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New Reduction Technique for Isobaric Interferences on Ba Using ICP-Mass Spectrometry

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A new technique for the removal of isobaric interferences on Ba has been developed for ICP-mass spectrometer. Mass spectrometric interferences on Ba by $^{138}La^+$, $^{136}Ce^+$, or $^{138}Ce^+$ isobaric signals were effectively eliminated by a selective production of oxide ions. The La$^+$ and Ce$^+$ ions could be quantitatively converted to oxide ions (LaO$^+$ and CeO$^+$) by the ICP ion source under the low-power operation. Production efficiency of oxide signals for La and Ce was remarkably enhanced, *i.e.*, >2,000,000 times the level obtained by the conventional ICP power (1.35 kW). Residual signal intensity of La$^+$ signal was almost the same level as the instrumental background. The overall contribution of isobaric ^{138}La and ^{138}Ce to ^{138}Ba signals were 0.02% and 0.1%, respectively, even with the presence of ×10,000 times higher concentration of La and Ce. The data obtained here demonstrate that the level of the isobaric interferences by ^{138}La, ^{136}Ce, and ^{138}Ce signals produced by the low-power ionisation was negligible within the analytical precision achieved in this study (∼1%). It should be noted that the analytical sensitivity for Ba obtained by the low-power ICP remains almost 85% of the level achieved by the conventional ICP power. This is very promising because the present technique can be applied to the laser ablation sampling technique which requires high sensitivity without chemical separation or purification procedures.

1. Introduction

Age of rock sample is one of the key information for the understanding of geological sequence of the Earth and the solar system. Earth scientists have been trying to understand the underlying order and inherent linkage of the events in the world based on the chronological description of the sample. Ages of the samples have been determined by means of the rate of erosion or sedimentation, fossils contained therein or nuclear decay of radioactive isotope. It is well recognised that isotopic chronometer based on radioactive decay of unstable nuclides, such as ^{87}Rb, ^{147}Sm, ^{238}U, or ^{235}U, can provide most accurate age data of the samples.[1, 2] Recent progress in analytical technique to measure small variation in isotopic composition with high sensitivity can enables us to determine precise chronological information. Atmospheric pressure inductively coupled plasmas (ICPs) are flame like electrical discharge that have revolutionised the practice of elemental and isotopic ratio analysis. The high temperatures available at atmospheric pressure in the plasmas make them very efficient excitation and ionisation sources. The ionisation efficiency to the singly charged state for most elements is approaching >80%,[3, 4] indicative of very attractive characteristics as an ion sources.[5]–[7] Many geologists are increasingly interested in processes in rocks that operate at the microscopic scale such as zoning or metamorphic recrystallisation. Because these processes have implications for the larger scale behavior of the Earth, new techniques for chemical and isotopic measurements at the μm scale need to be developed. Combination of laser ablation (LA) technique and ICP-MS has now become a fast and accurate method of *in situ* trace element and isotopic analysis.[8]–[15] In order to obtain accurate isotopic data, isobaric interferences onto the isotopes of interest must be removed. Chemical separation procedures such as chromatography or liquid–liquid distribution techniques have been widely used to separate the isobaric interferences from the analyte. However, in the case of laser ablation sample introduction technique, these conventional techniques can not be applied because sample aerosols produced by the laser ablation are directly introduced into the ICP. Recently, isobaric interference of ^{87}Rb onto ^{87}Sr was successfully minimised by means of collision or reaction cell technique.[16]–[19] However, in most cases, elemental sensitivity of the instrument can be lowered through this reaction process. Moreover, modification of the instrument is needed with the standard ICP-MS instruments.

La–Ba isotopic chronometer is based on radioactive decay of ^{138}La to ^{138}Ba with half-life of 1.1×10^{11} yrs. The La–Ba chronometer can provide precise chronological data for REE-bearing minerals or ores.[20, 21] In order to obtain accurate La-Ba age, precise isotopic ratio data on Ba are highly desired. However, even a small contribution of mass spectrometric interferences on ^{136}Ba and ^{138}Ba by ^{136}Ce, ^{138}Ce, and ^{138}La ionic signals can be a large source of analytical error (Fig. 1). To minimise the effect of isobaric interferences, prior to the isotopic analysis, Ba was chemically separated from La and Ce. Despite the obvious success in effective separation and high recovery achieved by the chemical separation procedure, this conventional technique can not be applied to the LA technique. In order to obtain *in-situ* La–Ba isotopic data using the LA technique, the isobaric interferences on Ba isotopes must be separated or removed within the mass spectrometer. In this study, I would like to show a new

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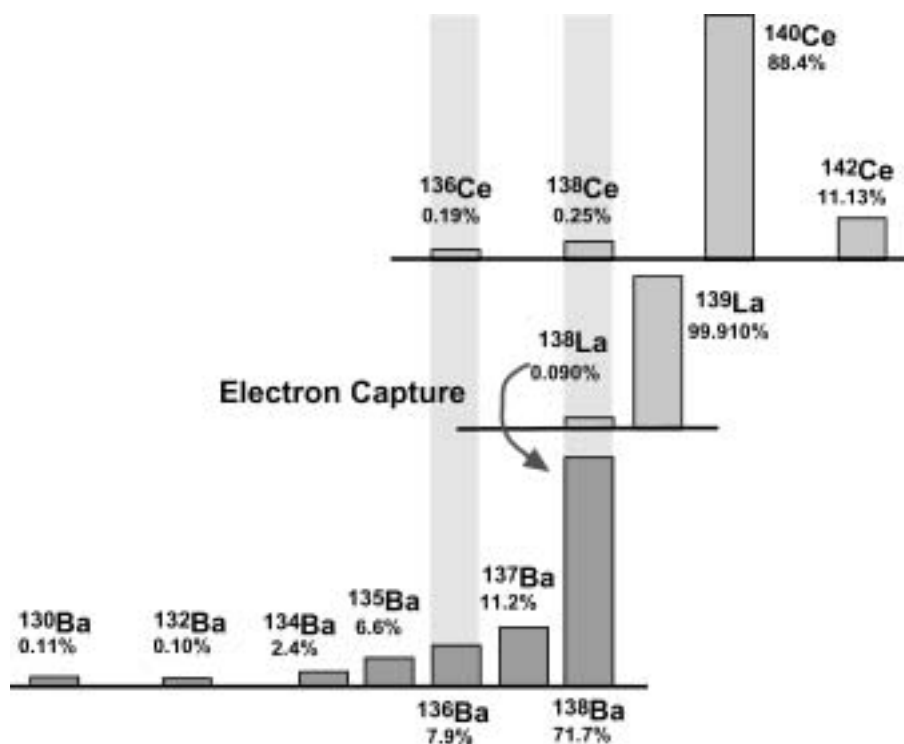
Fig. 1. Schematic diagram of isobaric interferences on Ba by La and Ce. The ^{136}Ba and ^{138}Ba signals were interfered by ^{138}La, ^{136}Ce, and ^{138}Ce isobaric signals. La–Ba isotopic chronometer is based on the small isotopic growth of ^{138}Ba due to radio-active decay of ^{138}La.

technique for reduction of isobaric interferences on Ba using a preferential conversion of La$^+$ and Ce$^+$ ions to LaO$^+$ and CeO$^+$ signals achieved by the low-power ICP operational condition.

The strength of ICP-MS lies with the ion source which achieves high ionisation efficiency for nearly all elements.[4] In order to take full advantage of the high ionisatin capability of the ICP, RF incident power of >1.2 kW was generally accepted as an ICP operation setting. Moreover, higher ICP operation power is very important to minimise the oxide (MO$^+$) production. The production of oxide has been evaluated by the MO$^+$/M$^+$ ratio. The MO$^+$/M$^+$ ratios of <0.05 can be achieved by the ICP ion source under the conventional power setting, whereas the ratio increased up to >0.1 when the lower ICP power (1,100 W) was applied.[22] Because of the lower elemental sensitivity of the instrument with higher oxide production (MO$^+$/M$^+$ ratio), the actual utility of the low-power ICP has been highly restricted. Despite these apparent drawbacks of the low ICP operation power, lower power (500 W) was applied to the ICP to enhance the oxide production aiming at removal of isobaric interferences on Ba.

2. Experimental

The ICP-mass spectrometer used in this study was a Thermo Electron (Winchester, UK) VG PlasmaQuad 2 Omega. This uses quadrupole mass spectrometer with $M/\Delta M=250$ (10% height) as a mass analyser. Conventional pneumatic nebuliser MicroMist (Glass Expansion, Melbourne, Australia) was used for solution introduction into the ICP. It is well recognised that secondary discharge between vacuum interface and the ICP becomes serious when low incident power was used.

The secondary discharge results in lowering the instrumental sensitivity. In this study, plasma shield technique was applied to minimise the formation of secondary discharge,[23] and no obvious discharge could be found even with RF incident power of 400 W. The pressure of analyser chamber (quadrupole housing) becomes high ($>10^{-4}$ Pa) when the lower ICP incident power (<400 W) was applied. This is mainly due to lowering of the gas temperature at the tip of the sampling orifice,[4] and this results in higher gas flux entering the vacuum chamber through the orifice. In this study, 500 W incident power was applied to test the low-power ICP operation because there was no significant increase in pressure of analyser housing.

Operational conditions of the ICPMS such as torch position, Ar gas flow rates, ion transfer lens biases or spray chamber temperature were tuned to maximise the signal intensity of ^{138}Ba. In the case of low-power ICP, optimum nebuliser gas flow rate were 0.75–0.8 L/min which was significantly lower than the values (0.95 L/min) required for the conventional ICP power (1.35 kW). This can be attributed to the poorer ionisation efficiency of the low-power ICP, and therefore the lower nebuliser gas flow rate avoids the further cooling of the plasma by the water load. Details of the instrument and the operational parameters used in this study are listed in Table 1. For comparison, operational settings used for conventional ICP operation were also listed in this table.

3. Results and Discussion

3.1 Production of oxide ions

It has been well recognised that oxide ions (MO$^+$) was enhanced when lower ICP power was applied.

Table 1.   ICP-MS Instrumentation and Operational Settings

1. ICP-mass spectrometer	
Instrument	: Thermo Electron VG PlasmaQuad 2 Omega
ICP incident power	: 1350 W (standard), 500 W (low-power operation)
Reflection	: <5 W
Vacuum interface	: S-option
Lens type	: CHICANE lens
Pressure (Pa)	
Expansion chamber	: 120
Intermediate chamber	: $<10^{-2}$
Analyzer chamber	: 2×10^{-4} (standard operation)
	6×10^{-4} (low-power operation)
2. Instrumental setting	
Nebuliser	: Glass Expansion MicroMist
Nebuliser gas flow rate	: 1.02 L/min (standard operation)
	0.75 L/min (low-power operation)
Solution uptake rate	: 1 mL/min (standard operation)
	0.8 mL/min (low-power operation)
Spray chamber	: Scott-type double path
Spray chamber temp.	: 4℃ (standard operation)
	12℃ (low-power operation)
Peristaltic pump	: not used
Sampling depth	: 20 mm above the load coil
Sensitivity for Ba	: 400 Mcps/$\mu g\ g^{-1}$ (standard operation)
	$\sim$360 Mcps/$\mu g\ g^{-1}$ (low-power operation)
Background	: <5 cps (at $m/z=101.5$)
3. Data acquisition	
Monitoring signals	: ^{134}Ba, ^{135}Ba, ^{136}(Ba+Ce), ^{137}Ba, ^{138}(Ba+La+Ce), ^{139}La, ^{140}Ce
Data acquisition time	: 15 s
Scan mode	: peak jump (3 points per isotopes; M and M$\pm$0.025 amu)
Dwell time	: 10 ms/point
Settled time	: 10 ms/isotope
Correction for mass discrimination	: not made

Note:
Standard operation: Standard power setting for ICP operation (1,350 W)
Low-power operation: low-power ICP operation (500 W)

Lichte *et al.*[22] reported that production ratio defined as MO^+/M^+ ratio increased up to 10% with the ICP incident power of 1,100 W.   More importantly, they pointed out that oxide production ratio is basically correlated with chemical affinity with oxygen. In this study, further lower power was used to enhance the production efficiency of oxide ions, aiming at separation of mass spectrometric interferences by shifting the interferences to heavier masses as oxide molecular ions.

Dependence of production ratio of oxide ions (MO^+/M^+) upon ICP incident power was examined. In this study, BaO^+/Ba^+ and LaO^+/La^+ ratios were monitored by introducing a mixed solution of Ba and La (1 ng/g each), and the resulting MO^+/M^+ ratios were plotted against the ICP incident power (Fig. 2). Uncertainties of the BaO^+/Ba^+ and LaO^+/La^+ ratios denote 2σ (standard deviation) calculated from 5 times repeated analysis. The BaO^+/Ba^+ and LaO^+/La^+ ratios obtained on the conventional ICP power (1,350 W) was 0.00052 ± 0.00008 and 0.0029 ± 0.0003, respectively. The level of oxide production increased dramatically when the ICP incident power was lower than 1,000 W, and the resulting BaO^+/Ba^+ and LaO^+/La^+ ratios found on the present low-power ICP (500 W) condition were 0.0912 ± 0.0047 and 6301 ± 205, respectively. The enhancement factors for oxide production defined by

$(MO^+/M^+)_{500\ W}/(MO^+/M^+)_{1350\ W}$ were 200 for Ba and $>2,000,000$ for La, suggesting that La^+ was preferentially converted to LaO^+ ions under the low-power ionisation condition.   Fig. 3 represents the resulting mass spectrum for Ba–La mass region obtained by the low-power ICP operation. It should be noted that resid-
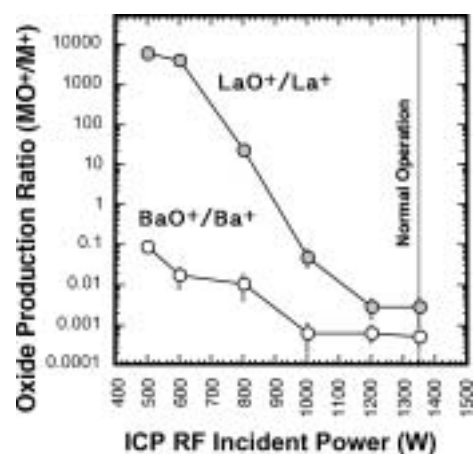

Fig. 2.   Level of oxide production (BaO^+/Ba^+ and LaO^+/La^+) as a function of ICP incident power. The resulting LaO^+/La^+ ratio increased $>2,000,000$ times when the low power (500 W) was applied.

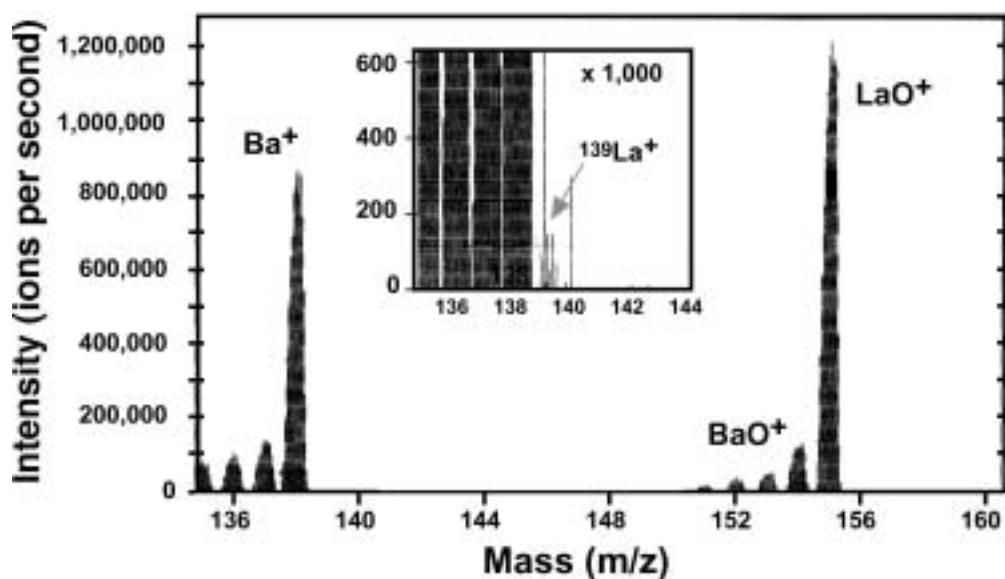Fig. 3. Mass spectrum obtained by the low-power ICP operation (incident power 500 W). The La$^+$ ion was quantitatively converted to LaO$^+$ ion, and residual signal intensity for ^{139}La was almost identical to the background count rate.

ual signal intensity at $m/z=139$ would be originated from the hydride ion (^{138}BaH$^+$) since production yield for hydride ions could also be increased with the low ICP power. However, this is not the case because the signal intensity at $m/z=139$ was independent upon the signal intensity of ^{138}Ba$^+$. Although it is not clear that residual signal at $m/z=139$ was originated either from ^{139}La$^+$ or other polyatomic ions, it is feasible that residual signal intensity at $m/z=139$ could reflect the upper limit of the residual signal intensity of ^{139}La$^+$ ions. The resulting signal intensity at $m/z=139$ was <10 ions/s which was almost same level as the background count of the instrument, and therefore, the most of the La$^+$ ion was quantitatively converted to LaO$^+$ ions under the low-power ICP operation. In strike contrast, only 10–15% fraction of Ba was converted to BaO ions even with the low-power ICP condition, and the main Ba ion produced by the ICP was still Ba$^+$. This indicates that contribution of isobaric interference on ^{138}Ba by ^{138}La could be remarkably reduced by the low-power ICP

achieved in this study. It should be noted that loss of elemental sensitivity for Ba under the low-power ICP conditions was only 15% level, and therefore, sensitive detection of Ba was still possible. The result obtained here reveals that contribution of isobaric interference on ^{138}Ba could be minimised by the preferential conversion of ^{138}La$^+$ to ^{154}LaO$^+$ signals. This is identical to that ion-molecule reaction chemistry through the collision or reaction cell techniques.[16)–19)]

In the case of isotopic analysis of Ba, not only ^{138}La but also ^{136}Ce and ^{138}Ce ions can become a mass spectrometric interferences on Ba. In order to validate the effectiveness of the conversion technique achieved by the low-power ICP, isotopic ratios of Ba for chemical reagents were measured.

3.2 Isotopic analysis of Ba

In this study, ^{134}Ba/^{137}Ba, ^{135}Ba/^{137}Ba, ^{136}Ba/^{137}Ba, and ^{138}Ba/^{137}Ba ratios for mixtures of Ba, La, and Ce from high purity chemical reagents have been meas-

Table 2. ^{134}Ba/^{137}Ba, ^{135}Ba/^{137}Ba, ^{136}Ba/^{137}Ba and ^{138}Ba/^{137}Ba Isotopic Ratios Obtained by ICP-MS with Different ICP Operation Power
No correction for the mass discrimination effect was made.

	ICP Power (Watts)	Ba (ng/g)	Ln*1 (ng/g)	^{134}Ba/^{137}Ba*2	^{135}Ba/^{137}Ba*2	^{136}Ba/^{137}Ba*2	^{138}Ba/^{137}Ba*2
Hot plasma	1,350	5	0	0.1955 ±0.0073	0.5805 ±0.0088	0.7014 ±0.0055	6.511 ±0.061
Cool plasma	500	5	0	0.2002 ±0.0050	0.5779 ±0.0065	0.7007 ±0.0063	6.455 ±0.064
		5	5	0.1922 ±0.0063	0.5842 ±0.0080	0.7017 ±0.0041	6.511 ±0.051
		5	5,000	0.1968 ±0.0055	0.5801 ±0.0089	0.7001 ±0.0052	6.501 ±0.058
		5	50,000	0.1955 ±0.0075	0.5822 ±0.0091	0.7008 ±0.0066	6.498 ±0.078

*1 Lanthanoid elements (La–Lu).
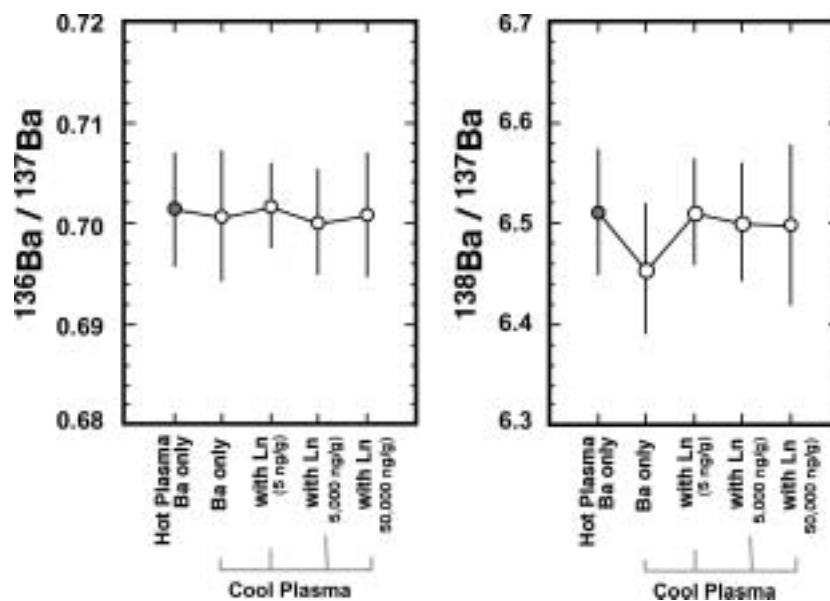*2 Errors are 2-sigma standard deviation calculated by 15 repeated analysis.

Fig. 4. Isotopic ratios of Ba ($^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$) obtained by the standard ICP operation and the low-power operation. There were no significant difference in resulting $^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$ ratios even with the presence of La and Ce (Ln/Ba=1–10,000).

ured in order to test the separation efficiency of isobaric interferences more rigorously. Four analytical solutions were made: first solution was 5 ng/g Ba solution simply diluted from the Ba standard solution. Second solution was a 5 ng/g Ba solution containing same concentrations of La and Ce (5 ng/g each). The third and fourth solutions was 5 ng/g Ba containing ×1,000 times and ×10,000 times higher concentrations of La and Ce, respectively. For further comparison, Ba isotopic ratios measurement was made under the standard ICP operation (1.35 kW). Data acquisition parameters such as signal integration area, integration time, mass-scan rate or number of scans were summarised in Table 1. The resulting $^{134}Ba/^{137}Ba$, $^{135}Ba/^{137}Ba$, $^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$ ratios were listed in Table 2. Among them, data for $^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$ ratios could vary due to possible isobaric interferences by La and Ce, and therefore, resulting $^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$ ratios were plotted for clarification (Fig. 4). All the isotopic ratio data including $^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$ ratios show excellent agreement to the data obtained by the pure Ba analytical solution within the analytical uncertainties (1%, 2SD). Moreover, no significant difference was found on the resulting isotopic ratios obtained by the low-power ICP operation from the data for pure-Ba solution obtained with the standard-power ICP operation. Contributions of ^{138}La and ^{138}Ce signals onto ^{138}Ba isotope were <0.02% and <0.1%, respectively, even with the presence of ×10,000 times higher concentrations of La and Ce, and therefore, level of isobaric interferences on Ba due to La and Ce were negligible within the precision of the measurement achieved in this study.

Allanite ((Ca, Ce, Y, La, Th)$_2$(AlFe)$_3$Si$_3$O$_{12}$(OH)) and monazite ((Ce, La, Y, Th)PO$_4$) are the typical REE (rare earth elements)-bearing minerals. Since La/Ba abundance ratio for the allanite or monazite is generally very high, age of these minerals can be well constrained by the La–Ba isotopic chronometer. In most cases, the La/Ba ratio for alanites or monazites is generally 50–5,000,[20)–21)] and this is significantly lower than the nominal La/Ba ratio simulated in this study (×10,000). This suggests that precise isotopic ratios of Ba can be made on bulk samples without chemical separation of Ba from La and Ce.

No correction of the mass discrimination effect was made for all the isotopic data for Ba ($^{134}Ba/^{137}Ba$, $^{135}Ba/^{137}Ba$, $^{136}Ba/^{137}Ba$, and $^{138}Ba/^{137}Ba$ ratios) given in Table 2 and Fig. 4. This indicates that accuracy and precision of the isotopic ratio measurements could be further improved when the mass discrimination effect is corrected internally. Moreover, further precise and accurate isotopic ratio measurements can be achieved by the combination of the present low-power ionisation technique and a multiple collector-ICP-mass spectrometer.

4. Conclusion

Isobaric interferences on Ba by La and Ce isotopes were effectively minimised by the preferential production of LaO$^+$ and CeO$^+$ molecular ions under the low-power ICP operation (500 W). Since the signal intensity of residual La$^+$ ions were almost the same level as the instrumental background (<10 ions/s), La$^+$ ions were quantitatively converted to LaO$^+$ ions under the low-power ICP operation. Resulting LaO$^+$/La$^+$ ratio observed on the low-power ICP operation was >2,000,000 times higher than the ratio obtained by the conventional operation with ICP power of 1.35 kW. In contrast, the main Ba signal observed on the low-power ICP was still Ba$^+$ ion. Instrumental sensitivity for Ba was still >300 MHz/μg g^{-1}, which was almost 85% level of that achieved by the standard ICP power. This is very important for the isotopic analysis of Ba with high sensitivity. No significant changes in $^{136}Ba/^{137}Ba$ and $^{138}Ba/^{137}Ba$ ratios was found even with the presence of ×10,000 times higher concentration of La and Ce (50,000 ng/g each), indicative of effective

removal of isobaric interferences by La and Ce isotopes. The removal of isobaric interferences by means of the selective conversion achieved with the low-power ICP can be applied for the isotopic analyses of various elements without any serious modification of the ICP-MS instruments.

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