

## NOTE

# Determination of $^9\text{Be}$ in geological standard samples, JA-2 and JB-2, and of $^9\text{Be}$ and $^{10}\text{Be}$ in a basaltic rock sample for evaluation of uncertainty involved in $^{10}\text{Be}/^9\text{Be}$ ratio measurements

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We determined the concentrations of  $^9\text{Be}$  in JB-2 and JA-2 geological standard samples using an inductively coupled plasma mass spectrometer (ICP-MS). We determined  $^9\text{Be}$  abundance in standard samples of JA-2 and JB-2 as  $2.26 \pm 0.10$  and  $0.241 \pm 0.010$  ppm, respectively, after comparing and selecting  $^9\text{Be}$  concentration data obtained by the internal standard method, the standard addition method and the column separation method. In the course of comparison, we identified a problem in the internal standard method, which is usually used for abundance analyses using an ICP-MS.

Repeated analyses of a basalt lava gave a standard deviation of  $^{10}\text{Be}$  abundance of 9% ( $1\sigma$ ,  $n = 5$ ). From the results, we estimated the uncertainty of  $^{10}\text{Be}/^9\text{Be}$  ratio as 10% ( $1\sigma$ ), considering a law of propagation of errors.

Keywords:  $^{10}\text{Be}$ ,  $^9\text{Be}$ , ICP-MS, AMS, uncertainty

## INTRODUCTION

Beryllium is a mildly incompatible element whose abundance is approximately 0.1–1 ppm in volcanic rocks (Ryan, 2002). Beryllium has a short-lived radioactive nuclide  $^{10}\text{Be}$  (with a half life of  $1.5 \times 10^6$  year), and is produced by spallation of nitrogen and oxygen in the air; this is washed away from the air by precipitation and subsequently transported to the sea. The  $^{10}\text{Be}$  in the seawater is scavenged and concentrated in marine sediments. Because  $^{10}\text{Be}$  does not exist in the Earth's interior, its presence in volcanic rocks derived from island-arc volcanism is direct evidence of the contribution of subducted sediment to arc-derived magmas; its abundance is a useful tracer to understand the behavior of slab-derived fluid in island-arc systems (Morris *et al.*, 2002). However,  $^{10}\text{Be}$  abundance can be modified by magmatic processes such as partial melting and fractional crystallization. The  $^{10}\text{Be}/^9\text{Be}$  ratio is therefore a better tracer, which can cancel out the influences of magmatic processes.

In the 1980s, the  $^9\text{Be}$  abundance was measured using either inductively coupled plasma (ICP) emission spectrometric methods (Morris and Tera, 1989) or the

direct-current generated plasma (DCP) emission spectrometric method (Ryan and Langmuir, 1988). After the invention of the ICP-MS,  $^9\text{Be}$  abundance was routinely analyzed using that instrument (Ryan, 2002).  $^{10}\text{Be}$  measurements require accelerator mass spectrometry. It is known that surface contamination of meteoric water increases  $^{10}\text{Be}$  in volcanic rocks. Although Shimaoka *et al.* (2004) proposed an acid leaching method to remove secondary contaminations of  $^{10}\text{Be}$  from meteoric water, the heterogeneity in  $^{10}\text{Be}$  distribution remaining after the acid leaching process has not been evaluated. The accuracy and precision of  $^9\text{Be}$  abundance and  $^{10}\text{Be}/^9\text{Be}$  ratio measurements, however, have not been fully investigated.

In this study we will report  $^9\text{Be}$  abundances of standard rocks of JA-2, andesite from Goshikidai sanukitoid, and JB-2, tholeiitic basalt from O-shima volcano, distributed by the Geological Survey of Japan, and discuss errors entailed depending on the choice of calibration or pretreatment methods. We will report the uncertainty of  $^{10}\text{Be}/^9\text{Be}$  measurements as a typical case by the repeated  $^{10}\text{Be}$  analyses of a basaltic rock from Niijima Island with an age of 2 kyr.

## METHODS

### $^9\text{Be}$ analysis

First, 30–50 mg samples were weighted in Teflon vi-

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als and digested using HF, HNO<sub>3</sub>, and HClO<sub>4</sub>. The Be abundance in sample solutions was analyzed using the following methods: (i) an internal standard method using indium without chemical separation, (ii) a standard addition method without chemical separation, (iii) a chemical separation method coupled with an In internal standard correction.

For the methods of internal standard and standard addition, the digested sample solutions were evaporated to dryness and subsequently re-dissolved in 2 wt.% HNO<sub>3</sub>. The solutions were diluted with 2 wt.% HNO<sub>3</sub> so that the dilution factor is around two thousand against the weight of the rock sample. The digested sample solutions were divided into four aliquots and a Be standard solution was added to three of them for analyses using the method of standard addition so that the added Be concentration in each became, respectively 1 ppb, 3 ppb, and 5 ppb. Then, In was added to a solution without Be addition. The data related to sample solutions without Be addition were shared for both the method of standard addition and the method of an internal standard. Abundance of Be was calculated for the method of standard addition as follows. The amount of Be added to a solution and a raw count of signal at  $m/z = 9$  were plotted respectively on the  $X$  and  $Y$  axes. Error in the  $X$  value was assigned as 0.1% and that in the  $Y$  value was assigned from the sum of stability of signals of standard solutions analyzed before and after the sample solution and counting statistics. A best fit line was regressed using the “IsoPlot” program (Ludwig, 1991). The abundance in the initial solution was calculated from the  $X$ -axis intercept. The uncertainty in Be abundance was estimated from the error associated with the  $X$ -axis intercept.

In the internal standard method, a count of signals at  $m/z = 9$  was compared with those of standard solutions before and after a sample solution, after the raw count at  $m/z = 9$  was corrected by an In internal standard. The uncertainty of each analysis was estimated from the sum of stability of signals of standard solutions analyzed before and after the sample solution and counting statistics.

For the method of column separation analyses of Be, we used 4.5-ml quartz columns filled with 4 ml of (200–400 mesh, H<sup>+</sup>-form, AG 50W-X8; Bio-Rad Laboratories Inc.). After the digested samples were dissolved in 0.1 M HCl, the sample solutions were loaded on the columns. The loaded samples were washed using 40 ml of 0.1 M HCl to remove the nonmetallic materials such as organic matter; subsequently these columns were washed with 12 ml of 1M HCl. After the wash, Be was recovered with 20 ml of 1M HCl. After the Be fractions were dried and re-dissolved in 2% HNO<sub>3</sub>, an indium internal standard was added. Abundance measurements were performed as in the internal standard methods. Uncertainty of each analysis was estimated as in the internal standard method. The

total Be blank for all three methods was less than 100 pg and blank contribution was negligible.

Be abundances in an artificial solution described later, JA-2 and a basalt sample from Niijima were analyzed using a Quadrupole-ICP-MS (PQ-3; VG Isotech) at the Earthquake Research Institute, The University of Tokyo. That in JB-2 was analyzed using an ICP-MS (7500a; Yokogawa Agilent) at the Faculty of Science, Gakushuin University.

#### <sup>10</sup>Be analysis

For investigation of the uncertainty of <sup>10</sup>Be abundance analysis, we used a sample of basaltic lava of Wakago from Niijima Island. The sample was treated with acid leaching following the method described by Shimaoka *et al.* (2004) to remove secondary contaminations of <sup>10</sup>Be from meteoric water. Rock powder finer than 50 mesh was subjected to ultrasonic cleaning for 2–4 h with 1 M HCl.

We modified a <sup>10</sup>Be purification procedure described in Shimaoka (1999). Three to five grams of dried samples after leaching were weighed in a Teflon beaker and the Be reagent, free of <sup>10</sup>Be (<sup>10</sup>Be/<sup>9</sup>Be ratio <1 × 10<sup>-14</sup>) of 150–200 μg was added as Be carrier. The samples were digested using HF, HNO<sub>3</sub>, and HClO<sub>4</sub> and dried. After the sample was re-dissolved in 1 M HCl, Be was separated and extracted from other major component elements of the rocks using the following multi-step procedures. First, the sample solution was Fe-coprecipitated with aqueous ammonia at a pH of greater than 8, and the supernatant was discarded. Then, sodium hydroxide tablets were added to the precipitate, and Al was removed by dissolving Al(OH)<sub>3</sub> from the precipitate at a pH of 13. The procedure described above was repeated twice. Next, the precipitate was dissolved in conc. HCl and di-isopropyl ether was added. The Fe in the solution is extracted in the organic phase. The aqueous phase from which Al and Fe were removed was dried and re-dissolved with 1 M HCl. Then, Be in the solution was extracted as the acetyl-acetone complex in CCl<sub>4</sub> under the presence of EDTA at a pH of 6.0–6.8. After Be was back-extracted from CCl<sub>4</sub> with 7 M HNO<sub>3</sub> it was dried and re-dissolved. Following this, Be was purified using cation-exchange chromatography with 1 M HCl. Aqueous ammonia was added to the purified Be and washed ultrasonically to remove boron. Finally, Be(OH)<sub>2</sub> was fumed at 900°C to form BeO powder. The ratio of <sup>10</sup>Be in a sample relative to the doped <sup>9</sup>Be was analyzed using the system of accelerator mass spectrometry (AMS) at MALT (Micro Analysis Laboratory, Tandem accelerator) at the Graduate School of Engineering, The University of Tokyo (Matsuzaki *et al.*, 2007). The <sup>10</sup>Be abundance in the initial rock powder was calculated by multiplying the amount of Be carrier added to the sample powder. The usage of

Table 1. Results of  $^9\text{Be}$  abundance analyses on JB-2, JA-2 and a basalt from Niijima with the three methods

Run	(A) Internal standard without separation	(B) Column separation method	(C) Standard addition method
JB-2			
1	$0.224 \pm 0.009$	$0.244 \pm 0.008$	$0.247 \pm 0.005$
2	$0.223 \pm 0.008$	$0.244 \pm 0.008$	$0.245 \pm 0.002$
3	$0.220 \pm 0.007$	$0.243 \pm 0.008$	$0.218 \pm 0.013$
4	$0.196 \pm 0.007$	$0.233 \pm 0.013$	$0.242 \pm 0.002$
5	$0.214 \pm 0.009$	$0.248 \pm 0.013$	$0.246 \pm 0.009$
6	$0.209 \pm 0.016$	$0.241 \pm 0.013$	$0.242 \pm 0.019$
Mean	$0.211 \pm 0.012$	$0.242 \pm 0.005$	$0.240 \pm 0.011$
Yoshida <i>et al.</i> (1992)	0.22		
JA-2			
1	$2.06 \pm 0.03$	$2.34 \pm 0.09$	$2.22 \pm 0.04$
2	$1.97 \pm 0.07$	$2.24 \pm 0.08$	$2.30 \pm 0.13$
3	$1.96 \pm 0.02$	$2.26 \pm 0.08$	$2.18 \pm 0.19$
4	$2.12 \pm 0.02$	$2.31 \pm 0.09$	$2.21 \pm 0.11$
Mean	$2.03 \pm 0.08$	$2.29 \pm 0.04$	$2.23 \pm 0.05$
Yoshida <i>et al.</i> (1992)	2.27		
Basalt from Niijima			
1	$0.345 \pm 0.009$	$0.405 \pm 0.030$	$0.398 \pm 0.010$
2	$0.329 \pm 0.010$	$0.407 \pm 0.031$	$0.397 \pm 0.010$
Mean	$0.337 \pm 0.011$	$0.406 \pm 0.002$	$0.397 \pm 0.001$

Error associated with each result was calculated as described in text.  
The error associated with average is  $1\sigma$ .

the Be carrier enables quantitative determination of  $^{10}\text{Be}$  even when the recovery was not quantitative. Recovery of Be was usually 60–80% in this study.

