6, 7 among many others]. One potential difficulty in analyzing

84 carbonates is that they are typically characterized by much lower REE abundances compared  
85 to other commonly studied rocks, such as basalts, granites and sediments. Using ICP-MS  
86 techniques, this difficulty can be generally successfully overcome by simply analyzing less  
87 diluted solutions. Another important issue when measuring REE concentrations in carbonates  
88 is that they can contain substantial amounts of Ba. During the course of ICP-MS analysis, a  
89 fraction of Ba atoms present in the plasma forms oxides, which can generate isobaric  
90 interferences with Eu isotopes (e.g.  $^{135}\text{Ba}^{16}\text{O}^+$  and  $^{134}\text{BaOH}^+$  with  $^{151}\text{Eu}$ ,  $^{137}\text{Ba}^{16}\text{O}$  and  
91  $^{136}\text{BaOH}^+$  with  $^{153}\text{Eu}$  [e.g., 14, 18-19]). Uncorrected isobaric interferences cannot be neglected  
92 because they typically result in the occurrence of non-natural positive Eu anomalies in studied  
93 samples. In most cases, the presence of isobaric interferences on Eu can be successfully  
94 corrected by monitoring the oxide formation rate during an analytical ICP-MS session, using  
95 a mono-elemental solution of Ba. Many rocks, such as basalts, granites, terrigenous sediments  
96 or peridotites commonly display Ba/Eu ratios  $< 1000$ . The contribution of Ba oxides to the  
97 151 or 153 Eu masses is not dominant here, and the correction is generally very satisfactory  
98 (Fig. 1). However, many marine or hydrothermal carbonates have much higher Ba/Eu ratios,  
99 frequently  $>10000$ . For these samples, the interference contribution to measured  $^{151}\text{Eu}$  and  
100  $^{153}\text{Eu}$  signals can become dominant. The corrections that can be made using estimates of  
101 oxide formation rates commonly yield Eu abundances with poor accuracy and/or associated  
102 with a relatively high uncertainty. The use of collision/reaction cells and/or of ICP-MS  
103 operated in high-resolution modes can provide efficient means for eliminating the formation  
104 of Ba oxides and allowing quantitative separation of  $\text{Eu}^+$  and  $\text{BaO}^+$  peaks, respectively.  
105 However, these options significantly reduce the signal intensities, and hence are generally not  
106 adapted to low-level samples such as carbonates. One alternative to resolve the specific  
107 problem raised by the potential occurrence of isobaric interferences upon carbonate analysis is  
108 to quantitatively separate REEs from Ba prior to ICP-MS measurements. Another advantage

109 of separating REEs is that it allows one to analyse less diluted solutions during ICP-MS  
110 measurements, hence improving the quality of data acquisition.

111         Several ion-exchange and diverse Fe-Mg hydroxide coprecipitation techniques have  
112 been developed for application to samples having low REE abundances [e.g., 10, 12, 20-28].  
113 Over the past twenty-five years, we have used one of these previously developed  
114 chromatographic methods, based on the use cation-exchange resins (e.g. 50WX12 or 50WX8,  
115 as first described by Strelow [29]), combined with the addition of a Tm spike in order to  
116 overcome the potential problem of any sample loss during handling and throughout the ion  
117 chromatography process [30]. It was initially designed for silicate rocks, and over time has  
118 proven particularly useful for analysing various minerals and rocks with very low REE  
119 abundances [e.g., 31-33]. The utility of this technique for measuring REE abundances in  
120 carbonates has been already demonstrated [9, 34]. However, this procedure also had some  
121 drawbacks, which required further improvements. First, the columns are small (1.6 ml resin),  
122 which restricts their use to small sample size only (<30 mg), hence being problematic when  
123 processing REE-depleted materials such as biogenic carbonates, for which larger amounts of  
124 material would be ideally required. Second, the procedure based on cation-exchange  
125 chromatography did not yield quantitative Ba removal, resulting in eluted solutions that still  
126 contain non-negligible amounts of this element. Finally, this procedure was also accompanied  
127 with poor recovery of Y, hence leading to non-reproducible determination of Y abundances.

128         Novel ion exchange resins have been developed and commercialized in recent years,  
129 including the DGA, normal resin. It is an extraction chromatographic resin based on  
130 N,N,N',N'-tetra-n-octyldiglycolamide extractant, commonly referred to as either DN Resin or  
131 TODGA in the literature. It has been previously used for the preconcentration of actinides and  
132 lanthanides from various samples for radioactive waste management [35, 36]. A complete set  
133 of partition coefficients has been published for this resin [37], and its capability for the

134 preconcentration of REEs for difficult geological samples has already been demonstrated [38,  
135 39]. In this study, we used the remarkable properties of this resin to separate the REEs from  
136 carbonates. We describe here a new procedure aimed at quantitatively separating REE from  
137 other elements in carbonate samples, and illustrate its utility using two international (JLs-1 and  
138 CAL-S) and one in-house standard from hereafter referred to as BEAN for **Brest carbonate**  
139 and available on request.

140

## 141 **2. Experimental techniques**

### 142 **Sample preparation and REE separation**

143 All sample preparations were conducted in a Class 1000 (ISO 6) clean laboratory. Deionized  
144 water purified with a Milli-Q system (Millipore®) at 18.2 M $\Omega$  (from hereafter referred to as  
145 ultrapure water) was used for material cleaning and acid dilutions. Nitric and hydrochloric  
146 acids were purified using sub-boiling systems.

147 Three carbonate reference materials displaying low REE abundances were selected for  
148 this study:

149 -JLs-1, a marine limestone prepared by the Geological Survey of Japan, which is one of the  
150 best characterized carbonate standard for REEs and Y abundances; this carbonate is depleted  
151 in REEs, but enriched in Ba, consequently displaying a Ba ( $\mu\text{g/g}$ )/Eu ( $\mu\text{g/g}$ ) ratio  $\sim 98000$ ;

152 -CAL-S, an Oxfordian limestone, locally known as “craie de Sorcy” (which is extensively  
153 exploited for its high purity), prepared and distributed twenty years ago by the Centre de  
154 Recherches Pétrographiques et Géochimiques (CRPG), Nancy; this carbonate has a low  
155 Ba/Eu ratio ( $\sim 80$ );

156 -BEAN (Brest carbonate), our in-house carbonate standard, is a pure calcium carbonate  
157 powder with a Ba/Eu ratio ~ 1300, sold by Acros Organics® (catalog number 42351), and  
158 available upon request to the first author.

159 Samples were precisely weighted and spiked with a solution of pure Tm. The spike  
160 solution was prepared with a Tm mono-elementary solution (custom grade, CGTM1-1,  
161 Inorganic Ventures Inc. ®). About 40 ng of Tm was added for 100-200 mg of sample.  
162 Samples were dissolved in a 30 ml screw-top Teflon vial. The spiked sample was first  
163 covered with a few ml of ultrapure water to prevent sample loss during effervescence, and  
164 drops of nitric acid were carefully added until the effervescence of the solution stops. About  
165 0.5 ml of 14 N HNO<sub>3</sub> was then added, and the vial was closed and let on a hot plate at 110°C  
166 during one hour to ensure the full dissolution of the sample. The vial was then opened, and  
167 after evaporation to dryness, the residue was taken up with 1.5 ml of 14 N HNO<sub>3</sub>.

168 Chromatographic columns (Triskem®, 2 ml, AC-142-TK) were loaded with 1 ml of  
169 DGA resin. A frit washer was placed on top of the resin bed to avoid any resin disturbance  
170 following subsequent addition of the eluant. As mentioned above, the properties of the DGA  
171 resin allow for a selective separation of REEs and Y as a group of coherent chemical elements  
172 (Fig. 2). To large extent, Ca, Mg and other alkaline earth metals are not adsorbed by the resin  
173 under concentrated (14 N) nitric conditions. Fe and many other transition metals are no more  
174 retained by the DGA resin with 2 N HNO<sub>3</sub> contrary to REEs . Previous work also showed that  
175 REEs are not retained by the resin under highly diluted HCl conditioning [34]. Based on the  
176 above findings, we set up a novel procedure that involves an initial cleaning step with 50 ml  
177 of 0.05 N HCl, followed by conditioning of the resin with 5 ml of 14 N HNO<sub>3</sub>. The sample  
178 solutions (corresponding to 100-200 mg of sample in 1.5 ml 14 N HNO<sub>3</sub>) were then loaded  
179 onto the columns, prior to subsequent addition of 7 ml 14 N HNO<sub>3</sub>, and 5 ml 2 N HNO<sub>3</sub>, in  
180 order to elute all matrix elements and Ba (Fig. 2). The final step corresponds to the elution of



181 REEs and Y using 25 ml 0.05 N HCl followed by evaporation on hotplate. After evaporation,  
182 note that the residues were the size of a pinhead, illustrating the efficiency of the procedure  
183 for separating Ca and other major matrix elements.

184 Columns were washed using 30 ml of 0.05 N HCl, followed by conditioning of the  
185 resin with 5 ml of 14 N HNO<sub>3</sub>, and were ready for next samples. While we did not evaluate  
186 the resin lifetime in this study, we systematically replaced the resin beds every four samples  
187 in order to prevent any effect related to resin aging, such as reduced binding efficiency.

188 For comparison, solutions of the three carbonate reference materials were prepared  
189 following the procedure described above. Aliquots containing the equivalent of 10 mg were  
190 placed in Teflon vials and evaporated to dryness. The residues were taken up in 10 ml of 0.4  
191 N HNO<sub>3</sub> with traces of HF (corresponding to a dilution factor of 1000), and analysed with the  
192 other solutions during the same analytical sessions.

193

#### 194 **Mass spectrometry**

195 The measurements were performed on a Thermo Scientific ELEMENT XR™  
196 spectrometer located at the “Pôle Spectrométrie Océan”, Institut Universitaire Européen de la  
197 Mer, Plouzané. Basic operating conditions, and selected masses are summarized in Table 1.  
198 Data were acquired with a routine sequence using the software supplied by the manufacturer,  
199 and processed as already reported in earlier studies. The reader is referred to previous papers  
200 where our routine sequence, calibration and calculations of concentrations with the Tm spike  
201 have been extensively described [e.g., 24-26, 30-33]. Briefly, Ba and REE oxides, and  
202 hydroxide formation rates were determined by analysing solutions of ultrapure water, Ba+Ce,  
203 Pr+Nd, and Sm+Eu+Gd+Tb at the beginning of the analytical session. During the course of  
204 the study, these rates remained systematically < 0.1 % for BaO<sup>+</sup>/Ba<sup>+</sup> and CeOH<sup>+</sup>/Ce<sup>+</sup>.

