

## Determination of trace element abundances in GSJ reference rock samples using lithium metaborate–lithium tetraborate fused solutions and inductively coupled plasma mass spectrometry

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### Abstract

This study aims to establish a quantitative method for determination of trace element abundances in rock samples using  $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$  fused solutions and inductively coupled plasma mass spectrometry (ICP-MS). Alkali fusion of rock powders has an advantage in assuring complete dissolution of refractory minerals, but the analyte solution diluted from the alkali-fused glass is known to cause matrix effects during ICP-MS analysis. The present study adopted the following procedures: (1) The alkali fusion of the rock powders was made using a rock:flux ratio of 1:2. (2) The alkali fused glass samples were digested using 5%  $\text{HNO}_3$ -0.1% HF to yield solutions with high dilution factors of 6000-8000 times. (3) The internal standard method was adopted to construct the calibration curves. Concentrations of the internal standard element (10 ppb In) were kept constant in the solutions of both the reference and unknown samples. The results show that abundances of Sc, V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Cs, Ba, 14 REEs, Hf, Ta, Pb, Th, and U were successfully determined in representative standards from the Geological Survey of Japan (JA-1, JA-2, JA-3, JB-1b, JB-2, JB-3, JG-1a, JG-2, JG-3, JGb-1, JR-1, JR-2, and JR-3).

**Key words:** Trace element,  $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$  fused solution, ICP-MS

### Introduction

Inductively coupled plasma mass spectrometer (ICP-MS) is a powerful tool for the determination of sub-part per million (ppm) concentrations of a large number of elements in a variety of materials. ICP-MS has also been widely utilized for quantitative analysis of trace elements in rock samples over the last few decades. Many researchers have developed and progressively modified the analytical method (e.g., Jarvis and Jarvis, 1985; Hirata *et al.*, 1988; Imai, 1990; Hall and Pelchat, 1990; Kimura *et al.*, 1995). These previous studies were very useful during our efforts to establish an accurate and reliable analytical procedure in our ICP-MS laboratory.

The first requirement for the analysis of geological materials by ICP-MS is to quantitatively transform the sample into solution. Mixed acids in open or closed digestion systems have been widely used to prepare such solutions, using a variety of heating times and temperatures (e.g. Chao and Sanzolone, 1992). These approaches are not always successful for all rock samples, because highly refractory minerals such as zircon, chromite, garnet, magnetite, and spinel may not be completely dissolved, resulting in an underestimate of concentrations of trace elements and REE (e.g. Ujiié and Imai, 1995). To overcome this problem, some analysts have used specialized equipment such as microwaves (e.g. Totland *et al.*, 1992) or PTFE-lined stainless steel bombs (e.g. Liang

*et al.*, 2000). Such methods may have budgetary implications. In contrast, lithium metaborate ( $\text{LiBO}_2$ ) and/or lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) fusion techniques that are incorporated into ICP-MS measurements are capable of complete dissolution of refractory minerals (e.g. Hall and Plant, 1992). This method is both rapid and cost-effective. Consequently we have recently established a new ICP-MS analytical method following sample digestion of  $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$  glasses using mixed-acid ( $\text{HF-HClO}_4\text{-HNO}_3\text{-HCl}$ ) for routine analysis in the Department of Geoscience of Shimane University. This paper describes the analytical method, and reports the results obtained for 31 elements in 13 representative standard rock samples produced by the Geological Survey of Japan (GSJ).

### Experimental Methods

#### 1. Reagents, labware and instrumentation

The  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$  used for the alkali fusion of rock powders were Spectromelt A20 and A10 (Merck Millipore, Germany), respectively. TAMAPURE-AA grade 38% HF, 70%  $\text{HClO}_4$ , 68%  $\text{HNO}_3$ , and 30% HCl (Tama Chemicals, Japan) were used for digestion of the alkali fused glasses, and TMSC (Tama Chemicals, Japan), EL grade 70%  $\text{HNO}_3$  and 36% HCl (Kanto Chemicals, Japan) were employed for cleaning of the labware. The distilled–deionized water used throughout the present experiment was prepared in a system using Milli-Q Academic A10 (Millipore, Japan) and Demineralizer WA570 (Yamato Scientific, Japan). The water is of high quality, with a resistivity of  $> 18.2 \text{ M}\Omega\text{-cm}$ .

PFA vials (Savillex, USA) with 7 ml capacity and 10 ml polystyrene test tubes (MI Chemical, Japan) were used for

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decomposition of the alkali fused glasses and for solution dilution, respectively. To avoid contamination and to achieve low blanks, the vial and test tubes were cleaned on a hot plate at 90°C, using de-ionized water for one night, 5% TMSO for one night, 6N-HNO<sub>3</sub> for three hours, and then 6N-HCl for three hours. The cleaned vials and tubes were then rinsed three times in de-ionized water held at 90°C for three hours.

An Agilent 7500a ICP-MS (Agilent Technologies, USA) was used for determination of the trace elements. Optimization was made using a 10 ppb tuning solution, as monitored at masses of <sup>59</sup>Co, <sup>89</sup>Y, <sup>140</sup>Ce, and <sup>205</sup>Tl, which were mainly employed to obtain highest sensitivity and resolution, minimum oxides (<sup>156</sup>CeO/<sup>140</sup>Ce < 1.0%) and doubly charged ions (<sup>70</sup>Ce<sup>2+</sup>/<sup>140</sup>Ce < 2.0%), and mass axis adjustment. The operating conditions of the instrument are summarized in Table 1. The Agilent 7500a is installed with an electron multiplier (EM) as the detector. Two modes are available for detecting signals, and hence it is possible to measure a wide range of abundances of various elements. The modes are the pulse counting mode (lower than 1 Mcps) and analog mode (1 Mcps to 4 Gcps). These two modes were adjusted for linear calibration curves by P/A factor tuning using a 100 ppb solution which contained all the elements analyzed in this study.

## 2. Internal and reference solutions

Indium (<sup>115</sup>In) was used as the internal standard element. A mono-elemental standard of 1000 ppm Indium (Wako Pure Chemical Industries, Japan) was diluted to a 100 ppb solution with 5% HNO<sub>3</sub>-0.1% HF. The stock internal standard was kept in a cleaned 100 ml PFA bottle.

Reference solutions of 0.005, 0.05, 0.5, 5, and 50 ppb were prepared in polystyrene test tubes by dilution of XSTC-1, -7, -8, and -331 (10 ppm multi-element standards: SPEX CertiPrep, USA) with 5% HNO<sub>3</sub>-0.1% HF. The final volume of each solution was nine ml, which was made up using 1 ml and 5 ml Eppendorf Research pipettes (Eppendorf, Germany). One ml of the stock internal standard (100 ppb In) was added to each nine ml solution before ICP-MS analysis. Consequently, the indium concentration of the reference solution was diluted to 10 ppb. All solutions were weighed to the fourth decimal place using an electronic balance to determine accurate dilution factors for each.

Calibration curves for each element were constructed in the following concentration ranges, in accordance with the expected concentrations in the samples: 0.05-50 ppb for V, Cr, Ni, Rb, Sr, Y, Zr, Ba, and Th, and 0.005-5 ppb for all other elements. The correlation coefficients (*r*) for each curve lay within the range 1.0000-0.9996. These coefficients thus fell within the permissible range of >0.995 for quantitative ICP-MS analysis suggested by Rüdél *et al.* (2011).

## 3. Sample preparation

The LiBO<sub>2</sub> and Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fluxes were dried at 110°C overnight, and then mixed at a ratio of 20% LiBO<sub>2</sub> and 80%

**Table 1.** Operating conditions for ICP-MS.

Instrument	Agilent 7500a
RF power	1500 W
RF matching	1.58 V
Sample depth	8.5 mm
Carrier gas	1.22 L/min
Makeup gas	0.00 L/min
Peri Pump	0.10 rps
Replicates	3 times
S/C (spray chamber) Temp	2 °C

Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. About 3 g of each GSJ standard rock powder were weighed in clean ceramic crucibles and then ignited in a muffle furnace for 2 hours at 1050°C to achieve anhydrous state. Glass fusion beads were prepared by mixing 1.8000±0.0005 g of the ignited GSJ standards powder with 3.6000±0.0005 g of the LiBO<sub>2</sub>-Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> flux. The mixtures were fused in platinum crucibles (95% Pt and 5% Au alloy) in a NT-2000 automatic bead sampler (Tokyo Kagaku, Japan), with preheat, fusion and agitation times of 120, 120 and 360 seconds, respectively. This procedure follows that described by Kimura and Yamada (1996) for X-ray Fluorescence (XRF) analysis of rocks.

The glass beads were then manually broken and reduced to small fragments in a tungsten carbide pestle and mortar. Fragments of the GSJ fused glasses weighing approximately 0.05 g were then placed in 7 ml PFA vials, with the weight of each accurately measured to the fourth decimal place using an electronic balance. Two ml of 6N-HCl and 0.3 ml of conc. HNO<sub>3</sub> were then added to each vial. The vials were then closed and heated on a hot plate at 90°C overnight. A jelly-like residue was sometimes present in the solutions the next morning. However, this residue was immediately dissolved by a next addition of 0.5 ml of conc. HF and 0.3 ml of conc. HClO<sub>4</sub>. The vials were again closed, and heated on a hot plate at 90°C for another night. The decomposed samples were then progressively evaporated in a draft chamber with clean air, at temperatures of 120°C for 12 hours, 165°C for 12 hours, and 195°C, until dryness was achieved. This procedure usually took one night. The progressive drying follows Yokoyama *et al.* (1999).

The dried residue was then dissolved in 5 ml of 5% HNO<sub>3</sub>-0.1% HF. The resulting solutions were colorless and transparent. An 0.4 ml aliquot of each sample solution was then transferred to a polystyrene test tube, followed by addition of 8.6 ml of 5% HNO<sub>3</sub>-0.1% HF. One ml of the stock internal standard (100 ppb In) solution was finally added before the ICP-MS analysis. The indium concentration in the final solution was thus 10 ppb. The weights of the sample solution, the 5% HNO<sub>3</sub>-0.1% HF and the stock internal standard were accurately measured to the fourth decimal place using an electronic balance. Total dilution factors of the samples were aimed to fall within 6000-8000x. The sample preparation procedure is summarized in Figure 1.

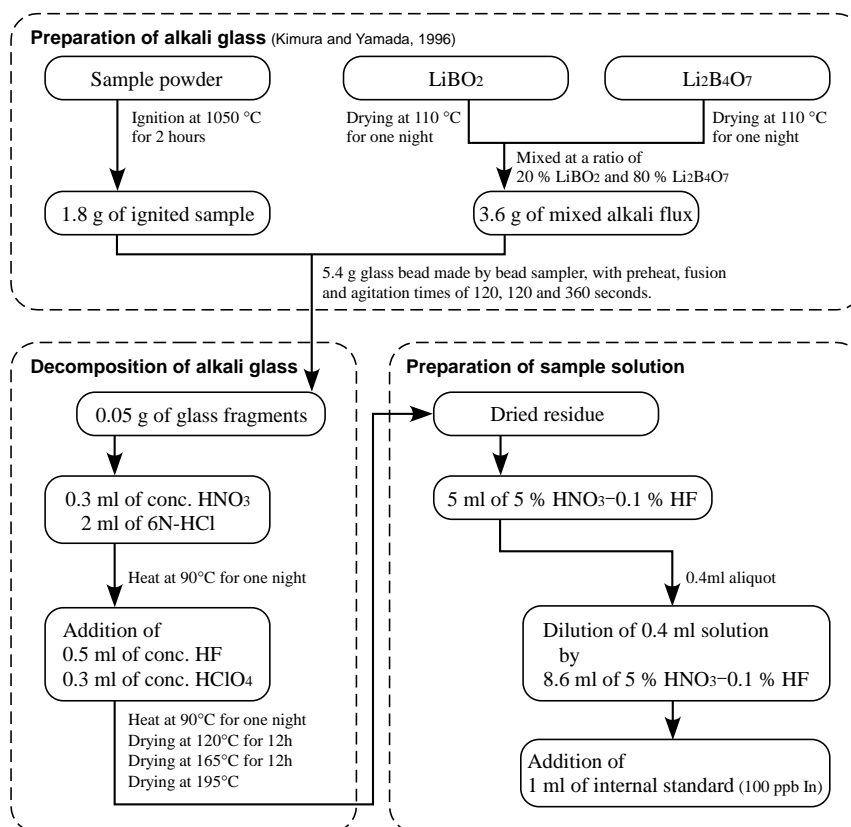


Fig. 1. Sample preparation procedure for ICP-MS analysis.

## Results

Representative rock standards from the GSJ (JA-1, JA-2, JA-3, JB-1b, JB-2, JB-3, JG-1a, JG-2, JG-3, JGb-1, JR-1, JR-2, and JR-3) were analyzed. These span the range in composition from gabbro through to granite and volcanic equivalents, and hence are typical of the natural variability that may be encountered in routine analysis. The results with errors are presented in Table 2. Some data are not listed (e.g. V for JB-2) because in a few cases the raw data fell off the calibration curves. Almost all the elements have relative standard deviations (RSD) of less than 5%. The analytical results are in mostly in good agreement with the recommended values, as reported by Imai *et al.* (1995) and Terashima *et al.* (1998) (Table 2 and Fig. 2). Chondrite normalized REE patterns of the analyzed standards also show good agreement with the recommended values (Fig. 3). However, the Nb and Y results tend to be slightly lower than the recommended values, although they are generally consistent with ICP-MS data produced by Yajima and Fujimaki (2002). Jochum *et al.* (1990), Robinson *et al.* (1999), Roser *et al.* (2000) and Yajima and Fujimaki (2002) noted that the recommended values for these two elements were strongly influenced by XRF data, and that ICP-MS results for Nb and Y were slightly lower than the XRF results.

## Discussion

### 1. Matrix effects from LiBO<sub>2</sub>-Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fusion

One advantage of incorporating LiBO<sub>2</sub> and/or Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fusion into ICP-MS measurement is that complete dissolution of highly refractory minerals such as zircon, chromite, garnet, magnetite, and spinel is assured (Totland *et al.*, 1992; Hall and Plant, 1992; Wei and Haraguchi, 1999; Yang and Pin, 2002; Panteeva *et al.*, 2003; Madinabeitia *et al.*, 2008; Nikolaeva *et al.*, 2008; Roy *et al.*, 2012). On the other hand, some disadvantages of such fusions have been also reported (e.g. Date and Stuart, 1988). The most important limitation is matrix effects during the ICP-MS analysis. This may cause signal inhibition, polyatomic ion interferences, and signal drift (e.g. Mochizuki *et al.*, 1990; Totland *et al.*, 1992; Madinabeitia *et al.* 2008).

Mochizuki *et al.* (1990) compared signal intensities for 41 elements from <sup>9</sup>Be to <sup>238</sup>U obtained with and without Li<sub>2</sub>CO<sub>3</sub>-H<sub>3</sub>BO<sub>3</sub> solutions. The intensities of all elements in 0.1 ppm Li<sub>2</sub>CO<sub>3</sub>-H<sub>3</sub>BO<sub>3</sub> solution were inhibited by 92 ± 2% compared to the Li<sub>2</sub>CO<sub>3</sub>-H<sub>3</sub>BO<sub>3</sub> free solution. Based on this result, Mochizuki *et al.* (1990) suggested that the internal standard method was thus preferable for quantitative measurements using Li-B additive solutions. Therefore, the internal standard method was adopted in this study. On the other hand, Mochizuki *et al.* (1990) also reported that inhibition effects did not occur with the

Table 2. Comparison between GSJ recommended values and analytical results.

mass	JA-1				JA-2				JA-3				JB-1b				JB-2				JB-3			
	R.V. (ppm)	ICP MS	SD (ppm)	RSD (%)	R.V. (ppm)	ICP MS	SD (ppm)	RSD (%)	R.V. (ppm)	ICP MS	SD (ppm)	RSD (%)	R.V. (ppm)	ICP MS	SD (ppm)	RSD (%)	R.V. (ppm)	ICP MS	SD (ppm)	RSD (%)	R.V. (ppm)	ICP MS	SD (ppm)	RSD (%)
45 Sc	28.5	28.0	1.0	3.6	19.6	19.7	0.4	1.8	22.0	20.4	0.1	0.5	29.9	0.8	2.6	53.5	54.0	1.4	2.7	33.8	32.3	0.2	0.6	
51 V	105	109	3	2.3	126	133	1	0.6	169	174	0	0.2	214	229	3	1.1	575	n.a.	-	-	372	407	5	1.2
53 Cr	7.83	7.38	0.64	8.6	436	445	1	0.3	66.2	63.9	1.4	2.2	439	446	7	1.7	28.1	27.6	0.7	2.4	58.1	57.3	0.9	1.5
59 Co	12.3	10.6	0.2	1.5	29.5	29.4	0.3	0.9	21.1	19.9	0.1	0.4	40.3	39.2	0.4	1.0	38.0	36.4	0.4	1.0	34.3	34.3	0.4	1.1
60 Ni	3.49	1.78	0.27	15.4	130	131	2	1.3	32.2	28.8	0.7	2.6	148	140	3	2.3	16.6	12.7	0.1	1.1	36.2	33.1	0.7	2.0
85 Rb	12.3	10.7	0.2	2.1	72.9	65.9	0.4	0.5	36.7	34.0	0.2	0.5	39.1	35.2	0.5	1.4	7.37	7.24	0.08	1.1	15.1	14.2	0.2	1.4
88 Sr	263	260	3	1.3	248	245	2	0.8	287	280	4	1.4	439	450	4	1.0	178	178	1	0.7	403	401	5	1.4
89 Y	30.6	28.7	0.4	1.4	18.3	16.9	0.2	0.9	21.2	19.6	0.2	1.1	21.9	0.1	0.6	24.9	23.2	0.4	1.7	26.9	25.9	0.4	1.4	
90 Zr	88.3	84.4	1.4	1.7	116	112	1	0.6	118	115	2	1.4	133	2	1.7	51.2	47.5	0.6	1.3	97.8	94.2	0.7	0.7	
93 Nb	1.85	1.23	0.05	3.9	9.47	8.82	0.11	1.2	3.41	2.98	0.04	1.3	26.4	0.5	1.8	1.58	0.510	0.033	6.5	2.47	1.96	0.06	2.9	
133 Cs	0.62	0.612	0.026	4.3	4.63	4.46	0.09	1.9	2.08	2.16	0.05	2.3	1.21	0.807	0.015	1.9	0.85	0.785	0.022	2.8	0.94	0.917	0.000	0.0
137 Ba	311	308	4	1.2	321	316	1	0.2	323	317	2	0.7	526	5	0.9	222	224	3	1.2	245	242	1	0.3	
139 La	5.24	4.97	0.10	1.9	15.8	15.5	0.2	1.2	9.33	9.22	0.13	1.4	40.3	0.4	1.0	2.35	2.36	0.06	2.7	8.81	8.45	0.04	0.5	
140 Ce	13.3	13.1	0.2	1.5	32.7	32.0	0.1	0.3	22.8	21.2	0.2	0.9	69.3	0.7	1.0	6.76	6.56	0.03	0.5	21.5	21.0	0.1	0.7	
141 Pr	1.71	2.13	0.03	1.4	3.84	3.71	0.10	2.8	2.40	2.80	0.06	2.0	7.38	0.11	1.5	1.01	1.16	0.02	2.1	3.11	3.24	0.06	1.7	
146 Nd	10.9	10.6	0.1	1.2	13.9	14.1	0.1	1.0	12.3	12.1	0.3	2.5	26.8	0.1	0.4	6.63	6.21	0.16	2.7	15.6	15.7	0.3	1.7	
147 Sm	3.52	3.38	0.02	0.7	3.11	3.15	0.05	1.5	3.05	3.05	0.11	3.5	5.25	0.26	5.0	2.31	2.28	0.12	5.2	4.27	4.35	0.18	4.1	
153 Eu	1.20	1.16	0.06	5.1	0.93	0.956	0.035	3.6	0.82	0.823	0.024	2.9	1.57	0.02	1.1	0.86	0.832	0.019	2.2	1.32	1.37	0.07	5.3	
157 Gd	4.36	4.31	0.14	3.2	3.06	3.07	0.11	3.6	2.96	3.31	0.16	5.0	5.04	0.06	1.2	3.28	3.15	0.04	1.1	4.67	4.70	0.17	3.5	
159 Tb	0.75	0.731	0.030	4.2	0.44	0.501	0.024	4.9	0.52	0.535	0.018	3.3	0.690	0.016	2.4	0.60	0.547	0.011	1.9	0.73	0.776	0.036	4.7	
163 Dy	4.55	4.84	0.01	0.2	2.80	2.89	0.03	1.1	3.01	3.28	0.13	4.0	4.14	0.06	1.4	3.73	3.90	0.09	2.4	4.54	4.61	0.08	1.8	
165 Ho	0.95	1.03	0.02	1.9	1.48	1.80	0.08	4.6	1.57	2.04	0.02	1.1	0.788	0.029	3.6	0.75	0.868	0.007	0.8	0.80	0.961	0.018	1.9	
166 Er	3.04	3.08	0.00	0.1	1.62	1.70	0.03	1.6	2.16	2.01	0.11	5.7	2.33	0.02	0.9	2.60	2.65	0.06	2.4	2.49	2.69	0.07	2.6	
169 Tm	0.47	0.462	0.010	2.2	0.28	0.285	0.009	3.2	0.28	0.303	0.014	4.5	0.326	0.003	0.8	0.41	0.394	0.013	3.2	0.42	0.437	0.013	3.0	
172 Yb	3.03	2.97	0.02	0.6	1.70	1.70	0.03	1.6	2.16	2.01	0.11	5.7	2.12	0.03	1.6	2.62	2.64	0.04	1.5	2.55	2.42	0.06	2.5	
175 Lu	0.47	0.464	0.008	1.7	0.27	0.273	0.016	6.0	0.32	0.303	0.010	3.4	0.302	0.014	4.6	0.40	0.382	0.006	1.6	0.39	0.390	0.021	5.4	
178 Hf	2.42	2.69	0.07	2.7	2.86	3.04	0.04	1.2	3.42	3.23	0.12	3.9	3.55	0.08	2.4	1.49	1.58	0.03	2.2	2.67	2.84	0.04	1.3	
181 Ta	0.13	0.157	0.010	6.4	0.80	0.766	0.028	3.7	0.27	0.269	0.013	4.8	1.61	0.05	3.3	0.13	0.173	0.019	11.0	0.15	0.331	0.028	8.5	
208 Pb	6.55	5.49	0.01	0.2	19.2	19.2	0.2	1.0	7.70	7.58	0.17	2.3	6.80	5.46	0.24	4.4	5.36	4.78	0.12	2.6	5.58	4.93	0.12	2.4
232 Th	0.82	0.699	0.026	3.8	5.03	4.68	0.05	1.2	3.25	3.12	0.10	3.1	9.53	0.25	2.6	0.35	0.292	0.025	8.7	1.27	1.25	0.05	3.8	
238 U	0.34	0.380	0.022	5.8	2.21	2.14	0.08	3.6	1.18	0.923	0.074	8.0	1.56	0.03	1.7	0.18	0.160	0.013	8.4	0.48	0.496	0.030	6.0	

R. V.: Recommended Value (Imai et al., 1995; Terashima et al., 1998). n.a.: not analysis.



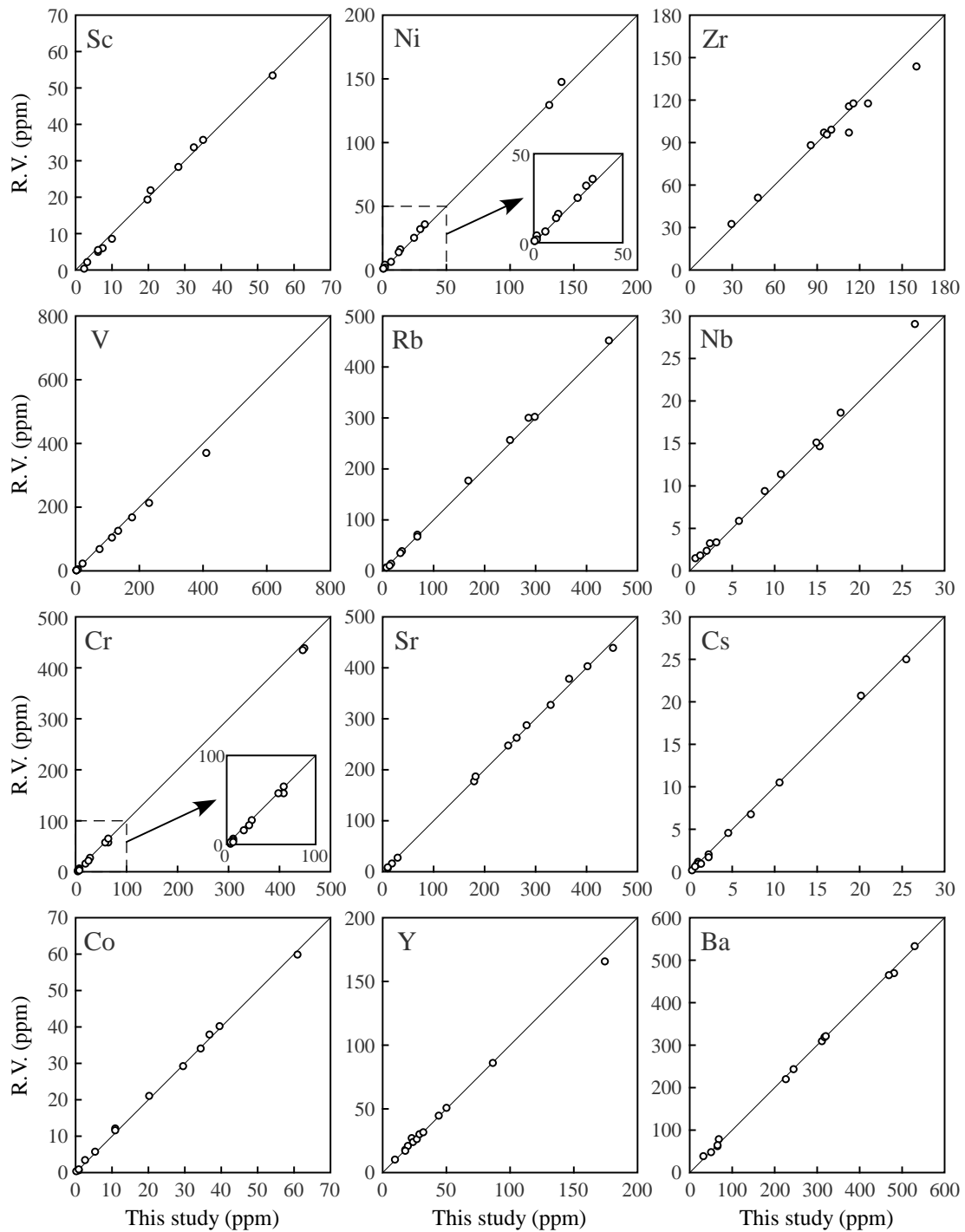


Fig. 2. Plots of recovery (ppm) for GSJ Reference Materials analyzed as unknowns.

variation of atomic weight from  $^9\text{B}$  to  $^{238}\text{U}$ , and ionization energy was also not affected. Consequently, this study did not consider any countermeasures for inhibition or ionization energy effects.

Polyatomic ion interference resulting from added Li-B fluxes has also been suggested as a matrix effect (Mochizuki *et al.*, 1990; Totland *et al.*, 1992). Mochizuki *et al.* (1990) found visible  $^{40}\text{Ar}^{11}\text{B}$  and  $^{40}\text{Ar}^7\text{Li}$  signals during analysis of flux-fused solutions, and suggested a possible interference

by  $^{40}\text{Ar}^{11}\text{B}$  when determining  $^{51}\text{V}$ . In general, higher dilution rates such as 6000-10000 times provides a viable means of decreasing the matrix effect (e.g. Tan and Horlick, 1987; Yajima and Fujimaki, 2002; Madinabeitia *et al.*, 2008). Therefore, the final dilution factor in this study was set to 6000-8000 times. As a result, quantitative analysis of V was successful (Fig. 2).

Several researchers have reported several ICP-MS methods using variable sample:flux ratios of 1:7-1:3 (Totland *et al.*,