## RESULTS AND DISCUSSION

### Comparison of analytical methods on $^9\text{Be}$ abundance measurements

We compared the results of  $^9\text{Be}$  abundance measurements on JA-2 and JB-2 obtained using the three methods. Table 1 shows average  $^9\text{Be}$  abundances and standard deviations ( $1\sigma$ ) of standard rocks. Yoshida *et al.* (1992) reported Be abundances of the standard rocks using ICP-MS with the indium internal standard method without chemical separation. Their results are also shown for comparison. The results of our experiments show that the average of the standard addition method and that of the column separation method gave consistent values. In contrast, the result of the internal standard method gave an average that was approximately 10% lower than those of the other methods. Therefore, our results suggested that the Be abundances in the standard rocks obtained using the internal standard method were underestimated by 10%. To confirm the problem with the internal standard method, we repeated the whole set of measurements using an arti-

ficial rock solution with a known concentration of Be and matrix elements without Si. The internal standard method produced an underestimation by as much as 13%, whereas the other two methods gave the correct value.

We now report  $^9\text{Be}$  abundance in the standard rocks JA-2 and JB-2 as  $2.26 \pm 0.10$  and  $0.241 \pm 0.010$  ppm, respectively, neglecting data by the internal standard method. We estimated the repeatability of the Be abundance analyses results which were obtained using methods of standard addition and column separation from the data as about 4–5% ( $1\sigma$ ).

### Uncertainty of $^{10}\text{Be}$ and Be isotopic ratio analysis

We analyzed  $^{10}\text{Be}/^9\text{Be}$  ratio of a basalt sample from Niijima. To evaluate uncertainty, we repeated  $^{10}\text{Be}$  analyses of the sample five-times over ten months. For the five analyses, three different aliquots of rock powder were used. Each aliquot was treated with acid leaching separately. In-run uncertainty (about 4–5%) was estimated from the sum of statistical error of  $^{10}\text{Be}$  counts of each sample (4–5%) and the stability of  $^{10}\text{Be}/^9\text{Be}$  ratio of a standard material (KN standard (Matsuzaki *et al.*, 2007)) with the MALT (1% in each day of analysis). Average and standard deviation of the repeated measurements were  $(9.3 \pm 0.8) \times 10^5$  atoms  $\text{g}^{-1}$  ( $1\sigma$ ). We estimated uncer-

tainty ( $1\sigma$ ) as about 9% from the results.

The  $^9\text{Be}$  abundance of the sample was determined as 0.397 ppm by the method of standard addition as shown in Table 1. The  $^{10}\text{Be}/^9\text{Be}$  ratio of the sample is calculated as  $3.5 \times 10^{-11}$ . For  $^9\text{Be}$  analysis, we determined the uncertainty of 4–5% ( $1\sigma$ ), as described in the previous section. Combining two values, the uncertainty of Be isotopic ratio analysis in the volcanic rock was estimated as approximately 10% ( $1\sigma$ ) considering a law of propagation of errors. This uncertainty includes heterogeneous distribution of  $^{10}\text{Be}$  in the rocks. When we treat a rock sample with age of a few thousand years, which might have been influenced by surface processes, we might have to admit this level of uncertainty. Our results also demonstrate that the use of  $^9\text{Be}$  abundance obtained using the internal standard method would generate an overestimation of  $^{10}\text{Be}/^9\text{Be}$  by more than 10%.

Several references describe the precision of  $^{10}\text{Be}/^9\text{Be}$  ratio measurements. Morris and Tera (1989) and Gill *et al.* (1993) reported reproducibility of  $^{10}\text{Be}$  concentrations of 15% ( $1\sigma$ ) based on replicate analyses of low concentration standards with a Be concentration comparable to the volcanic samples. Gill *et al.* (1993) measured  $^9\text{Be}$  concentrations with an ICP spectroscopy and reported uncertainty as 5–10% for samples with Be of  $>0.3$  ppm, and 20% for samples with Be of  $<0.3$  ppm. They reported reproducibility of  $^{10}\text{Be}/^9\text{Be}$  ratio as less than 22%. George *et al.* (2003) reported that reproducibility on  $^{10}\text{Be}$  measurements are typically 5% ( $1\sigma$ ) at concentrations  $>1 \times 10^6$  atoms  $\text{g}^{-1}$  without detailed descriptions. Our uncertainty as 9% ( $1\sigma$ ) is larger than that reported in George *et al.* (2003). Our uncertainty, however, may include heterogeneous distribution of  $^{10}\text{Be}$  and it is not clear if it can be compared with that reported in George *et al.* (2003) directly.

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