205 Measured sample data were corrected from the contribution of procedural blank, drift  
206 corrected, and interference corrected assuming constant rates of oxides and hydroxide  
207 formation during the session. Note that our results are given relative to our working values for  
208 the USGS basalt BHVO-2 (Table 2). In the event of future change to these BHVO-2 values,  
209 the data need only to be corrected by the ratio of the new and old values. Moreover, these  
210 working values can be used to evaluate possible inter-laboratory bias.

211

### 212 **3. Results and discussion**

213 The results for the three carbonate samples investigated in this study are given in  
214 Table 2, while corresponding REE patterns normalized to Post Archaean Australian Shale  
215 (PAAS, [38]) are shown in Figure 3. Concentrations obtained from samples with or without  
216 separation are analytically indistinguishable, and in excellent agreement with literature values.  
217 This confirms that the recovery of rare earths and yttrium with our procedure is complete. For  
218 the case of JLs-1, i.e. the studied carbonate having the lowest and the highest REE and Ba  
219 abundances, respectively, the Eu and Gd concentrations obtained without initial ion-exchange  
220 separation are higher than those obtained from the DGA purified solutions. Barium was very  
221 well separated by the columns, and the solutions were nearly devoid of it with levels similar  
222 to the procedural blanks (Table 2). Interferences of Ba oxides on Eu were practically absent  
223 for the solutions obtained with the columns, contrary to the solutions without separation for  
224 which Ba oxides contributed more than 90 % of the measured signal for mass 151 used to  
225 determine Eu abundances. The positive anomaly in Gd determined in the samples without  
226 initial ion-exchange separation is the result of an insufficient correction of  $^{140}\text{Ce}^{16}\text{OH}^+$  and  
227  $^{141}\text{Pr}^{16}\text{O}$  on the 157 mass signal used for quantifying Gd concentrations. This artifact is  
228 probably amplified by the weak signal obtained with these solutions containing little Gd (20  
229 pg/g), and by the uncertainties in the rates of formation of light REE oxides and hydroxides in

230 plasma for solutions containing high total dissolved solids. These bad interference corrections  
231 for Ba and Gd are accompanied by relative standard deviations (RSD) higher than 10 %. In  
232 comparison, RSDs are generally less than 2 % for abundances, element ratios including REE  
233 anomalies like  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}/\text{Ce}^*$  or  $\text{La}/\text{La}^*$  for analyses made with the solutions obtained with  
234 the columns, having much lower total dissolved contents.

235 The lack of consensual or certified data for carbonate standards with ultra-low REE  
236 concentrations does not allow us to illustrate the analytical accuracy of our procedure for such  
237 samples. However, the entire procedure requires only limited amounts of acids, and  
238 procedural blanks are very low (Table 2). During the course of the study, we have limited the  
239 mass of sample loaded on the columns to 200 mg, but since Ca is not retained on the resin,  
240 much larger quantities could be considered, in order to improve the accuracy of results  
241 obtained on samples displaying even lower REE concentrations.

242 For CAL-S and BEAN, both being characterized by relatively enriched REE  
243 abundances and low Ba/Eu ratios, our novel procedure yields results that are similar in terms  
244 of accuracy and precision to what can be achieved using existing analytical protocols. In  
245 particular, their low Ba/Eu ratios are such that the interferences produced can be easily  
246 corrected. However, for the case of JLs-1 or any other REE-depleted carbonate material, such  
247 as hydrothermal carbonates, corals or shells, our new method is particularly well suited,  
248 allowing one to obtain high quality data for the entire suite of REE, including for the  
249 analytically-challenging Eu and Gd.

250

## 251 **4. Conclusions**

252 We report on a novel analytical protocol for rapid and efficient separation of REEs and  
253 Y from carbonate samples, which results in quantitative removal of Ba and other major

254 alkaline earth matrix elements. This procedure was validated using a suite of three carbonate  
255 reference materials (CAL-S, JLS-1; BEAN) analysed by Element XR ICP-MS, providing  
256 precise and accurate REE data even for depleted carbonate material characterized by high Ba  
257 abundances, for which efficient Ba removal prior to analysis can prevent the formation of  
258 isobaric interferences that would otherwise complicate the measurement of Eu. Overall, this  
259 new protocol offers interesting perspectives for future geochemical investigations of  
260 carbonates in earth sciences, but also in the field of environmental and biological sciences  
261 (pollution). It can be easily adapted to the specific case of much smaller samples ( $\approx 1$  mg). The  
262 use of smaller columns containing less resin (0.1 ml of resin) is better suited to this type of  
263 sample. It also allows the use of less acid, and reduces blanks.

264         Nothing prevents the use of this protocol for rocks and silicates, but also for organic  
265 matter, while taking care to load smaller quantities of samples on the columns.

266

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272

### 273 **CRedit authorship contribution statement**

274 **Jean-Alix Barrat, Germain Bayon:** Conceptualization, Supervision, Methodology,  
275 Investigation, Validation, Writing – original draft. **Xudong Wang, Samuel Le Goff, Marie-**  
276 **Laure Rouget, Bleuenn Gueguen:** Investigation, Validation. **Douraid Ben Salem:**  
277 Conceptualization.

278

### 279 **Declaration of competing interests**

280 The authors declare that they have no known competing financial interests or personal  
281 relationships that could have appeared to influence the work reported in this paper.

282

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Table 1. ICP-MS instrument operating conditions

|                            |   |
|----------------------------|---|
| RF power                   | 1200 W  |
| Sample uptake rate         | 100 $\mu$ l / min   |
| Coolant argon flow rates   | 16 l / min  |
| Auxiliary argon flow rates | 0.9 l / min   |
| Nebuliser argon flow rates | 1.031 l / min   |
| Torch                      | Quartz  |
| Nebuliser                  | PFA ST micro-flow   |
| Spray chamber              | Quartz cyclonic   |
| Cones                      | Nickel  |
| Low resolution mode (LRM)  | $^{135}\text{Ba}$ , $^{139}\text{La}$ , $^{140}\text{Ce}$ , $^{141}\text{Pr}$ , $^{143,146}\text{Nd}$ , $^{147,149}\text{Sm}$ , $^{151}\text{Eu}$ , $^{157}\text{Gd}$ , $^{159}\text{Tb}$ , $^{163}\text{Dy}$ , $^{165}\text{Ho}$ , $^{167}\text{Er}$ , $^{169}\text{Tm}$ , $^{174}\text{Yb}$ , $^{175}\text{Lu}$ |
| Acquisition mode           | Mass Accuracy   |
| Number of scans            | 3*2   |
| Ion lens settings          | Acquisition to obtain maximum signal intensity  |
| Wash time                  | 100 s   |

Table 2. Procedural blanks, BHVO-2, PAAS (adjusted to our values of BHVO-2), JLS-1, Cal-S, and BEAN abundances (in ng/g).

|        | procedural<br>blank<br>(pg) | PAAS<br>Pourmand<br>et al.<br>[38] | BHVO-2<br>Barrat<br>et al.<br>[40] | JLS-1                      |              |                         |             |                          |                |                       |                               |                       |
|--------|-----------------------------|------------------------------------|------------------------------------|----------------------------|--------------|-------------------------|-------------|--------------------------|----------------|-----------------------|-------------------------------|-----------------------|
|        |                             |                                    |                                    | this                       |              | study                   |             | Kawabe<br>et al.<br>[41] | Dulski<br>[16] | Bau<br>et al.<br>[21] | Ponnurangam<br>et al.<br>[42] | Kim<br>et al.<br>[28] |
|        |                             |                                    |                                    | without separation<br>n=12 | RSD (%)      | with separation<br>n=39 | RSD (%)     |                          |                |                       |                               |                       |
| Y      | <32                         | 32200                              | 27600                              | <b>241</b>                 | <b>1.72</b>  | <b>249</b>              | <b>1.32</b> | 233                      | 216            | 210                   | 199                           |                       |
| Ba     | <340                        |                                    | 131000                             | <b>449171</b>              | <b>1.73</b>  |                         |             |                          |                |                       |                               |                       |
| La     | <30                         | 44750                              | 15200                              | <b>96.7</b>                | <b>1.27</b>  | <b>99.8</b>             | <b>2.76</b> | 101                      | 107            | 84.7                  | 97.1                          | 91                    |
| Ce     | <33                         | 87290                              | 37500                              | <b>170</b>                 | <b>1.72</b>  | <b>185</b>              | <b>1.54</b> | 174                      | 187            | 168.7                 | 175                           | 148                   |
| Pr     | <5                          | 10100                              | 5310                               | <b>21.02</b>               | <b>2.13</b>  | <b>22.84</b>            | <b>1.82</b> | 24.6                     | 23.6           | 21.1                  | 22                            | 18                    |
| Nd     | <12                         | 36980                              | 24500                              | <b>88.0</b>                | <b>1.74</b>  | <b>92.5</b>             | <b>1.44</b> | 94.2                     | 90.2           | 87.6                  | 83.7                          | 81                    |
| Sm     | <2.5                        | 6908                               | 6070                               | <b>19.22</b>               | <b>1.62</b>  | <b>19.59</b>            | <b>1.34</b> | 19.7                     | 18.5           | 18.9                  | 18.51                         | 19                    |
| Eu     | <1                          | 1188                               | 2070                               | <b>11.63</b>               | <b>10.57</b> | <b>4.59</b>             | <b>1.47</b> | 3.7                      | 4.6            | 4.5                   | 4.54                          | 3                     |
| Gd     | <1.8                        | 5958                               | 6240                               | <b>34.79</b>               | <b>10.86</b> | <b>20.82</b>            | <b>1.42</b> | 19.7                     | 21.4           | 20.9                  | 22.01                         | 21                    |
| Tb     | <0.5                        | 894                                | 940                                | <b>2.83</b>                | <b>2.55</b>  | <b>3.14</b>             | <b>1.34</b> |                          | 3.1            | 3.1                   | 3.11                          | 3                     |
| Dy     | <2.8                        | 5272                               | 5310                               | <b>19.31</b>               | <b>2.13</b>  | <b>19.60</b>            | <b>1.39</b> | 19.7                     | 20             | 19.8                  | 19.99                         | 18                    |
| Ho     | <0.6                        | 1078                               | 1000                               | <b>4.41</b>                | <b>2.05</b>  | <b>4.44</b>             | <b>1.32</b> | 4.6                      | 4.5            | 4.4                   | 4.28                          | 4                     |
| Er     | <1.4                        | 3094                               | 2540                               | <b>13.43</b>               | <b>1.54</b>  | <b>13.24</b>            | <b>1.39</b> | 14.3                     | 13.6           | 13.7                  | 13.22                         | 14                    |
| Tm     | <1.8                        | 468                                | 340                                |                            |              |                         |             |                          | 2              |                       |                               | 2                     |
| Yb     | <1.5                        | 3028                               | 2000                               | <b>11.51</b>               | <b>2.31</b>  | <b>11.68</b>            | <b>1.34</b> | 12.7                     | 12.6           | 11.7                  | 11.74                         | 12                    |
| Lu     | <0.3                        | 438                                | 270                                | <b>1.88</b>                | <b>3.00</b>  | <b>1.80</b>             | <b>1.32</b> | 2.05                     | 2              | 1.9                   | 1.75                          | 2                     |
| La/La* |                             | 1                                  | 1.03                               | <b>1.36</b>                | <b>3.04</b>  | <b>1.21</b>             | <b>0.99</b> | 1.01                     | 1.12           | 1.16                  | 1.07                          | 1.72                  |
| Ce/Ce* |                             | 1                                  | 1.03                               | <b>1.10</b>                | <b>1.86</b>  | <b>1.04</b>             | <b>1.44</b> | 0.86                     | 0.96           | 1.05                  | 0.96                          | 1.17                  |
| Eu/Eu* |                             | 1                                  | 1.82                               | <b>2.43</b>                | <b>14.71</b> | <b>1.23</b>             | <b>0.56</b> | 1.01                     | 1.25           | 1.22                  | 1.21                          | 0.81                  |
| Y/Ho   |                             | 29.9                               | 27.6                               | <b>54.6</b>                | <b>1.95</b>  | <b>56.1</b>             | <b>0.46</b> | 50.65                    | 48.00          | 47.72                 | 46.49                         |                       |

Table 2 (continue)

|        | CAL-S                      |             |                         |             |                         | BEAN                     |                            |             |                         |             |
|--------|----------------------------|-------------|-------------------------|-------------|-------------------------|--------------------------|----------------------------|-------------|-------------------------|-------------|
|        | this                       |             | study                   |             | Potts<br>et al.<br>[43] | Le Goff<br>et al.<br>[9] | this                       |             | study                   |             |
|        | without separation<br>n=15 | RSD (%)     | with separation<br>n=41 | RSD (%)     |                         |                          | without separation<br>n=15 | RSD (%)     | with separation<br>n=41 | RSD (%)     |
| Y      | <b>1948</b>                | <b>1.79</b> | <b>2177</b>             | <b>3.58</b> | 1944                    | 2065                     | <b>5373</b>                | <b>0.72</b> | <b>6078</b>             | <b>1.69</b> |
| Ba     | <b>1180</b>                | <b>2.57</b> |                         |             | 1382                    |                          | <b>88265</b>               | <b>0.40</b> |                         |             |
| La     | <b>745</b>                 | <b>1.68</b> | <b>806</b>              | <b>1.33</b> | 787                     | 793                      | <b>2028</b>                | <b>2.48</b> | <b>2269</b>             | <b>2.01</b> |
| Ce     | <b>286</b>                 | <b>3.88</b> | <b>313</b>              | <b>2.72</b> | 333                     | 302                      | <b>786</b>                 | <b>1.56</b> | <b>805</b>              | <b>1.79</b> |
| Pr     | <b>82.6</b>                | <b>1.88</b> | <b>89.2</b>             | <b>1.70</b> | 90                      | 87.1                     | <b>282</b>                 | <b>1.42</b> | <b>292</b>              | <b>1.76</b> |
| Nd     | <b>342</b>                 | <b>1.77</b> | <b>363</b>              | <b>1.70</b> | 357                     | 359                      | <b>1237</b>                | <b>1.15</b> | <b>1273</b>             | <b>1.68</b> |
| Sm     | <b>60.2</b>                | <b>1.59</b> | <b>63.7</b>             | <b>1.68</b> | 64                      | 62.4                     | <b>256</b>                 | <b>0.84</b> | <b>262</b>              | <b>1.65</b> |
| Eu     | <b>14.8</b>                | <b>1.84</b> | <b>15.85</b>            | <b>1.33</b> | 16                      | 15.49                    | <b>67.6</b>                | <b>2.05</b> | <b>66.7</b>             | <b>1.74</b> |
| Gd     | <b>89.9</b>                | <b>3.26</b> | <b>92.3</b>             | <b>1.41</b> | 93                      | 91.6                     | <b>378</b>                 | <b>0.86</b> | <b>380</b>              | <b>2.08</b> |
| Tb     | <b>13.4</b>                | <b>1.45</b> | <b>13.90</b>            | <b>1.23</b> | 14                      | 13.72                    | <b>55.1</b>                | <b>0.94</b> | <b>54.9</b>             | <b>1.66</b> |
| Dy     | <b>97.2</b>                | <b>1.34</b> | <b>100</b>              | <b>1.29</b> | 100                     | 98.3                     | <b>360</b>                 | <b>0.62</b> | <b>361</b>              | <b>1.51</b> |
| Ho     | <b>25.8</b>                | <b>1.39</b> | <b>26.33</b>            | <b>1.12</b> | 26                      | 26.02                    | <b>84.9</b>                | <b>0.85</b> | <b>84.6</b>             | <b>1.60</b> |
| Er     | <b>80.7</b>                | <b>1.58</b> | <b>82.0</b>             | <b>1.11</b> | 81                      | 81                       | <b>241</b>                 | <b>0.69</b> | <b>237</b>              | <b>1.58</b> |
| Tm     |                            |             |                         |             |                         |                          |                            |             |                         |             |
| Yb     | <b>65.2</b>                | <b>1.44</b> | <b>67.1</b>             | <b>1.23</b> | 68                      | 66.3                     | <b>173</b>                 | <b>0.71</b> | <b>173</b>              | <b>1.71</b> |
| Lu     | <b>10.2</b>                | <b>2.10</b> | <b>10.31</b>            | <b>1.22</b> | 11                      | 10.16                    | <b>25.43</b>               | <b>0.80</b> | <b>24.85</b>            | <b>1.66</b> |
| La/La* | <b>2.60</b>                | <b>1.86</b> | <b>2.52</b>             | <b>0.80</b> | 2.32                    | 2.60                     | <b>2.33</b>                | <b>1.61</b> | <b>2.49</b>             | <b>0.64</b> |
| Ce/Ce* | <b>0.45</b>                | <b>2.07</b> | <b>0.45</b>             | <b>1.23</b> | 0.46                    | 0.45                     | <b>0.39</b>                | <b>1.05</b> | <b>0.38</b>             | <b>0.37</b> |
| Eu/Eu* | <b>1.09</b>                | <b>1.61</b> | <b>1.12</b>             | <b>0.50</b> | 1.12                    | 1.11                     | <b>1.17</b>                | <b>1.78</b> | <b>1.14</b>             | <b>0.52</b> |
| Y/Ho   | <b>75.5</b>                | <b>1.28</b> | <b>82.7</b>             | <b>3.34</b> | 74.8                    | 79.4                     | <b>63.3</b>                | <b>0.61</b> | <b>71.8</b>             | <b>0.86</b> |

