

## Rapid Two-Column Separation Method for Determining Barium Isotopic Compositions Using MC-ICP-MS

Yishan Cheng,<sup>a</sup> Yifan Du,<sup>a</sup> Kaiyun Chen,<sup>a,\*</sup> Chunlei Zong,<sup>a</sup> Jian Zhao,<sup>a</sup> and Li-Hui Chen<sup>a</sup>

<sup>a</sup> State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, P. R. China

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**ABSTRACT:** In recent years, the stable isotope composition of barium has emerged as a powerful tracer for understanding crucial geo-social processes; therefore, it is necessary to develop an efficient method for Ba isotopic ratios. Herein, we describe a rapid method for determining the isotopic ratios of Ba using a multi-collector inductively coupled plasma mass spectrometer in the low-resolution mode (Neptune Plus). In this method, the exact amount of the resin and the low eluted volume of the acid used in column purification significantly reduce the time required for Ba separation. Instrumental mass bias calibrations were performed for both standard-sample bracketing (SSB) and double-spike methods. The results show that the double-spike method provided Ba isotopic ratios with higher precision than the SSB technique. The effects of acid molarity and concentration mismatch, as well as the potential matrix effect, were investigated in the wet plasma mode. We evaluated the Ba isotopic compositions of ten geological reference materials, namely, BCR-2, BHVO-2, AGV-2, GSP-2, RGM-2, G-2, GSR-3, GSR-5, GSR-8, and GSR-11. Results indicated that these compositions were highly accurate with respect to the international Ba isotope standard, NIST SRM 3104a. Furthermore, the Ba isotopic compositions of most geological reference materials examined in this study agreed well with previously published data within the quoted analytical uncertainties. The long-term reproducibility analyses of all standards indicated that the obtained isotopic ratios were highly reproducible for  $\delta^{138/134}\text{Ba}$ , with precisions of  $\leq \pm 0.05\%$  (2SD). Compared to previous reports, we optimized the process of chemical purification, separated Ba samples faster, and improved the efficiency of the analyses employed in this study.

## INTRODUCTION

Barium is an alkaline earth metal of the second main group of the sixth period of the periodic table. The atomic number of Ba is 56 with a relative atomic mass is 137.32. Elemental Ba does not exist in nature because of its high chemical reactivity. The main minerals of Ba found in nature are barite or baryte ( $\text{BaSO}_4$ ) and witherite ( $\text{BaCO}_3$ ), which are both insoluble in water.<sup>1</sup> Ba is broadly distributed in seawater, river water, river sediments, and soil pore water.<sup>2</sup> Ba is a large-ion lithophile element and highly incompatible during the melting of the Earth's mantle.<sup>1, 3-8</sup> The amounts of Ba in chondrite and silicate minerals are 2.41 and 6.60  $\mu\text{g g}^{-1}$ , respectively, both considerably lower than those found in the upper continental crust and sediments (628 and 768  $\mu\text{g g}^{-1}$ ,

respectively).<sup>4, 9-12</sup> Upon subduction, fluid Ba is first released from the subducting slab with the fluid, and then enters the mantle wedge.<sup>13</sup> The introduction of small amounts of surface materials into the mantle can cause significant changes in its Ba content. Therefore, Ba can be used to trace not only subduction-related activities but also crustal material recycling.<sup>14, 15</sup> In addition, Ba is a well-known geochemical proxy used to trace oceanic biogeochemical cycling and the diagenetic alteration of sediments. In sediments, bio-barite is often used for reconstructing the ocean paleoproductivity because the accumulation rate of bio-barite strongly correlates with the output flux of organic carbon.<sup>16-18</sup> The elemental and isotopic composition of Ba has been used to study elemental cycling in the marine systems, hypergene environment, paleoenvironments, and subduction zones.<sup>19-22</sup>

Ba has seven stable isotopes, namely,  $^{130}\text{Ba}$ ,  $^{132}\text{Ba}$ ,  $^{134}\text{Ba}$ ,  $^{135}\text{Ba}$ ,  $^{136}\text{Ba}$ ,  $^{137}\text{Ba}$ , and  $^{138}\text{Ba}$ , with percent abundances of 0.1058%, 0.1012%, 2.417%, 6.592%, 7.853%, 11.232% and 71.699%, respectively.<sup>3</sup> In the previous studies<sup>3, 23</sup>, Ba isotopic composition was determined by thermal ionization mass spectrometry (TIMS); however, the analytical precision was low due to the limitations associated with the instruments used. Nier<sup>23</sup> was the first to determine the stable isotopic composition of Ba using TIMS. Eugster *et al.*<sup>3</sup> used the double-spike (DS) method ( $^{134}\text{Ba}$ - $^{137}\text{Ba}$ ) and TIMS to improve the precision of Ba isotope analysis to 1‰. In the mid-to-late 20th century, the Ba isotopic compositions of meteorite samples and natural fission reactors were mostly studied. For example, the heterogeneity of the early solar system can be assessed by Ba isotopic anomalies in carbonaceous chondrites.<sup>24, 25</sup> With the rapid development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), von Allmen *et al.*<sup>26</sup> used the DS method ( $^{130}\text{Ba}$ - $^{135}\text{Ba}$ ) to improve the analytical precision to 0.14‰ ( $\delta^{137/134}\text{Ba}$ , 2SD). Miyazaki *et al.*<sup>5</sup> achieved an optimal dilution ratio of the DS to the sample and improved the analytical precision to 0.03‰ ( $\delta^{137/134}\text{Ba}$ , 2SD) for Ba isotopes. Nan *et al.*<sup>8</sup> used both Ce-doping and the DS method ( $^{135}\text{Ba}$ - $^{136}\text{Ba}$ ) to measure Ba isotopic composition and reported an accuracy of 0.05‰ ( $\delta^{137/134}\text{Ba}$ , 2SD). Tian *et al.*<sup>27</sup> used the  $\text{Na}_2\text{CO}_3$  exchange reaction and  $^{135}\text{Ba}$ - $^{136}\text{Ba}$  DS method to measure Ba isotopes in barite with a precision of 0.05‰ ( $\delta^{137/134}\text{Ba}$ , 2SD). Owing to the extensive application of MC-ICP-MS and TIMS, high-precision Ba isotopic analysis methods have been gradually developed and improved. Several previous studies involved the application of Ba isotopes for tracing high- and low-temperature geochemical processes.<sup>17, 22, 28-30</sup> Natural Ba samples, experimental Ba precipitation, and diffusion experiments exhibit large variations in Ba isotope fractionation.<sup>31-34</sup> Highly precise and accurate data are prerequisites for the application of Ba isotopes. Studies on Ba isotopes, which are rapidly increasing in number, require reference materials for the validation of different analytical methods and comparison of the data acquired in different laboratories. However, Ba isotopic data for the reference materials used for comparison are still limited.

This paper describes a highly precise analytical method for determining Ba isotopic compositions by applying the sample-standard bracketing and DS methods. Our method includes a simplified chemical purification process for Ba separation and a direct approach for the correction of instrumental mass bias. We used ion-exchange and Sr resin columns to separate Ba from the matrix elements, including major and rare-earth elements (REEs). The Ba isotopic ratios of ten geological samples, including basalt, granodiorite, andesite, shale, trachyte, granite, and rhyolite, were measured using MC-ICP-MS and two correction methods. Herein, we report creating a comprehensive database for method validation by introducing an efficient chemical pretreatment method for geological reference materials. Moreover, we present

new data on Ba isotopic ratios in geological reference materials, facilitating the application of Ba isotopes in the study of geochemical processes.

## EXPERIMENTAL

**Reagents and materials.** The experiments were conducted in an ISO-class 6 clean room at the State Key Laboratory of Continental Dynamics (SKLCD), Northwest University, China. To obtain high-purity acids, guaranteed reagent (GR) –grade hydrochloric acid (HCl) and nitric acid ( $\text{HNO}_3$ ) were distilled twice using a sub-boiling distillation system, Savillex DS-1000 (Savillex, Eden Prairie, MN, USA). Ultrapure water (resistivity of  $18.2 \text{ M}\Omega\text{-cm}$ ) was procured from a Milli-Q Element water purification system (Elix-Millipore, Billerica, MA, USA) and used for acid dilutions and washing solid samples. First, 1.1 mL of the cation exchange resin (AG 50 W-X8 200–400 mesh, Bio-Rad, USA) was pre-cleaned and packed in a polyacrylamide column (8 mm OD  $\times$  63 mm Length); thereafter, 0.5 mL of Eichrom's Sr-spec<sup>TM</sup> resin was packed in an ion-exchange column (6 mm  $\times$  104 mm).  $\text{H}_2\text{O}_2$  (approximately 30%) was obtained from Alfa Aesar (USA). All beakers, Teflon bottles, and vials (Savillex<sup>®</sup>) were cleaned with GR–grade  $\text{HNO}_3$ , GR–grade HCl, high-purity  $\text{HNO}_3$ , high-purity HCl, and ultrapure Milli-Q water prior to use.

Ten reference materials were used; these included igneous rocks, namely, rhyolite RGM-2, GBW07113 (GSR-11), granite G-2, trachyte GBW07110 (GSR-8), andesite AGV-2, granodiorite GSP-2, basalt BCR-2, BHVO-2, and GBW07105 (GSR-3), and sedimentary rocks, namely, shale GBW07108 (GSR-5). These geological samples were approved as reference materials by the United States Geological Survey (USGS) and the Institute of Geophysical and Geochemical Exploration (IGGE) of the Chinese Academy of Geological Sciences (CAS). Three pure Ba standard solutions were used to evaluate the stability of the instrument during measurements. The two standard solutions included a Ba ICP-MS standard solution (Alfa Ba,  $10 \text{ mg mL}^{-1}$  Ba diluted in  $\text{HNO}_3$  (5 v/v%), LOT # 9177497) procured from Alfa Aesar (USA) and a GSB Ba standard solution (GSB 04-1717-2004,  $10 \text{ mg mL}^{-1}$  Ba diluted in  $1 \text{ mol L}^{-1}$   $\text{HNO}_3$ ) procured from the Key Laboratory of Isotopic Geology, Ministry of Land and Resources, China. The Ba isotope, NIST-standard-certified SRM 3104a (NIST 3104a,  $10 \text{ mg mL}^{-1}$  diluted in  $\text{HNO}_3$  (1%), LOT # 140909) from the National Institute of Standards and Technology (NIST), was diluted and used as the bracketing standard.

The DS ( $^{135}\text{Ba}$ - $^{136}\text{Ba}$ ) method was modified based on a previous report by Tian *et al.*<sup>27</sup>. Isolution 2.0<sup>35, 36</sup> software (<http://isolution.net.cn/en/>) was used to calculate the optimized isotopic composition of the DS of  $^{135}\text{Ba}$ - $^{136}\text{Ba}$ . The results showed that the optimal composition of the DS ( $^{135}\text{Ba}$ / $^{136}\text{Ba}$ ) is 1.78, and

**Fig. 1** Effects of the isotopic compositions and proportions of the double spike (DS) in the DS sample mixture. The vertical and horizontal axes indicate the proportions of  $^{135}\text{Ba}$  and  $^{135}\text{Ba}/^{136}\text{Ba}$  in the double-spike-sample mixture, respectively. The isotopic ratio of the DS is calculated using the Monte Carlo Simulation method, and the calculation error propagation process was different from Rudge *et al.* (2009). The plot is generated using the Isolution 2.0 software (<http://isolution.net.cn/en/>), which uses the principle of Pascal code to obtain the most ideal isotopic composition of the  $^{135}\text{Ba}/^{136}\text{Ba}$  DS. The optimal composition of the DS ( $^{135}\text{Ba}/^{136}\text{Ba}$ ) is 1.78, and the optimal molar fraction of the DS for the  $^{135}\text{Ba}/^{134}\text{Ba}-^{136}\text{Ba}/^{134}\text{Ba}-^{138}\text{Ba}/^{134}\text{Ba}$  isotope spaces relative to the mixed Ba solution is 0.52.

**Fig. 2** Elution curves of the matrix elements obtained with the cation resin AG 50W-X8 column (step 1). Element concentrations are measured using Agilent 8900 ICP-MS. Each aliquot corresponds to 1 mL of an acidic eluent. The vertical dotted line represents the concentration change of the acid used.

**Fig. 3** Elution curves of rare-earth elements obtained with the Sr resin column (step 2). Element concentrations are measured on Agilent 8900 ICP-MS. Each aliquot corresponds to 1 mL of an acidic eluent. The vertical dotted line represents the concentration change of the acid used.

the optimal molar fraction of the DS relative to the mixed Ba solution was 0.52 for the  $^{135}\text{Ba}/^{134}\text{Ba}-^{136}\text{Ba}/^{134}\text{Ba}-^{138}\text{Ba}/^{134}\text{Ba}$  isotope spaces (Fig. 1). Briefly, 100 mg of  $^{135}\text{BaCO}_3$  (94.9%) and 100 mg of  $^{136}\text{BaCO}_3$  (95.4%) powder procured from ISOFLEX (San Francisco, California, USA) were dissolved in  $\text{HNO}_3$  (2 v/v%). A  $^{135}\text{Ba}-^{136}\text{Ba}$  spike solution with a ratio of 1.78 was obtained by mixing the two previously prepared solutions; subsequently, this solution was diluted with  $\text{HNO}_3$  (2 v/v%) for further isotopic measurements. An appropriate amount of the prepared  $^{135}\text{Ba}-^{136}\text{Ba}$  spike solution was added to the sample solution, which contained almost the same amount of Ba as the sample. The mixed solutions were expected to have a  $^{136}\text{Ba}/^{135}\text{Ba}$  ratio of approximately 0.52. Although similar calculations have been previously performed for  $^{135}\text{Ba}/^{134}\text{Ba}-^{136}\text{Ba}/^{134}\text{Ba}-^{137}\text{Ba}/^{134}\text{Ba}$  isotopes, it is necessary to re-simulate the  $^{135}\text{Ba}/^{134}\text{Ba}-^{136}\text{Ba}/^{134}\text{Ba}-^{138}\text{Ba}/^{134}\text{Ba}$  isotope space.

**Sample digestion.** Sample digestion and column chromatography were conducted in class 100 laminar flow hoods. To obtain approximately 10  $\mu\text{g}$  of Ba for high-precision isotopic analysis, 10–96 mg of each rock sample was weighed into 15-mL pre-cleaned PFA vials. The weighed samples were mixed with 3 mL of concentrated  $\text{HNO}_3$ -HF (1:1, v/v) and allowed to decompose for 48 h at 120 °C on the electricity hot plate. For insoluble silicate samples, 300  $\mu\text{l}$   $\text{HClO}_4$  was added to dissolve the silicates. After evaporation on the electricity hot plate, the samples were dissolved in 4 mL  $\text{HNO}_3$ -HCl (1:3, v/v) and allowed to decompose for 48 h at 120 °C to dissolve residual fluorides. The obtained clear sample solutions were evaporated and redissolved in concentrated HCl to ensure that the medium was completely converted to HCl, after which they were evaporated to dryness. Lastly, all samples were individually dissolved in 0.5 mL of 2.5 M HCl for subsequent measurement.

**Ba double spike.** Double spikes can correct mass fractionation during chromatographic separation and MC-ICP-MS analysis.<sup>7,26,28,29,31,32</sup> Most recent studies on Ba isotopes involved using the DS method to correct instrumental mass fractionation. The DS solution was made using  $^{135}\text{Ba}$ - and  $^{136}\text{Ba}$ -enriched carbonate salts from ISOFLEX (San Francisco, California, USA) and calibrated by measuring mixtures of the DS solution with the NIST 3104a standard solution. An optimal dilution ratio of 1.78 for the  $^{135}\text{Ba}-^{136}\text{Ba}$  DS was used to calibrate the mass-dependent fractionation caused by the instrument.<sup>36</sup> Before loading the samples into the columns, a calibrated double Ba isotope spike solution with known Ba concentration was added to the dissolved samples.

**Chromatographic separation.** The column chromatography procedure was improved based on previous studies by van Zuilen *et al.*<sup>7</sup> and Yobregat *et al.*<sup>37</sup>. Purification was conducted in two separate columns. In the first column, we used a cation resin, while in the second column, we used a Sr resin (Eichrom™). Prior to loading the samples into the columns, all samples were dissolved

in 0.5 mL of 2.5 M HCl, allowed to rest and equilibrate, and sonicated in an ultrasonic bath for 40 min to ensure the best dissolution. Next, 0.5 mL of the sample solutions containing equivalent Ba masses (approximately 10 µg) was loaded onto the resin. Thereafter, the samples were passed through a 1.1-mL AG 50 W-X8 (200-400 mesh) resin column by adding 9 mL of 2.5 M HCl to remove Mg, Fe and other matrix elements as described in step 1 (Fig. 2). During leaching, some middle and heavy REEs partially overlapped with the recovering range of Ba. The eluent (containing Ba and REEs) was collected and evaporated to dryness for subsequent separation. The dried eluent was then re-dissolved in 1 mL of 3 M HNO<sub>3</sub>, allowed to equilibrate, and sonicated again. In step 2, REEs and remaining matrix elements were removed by passing through 0.5 mL of the Sr resin (Fig. 3). High-purity Ba was eluted from the column using 10 mL 7.5 M HNO<sub>3</sub>. Ba eluents were evaporated at 120 °C, and organic residuals were removed by adding a mixture of concentrated HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (~30%) dropwise and evaporating to dryness. If the REE content of the sample was low, purification using only the first column was required. After column chromatography, the Ba recovery rate and total process blank of the chemical separation method were determined using an Agilent 8900 ICP-MS unit. Ba eluents were re-dissolved in HNO<sub>3</sub> (2 v/v%) and diluted to 0.5 µg g<sup>-1</sup> for Ba isotopic measurement. The separation protocols are summarized in Table 1.

**Mass spectrometry.** One of the instruments used in this study was a Thermo Fisher Scientific (USA) Neptune Plus<sup>®</sup> MC-ICP-MS unit, located in the SKLCD (Northwest University, China). This instrument is equipped with nine Faraday cups connected to 10<sup>11</sup> Ω amplifiers. It has a double-focus sector magnetic field that allows resolutions above 8,000 while maintaining a flat top peak for high precision and the simultaneous collection of multiple isotopic signals. Ba isotopes, namely, <sup>132</sup>Ba, <sup>134</sup>Ba, <sup>135</sup>Ba, <sup>136</sup>Ba, <sup>137</sup>Ba, <sup>138</sup>Ba, were simultaneously measured in six Faraday cups. Isobaric interferences from Xe and Ce were monitored by measuring <sup>131</sup>Xe and <sup>140</sup>Ce isotopes on two additional Faraday cups (Table 2). Isobaric interferences of Xe and Ce were deduced from an exponential fit assuming that the mass fractionation factors were the same as those for Ba. All isotopes were measured using Faraday cups with 10<sup>11</sup> Ω amplifiers. Xe is present in the atmosphere and can have different concentrations in the argon gas used for MC-ICP-MS analysis, with interfering masses of 134 and 136 (10.44% and 8.87% of total Xe). Cerium is an isobaric interference of Ba at masses of 136 (<sup>136</sup>Ce = 0.185% of total Ce), and 138 (<sup>138</sup>Ce = 0.251% of total Ce).<sup>38</sup> Wet plasma with a standard Ni sampler and Ni H skimmer cones was used for Ba isotopic measurements. The sample solutions were introduced into MC-ICP-MS using a dual cyclonic double-pass ISIS quartz spray chamber containing a PFA concentric nebulizer at an uptake rate of 50 µL min<sup>-1</sup>. The other operating parameters for Ba isotopic measurements are listed in Table 2. All isotopes were measured in the low-resolution mode with robust plasma to avoid polyatomic

**Table 1** Chromatographic separation procedures

Step 1: Separation of Ba and matrix removal		
AG50-X8 200-400 mesh size	Eluent	Volume (mL)
Clean resin	6.4 M HCl	10
Condition resin	2.5 M HCl	4
Load sample	2.5 M HCl	1
Remove matrix	2.5 M HCl	9
Elute Ba	6.4 M HCl	9
Step 2: Removal of REE		
Eichrom Sr resin	Eluent	Volume (mL)
	MQ	5
Clean resin	1 M HCL	5
	MQ	5
	0.5 M HNO <sub>3</sub>	5
Condition resin	3 M HNO <sub>3</sub>	2
Load sample	3 M HNO <sub>3</sub>	1
Remove REE	3 M HNO <sub>3</sub>	3
Elute Ba	7.5 M HNO <sub>3</sub>	10

**Table 2** Instrument parameters

MC-ICP-MS	Thermo Fisher Scientific, Neptune Plus								
RF power	1200W								
Cooling Ar	~15 L min <sup>-1</sup>								
Auxiliary Ar	~0.8 L min <sup>-1</sup>								
Nebulizer Ar	~1.07 L min <sup>-1</sup>								
Mass resolution	Low resolution								
Sensitivity	~60V ppm <sup>-1</sup> for <sup>138</sup> Ba								
Cones	Ni standard sample cone and Ni H skimmer cone								
Solution uptake	~50 µL min <sup>-1</sup>								
	Faraday cup configuration								
Detector mode	L4	L3	L2	C	H1	H2	H3	H4	L4
	<sup>131</sup> Xe	<sup>132</sup> Ba	<sup>134</sup> Ba	<sup>136</sup> Ba	<sup>138</sup> Ba	<sup>137</sup> Ba	<sup>138</sup> Ba	<sup>140</sup> Ce	<sup>131</sup> Xe

