JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

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

Xiaoyun Nan,[a] Fei Wu,[a] Zhaofeng Zhang,[b] Zhenhui Hou,[a] Fang Huang,[a] Huimin Yu* [a]

[a]CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Anhui, 230026, China
[b]State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemisty, the Chinese Academy of Sciences, Guangzhou 510640, China.

Abstract

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 cation exchange resin (AG50W-X12, 200-400 mesh). Instrumental mass bias of Ba isotopes was corrected by sample-standard bracketing method using SRM3104a as the bracketing standard. Potential effects of different matrices from resin and samples, acid molarities and concentrations mismatch were rigorously evaluated in this study. The precision and accuracy of this method was tested by measurement of a synthetic solution made by mixing SRM3104a Ba with other matrix elements. The average $\delta^{137/134}$Ba of the synthetic solution is -0.005 ± 0.047‰ (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 $\delta^{137/134}$Ba of basalt standards BCR-2, BHVO-2, JB-2 are 0.050 ± 0.039‰ (2SD, n=13), 0.047 ± 0.028‰ (2SD, n=22), 0.085 ± 0.035‰ (2SD, n=19), respectively; diabase standard W-2 is 0.035 ± 0.022‰ (2SD, n=11); andesite standard AGV-1 is 0.047 ± 0.040‰ (2SD, n=11) and JA-2 is 0.038 ± 0.048‰ (2SD,

n=17); rhyolite standard RGM-1 is 0.142 ± 0.030‰ (2SD, n=15); and granodiorite standard GSP-2 is 0.013 ± 0.046‰ (2SD, n=15). Two late Mesozoic basalts from China have $\delta^{137/134}$Ba of -0.132 ± 0.020‰ (2SD, n=7) and 0.001 ± 0.034‰ (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 ±0.05‰, much smaller than the variation of $\delta^{137/134}$Ba in these reference standards and samples (up to 0.27‰). Therefore, Ba isotopic composition can be used as a novel tracer to study geochemical processes.

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 silicate Earth is 6.60 ppm,[2] much lower than the values in upper continental crust (~628 μg/g)[3] and sediments (~768 μg/g).[4] During subduction, as a fluid mobile element, Ba can be released from the subduction slab with fluid, and then added to the mantle wedge. Therefore, Ba abundance in arc lavas has been used to track the subducted related fluid in arc magmas (*e.g.* Hawkesworth and Norry[5]) or the recycled sediments in the mantle (*e.g.* Murphy *et al.*;[6] Kuritani *et al.*[7]). Previous studies of the alkaline Earth elements reveal significant Mg, Ca, and Sr stable isotopic 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] 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 $\delta^{137/134}$Ba in low temperature environment.[13]

Fractionations of Mg, Ca, and Sr stable isotopes among igneous rocks have been used to constrain recycling of crustal material and magmatic differentiation.[9, 11, 12, 14] Because Ba abundance in mantle is much lower than the crust and sediments, the Ba isotopes could be more sensitive than Ca and Mg isotopes in tracing the recycled materials. However, the Ba isotope 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 isotope compositions of the important reservoirs of the Earth.

Barium have seven stable isotopes, ^{130}Ba, ^{132}Ba, ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba and ^{138}Ba, and the abundances are 0.1058%, 0.1012%, 2.417%, 6.592%, 7.853%, 11.232%, and 71.699%, respectively.[15] Since Nier[16] 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 spectrometry (TIMS). With the quick advance of analytical technique 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 $\delta^{137/134}$Ba ($\delta^{137/134}\text{Ba} = [(^{137/134}\text{Ba}_{\text{sample}})/(^{137/134}\text{Ba}_{\text{standard}})-1] \times 1000$) of ± 0.15‰ (2SD). Miyazaki *et al.*[23] improved this method with the achievable repeatability of 0.032‰ (2SD) in $\delta^{137/134}$Ba. Both methods used double spike technique to correct fractionation of Ba isotopes during Ba separation in exchange chromatography and mass bias produced by instrument. However, Ba isotope data of reference materials for inter-laboratories 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 for eight well-characterized reference materials and two natural basalts using NIST SRM3104a as a bracketing standard. The reference materials include igneous rock standards from 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 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 high purity after double distilling. All reagents were then diluted from concentrated acids by 18.2MΩ ultra-pure water. Rock reference standards were weighed into 7 mL Teflon® PFA screw cap vials (Savillex®). After decomposing by a 1:2 mixture of concentrated HNO_3 and HF, they were dried down and fluxed by 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) by only one ion exchange column. To avoid the effect from 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 mm ID x 9.6 mm OD (Savillex®). Two mili-liter cation exchange resin (AG50W-X12, 200-400 mesh, Bio-Rad, USA) was cleaned alternatively by 6 mol L^{-1} HCl and 18.2 MΩ H_2O for three times, and loaded into the column. And then, the resin was finally cleaned by 8 mL of 6 mol L^{-1} HNO_3 and 6 mL of 6 mol L^{-1} HCl, and conditioned by 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 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 Ba elution curve drifted during the chromatography process.

The second column was polypropylene spin column from Bio-Rad with 1.2 mL bed volume and 6.5 mm ID. Half milliliter of the same cation resin was loaded to the column. Similar procedure as 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 by 2% (m/m) HNO_3, and then ready for instrument analysis.

2.1.1 Effect of acid molarities on Ba elution

In order to use minimum volume of acid to purify Ba and avoid potential contamination, different molarities of acid were used to examine for 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 4mol L^{-1}). Figure 2 shows that cations were eluted faster when using more concentrated acid, and the elution curve of matrix elements were wide when using 2 mol L^{-1} HCl (＞ 20 mL, Fig. 2 a 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 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}, matrix elements (including Ca and part of Sr) can be eluted within 20 ml of HCl (Fig. 2c-f). The left 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 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. Total procedure blank (from sample dissolution to instrumental analysis) was ~2.9 ng.

2.1.2 Effect of Ba mass loaded on 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 the tails of matrix elements. Furthermore, based on the research for other metal stable isotopes (*e.g.* Mg[25]), the elution curves could shift with the variations of the amount of target element loaded to the columns or the types of matrix elements. To achieve 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 (the 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 by 3 mol L^{-1} HCl (Fig. 3). When the mass of Ba loaded into column is $\leq$ 20 μg, regardless of the mass of Ba, all elution curves of Ba overlap with each other. However, if the sample loaded to the column contained extremely high Ba, 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. Figure 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 to the columns are same, indicating the elution procedure is not sensitive to the types of samples. Therefore, if less than 20 μg Ba loading to 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 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 isotopes analyses. The sensitivity of ^{137}Ba is ~75v/ppm under dry plasma using Aridus II desolvator (CETAC Technologies). The cup configuration and parameters for instrument are summarized in Table 1. Five Ba isotopes (^{132}Ba, ^{134}Ba, ^{135}Ba, ^{136}Ba, and ^{137}Ba) were collected on L1, C, H1, H2, and H3 Faraday cups, respectively. The ^{131}Xe was also simultaneously collected on 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 second per cycle. The sample is bracketed before and after by the standard, and the analyses repeated ≥ 3 times for the same sample solution. Between each measurement, the sample introduction system was cleaned by 2% HNO_3 (m/m) for 5 min to eliminate the potential cross-contamination, until the ^{137}Ba signal is less than 10mv.

The Ar gas always contains trace amount of Xe, producing isobaric interferences on Ba isotopes (^{134}Xe on ^{134}Ba and ^{136}Xe on ^{136}Ba). To correct the effect of Xe interference, we first analyzed 2 % HNO_3 (m/m) for ~2 min as on-peak background before each sequence. And then Ba signal (~7mv of ^{137}Ba) in the background was subtracted from the analyzed data. Because 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 ^{134}Xe and ^{136}Xe interferences based on the signal of ^{131}Xe assuming that the fractionation factor (β) was same to Ba using an exponential law of fractionation. The Ba isotope ratios were then corrected by subtracting ^{134}Xe and ^{136}Xe from ^{134}Ba and ^{136}Ba.

2.3 Standards for sample-standard bracketing

The bracketing standard used in previous studies was Fluka, a barium nitrate ($Ba(NO_3)_2$) ICP-OES standard solution from Aldrich Company.[13,23] In this study, we calibrated a new bracketing standard, SRM3104a, which is a 50 mL $Ba(NO_3)_2$ 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 ± 0.036 mg/g. This standard was diluted to ~500 μg/g and stored in a Teflon® bottle. During measurement, the standard and sample solutions were further diluted to 200 ng/g.

2.4 Reference materials and samples

In this study, we analyzed 8 USGS and GSJ rock standards, including basalt (BCR-2, BHVO-2, JB-2), andesite (AGV-1, JA-2), diabase (W-2), granite (GSP-2), and rhyolite (RGM-1). Barium abundances of these standards vary from 130 to 1340 μg/g, and more detailed information of 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 higher Ba abundance (767 μg/g) and higher $^{87}Sr/^{86}Sr$ ratio (0.709170) compared with MZ834 which contained 267 μg/g of Ba and 0.705832 of $^{87}Sr/^{86}Sr$. The high Ba abundance and $^{87}Sr/^{86}Sr$ ratio of MZ815 may reflect addition of altered oceanic crust into the mantle source by subduction.[26] These two samples can provide preliminary information for Ba isotopic compositions of the upper mantle metasomatized by recycled crust material.

3. Accuracy and precision

3.1 Effects of acid molarities and concentrations mismatch

The purified samples were normally dissolved by 2% HNO_3 (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] Teng and Yang[29]). 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 with 2 % HNO_3 (m/m) to bracket 200 ng/g SRM3104a solutions diluted by HNO_3 from 1 to 3 % (m/m). Figure 5 shows that there is no Ba isotopic offset between the SRM3104a diluted in 1 % (m/m) to 3 % (m/m) HNO_3, 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 concentrations mismatch of standard and samples on Ba isotope analysis, we also bracketed a series of Ba standard solutions with concentrations varied from 70 ng/g to 410 ng/g by the same standard with concentration of 200 ng/g. Figure 6 exhibites that Ba isotopes analyses are not sensitive with 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 $\delta^{137/134}$Ba relative to the bracketing standard. Nonetheless, we still carefully adjusted concentrations of sample solutions within 20% difference to the SRM3104a standard solution.

3.2 Effects of 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 solution, 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 measurement. Variable amount of pure Ba standard solutions (SRM3104a) were loaded to 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 into the resin, and then the collected Ba cut were analyzed as unknown samples. There should be no isotopic offset between sample and standard ($\delta^{137/134}$Ba should be zero) if the matrices from column do not affect Ba isotope analyses. Figure 7 shows that, when only loading 2 μg Ba into 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 to the columns. When the loaded Ba is more than 6 μg, the column matrix effect is negligible (<0.05‰). Therefore, all of the sample solutions loaded to the columns in this study contained ~ 10 μg 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 form isobaric interferences. For example, $^{94}Zr^{40}Ar$ and $^{54}Fe(^{40}Ar)_2$ are isobaric effects for ^{134}Ba, and $^{97}Mo^{40}Ar$ and $^{87}Sr^{38}Ar^{12}C$ can affect ^{137}Ba. Some matrix elements will not form isobaric interferences, but still can change 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 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, matrix effect on $\delta^{137/134}$Ba analyses is negligible when the purified samples have Ca/Ba ≤ 1, Mg/Ba ≤ 1, Na/Ba ≤ 0.5, Sr/Ba ≤ 0.5, K/Ba ≤0.1, Fe/Ba ≤ 0.05, and Al/Ba ≤ 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 by 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 Ba isotopic composition of the synthetic standard to ensure that there is no isotope fractionation during chemical separation and instrumental measurement. Second, precision and accuracy of our method were monitored by the repeating measurements of the same samples, including the same solution measured in different time, the same bulk raw solution with different chemistry separation, and independent digestion 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-steps cation exchange columns and analyzed by MC-ICP-MS. The average $\delta^{137/134}$Ba (relative to the pure SRM3104a) of the synthetic solution is -0.005 ± 0.047‰ (2SD, n=36), indicating that chemical procedure and instrumental analyses did not produce significant artifacts.

The Ba isotopic ratios of the standards and samples are listed in Table 2 and Table 3. All standards and samples were repeatedly measured for 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 repeated runs (bracketed for more than three times) of the same solution, the precision of the measured $\delta^{137/134}$Ba is ≤ 0.05‰ (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 $\delta^{137/134}$Ba of IAEA-CO-9 is 0.017 ± 0.049‰ (2SD, n=13). Because of the lack of Fluka standard, we cannot directly compare our results with previous work of Miyazaki *et al.*[23] Therefore, we 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 $\delta^{137/134}$Ba of JA-2, JB-2, and BHVO-2 relative to IAEA-CO-9 are 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 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 $\delta^{137/134}$Ba and $\delta^{136}/^{134}$Ba fractionation line is Y = (1.447 ± 0.058)X - (0.007 ± 0.003) (R^2=0.944), consistent with the slope values of kinetic (1.494) or equilibrium (1.489) fractionation within error.[32] Simultaneously, the slope of $\delta^{137/134}$Ba and $\delta^{135}/^{134}$Ba fractionation line is Y = (2.885 ± 0.122)X + (0.001 ± 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. $\delta^{137/134}$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 $\delta^{137/134}$Ba in the reference materials is 0.129‰, larger than the error of our method (2SD, 0.05‰). There is no correlation between SiO_2 abundance and Ba isotopic compositions (not shown). The granodiorite GSP-2 has the lightest $\delta^{137/134}$Ba (0.013 ± 0.046‰), and the rhyolite RGM-1 has the highest $\delta^{137/134}$Ba (0.142 ± 0.030‰), indicating that the 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 exhibited that sample MZ815 has lighter $\delta^{137/134}$Ba (-0.132 ± 0.020‰) with higher Ba abundance (767 μg/g) and ^{87}Sr/^{86}Sr (0.709170) than MZ834 with $\delta^{137/134}$Ba of 0.001 ± 0.034‰, lower Ba abundance (267 μg/g), and lower ^{87}Sr/^{86}Sr (0.705832).[26] Cui *et al.*[26] suggested that the high Ba abundance and ^{87}Sr/^{86}Sr ratios of MZ815 might be due to addition of altered oceanic crust into its mantle source by subduction. If this is true, the recycled altered oceanic crust would contaminate mantle producing a light $\delta^{137/134}$Ba signature.

5. Conclusions

We developed a method for high precision Ba isotope analyses using sample-standard bracketing in the Neptune plus MC-ICP-MS. After samples were purified by 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 measurement, including matrix effects and mismatch in acid molarities and Ba concentrations between samples and bracketing standard. No significant analytical artifact was observed when the sample-standard Ba concentration difference is $<$50% or the dilution acid molarity difference varies from 50% to 150%. Further tests showed that Ba isotope measurement is not affected by the matrices when the loaded sample contains more than 6 μg Ba and the purified samples have Ca/Ba $\leq$ 1, Mg/Ba $\leq$ 1, Na/Ba $\leq$ 0.5, Sr/Ba $\leq$ 0.5, K/Ba $\leq$0.1, Fe/Ba $\leq$ 0.05, and 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 $\delta^{137/134}$Ba is better than ± 0.05‰ (2SD). With our method, we determined the $\delta^{137/134}$Ba values of 8 reference materials. $\delta^{137/134}$Ba of basalt standards BCR-2, BHVO-2, JB-2 are 0.050 ± 0.039‰ (2SD, n=13), 0.047 ± 0.028‰ (2SD, n=22) and 0.085 ± 0.035‰ (2SD, n=19), respectively; diabase standard W-2 is 0.035 ± 0.022‰ (2SD, n=11); andesite standards AGV-1 and JA-2 are 0.047 ± 0.040‰ (2SD, n=11) and 0.038 ± 0.048‰ (2SD, n=17), respectively; rhyolite standard RGM-1 is 0.142 ± 0.030‰ (2SD, n=15); and granodiorite standard GSP-2 is 0.013 ± 0.046‰ (2SD, n=15). The $\delta^{137/134}$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 $\delta^{137/134}$Ba in igenous rock standards and samples in this study is 0.274‰, implying that Ba isotopes can be fractionated in 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 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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Figure captions:

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

Figure 2. Elution curves for Ba purification procedures using different reagents.

Figure 3. Drifting of the center of Ba elution curves with different masses of Ba loaded to the columns. Matrix elements (such as Na, K, Ca, and Sr) are not shown in the plot as most of them were removed by 28 ml of HCl before adding HNO_3.

Figure 4. Elution curves for Ba purification procedures using different rock standards. Despite of the different set 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.

Figure 5. $\delta^{137/134}$Ba variations during measurement of Ba standard solutions diluted by different HNO_3 acid strengths. The error bars (2SD) are based on at least 3 replicate measurements. The HNO_3 molarities in this test changed from 1% to 3% (m/m).

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

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

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

Figure 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 $\delta^{137/134}$Ba-$\delta^{136/134}$Ba fractionation line and 2.885 ± 0.122 in $\delta^{137/134}$Ba-$\delta^{135/134}$Ba fractionation line.

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	~0.8 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 mL min^{-1}					
N_2 gas	2-3 mL min^{-1}					
Solution uptake	~50µL min^{-1}					
Detector mode	Faraday cup static 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

Table 2 Ba isotopic composition of standards

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

n is the times of repeated measurement of the same solution.

M is the times of independent digestions of the same standard powder.

* Same bulk raw solution with different chemistry separations.

[a] The total number of repeated runs of the same sample, including different digestions.

‡ The difference between two samples instead of two standard deviation.

2SD = 2 times the standard deviation of the population of *n* repeat measurements.

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

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	Ba	$^{87}Sr/^{86}Sr$	$\delta^{137/134}Ba$（‰）	2SD	n
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
															-0.137	0.007	3
Average (M=2)															**-0.132**	**0.020**	**7**[a]
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
															0.001	0.038	4
Average (M=2)															**0.001**	**0.034**	**7**[a]

The major elements in wt%, Ba in μg/g. Data of major elements, Ba abundance and $^{87}Sr/^{86}Sr$ ratios are from Cui et al.[26] Each sample has two independent digestions.

[a] The total number of repeated runs of the same sample, including different 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.

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

Sample	**$\Delta^{137/134}Ba_{IAEA\text{-}CO\text{-}9}$ (‰)**	
	This study	Miyazaki *et al.*[17]
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

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

Figure 1

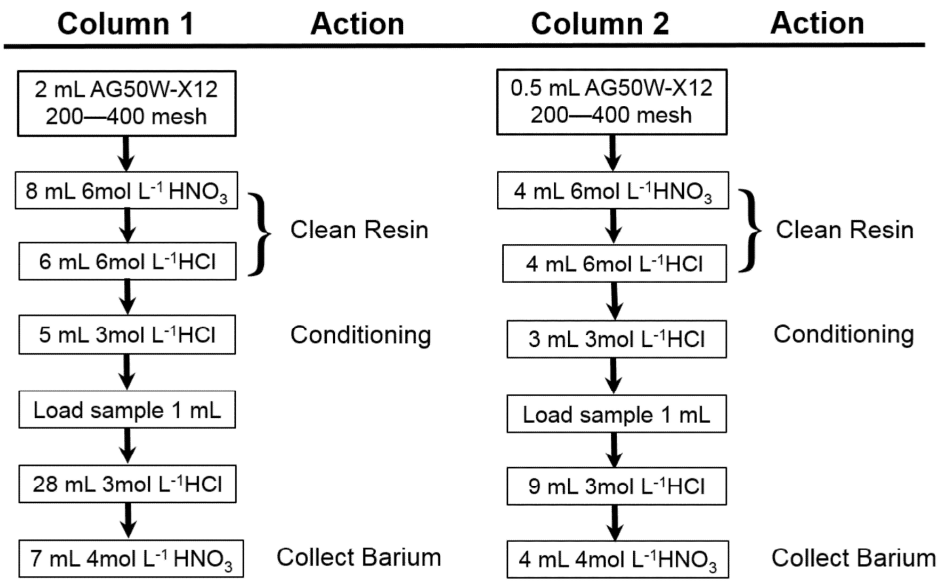

Column 1
Action
Column 2
Action
2 mL AG50W-X12 200—400 mesh
8 mL 6mol L^{-1} HNO$_3$
6 mL 6mol L^{-1}HCl
Clean Resin
5 mL 3mol L^{-1}HCl
Conditioning
Load sample 1 mL
28 mL 3mol L^{-1}HCl
7 mL 4mol L^{-1} HNO$_3$
Collect Barium
0.5 mL AG50W-X12 200—400 mesh
4 mL 6mol L^{-1}HNO$_3$
4 mL 6mol L^{-1}HCl
Clean Resin
3 mL 3mol L^{-1}HCl
Conditioning
Load sample 1 mL
9 mL 3mol L^{-1}HCl
4 mL 4mol L^{-1}HNO$_3$
Collect Barium

Figure 2

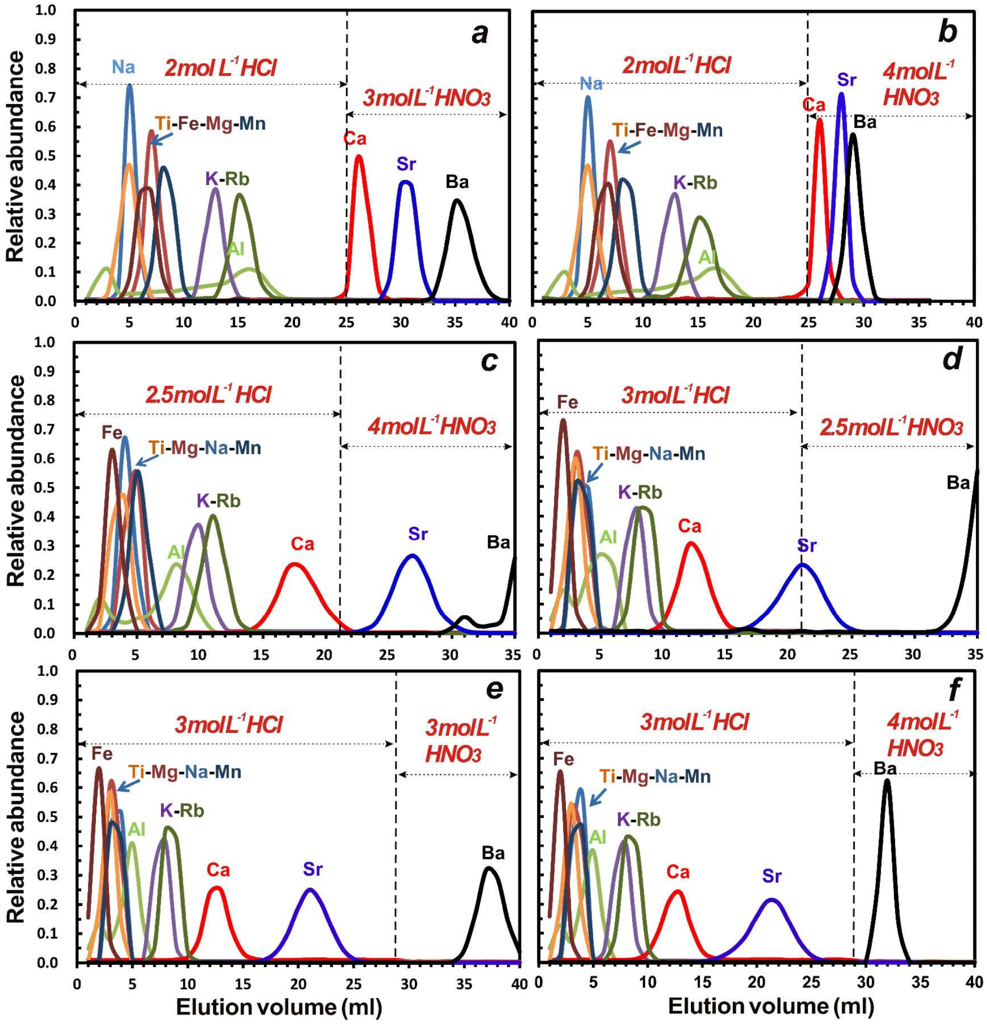

a
2mol L-1 HCl
3molL-1 HNO3
Na
Ti-Fe-Mg-Mn
K-Rb
Al
Ca
Sr
Ba
b
2molL-1 HCl
4molL-1 HNO3
Na
Ti-Fe-Mg-Mn
K-Rb
Al
Ca
Sr
Ba
c
2.5molL-1 HCl
4molL-1 HNO3
Fe
Ti-Mg-Na-Mn
K-Rb
Al
Ca
Sr
Ba
d
3molL-1 HCl
2.5molL-1 HNO3
Fe
Ti-Mg-Na-Mn
K-Rb
Al
Ca
Sr
Ba
e
3molL-1 HCl
3molL-1 HNO3
Fe
Ti-Mg-Na-Mn
Al
K-Rb
Ca
Sr
Ba
f
3molL-1 HCl
4molL-1 HNO3
Fe
Ti-Mg-Na-Mn
Al
K-Rb
Ca
Sr
Ba
Relative abundance
Elution volume (ml)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
5
10
15
20
25
30
35
40

Figure 3

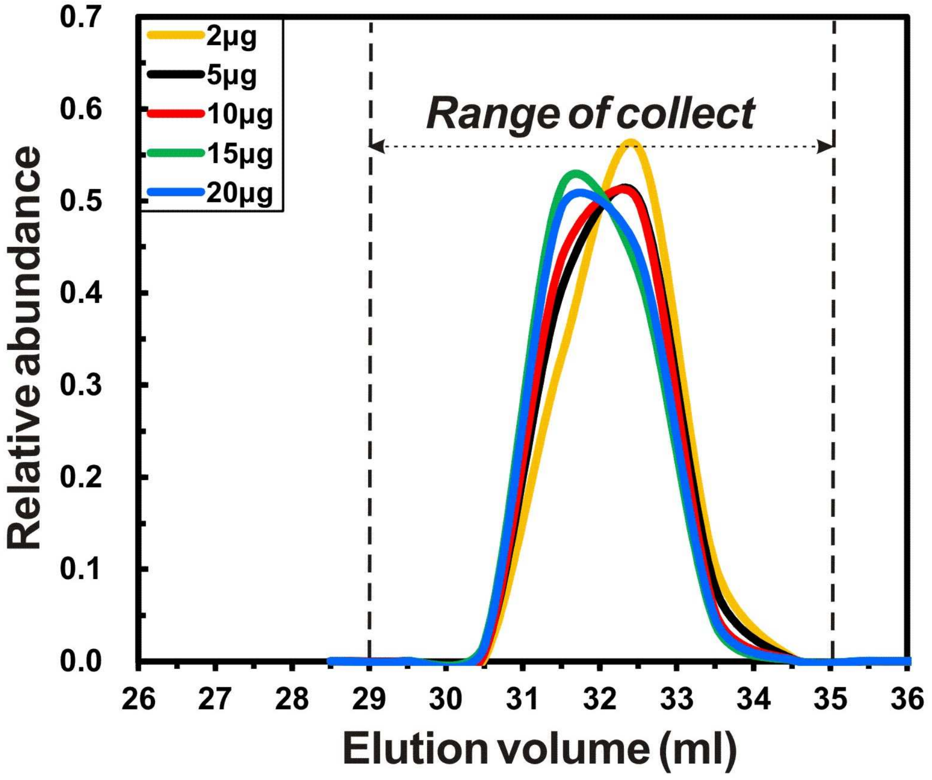

2μg
5μg
10μg
15μg
20μg
Range of collect
Relative abundance
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
26
27
28
29
30
31
32
33
34
35
36
Elution volume (ml)

Figure 4

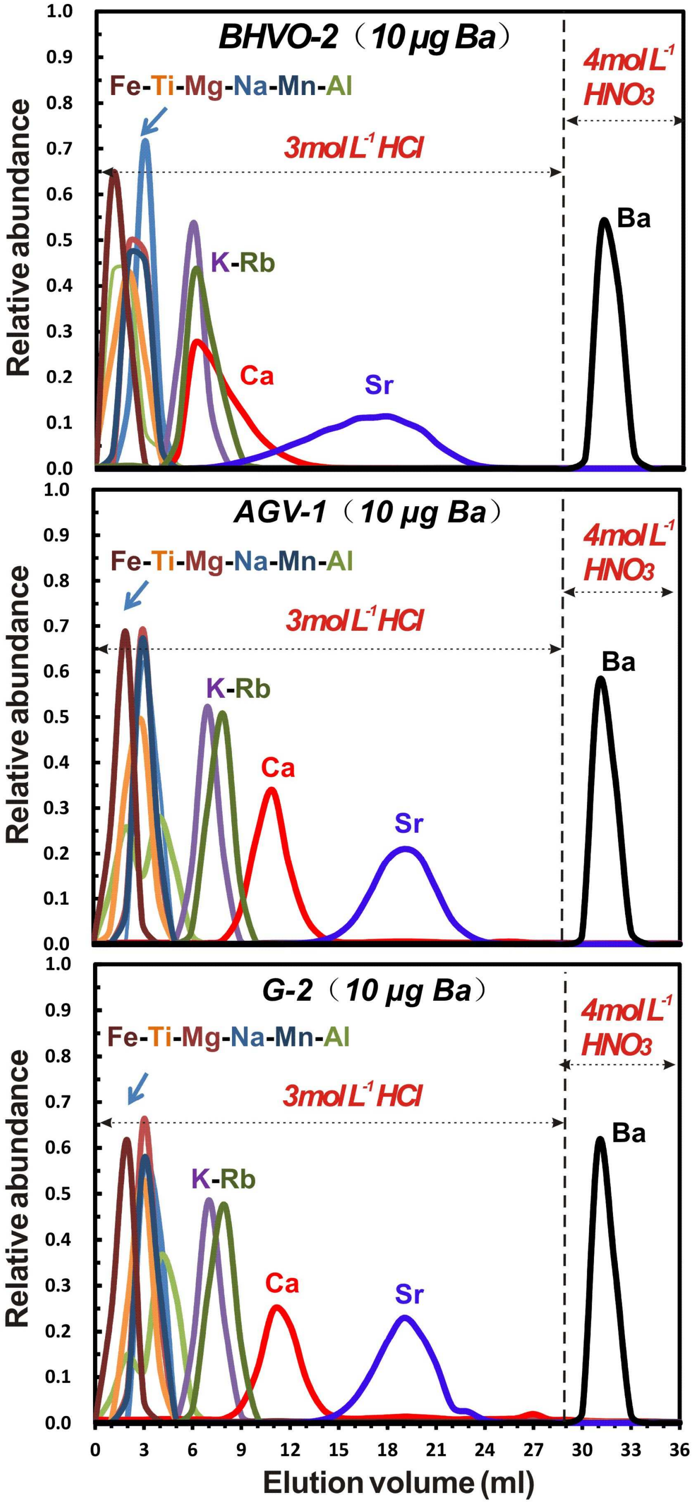
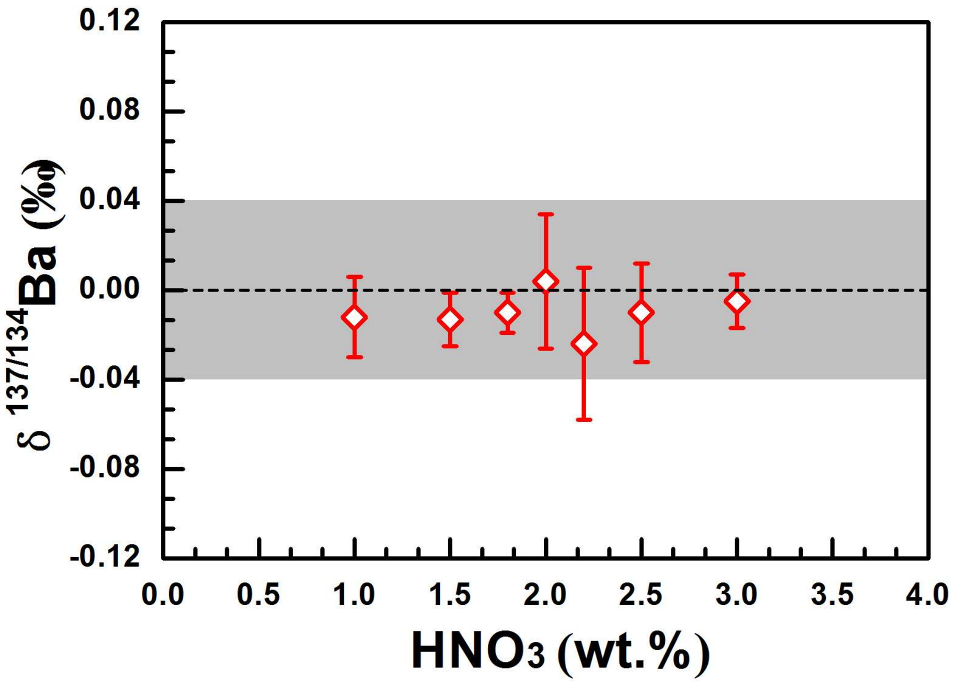

BHVO-2（10 µg Ba）
AGV-1（10 µg Ba）
G-2（10 µg Ba）
Fe-Ti-Mg-Na-Mn-Al
3mol L⁻¹ HCl
4mol L⁻¹ HNO3
K-Rb
Ca
Sr
Ba
Relative abundance
Elution volume (ml)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
3
6
9
12
15
18
21
24
27
30
33
36

Figure 5



0.12
0.08
0.04
0.00
-0.04
-0.08
-0.12
$\delta\ ^{137/134}Ba$ (‰)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
HNO_3 (wt.%)