The La, Ce and Eu anomalies are calculated using the X/X\* ratios, where X\* is the extrapolated X concentration for a smooth PAAS-normalised REE pattern and X<sub>sn</sub> is the concentration of element X normalised to PAAS:  $La_{sn}^* = Pr_{sn}^3 / Nd_{sn}^2$ ,  $Ce_{sn}^* = Pr_{sn}^2 / Nd_{sn}$ ,  $Eu_{sn}^* = (Sm_{sn} \cdot Gd_{sn})^{1/2}$ .

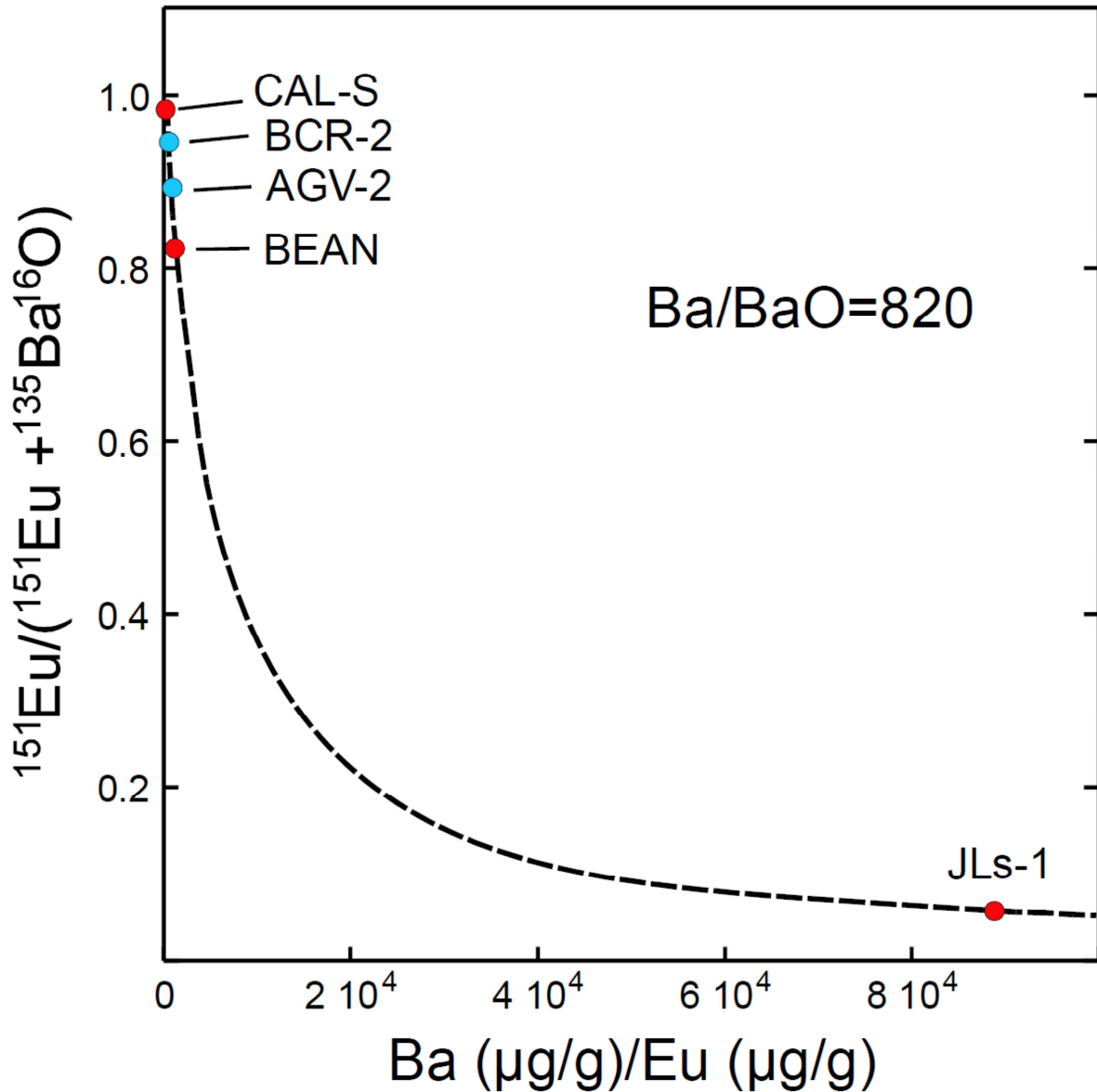


Figure 1.  $^{151}\text{Eu}/(^{151}\text{Eu} + ^{135}\text{Ba}^{16}\text{O})$  vs. Ba/Eu plot showing the contribution of BaO on the mass 151 used to determine the Eu abundances, calculated using a Ba/BaO ratio of 820 (as generally observed during our ICP-MS sessions). This contribution is satisfactorily corrected for samples with Ba/Eu < 1500 as exemplified by BCR-2 (basalt), AGV-2 (andesite), CAL-S and BEAN (carbonates). For marine limestone like JLS-1, the BaO contribution is huge, and generally not well corrected.

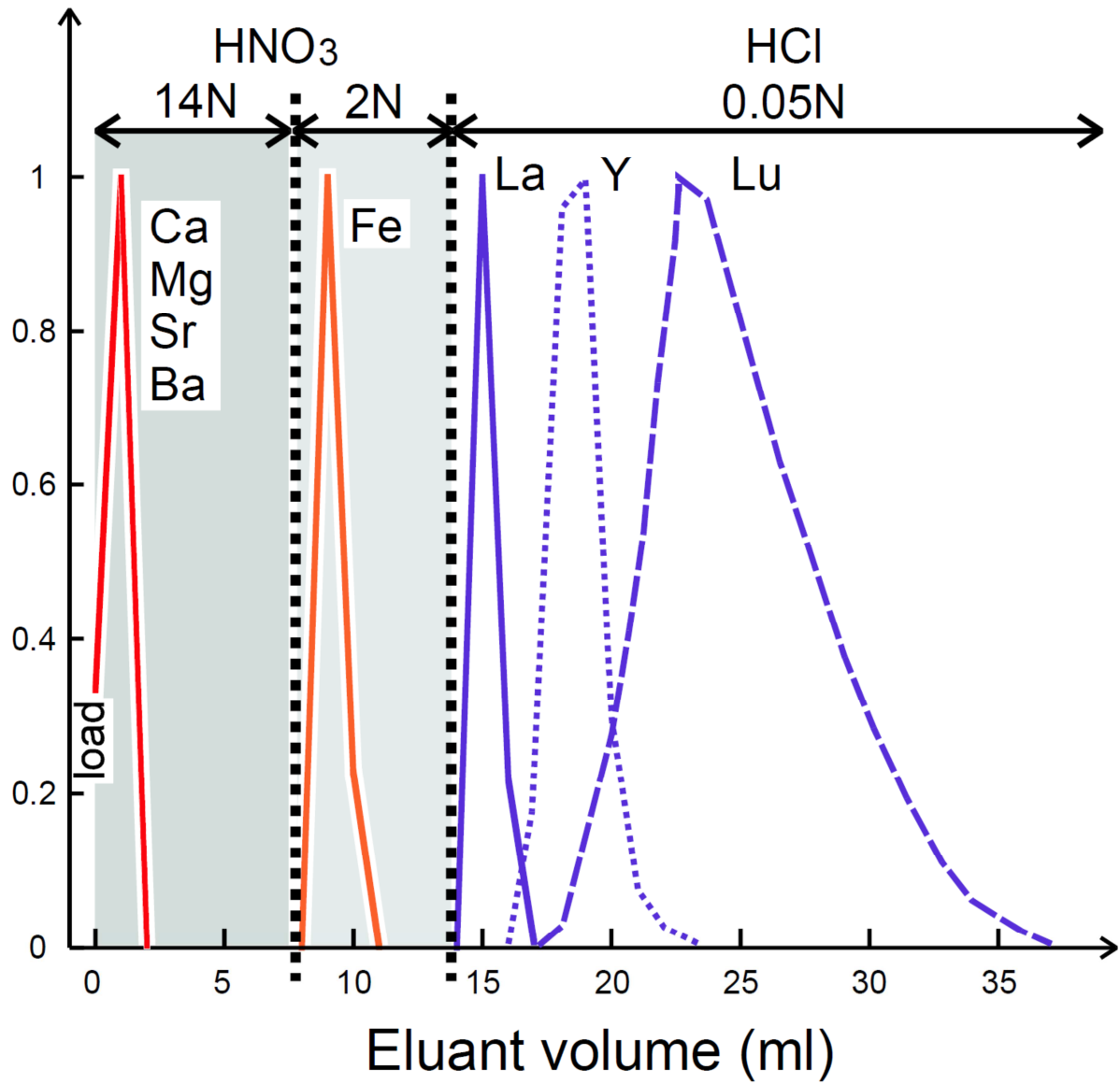


Figure 2. Elution curves for various elements using a small chromatographic column loaded with 1 ml of DGA resin. The vertical scale (concentration) is in arbitrary units.

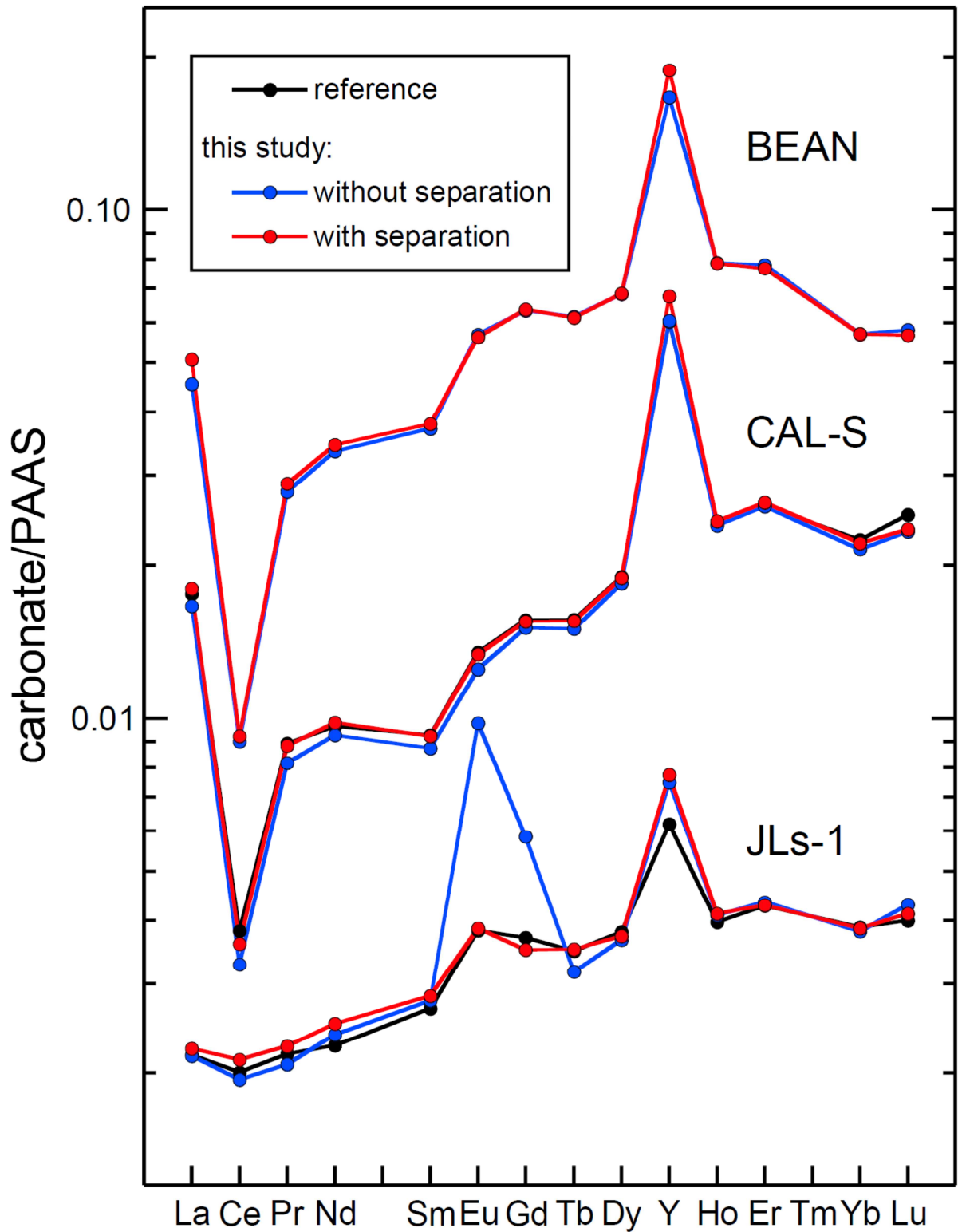


Figure 3. REE+Y patterns normalised to Post Archaean Australian Shale (Pourmand et al., 1991, adjusted to our BHVO-2 values) for the three carbonates analysed during the course of the study. Reference values are from Potts et al. [43] for CAL-S, and Dulski [16] for JLS-1.



## Highlights

- A novel cation exchange method was developed for the analysis of REE+Y in carbonates by ICP-MS.
- Measurements of REEs were free of Ba interferences.
- Low blanks and high enrichment-factor for REEs+Y are achieved, and allow the analysis of ultradepleted samples.
- Precision better than 3 % RSD was achieved for most elements analyzed.

**CRedit authorship contribution statement**

**Jean-Alix Barrat, Germain Bayon:** Conceptualization, Supervision, Methodology, Investigation, Validation, Writing – original draft. **Xudong Wang, Samuel Le Goff, Marie-Laure Rouget, Bleuenn Gueguen:** Investigation, Validation. **Douraid Ben Salem:** Conceptualization.

Journal Pre-proof

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: