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To cite this version:

Jean-Alix Barrat, Germain Bayon, Xudong Wang, Samuel Le Goff, Marie-Laure Rouget, et al.. A new chemical separation procedure for the determination of rare earth elements and yttrium abundances in carbonates by ICP-MS. Talanta, 2020, 219, pp.121244. 10.1016/j.talanta.2020.121244 . hal-02975503

HAL Id: hal-02975503

https://hal.univ-brest.fr/hal-02975503v1

Submitted on 22 Jul 2024

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

By

Jean-Alix Barrat[1,2]*, Germain Bayon[3], Xudong Wang[3,4], Samuel Le Goff[1,5], Marie-Laure Rouget[1,6], Bleuenn Gueguen[1,6], Douraied Ben Salem[7]

1 Univ Brest, CNRS, UMR 6538 (Laboratoire Géosciences Océan), Institut Universitaire Européen de la Mer (IUEM), Place Nicolas Copernic, 29280 Plouzané, France.

2 Univ Brest, CNRS, UMR 6539 (Laboratoire des Sciences de l'Environnement Marin), LIA BeBEST, Institut Universitaire Européen de la Mer (IUEM), Place Nicolas Copernic, 29280 Plouzané, France

3 IFREMER, Marine Geosciences Unit, F-29280 Plouzané, France

4 Shanghai Engineering Research Center of Hadal Science and Technology, College of Marine Sciences, Shanghai Ocean University, Shanghai 201306, China.

5 ENS Lyon, CNRS, UMR 5276, LGLTPE, 46 Allée Italie, F-69342 Lyon, France

6 CNRS, Univ Brest, UMS 3113, F-29280 Plouzané, France.

7 LaTIM (INSERM UMR 1101) Université de Bretagne Occidentale. 22, avenue C. Desmoulins, 29238, Brest Cedex 3, France.

*corresponding author (E-Mail : barrat@univ-brest.fr).

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.

Key words: Rare Earth Elements, DGA resin, carbonate, ICP-MS, CAL-S, JLs-1

1. Introduction

The lanthanides and other rare earth elements (REEs) are amongst the most studied chemical elements in geochemistry, being of prime importance for addressing a wide range of issues in earth and planetary sciences, such as e.g. the condensation of the first solids in the Solar System, the formation of magmas, the reconstruction of present and past ocean circulation patterns [e.g., 1]. The usefulness of REE as unique tracers of geochemical processes comes first from their overall very consistent behavior in nature, which enables the modelling of their abundance in geochemical reservoirs. Most REEs are trivalent and, as a consequence, cannot be easily fractionated from each other during petrogenetic processes. However, two REEs, Ce and Eu, can also exist in different valence states (Ce^{4+} and Eu^{2+}, respectively), which implies that they can be decoupled from the other REEs, resulting in quantifiable abundance anomalies, which, in turn, can be used to provide constraints on rock formation processes and other redox-sensitive bio-geochemical reactions. Another important field of application of REE geochemistry is based on the use of particular radioactive and radiogenic isotopes for geochronological purposes (i.e. the La/Ce, Sm/Nd, and Lu/Hf isotope systematics).

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

Since the 1990s, ICP-MS has become the method of choice for determining trace element concentrations in rocks, minerals and waters. A multitude of protocols have been described to date, and successfully applied to a wide range of materials [e.g., 10-17]. The very high sensitivity of ICP-MS instruments makes it possible to determine very low trace element abundances in solution, with dilution factors (=solution weight/sample weight) up to several tens of thousands. Compared to previous state-of-the-art techniques, such as isotope dilution-thermo-ionization mass spectrometry (ID-TIMS) or instrumental neutron activation analyses (INAA), the use of ICP-MS allows high sample throughput at comparatively low analytical costs. The dissolution of biogenic and chemical carbonate samples is generally relatively straightforward, so that high quality trace element data can be obtained in the vast majority of case studies [e.g., 2, 4, 6, 7 among many others]. One potential difficulty in analyzing carbonates is that they are typically characterized by much lower REE abundances compared to other commonly studied rocks, such as basalts, granites and sediments. Using ICP-MS techniques, this difficulty can be generally successfully overcome by simply analyzing less diluted solutions. Another important issue when measuring REE concentrations in carbonates is that they can contain substantial amounts of Ba. During the course of ICP-MS analysis, a fraction of Ba atoms present in the plasma forms oxides, which can generate isobaric interferences with Eu isotopes (e.g. $^{135}Ba^{16}O^+$ and $^{134}BaOH^+$ with ^{151}Eu, $^{137}Ba^{16}O$ and $^{136}BaOH^+$with ^{153}Eu [e.g., 14, 18-19]). Uncorrected isobaric interferences cannot be neglected because they typically result in the occurrence of non-natural positive Eu anomalies in studied samples. In most cases, the presence of isobaric interferences on Eu can be successfully corrected by monitoring the oxide formation rate during an analytical ICP-MS session, using a mono-elemental solution of Ba. Many rocks, such as basalts, granites, terrigenous sediments or peridotites commonly display Ba/Eu ratios < 1000. The contribution of Ba oxides to the 151 or 153 Eu masses is not dominant here, and the correction is generally very satisfactory (Fig. 1). However, many marine or hydrothermal carbonates have much higher Ba/Eu ratios, frequently >10000. For these samples, the interference contribution to measured ^{151}Eu and ^{153}Eu signals can become dominant. The corrections that can be made using estimates of oxide formation rates commonly yield Eu abundances with poor accuracy and/or associated with a relatively high uncertainty. The use of collision/reaction cells and/or of ICP-MS operated in high-resolution modes can provide efficient means for eliminating the formation of Ba oxides and allowing quantitative separation of Eu+ and BaO+ peaks, respectively. However, these options significantly reduce the signal intensities, and hence are generally not adapted to low-level samples such as carbonates. One alternative to resolve the specific problem raised by the potential occurrence of isobaric interferences upon carbonate analysis is to quantitatively separate REEs from Ba prior to ICP-MS measurements. Another advantage of separating REEs is that it allows one to analyse less diluted solutions during ICP-MS measurements, hence improving the quality of data acquisition.

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

Novel ion exchange resins have been developed and commercialized in recent years, including the DGA, normal resin. It is an extraction chromatographic resin based on N,N,N’,N’-tetra-n-octyldiglycolamide extractant, commonly referred to as either DN Resin or TODGA in the literature. It has been previously used for the preconcentration of actinides and lanthanides from various samples for radioactive waste management [35, 36]. A complete set of partition coefficients has been published for this resin [37], and its capability for the preconcentration of REEs for difficult geological samples has already been demonstrated [38, 39]. In this study, we used the remarkable properties of this resin to separate the REEs from carbonates. We describe here a new procedure aimed at quantitatively separating REE from other elements in carbonate samples, and illustrate its utility using two international (JLs-1and CAL-S) and one in-house standard from hereafter referred to as BEAN for **Br**est c**a**rbo**n**ate and available on request.

2. Experimental techniques

Sample preparation and REE separation

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

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

-JLs-1, a marine limestone prepared by the Geological Survey of Japan, which is one of the best characterized carbonate standard for REEs and Y abundances; this carbonate is depleted in REEs, but enriched in Ba, consequently displaying a Ba (µg/g)/Eu (µg/g) ratio ~ 98000;

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

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

Samples were precisely weighted and spiked with a solution of pure Tm. The spike solution was prepared with a Tm mono-elementary solution (custom grade, CGTM1-1, Inorganic Ventures Inc. ®). About 40 ng of Tm was added for 100-200 mg of sample. Samples were dissolved in a 30 ml screw-top Teflon vial. The spiked sample was first covered with a few ml of ultrapure water to prevent sample loss during effervescence, and drops of nitric acid were carefully added until the effervescence of the solution stops. About 0.5 ml of 14 N HNO_3 was then added, and the vial was closed and let on a hot plate at 110°C during one hour to ensure the full dissolution of the sample. The vial was then opened, and after evaporation to dryness, the residue was taken up with 1.5 ml of 14 N HNO_3.

Chromatographic columns (Triskem®, 2 ml, AC-142-TK) were loaded with 1 ml of DGA resin. A frit washer was placed on top of the resin bed to avoid any resin disturbance following subsequent addition of the eluant. As mentioned above, the properties of the DGA resin allow for a selective separation of REEs and Y as a group of coherent chemical elements (Fig. 2). To large extent, Ca, Mg and other alkaline earth metals are not adsorbed by the resin under concentrated (14 N) nitric conditions. Fe and many other transition metals are no more retained by the DGA resin with 2 N HNO_3 contrary to REEs . Previous work also showed that REEs are not retained by the resin under highly diluted HCl conditioning [34]. Based on the above findings, we set up a novel procedure that involves an initial cleaning step with 50 ml of 0.05 N HCl, followed by conditioning of the resin with 5 ml of 14 N HNO_3. The sample solutions (corresponding to 100-200 mg of sample in 1.5 ml 14 N HNO_3) were then loaded onto the columns, prior to subsequent addition of 7 ml 14 N HNO_3, and 5 ml 2 N HNO_3, in order to elute all matrix elements and Ba (Fig. 2). The final step corresponds to the elution of

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

Columns were washed using 30 ml of 0.05 N HCl, followed by conditioning of the resin with 5 ml of 14 N HNO_3, and were ready for next samples. While we did not evaluate the resin lifetime in this study, we systematically replaced the resin beds every four samples in order to prevent any effect related to resin aging, such as reduced binding efficiency.

For comparison, solutions of the three carbonate reference materials were prepared following the procedure described above. Aliquots containing the equivalent of 10 mg were placed in Teflon vials and evaporated to dryness. The residues were taken up in 10 ml of 0.4 N HNO_3 with traces of HF (corresponding to a dilution factor of 1000), and analysed with the other solutions during the same analytical sessions.

Mass spectrometry

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

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

3. Results and discussion

The results for the three carbonate samples investigated in this study are given in Table 2, while corresponding REE patterns normalized to Post Archaean Australian Shale (PAAS, [38]) are shown in Figure 3. Concentrations obtained from samples with or without separation are analytically indistinguishable, and in excellent agreement with literature values. This confirms that the recovery of rare earths and yttrium with our procedure is complete. For the case of JLs-1, i.e. the studied carbonate having the lowest and the highest REE and Ba abundances, respectively, the Eu and Gd concentrations obtained without initial ion-exchange separation are higher than those obtained from the DGA purified solutions. Barium was very well separated by the columns, and the solutions were nearly devoid of it with levels similar to the procedural blanks (Table 2). Interferences of Ba oxides on Eu were practically absent for the solutions obtained with the columns, contrary to the solutions without separation for which Ba oxides contributed more than 90 % of the measured signal for mass 151 used to determine Eu abundances. The positive anomaly in Gd determined in the samples without initial ion-exchange separation is the result of an insufficient correction of $^{140}Ce^{16}OH^+$ and $^{141}Pr^{16}O$ on the 157 mass signal used for quantifying Gd concentrations. This artifact is probably amplified by the weak signal obtained with these solutions containing little Gd (20 pg/g), and by the uncertainties in the rates of formation of light REE oxides and hydroxides in plasma for solutions containing high total dissolved solids. These bad interference corrections for Ba and Gd are accompanied by relative standard deviations (RSD) higher than 10 %. In comparison, RSDs are generally less than 2 % for abundances, element ratios including REE anomalies like Eu/Eu*, Ce/Ce* or La/La* for analyses made with the solutions obtained with the columns, having much lower total dissolved contents.

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

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

4. Conclusions

We report on a novel analytical protocol for rapid and efficient separation of REEs and Y from carbonate samples, which results in quantitative removal of Ba and other major alkaline earth matrix elements. This procedure was validated using a suite of three carbonate reference materials (CAL-S, JLs-1; BEAN) analysed by Element XR ICP-MS, providing precise and accurate REE data even for depleted carbonate material characterized by high Ba abundances, for which efficient Ba removal prior to analysis can prevent the formation of isobaric interferences that would otherwise complicate the measurement of Eu. Overall, this new protocol offers interesting perspectives for future geochemical investigations of carbonates in earth sciences, but also in the field of environmental and biological sciences (pollution). It can be easily adapted to the specific case of much smaller samples (≈1 mg). The use of smaller columns containing less resin (0.1 ml of resin) is better suited to this type of sample. It also allows the use of less acid, and reduces blanks.

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

Acknowledgements: We thank Jean-Michel Kauffmann for the editorial handling, and the two anonymous reviewers for constructive comments. We thank Stefan Lalonde for providing the Acros Organics® carbonate. This work was supported by the "Laboratoire d'Excellence" LabexMER (ANR-10-LABX-19) and funded by grants from the French Government under the program "Investissements d'Avenir".

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. **Douraied Ben Salem:** Conceptualization.

Declaration of competing 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.

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[43] P.J. Potts, M. Thompson, J.S. Kane, P.C. Webb, J. Carignan, GeoPT6. An international proficiency test. for analytical geochemistry laboratories - report on round 6 (OU3: Nanhoron microgranite) and 6A (CAL-S: CRPG limestone). Geostandards Newsletter 24 (2002), E1–E37.

Table 1. ICP-MS instrument operating conditions

RF power	1200 W
Sample uptake rate	100 µl / 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}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143,146}Nd, ^{147,149}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{174}Yb, ^{175}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	**PAAS**	**BHVO-2**	**JLs-1**								
	blank	Pourmand	Barrat	this study				Kawabe	Dulski	Bau	Ponnurangam	Kim
	(pg)	et al.	et al.	without separation		with separation		et al.	[16]	et al.	et al.	et al.
		[38]	[40]	n=12	RSD (%)	n=39	RSD (%)	[41]		[21]	[42]	[28]
Y	<32	32200	27600	**241**	**1.72**	**249**	**1.32**	233	216	210	199	
Ba	<340		131000	**449171**	**1.73**							
La	<30	44750	15200	**96.7**	**1.27**	**99.8**	**2.76**	101	107	84.7	97.1	91
Ce	<33	87290	37500	**170**	**1.72**	**185**	**1.54**	174	187	168.7	175	148
Pr	<5	10100	5310	**21.02**	**2.13**	**22.84**	**1.82**	24.6	23.6	21.1	22	18
Nd	<12	36980	24500	**88.0**	**1.74**	**92.5**	**1.44**	94.2	90.2	87.6	83.7	81
Sm	<2.5	6908	6070	**19.22**	**1.62**	**19.59**	**1.34**	19.7	18.5	18.9	18.51	19
Eu	<1	1188	2070	**11.63**	**10.57**	**4.59**	**1.47**	3.7	4.6	4.5	4.54	3
Gd	<1.8	5958	6240	**34.79**	**10.86**	**20.82**	**1.42**	19.7	21.4	20.9	22.01	21
Tb	<0.5	894	940	**2.83**	**2.55**	**3.14**	**1.34**		3.1	3.1	3.11	3
Dy	<2.8	5272	5310	**19.31**	**2.13**	**19.60**	**1.39**	19.7	20	19.8	19.99	18
Ho	<0.6	1078	1000	**4.41**	**2.05**	**4.44**	**1.32**	4.6	4.5	4.4	4.28	4
Er	<1.4	3094	2540	**13.43**	**1.54**	**13.24**	**1.39**	14.3	13.6	13.7	13.22	14
Tm	<1.8	468	340						2			2
Yb	<1.5	3028	2000	**11.51**	**2.31**	**11.68**	**1.34**	12.7	12.6	11.7	11.74	12
Lu	<0.3	438	270	**1.88**	**3.00**	**1.80**	**1.32**	2.05	2	1.9	1.75	2
La/La*		1	1.03	**1.36**	**3.04**	**1.21**	**0.99**	1.01	1.12	1.16	1.07	1.72
Ce/Ce*		1	1.03	**1.10**	**1.86**	**1.04**	**1.44**	0.86	0.96	1.05	0.96	1.17
Eu/Eu*		1	1.82	**2.43**	**14.71**	**1.23**	**0.56**	1.01	1.25	1.22	1.21	0.81
Y/Ho		29.9	27.6	**54.6**	**1.95**	**56.1**	**0.46**	50.65	48.00	47.72	46.49	

Table 2 (continue)

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

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_{sn} is the concentration of element X normalised to PAAS: $La_{sn}^* = Pr_{sn}^3/Nd_{sn}^2$, $Ce_{sn}^* = Pr_{sn}^2/Nd_{sn}$, $Eu_{sn}^* = (Sm_{sn} . Gd_{sn})^{1/2}$.

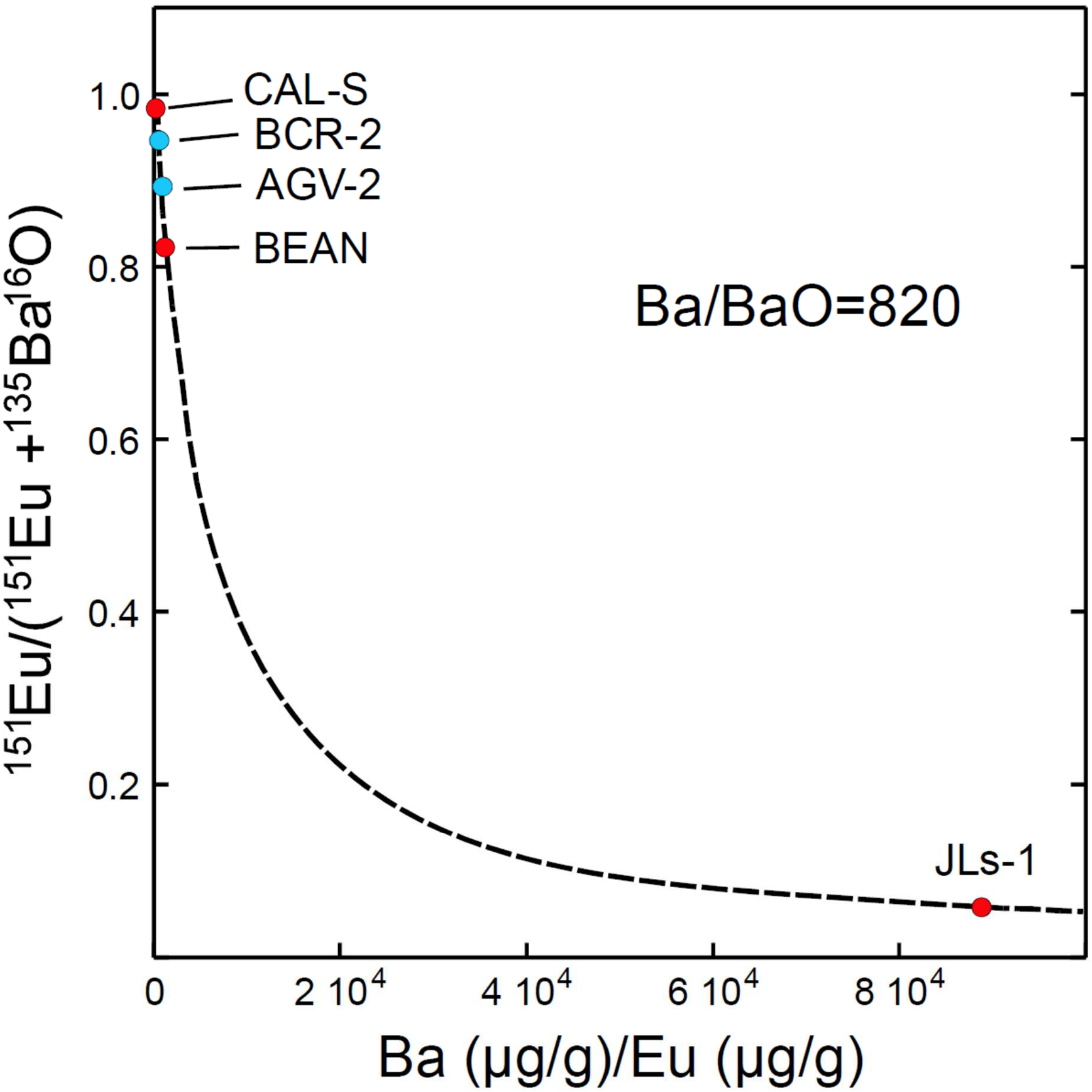


Figure 1. $^{151}Eu/(^{151}Eu+^{135}Ba^{16}O)$ vs. Ba/Eu plot showing the contribution of BaO on the mass 151 used to determine the Eu abundances, calculated using a Ba/BaO ratio of 820 (as generally observed during our ICP-MS sessions). This contribution is satisfactorily corrected for samples with 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.

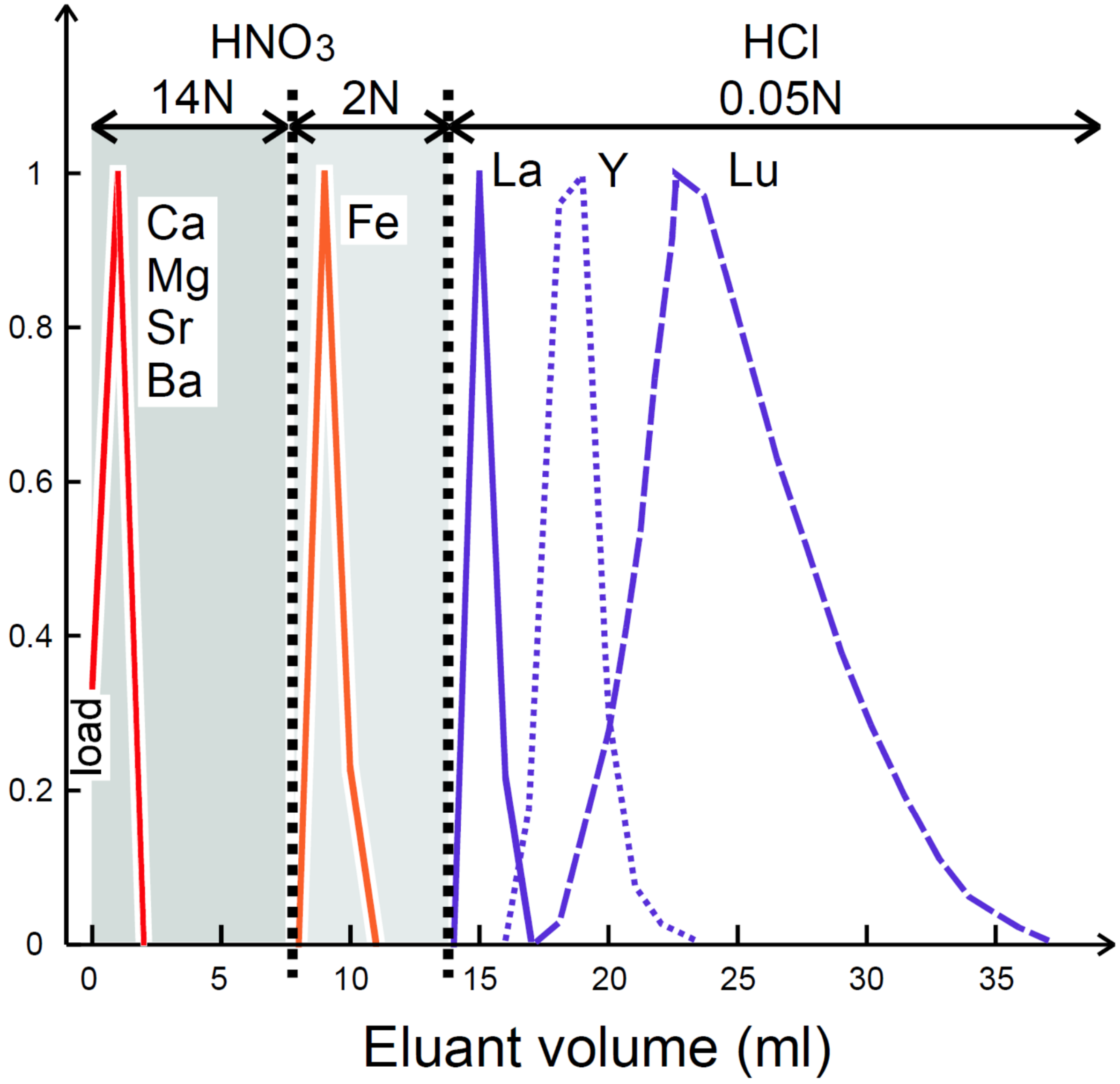


Figure 2. Elution curves for various elements using a small chromatographic column loaded with 1 ml of DGA resin. The vertical scale (concentration) is in arbitrary units.

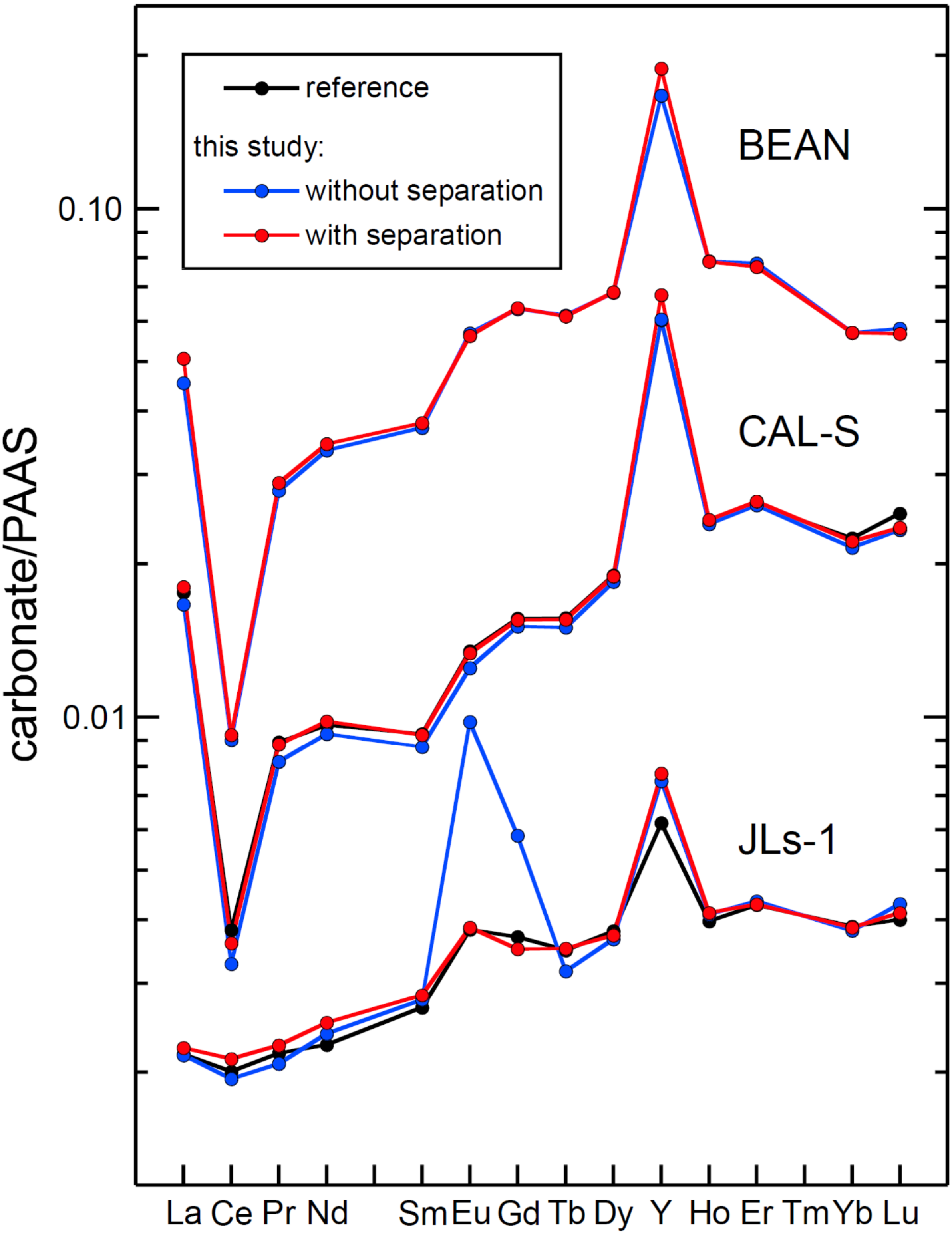
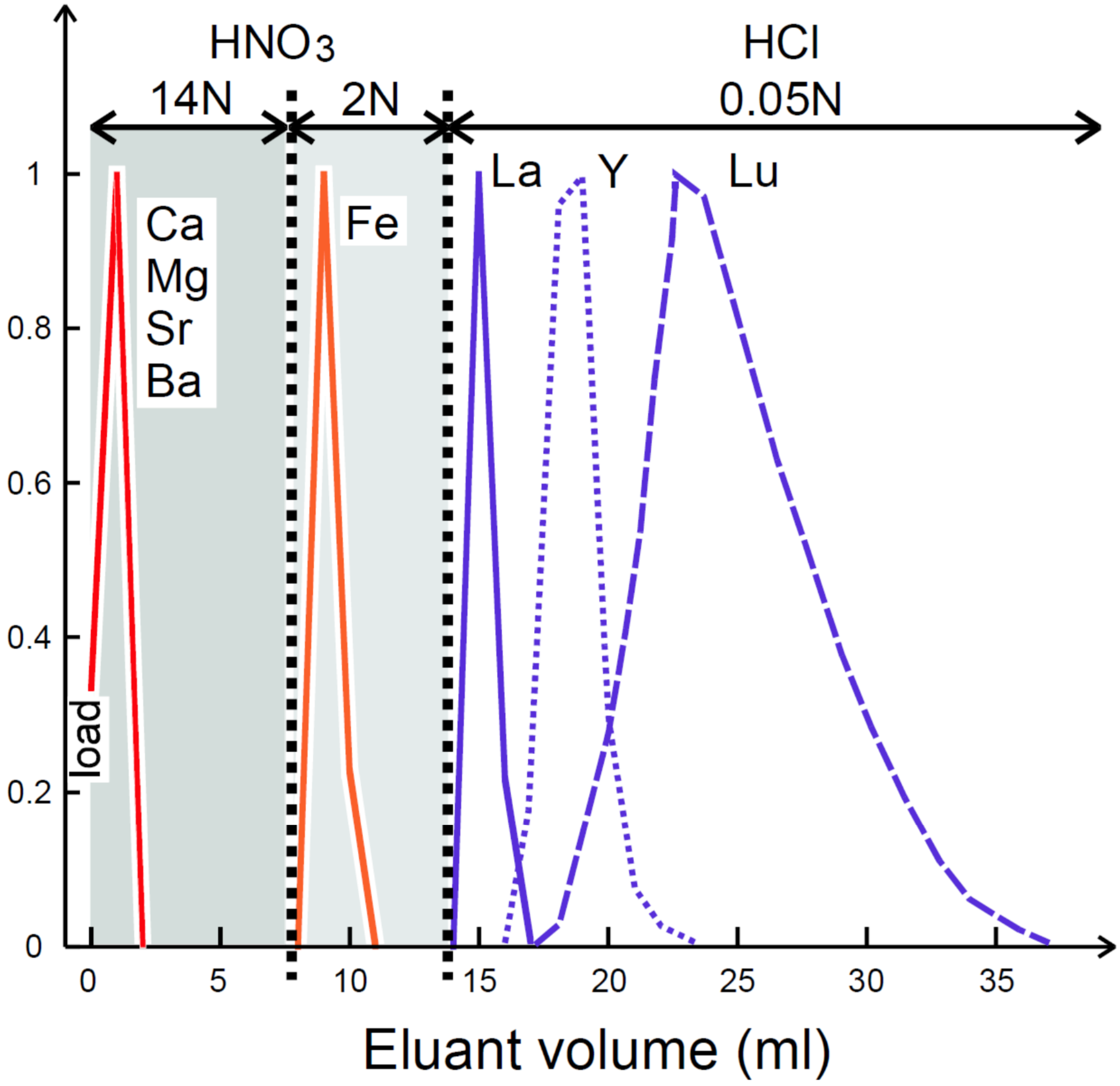


Figure 3. REE+Y patterns normalised to Post Archaean Australian Shale (Pourmand et al., 1991, adjusted to our BHVO-2 values) for the three carbonates analysed during the course of the study. References values are from Potts et al. [43] for CAL-S, and Dulski [16] for JLs-1.


HNO3
14N
2N
HCl
0.05N
1
0.8
0.6
0.4
0.2
0
load
Ca
Mg
Sr
Ba
Fe
La
Y
Lu
0
5
10
15
20
25
30
35
Eluant volume (ml)