Figure 6

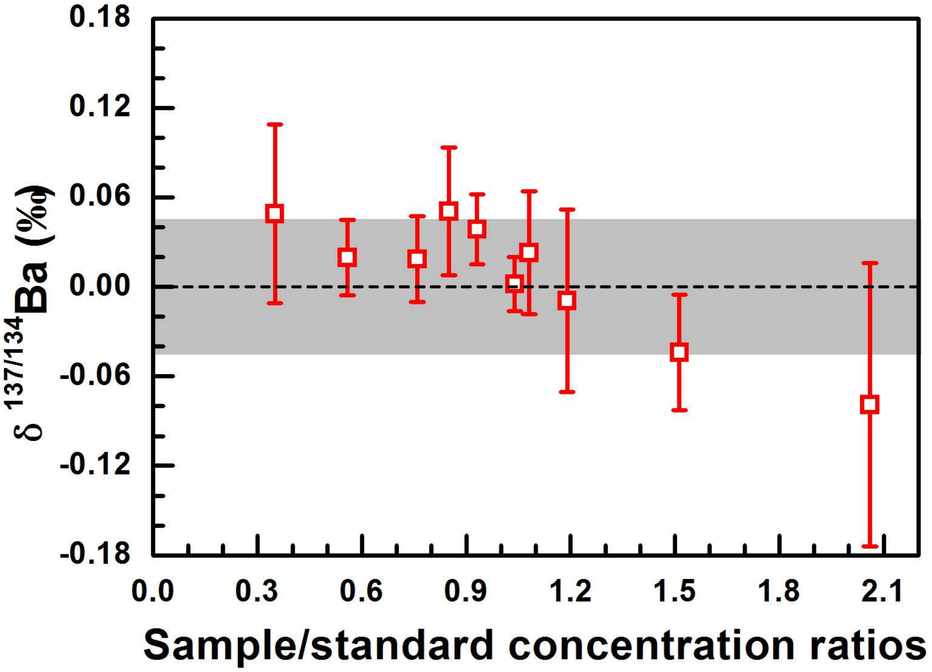

0.18
0.12
0.06
0.00
-0.06
-0.12
-0.18
δ 137/134Ba (‰)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
Sample/standard concentration ratios

Figure 7

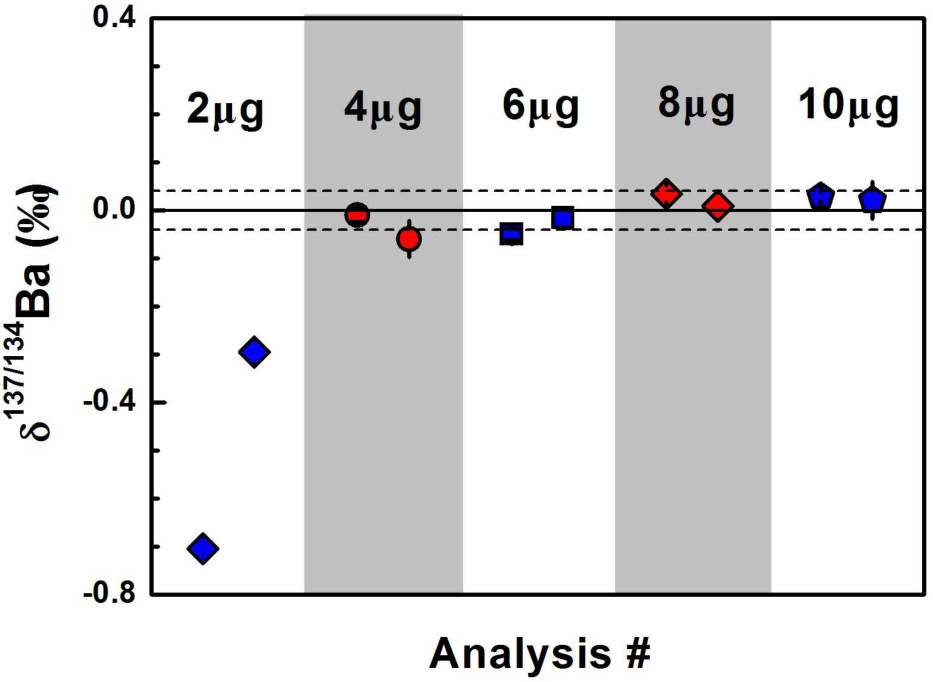


Figure 8

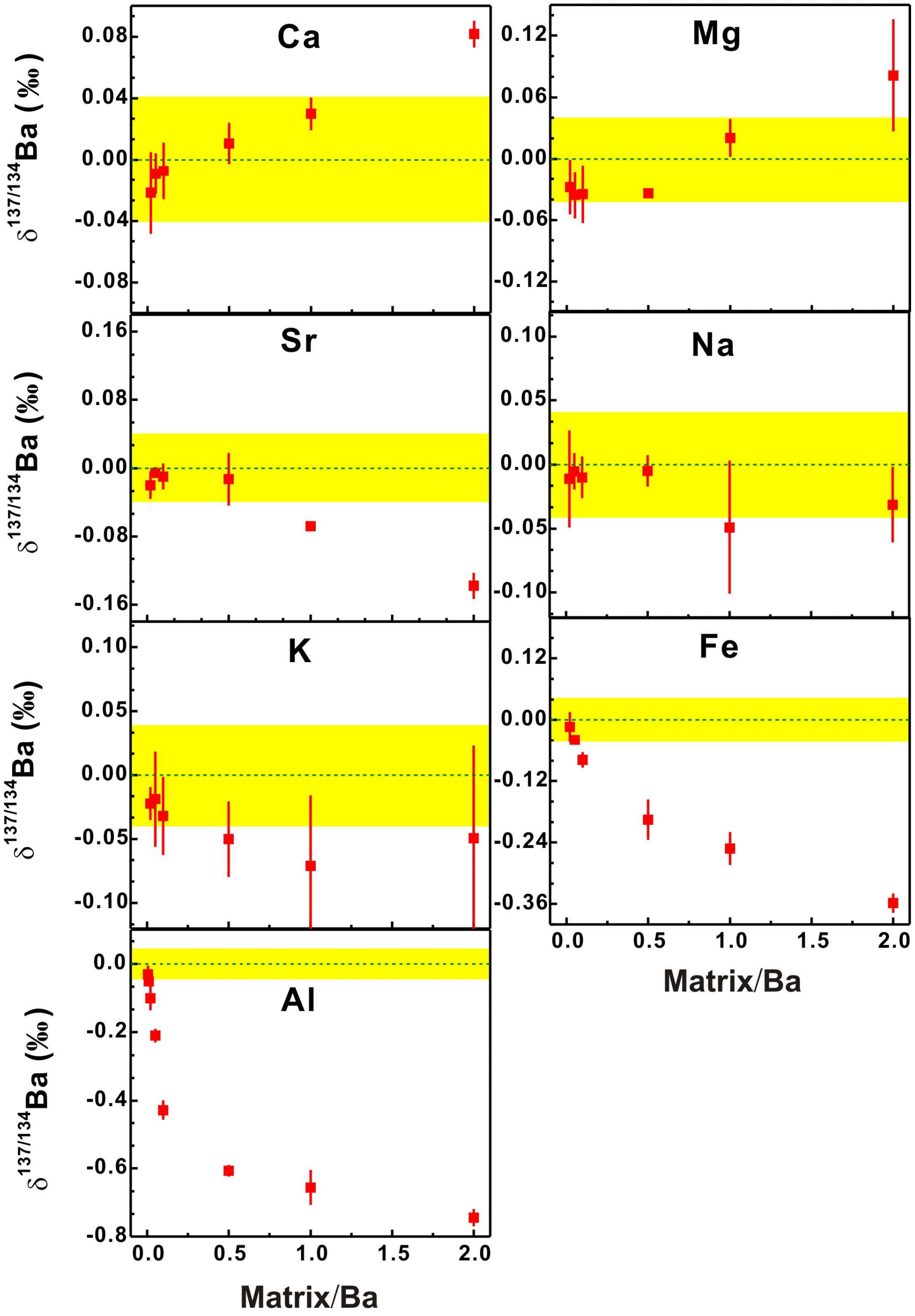
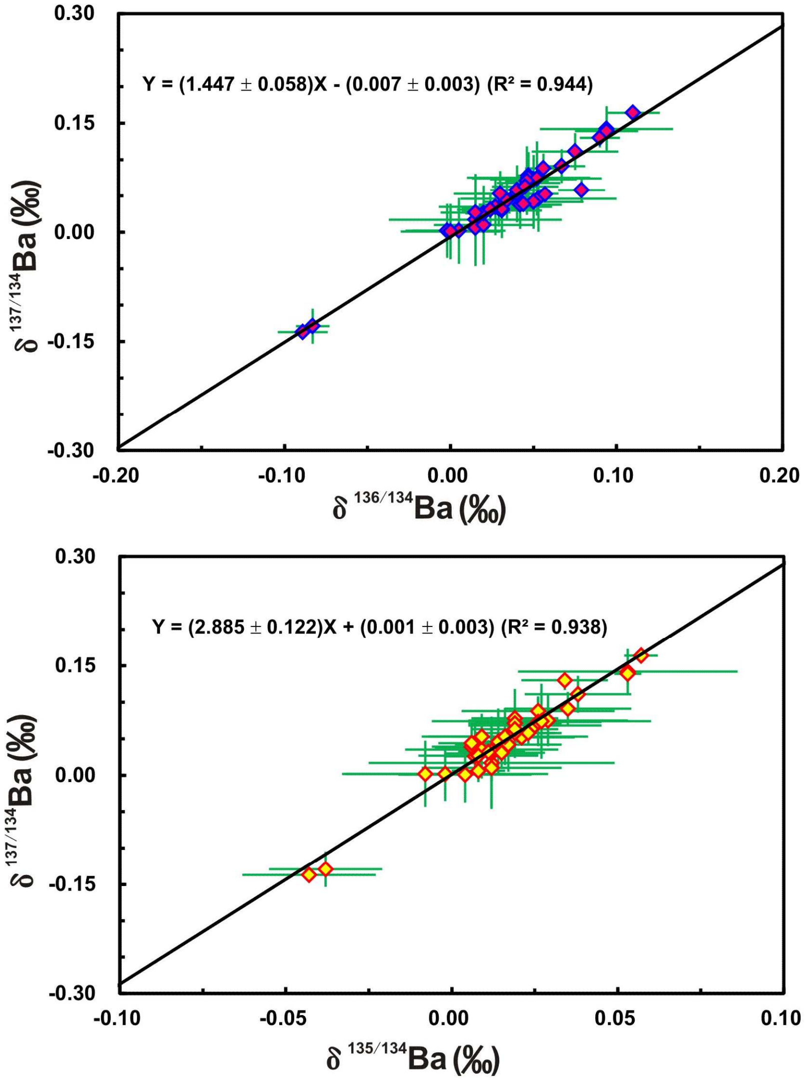
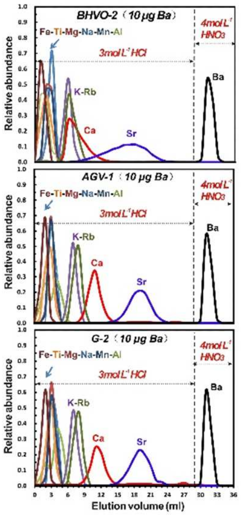

Ca
Mg
Sr
Na
K
Fe
Al
δ137/134Ba (‰)
0.08
0.04
0.00
-0.04
-0.08
0.12
0.06
0.00
-0.06
-0.12
0.16
0.08
0.00
-0.08
-0.16
0.10
0.05
0.00
-0.05
-0.10
0.12
0.00
-0.12
-0.24
-0.36
0.0
-0.2
-0.4
-0.6
-0.8
0.0
0.5
1.0
1.5
2.0
Matrix/Ba

Figure 9


Y = (1.447 ± 0.058)X - (0.007 ± 0.003) (R² = 0.944)
0.30
0.15
0.00
-0.15
-0.30
-0.20
-0.10
0.00
0.10
0.20
δ 137/134Ba (‰)
δ 136/134Ba (‰)
Y = (2.885 ± 0.122)X + (0.001 ± 0.003) (R² = 0.938)
0.30
0.15
0.00
-0.15
-0.30
-0.10
-0.05
0.00
0.05
0.10
δ 137/134Ba (‰)
δ 135/134Ba (‰)



This article presents a high precision method for Ba isotope measurement using multiple-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS).