

Whole rock multiple trace element analyses using fused glass bead by laser ablation-ICP-MS

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Abstract: A simple analytical method for whole rock trace elements covering a mass range of ^{45}Sc – ^{238}U using laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with a high-dilution ratio (sample:flux = 1:10) glass bead for X-ray fluorescence spectrometry (XRF) has been established. The reproducibility (shown as relative standard deviation of signal intensities) of analytical results of the Geological Survey of Japan (GSJ) geochemical reference materials was mostly < 30%, except for elements of very low contents. A comparison with the compilation values from literature values and the analytical results of this study show < 30% difference (DIF) for 194 out of 225 elements analyzed from JB-2, JA-1, JR-1, JGb-1 and JG-1a. Results of > 30% DIF were elements of very low contents in most cases. Analytical results of JB-1b obtained in this study were concordant with the literature values. The quantitative values obtained in this study can be used for petrological and geochemical discussions of whole rock trace elements.

Keywords: Trace elements, Laser Ablation ICP-MS (LA-ICP-MS), GSJ geochemical reference materials, glass bead, GSJ-Lab

1. Introduction

Whole rock chemical composition of geological rock samples is one of the most fundamental and important data for earth science studies. Recent advances in analytical methods and a rapid growth in the use of analytical instruments have enabled easy and precise analysis of whole rock chemical compositions. For major elements, an X-ray fluorescence spectrometry (XRF) is widely used. For trace element analyses, XRF, instrumental neutron activation analysis (INAA), atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and ICP-mass spectrometry (ICP-MS) are available for simultaneous multiple elemental analysis. Among such techniques, both XRF and ICP-MS are widely used in many institutions.

In XRF analysis, low-dilution ratios (1:5 and 1:2) of glass beads (e.g., Kimura and Yamada, 1996; Takahashi and Shuto, 1997; Tanaka and Orihashi, 1997) or pressed powder pellets (e.g., Hattori and Shibata, 1969; Terashima, 1977; Sugisaki *et al.*, 1981; Ogasawara, 1987) have generally been used for trace

element analyses. However, acceptable analytical precision of measurements could not be achieved for geochemical studies because some target samples containing low concentrations for trace elements show low signal intensities. Thus, in general, quantitative analyses of such samples by XRF suffers from limitations. At the same time, XRF analysis also offers an advantage, as it enables the measurement of both major and trace elements using the same instrument. Furthermore, in XRF a single glass bead can be used to measure both the major and trace elements with low-dilution ratios.

Compared with XRF, ICP-MS enables the simultaneous measurement of a large number of multi-elements in ppb- and ppt- orders. Although solution method requiring a few thousandfold dilution of nitric acid following acid digestion of rock samples is the common method used for the whole rock analysis using ICP-MS, the laser ablation (LA) method using glass beads or rock powder pellets has also been recently adopted (e.g., Morrison *et al.*, 1995; Becker and Dietze, 1999; Günther *et al.*, 2001; Eggins, 2003; Orihashi and Hirata, 2003; Kurosawa *et al.*, 2006). Advantages and disadvantages of the solution and

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LA methods have been described by Yamasaki *et al.* (2015). In brief, the following are the advantages of the LA method: relative ease of rock analysis, including acid digestion-resistant minerals; reduction of the effect of interference elements due to oxide production from the acid solvent; absence of unavoidable errors on solution making; and no need to closely monitor the contamination owing to direct ablation of samples. Because of these advantages, the LA method can be used to obtain stable data of constant quality without expertise for instrumental operation when the laser ablation settings and instrumental analytical conditions for samples are optimized (e.g., Kimura *et al.*, 1996; Satoh *et al.*, 2001). In particular, since the sample preparation of the LA method is essentially the same as that of XRF, the LA method is a very facile method compared to the solution method, which generally requires highly complicated and time-consuming chemical decomposition processes (often using a strong acid for digestion). In addition, whole rock major and trace elements, including rare-earth elements (REEs), can be measured using a single glass bead with high-dilution ratio for major element analysis.

The shared research facilities of the Geological Survey of Japan, AIST (GSJ-Lab, AIST), is used as a cooperative managing analytical laboratory for common basic analyses in geological studies (e.g., Ogasawara, 2013a,b). For analytical instruments, it is essential that a simple and clear analytical protocol and a hardware system are established for users with various specialties, and such users should understand the precision, accuracy, and limitation of instruments being used. In this paper, we report an analytical method and the precision of whole rock multiple trace element analysis for the mass range ^{45}Sc – ^{238}U for geological samples using a high-dilution ratio (sample:flux = 1:10) glass bead with LA-ICP-MS in GSJ-Lab, AIST. This study aimed to establish a multipurpose and the simplest protocol to analyze as many elements as possible that can be used for geological discussions.

2. Experimental

2.1 Instrumentation and operating conditions

Instruments and operating conditions used in this study are shown in Table 1. The LA-ICP-MS system at the GSJ Lab consisted of a New Wave Research NWR213 LA system coupled to an Agilent 7700 x quadrupole ICP-MS. The LA system consisted of a Nd:YAG laser that generated an output wavelength of 213 nm and a maximum pulse energy (fluence) of $> 30 \text{ J cm}^{-2}$. Detailed information about the instrument is given in Yamasaki *et al.* (2015). The large sample chamber allowed nine glass beads, including the calibration reference material, to be loaded and analyzed in a single uninterrupted session.

Table 1 LA-ICP-MS operating parameters.

Laser	New Wave NWR213 Nd:YAG Laser
Wavelength	213 nm
Maximum pulse energy	$> 30 \text{ J cm}^{-2}$ (Fluence)
Repetition rate	10 Hz
Spot size	100 μm
Raster speed	55 $\mu\text{m sec}^{-1}$
ICP-MS	Agilent 7700x
Forward power	1,550 W
Nebuliser gas flow	1.03 L min^{-1} (Ar)
Plasma gas flow	15 L min^{-1}
Cones	Ni sample cone Ni skimmer cone
Scanning mode	peak jump
Detector mode	pulse-counting/analog-counting automatic switching mode

Flow rates of the He carrier gas were chosen as 0.5 L min^{-1} following the results of Yamasaki *et al.* (2015). Prior to analysis, the LA-ICP-MS system was calibrated using NIST613 reference glass for high sensitivity over a large mass range and low production rate of oxides. The production rate of oxide in this study was monitored using ^{248}ThO ($^{232}\text{Th}^{16}\text{O}$)/ ^{232}Th and was maintained below 0.5 %. Other potentially interfering oxides were assumed to be negligible compared with the relative ease of production of Th oxide (e.g., Leichte *et al.*, 1987; Orihashi and Hirata, 2003; Kon *et al.*, 2011).

Laser settings were used under the following conditions of stable and the highest intensity from glass bead samples: a spot size of 100 μm and a laser emission repetition rate of 10 Hz. Raster ablation (55 $\mu\text{m/s}$) was adopted, which provides a stable signal intensity profile and minimizes elemental fractionation, compared to when spot ablation was used. The laser energy was fixed at 60 % (fluence *ca.* 20 J cm^{-2}), unless otherwise specified.

2.2 Analytical elements, standard, and data reduction

The same analytical elements were used as those in the full elemental set of Yamasaki *et al.* (2015), and 100 sweeps of 45 elements from ^{45}Sc to ^{238}U with dwell times shown in Table 2 were replicated three times in the peak hopping and spectrum modes. The acquisition time on ICP-MS was *ca.* 40 s, and the total time for one analysis was *ca.* 85 s, including 10 s for both the shuttered laser warm-up and laser stabilization. After completing the ablation, signal intensities returned to background levels after approximately 25 s (Yamasaki *et al.*, 2015). All signal intensities were corrected with respect to the background signal obtained from the measurement of a gas blank for 40 s prior to initiating the calibration standard and unknown measurements. The internal standard ^{42}Ca was used for all the measurements in

Table 2 Analytical elements, mass number and dwell time per element.

Element	Mass number	Dwell Time (sec.)
Ca	42	0.05
Sc	45	0.3
Ti	47	0.3
V	51	0.3
Cr	53	0.3
Mn	55	0.1
Co	59	0.25
Ni	60	0.3
Cu	63	0.25
Zn	66	0.25
Ga	69	0.25
Ge	72	0.1
As	75	0.25
Rb	85	0.25
Sr	88	0.25
Y	89	0.25
Zr	90	0.25
Nb	93	0.25
Mo	95	0.25
Cd	111	0.4
Sn	118	0.25
Sb	121	0.25
Cs	133	0.1
Ba	137	0.4
La	139	0.25
Ce	140	0.25
Pr	141	0.25
Nd	146	0.25
Sm	147	0.25
Eu	153	0.25
Gd	157	0.3
Tb	159	0.25
Dy	163	0.4
Ho	165	0.25
Er	166	0.4
Tm	169	0.3
Yb	172	0.3
Lu	175	0.3
Hf	178	0.3
Ta	181	0.3
W	182	0.3
Tl	205	0.3
Pb	208	0.3
Bi	209	0.3
Th	232	0.3
U	238	0.3

this study. A pulse-counting/analog automatic switching mode was adopted, and as a result, all measurements were carried out using the pulse-counting mode. It is noted that the counting mode would be automatically switched to the analog mode in the case of unknown analyses, depending on the concentration of an element. In such case, a careful optimization of the pulse-counting/analog factor (P/A factor) would be needed (Kon *et al.*, 2011).

The GSJ geochemical reference materials were used as the external calibration standard materials. The use of a natural reference material offers following several advantages over synthetic external calibration standard. 1) The matrix effect can be corrected by using reference materials that have a

similar matrix to that of the samples. 2) A simple, equivalent, and reproducible preparation procedure for both samples and standards can be realized (Eggs *et al.*, 1997). It is suggested that the compilation values of the GSJ geochemical reference materials (e.g., Imai *et al.*, 1995) potentially included low-quality data due to the statistical calculation of the data from many institutions (e.g., Goto and Tatsumi, 1991). Thus, using the compilation value is not the best choice for a standard value for a calibration line method such as sensitive trace element analysis by ICP-MS. In this study, we chose values of external calibration standard ensuring that the analytical data were obtained by an externally quantitative method such as standard solution or isotope dilution method, or based on such methods, and the data were obtained from a single institution. Using such values enables an objective evaluation of reference materials.

Kon *et al.* (2011) reported an analytical method using a glass bead of the GSJ reference materials with a sample to flux ratio of 1:10 using a multi-point calibration line method. However, single-point calibration line method is rather common in LA-ICP-MS with, for example, NIST reference materials, and the use of the GSJ reference materials as an external calibration standard has already been established in solution method (Awaji *et al.*, 2006). If the accuracy could be made sufficient for use in geochemical and petrological discussions, then the single-point calibration line method offers great advantages in terms of the feasibility of the evaluation of the GSJ reference materials prepared by users for monitoring analytical quality; most importantly, it is a very simple method that fits the GSJ-Lab's purpose. However, calibration line method using a glass bead inevitably suffers from an effect of elements contained in the flux. Thus, we adopted a two-point calibration method, in order to compensate the effect of flux. Detailed evaluation of calibration line method and the effects of the elements in the flux have been discussed later.

Based on above considerations, the GSJ geochemical reference materials JP-1 and JB-3 were used as the external calibration standard materials. The use of the JB-3 standard enables a simple simultaneous multi-elemental analysis, because it contains most elements in high concentration. In this study, we used the concentration data for JP-1 and JB-3 as follows: for Ca, Sc, V, Mn, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Cs, Ba, lanthanides, Pb, Th, and U: Makishima and Nakamura (2006); for Zr, Nb, Hf, and Ta: Makishima *et al.* (1999); for Mo, Sb, and W: Makishima and Nakamura (1999); for Cd, In, Tl, and Bi: Makishima *et al.* (2011); for Ti: Makishima and Nakamura (2000); for Cr: Makishima *et al.* (2002); and for Ge, As, and Sn: Imai *et al.* (1995). Although we tentatively used values from Imai *et al.* (1995) for Ge, As, and Sn due to lack of appropriate values, it should be noted that these data do not have the same quality or

meaning as the external calibration values compared to other values from literatures by Makishima and co-workers. Instead of JB-3, JB-2 and JA-1 can also be used as calibration standard materials.

The glass beads were prepared by essentially the same method used by Yamasaki (2014). The flux ($\text{Li}_2\text{B}_4\text{O}_7$: MERK Co. Ltd., Spectromelt A10, #10783) was ignited at 700°C for 2 h prior to weighing, and cooled in a desiccator. Reference materials in the powder form were weighed in a ceramic crucible and ignited in a muffle furnace at 900°C for 2 h. The glass beads were made by mixing 0.5 g of reference material powder with 5.0 g of lithium tetraborate flux (sample:flux = 1:10). The mixture was put into a platinum crucible (95 % Pt-5% Au alloy) and two drops of aqueous lithium bromide solution ($\text{LiBr}\cdot\text{H}_2\text{O}$: H_2O = 1:1) were added as an exfoliation agent. Fusing and agitation were carried out with an automated high frequency bead sampler (Tokyo Kagaku Co. Ltd. TK-4500); 120 s pre-fusion ($\sim 1,070^\circ\text{C}$), 180 s fusion ($\sim 1,070^\circ\text{C}$), and 180 s agitation.

Data reduction was conducted using MassHunter Workstation software installed with the Agilent 7700 x. Calibration lines were calculated with the calibration standard, and a series of data reduction, which involved subtraction of the gas blank intensity and calculation of the concentration after normalization using the internal standard element, was performed with the MassHunter software. The signal count rate, concentration, and relative standard deviation (RSD) of the signal intensity for each element were reported as standard form. The concentration, signal intensity rate, and type of detectors for each element and each scan could also be confirmed and exported.

3. Results and discussion

3.1 Effect of elements contained in the flux and exfoliation agent

Since flux-mixed glass beads were used for analyses, elements contained in the flux and exfoliation agent (collectively referred as the “flux blank” hereafter) were included in the analytical results. In order to compensate this effect, several theoretically possible methods can be considered: 1) a one-point calibration line method using a flux blank as the origin (original point), 2) subtracting the signal intensities of a flux blank (including gas blank intensity) from all the calibration standards and unknown analytical samples, and 3) a two (or more)-point calibration line method using calibration standard glass beads made by using the same procedures with unknown analytical samples (e.g., Kon *et al.*, 2011). To examine these methods, signal intensities of the gas blank and flux blank (including gas blank) are shown in Table 3.

Net signal intensities of the flux blank have been shown as the

number that remains after the subtraction of gas blank intensities from gas + flux blank intensities (Net Flux Blk in Table 3). These numbers (in counts per second, CPS) were several dozen to more than a hundred times the gas blank intensities. In addition, the contribution ratio of net flux blank intensities to the JB-3 calibration standard (Flux Blk/JB-3 in Table 3) were $> 20\%$ for Cr, Ni, Zn, As, Mo, Cd, Sn, Sb, W, Tl, Pb, Bi, Th and U, although many elements were within the RSD of the signal intensity of JB-3 (Table 3).

Because gas blank intensities are subtracted from both calibration standard and unknown analytical samples, counts of the net flux blank intensities (Net Flux Blk shown in Table 3) were included in the corresponding signal intensities. It should be noted that the effective meaning of the Net Flux Blk in the standard and unknown samples depend on the concentration of the internal standard element (^{42}Ca) and elements in each sample. In other words, the effective meaning of the Net Flux Blk varied with concentration of analytical elements in samples. Therefore, it is impossible to subtract uniform value as concentration from samples. In addition, the concentration of the flux blank intensities was always almost zero after normalizing the internal standard element (^{42}Ca), irrespective of the signal intensities. The reason is as follows: (1) Concentration of various analytical elements was calculated from ratio of signal intensities between objective element and internal standard element, using content of internal standard element. (2) Since Ca content of flux blank is zero, concentration of analytical elements in the flux blank was also zero. Therefore, flux blank is not able to use as the origin as above first method. The second method involving the subtraction of flux blank signal intensities from the calibration standard and unknown analytical samples requires analysis of the flux blank as a background for every sample. This frequent analysis of the flux blank causes a high background due to contamination of the instrument and would cause long-term damage of the instrument. In addition, in cases of samples with a smaller signal/background (= flux blank) ratio, signal intensities are frequently smaller than the background intensities due to elevation of background-level. Therefore, it is concluded that the multi-point calibration method is the appropriate calibration method for this study.

Kon *et al.* (2011) made regression lines of 33 trace elements using glass beads of 12 GSJ geochemical reference materials, and the results show good linear correlation between the signal intensity and concentration, except for low-concentration Ga and As. The dispersion in low-concentration Ga and As was probably due to the reliability of their reference values rather than effect of flux blank, because those values in Imai *et al.* (1995) have been classified as “preferable values”. Therefore, we adopted the simplest, two-point calibration line method in this study. JP-1 was intended as a lower-concentration calibration standard

Table 3 Counts (CPS) for gas blank, flux blank and calibration standard (JB-3).

Mass Number	Element	Gas Blk	Gas + Flux Blk	Net Flux Blk	JB-3		Flux Blk/JB-3
		Count (CPS)	Count (CPS)	Count (CPS)	Count (CPS)	RSD (%)	Count ratio (%)
45	Sc	762.24	1586.74	824.50	24744.77	5.5	3.2
47	Ti	53.33	301.11	247.78	315525.25	3.3	0.1
51	V	63.33	7628.35	7565.02	270355.59	0.8	2.7
53	Cr	114.44	1373.39	1258.95	4658.39	5.5	21.3
55	Mn	4987.39	22457.81	17470.41	1180060.04	20.0	1.5
59	Co	13.33	1358.77	1345.43	23347.24	0.8	5.4
60	Ni	328.89	3218.08	2889.19	6265.55	1.0	31.6
63	Cu	138.67	9637.32	9498.65	57850.70	10.7	14.1
66	Zn	93.33	2915.81	2822.48	5484.85	4.6	34.0
69	Ga	20.00	492.02	472.02	10966.09	4.9	4.1
72	Ge	156.67	220.00	63.33	610.01	10.2	9.4
75	As	40.00	110.67	70.67	132.00	13.9	34.9
85	Rb	497.34	1305.42	808.07	9031.68	2.0	8.2
88	Sr	1.33	3657.87	3656.53	353678.09	2.6	1.0
89	Y	0.00	252.01	252.01	24621.40	1.2	1.0
90	Zr	2.67	461.34	458.68	48196.10	1.7	0.9
93	Nb	1.33	201.34	200.01	1982.78	7.1	9.2
95	Mo	2.67	157.34	154.67	182.67	17.7	45.9
111	Cd	5.83	26.67	20.83	16.67	31.2	55.6
118	Sn	104.00	2034.83	1930.83	405.34	9.7	82.6
121	Sb	18.67	522.68	504.02	62.67	20.5	88.9
133	Cs	2836.92	3567.06	730.14	5150.79	1.9	12.4
137	Ba	1.67	746.75	745.09	31066.31	3.4	2.3
139	La	0.00	682.68	682.68	9722.85	4.2	6.6
140	Ce	1.33	1260.17	1258.84	24162.82	4.0	5.0
141	Pr	1.33	114.67	113.34	4215.20	10.6	2.6
146	Nd	0.00	37.33	37.33	3591.06	3.7	1.0
147	Sm	2.67	17.33	14.67	826.69	8.0	1.7
153	Eu	0.00	52.00	52.00	920.03	7.2	5.3
157	Gd	0.00	6.67	6.67	1050.03	10.8	0.6
159	Tb	0.00	129.34	129.34	1032.03	8.9	11.1
163	Dy	0.83	22.50	21.67	1498.40	0.8	1.4
165	Ho	0.00	116.00	116.00	1289.38	8.7	8.3
166	Er	0.00	30.00	30.00	1201.71	3.5	2.4
169	Tm	0.00	75.56	75.56	514.45	7.7	12.8
172	Yb	1.11	31.11	30.00	754.47	8.9	3.8
175	Lu	1.11	106.67	105.56	456.67	9.5	18.8
178	Hf	1.11	16.67	15.56	1133.38	9.5	1.4
181	Ta	0.00	37.78	37.78	194.45	6.9	16.3
182	W	4.44	453.35	448.90	561.12	4.3	44.4
205	Tl	3.33	48.89	45.55	12.22	68.7	78.8
208	Pb	110.00	3277.13	3167.13	3331.47	5.1	48.7
209	Bi	13.33	188.89	175.56	35.55	44.3	83.2
232	Th	0.00	211221.98	211221.98	1390.07	12.3	99.3
238	U	3.33	130.01	126.67	496.68	23.9	20.3
42	Ca (ISTD)	22954.58	23682.14	727.56	323284.83	4.98	0.2

Blk, RSD, CPS and ISTD denote blank, relative standard deviation, counts per second, and internal standard, respectively.

except for Ni and Co, and the concentrations of JP-1 were nearly equal to the flux blank-level in most of the elements. The concentrations of Ni and Co of JP-1 correspond to the higher concentrations of the calibration lines. In the case of two-point calibration line method using JP-1 as the lower-content calibration standard, sometimes signal intensity of an unknown analytical sample with lower concentrations becomes lower than that of the background. The major cause of this phenomenon was the propagation of errors, depending on the analytical precision of JP-1. If the effect of the flux blank was negligible, calibration lines without the low concentration calibration standard (JP-1) result in the reduction of such error propagation. For example,

the contribution ratio of the flux blank to the signal intensity of JB-3 (including flux blank) is lower than the RSD of the signal intensity for some elements (Table 3). In these cases, the effect of the signal intensity of the flux blank is virtually negligible or indistinguishable from the errors of the signal counting of a one-point calibration of JB-3. Therefore, in cases where the use of the two-point calibration method caused low concentration/signal intensity, the one-point calibration method for elements with a smaller contribution of the flux blank could be adopted.

3.2 Sensitivity and detection limits

Analytical results, sensitivity, and lower limits of detection

(DL) of JB-2, JA-1, JR-1, JGb-1, and JG-1a obtained by five replicate analyses using JP-1 and JB-3 as external calibration standard are shown in Table 4. The sensitivity and DL were the average values calculated in each run following the method of Longerich *et al.* (1996).

Only Tl for JB-2 was lower than the values of DL, but Tl in the other reference materials were higher than DL. On the other hand, the amount of Tl in JG-1a was not determined due to a small signal/background ratio. A lower concentration and corresponding lower signal intensities in individual samples would be the main cause for the results under the DL or no detection. As emphasized in Longerich *et al.* (1996), it is necessary that the sensitivity and DL should be calculated sample by sample, and thus we have not specified the absolute values of sensitivity and DL for this method and instrument.

3.3 Analytical precisions and comparison to compilation values

As described above, results of five times replicate analyses of JB-2, JA-1, JR-1, JGb-1, and JG-1a using JP-1 and JB-3 as the external calibration standard are shown in Table 4. Analyses of JR-1 were carried out using 70% of the laser energy (fluence $\sim 35 \text{ J cm}^{-2}$), which gave stable high-signal intensity. Averaged values of replicate analyses, difference (absolute values, DIF, and percentages of absolute values to quantitative values, DIF%) between the analytical results and the compilation values from Imai *et al.* (1995), standard deviation (SD), and RSD of the replicate analyses are also shown. The results for the calibration blank measured before each five replicate analyses are shown as a typical background count because the background drifts during the replicate analyses. Reproducibility as precision and DIF % are also shown in Fig. 1 and summarized in Table 5.

Analytical precision was evaluated by reproducibility of five times replicate analyses of GSJ geochemical reference materials. Reproducibility shown by RSD were mostly $< 30\%$, except for Cd, Sn, Ta, Tl and Bi in JB-2; Tl and Bi in JA-1; Cr, Ni and Cd in JR-1; Ge, Mo, Cd, Sb, Cs, Bi and U in JGb-1; Bi in JG-1a (Table 4 and Table 5A and Fig.1). The amount of Tl in JG-1a was not determined. Elements with $> 30\%$ RSD for all samples are not observed; thus, it is regarded that the RSD essentially depends on the concentration and/or signal intensity of the sample.

A comparison with the compilation values from Imai *et al.* (1995) and the analytical results of this study were shown as DIFs. Using the compilation values by Imai *et al.* (1995) enables the comparison of the quality of the analytical results with that of an instrument in other institutions. Results of DIFs are summarized in Table 5B. DIFs were $< 30\%$ for 194 out of 225 elements and $> 30\%$ for 31 elements (Table 4 and Table 5B and Fig. 1). Elements with DIF $> 40\%$ in more than two samples

were as follows: Ni in JA-1 and JR-1; Cu and Cd, in JR-1 and JG-1a; Sb in JA-1 and JG-1a; W in JB-2, JA-1, and JR-1; Tl in JA-1, JR-1 and JGb-1; and Bi in JB-2, JR-1 and JG-1a (Table 4). For many of these values, however, the compilation values were less reliable because they were reported as the “preferable values” in Imai *et al.* (1995). Thus, these data have not been discussed here. As a result, elements with DIF $> 40\%$ in more than two samples were only Cu in JR-1 and JG-1a (Table 4). Since precisions of both analytical results were acceptable, cause of this difference is unclear. One of the possibilities is difference in values of calibration standards and compilation values. Contents of Cu in JP-1 and JB-3 were 4.25 ppm and 179 ppm respectively in Makishima and Nakamura (2006), instead of 6.72 ppm and 194 ppm in Imai *et al.* (1995). This difference in Cu content, particularly for JP-1, could be result in difference between analytical results and compilation values within the range of 3 to 6 ppm.

In summary, elements with concentrations of DIF $< 30\%$ could be used as quantitative results for geochemical and petrological discussions. The precision and DIFs were at the same level as other instruments/institutions (e.g., Orihashi and Hirata, 2003; Shindo *et al.*, 2009; Kon *et al.*, 2011; Nakano *et al.*, 2012). In the case of unknown analyses, the reliability of quantitative values could be evaluated from the RSD in signal count rates and quantitative values, and estimated DL.

3.4 Application

Quantitative analytical results, sensitivity, and DL of five replicate analyses of JB-1b using this method are shown in Table 4. The DL and sensitivity were calculated according to the widely used method reported by Longerich *et al.* (1996). It is assumed that the users of XRF in the GSJ-Lab used JB-1b as a quality-monitor sample; such a sample could be used in LA-ICP-MS analyses for the same purpose. Thus, this result could be used for comparing the analytical results of JB-1b glass beads prepared by each user. Note, however, the quantitative values of some elements were under the DL, and the reliability of the quantitative results for some elements with very low concentrations, even values higher than the DL, requires careful evaluation, as mentioned above.

The multiple trace element pattern normalized by N-MORB (Sun and McDonough, 1989) is shown in Fig. 2. The pattern calculated from the values of Kon *et al.* (2011) is also shown for comparison. Although analytical errors are shown in Fig. 2, all errors were within the symbols except for Cs. The result of this study agrees well with the quantitative values of Kon *et al.* (2011), and the quantitative values of this method are of acceptable quality for discussion on geochemical and petrological studies using multi-element patterns.

Table 4 Replicate analyses (N=5) of GSJ geochemical reference materials and comparison with reference values.

Element	JB-2										JA-1									
	B.G. (cps)	Av. ($\mu\text{g g}^{-1}$)	R.V. ($\mu\text{g g}^{-1}$)	DIF ($\mu\text{g g}^{-1}$)	DIF% (%)	S.D. (1s) ($\mu\text{g g}^{-1}$)	RSD (%)	Sensitivity (cps/ $\mu\text{g g}^{-1}$)	DL ($\mu\text{g g}^{-1}$)	Av. ($\mu\text{g g}^{-1}$)	R.V. ($\mu\text{g g}^{-1}$)	DIF ($\mu\text{g g}^{-1}$)	DIF% (%)	S.D. (1s) ($\mu\text{g g}^{-1}$)	RSD (%)	Sensitivity (cps/ $\mu\text{g g}^{-1}$)	DL ($\mu\text{g g}^{-1}$)			
Sc	475.6	53.5	0.4	0.8	0.8	1.3	2.3	804	0.0011	29.4	28.5	0.9	3.2	0.8	2.9	887	0.0010			
Ti	433	7091	7097	6	0.1	98	1.4	33	0.00264	5031	5132	102	2.0	62	1.2	37	0.00174			
V	16.7	577	575	2	0.4	12	2.1	761	0.00009	105	105	0	0.1	3	2.4	876	0.00012			
Cr	67.8	18.2	28.1	9.9	35.2	1.1	5.9	112	0.00173	8.7	7.83	0.9	11.6	0.6	7.1	64	0.00710			
Mn	1360.1	1727	1679	48	2.9	142	7.3	941	0.00014	1244	1224	20	1.6	34	2.7	1056	0.00014			
Co	5.3	36.8	38.0	1.2	3.0	0.8	2.1	499	0.00015	11.0	12.3	1.3	10.5	0.7	6.8	561	0.00033			
Ni	183.3	16.40	16.6	0.20	1.2	1.27	7.7	112	0.00150	5.54	3.49	2.05	58.6	0.26	4.6	123	0.00240			
Cu	108.0	206	225	19	8.6	33	16.3	264	0.00061	41	43	2	5.6	3	8.3	477	0.00051			
Zn	57.3	112.5	108	4.5	4.2	3.0	2.6	48	0.00234	95.8	90.9	4.9	5.4	3.2	3.3	39	0.00334			
Ga	10.7	17.6	17	0.6	3.5	0.4	2.2	531	0.00022	18.2	16.7	1.5	9.2	0.8	4.6	617	0.00027			
Ge	200.0	0.99	1.35	0.36	26.9	0.50	28.5	323	0.00330	1.10	1.33	0.23	17.2	0.08	7.5	331	0.00175			
As	16.0	2.32	2.87	0.55	19.1	0.43	11.2	67	0.01043	2.34	2.78	0.44	16.0	0.15	6.6	64	0.00831			
Rb	56.0	6.24	7.37	1.13	15.3	0.16	2.5	515	0.00029	10.86	12.3	1.44	11.7	0.52	4.8	581	0.00016			
Sr	0.0	185	178	7	3.8	2	1.2	830	0.00010	262	263	1	0.2	3	1.3	746	0.00012			
Y	0.0	20.9	24.9	4.0	16.1	0.5	2.3	865	0.00011	25.5	30.6	5.1	16.5	0.8	3.3	1208	0.00008			
Zr	1.3	45.3	51.2	5.9	11.5	0.9	2.0	426	0.00021	80.2	88.3	8.1	9.2	2.9	3.7	593	0.00019			
Nb	2.7	0.63	1.58	0.95	60.1	0.15	23.0	823	0.00103	1.25	1.85	0.60	32.3	0.15	11.9	896	0.00041			
Mo	2.7	1.06	1.08	0.02	1.4	0.10	9.3	123	0.00443	1.78	1.59	0.19	11.8	0.08	4.6	193	0.00195			
Cd	10.0	0.12	0.14	0.02	17.4	0.09	48.5	44	0.04476	0.11	0.11	0.00	2.0	0.01	12.9	70	0.03462			
Sn	110.7	0.61	0.95	0.34	36.2	2.10	68.7	443	0.00089	0.82	1.16	0.34	29.5	0.24	29.3	389	0.00108			
Sb	28.0	0.247	0.25	0.003	1.1	0.047	19.0	537	0.00268	0.124	0.22	0.096	43.7	0.018	14.2	817	0.00111			
Cs	506.7	0.858	0.85	0.008	0.9	0.315	22.3	846	0.00067	0.743	0.62	0.123	19.9	0.117	15.8	892	0.00095			
Ba	0.0	221	222	1	0.3	4	2.0	114	0.00062	311	311	0	0.1	6	2.0	131	0.00097			
La	4.0	2.19	2.35	0.16	6.7	0.10	4.5	909	0.00020	4.85	5.24	0.39	7.5	0.15	3.1	1188	0.00020			
Ce	1.3	6.4	6.76	0.4	5.6	0.2	3.4	831	0.00009	13.4	13.3	0.1	0.5	0.3	2.4	1117	0.00009			
Pr	1.3	1.11	1.01	0.10	10.3	0.08	6.8	951	0.00020	2.06	1.71	0.35	20.3	0.08	3.7	1070	0.00022			
Nd	1.3	6.5	6.63	0.1	1.9	0.4	6.1	159	0.00127	11.4	10.9	0.5	4.3	0.6	5.2	215	0.00074			
Sm	4.0	2.29	2.31	0.02	0.9	0.21	9.4	138	0.00351	3.67	3.52	0.15	4.2	0.20	5.3	147	0.00240			
Eu	5.3	0.8	0.86	0.0	1.9	0.0	4.0	495	0.00062	1.1	1.2	0.1	9.9	0.1	5.7	708	0.00051			
Gd	1.1	3.27	3.28	0.01	0.3	0.21	6.5	167	0.00222	4.42	4.36	0.06	1.4	0.19	4.2	146	0.00211			
Tb	0.0	0.600	0.6	0.000	0.1	0.017	3.2	1105	0.00019	0.775	0.75	0.025	3.3	0.025	3.3	1230	0.00018			
Dy	1.7	3.96	3.73	0.23	6.2	0.09	2.0	274	0.00054	4.62	4.55	0.07	1.5	0.20	4.4	249	0.00068			
Ho	0.0	0.84	0.75	0.09	11.9	0.02	2.9	889	0.00024	1.00	0.95	0.05	5.5	0.06	6.4	962	0.00027			
Er	2.5	2.72	2.6	0.12	4.8	0.12	4.6	288	0.00075	2.96	3.04	0.08	2.8	0.12	4.0	342	0.00066			
Tm	0.0	0.39	0.41	0.02	5.3	0.03	8.1	859	0.00043	0.45	0.47	0.02	3.9	0.04	8.3	1217	0.00026			
Yb	1.1	2.68	2.62	0.06	2.1	0.10	3.7	192	0.00132	3.07	3.03	0.04	1.3	0.14	4.6	268	0.00088			
Lu	2.2	0.396	0.4	0.004	1.0	0.019	5.0	1023	0.00024	0.450	0.47	0.020	4.4	0.021	4.6	1205	0.00025			
Hf	3.3	1.24	1.49	0.25	16.6	0.14	11.8	372	0.00116	2.29	2.42	0.13	5.2	0.21	9.4	392	0.00091			
Ta	1.1	0.071	0.13	0.059	45.6	0.027	37.6	843	0.00106	0.114	0.13	0.016	12.6	0.011	9.4	1021	0.00062			
W	1.1	0.807	0.26	0.547	210.4	0.181	4.4	1875	0.00007	0.740	0.34	0.400	117.5	0.068	9.2	345	0.00197			
Tl	4.4	0.028	0.042	0.014	32.5	0.216	76.2	118	0.12471	0.201	0.13	0.071	55.0	0.088	43.7	26	0.12484			
Pb	127.8	5.52	5.36	0.16	2.9	0.41	7.5	402	0.00059	6.25	6.55	0.30	4.6	0.42	6.7	444	0.00048			
Bi	5.6	0.319	0.033	0.286	866.4	0.143	44.9	151	0.00523	0.117	0.091	0.026	28.0	0.202	173.6	511	0.00738			
Th	2.2	0.29	0.35	0.06	18.4	0.03	10.4	607	0.00062	0.75	0.82	0.07	8.5	0.06	7.7	939	0.00049			
U	1.1	0.17	0.18	0.01	7.7	0.01	3.9	709	0.00137	0.35	0.34	0.01	1.9	0.03	7.4	845	0.00040			

B.G.: typical background, n.d.: not determined, RV: reference value of Imai *et al.* (1995), AV: averaged value of analytical result, DIF: difference from reference value, DIF%: percentage of DIF against RV, SD: standard deviation of analytical values, RSD: relative standard deviation of analytical values, DL: lower limit of detection. *Values shown by *italic* are below the lower limits of detection.

Table 4 Continued.

Element	JR-1						JGb-1									
	Av. ($\mu\text{g g}^{-1}$)	R.V. ($\mu\text{g g}^{-1}$)	DIF ($\mu\text{g g}^{-1}$)	DIF% (%)	S.D. (1s) ($\mu\text{g g}^{-1}$)	RSD (%)	Sensitivity (cps/ $\mu\text{g g}^{-1}$)	DL ($\mu\text{g g}^{-1}$)	Av. ($\mu\text{g g}^{-1}$)	R.V. ($\mu\text{g g}^{-1}$)	DIF ($\mu\text{g g}^{-1}$)	DIF% (%)	S.D. (1s) ($\mu\text{g g}^{-1}$)	RSD (%)	Sensitivity (cps/ $\mu\text{g g}^{-1}$)	DL ($\mu\text{g g}^{-1}$)
Sc	5.5	5.1	0.4	8.8	0.1	2.5	1693	0.00010	36.2	35.8	0.4	1.2	1.0	2.6	574	0.00018
Ti	618	669	51	7.6	11	1.8	116	0.00075	9641	9667	27	0.3	246	2.6	33	0.00319
V	6	7	1	12.0	0	2.4	2680	0.00004	649	635	14	2.2	15	2.3	597	0.00015
Cr	9.4	2.8	6.6	232.7	3.7	39.0	177	0.00405	53.9	57.8	3.9	6.7	0.9	1.7	63	0.00234
Mn	846	777	68	8.8	21	2.5	1919	0.00013	1469	1475	6	0.4	84	5.7	711	0.00043
Co	1.0	0.8	0.2	19.3	0.2	24.5	1549	0.00027	57.4	60.1	2.7	4.5	1.1	1.9	540	0.00015
Ni	3.53	1.67	1.86	111.2	1.24	124.1	1302	0.00286	27.06	25.4	1.66	6.5	1.02	3.8	114	0.00174
Cu	6	3	3	121.6	2	26.9	1976	0.00016	63	85.7	23	26.6	9	14.1	331	0.00070
Zn	35.1	30.6	4.5	14.6	1.4	3.9	150	0.00058	108.1	109.0	0.9	0.8	6.7	6.2	39	0.00388
Ga	19.0	16.1	2.9	18.1	0.1	0.7	1613	0.00007	18.2	17.9	0.3	1.5	0.7	3.8	440	0.00028
Ge	2.59	1.88	0.71	37.8	0.14	5.4	479	0.00102	1.13	1.01	0.12	12.1	0.53	47.1	175	0.01497
As	17.30	16.30	1.00	6.1	0.69	4.0	133	0.00161	1.02	1.09	0.07	6.8	0.26	25.7	57	0.01074
Rb	269.04	257.00	12.04	4.7	2.66	1.0	1809	0.00003	6.29	6.87	0.58	8.4	1.46	23.3	535	0.00111
Sr	28	29	1	4.8	1	3.2	2099	0.00010	334	327	7	2.2	11	3.3	717	0.00010
Y	35.7	45.1	9.4	20.9	0.8	2.3	3370	0.00002	9.2	10.4	1.2	11.7	0.3	3.6	863	0.00013
Zr	87.7	99.9	12.2	12.2	1.7	1.9	1638	0.00004	29.1	32.8	3.7	11.2	1.4	4.7	429	0.00020
Nb	13.25	15.20	1.95	12.8	0.22	1.7	2436	0.00009	2.15	3.34	1.19	35.6	0.09	4.3	748	0.00030
Mo	2.89	3.25	0.36	11.2	0.11	3.9	492	0.00037	0.51	0.59	0.08	13.2	0.31	60.2	125	0.00810
Cd	0.04	0.03	0.01	47.7	0.02	50.5	253	0.01208	0.07	0.087	0.02	20.6	0.12	35.1	80	0.04765
Sn	2.92	2.86	0.06	1.9	0.17	5.8	1025	0.00009	0.56	0.48	0.08	16.8	0.12	20.6	403	0.00139
Sb	1.060	1.190	0.130	10.9	0.129	12.2	1243	0.00021	0.093	0.085	0.008	9.6	0.058	61.7	851	0.00219
Cs	24.757	20.800	3.957	19.0	0.649	2.6	2262	0.00004	0.443	0.26	0.183	70.5	0.133	30.1	1578	0.00051
Ba	47	50	3	5.9	3	5.5	313	0.00072	64	64.3	0	0.5	1	2.3	108	0.00128
La	17.60	19.70	2.10	10.6	0.38	2.2	3608	0.00002	3.58	3.6	0.02	0.4	0.17	4.7	826	0.00028
Ce	45.4	47.2	1.8	3.7	0.8	1.8	3419	0.00002	8.4	8.17	0.2	2.3	0.1	1.4	801	0.00026
Pr	5.46	5.58	0.12	2.1	0.11	2.1	4099	0.00002	1.12	1.13	0.01	1.2	0.06	5.5	941	0.00034
Nd	21.8	23.3	1.5	6.3	0.4	2.0	715	0.00009	5.6	5.47	0.1	1.9	0.3	5.0	153	0.00172
Sm	5.78	6.03	0.25	4.1	0.17	3.0	584	0.00023	1.44	1.49	0.05	3.4	0.11	7.7	147	0.00379
Eu	0.3	0.3	0.0	7.5	0.0	6.2	2289	0.00011	0.6	0.62	0.1	9.7	0.0	8.6	626	0.00072
Gd	5.41	5.06	0.35	6.9	0.16	3.0	615	0.00012	1.84	1.61	0.23	14.1	0.28	15.4	133	0.00366
Tb	0.987	1.010	0.023	2.3	0.016	1.6	3907	0.00003	0.300	0.29	0.010	3.3	0.041	13.7	1116	0.00033
Dy	5.77	5.69	0.08	1.4	0.12	2.1	1057	0.00008	1.99	1.56	0.43	27.4	0.18	9.0	248	0.00161
Ho	1.17	1.11	0.06	5.2	0.06	5.5	3320	0.00006	0.41	0.33	0.08	24.7	0.04	10.2	979	0.00045
Er	3.89	3.61	0.28	7.6	0.12	3.0	1365	0.00007	1.04	1.04	0.00	0.0	0.09	8.7	284	0.00139
Tm	0.63	0.67	0.04	6.7	0.02	2.9	4186	0.00003	0.17	0.16	0.01	5.4	0.03	17.3	940	0.00099
Yb	4.47	4.55	0.08	1.7	0.13	2.9	683	0.00024	1.06	1.06	0.00	0.3	0.07	6.9	193	0.00166
Lu	0.714	0.710	0.004	0.5	0.027	3.7	2916	0.00006	0.161	0.15	0.011	7.2	0.007	4.1	708	0.00117
Hf	4.48	4.51	0.03	0.6	0.02	3.5	1264	0.00007	0.86	0.88	0.02	2.4	0.08	8.8	268	0.00160
Ta	1.381	1.860	0.479	25.8	0.036	2.6	3501	0.00006	0.160	0.18	0.020	11.0	0.043	26.6	1038	0.00078
W	0.843	1.590	0.747	47.0	0.021	2.4	6416	0.00004	1.010	0.81	0.200	24.7	0.009	0.9	648	0.00051
Tl	0.583	1.560	0.977	62.6	0.071	12.1	701	0.00062	0.037	0.066	0.029	43.9	0.008	21.2	173	0.01203
Pb	20.57	19.30	1.27	6.6	0.31	1.5	1904	0.00006	0.55	1.92	1.37	71.3	0.009	13.5	1764	0.00016
Bi	1.672	0.560	1.112	198.6	0.079	4.7	824	0.00024	0.011	0.014	0.003	19.9	0.009	82.3	3555	0.00060
Th	28.50	26.70	1.80	6.7	3.26	11.4	2702	0.00025	0.49	0.48	0.01	3.0	0.05	9.2	828	0.00075
U	9.41	8.88	0.53	6.0	0.29	3.1	2397	0.00009	0.11	0.13	0.02	12.2	0.06	54.7	1373	0.00088

Table 4 Continued.

Element	JG-1a					JB-1b							
	Av. ($\mu\text{g g}^{-1}$)	R.V. ($\mu\text{g g}^{-1}$)	DIF ($\mu\text{g g}^{-1}$)	DIF% (%)	S.D. (1s) ($\mu\text{g g}^{-1}$)	RSD (%)	Sensitivity (cps/ $\mu\text{g g}^{-1}$)	DL ($\mu\text{g g}^{-1}$)	Av. ($\mu\text{g g}^{-1}$)	S.D. (1s) ($\mu\text{g g}^{-1}$)	RSD (%)	Sensitivity (cps/ $\mu\text{g g}^{-1}$)	DL ($\mu\text{g g}^{-1}$)
Sc	6.4	6.21	0.2	3.4	0.4	6.5	2783	0.00003	29.4	0.8	2.7	475	0.00024
Ti	1463	1512	49	3.2	48	3.3	135	0.00047	7437	127	1.7	26	0.00344
V	22	22.7	1	4.5	1	4.2	2629	0.00003	219	3	1.4	538	0.00019
Cr	13.4	17.6	4.2	24.1	0.4	3.1	427	0.00027	440.6	10.6	2.4	49	0.00232
Mn	516	445	70	15.8	52	10.1	1943	0.00007	1231	19	1.5	580	0.00018
Co	6.0	5.9	0.1	1.0	0.0	0.5	1627	0.00007	37.5	0.8	2.2	448	0.00032
Ni	4.21	6.91	2.70	39.0	0.39	9.3	1171	0.00011	131.77	1.98	1.5	101	0.00151
Cu	6	3	4	144.8	1	9.0	939	0.00021	17	1	6.6	241	0.00081
Zn	46.0	36.5	9.5	25.9	3.2	7.0	170	0.00098	90.9	4.9	5.4	34	0.00374
Ga	21.8	16.5	5.3	31.9	0.3	1.5	1765	0.00002	20.8	0.5	2.3	418	0.00028
Ge	3.24	1.5	1.74	116.3	0.31	9.7	299	0.00192	1.15	0.21	17.9	199	0.00519
As	0.52	0.43	0.09	20.7	0.10	19.1	269	0.00340	1.80	0.40	22.4	43	0.03169
Rb	190.84	178	12.84	7.2	2.53	1.3	2096	0.00002	36.04	0.37	1.0	472	0.00025
Sr	181	187	6	3.2	7	3.8	2313	0.00004	478	6	1.4	691	0.00012
Y	25.0	32.1	7.1	22.0	1.6	6.4	2899	0.00004	20.7	0.5	2.3	835	0.00009
Zr	112.2	118	5.8	4.9	6.4	5.7	1479	0.00005	128.6	1.7	1.3	411	0.00026
Nb	10.42	11.4	0.98	8.6	0.30	2.9	2623	0.00006	25.83	0.58	2.2	708	0.00016
Mo	0.49	0.45	0.04	9.0	0.10	20.3	657	0.00069	1.14	0.11	9.8	144	0.00376
Cd	0.23	0.026	0.21	792.3	0.02	10.1	203	0.00433	0.20	0.05	22.9	51	0.03925
Sn	4.49	4.47	0.02	0.3	0.14	3.2	923	0.00020	2.45	0.23	9.5	164	0.00145
Sb	0.179	0.048	0.131	273.3	0.025	14.1	2037	0.00046	0.107	0.029	27.2	1203	0.00087
Cs	12.339	10.6	1.739	16.4	0.281	2.3	3054	0.00002	0.985	0.344	35.0	843	0.00116
Ba	481	470	11	2.2	15	3.1	345	0.00028	547	5	0.8	104	0.00101
La	19.65	21.3	1.65	7.7	0.45	2.3	3883	0.00002	40.38	0.71	1.7	938	0.00008
Ce	44.9	45	0.1	0.3	1.3	2.8	3051	0.00003	68.2	1.2	1.8	972	0.00008
Pr	4.73	5.63	0.90	16.1	0.13	2.8	3731	0.00003	7.00	0.12	1.8	1177	0.00015
Nd	18.7	20.4	1.7	8.4	0.4	2.2	761	0.00012	27.9	1.0	3.7	195	0.00055
Sm	4.12	4.53	0.41	9.1	0.21	5.0	667	0.00025	4.98	0.23	4.5	187	0.00098
Eu	0.7	0.7	0.0	5.0	0.0	4.1	2542	0.00007	1.6	0.1	5.8	549	0.00048
Gd	4.19	4.08	0.11	2.8	0.28	6.7	536	0.00017	4.91	0.13	2.6	165	0.00096
Tb	0.676	0.810	0.134	16.6	0.032	4.7	3847	0.00004	0.704	0.032	4.5	1069	0.00029
Dy	4.60	4.44	0.16	3.7	0.28	6.0	860	0.00017	4.18	0.09	2.1	302	0.00076
Ho	0.93	0.82	0.11	13.1	0.03	3.3	4347	0.00003	0.83	0.06	6.8	1023	0.00031
Er	2.83	2.57	0.26	10.1	0.05	1.7	1415	0.00005	2.17	0.10	4.8	428	0.00049
Tm	0.38	0.38	0.00	0.9	0.01	3.3	4939	0.00002	0.32	0.03	8.3	1050	0.00038
Yb	2.89	2.70	0.19	7.0	0.23	7.8	787	0.00025	1.86	0.13	6.9	291	0.00108
Lu	0.415	0.44	0.025	5.8	0.017	4.0	4600	0.00003	0.328	0.039	11.8	1059	0.00025
Hf	3.47	3.59	0.12	3.5	0.29	8.5	1121	0.00013	3.11	0.12	3.9	357	0.00049
Ta	1.822	1.9	0.078	4.1	0.112	6.2	2979	0.00004	1.028	0.022	2.1	1788	0.00010
W	10.637	12.4	1.763	14.2	0.379	3.6	1110	0.00023	1.146	0.017	1.4	400	0.00086
Tl	n.d.	0.98	-	-	-	-	-	-	0.042	0.011	27.0	631	0.00277
Pb	27.84	26.4	1.44	5.5	0.26	0.9	2004	0.00002	2.33	0.15	6.3	1537	0.00017
Bi	1.395	0.43	0.965	224.4	0.458	32.8	796	0.00079	0.004	0.001	29.0	6676	0.00026
Th	13.48	12.8	0.68	5.3	2.87	21.3	2724	0.00018	8.56	0.24	2.8	1172	0.00009
U	4.64	4.69	0.05	1.1	0.19	4.1	3005	0.00004	1.33	0.09	7.0	1386	0.00019

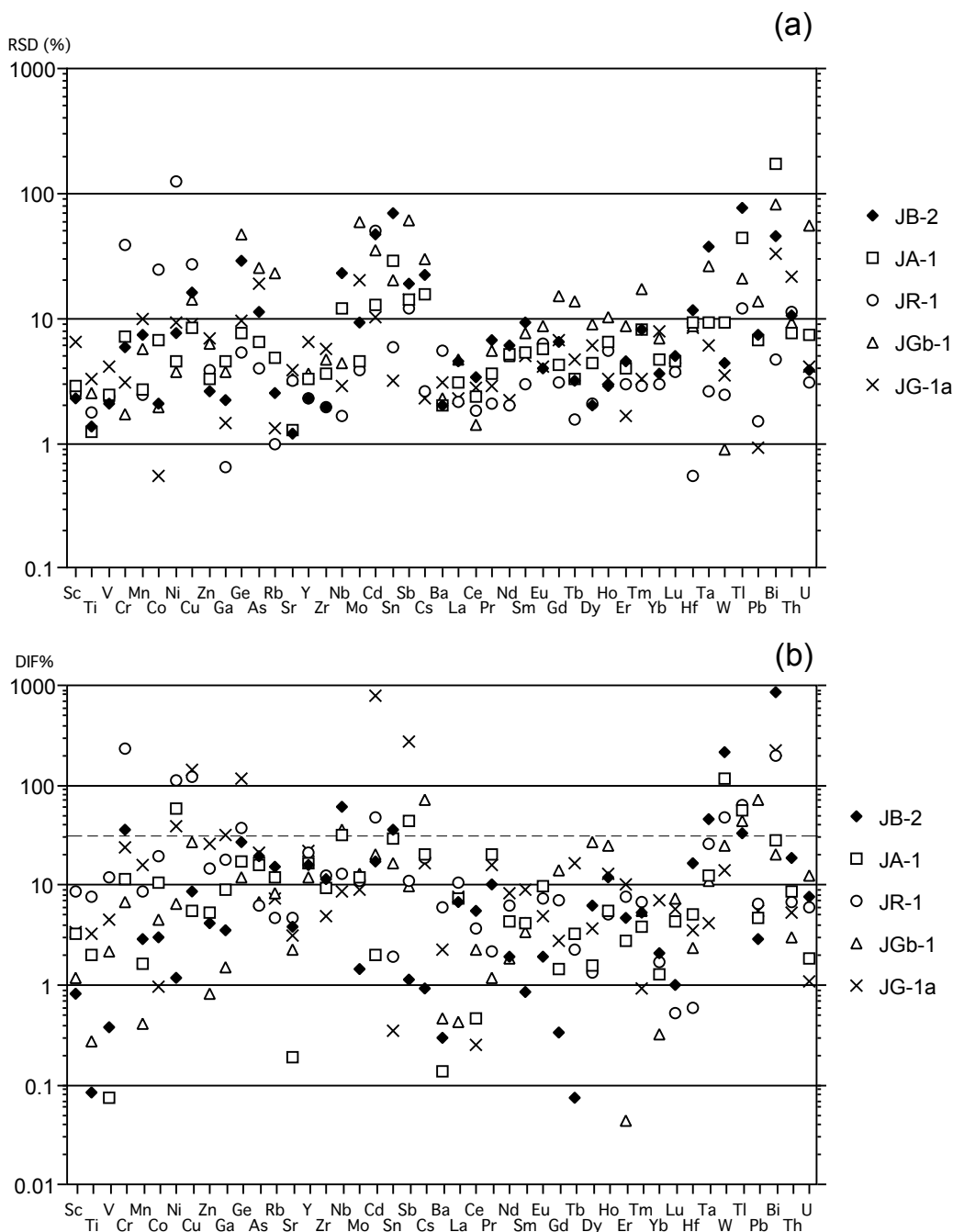


Fig. 1 Reproducibility and difference of the compilation values for five GSJ reference materials. (a) Relative standard deviation (RSD) of GSJ reference materials. (b) Percentage of difference (DIF%) between the analytical results and compilation values of GSJ reference materials (Imai *et al.*, 1995).

4. Summary

The simple analytical method for whole rock 45 trace elements ranging from ^{45}Sc to ^{238}U by LA-ICP-MS using a high-dilution ratio (sample:flux = 1:10) glass bead has been established. The precision of the analytical results of the GSJ geochemical reference materials was mostly <30% except for elements of

very low contents. A comparison with the compilation values from the literature and the analytical results of this study show <30% DIF for 194 out of 225 elements analyzed from JB-2, JA-1, JR-1, JGb-1, and JG-1a. Most of the elements with DIF >30% were of very low concentration and/or the compilation values were less reliable. In the case of unknown analyses, the reliability of the quantitative values could be evaluated from the RSD of

Table 5 Summary of reproducibility and difference of the compilation values for five GSJ reference materials.

(A) Reproducibility (precision) shown by RSD (%).			(B) Difference (DIF) between the analytical results and the compilation values of Imai <i>et al.</i> (1995).		
Std.	RSD(%)	Elements	Std.	DIF(%)	Elements
JB-2	<10%	Sc, Ti, V, Cr, Mn, Co, Ni, Zn, Ga, Rb, Sr, Y, Zr, Mo, Ba, lanthanides, W, Pb, U	JB-2	<10%	Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Ga, Sr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Pb, U
	<15%	As, Hf, Th		<15%	Zr, Pr, Ho
	<30%	Cu, Ge, Nb, Sb, Cs		<30%	Ge, As, Rb, Y, Cd, Hf, Th
	>30%	Cd, Sn, Ta, Tl, Bi		>30%	Cr, Nb, Sn, Ta, W, Tl, Bi
JA-1	<10%	Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Mo, Ba, lanthanides, Hf, Ta, W, Pb, Th, U	JA-1	<10%	Sc, Ti, V, Mn, Cu, Zn, Ga, Sr, Zr, Cd, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th, U
	<15%	Nb, Cd, Sb		<15%	Cr, Co, Rb, Mo, Ta
	<30%	Sn, Cs		<30%	Ge, As, Y, Sn, Cs, Pr, Bi
	>30%	Tl, Bi		>30%	Ni, Nb, Sb, W, Tl
JR-1	<10%	Sc, Ti, V, Mn, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, lanthanides, Hf, Ta, W, Pb, Bi, U	JR-1	<10%	Sc, Ti, Mn, As, Rb, Sr, Sn, Ba, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th, U
	<15%	Sb, Tl, Th		<15%	V, Zn, Zr, Nb, Mo, Sb, La
	<30%	Co, Cu		<30%	Co, Ga, Y, Cs, Ta
	>30%	Cr, Ni, Cd		>30%	Cr, Ni, Cu, Ge, Cd, W, Tl, Bi
JGb-1	<10%	Sc, Ti, V, Cr, Mn, Co, Ni, Zn, Ga, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Dy, Er, Yb, Lu, W, Th	JGb-1	<10%	Sc, Ti, V, Cr, Mn, Co, Ni, Zn, Ga, Ge, As, Rb, Sr, Sb, Ba, La, Ce, Pr, Nd, Sm, Eu, Tb, Er, Tm, Yb, Lu, Hf, Th
	<15%	Cu, Tb, Ho, Pb		<15%	Y, Zr, Mo, Gd, Ta, U
	<30%	As, Rb, Sn, Gd, Tm, Ta, Tl		<30%	Cu, Cd, Sn, Dy, Ho, W, Bi
	>30%	Ge, Mo, Cd, Sb, Cs, Bi, U		>30%	Nb, Cs, Tl, Pb
JG-1a	<10%	Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, lanthanides, Hf, Ta, W, Pb, U	JG-1a	<10%	Sc, Ti, V, Co, Rb, Sr, Zr, Nb, Mo, Sn, Ba, La, Ce, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu, Hf, Ta, Pb, Th, U
	<15%	Mn, Cd, Sb		<15%	Ho, Er, W
	<30%	As, Mo, Th		<30%	Cr, Mn, Zn, As, Y, Cs, Pr, Tb
	>30%	Bi		>30%	Ni, Cu, Ga, Ge, Cd, Sb, Bi

Std. denotes GSJ reference materials.

Std. denotes GSJ reference materials.

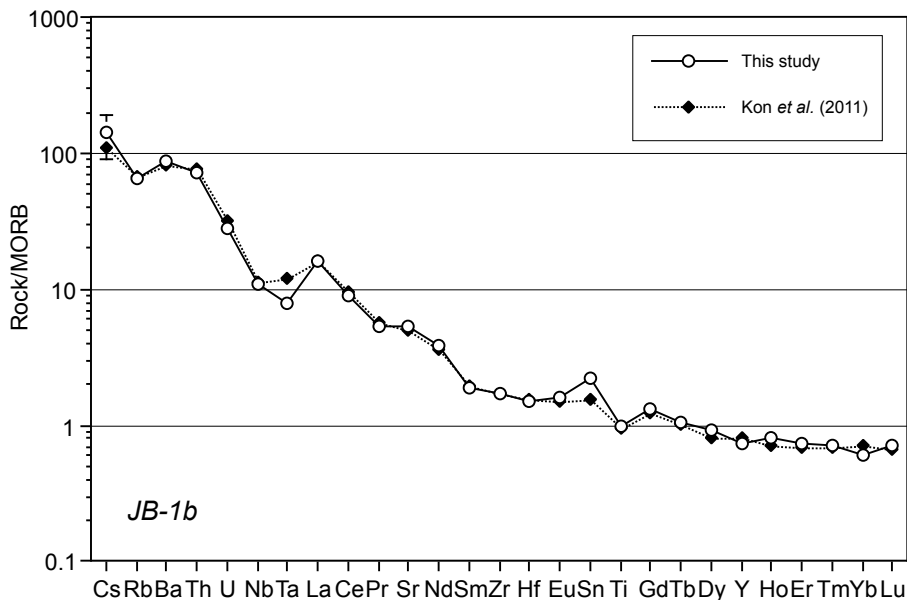


Fig. 2 Comparison between the quantitative values of JB-1b from this study ($N=5$) and those from Kon *et al.* (2011). The values are normalized by N-MORB composition from Sun and McDonough (1989). Analytical errors of this study are shown as error bars. All errors were within the symbols except for Cs.

signal count rates and quantitative values, and estimated DL. The analytical values of JB-1b in this study were concordant with the literature values, and this result suggests that the analytical results of this study can be adequately used for petrological and geochemical discussions.

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ガラスビード試料を用いたレーザーアブレーション誘導結合プラズマ質量分析計 (LA-ICP-MS) による全岩微量元素分析

山崎 徹・山下康平

要 旨

XRF分析用の高希釈ガラスビード(試料・融剤比1:10)を用いて、レーザーアブレーション誘導結合プラズマ質量分析計(LA-ICP-MS)によって、 ^{45}Sc から ^{238}U までの質量範囲をカバーする全岩微量元素測定を行う簡便な手法を構築した。地質調査総合センター岩石標準試料のガラスビードを用いて、5回の繰り返し測定によるシグナル・カウントの相対標準偏差(RSD)を繰り返し測定精度として検討した結果、著しく含有量の乏しい元素を除いて概ねRSD<30%であった。標準値との比較においては、JB-2、JA-1、JR-1、JGb-1及びJG-1aの5試料において測定した延べ225元素のうち194元素(約85%)において、差が一般的に定量分析における精度の許容範囲の目安とされている30%以下であった。標準値との差が30%以上であった試料・元素のほとんどは、含有量が乏しいものであった。JB-1bの測定結果は既存のLA-ICP-MSによる測定値とよく一致し、本手法による分析結果は十分に岩石学的・地球化学的議論に使用可能であることを示す。