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

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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 $-0.005 \pm 0.047\%$ (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 $0.050 \pm 0.039\%$ (2SD, $n=13$), $0.047 \pm 0.028\%$ (2SD, $n=22$), $0.085 \pm 0.035\%$ (2SD, $n=19$), respectively; diabase standard W-2 is $0.035 \pm 0.022\%$ (2SD, $n=11$); andesite standard AGV-1 is $0.047 \pm 0.040\%$ (2SD, $n=11$) and JA-2 is $0.038 \pm 0.048\%$ (2SD, $n=11$).
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 δ\(^{137/134}\)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 δ\(^{137/134}\)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 δ\(^{137/134}\)Ba in low temperature environment.\textsuperscript{13}

Fractionations of Mg, Ca, and Sr stable isotopes among igneous rocks have been used to constrain recycling of crustal material and magmatic differentiation.\textsuperscript{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.\textsuperscript{15} Since Nier\textsuperscript{16} first analyzed Ba isotopes, Ba isotopic compositions have been used to study meteorite samples and natural fission reactors.\textsuperscript{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.\textsuperscript{13} developed a high precision analytical method with the repeatability of δ\(^{137/134}\)Ba (δ\(^{137/134}\)Ba = [(\(^{137/134}\)Ba\textsuperscript{sample})/(\(^{137/134}\)Ba\textsuperscript{standard})-1] x 1000) of ± 0.15‰ (2SD). Miyazaki et al.\textsuperscript{23} improved this method with the achievable repeatability of 0.032‰ (2SD) in δ\(^{137/134}\)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 HNO₃ 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, BioRad, USA) was cleaned alternatively by 6 mol L\(^{-1}\) HCl and 18.2 MΩ H\(_2\)O 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 4 mol 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. 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 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, 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), 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 ≤ 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 (\(^{134}\text{Xe}\) on \(^{134}\text{Ba}\) and \(^{136}\text{Xe}\) on \(^{136}\text{Ba}\)). 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 (~7 mV of \(^{137}\text{Ba}\)) 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 \(^{134}\text{Xe}\) and \(^{136}\text{Xe}\) interferences based on the signal of \(^{131}\text{Xe}\) assuming that the fractionation factor (\(\beta\)) was same to Ba using an exponential law of fractionation. The Ba isotope ratios were then corrected by subtracting \(^{134}\text{Xe}\) and \(^{136}\text{Xe}\) from \(^{134}\text{Ba}\) and \(^{136}\text{Ba}\).

### 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.\textsuperscript{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.\textsuperscript{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\textsubscript{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.;\textsuperscript{25} Malinovsky et al.;\textsuperscript{27} Liu et al.;\textsuperscript{28} Teng and Yang\textsuperscript{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 % HNO₃ (m/m) to bracket 200 ng/g SRM3104a solutions diluted by HNO₃ 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) 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 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 exhibits 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 δ¹⁳⁷/¹³⁴Ba 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. 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 (δ^{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 δ^{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.\textsuperscript{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 $-0.005 \pm 0.047\%$ (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 $\leq 0.05\%$ (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 $0.017 \pm 0.049\%$ (2SD, n=13). Because of the lack of Fluka standard, we cannot directly compare our results with previous work of Miyazaki et al.\textsuperscript{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.\textsuperscript{23} The $\delta^{137/134}$Ba of JA-2, JB-2, and BHVO-2 relative to IAEA-CO-9 are $0.021 \pm 0.069\%$, $0.068 \pm 0.060\%$, and $0.030 \pm 0.056\%$ in this study, consistent with $-0.016 \pm 0.038\%$, $0.054 \pm 0.024\%$, and $0.026 \pm 0.026\%$ in Miyazaki et al.,\textsuperscript{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 $Y = (1.447 \pm 0.058)X - (0.007 \pm 0.003)$ ($R^2=0.944$), consistent with the slope values of kinetic (1.494) or equilibrium (1.489) fractionation within error.\textsuperscript{32} Simultaneously, the slope of $\delta^{137/134}$Ba and $\delta^{135/134}$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.\textsuperscript{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). Cui et al. 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 ≤ 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.

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, JB-2 are $0.050 \pm 0.039\%$ (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 are $0.047 \pm 0.040\%$ (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 in high-temperature rocks.

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References:


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 HNO₃.

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. δ¹³⁷/¹³⁴Ba variations during measurement of Ba standard solutions diluted by 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).

Figure 6. The effect of Ba concentration mismatches between sample and standard on δ¹³⁷/¹³⁴Ba analyses.

Figure 7. δ¹³⁷/¹³⁴Ba variations with the different masses of Ba loaded to the columns.

Figure 8. Doping experiments to test the matrix effect on δ¹³⁷/¹³⁴Ba 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 δ¹³⁷/¹³⁴Ba-δ¹³⁶/¹³⁴Ba fractionation line and 2.885 ± 0.122 in δ¹³⁷/¹³⁴Ba-δ¹³⁵/¹³⁴Ba fractionation line.
### Table 1 Instrumental operating conditions for Ba isotopic measurements

<table>
<thead>
<tr>
<th>MC-ICP-MS</th>
<th>Thermo Fisher Scientific, Neptune Plus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling Ar</td>
<td>~16 L min⁻¹</td>
</tr>
<tr>
<td>Auxiliary Ar</td>
<td>~0.8 L min⁻¹</td>
</tr>
<tr>
<td>Nebulizer Ar</td>
<td>~0.85 L min⁻¹</td>
</tr>
<tr>
<td>Mass resolution</td>
<td>Low resolution</td>
</tr>
<tr>
<td>Typical sensitivity</td>
<td>~75V ppm⁻¹ for $^{137}$Ba</td>
</tr>
<tr>
<td>Cones</td>
<td>Ni Sampler cone, X-skimmer cone</td>
</tr>
<tr>
<td>Desolvator</td>
<td>Aridus II</td>
</tr>
<tr>
<td>Ar sweep</td>
<td>~ 5.45 mL min⁻¹</td>
</tr>
<tr>
<td>N₂ gas</td>
<td>2-3 mL min⁻¹</td>
</tr>
<tr>
<td>Solution uptake</td>
<td>~50µL min⁻¹</td>
</tr>
<tr>
<td>Detector mode</td>
<td>Faraday cup static mode</td>
</tr>
<tr>
<td>L₂-F</td>
<td>$^{131}$Xe $^{132}$Ba $^{134}$Ba $^{135}$Ba $^{136}$Ba $^{137}$Ba</td>
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<tr>
<td>L₁-F</td>
<td></td>
</tr>
<tr>
<td>C-F</td>
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<td>H₁-F</td>
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<td>H₂-F</td>
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<td>H₃-F</td>
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</table>
Table 2. Ba isotopic composition of standards

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

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.
‡ 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>LOI</th>
<th>Total</th>
<th>Ba</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>$\delta^{137/134}$Ba (‰)</th>
<th>2SD</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ815</td>
<td>50.51</td>
<td>17.05</td>
<td>1.47</td>
<td>9.78</td>
<td>0.15</td>
<td>4.33</td>
<td>5.81</td>
<td>4.19</td>
<td>2.53</td>
<td>0.36</td>
<td>2.94</td>
<td>99.43</td>
<td>767</td>
<td>-0.129</td>
<td>0.024</td>
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<tr>
<td>Average (M=2)</td>
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<td><strong>-0.132</strong></td>
<td><strong>0.020</strong></td>
<td>7a</td>
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<tr>
<td>MZ834</td>
<td>48.93</td>
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<td>1.43</td>
<td>10.46</td>
<td>0.19</td>
<td>5.28</td>
<td>8.09</td>
<td>2.19</td>
<td>1.51</td>
<td>0.63</td>
<td>3.29</td>
<td>99.57</td>
<td>267</td>
<td>0.002</td>
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<td></td>
<td>0.001</td>
<td>0.038</td>
<td>4</td>
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<tr>
<td>Average (M=2)</td>
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<td></td>
<td><strong>0.001</strong></td>
<td><strong>0.034</strong></td>
<td>7a</td>
<td></td>
</tr>
</tbody>
</table>

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. 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 relative to IAEA-CO-9 in our study and Miyazaki et al. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta^{137/134}$Ba$_{\text{IAEA-CO-9}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This study</td>
</tr>
<tr>
<td>JA-2</td>
<td>0.021 ± 0.069</td>
</tr>
<tr>
<td>JB-2</td>
<td>0.068 ± 0.060</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>0.030 ± 0.056</td>
</tr>
</tbody>
</table>

The error was 2SD, which was calculated based on error propagation.
Figure 1

<table>
<thead>
<tr>
<th>Column 1</th>
<th>Action</th>
<th>Column 2</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mL AG50W-X12 200-400 mesh</td>
<td>Clean Resin</td>
<td>0.5 mL AG50W-X12 200-400 mesh</td>
<td>Clean Resin</td>
</tr>
<tr>
<td>8 mL 6mol L⁻¹ HNO₃</td>
<td>Conditioning</td>
<td>4 mL 6mol L⁻¹ HNO₃</td>
<td>Conditioning</td>
</tr>
<tr>
<td>6 mL 6mol L⁻¹ HCl</td>
<td>Load sample 1 mL</td>
<td>4 mL 6mol L⁻¹ HCl</td>
<td>Load sample 1 mL</td>
</tr>
<tr>
<td>5 mL 3mol L⁻¹ HCl</td>
<td>28 mL 3mol L⁻¹ HCl</td>
<td>9 mL 3mol L⁻¹ HCl</td>
<td>4 mL 4mol L⁻¹ HNO₃</td>
</tr>
<tr>
<td>7 mL 4mol L⁻¹ HNO₃</td>
<td>Collect Barium</td>
<td>4 mL 4mol L⁻¹ HNO₃</td>
<td>Collect Barium</td>
</tr>
</tbody>
</table>
Figure 2
Figure 3

![Diagram showing elution volume (ml) vs. relative abundance for different concentrations (2µg, 5µg, 10µg, 15µg, 20µg). The range of collect is indicated by a dashed line between 30.5 and 31.5 ml.]
Figure 4

BHVO-2 (10 μg Ba)

Fe-Ti-Mg-Na-Mn-Al

3 mol L⁻¹ HCl

K-Rb

Ca

Sr

Ba

AGV-1 (10 μg Ba)

Fe-Ti-Mg-Na-Mn-Al

3 mol L⁻¹ HCl

K-Rb

Ca

Sr

Ba

G-2 (10 μg Ba)

Fe-Ti-Mg-Na-Mn-Al

3 mol L⁻¹ HCl

K-Rb

Ca

Sr

Ba

Elution volume (ml)
Figure 5
Figure 7

![Graph showing δ^{137/134}Ba (%) for different concentrations of Ba. The graph has a y-axis labeled δ^{137/134}Ba (%) with values ranging from -0.8 to 0.4, and an x-axis labeled Analysis #. The concentrations are marked as 2μg, 4μg, 6μg, 8μg, and 10μg. The graph includes data points for each concentration level.](image-url)
Figure 8
Figure 9

\[ Y = (1.447 \pm 0.058)X - (0.007 \pm 0.003) \quad (R^2 = 0.944) \]

\[ Y = (2.885 \pm 0.122)X + (0.001 \pm 0.003) \quad (R^2 = 0.938) \]
This article presents a high precision method for Ba isotope measurement using multiple-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS).