TECHNICAL NOTE 30814

Ba isotope analysis using 10^{13} Ω amplifiers

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Keywords: $\delta^{138/134}$Ba, Isotope Ratio, TIMS, 10^{13} Ω Amplifier Technology

Introduction

Barium (Ba) is an alkaline earth metal with high mobility during crust-mantle melt/fluid activity, surficial weathering and oceanic circulation. Ba has seven stable isotopes, ^{130}Ba (0.106 % natural abundance), ^{132}Ba (0.101 %), ^{134}Ba (2.417 %), ^{135}Ba (6.592 %), ^{136}Ba (7.854 %), ^{137}Ba (11.232 %) and ^{138}Ba (71.698 %). Previous studies have shown that Ba isotopes have the potential to track both high-temperature (e.g. crust-mantle recycling[1,2]) and low-temperature geochemical processes (e.g. oceanic circulation and paleo-ocean productivity reconstruction[3,4]).

Both thermal ionization mass spectrometry (TIMS)[5, 6] and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS)[7, 8] have been used for Ba isotope measurements. To achieve high precision and accuracy Ba isotope data (2 SD < ± 0.1 ‰), more than 50 ng Ba is required to guarantee that the beam size of the Ba isotope of interest with lowest abundance (i.e. ^{134}Ba) is higher than 300-500 mV with the default 10^{11} Ω amplifiers. A recent advance for the mass spectrometer is the development of state-of-the-art Thermo Scientific™ 10^{13} Ω Amplifier Technology™ for the collection of the small ion beams[9,10]. Compared to default 10^{11} Ω amplifiers, the use of a high-resistance 10^{13} Ω amplifiers results in a theoretical ten-fold improvement in the signal-to-Johnson-noise ratio, and thus should correspond to a similar improvement in isotope ratio precision for analyses of small ion beams. In this work, the Ba isotope analysis of pure solution standards and complex matrix reference materials (RMs) by TIMS demonstrates the remarkable improvements in accuracy and precision for low intensity ion beams afforded by the 10^{13} Ω Amplifier Technology. The data shows that for samples with low Ba abundance, the amount of sample required when measuring with the 10^{13} Ω Amplifier Technology can be reduced by a factor of 12-14 in order to achieve comparable uncertainties to 10^{11} Ω amplifiers. This technique thereby opens up new possibilities for analysis of samples that have low Ba concentration (e.g. mantle peridotite) or were otherwise impossible to obtain in sufficient quantities (e.g. small pieces from foraminifera, shellfish, or coral).

Method

Barium isotope ratio analysis was performed on three pure solution standard (NIST™ SRM3104a, ICPUS-Ba and USTC-Ba) and four rock RMs (BHVO-2, BCR-2, PCC-1 and DTS-1). Sample processing and Ba isotope measurement are performed in the Macquarie University—Thermo Scientific™ isotope development laboratory. For the RMs, samples were first digested using HF-HCl-HNO_3 and then are purified from the matrix using cation exchange columns with AG® 50W-X12 resin (200–400 mesh, Bio Rad, USA) following established procedures[3]. Samples were weighed and spiked with a ^{135}Ba–^{136}Ba double-spike to allow correction for mass fractionation during chemical purification and instrument analysis. A mixed spike-to-sample ratio of about 1:1 is targeted (ratio of total Ba) based on estimates of [Ba] at samples.

Barium isotope measurements were performed using a Thermo Scientific™ Triton Plus™ TIMS. Purified Ba samples were dissolved in 2 µL of distilled 3 M HCl and loaded onto previously outgassed single Re filaments. A current of 0.7 A is continuously applied during the loading. Before and after loading sample, 1 µL of activator gel (a mixture of 250 mg Ta_2O_5 powder and 20 mL 5 % H_3PO_4) was loaded onto the filament at the bottom and top of the sample. In such ways, stable ion beams are achieved during heating. During analysis, ion beams at atomic masses 134 (Ba), 135 (Ba), 136 (Ba), 137 (Ba), 138 (Ba), 139 (La) and 140 (Ce) were monitored in 7 Faraday cups simultaneously. Measurements were made with two different amplifier configurations, one using standard 10^{11} Ω amplifiers and one using the new 10^{13} Ω Amplifier Technology, for the isotopes used in the double-spike inversion (Table 1). Aside from the amplifier configuration and EVAP current (i.e. heating temperature), all other operating parameters were kept identical between these two configurations.

Ion beams were collected in 40 blocks of 10 integrations lasting 8.4 s each. Before each analysis, ion beams were deflected to measure the electronic baseline and then a peak center was run. ^{134}Ba, ^{135}Ba, ^{136}Ba and ^{138}Ba are used in the double-spike inversion. The ion beams at atomic masses 139 (La) and 140 (Ce) are monitored to assess potential isobaric inferences on ^{136}Ba and ^{138}Ba. During all analyses, no detectable signal was observed. Barium isotope ratios are typically reported in delta notation relative to the National Institute of Standards and Technology (NIST™) reference material SRM3104a:

$$\delta^{138/134}\text{Ba} = [(^{138/134}\text{Ba}_{\text{sample}})/(^{138/134}\text{Ba}_{\text{SRM3104a}}) - 1] \times 1000 \text{ in ‰}.$$

Result

To ascertain the precision and accuracy of the $\delta^{138/134}$Ba data with 10^{13} Ω Amplifier Technology using the Triton Plus TIMS, samples were also analyzed on the same instrument using the conventional 10^{11} Ω amplifier set-up (Table 1). Therein, the data with 10^{11} Ω and 10^{13} Ω amplifier configurations were measured with ^{134}Ba beam intensities of 400 mV and 10 mV, respectively. Note that to ensure a consistent reference frame, gain-corrected voltages are always reported relative to 10^{11} Ω amplifiers; the 10^{13} Ω amplifiers used a relative gain of ca. 0.01 and thus, for a given ion beam, the same intensity is reported for both amplifiers. The results of four well-studied standards (ICPUS-Ba, USTC-Ba, BHVO-2 and BCR-2) obtained using the 10^{13} Ω Amplifier Technology, given in Table 2 and shown on Figure 1, are in excellent agreement to

Table 1. Cup configuration for Ba isotopes with 10^{11} Ω and 10^{13} Ω Amplifier Technology on the Triton Plus TIMS. ^{139}La and ^{140}Ce are measured to monitor the potential isobaric interferences.

10^{11} Ω configuration									
Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass		134	135	136	137	138	139	140	
Metal		Ba	Ba	Ba	Ba	Ba	La	Ce	
Amp		10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{13}	10^{13}	
10^{13} Ω configuration									
Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass		134	135	136	137	138	139	140	
Metal		Ba	Ba	Ba	Ba	Ba	La	Ce	
Amp		10^{13}	10^{13}	10^{13}	10^{13}	10^{13}	10^{11}	10^{11}	

those using the 10^{11} Ω amplifier configuration with only slightly higher uncertainties (±0.06 ‰ vs ±0.02 ‰, external precision of 2 SD). The results are consistent with previously published reference values.

Ba isotope measurements were also conducted on two depleted peridotite rock standards (PCC-1 and DTS-1) with very low Ba abundances. For PCC-1 with Ba abundance of 0.63 μg g^{-1}, more than 100 mg sample powder is required to obtain sufficient Ba (~80 ng) for a complete analysis on the TIMS with conventional 10^{11} Ω amplifier set-up. For comparison, ~5 ng Ba is needed for isotopic analysis on the TIMS using the 10^{13} Ω Amplifier Technology, thus 10 mg sample powder is more than sufficient. The average $\delta^{138/134}$Ba value of PCC-1 obtained with the 10^{13} Ω Amplifier Technology, with much less sample consumption, is in agreement within uncertainty with that obtained with the 10^{11} Ω amplifiers (Table 2). Moreover, the application of the 10^{13} Ω Amplifier Technology makes it possible to obtain the $\delta^{138/134}$Ba value for samples with extremely low Ba abundance like DTS-1 (0.19 μg g^{-1}), as shown in Table 2 and Figure 1. This is very difficult for Ba isotope analysis with the conventional 10^{11} Ω amplifier set-up. All these results demonstrate that high-precision Ba isotope data could be obtained by TIMS using 10^{13} Ω Amplifier Technology, with much less sample consumption compared to that with 10^{11} Ω amplifiers.

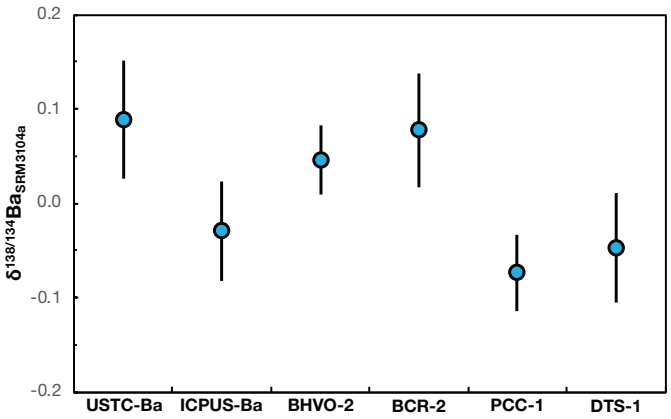

Figure 1. Mean $\delta^{138/134}$Ba of two pure solution standards (ICPUS-Ba and USTC-Ba) and four USGS reference rocks (BHVO-2, BCR-2, PCC-1 and DTS-1) for 10^{13} Ω amplifier configurations. NIST SRM3104a was used as the external standard ($\delta^{138/134}$Ba = 0.0). Error bars represent 2SD.

For direct comparison with analyses made on the 10^{13} Ω Amplifier Technology, Ba isotope measurements are conducted under 10^{11} Ω amplifier configurations with various ^{134}Ba beam intensities from the 400 mV to 10 mV, which is same as the typical ^{134}Ba beam intensity for analyses using the 10^{13} Ω Amplifier Technology. Given that all other parameters remained the same between the two different amplifier configurations, this permits a direct determination of the improvement in uncertainties arising from the lower noise of the 10^{13} Ω Amplifier Technology. The results of this test (Table 3 and Figure 2) show that for the 10^{11} Ω configuration, the data analyzed at lower intensities had predictably poorer reproducibility. Therein, ICPUS-Ba and USTC-Ba analyzed at ^{134}Ba beam intensity

Table 2. Summary of Ba isotope data for 10^{11} Ω and 10^{13} Ω amplifier configurations compared with reference values.

Sample	Configuration	$\delta^{138/134}$Ba (‰)	2SD	n	Ba concentration (μg g-1)
ICPUS-Ba	10^{13} Ω	-0.03	0.05	18	
	10^{11} Ω	-0.03	0.02	12	
	Wu et al. (2020)[2]	-0.03	0.04		
USTC-Ba	10^{13} Ω	0.09	0.06	16	
	10^{11} Ω	0.09	0.02	11	
	Wu et al. (2020)[2]	0.09	0.04		
BHVO-2	10^{13} Ω	0.05	0.04	7	130
	10^{11} Ω	0.04	0.02	5	
	Wu et al. (2020)[2]	0.04	0.03		
BCR-2	10^{13} Ω	0.08	0.06	7	683
	10^{11} Ω	0.07	0.02	7	
	Wu et al. (2020)[2]	0.07	0.04		
PCC-1	10^{13} Ω	-0.07	0.04	5	0.63
	10^{11} Ω	-0.05	0.00	2	
DTS-1	10^{13} Ω	-0.05	0.06	4	0.19

of 10 mV with 10^{11} Ω amplifiers give average $\delta^{138/134}$Ba values of 0.00 ± 0.69 ‰ (2SD, n = 3) and 0.09 ± 0.76 ‰ (2SD, n = 3), respectively. Analyses under the same beam intensity using the 10^{13} Ω Amplifier Technology show much better data, yielding average $\delta^{138/134}$Ba value of -0.03 ± 0.05 ‰ (2SD, n = 18) for ICPUS-Ba, and 0.09 ± 0.06 ‰ (2SD, n = 16) for USTC-Ba. These data show that the 10^{13} Ω Amplifier Technology leads to a significant improvement in the reproducibility for these measurements of small ion beams.

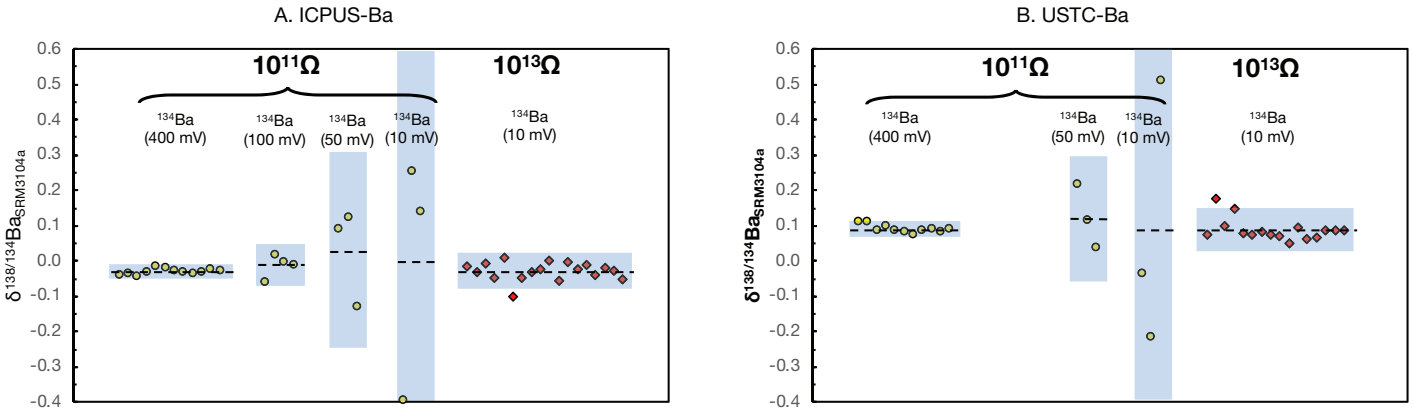

Figure 2. Barium isotope data acquired using the 10^{11} Ω vs 10^{13} Ω amplifier configurations for the pure solution standards (A) ICPUS-Ba and (B) USTC-Ba. The data with 10^{11} Ω amplifier configurations are measured under ^{134}Ba beam intensity from 10 mV to 400 mV. The data with 10^{13} Ω Amplifier Technology are measured under ^{134}Ba beam intensity 10 mV. To ensure a consistent reference frame, gain corrected voltages are always reported relative to 10^{11} Ω amplifiers; 10^{13} Ω amplifiers use a relative gain of ca. 0.01, and thus for a given ion beam, the same intensity will be reported for both amplifiers. NIST SRM3104a was used as the external standard ($\delta^{138/134}$Ba = 0.0). Dashed lines represent the average $\delta^{138/134}$Ba values under each setting. Shaded areas represent the 2SD of the analyses they enclose.

Table 3. Comparison of $\delta^{138/134}$Ba results of pure solution standards between 10^{11} Ω and 10^{13} Ω amplifier configurations. The data with 10^{11} Ω amplifier configurations are measured under ^{134}Ba beam intensity from 400 mV to 10 mV. The data with 10^{13} Ω Amplifier Technology are measured under ^{134}Ba beam intensity of 10 mV. To ensure a consistent reference frame, gain corrected voltages are always reported relative to 10^{11} Ω amplifiers; 10^{13} Ω amplifiers use a relative gain of ca. 0.01, and thus for a given ion beam, the same intensity will be reported for both amplifiers.

^{134}Ba beam intensity (mV)	ICPUS-Ba						USTC-Ba					
	10^{11} Ω configuration			10^{13} Ω configuration			10^{11} Ω configuration			10^{13} Ω configuration		
	$\delta^{138/134}$Ba (‰)	2SD	n	$\delta^{138/134}$Ba (‰)	2SD	n	$\delta^{138/134}$Ba (‰)	2SD	n	$\delta^{138/134}$Ba (‰)	2SD	n
400	-0.03	0.02	12				0.09	0.02	11			
100	-0.01	0.06	4									
50	0.03	0.28	3				0.12	0.18	3			
10	0.00	0.69	3	0.03	0.05	18	0.09	0.76	3	0.09	0.06	16

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Conclusion

We show that high precision Ba isotope measurement of small ion beam currents could be achieved with the application of the 10^{13} Ω Amplifier Technology on the Triton Plus TIMS. The required sample masses can be reduced by a factor of 12-14 and still achieve comparable measurement uncertainty. Therefore, the use of 10^{13} Ω Amplifier Technology may enable the analysis of samples that were hereto impractical, such as depleted mantle peridotites and other rare materials.

Acknowledgment

The authors wish to thank Peter Wieland, Yi-Jen Lai and John Creech for technical and analytical support in the Macquarie GeoAnalytical (MQGA) laboratories and Thermo Fisher Scientific™ and the DVCR for support of equipment and post-doctoral salaries in the Macquarie University—Thermo Scientific™ Isotope Development Laboratories.

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