interferences, such as <sup>94</sup>Zr<sup>40</sup>Ar and <sup>98</sup>Mo<sup>40</sup>Ar on <sup>134</sup>Ba and <sup>138</sup>Ba, respectively. Samples were re-dissolved to 0.5 µg g<sup>-1</sup> in HNO<sub>3</sub> (2 v/v%) and transferred to acid-washed 5-mL centrifuge tubes (2 mL of the Ba solution) for MC-ICP-MS analysis. The typical sensitivity of <sup>138</sup>Ba was 28 V for 0.5 µg g<sup>-1</sup> Ba solution. Before each sample/standard analysis, the sample spray system was washed with HNO<sub>3</sub> (2 v/v%) until the signal intensity of <sup>138</sup>Ba decreased to less than 5 mV. The blank sample was measured using the peak mass, and the measured blank value was subtracted from the Ba sample value. Each run consisted of one block of 42 cycles with an integration time of approximately 4.192 s. The isotopic ratio of Ba, δ<sup>138</sup>Ba, which is the per mil deviation between the <sup>138</sup>Ba/<sup>134</sup>Ba ratio in the sample and NIST 3104a standard, can be calculated as follows:

$$\delta^{138}\text{Ba} = [({}^{138}\text{Ba}/{}^{134}\text{Ba})_{\text{sample}} / ({}^{138}\text{Ba}/{}^{134}\text{Ba})_{\text{NIST 3104a}} - 1] \times 10^3.$$

The analysis of every three to four samples was bracketed by the spiked Alfa Ba/GSB Ba standard sample with similar Ba concentrations to monitor the instrument stability. No distinct systematic variation in δ<sup>138</sup>Ba was observed within the signal intensity range. The mass fractionation of the sample was corrected by an iterative normalization of the <sup>136</sup>Ba/<sup>135</sup>Ba ratio of the DS using an exponential fit.

## RESULTS AND DISCUSSION

**Ba purification column.** During elution, the volume of reagents, choice and amount of resin, and shape of the resin-bearing column are closely related to the time required for the separation of different elements. Using our method, we could reduce the amount of acid used for elution while maintaining the separation effect. This, in turn, not only reduces the amount of the blank sample used but also results in a shorter elution time. Hydrochloric and nitric acid were used as eluents in the chromatography columns. The total amount of the acid used from sample loading to Ba recovery was only 33 mL, and the total time was approximately 6 h (not including the time for cleaning and column conditioning). The blank results indicated that the amount of background Ba was <5 ng, which was considerably lower than the Ba content of the samples; therefore, the effect on Ba isotopic analysis was likely negligible. The sample recovery rate was guaranteed to be 99.8%, which confirms the efficiency and speed of our method. By referring to previously reported methods, we separated REEs that were not of particular concern in the method reported by van Zuilen *et al.*<sup>7</sup>. Furthermore, compared to the methods reported by Nan *et al.*<sup>28</sup> and Yobregat *et al.*<sup>37</sup>, our purification process saves time because of the different choices of resins and columns available. And while ensuring the separation efficiency and recovery rate, our work procedure is also more concise. For samples with low REE contents, as Ba purification could be conducted using only the first column, it could be completed in only three and a half hours (from sample loading to Ba collection). The time required for purification previously reported by Matecha *et al.*<sup>38</sup> is similar; however, they only considered two rock standards and extensively used acids. The purification efficiency of our method is considerably better than those of previously reported separation methods, and our method allows two samples to be sequentially separated in one day using a single column.

**Effects of acidity and concentration.** Previous studies have shown that the deviation in metal stable isotopic analyses can be caused by concentration and acidity mismatches during mass spectrometry.<sup>28, 39–42</sup> In this study, purified samples were dissolved in HNO<sub>3</sub> (2 v/v%) as the medium of choice for Ba isotopic analyses. The effects of acidity mismatch between the sample and standard solutions were tested using a series of 0.5 μg g<sup>-1</sup> GSB Ba solutions diluted with 0.5–3.0 v/v% of HNO<sub>3</sub>. The standard-sample bracketing (SSB) method using the NIST SRM3104a solution as an internal standard was used to correct the instrument mass bias for Ba isotopic analysis. Fig. 4 shows that there is a distinct Ba isotopic offset between GSB Ba solutions diluted with 0.5–3.0 v/v% of HNO<sub>3</sub>, indicating that Ba isotopic analysis is susceptible to the differences in acid molarities between the bracketing standards and samples. To eliminate the possible effects of the acidity mismatch, all dried samples were diluted with HNO<sub>3</sub> (2 v/v%) to ensure that the acidity differences were as small as possible before conducting mass spectrometry measurements.

**Fig. 4** Ba isotopic ratio variations,  $\delta^{138}\text{Ba}$ , during the measurement of Ba standard solutions diluted in HNO<sub>3</sub> with different concentrations. The error bars (2SD) are based on at least three replicate measurements. The HNO<sub>3</sub> molarities in this test changed from 0.5 to 3.0 v/v%. The gray region indicates the 2SD range ( $\pm 0.05\%$ ).

**Fig. 5** Ba isotopic ratio variations,  $\delta^{138}\text{Ba}$ , of Ba standard solutions with different Ba concentrations ranging from 0.1–2.5 μg g<sup>-1</sup>. Errors are presented at the 2SD level obtained by three repeated measurements. The dotted line indicates the reference value. The gray region indicates the 2SD range ( $\pm 0.05\%$ ).

To investigate the effects of concentration mismatches between the sample and standard solutions on Ba isotopic analysis, we also bracketed a series of Ba standard solutions with different Ba concentrations ranging from 0.05–0.5 μg g<sup>-1</sup>. We found that the weaker the effect of the concentration mismatch, the closer the  $\delta^{138}\text{Ba}$  values were to 0. Our results also indicated that the differences in concentrations did not affect the sample/standard concentration ratios when the wet plasma method was used (Fig. 5). For sample/standard concentration ratios ranging from 0.1–2.5 μg g<sup>-1</sup>, the  $\delta^{138}\text{Ba}$  values of all samples lied within  $\pm 0.05\%$  (2SD). Nevertheless, the sample/standard concentration ratios were maintained at less than  $\pm 20\%$  to achieve high precision and accuracy.

**Effect of matrix elements.** Matrix elements can cause an instrumental mass fractionation bias for Ba isotopic measurements.



**Fig. 6** Ba isotopic ratio variation,  $\delta^{138}\text{Ba}$ , values of GSB Ba (GSB 04-1717-2004) solutions containing added matrix elements in different proportions relative to Ba. The Ba concentration of the samples and bracketed standards (NIST SRM 3104a) is  $0.5 \mu\text{g g}^{-1}$ . The errors(2SD) were obtained by four repeated measurements. The dotted line indicates the reference value. The grey region indicates the 2SD range ( $\pm 0.05\%$ ).

**Fig. 7** Comparison of the Ba isotopic ratio variation,  $\delta^{138}\text{Ba}$ , values measured using the sample standard bracketing and DS methods. The GSB Ba solution was used as the internal standard for long-term monitoring experiments in the laboratory. It was measured 121 times using MC-ICP-MS in 2021 and 2022. Error bars reflect the 2SD range.

**Fig. 8** Comparison of the Ba isotopic ratio variation,  $\delta^{138}\text{Ba}$ , values in selected geological reference materials measured in this and previous studies using MC-ICP-MS. Circles represent the data measured using the DS method, whereas diamonds represent the data measured using the sample-standard bracketing method. The data compared with RGM-2 in the figure is RGM-1 quoted from Nan *et al.*(2015). The gray bar indicates the intermediate measurement precision of  $\pm 0.05\%$  (2SD).

Previous studies have found that matrix effects originate from residual cations in the sample solution and organic residuals eluted from the resin.<sup>43</sup> In this study, 12 matrix elements, namely, Na, Mg, K, Ca, Fe, Al, Sr, Mn, Ce, Mo, Ti, and Pb, of different concentrations were added to GSB Ba solutions ( $0.5 \mu\text{g g}^{-1}$ ) to quantitatively determine a potential matrix effect on Ba isotopic measurements. These elements represent the matrix elements that may be present in the sample solution after chemical separation. The results of these analyses were shown in Fig. 6. The matrix effect on the Ba isotopic ratio variations ( $\delta^{138}\text{Ba}$ ) is insignificant when the purified samples have the following proportions of added matrix elements relative to Ba:  $\text{Ca/Ba} \leq 0.8$ ,  $\text{Mg/Ba} \leq 1$ ,  $\text{Na/Ba} \leq 0.1$ ,  $\text{Sr/Ba} \leq 1$ ,  $\text{K/Ba} \leq 1$ ,  $\text{Fe/Ba} \leq 0.5$ ,  $\text{Al/Ba} \leq 0.01$ ,  $\text{Mn/Ba} \leq 0.1$ ,  $\text{Ti/Ba} \leq 1$ ,  $\text{Mo/Ba} \leq 0.1$ , and  $\text{Pb/Ba} \leq 0.01$ . Nonetheless, small amounts of Ce residues in Ba solutions may significantly affect the Ba isotopic ratios because of the strong isobaric interferences of  $^{136}\text{Ce}$  and  $^{138}\text{Ce}$  on  $^{136}\text{Ba}$  and  $^{138}\text{Ba}$ , respectively; this requires further investigation. The signal of the  $^{136}\text{Ba}$  isotope is typically corrected by monitoring the  $^{140}\text{Ce}$  isotope signal. The matrix effects of Ce on the Ba isotopic ratios are also shown in Fig. 6. Tests with GSB Ba solutions, where Ce was added at different concentrations, showed that the measured

**Table 3** Barium isotopic compositions of reference materials in this study

Sample	Rock type	Ba ( $\mu\text{g g}^{-1}$ ) <sup>a</sup>	Reference	Correction method	$\delta^{138}\text{Ba}$	2SD	N <sup>c</sup>	
G-2(USGS)	Granite	1860	This study	SSB	0.07	0.04	4	
				Average	0.02	0.00	3	
				van Zuilen <i>et al.</i> , 2016	DS( <sup>130</sup> Ba- <sup>135</sup> Ba)	0.04	0.06	7
					DS( <sup>132</sup> Ba- <sup>136</sup> Ba)	0.03 <sup>b</sup>	0.04 <sup>b</sup>	4
				Nan <i>et al.</i> , 2018	Ce-doping	0.07 <sup>b</sup>	0.08 <sup>b</sup>	4
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.04 <sup>b</sup>	0.08 <sup>b</sup>	6
				Deng <i>et al.</i> , 2020	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.04 <sup>b</sup>	0.03 <sup>b</sup>	5
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.03	0.03	6
					SSB	0.08	0.05	4
					Average	0.05	0.02	4
AGV-2(USGS)	Andesite	1134	This study	SSB	0.10	0.02	3	
				Average	0.08	0.05	11	
				Gou and Deng, 2019	SSB	0.07	0.09	6
					SSB	0.07	0.04	6
					SSB	0.05	0.05	6
					SSB	0.03	0.07	3
					SSB	0.06	0.06	3
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.05	0.04	4
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.05	0.06	4
					Average	0.05	0.05	26
BCR-2(USGS)	Basalt	683	Nan <i>et al.</i> , 2015	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.05	0.01	3	
				SSB	0.01 <sup>b</sup>	0.07 <sup>b</sup>	15	
				Ce-doping	0.05 <sup>b</sup>	0.05 <sup>b</sup>	3	
				Nan <i>et al.</i> , 2018	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.08 <sup>b</sup>	0.01 <sup>b</sup>	10
				Li <i>et al.</i> , 2019	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.05 <sup>b</sup>	0.05 <sup>b</sup>	10
				Gong <i>et al.</i> , 2019	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.08 <sup>b</sup>	0.05 <sup>b</sup>	2
				Gong <i>et al.</i> , 2020	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.08 <sup>b</sup>	0.01 <sup>b</sup>	4
				An <i>et al.</i> , 2020	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.06 <sup>b</sup>	0.06 <sup>b</sup>	6
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.02	0.03	3
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.03	0.01	3
					SSB	-0.01	0.04	3
					SSB	0.02	0.04	4
					SSB	0.04	0.04	3
					Average	0.02	0.04	16
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.05	0.02	4
BHVO-2(USGS)	Basalt	130	Miyazaki <i>et al.</i> , 2014	DS( <sup>130</sup> Ba- <sup>135</sup> Ba)	0.11 <sup>b</sup>		5	
				Nan <i>et al.</i> , 2015	SSB	0.07 <sup>b</sup>	0.04 <sup>b</sup>	22
				Bullen and Chadwick, 2016	DS( <sup>132</sup> Ba- <sup>136</sup> Ba)	0.07 <sup>b</sup>	0.05 <sup>b</sup>	
				Li <i>et al.</i> , 2019	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.03 <sup>b</sup>	0.04 <sup>b</sup>	6
				Lin <i>et al.</i> , 2019	DS( <sup>130</sup> Ba- <sup>135</sup> Ba)	0.07	0.02	6
				Gong <i>et al.</i> , 2019	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.03 <sup>b</sup>	0.04 <sup>b</sup>	3
				Gou and Deng, 2019	SSB	-0.03	0.03	6
				An <i>et al.</i> , 2020	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.02	0.03	6
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.04	0.06	4
					SSB	0.05	0.03	3
					Average	0.05	0.05	7
					DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.00	0.06	6
GSR-3 (IGGE)	Basalt	527	This study	SSB	-0.15	0.04	4	
				DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	-0.21	0.05	3	
				DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	-0.13	0.05	6	
GSR-8 (IGGE)	Trachyte	1053	This study	SSB	0.00	0.07	3	
				SSB	0.03	0.04	3	
				SSB	0.01	0.06	6	
GSP-2(USGS)	Granodiorite	1340	Nan <i>et al.</i> , 2015	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.01 <sup>b</sup>	0.07 <sup>b</sup>	15	
				Nan <i>et al.</i> , 2018	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.00 <sup>b</sup>	0.04 <sup>b</sup>	3
				Gong <i>et al.</i> , 2019	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.03 <sup>b</sup>	0.04 <sup>b</sup>	3
				An <i>et al.</i> , 2020	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.03	0.02	4
				Deng <i>et al.</i> , 2021	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.00	0.03	6
					SSB	0.17	0.04	3
					SSB	0.14	0.08	3
RGM-2(USGS)	Rhyolite	826.8	This study	Average	0.15	0.06	6	
				DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.19	0.01	4	
				SSB	-0.27	0.03	3	
GSR-11(IGGE)	Rhyolite	506	This study	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	-0.33	0.03	3	
				DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	-0.24	0.03	10	
				SSB	0.36	0.06	4	
GSR-5(IGGE)	Shale	450	This study	DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.35	0.05	3	
				DS( <sup>135</sup> Ba- <sup>136</sup> Ba)	0.37	0.03	12	

<sup>a</sup> Data from Georem <http://georem.mpch-mainz.gwdg.de/>.

<sup>b</sup> Converted by  $\delta^{138/134}\text{Ba} \approx 1.33 \times \delta^{137/134}\text{Ba}$ .

<sup>c</sup> The Number of analyses.

$\delta^{138}\text{Ba}$  values in GSB Ba solutions were not affected even when the Ce/Ba ratio exceeded 0.5. Hence, the influence of  $^{136}\text{Ce}$  and  $^{138}\text{Ce}$  on the Ba isotopic measurements of the samples can be neglected because the Ce/Ba in the purified solutions was always  $<0.001$ . Therefore, for precise and accurate analysis, purified Ba solutions should be extensively examined for all matrix elements by ICP-MS prior to Ba isotopic analysis. In addition, to avoid interference caused by organic residues, the loading amount of Ba was increased, and the organic residues were removed by hydrogen peroxide and concentrated nitric acid after column chromatography.

**Precision and Accuracy.** In this study, we used two methods to ensure precise and accurate Ba isotopic analysis. First, the precision and accuracy of the reported methods were monitored by repeating the digestion, purification and measurement steps for the same samples using different analytical processes. Second, the accuracy of our method was validated by comparing the Ba standard data acquired in our laboratory with previously reported data. The Ba isotopic ratios of the reference materials are listed in Table 3. From digestion to isotopic analysis, all reference materials were measured 2–3 times in duplicate. In addition, we determined the average isotopic compositions of the same solutions analyzed on different days. Based on repeated measurements (bracketed more than three times) of the same solution, the precision of the measured Ba isotopic ratio variations,  $\delta^{138}\text{Ba}$ , was  $\leq 0.06\text{‰}$  (2SD). The long-term external precision was monitored by analyzing pure Ba standard solutions (Alfa Ba and GSB Ba solutions) and Ba silicate standards (BCR-2 and BHVO-2) over six months. Fig. 7 shows that the  $\delta^{138}\text{Ba}$  value of GSB Ba solutions obtained using SSB method is  $0.02 \pm 0.05\text{‰}$  (2SD,  $n = 86$ ), which is consistent with that obtained using the DS method ( $0.03 \pm 0.04\text{‰}$  2SD,  $n = 35$ ). The average  $\delta^{138}\text{Ba}$  values of the BCR-2 standard are  $0.05 \pm 0.05\text{‰}$  (2SD,  $n = 21$ , SSB) and  $0.05 \pm 0.01\text{‰}$  (2SD,  $n = 3$ , DS), and those of the BHVO-2 standard are  $0.02 \pm 0.04\text{‰}$  (2SD,  $n = 16$ , SSB) and  $0.05 \pm 0.02\text{‰}$  (2SD,  $n = 4$ , DS).

As shown in Fig. 8, the mean  $\delta^{138}\text{Ba}$  values of the G-2, AGV-2, GSP-2, BCR-2, BHVO-2, GSR-3, GSR-5, GSR-8, and GSR-11 standards agree with those previously reported,<sup>7, 8, 20, 28, 32, 33, 44-48</sup> confirming that they are highly precise and accurate.

**Ba isotopic composition in geological reference materials.** The Ba isotopic ratio variation,  $\delta^{138}\text{Ba}$ , values of ten reference materials were reported in this study, the Ba isotopic ratio variation value of the RGM-2 sample was reported for the first time. The  $\delta^{138}\text{Ba}$  values ranged from  $-0.33\text{‰}$  to  $0.36\text{‰}$  (Table 3). Currently, only limited data on Ba isotopes are available for silicate rocks, and more comprehensive studies are required on the behavior of Ba isotopes during magmatic evolution. The nine igneous rock reference materials included basalt, granodiorite, andesite, trachyte, granite, and rhyolite. The  $\text{SiO}_2$  contents of these samples range from 44.5–74.7 m/m%. Furthermore, we observed a large

Ba isotopic variation (approximately 0.52‰) across the reference materials. Herein, the  $\delta^{138}\text{Ba}$  values of the RGM-2 (rhyolite) sample were reported for the first time; these were  $0.19 \pm 0.01\text{‰}$  (2SD,  $n = 4$ , DS) and  $0.15 \pm 0.06\text{‰}$  (2SD,  $n = 6$ , SSB), similar to that of RGM-1 (rhyolite,  $0.19 \pm 0.04\text{‰}$ ). The shale reference material (GSR-5) had the highest  $\delta^{138}\text{Ba}$  value ( $0.36 \pm 0.06\text{‰}$ ) among the ten reference materials evaluated in this study, which may be related to the redox processes it underwent in the depositional environment.

## CONCLUSIONS

Herein, we described a rapid separation method for the determination of Ba isotopic compositions using SSB and DS methods by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), which is suitable for silicate matrices. Chromatographic purification was performed using a two-column process with cation exchange and Sr resins. In this study, a lower elution volume and more suitable column capacity enabled efficient and simultaneous Ba separation in multiple samples, which reduced the separation time. Ba isotopic measurements were not affected by concentration mismatches within sample/standard concentration ratios ranging from 0.1–2.5  $\mu\text{g g}^{-1}$ . However, the acidity mismatch had a crucial effect on Ba isotopic ratios even after the acidity was carefully matched within the 5% difference. Furthermore, matrix effects on Ba isotopic measurements could be neglected when the purified samples had  $\text{Ca/Ba} \leq 0.8$ ,  $\text{Mg/Ba} \leq 1$ ,  $\text{Na/Ba} \leq 0.1$ ,  $\text{Sr/Ba} \leq 1$ ,  $\text{K/Ba} \leq 1$ ,  $\text{Fe/Ba} \leq 0.5$ ,  $\text{Al/Ba} \leq 0.01$ ,  $\text{Mn/Ba} \leq 0.1$ ,  $\text{Ti/Ba} \leq 1$ ,  $\text{Mo/Ba} \leq 0.1$ , and  $\text{Pb/Ba} \leq 0.01$ . The isobaric interference of Ce did not affect the Ba isotopic ratios because of the extremely low Ce/Ba ratio in the purified solutions. Ba isotopic ratio variation,  $\delta^{138}\text{Ba}$ , values of ten GRMs were measured by SSB and DS methods using MC-ICP-MS. Repetitive sample digestion, chemical purification and instrumental measurements had a precision of less than 0.05‰ (2SD). Nine rock samples had been measured previously, and the values obtained in the present study were in agreement with the previously reported, confirming that the data reported in this study are highly precise and accurate. Ba isotopic ratio variation,  $\delta^{138}\text{Ba}$ , values for the RGM-2 sample (ranging between 0.15‰ and 0.19‰) were reported for the first time herein.

## AUTHOR INFORMATION



**Kai-Yun Chen** is an engineer at State Key Laboratory of Continental Dynamics (SKLCD), Northwest University. He completed his Ph.D. in geochemistry from Northwest University in 2014. His research interests primarily focus on analytical geochemistry and isotope geochemistry. He has made significant



progress in the high-precision micro-analysis technology of Pb, Si, and Fe isotopes. Kai-Yun Chen is the author or co-author of over 20 articles published in peer-reviewed scientific journals.

## Corresponding Author

\*K. Y. Chen

Email address: kychen@nwu.edu.cn

## Notes

The authors declare no competing financial interest.

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