



Cite this: *J. Anal. At. Spectrom.*, 2015, **30**, 2307

High-precision barium isotope measurements by MC-ICP-MS

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We present a high precision method to measure Ba isotopes by multiple-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). Barium is separated from matrices by using a cation exchange resin (AG50W-X12, 200–400 mesh). Instrumental mass bias of Ba isotopes was corrected by a sample-standard bracketing method using SRM3104a as the bracketing standard. Potential effects of different matrices from resin and samples, and acid molarity and concentration mismatch were rigorously evaluated in this study. The precision and accuracy of this method were tested by the measurement of a synthetic solution made by mixing SRM3104a Ba with other matrix elements. The average $\delta^{137/134}\text{Ba}$ of the synthetic solution is $-0.005 \pm 0.047\text{‰}$ (2SD, $n = 36$) relative to SRM3104a. The robustness of this method was further assessed by replicated analyses of 8 reference materials, including igneous rocks with mafic to felsic compositions. The $\delta^{137/134}\text{Ba}$ of basalt standards BCR-2, BHVO-2, and JB-2 is $0.050 \pm 0.039\text{‰}$ (2SD, $n = 13$), $0.047 \pm 0.028\text{‰}$ (2SD, $n = 22$), and $0.085 \pm 0.035\text{‰}$ (2SD, $n = 19$), respectively; diabase standard W-2 is $0.035 \pm 0.022\text{‰}$ (2SD, $n = 11$); andesite standard AGV-1 is $0.047 \pm 0.040\text{‰}$ (2SD, $n = 11$) and JA-2 is $0.038 \pm 0.048\text{‰}$ (2SD, $n = 17$); rhyolite standard RGM-1 is $0.142 \pm 0.030\text{‰}$ (2SD, $n = 15$); and granodiorite standard GSP-2 is $0.013 \pm 0.046\text{‰}$ (2SD, $n = 15$). Two late Mesozoic basalts from China have a $\delta^{137/134}\text{Ba}$ of $-0.132 \pm 0.020\text{‰}$ (2SD, $n = 7$) and $0.001 \pm 0.034\text{‰}$ (2SD, $n = 7$), respectively. Based on repeated analyses of the synthetic standard and a carbonate standard IAEA-CO-9, the long-term external precision of our method is better than $\pm 0.05\text{‰}$, much smaller than the variation of $\delta^{137/134}\text{Ba}$ in these reference standards and samples (up to 0.27‰). Therefore, the Ba isotopic composition can be used as a novel tracer to study geochemical processes.

Received 3rd May 2015
Accepted 25th August 2015

DOI: 10.1039/c5ja00166h

www.rsc.org/jaas

1. Introduction

Barium (Ba) is a large ion lithophile element (LILE) and an incompatible element during magmatism.¹ The abundance of Ba in chondrite is 2.41 ppm and in the silicate Earth is 6.60 ppm,² much lower than the values in the upper continental crust ($\sim 628 \mu\text{g g}^{-1}$)³ and sediments ($\sim 768 \mu\text{g g}^{-1}$).⁴ During subduction, as a fluid mobile element, Ba can be released from the subducting slab along with fluid, and then added to the mantle wedge. Therefore, Ba abundance in arc lavas has been used to track the subduction related fluid in arc magmas (*e.g.* Hawkesworth and Norry⁵) or the recycled sediments in the mantle (*e.g.* Murphy *et al.*⁶ and Kuritani *et al.*⁷). Previous studies of the alkaline Earth elements reveal significant Mg, Ca, and Sr stable isotope fractionations in terrestrial samples and/or extraterrestrial samples (*e.g.* Griffith *et al.*,⁸ Moynier *et al.*,⁹ Tipper *et al.*,¹⁰ Teng *et al.*¹¹ and Valdes *et al.*¹²). We predict that

Ba isotopes could also be fractionated in geological processes. Indeed, the preliminary experimental study has reported that Ba isotopes can be fractionated by 0.3‰ in $\delta^{137/134}\text{Ba}$ in low temperature environments.¹³

Fractionations of Mg, Ca, and Sr stable isotopes among igneous rocks have been used to constrain the recycling of the crustal material and magmatic differentiation.^{9,11,12,14} Because Ba abundance in the mantle is much lower than that in the crust and sediments, the Ba isotopes could be more sensitive than Ca and Mg isotopes in tracing the recycled materials. However, the Ba isotopic compositions of different sources of the Earth, such as mid-ocean ridge basalts, continental crust and sediments, are not known. It is therefore important to improve the analytical method to determine the Ba isotopic compositions of the important reservoirs of the Earth.

Barium has seven stable isotopes, ¹³⁰Ba, ¹³²Ba, ¹³⁴Ba, ¹³⁵Ba, ¹³⁶Ba, ¹³⁷Ba and ¹³⁸Ba, and the abundances are 0.1058%, 0.1012%, 2.417%, 6.592%, 7.853%, 11.232%, and 71.699%, respectively.¹⁵ Since Nier¹⁶ first analyzed Ba isotopes, Ba isotopic compositions have been used to study meteorite samples and natural fission reactors.^{15–22} In previous studies, Ba isotopes have been mostly analyzed by thermal ionization mass

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spectrometry (TIMS). With the quick advance of analytical techniques based on multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), von Allmen *et al.*¹³ developed a high precision analytical method with the repeatability of $\delta^{137/134}\text{Ba}$ ($\delta^{137/134}\text{Ba} = [({}^{137/134}\text{Ba}_{\text{sample}}/{}^{137/134}\text{Ba}_{\text{standard}}) - 1] \times 1000$) of $\pm 0.15\%$ (2SD). Miyazaki *et al.*²³ improved this method with the achievable repeatability of 0.032% (2SD) in $\delta^{137/134}\text{Ba}$. Both methods used a double spike technique to correct the fractionation of Ba isotopes during Ba separation in ion exchange chromatography and mass bias produced by the instrument. However, Ba isotope data of reference materials for inter-laboratory comparison are still rare.

Here, we present a high precision Ba isotope analysis method by MC-ICP-MS using the sample-standard bracketing technique, with a simplified chemical purification procedure and straightforward instrumental mass bias calibration method. Most importantly, we measured Ba isotopic compositions of eight well-characterized reference materials and two natural basalts using NIST SRM3104a as a bracketing standard. The reference materials include igneous rock standards from the United States Geological Survey (USGS) and Geological Survey of Japan (GSJ), while the two natural basalts are from Southeastern Zhejiang Province, China. Our results will be really helpful for the application of Ba isotopes to the studies of geochemical processes on the Earth.

2. Analytical methods

2.1. Chemical purification procedure

Chemical purification procedures were performed in an ISO-class 6 clean room. The concentrated acids were of high purity after double distillation. All reagents were then diluted from concentrated acids with $18.2\text{ M}\Omega\text{ cm}$ ultra-pure water. Rock reference standards were weighed into 7 mL Teflon® PFA screw cap vials (Saville®). After decomposing by using a 1 : 2 mixture of concentrated HNO_3 and HF, they were dried down and fluxed with 11 mol L^{-1} HCl. Finally, the samples were dissolved in 1 mL of 3 mol L^{-1} HCl for further purification.

The procedures of chemical purification are listed in Fig. 1. Since barium is a trace element, it is difficult to completely separate Ba with matrix elements (especially major elements) using only one ion exchange column. To avoid the effect from the residue of matrix elements (see details in Section 3.2), samples were purified twice through the cation exchange columns. The first column used a 30 mL Teflon® micro-column with $6.4\text{ mm ID} \times 9.6\text{ mm OD}$ (Saville®). Two milli-liter cation exchange resin (AG50W-X12, 200–400 mesh, Bio-Rad, USA) was cleaned alternatively with 6 mol L^{-1} HCl and $18.2\text{ M}\Omega\text{ cm H}_2\text{O}$ three times, and loaded onto the column. And then, the resin was finally cleaned with 8 mL of 6 mol L^{-1} HNO_3 and 6 mL of 6 mol L^{-1} HCl, and conditioned with 5 mL of 3 mol L^{-1} HCl. The samples were loaded in 1 mL of 3 mol L^{-1} HCl, and 28 mL of 3 mol L^{-1} HCl was used to elute the matrix elements. Barium was collected with 7 mL of 4 mol L^{-1} HNO_3 , and both 1 mL aliquots before and after the “Ba-cut” were collected to test whether the Ba elution curve drifted during the chromatographic process.

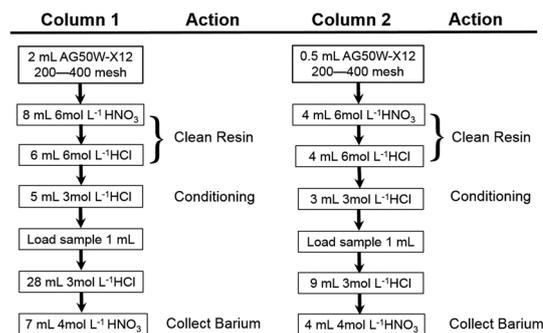


Fig. 1 Summary of the two column procedures to separate Ba from matrices.

The second column was a polypropylene spin column from Bio-Rad with a 1.2 mL bed volume and 6.5 mm ID. Half milliliter of the same cation resin was loaded onto the column. A similar procedure to that used for the first column was used for the second column, but the volumes of acid used were different (Fig. 1). The Ba cut collected in 4 mol L^{-1} HNO_3 was dried up and diluted into 200 ppb solution with 2% (m/m) HNO_3 , and then made ready for instrument analysis.

2.1.1. Effect of acid molarities on Ba elution. In order to use a minimum volume of acid to purify Ba and avoid potential contamination, different molarities of acid were used to examine the effect on separating Ba with other elements. We examined the effect using different molarities of HCl (2 mol L^{-1} , 2.5 mol L^{-1} , and 3 mol L^{-1}) and HNO_3 (2.5 mol L^{-1} , 3 mol L^{-1} , and 4 mol L^{-1}). Fig. 2 shows that cations were eluted faster when using more concentrated acid, and the elution curves of the matrix elements were wide when using 2 mol L^{-1} HCl ($>20\text{ mL}$, Fig. 2a and b). After elution using 2 mol L^{-1} HCl, neither 3 mol L^{-1} HNO_3 nor 4 mol L^{-1} HNO_3 can completely separate Ba from Ca and Sr. If using more diluted HNO_3 , the whole procedure needs more acid volumes, which lowers the purification efficiency and extends the time required for the whole procedure. Therefore, we chose 3 mol L^{-1} HCl for Ba purification. When the molarities of HCl increased to 3 mol L^{-1} , the matrix elements (including Ca and part of Sr) can be eluted within 20 mL of HCl (Fig. 2c–f). The remaining Ca and Sr would be separated well from Ba by eluting with HNO_3 .

We also tested the elution curves of Ba by using different molarities of HNO_3 . The volumes of diluted HNO_3 required to collect Ba is much larger than that when using more concentrated HNO_3 . Based on these tests, we finally used 28 mL of 3 mol L^{-1} HCl to elute the matrix elements and 7 mL of 4 mol L^{-1} HNO_3 to collect Ba (Fig. 2f). The purified Ba was evaporated to dryness and re-dissolved in 2% (m/m) HNO_3 prior to isotope analyses. The total procedure blank (from sample dissolution to instrumental analysis) was $\sim 2.9\text{ ng}$.

2.1.2. Effect of Ba mass loaded onto the column. Because metal stable isotopes can be dramatically fractionated during ion exchange chromatography,²⁴ the yield of Ba should be close to 100% to avoid the mass fractionation of Ba isotopes. This requires that the Ba cut should be appropriate, not too narrow to lose the elution tail of Ba, but not too wide either to introduce

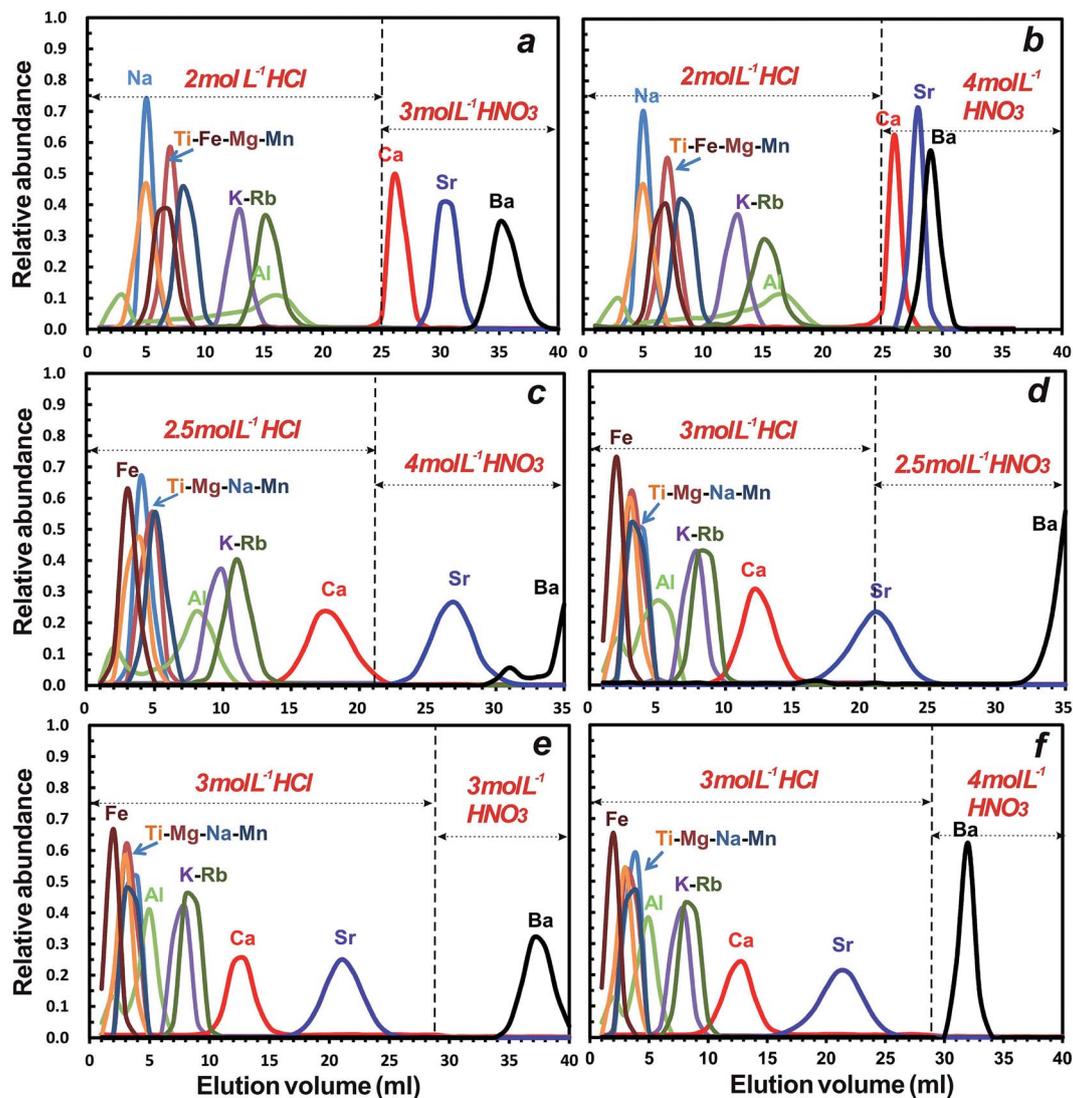


Fig. 2 Elution curves of Ba purification procedures using different reagents.

the tails of the matrix elements. Furthermore, based on the research on other metal stable isotopes (e.g. Mg^{25}), the elution curves could shift with the variations of the amount of target elements loaded onto the columns or the types of matrix elements. To achieve a 100% recovery rate of Ba for different types of samples, it is necessary to test whether their Ba elution curves drift with sample matrices. We tested this by two methods. First, we doped different amounts of Ba into a matrix solution (containing major and trace elements but no Ba) to test the drifting of elution curves for Ba. Second, we fixed the mass of Ba, and changed the matrix elements to test how the matrices would affect the elution curve of Ba.

In the first test, we split one synthetic solution (a similar composition as basalt, but without Ba) into 5 aliquots and doped with 2, 5, 10, 15, and 20 μg Ba, respectively. Barium was collected in 7 mL of 4 mol L^{-1} HNO_3 after the matrix elements were eluted with 3 mol L^{-1} HCl (Fig. 3). When the mass of Ba loaded onto the column is ≤ 20 μg , regardless of the mass of Ba, all elution curves of Ba overlap with each other. However, if the

sample loaded onto the column contained an extremely high Ba concentration, the Ba elution curve may shift.

In the second test, we loaded solutions of basalt (BHVO-2), andesite (AGV-1), and granite (G-2) containing 10 μg of Ba into columns. Fig. 4 exhibits that the elution curves of Ba in these samples overlap with each other, showing independence on the matrix compositions in the solution if the Ba masses loaded onto the columns are the same, indicating that the elution procedure is not sensitive to the types of samples. Therefore, if less than 20 μg Ba is loaded onto the column, the elution curve of Ba will not be affected by either the amount of loaded Ba or the matrix compositions. The yields of all samples analyzed in this study are $>99\%$.

2.2. Mass spectrometry

Barium isotopic ratios were determined on a Thermo-Fisher Scientific Neptune Plus (MC-ICP-MS, Bremen, Germany) in the CAS Key Laboratory of Crust-Mantle and Environments at the

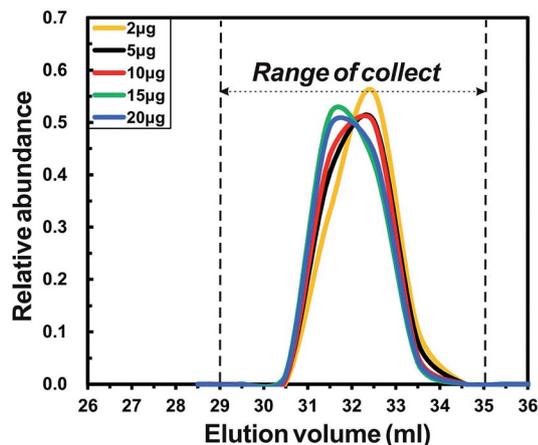


Fig. 3 Drifting of the center of Ba elution curves with different masses of Ba loaded onto the columns. Matrix elements (such as Na, K, Ca, and Sr) are not shown in the plot as most of them were removed using 28 mL of HCl before adding HNO₃.

University of Science and Technology of China (USTC), Hefei. Normal Ni sampling and Ni X skimmer cones (Thermo Fisher, Bremen, Germany) were used for Ba isotope analyses. The sensitivity of ¹³⁷Ba is ~75 V per ppm under dry plasma using an Aridus II desolvator (CETAC Technologies). The cup configuration and parameters for the instrument are summarized in Table 1. Five Ba isotopes (¹³²Ba, ¹³⁴Ba, ¹³⁵Ba, ¹³⁶Ba, and ¹³⁷Ba) were collected on L1, C, H1, H2, and H3 Faraday cups, respectively. ¹³¹Xe was also simultaneously collected on a L2 Faraday cup for correcting the isobaric effect. Each block of analysis consisted of 60 cycles of data with an integration time of 2.097 seconds per cycle. The sample is bracketed before and after with the standard, and the analyses were repeated ≥3 times for the same sample solution. Between each measurement, the sample introduction system was cleaned with 2% HNO₃ (m/m) for 5 minutes to eliminate the potential cross-contamination, until the ¹³⁷Ba signal is less than 10 mV.

The Ar gas always contains a trace amount of Xe, producing isobaric interferences on Ba isotopes (¹³⁴Xe on ¹³⁴Ba and ¹³⁶Xe on ¹³⁶Ba). To correct the effect of Xe interferences, we first analyzed 2% HNO₃ (m/m) for ~2 min as an on-peak background before each sequence. And then the Ba signal (~7 mV of ¹³⁷Ba) in the background was subtracted from the analyzed data. Because the Xe signal was not stable and changed with Ar tank pressure, Xe interferences cannot be directly corrected by on-peak background subtraction. We calculated the ¹³⁴Xe and ¹³⁶Xe interferences based on the signal of ¹³¹Xe assuming that the fractionation factor (β) was the same as that of Ba using an exponential law of fractionation. The Ba isotopic ratios were then corrected by subtracting ¹³⁴Xe and ¹³⁶Xe from ¹³⁴Ba and ¹³⁶Ba.

2.3. Standards for sample-standard bracketing

The bracketing standard used in previous studies was Fluka, a barium nitrate (Ba(NO₃)₂) ICP-OES standard solution from Aldrich company.^{13,23} In this study, we calibrated a new

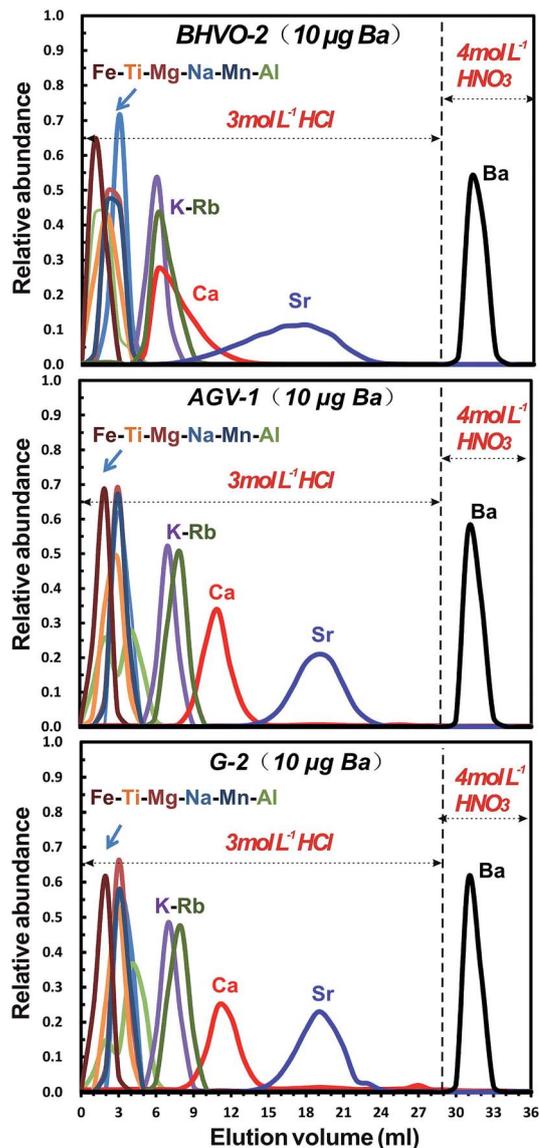


Fig. 4 Elution curves of Ba purification procedures using different rock standards. Despite the different sets of matrix elements, the Ba peaks of BHVO-2, AGV-1, and G-2 were eluted at the same location. But the peaks of the other elements were eluted differently in different samples.

bracketing standard, SRM3104a, which is a 50 mL Ba(NO₃)₂ standard solution provided by the National Institute of Standards and Technology (NIST) and the certified concentration value of barium in this standard is 10.014 mg g⁻¹ ± 0.036 mg g⁻¹. This standard was diluted to ~500 µg g⁻¹ and stored in a Teflon® bottle. During the measurement, the standard and sample solutions were further diluted to 200 ng g⁻¹.

2.4. Reference materials and samples

In this study, we analyzed 8 USGS and GSJ rock standards, including basalt (BCR-2, BHVO-2, and JB-2), andesite (AGV-1 and JA-2), diabase (W-2), granite (GSP-2), and rhyolite (RGM-1). Barium abundances of these standards vary from 130 to

Table 1 Instrumental operating conditions for Ba isotopic measurements

MC-ICP-MS	Thermo Fisher Scientific, Neptune Plus					
Cooling Ar	~16 L min ⁻¹					
Auxiliary Ar	~0.80 L min ⁻¹					
Nebulizer Ar	~0.85 L min ⁻¹					
Mass resolution	Low resolution					
Typical sensitivity	~75V ppm ⁻¹ for ¹³⁷ Ba					
Cones	Ni sampler cone, X-skimmer cone					
Desolvator	Aridus II					
Ar sweep	~5.45 L min ⁻¹					
N ₂ gas	2–3 mL min ⁻¹					
Solution uptake	~50 μL min ⁻¹					
	Faraday cup static mode					
Detector mode	L2-F	L1-F	C-F	H1-F	H2-F	H3-F
	¹³¹ Xe	¹³² Ba	¹³⁴ Ba	¹³⁵ Ba	¹³⁶ Ba	¹³⁷ Ba

1340 μg g⁻¹, and more detailed information on these standards can be found on the USGS and GSJ websites. The international reference material of Ba carbonate (IAEA-CO-9) was also analyzed.

Besides these standards, we analyzed two well-characterized late Mesozoic basalts (MZ815 and MZ834) from Southeastern Zhejiang Province, China. The major elements, trace elements, and Sr–Nd–Pb isotopic compositions were reported by Cui *et al.*²⁶ Sample MZ815 has a higher Ba abundance (767 μg g⁻¹) and higher ⁸⁷Sr/⁸⁶Sr ratio (0.709170) compared with MZ834 which contained 267 μg g⁻¹ of Ba and 0.705832 of ⁸⁷Sr/⁸⁶Sr. The high Ba abundance and ⁸⁷Sr/⁸⁶Sr ratio of MZ815 may reflect the addition of the altered oceanic crust into the mantle source by subduction.²⁶ These two samples can provide preliminary information on Ba isotopic compositions of the upper mantle metasomatized by the recycled crust material.

3. Accuracy and precision

3.1. Effects of acid molarity and concentration mismatch

The purified samples were normally dissolved using 2% HNO₃ (m/m), and then introduced into MC-ICP-MS. Previous studies have shown that different molarities of nitric acid using in sample/standard dilution may cause artifacts in metal stable isotope analyses (*e.g.* An *et al.*,²⁵ Malinovsky *et al.*,²⁷ Liu *et al.*²⁸ and Teng and Yang²⁹). To test the influence of diluting acid molarities on Ba isotope analyses, a series of tests have been done in this study. One aliquot of SRM3104a solution was diluted to 200 ng g⁻¹ with 2% HNO₃ (m/m) to bracket 200 ng g⁻¹ SRM3104a solutions diluted by HNO₃ from 1 to 3% (m/m). Fig. 5 shows that there is no Ba isotopic offset between SRM3104a diluted in 1% (m/m) to 3% (m/m) HNO₃, indicating that Ba isotope analyses are not sensitive to the differences of acid molarities between the bracketing standards and samples.

To understand the effect of Ba concentration mismatch of the standard and samples on Ba isotope analysis, we also

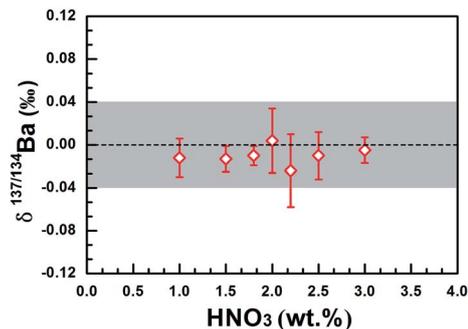


Fig. 5 $\delta^{137/134}\text{Ba}$ variations during the measurement of Ba standard solutions diluted with different HNO₃ acid strengths. The error bars (2SD) are based on at least 3 replicate measurements. The HNO₃ molarities in this test changed from 1% to 3% (m/m).

bracketed a series of Ba standard solutions with concentrations varied from 70 ng g⁻¹ to 410 ng g⁻¹ using the same standard with a concentration of 200 ng g⁻¹. Fig. 6 exhibits that Ba isotope analyses are not sensitive to the standard/sample concentration ratios ranging from 0.35 to 1.5. Only when the sample/standard concentration ratio is lower than 0.35 or higher than 1.5, we can observe the obvious offset of $\delta^{137/134}\text{Ba}$ relative to the bracketing standard. Nonetheless, we still carefully adjusted the concentrations of sample solutions within 20% difference to the SRM3104a standard solution.

3.2. Effects of the matrix from ion exchange resin and from samples

The sample-standard bracketing method is susceptible to matrix effects. Previous studies found that the matrix effects result from not only the residue cations in sample solutions, but also the dissolved organic material from the resin.^{30,31} Therefore, it is necessary to test the effect of column matrices on Ba isotope measurements. Variable amounts of pure Ba standard solutions (SRM3104a) were loaded onto the cation resin columns to test the matrix effects corresponding to the amount of Ba. Masses of 2, 4, 6, 8, and 10 μg Ba were loaded onto the resin, and then the collected Ba cut were analyzed as unknown samples. There should be no isotopic offset between the sample and standard ($\delta^{137/134}\text{Ba}$ should be zero) if the matrices from the

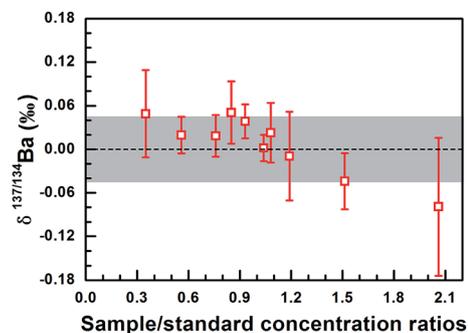


Fig. 6 The effect of Ba concentration mismatches between the sample and standard on $\delta^{137/134}\text{Ba}$ analyses.

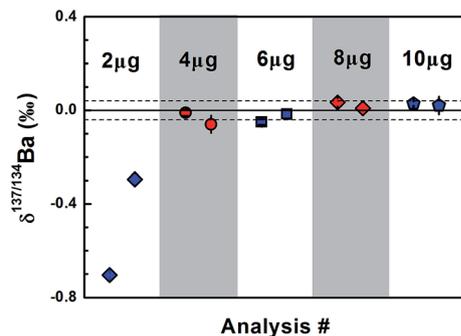


Fig. 7 $\delta^{137/134}\text{Ba}$ variations with different masses of Ba loaded onto the columns.

columns do not affect Ba isotope analyses. Fig. 7 shows that, when only 2 μg Ba was loaded onto the column, the dissolved organic material caused significant Ba isotopic artifacts as large as -0.705‰ . The column matrix effect decreases with increasing the Ba amount loaded onto the columns. When the loaded Ba is more than 6 μg , the column matrix effect is negligible ($<0.05\text{‰}$). Therefore, all of the sample solutions loaded onto the columns in this study contained $\sim 10\text{ }\mu\text{g}$ of Ba to ensure that the column matrix effect does not affect the precision and accuracy of Ba isotopic analyses.

It is also well-known that the inorganic matrices in the sample solutions can affect the Ba isotope analyses by two different ways. Some matrix elements can cause isobaric interferences. For example, $^{94}\text{Zr}^{40}\text{Ar}$ and $^{54}\text{Fe}^{(40}\text{Ar})_2$ have isobaric effects on ^{134}Ba , and $^{97}\text{Mo}^{40}\text{Ar}$ and $^{87}\text{Sr}^{38}\text{Ar}^{12}\text{C}$ can affect ^{137}Ba . Some matrix elements will not cause isobaric interferences, but still can change the instrumental mass bias for Ba isotopes. In this study, different amounts of Na, K, Ca, Mg, Al, Fe, and Sr were doped into 200 ng g^{-1} SRM3104a solutions to test the matrix effect on Ba isotope analyses. These doping elements represent the possible matrix elements left in sample solutions after chemical separation. As Fig. 8 shows, the matrix effect on $\delta^{137/134}\text{Ba}$ analyses is negligible when the purified samples have $\text{Ca}/\text{Ba} \leq 1$, $\text{Mg}/\text{Ba} \leq 1$, $\text{Na}/\text{Ba} \leq 0.5$, $\text{Sr}/\text{Ba} \leq 0.5$, $\text{K}/\text{Ba} \leq 0.1$, $\text{Fe}/\text{Ba} \leq 0.05$, and $\text{Al}/\text{Ba} \leq 0.01$. Because Na, K, Fe and Al are major elements in most natural samples and Ba is a trace element, it is almost impossible to separate major elements from Ba using only one column. Therefore, a two-step column procedure is recommended to purify natural samples. In order to achieve precise and accurate analyses, all matrix elements of purified Ba solution should be strictly monitored by ICP-MS before Ba isotope analyses.

3.3. Precision and accuracy

In this study, we used three ways to show the precision and accuracy of Ba isotope analyses. First, we analyzed the Ba isotopic composition of the synthetic standard to ensure that there is no isotope fractionation during chemical separation and instrumental measurements. Second, the precision and accuracy of our method were monitored by the repeated measurements of the same samples, including the same

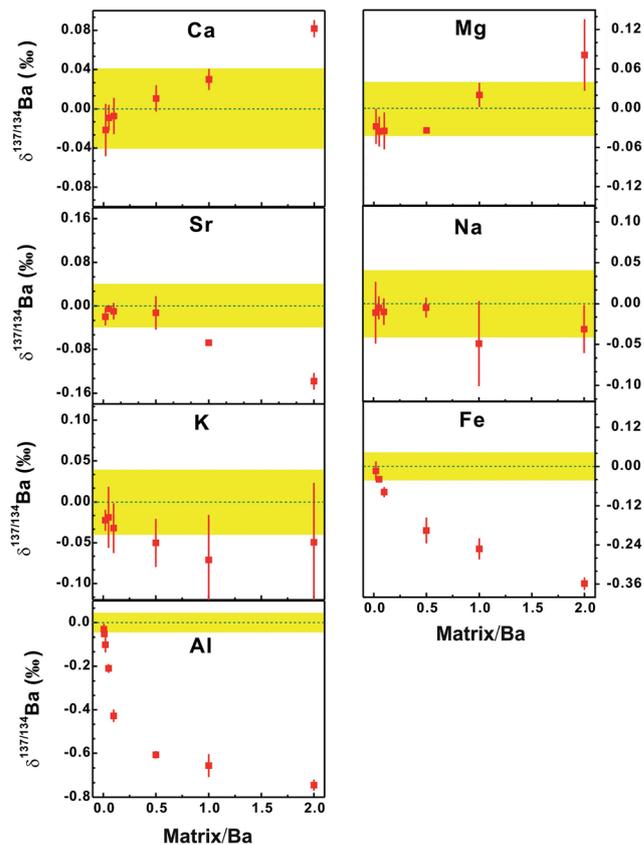


Fig. 8 Doping experiments to test the matrix effect on $\delta^{137/134}\text{Ba}$ analyses.

solution measured at different times, the same bulk raw solution with different chemistry separations, and independent digestions of the same sample powders. Third, the accuracy of our method was verified by comparing the few Ba standard data (IAEA-CO-9, BHVO-2, JA-2, and JB-2) measured in our lab with the values reported in the literature.^{13,23}

The synthetic solution was made by mixing SRM3104a Ba with rock matrices. It was purified through the two-step cation exchange columns and analyzed by MC-ICP-MS. The average $\delta^{137/134}\text{Ba}$ (relative to the pure SRM3104a) of the synthetic solution is $-0.005 \pm 0.047\text{‰}$ (2SD, $n = 36$), indicating that the chemical procedure and instrumental analyses did not produce significant artifacts.

The Ba isotopic ratios of the standards and samples are listed in Tables 2 and 3. All standards and samples were repeatedly measured twice or three times from digestion to isotopic analysis. For the same solution analyzed in different days, we present the average isotopic compositions. Based on the repeated runs (bracketed for more than three times) of the same solution, the precision of the measured $\delta^{137/134}\text{Ba}$ is $\leq 0.05\text{‰}$ (2SD). The long term external precision was monitored by analyzing the synthetic standard and Ba carbonate standard, IAEA-CO-9, over four months. The average $\delta^{137/134}\text{Ba}$ of IAEA-CO-9 is $0.017 \pm 0.049\text{‰}$ (2SD, $n = 13$). Because of the lack of the Fluka standard, we cannot directly compare our results with those of the previous work of Miyazaki *et al.*²³ Therefore, we

Table 2 Ba isotopic composition of standards^a

Sample	Standard description	$\delta^{137/134}\text{Ba}$ (‰)	2SD	<i>n</i>
Synthetic std.	SRM3104a (doped with matrices)	-0.010	0.039	7
		-0.020	0.031	6
		0.024	0.014	6
		0.002	0.040	8
		-0.017	0.046	9
Average (<i>M</i> = 5)		-0.005	0.047	36^c
IAEA-CO-9	Carbonate	0.023	0.029	4
		0.048	0.031	3
		0.000	0.045	3
		-0.003	0.008	3
		Average (<i>M</i> = 4)		0.017
JB-2	Basalt	0.084	0.040	13
		0.087	0.023	6
		0.085	0.035	19^c
JA-2	Andesite	0.048	0.041	10
		0.023	0.044	7
		0.038	0.048	17^c
BHVO-2	Basalt	0.040	0.033	7
		0.048	0.025	12
		0.058	0.016	3
Average (<i>M</i> = 3)		0.047	0.028	22^c
BCR-2	Basalt	0.065	0.043	3 ^b
		0.058	0.010	4 ^b
		0.026	0.016	4
		0.058	0.007 ^d	2
Average (<i>M</i> = 3)		0.050	0.039	13^c
AGV-1	Andesite	0.038	0.038	7
		0.063	0.022	4
		0.047	0.040	11^c
GSP-2	Granodiorite	0.014	0.049	7
		0.012	0.046	8
		0.013	0.046	15^c
RGM-1	Rhyolite	0.144	0.038	7
		0.140	0.023	8
		0.142	0.030	15^c
W-2	Diabase	0.032	0.016	4
		0.037	0.025	7
		0.035	0.022	11^c

^a *n* is the times of repeated measurements of the same solution. *M* is the times of independent digestions of the same standard powder. 2SD = 2 times the standard deviation of the population of *n* repeat measurements. ^b The same bulk raw solution with different chemistry separations. ^c The total number of repeated runs of the same sample, including different digestions. ^d The difference between two samples instead of two standard deviations.

Table 4 Comparisons of $\delta^{137/134}\text{Ba}$ of JA-2, JB-2 and BHVO-2 relative to IAEA-CO-9 in our study and that of Miyazaki *et al.*^{23,a}

Sample	$\delta^{137/134}\text{Ba}_{\text{IAEA-CO-9}}$ (‰)	
	This study	Miyazaki <i>et al.</i> ²³
JA-2	0.021 ± 0.069	-0.016 ± 0.038
JB-2	0.068 ± 0.060	0.054 ± 0.024
BHVO-2	0.030 ± 0.056	0.026 ± 0.026

^a The error was 2SD, which was calculated based on error propagation.

calibrated average Ba isotopic ratios of BHVO-2, JB-2, and JA-2 in this study relative to IAEA-CO-9 (Table 4), and an approach similar to data of Miyazaki *et al.*²³ The $\delta^{137/134}\text{Ba}$ of JA-2, JB-2, and BHVO-2 relative to IAEA-CO-9 is 0.021 ± 0.069‰, 0.068 ± 0.060‰, and 0.030 ± 0.056‰ in this study, consistent with -0.016 ± 0.038‰, 0.054 ± 0.024‰, and 0.026 ± 0.026‰ in data of Miyazaki *et al.*,²³ respectively.

The Ba three isotope plots for all reference materials and two basalt samples are shown in Fig. 9. The slope of the $\delta^{137/134}\text{Ba}$ and $\delta^{136/134}\text{Ba}$ fractionation line is $Y = (1.447 \pm 0.058)X - (0.007 \pm 0.003)$ ($R^2 = 0.944$), consistent with the slope values of kinetic (1.494) or equilibrium (1.489) fractionation within the error.³² Simultaneously, the slope of the $\delta^{137/134}\text{Ba}$ and $\delta^{135/134}\text{Ba}$ fractionation line is $Y = (2.885 \pm 0.122)X + (0.001 \pm 0.003)$ ($R^2 = 0.938$), also consistent with the slope values of kinetic (2.978) or equilibrium (2.956) fractionation within error.³²

4. $\delta^{137/134}\text{Ba}$ of igneous rocks

We measured Ba isotopic compositions for 10 igneous rocks using the method developed in this study, including eight whole rock reference materials (basalt: BCR-2, BHVO-2, and JB-2; diabase: W-2; andesite: AGV-1 and JA-2; rhyolite: RGM-1; and granodiorite: GSP-2) and two basalts from Southeastern China. As Table 2 shows, the variation of $\delta^{137/134}\text{Ba}$ in the reference materials is 0.129‰, larger than the error of our method (2SD, 0.05‰). There is no correlation between SiO₂ abundance and Ba isotopic compositions (not shown). The granodiorite GSP-2 has the lightest $\delta^{137/134}\text{Ba}$ (0.013 ± 0.046‰), and the rhyolite RGM-1 has the highest $\delta^{137/134}\text{Ba}$ (0.142 ± 0.030‰), indicating that the

Table 3 Major and trace elements and the Ba isotopic composition of the two samples^a

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Ba	⁸⁷ Sr/ ⁸⁶ Sr	$\delta^{137/134}\text{Ba}$ (‰)	2SD	<i>n</i>
MZ815	50.51	17.05	1.47	9.78	0.15	4.33	5.81	4.19	2.53	0.36	2.94	99.43	767	0.709170	-0.129	0.024	4
Average (<i>M</i> = 2)															-0.137	0.007	3
															-0.132	0.020	7^b
MZ834	48.93	17.12	1.43	10.46	0.19	5.28	8.09	2.19	1.51	0.63	3.29	99.57	267	0.705832	0.002	0.037	3
Average (<i>M</i> = 2)															0.001	0.038	4
															0.001	0.034	7^b

^a The major elements in wt%, Ba in $\mu\text{g g}^{-1}$. Data of major elements, Ba abundance and ⁸⁷Sr/⁸⁶Sr ratios are from Cui *et al.*²⁶ Each sample has two independent digestions. *M* is the times of separated digestions of the same sample powder. 2SD = 2 times the standard deviation of the population of *n* repeat measurements. ^b The total number of repeated runs of the same sample, including different digestions.

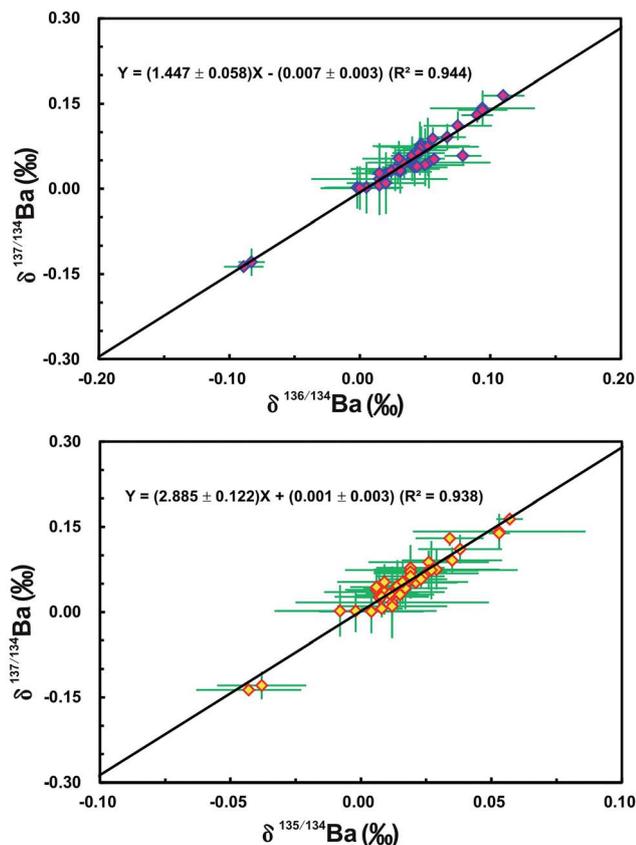


Fig. 9 Barium three isotope plot of all standards and samples analyzed in this study defines a line with a slope of 1.447 ± 0.058 in the $\delta^{137/134}\text{Ba}-\delta^{136/134}\text{Ba}$ fractionation line and 2.885 ± 0.122 in the $\delta^{137/134}\text{Ba}-\delta^{135/134}\text{Ba}$ fractionation line.

Ba isotopic composition of these igneous reference materials are heterogeneous.

The two late Mesozoic basalts from China (MZ815 and MZ834) also have different Ba isotopic compositions. Table 3 exhibits that sample MZ815 has lighter $\delta^{137/134}\text{Ba}$ ($-0.132 \pm 0.020\%$) with higher Ba abundance ($767 \mu\text{g g}^{-1}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ (0.709170) than MZ834 with a $\delta^{137/134}\text{Ba}$ of $0.001 \pm 0.034\%$, lower Ba abundance ($267 \mu\text{g g}^{-1}$), and lower $^{87}\text{Sr}/^{86}\text{Sr}$ (0.705832).²⁶ Cui *et al.*²⁶ suggested that the high Ba abundance and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of MZ815 might be due to the addition of the altered oceanic crust into its mantle source by subduction. If this is true, the recycled altered oceanic crust would contaminate the mantle producing a light $\delta^{137/134}\text{Ba}$ signature.

5. Conclusions

We developed a method for high precision Ba isotope analyses using sample-standard bracketing in a Neptune Plus MC-ICP-MS. After the samples were purified by a chromatographic method using a two-column procedure with AG50W-X12 resin, the Ba isotopic compositions were measured by MC-ICP-MS using SRM3104a as the bracketing standard. We systematically tested the possible parameters which might affect the precision and accuracy of Ba isotope measurements, including matrix

effects and mismatch in acid molarities and Ba concentrations between samples and bracketing standards. No significant analytical artifact was observed when the sample-standard Ba concentration difference was $<50\%$ or the dilution acid molarity difference varies from 50% to 150%. Further tests showed that Ba isotope measurements are not affected by the matrices when the loaded sample contains more than $6 \mu\text{g Ba}$ and the purified samples have $\text{Ca/Ba} \leq 1$, $\text{Mg/Ba} \leq 1$, $\text{Na/Ba} \leq 0.5$, $\text{Sr/Ba} \leq 0.5$, $\text{K/Ba} \leq 0.1$, $\text{Fe/Ba} \leq 0.05$, and $\text{Al/Ba} \leq 0.01$.

Based on repeated measurements of standards (such as IAEA-CO-9 and BHVO-2), the long-term external precision of $\delta^{137/134}\text{Ba}$ is better than $\pm 0.05\%$ (2SD). With our method, we determined the $\delta^{137/134}\text{Ba}$ values of 8 reference materials. $\delta^{137/134}\text{Ba}$ of basalt standards BCR-2, BHVO-2, and JB-2 is $0.050 \pm 0.039\%$ (2SD, $n = 13$), $0.047 \pm 0.028\%$ (2SD, $n = 22$) and $0.085 \pm 0.035\%$ (2SD, $n = 19$), respectively; diabase standard W-2 is $0.035 \pm 0.022\%$ (2SD, $n = 11$); andesite standards AGV-1 and JA-2 is $0.047 \pm 0.040\%$ (2SD, $n = 11$) and $0.038 \pm 0.048\%$ (2SD, $n = 17$), respectively; rhyolite standard RGM-1 is $0.142 \pm 0.030\%$ (2SD, $n = 15$); and granodiorite standard GSP-2 is $0.013 \pm 0.046\%$ (2SD, $n = 15$). The $\delta^{137/134}\text{Ba}$ of the late Mesozoic basalts from China has a variation of 0.133% , indicating that their mantle source is heterogeneous. The total variation of $\delta^{137/134}\text{Ba}$ in igneous rock standards and samples in this study is 0.274% , implying that Ba isotopes can be fractionated from high-temperature rocks.

Acknowledgements

This research was financially supported by the National Science Foundation of China (41173031, 41325011 and 41373007) and the 111 project, the Fundamental Research Funds for the Central Universities (WK3410000004), and the State Key Laboratory of Isotope Geochemistry grants (SKLIG-KF-12-05, SKLIG-KF-13-03). We are grateful to Dr Thomas F. Nägler for sharing the Ba standards and to Dr Zhi Xie for providing the Mesozoic basalt samples. We also thank two anonymous reviewers for their constructive comments.

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