

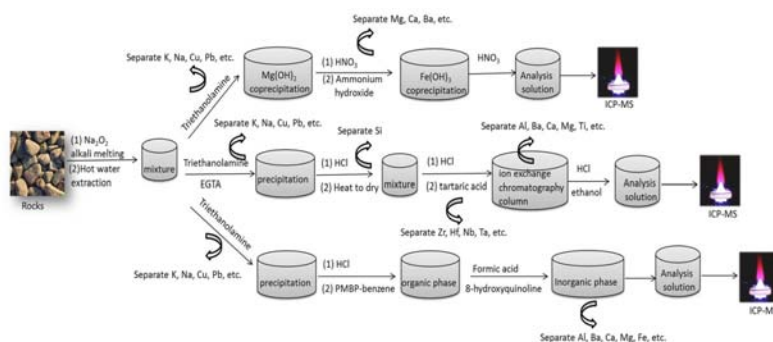
## ALKALI FUSION CO-PRECIIPITATION/CATION EXCHANGE/EXTRACTION ENRICHMENT FOR DETERMINATION OF TRACE RARE EARTH ELEMENTS IN ROCKS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Wenzhi ZHAO,\* Chuanfang ZHOU, Bing LU, Junbo YU and Yuan ZHANG

Center for Harbin Natural Resources Comprehensive Survey, China Geological Survey,  
Harbin, 150039, P. R. China

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In this paper, three separation and pre-enrichment methods of  $Mg(OH)_2$  and  $Fe(OH)_3$  co-precipitation, cation exchange and 1-phenyl-3-methyl-4-benzoyl-pyrazolone (PMBP) extraction were established by sodium peroxide alkali fusion digestion. Ca, Na and K, etc. were virtually eliminated from the analysis solutions using three sample processing procedures, thereby avoiding potential matrix interference and mass spectrometry interference due to high salt content. The detection limits of three methods were 0.0009–0.0076 mg/kg, 0.0011–0.0062 mg/kg, 0.0023–0.0114 mg/kg, respectively; the relative deviations of the determined rare earth elements (REEs) were -6.9–7.6%, -9.1–6.6% and -8.4–12.3%, respectively. The % RSD values of the three methods were lower than 10%, demonstrating good precision. The fit for purpose of the results was also evaluated by the quality criteria test proposed by the International Geological Correlation Programme (IGCP), from which it can be deduced that the three methods were adequate considering geochemical mapping application. The three sample processing procedures can be applied for the determination of rare earth elements in rocks.



### INTRODUCTION

Rare earth elements (REEs) have similar geochemical characteristics, stable chemical properties and high degree of uniformity. This unique geochemical property is often used to study mineral sources, evolution processes, rock genesis and magmatism, reflecting the element migration, enrichment and environmental change during the formation of geological bodies.<sup>1-3</sup> Therefore, there is a deep necessity for research in the determination and distribution of trace lanthanides in rocks. The physical and chemical properties of REEs are very similar

and they are also closely symbiotic in nature. Therefore, REEs are often considered as a whole. However, the characteristics that distinguish each REE from other REEs cannot be ignored.<sup>4-5</sup>

The term REEs is related to the elements of Group 3 in the Periodic Table: Sc, Y and the lanthanides, which comprises a group of 15 elements from La to Lu. However, Pm does not occur in the nature. Rare earth elements exist predominantly in the trivalent oxidation state. Sm, Eu and Y can be reduced to bivalent state and Ce, Pr and Tb can be oxidized to tetravalent state depending on the redox conditions. REEs are

\* Corresponding author: zhaowenzi817@163.com

classified according to the separation process, and they can be divided into light REEs (LREEs), including La, Ce, Pr, Nd, Pm, Sm, Eu and heavy REEs (HREEs), including Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y.<sup>6,7</sup>

At present, the determination of REEs mainly uses neutron activation analysis (NAA),<sup>8,9</sup> inductively coupled plasma mass spectrometry (ICP-MS),<sup>10-13</sup> inductively coupled plasma emission spectrometry (ICP-OES)<sup>14,15</sup> and X-ray fluorescence spectrometry (XRF).<sup>16,17</sup> ICP-MS is widely used in the analysis of REEs in geological samples due to its high sensitivity, low detection limit and wide linear dynamic range.<sup>18-20</sup> However, the direct determination of REEs in rocks is still difficult for various reasons. The content of REEs in some polymetallic ores is very low (0.1–1 mg/kg), while the content of matrix elements (Mg, Fe, Na, Ca, etc.) is very high. Using conventional sample preparation methods such as alkali melting, microwave digestion, mixed acid digestion and high pressure closed digestion to analyze by ICP-MS, generally needs multiple dilution (1000 times), which will lower the content of trace REEs below the detection limit of the instrument, therefore the content of REEs cannot be accurately analyzed.<sup>21,22</sup>

In this paper, sodium peroxide ( $\text{Na}_2\text{O}_2$ ) alkali melting digestion was used.  $\text{Mg}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  co-precipitation, and enrichment by cation exchange or PMBP extraction were selected to separate REEs from other rock-forming elements (Mg, Fe, Na, Ca, etc.), avoiding potential matrix interference and mass spectrometry interference caused by high salt content. The effects of three sample processing procedures on the determination of trace REEs were discussed and the detection

limits, accuracy and precision of the three methods were compared.

## RESULTS AND DISCUSSION

The separation and pre-enrichment route for the determination of REEs by ICP-MS is shown in Figure 1.

### 1. Matrix interference

Matrix elements such as Mg, Fe, Na, Ca, etc. in rocks have an influence on the determination of REEs. First of all, triethanolamine (TEA) forms a complex with Fe, Mg forms  $\text{Mg}(\text{OH})_2$  precipitate, co-precipitating REEs onto  $\text{Mg}(\text{OH})_2$ , so most of Fe, K, and Na are separated; secondly, after adjusting the pH value with ammonia solution, iron precipitates as  $\text{Fe}(\text{OH})_3$ . REE co-precipitate with it, allowing their isolation from other major matrix elements such as Mg, Ca and Ba. In cation exchange enrichment, the affinity of REEs for the cation exchange resin on elution with HCl is much larger than in the case of other elements, so K, Na, Al, Ca, Mg, Ba, Fe, etc. are separated by eluting with different concentrations of HCl. In PMBP extraction enrichment, PMBP forms benzene-extractable complexes with REEs. K, Na, Al, Ca, Mg, Ba, Fe, etc. are separated by back extraction with a mixture of formic acid and 8-hydroxyquinoline. The separation and enrichment by the above three methods reduce the dilution factor and improve the accuracy of ICP-MS determination.

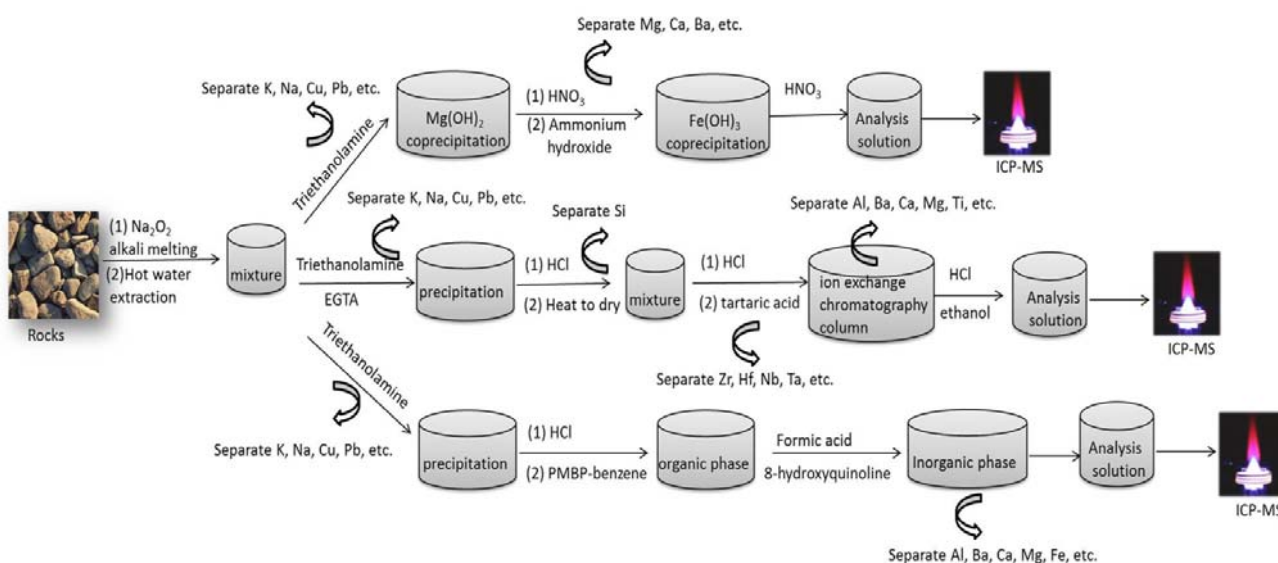


Fig. 1 – The separation and pre-enrichment route for determination of REEs by ICP-MS.

Table 1

Calibration functions and determination coefficients of REEs

Elements	Calibration functions <sup>a</sup>	Determination coefficients	Elements	Calibration functions	Determination coefficients
La	Y=4299.7x+3193.5	0.9992	Tb	Y=4775.1x+2257.1	0.9994
Ce	Y=4357.2x-1108.3	0.9991	Dy	Y=1433.8x+716.7	0.9995
Pr	Y=3057.9x-251.1	0.9994	Ho	Y=2001.2x+1444.4	0.9991
Nd	Y=2250.3x-446.1	0.9991	Er	Y=2844.7x-1217.6	0.9993
Sm	Y=3049.6x+1347.7	0.9990	Tm	Y=2003.2x+589.0	0.9996
Eu	Y=2942.7x+254.1	0.9997	Yb	Y=3237.8x-765.4	0.9996
Gd	Y=3880.2x+1662.5	0.9996	Lu	Y=2132.4x-917.5	0.9991

<sup>a</sup>X: concentration in µg/L, Y: signal intensity (CPS)

Table 2

Quantification limits of REEs

Elements	LOQ (mg/kg)			Elements	LOQ (mg/kg)		
	Co-precipitation	Cation exchange	DMBP-extraction		Co-precipitation	Cation exchange	DMBP-extraction
La	0.0137	0.0183	0.0247	Tb	0.0093	0.0037	0.0120
Ce	0.0253	0.0207	0.0380	Dy	0.0067	0.0090	0.0127
Pr	0.0093	0.0080	0.0143	Ho	0.0030	0.0047	0.0250
Nd	0.0057	0.0080	0.0147	Er	0.0150	0.0077	0.0200
Sm	0.0067	0.0087	0.0173	Tm	0.0207	0.0117	0.0257
Eu	0.0040	0.0073	0.0077	Yb	0.0043	0.0080	0.0187
Gd	0.0197	0.0173	0.0380	Lu	0.0217	0.0123	0.0370

## 2. Mass spectrum interference

The mass spectral interferences of REEs mainly come from oxides, polyatomic ions, and isotopes. In ICP-MS analysis, BaO interferes with Eu and LREEs oxides interfere with HREEs. In the pretreatment process, Ba has been separated from REEs. At the same time, after optimizing the operating parameters of the instrument, the oxide yield is less than 1%. Therefore, the interference of BaO on Eu and the interference of LREEs oxides on HREEs are both negligible.<sup>23</sup> According to the principle of non-interference, the determination of isotopes was performed. Therefore, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>151</sup>Eu, <sup>158</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, and <sup>175</sup>Lu were selected as the analysis isotopes.

## 3. Calibration and quantification limits

REEs stock standard solutions were diluted step by step with 2% HNO<sub>3</sub> into a mixing standard series of 0.0, 0.1, 0.5, 1.0, 10.0, 50.0 and 100.0 µg/L. The calibration functions were obtained

using optimized instrument working conditions. As shown in Table 1, the instrument response and concentration of REEs enjoy a good linear relationship in the 0.0-100.0 µg/L range.

The whole process blank solution (n=12) was prepared according to the prescribed method, and the contents of REEs were continuously determined under the selected instrument operating parameters. The quantification limits (LOQs) were calculated from the calibration curves as the concentration equivalent to ten times the standard deviation of blank signal (dilution factor DF= 250). The LOQs of REEs obtained in the analysis are listed in Table 2. It can be seen from Table 1 that the LOQs of the three sample processing procedures are 0.0030–0.0253 mg/kg, 0.0037–0.0207 mg/kg, 0.007–0.0380 mg/kg, respectively. The detection limits obtained by co-precipitation and cation exchange are better than those of PMBP-extraction. The three sample processing procedures have good detection ability, which can well meet the requirements for the determination of REEs in rocks.

Table 3

Concentrations determined of REEs in reference samples by ICP-MS under three methods

Elements	Reference samples	Certified (mg/kg)	Co-precipitation			Cation exchange			DMBP-extraction		
			Measured (mg/kg)	$\Delta \log C$	RSD%	Measured (mg/kg)	$\Delta \log C$	RSD%	Measured (mg/kg)	$\Delta \log C$	RSD%
La	GBW07108	15±4	15±0.4	0.006	2.35	15±1	0.009	6.5	17±1	0.049	9.16
	GBW07120	2.3±0.2	2.2±0.1	-0.011	5.13	2.2±0.2	-0.013	7.56	2.2±0.2	-0.024	9.50
	GBW07121	25±2	26±1	0.010	3.06	26±1	0.023	4.02	25±1	-0.003	4.78
Ce	GBW07108	25±3	25±1	0.006	3.77	25±1	0.003	3.8	24±1	-0.012	5.00
	GBW07120	4.6±0.4	4.7±0.4	0.013	8.09	4.8±0.3	0.017	7.03	4.2±0.3	-0.037	5.69
	GBW07121	48±3	46±2	-0.019	4.73	50±3	0.018	5.46	45±2	-0.027	4.19
Pr	GBW07108	3.4±0.4	3.3±0.3	-0.010	7.58	3.3±0.1	-0.016	2.28	3.6±0.2	0.024	6.03
	GBW07120	0.60±0.14	0.65±0.05	0.032	8.29	0.64±0.04	0.028	7.3	0.56±0.05	-0.034	7.58
	GBW07121	5.8±0.8	6.0±0.3	0.016	4.29	5.5±0.4	-0.026	6.71	5.3±0.3	-0.038	5.75
Nd	GBW07108	12.0±1.0	12.2±1.0	0.007	8.56	12.7±0.8	0.025	6.50	11.6±0.9	-0.014	7.5
	GBW07120	1.96±0.14	2.01±0.11	0.01	5.38	1.87±0.09	-0.021	4.44	1.83±0.10	-0.03	5.07
	GBW07121	21±4	20±2	-0.011	8.49	22±1	0.013	4.75	21±1	0.008	6.45
Sm	GBW07108	2.4±0.2	2.4±0.2	-0.009	6.89	2.4±0.2	-0.003	6.74	2.3±0.1	-0.015	4.03
	GBW07120	0.40±0.05	0.42±0.03	0.02	7.12	0.42±0.03	0.019	8.41	0.38±0.02	-0.021	4.38
	GBW07121	3.3±0.3	3.2±0.1	-0.009	3.04	3.4±0.2	0.013	5.68	3.2±0.2	-0.012	5.93
Eu	GBW07108	0.51±0.05	0.51±0.02	-0.004	3.97	0.52±0.03	0.006	5.39	0.52±0.02	0.006	4.37
	GBW07120	0.082±0.019	0.085±0.011	0.016	6.35	0.086±0.013	0.021	6.65	0.076±0.004	-0.035	4.56
	GBW07121	1.0±0.2	1.0±0.1	0.011	6.17	1.0±0.1	0.011	5.28	1.0±0.1	0.011	4.6
Gd	GBW07108	1.9±0.2	1.9±0.1	0.008	2.34	1.9±0.1	0.002	4.73	1.9±0.1	0.004	6.25
	GBW07120	0.36±0.08	0.36±0.01	-0.006	3.02	0.35±0.03	-0.013	8.69	0.39±0.03	0.036	7.46
	GBW07121	2.4±0.3	2.45±0.19	0.008	7.73	2.3±0.1	-0.011	5.91	2.6±0.2	0.026	6.08
Tb	GBW07108	0.35±0.05	0.35±0.02	0.019	4.81	0.34±0.01	-0.014	3.75	0.36±0.02	0.011	6.72
	GBW07120	0.054±0.010	0.057±0.004	0.023	7.40	0.051±0.001	-0.024	7.51	0.058±0.004	0.028	7.95
	GBW07121	0.29±0.03	0.30±0.02	0.019	5.84	0.28±0.01	-0.014	2.94	0.31±0.01	0.027	4.1
Dy	GBW07108	1.6±0.2	1.5±0.1	-0.016	7.03	1.5±0.1	-0.023	7.14	1.7±0.12	0.029	7.64
	GBW07120	0.28±0.07	0.27±0.02	-0.012	6.2	0.26±0.02	-0.032	5.51	0.27±0.01	-0.024	3.67

Elements	Reference samples	Certified (mg/kg)	Co-precipitation			Cation exchange			DMBP-extraction		
			Measured (mg/kg)	$\Delta\log C$	RSD%	Measured (mg/kg)	$\Delta\log C$	RSD%	Measured (mg/kg)	$\Delta\log C$	RSD%
Ho	GBW07121	1.52±0.14	1.41±0.11	-0.031	7.53	1.62±0.10	0.027	6.45	1.65±0.08	0.036	5.49
	GBW07108	0.33±0.05	0.32±0.02	-0.016	6.59	0.31±0.02	-0.028	5.49	0.35±0.03	0.027	8.25
	GBW07120	(0.045)	0.047±0.004	0.015	8.88	0.043±0.003	-0.021	7.06	0.044±0.002	-0.011	5.03
	GBW07121	0.27±0.03	0.28±0.01	0.02	4.9	0.28±0.01	0.01	3.45	0.29±0.02	0.028	8.22
Er	GBW07108	1.0±0.2	1.0±0.1	0.009	6.44	1.1±0.1	0.024	9.92	1.1±0.1	0.027	8.86
	GBW07120	(0.17)	0.18±0.01	0.018	6.32	0.16±0.01	-0.02	5.34	0.16±0.01	-0.021	5.2
	GBW07121	0.76±0.08	0.73±0.05	-0.021	6.53	0.73±0.05	-0.02	6.57	0.80±0.07	0.023	9.33
Tm	GBW07108	0.17±0.04	0.18±0.01	0.016	8.19	0.16±0.01	-0.018	7.22	0.18±0.01	0.022	5.61
	GBW07120	(0.024)	0.025±0.002	0.02	7.15	0.025±0.001	0.023	5.71	0.026±0.002	0.042	6.52
	GBW07121	0.11±0.02	0.11±0.01	0.012	8.3	0.10±0.01	-0.033	9.21	0.11±0.01	0.018	8.8
Yb	GBW07108	0.90±0.11	0.86±0.04	-0.021	4.99	0.82±0.08	-0.042	9.27	1.00±0.05	0.048	5.05
	GBW07120	0.15±0.05	0.15±0.01	-0.012	4.79	0.16±0.01	0.023	7.33	0.16±0.01	0.03	6.28
	GBW07121	0.69±0.08	0.72±0.04	0.018	5.73	0.70±0.04	0.004	5.57	0.77±0.04	0.045	5.12
Lu	GBW07108	0.14±0.03	0.15±0.01	0.026	5.81	0.14±0.01	-0.01	6.19	0.14±0.01	-0.013	4.43
	GBW07120	0.023±0.007	0.022±0.002	-0.023	8.86	0.022±0.002	-0.026	8.96	0.021±0.001	-0.038	6.28
	GBW07121	0.11±0.01	0.12±0.01	0.024	6.29	0.11±0.01	0.007	6.71	0.12±0.01	0.027	8.12

Values are for mean±standard deviation of twelve replicate measurements (n = 12).

#### 4. Comparison of accuracy and precision

According to the specified method, the national first-class reference samples GBW07108 (marly limestone), GBW07120 (limestone), and GBW07121 (granite gneiss) were measured. For each analyzed reference sample, the average determined value ( $n=12$ ), certified value, accuracy results ( $\Delta \log C$ ) and relative standard deviation (%RSD) ( $n=12$ ) were collected in Table 3.

As shown in Table 3 and Fig. 2, the measured

values of HREEs after cation exchange enrichment were lower than the certified values. This may be due to the high distribution coefficient of REEs in strongly acidic cation exchange resin and 1–2 mol/L HCl. The distribution coefficient decreases with the increase of the atomic number of REEs, the distribution coefficient of LREEs is greater than that of HREEs, resulting in incomplete exchange of HREEs, which results in lower measurement results.

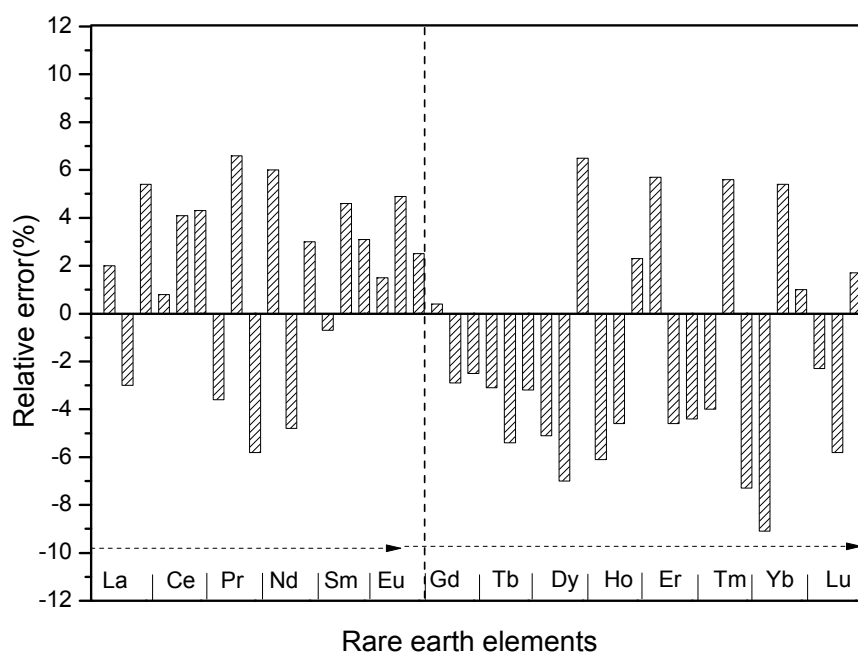


Fig. 2 – Schematic diagram of the accuracy of cation exchange.

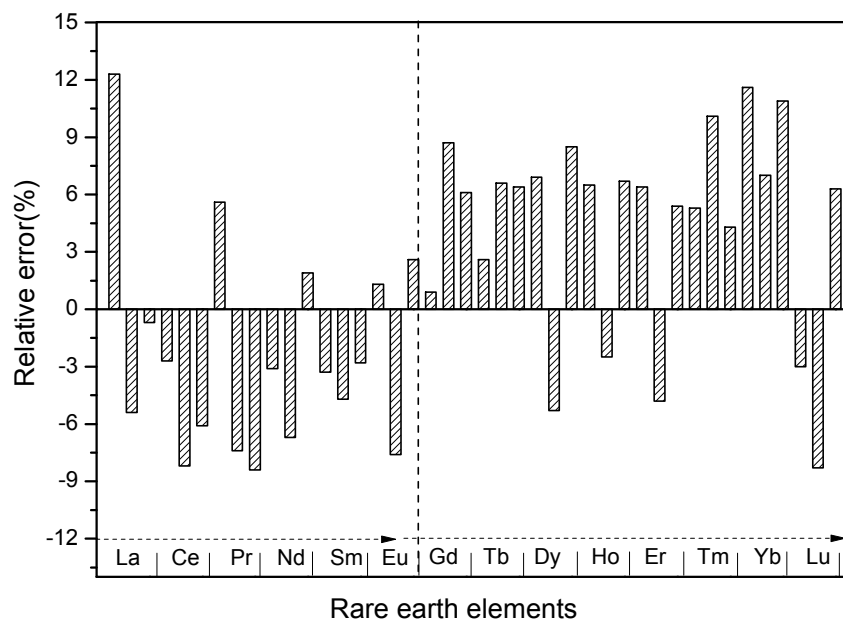


Fig. 3 – Schematic diagram of the accuracy of DMBP-extraction enrichment.

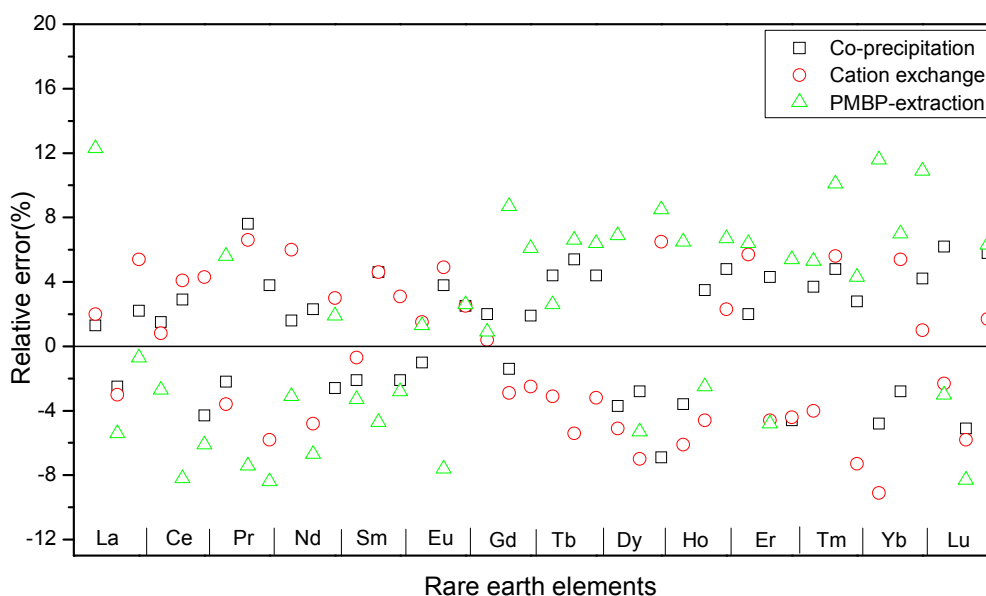


Fig. 4 – Comparison of the accuracy of three different pre-processing methods.

The measured values of LREEs by the PMBP-extraction were lower than the certified values, as shown in Table 3 and Figure 3. The reason may be that due to the “lanthanum shrinkage” of REEs, the ion radius gradually decreases from La to Lu. Therefore, the basicity of lanthanides gradually decreases from La to Lu. When  $\text{pH} < 5$ , the extraction of LREEs may be incomplete, while HREEs can be completely extracted; when  $\text{pH} > 5$ , LREEs are completely eluted, while HREEs are somewhat less. Most of the very low values in the reference samples selected in this article are in HREEs. Therefore, the pH value is set to 4.5 to ensure the complete extraction of low content HREEs, which may lead to incomplete extraction of some LREEs, making its measurement results low.<sup>24</sup>

The relative error (%RE) was adopted to evaluate the accuracy of twelve replicates of each sample. The concentrations of REEs by co-precipitation, cation exchange and PMBP-extraction were compared with certified values. The relative standard deviations of the levels of REEs determined after sample co-precipitation ranged from -6.9 to 7.6 %, while for cation exchange sample processing they varied from -9.1 to 6.6 % and extended from -8.4 to 12.3 % when PMBP extraction was applied. All the determination data by the three methods were reasonable and acceptable. The comparison of experimental results showed better accuracy after sample processing by co-precipitation and cation exchange than when using PMBP extraction (Fig. 4).

Results accuracy was also evaluated by the quality test proposed by the International Geological

Correlation Programme (IGCP),<sup>25</sup> which compares the differences between obtained and recommended values by the expression of  $\Delta \log C$  ( $\log C_s - \log C_i$ ), where  $C_i$  and  $C_s$  are the certified and measured value, respectively. According to IGCP criteria,  $\Delta \log C$  of the reference samples analyzed in this work would be between -0.05 and 0.05 for REEs. The results in Table 3 showed that  $\Delta \log C$  of REEs determination were -0.031-0.032 for co-precipitation and -0.042-0.028 for cation exchange and -0.038-0.049 for PMBP-extraction, which shows good accuracy. It can be deduced that all the three sample processing procedures are adequate for geochemical mapping application. The precision of twelve replicates of each sample is expressed as the relative standard deviation (%RSD). It can be seen from Table 3 that the %RSD values of REEs determination were lower than 8.88% for co-precipitation and lower than 9.92% for cation exchange and lower than 9.50% for PMBP-extraction. Consequently, all three methods developed in this study are demonstrated to be a valid method for determining REEs in rocks.

## EXPERIMENTAL

### 1. Instruments and operation conditions

An ICP-MS (X Series II, Thermofisher Scientific, USA) was used for the determination of trace REEs. The sensitivity, oxide yield (<1.0%) and double charge yield (<3.0%) were adjusted by the tuning solution. Details of the instrument and the operating parameters are summarized in Table 4.

Table 4

## Operating conditions of ICP-MS

Item	Parameter
RF power (W)	1300
Nebulizer gas flow (L·min <sup>-1</sup> )	0.8
Cooling gas flow (L·min <sup>-1</sup> )	13.5
Auxiliary gas flow (L·min <sup>-1</sup> )	0.78
Sampling depth (mm)	13
Dwell time (ms)	10
Integration time (s)	15
Rising speed (mL·min <sup>-1</sup> )	1.0
Sample cone (Aperture/mm)	Nickel (1.0)
Skimmer cone (Aperture/mm)	Nickel (0.7)

## 2. Reagents and solutions

Reference samples GBW07108 (marly limestone, IGGE, China), GBW07120 (limestone, IGGE, China), and GBW07121 (granite gneiss, IGGE, China) were used for method validation; hydrochloric acid (36.0-38.0%), hydrofluoric acid ( $\geq 40.0\%$ ), nitric acid (65.0-68.0%), sodium peroxide ( $\geq 95.0\%$ ), triethanolamine (TEA) ( $\geq 99.0\%$ ), ethylene glycol-bis( $\beta$ -aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA) ( $\geq 99.0\%$ ), ammonium chloride ( $\geq 99.8\%$ ), ammonia (25.0-28.0%), magnesium chloride ( $\geq 98.0\%$ ), tartaric acid ( $\geq 99.5\%$ ), anhydrous ethanol ( $\geq 99.8\%$ ), acetic acid ( $\geq 99.8\%$ ), sodium acetate ( $\geq 95.0\%$ ), PMBP ( $\geq 98.0\%$ ), benzene ( $\geq 99.8\%$ ) and 8-hydroxyquinoline ( $\geq 99.5\%$ ) (Sinopharm Chemical Reagent Co. Ltd, China) were all analytical grade reagent; tuning solution was purchased from Thermofisher Scientific (USA); AG 50W-X8 hydrogen type strong cation exchange resin (0.38-0.76  $\mu\text{m}$ ) and Poly-Prep polypropylene separation column (0.8  $\text{cm} \times 4 \text{ cm}$ ) were purchased from Beijing Fuxing Chemical Industry Co. Ltd (China).

Standard solutions used to build the ICP-MS calibration curves were prepared by the appropriate dilution of stock standard solutions containing 100 mg/L REEs (IGGE, China) in 2% (v/v) HNO<sub>3</sub>; <sup>103</sup>Rh used as internal standard solution was prepared by the appropriate dilution of stock standard solutions (IGGE, China) in 2% (v/v) HNO<sub>3</sub>. All solutions were prepared using high purity water (18.2 M $\Omega$  cm resistivity) obtained from GN-RO-500 Total Water System (Shuangfeng, Beijing, China).

## 3. Separation and pre-enrichment methods

### 3.1. Method for co-precipitation of Mg(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>

0.2000 g sample, 2.0 g Na<sub>2</sub>O<sub>2</sub> were added to the corundum crucible, mixed, then 1.0 g Na<sub>2</sub>O<sub>2</sub> was added to the surface of the sample and melted at 700 °C in muffle furnace for 15 min. After cooling to room temperature, the mixture was transferred into a beaker containing 5 mL TEA, 50% solution. 30 mL hot water were added for extraction, followed by 5 min heating, and crucible rinsing. The mixture was centrifuged at 3200 r/min for 3 min, the remaining liquid discarded, 1 mL 5% HNO<sub>3</sub> was added to dissolve the precipitate, then 10 mL pure water were added. The pH was adjusted with 50% NH<sub>3</sub> to precipitate iron hydroxide, followed by water addition to 25 mL, and 10 mL NH<sub>4</sub>Cl-NH<sub>3</sub> buffer solution (pH = 9). The resulting mixture was centrifuged at 3200 r/min for 3 min, the liquid was discarded, another 35 mL pure water were added and 0.5 mL ammonia. After centrifugation, the liquid was discarded, 1 mL nitric acid was added to dissolve the precipitate, and made up to 25 mL with water.

### 3.2. Method for cation exchange

The alkali melting stage was the same as in Section 3.3.1. After cooling to room temperature, the mixture was transferred into a beaker containing 10 mL TEA, 5 mL EGTA. 30 mL hot water were added for extraction, followed by crucible rinsing, dilution with water to 100 mL, boiling for 5 min. After cooling and filtering, the precipitate was washed with 2% NaOH and dissolved with hot 1: 1 HCl, heated to dryness. 3 mL HCl were added to wet the residue, and mixed with 2 g tartaric acid and 30 mL water, then heated for complete dissolution. The solution was transferred to an ion exchange chromatography column and run through the column at a rate of 0.5–0.8 mL/min. Fe, Al, Ca, etc. were rinsed with 2 mol/L HCl-20% C<sub>2</sub>H<sub>5</sub>OH. The REEs were leached with 3 mol/L HCl-20% C<sub>2</sub>H<sub>5</sub>OH. The REEs eluate was heated and evaporated to 10 mL, and diluted to 25 mL.

### 3.3. Method for PMBP-extraction enrichment

The alkali melting stage was the same as in Section 3.3.1. After cooling to room temperature, the mixture was transferred into a beaker containing 5 mL TEA. 30 mL hot water were added for extraction, followed by crucible rinsing, dilution with water to 100 mL, and boiling for 5 min. After cooling and filtering, the precipitate was washed with 2% NaOH and dissolved with hot 1: 1 HCl; 5% HCl was used to adjust the pH to about 5, then 5 mL acetic acid-sodium acetate buffer solution (pH=4.5) were added, and 15 mL 0.01 mol/L PMBP-C<sub>6</sub>H<sub>6</sub> solution. Extraction was performed for 1min, the aqueous layer was discarded. 15 mL formic acid-8-hydroxyquinoline mixtures were added in the organic phase for back extraction, phases were mixed for 1 min; the organic phase was discarded, and the aqueous phase was diluted to 25 mL.

## CONCLUSIONS

In this paper, the sample processing procedures of Mg(OH)<sub>2</sub> and Fe(OH)<sub>3</sub> co-precipitation, cation exchange and PMBP-extraction were proposed to separate REEs from matrix elements to eliminate matrix interference and mass spectrum interferences. Sample processing by co-precipitation and cation exchange gave better results in terms of accuracy than PMBP-extraction. According to the quality criteria test proposed by IGCP,  $\Delta \log C$  of all REEs determinations are between -0.05 and 0.05, demonstrating good accuracy. It can be deduced



that all three sample processing procedures are adequate considering geochemical mapping application. The %RSD values of the three sample processing procedures were lower than 10%, performing good precision. Consequently, all three methods can be applied for the determination of REEs in rocks.

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