

Separation of Rare Earth Elements in Geological Samples with High Concentrations of Barium Using RE Resin

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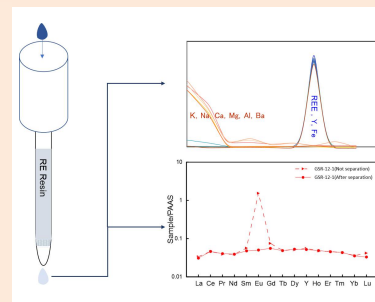
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ABSTRACT: Rare earth elements (REE) are important tools in geological studies. Accurate determination of REE concentrations can be affected in geological samples with low REE levels and/or high levels of interfering barium. Development of chemical separation methods allowing to isolate REE from other matrix components is a thorough approach to overcome this issue. In this study, a simple, RE resin-based separation method was developed and tested for a variety of sample solutions (mixed element solutions, shale, carbonate and granite). The method shows a good REE recovery and is efficient for the removal of matrix element, and notably Ba. The method is suitable for precise determination of the Eu contents in rock samples with high barium content.



INTRODUCTION

Rare earth elements (REE) are one of the main geochemical tools that play an important role in the genesis of rocks, the origin of ore-forming materials, and the redox environments of paleo-oceans.¹⁻⁵ The determination of REEs in geological samples is usually performed after acid digestion by inductively coupled plasma mass spectrometry (ICP-MS).⁶ However, for samples with high matrix elements, such as carbonates, siliceous rocks, seawater and sulfides, and low REE concentrations, the determination of their REE concentrations has always been problematic. Highly diluted sample solutions tend to have low intensities during ICP-MS measurements, resulting in high uncertainties in the results. On the other hand, the interferences imposed by matrix elements in less diluted sample solutions would be amplified, leading to the stability of the signals. Notably, for samples with high Ba concentrations, Ba imposes significant polyatomic interferences on Eu. Specifically, $^{151}\text{Eu}^+$ and $^{153}\text{Eu}^+$ can be superimposed by $^{135}\text{Ba}^{16}\text{O}^+$ and $^{137}\text{Ba}^{16}\text{O}^+$, respectively. Correction protocols based on monitoring the oxide production rates have been proposed to minimize the oxide interferences by BaO^+ .⁷⁻¹⁰ However, the main disadvantage of this method lies in the fact that the relative standard deviations associated with high Ba concentrations would limit the precision of the determined Eu values.^{7,11} In some cases,

ICP-MS may counteract the interferences during analysis.¹² For example, the interference can be eliminated by collision reaction cell (quadrupole mass spectrometer) or using the high resolution method (magnetic sector field mass spectrometer) during analysis, but the methods are less effective for samples with Ba/Eu ratios > 1000 and/or very low REE concentrations.^{11,13} Therefore, the pre-concentration of REEs and their separation from the matrix elements and Ba are usually necessary prior to ICP-MS measurement.

Co-precipitation and column chromatography have also been used for the separation of REEs from matrix elements. The former method employed $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and $\text{Ti}(\text{OH})_4$ for separation, but a new matrix element (e.g., Mg, Fe and Ti) could be introduced.¹⁴⁻¹⁷ Moreover, the removal efficiency of Ba by this method has rarely been evaluated. On the other hand, the column chromatography method usually adopted a chelating resin that is highly sensitive to the pH. In this way, addition of a buffering agent, such as ammonium citrate, is required, which adds to the complexity of the chemical procedure.¹⁸⁻²¹ Alternatively, the RE resin, prepared by dissolving octyl-N, N-diisobutylcarbamoylmethyl phosphine oxide in tributyl phosphate and impregnating an inert carrier, can also be used for REE separation.²² This resin is characterized by the high adsorption

capacity for REEs. In a study by Esser *et al.*,²² a technique using RE resin for the enrichment of REEs in natural waters was developed. Their results showed a high recovery of more than 80% and an effective separation of the REEs from Ba. Compared to other methods, the application of the RE resin is characterized by high recoveries and using a simpler experimental procedure, with less potential contamination and less laboratory time.

Barium (Ba) is a large ion lithophile element (LILE) and an incompatible element during magmatism.¹ Therefore, the upper continental crust and sediments have high Ba concentrations with average values of 628 mg/g and 768 mg/g, respectively.²³ For sedimentary rocks like shales and carbonates, the high Ba concentrations usually prohibit the precise determination of Eu and further leads to problematic interpretation of the Eu data. However, little attention has been paid in the literature to address this problem.²⁴⁻²⁷

In this study, we established a RE resin-based method for the analysis of REEs in samples with diverse matrices and Ba concentrations. This method is applied to a variety of geological samples, including shale, carbonate and granite that may potentially have Ba enrichment. The accuracy of the REE results was evaluated by the analysis of certified reference materials. The performance of the method on samples with extremely high Ba concentrations was evaluated by addition of Ba to certified reference materials.

EXPERIMENTAL

Reagents and samples. All solutions in the experiment were prepared using deionized water (18.2 MΩ, Millipore Corporation, USA). Nitric and hydrofluoric acids of analytical grade were purified by double-distillation using a PFA DAT 1000 system (Savillex, USA). REE multi-elemental standard solutions (100 mg/L for each REE) and single-element solutions for Ba, K, Na, Ca, Mg, Al and Fe (1000 mg/L) were obtained from Spex Certiprep (USA). The RE resin (100-150 μm) was obtained from Triskem (USA).

Geological certified reference materials were used to verify the performance of the method. They include: GSR-5 (Shale), GSR-12 (Dolomite), JDO-1 (Dolomite), and GSR-1 (Granite). GSR-5, GSR-12 and GSR-1 from the Institute of Geophysical and Geochemical Exploration (P.R. China) and JDO-1 from the Geological Survey of Japan.^{27,28}

Chemical procedure. Sample preparation. A mixture of standard solutions was prepared by adding calculated amounts of the REE multi-elements and single-element standard solutions to a PFA vessel. The solution was placed on a hot plate, set at 130 °C, and evaporated to dryness. Afterwards, 1 mL of 6 M HNO₃ was added to dissolve the solids and the solution was then diluted with water. The concentrations in the obtained solution were 10 μg/L for each

Table 1. Chemical Separation Procedures for RE Resin

Eluting fractions	Reagents	Volume (mL)
Resin prewashing	H ₂ O	5
	0.05 M HF	5
	6 M HNO ₃	5
Resin preconditioning	6 M HNO ₃	5
Sample loading		1
Washing	6 M HNO ₃	1
	6 M HNO ₃	1
	6 M HNO ₃	1
	6 M HNO ₃	1
	6 M HNO ₃	1
Collecting REE	0.01 M HNO ₃	5
	0.01 M HNO ₃	5
	0.01 M HNO ₃	5

REE: 1 mg/L for K, Ca, Mg, Fe, Al; 5 mg/L for Ba; and 20 mg/L for Na. This solution is labeled as MS.

For JDO-1 and GSR-12, which exclusively contain carbonate minerals, nitric acid was used for digestion. Approximately 100 mg of rock powder was weighed into a PFA vessel, and 3 mL of 1M concentrated HNO₃ was added. The vessel was put in an ultrasonic bath for 30 minutes. Afterwards, the solution was placed on a 120 °C hot plate to evaporate to dryness, followed by addition of 1 mL of 6 M HNO₃. The obtained solutions were labeled as GSR-12 and JDO-1, respectively.

For GSR-5 and GSR-1, approximately 100 mg of rock powder was weighed directly into a steel-jacketed high-pressure PTFE bomb, then dissolved using an acid mixture of 3 mL of concentrated HF and 2 mL of concentrated HNO₃ at 190 °C for 72 hours. The digested solution was evaporated to dryness and treated twice with 1 mL of concentrated HNO₃ to avoid formation of fluorides. Next, 3 mL of HNO₃ and 4 mL of water were added. The solution was then placed in the steel-jacket can and transferred to an oven at 120°C for another 12 hours. Finally, the solution was evaporated to dryness on a hot plate at 140 °C, then 1 mL of 6 M HNO₃ was added immediately. The obtained solutions were labeled GSR-5 and GSR-1, respectively.

In order to evaluate the performance of this method for samples with high Ba concentrations, 0.5 mL of the GSR-5 and GSR-12 solutions were taken, respectively. The calculated amounts of the standard Ba solution were then added. Finally, the solution contained Ba concentrations of about 10 mg/L and 100 mg/L, respectively. The solutions were labeled GSR-5-1 and GSR-12-1, respectively. For comparison, 0.5 mL of each sample solution (diluted with 6 M HNO₃ to 1 mL) was taken for column chemistry and the other 0.5 mL was measured directly for elemental concentrations.

Column Chemistry. The RE resin was soaked in 0.1 M HF at

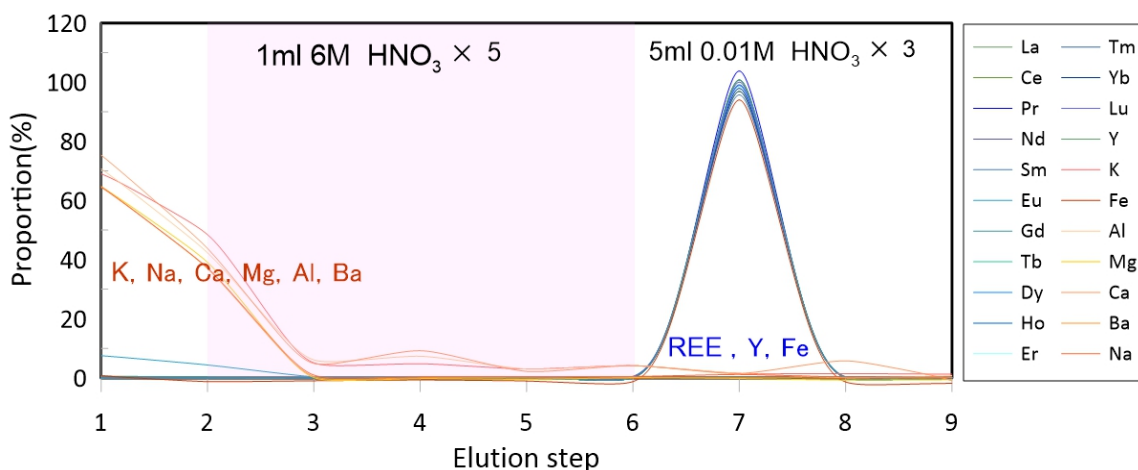


Fig. 1 Elution curve of the MS solution. (The proportion for all elements represented the percentage content in each elution fraction).

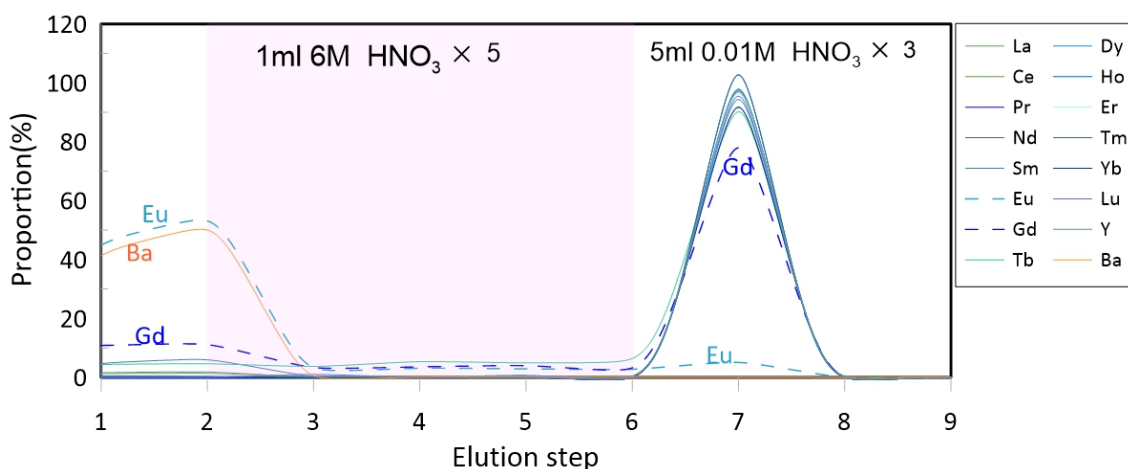


Fig. 2 The separation of Ba - REE by RE resin.

70 °C for 48 h, then rinsed three times with deionized water and stored in deionized water. Before use, 0.45 mL of the resin was filled into a PP column of 3 mm × 12 cm size (inner diameter × height).

Chemical separation process (Table 1):

(1) The resin was prewashed and preconditioned with 5 mL deionized water, 6 M HNO₃, 0.05 M HF, and 6 M HNO₃.

(2) After washing, 1 mL of sample solution (in 6 M HNO₃) was loaded.

(3) The matrix elements were eluted with five addition of 1 mL of 6 M HNO₃.

(4) Finally, the REEs were collected 3 times with 5 mL of 0.01 M HNO₃.

The MS and GSR-12-1 solutions were collected from step (2) to step (4) to generate elution curves (Fig. 1 and Fig. 2). For other solutions, the first 5 mL at step (4) were collected.

Instruments. All solutions were evaporated to dryness on a hot

Table 2. Operating Conditions of ICP-MS and ICP-OES

Parameter	ICP-MS	ICP-OES
Nebulizer type	Concentric glass Nebulizer	
Chamber type	Glass cyclonic spray chamber	
sampling mode	Liquid	
Autosampler	ASX-280	
Analysis mode	Normal/ Low-Resolution (LR)	Radial
Cool gas	15 L/min	12 L/min
Auxiliary gas	0.8 L/min	0.5 L/min
Nebulizer gas	1.05 L/min	0.5 L/min
RF Power	1200 W	1150 W

plate at 140°C before dilution to 10 ml and spiked with 10 ng/mL Rh. The REE concentrations were measured using an ICP-MS (Element XR, ThermoFisher, USA) and the concentrations for Ba, K, Na, Ca, Mg, Al, Fe were measured using an ICP-OES (iCAP 7200, ThermoFisher, USA). The detailed operating parameters are listed in Table 2. Possible spectroscopic interferences on the REE isotopes (for ICP-MS analysis) and elements (for ICP-OES analysis) are listed in Table 3.

Table 3. Isotopes and Spectrum Lines Selected in This Work

ICP-MS Analysis			
Isotope	Possible mass spectrum interferences	Isotope	Possible mass spectrum interferences
⁸⁹ Y	⁸⁸ Sr ¹ H	¹⁵⁹ Tb	
¹³⁹ La	¹³⁸ Ba ¹ H	¹⁶³ Dy	
¹⁴⁰ Ce	¹³⁸ Ba ¹ H ¹ H	¹⁶⁵ Ho	
¹⁴¹ Pr		¹⁶⁶ Er	
¹⁴⁶ Nd	¹³⁰ Ba ¹⁶ O	¹⁶⁹ Tm	
¹⁴⁷ Sm	¹³⁰ Ba ¹⁶ O ¹ H	¹⁷² Yb	¹³⁷ Ba ³⁵ Cl, ¹³⁵ Ba ³⁷ Cl
¹⁵³ Eu	¹³⁷ Ba ¹⁶ O, ¹³⁶ Ba ¹⁶ O ¹ H	¹⁷⁵ Lu	¹³⁸ Ba ³⁷ Cl, ¹³⁵ Ba ⁴⁰ Ar
¹⁵⁷ Gd	¹³⁸ Ba ¹⁸ O ¹ H	¹⁰³ Rh	

ICP-OES Analysis			
Spectrum line(nm)	Possible spectroscopic interferences	Spectrum line(nm)	Possible spectroscopic interferences
K 766.491	Cu, Fe, W, La	Mg 279.533	Mn
Na 589.592	Pb, Mo	Al 308.215	Na, Mn, V, Mo, Ce
Ca 317.933	Fe, Na, B, U	Fe 239.940	Cr, W
Ba 455.403	Fe		

Calibration was performed with external standard solutions for both ICP-MS and ICP-OES analysis. A series of standards with various elemental concentrations were used to build the calibration curves. For ICP-MS analysis of the REEs, ¹⁰³Rh was used as an internal standard to correct signal drifts. All calibration curves exhibited good linearity ($R^2 > 0.999$).

RESULTS AND DISCUSSION

Separation of REEs and the major matrix elements. As shown in Fig. 1, most of the matrix elements (K, Na, Ca, Mg, Al) were removed in the washing steps (pink area), except Fe. This probably is due to the low capabilities of these elements in forming stable complex ions at high concentrations of HNO₃.²² Therefore, it is difficult for them to be adsorbed by the resin. Meanwhile and since the REEs can form stable complexes in concentrated HNO₃, they exhibited stronger affinity to the RE resin in the washing steps. Since the HNO₃ concentrations decreased, the complexes formed

Table 4. LOD, LOQ, and Blank data of REEs (ng/mL)

REE	LOD	LOQ	Method Blank
Y	0.0019	0.0062	-
La	0.0003	0.0011	-
Ce	0.0013	0.0043	-
Pr	0.0009	0.003	0.005
Nd	0.0038	0.0127	-
Sm	0.001	0.0035	-
Eu	0.0004	0.0012	-
Gd	0.0016	0.0053	-
Tb	0.0002	0.0008	-
Dy	0.0006	0.002	-
Ho	0	0.0001	-
Er	0.0003	0.001	-
Tm	0.0002	0.0008	-
Yb	0.0003	0.0009	0.026
Lu	0.0002	0.0008	0.003

by the REEs became less stable and were eluted from the RE resin.²² Although some of the retained Fe will be eluted along with the REEs (Fig. 1), the influence on the precise determination of the REEs was negligible for all of the samples analyzed (see discussion below). The samples used in this study have Fe concentrations of less than 1.1%. For geological samples with higher Fe concentrations, such as iron ore, the influence of Fe awaits further exploration. In summary, by changing the concentration of the HNO₃ eluents, separation of the REEs from the matrix elements was achieved.

Separation of REEs and barium. The interference of Ba on the ICP-MS measurement of REEs has been a long-standing challenge.¹⁶ The two isotopes of Ba in geological samples are usually orders of magnitude higher than that of Eu, and the two isotopes of Eu (¹⁵¹Eu and ¹⁵³Eu) can be significantly affected by Ba oxides (¹³⁵Ba¹⁶O, ¹³⁷Ba¹⁶O) and hydroxides (¹³⁴Ba¹⁶OH, ¹³⁶Ba¹⁶OH). As a result, the measured Eu values in geological samples with high Ba concentrations can be largely overestimated by the presence of BaO, leading to erroneous Eu positive anomalies. In Fig. 1, it can be observed that Ba was eluted during the washing steps. For sample GSR-12-1, which had the highest Ba concentration (100 mg/L) and Ba/Eu ratio (ca. 200,000), the separation of Ba from the REEs was effective (Fig. 2). It is noticeable that a peak in Eu parallel to the Ba curve was observed in steps 1-3 (Fig. 2). This formation of the peak is due to the interference of BaO⁺ and BaOH⁺ and thus represents a “false” signal of Eu. A similar observation was found in the ¹⁵⁷Gd curve, which is linked to the influence from the formation of Ba hydroxide (¹³⁸Ba¹⁸O¹H) (Table 3).

Limits of detection and method blanks. The detection limits, the quantification limits and the procedural blanks in the experiment are listed in Table 4. Following the IUPAC definition, the detection limits (3σ) and quantification limits (10σ) were less than 0.004 ng/ml and 0.013 ng/ml, respectively. The blanks of most elements were below the detection limits, except for Yb, Lu and Pr. For sample solutions with the lowest Yb, Lu and Pr (GSR-12), the contributions of the blanks were less than 6% for Yb, less than 5% for Lu and less than 1% for Pr. The generally low blank contributions, which indicate the influences by the blanks, were only minimal in the determination of the REEs.

REE results of the analyzed samples. The recoveries of the REEs were calculated as the ratio of the determined elemental concentrations with and without column chemistry. As shown in Table 5, the recoveries for all REEs (except Eu) were excellent, ranging from 90% and 110%. The relatively low recovery of Eu is attributed to the interference by Ba on Eu for samples without chemical separation, which will be discussed in a section below.

The REE distribution patterns (normalized against PAAS²⁹) of the analyzed samples are shown in Fig. 3. For samples with Ba/Eu < 400 (GSR-1, GSR-5, JDO-1), the REE results before and after column chemistry are consistent recommended values of these

Table 5. REE Concentrations in the Certified Reference Materials

CRMs		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
MS	Content of REE (ng/g)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
	After separation (ng/g)	9.20	9.50	9.60	9.40	9.30	9.30	9.40	9.50	9.70	9.70	10.30	10.20	10.40	10.10	10.40
	Recovery (%)	92	95	96	94	93	93	94	95	97	97	103	102	104	101	104
	Preferred Values (µg/g) ²⁸	7.93	2.49	0.96	5.25	0.79	0.18	0.87	0.12	0.81	10.3	0.16	0.44	0.06	0.32	0.05
JDO-1	Not separation (µg/g)	7.47	2.34	1.02	4.95	0.72	0.17	0.92	0.11	0.79	10.37	0.17	0.48	0.06	0.32	0.05
	After separation (µg/g)	7.79	2.42	1.03	4.87	0.71	0.17	0.88	0.11	0.78	10.16	0.17	0.47	0.06	0.31	0.05
	Recovery (%)	104	103	101	100	100	98	95	97	99	98	99	100	100	97	103
	Preferred Values (µg/g) ²⁷	1.34	3.58	0.44	1.39	0.25	0.05	0.18	0.05	0.19	1.40	0.04	0.09	-	0.09	0.02
GSR-12	Not separation (µg/g)	1.33	4.13	0.38	1.40	0.28	0.07	0.23	0.04	0.26	1.47	0.05	0.14	0.02	0.10	0.02
	After separation (µg/g)	1.28	3.95	0.38	1.41	0.28	0.06	0.25	0.04	0.26	1.43	0.05	0.14	0.02	0.10	0.01
	Recovery (%)	96	96	100	101	99	82	106	99	98	97	100	101	99	103	95
	Not separation (µg/g)	1.29	3.68	0.35	1.33	0.31	1.66	0.35	0.04	0.24	1.5	0.05	0.13	0.02	0.1	0.018
GSR-12-1	After separation (µg/g)	1.19	3.66	0.36	1.33	0.27	0.05	0.26	0.04	0.25	1.39	0.05	0.13	0.02	0.1	0.014
	Preferred Values (µg/g) ²⁷	62.08	108.7	13.52	47.8	8.30	1.73	6.72	1.06	5.23	25.9	1.00	2.76	0.42	2.59	0.42
	Not separation (µg/g)	59.61	113.0	13.12	48.9	8.43	1.94	6.63	1.10	5.55	26.7	1.06	2.81	0.46	3.04	0.47
	After separation (µg/g)	54.56	110.9	13.13	48.9	8.42	1.71	6.44	1.08	5.44	25.9	1.04	2.78	0.45	2.87	0.45
GSR-5	Recovery (%)	92	98	100	100	100	88	97	98	98	97	98	99	97	94	97
	Not separation (µg/g)	60.22	111.1	12.99	46.6	8.00	2.94	6.44	1.00	4.98	26.1	0.95	2.54	0.40	2.55	0.44
	After separation (µg/g)	49.76	108.4	12.59	46.9	8.09	1.73	6.37	1.06	5.33	25.6	1.02	2.70	0.44	2.92	0.45
	Preferred Values (µg/g) ²⁷	54	108	12.7	47	9.7	0.85	9.3	1.65	10.2	62	2.05	6.5	1.06	7.4	1.15
GSR-5-1	Not separation (µg/g)	52.87	110.5	13.09	47.2	9.49	0.93	9.38	1.37	10.29	65.3	2.00	6.31	1.12	7.41	1.18
	After separation (µg/g)	52.69	104.3	13.06	48.0	9.25	0.80	9.32	1.33	9.97	61.5	2.06	6.21	1.06	7.40	1.04
	Recovery (%)	100	94	100	102	97	86	99	97	97	94	103	99	95	100	88

Fig. 3 Comparison of rare earth element partition patterns before and after RE resin separation in geological samples (A. JDO-1; B. GSR-12; C. GSR-5; D. GSR-1). (PAAS value after Taylor and McLennan,(1985)²⁹).

certified reference materials, indicating that the separation was effective. For GSR-12 (Ba/Eu: ca. 850), GSR-5-1 (Ba/Eu: ca. 900) and GSR-12-1 (Ba/Eu: ca. 200000) with high Ba/Eu ratios, the determined Eu contents without column chemistry were significantly higher than the recommended values, and

pronounced positive Eu and Gd anomalies were observed. The highest Eu and Gd anomalies are shown in GSR-12-1 with highest Ba/Eu. In contrast, the samples exhibited no Eu and Gd anomalies after separation, with measured REE concentrations consistent with the recommended values.

These results strongly support that the method proposed in this study can effectively separate Ba from REEs in clastic, silicates, and carbonates samples.

CONCLUSIONS

In the present study, a technique using RE resin was developed to separate REEs from matrix elements, notably Ba, from geological samples. For a variety of geological samples (carbonate, shale, granite) which usually exhibit high Ba concentrations, major matrix elements and Ba can be effectively removed with high recoveries for all REEs. Compared to previous techniques based on a chelating resin, the advantages of our method are low consumption of chemical reagents, no requirement for pH and less time-consuming.

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Notes

The authors declare no competing financial interest.

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