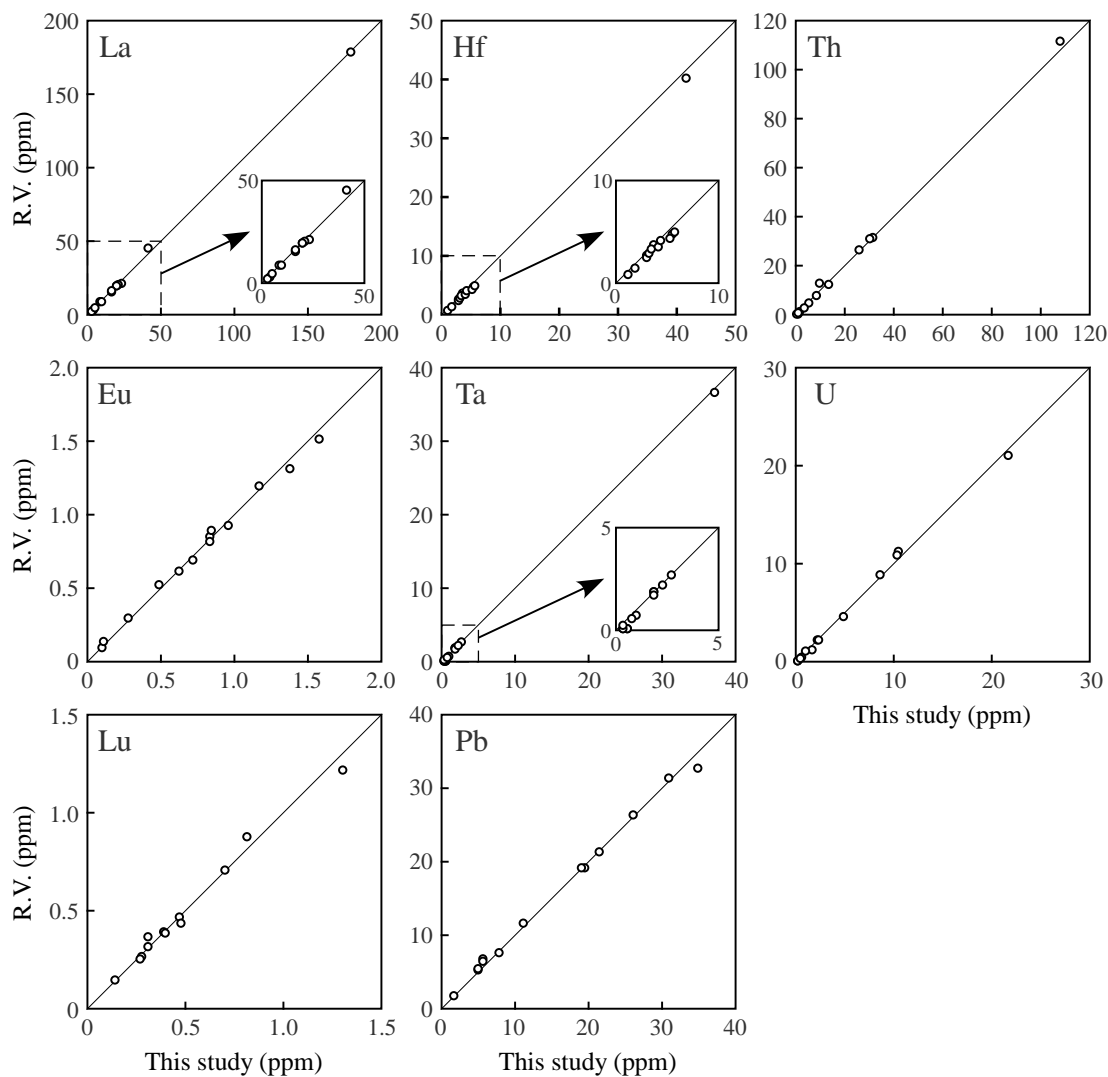


Fig. 2. Continued.

1992; Ramsey *et al.*, 1995; Nikolaeva *et al.* 2008). However, Madinabeitia *et al.* (2008) found significant signal drift during a short experiment in the case of low sample:flux ratio of 1:5, compared to a higher sample:flux ratio of 1:2, and concluded that the 1:2 ratio, combined with a higher dilution factor of 6500 times, was the better procedure for sample preparation. In this study, the 1:2 sample/flux ratio was therefore adopted. Madinabeitia *et al.* (2008) also commented that the drift problem was eliminated by using a solution of the same composition as the matrix for inter-sample washout, although this study did not incorporate this method. On the other hand, the acid digestion of alkali glass may result in loss of Pb (Totland *et al.*, 1992). However, this problem was not recognized in the analytical results in this present study (Fig. 2).

## 2. Adjustment of internal standard contents

The calibration curves were drawn using the linear equation:

$$Y = aX + b \quad (1)$$

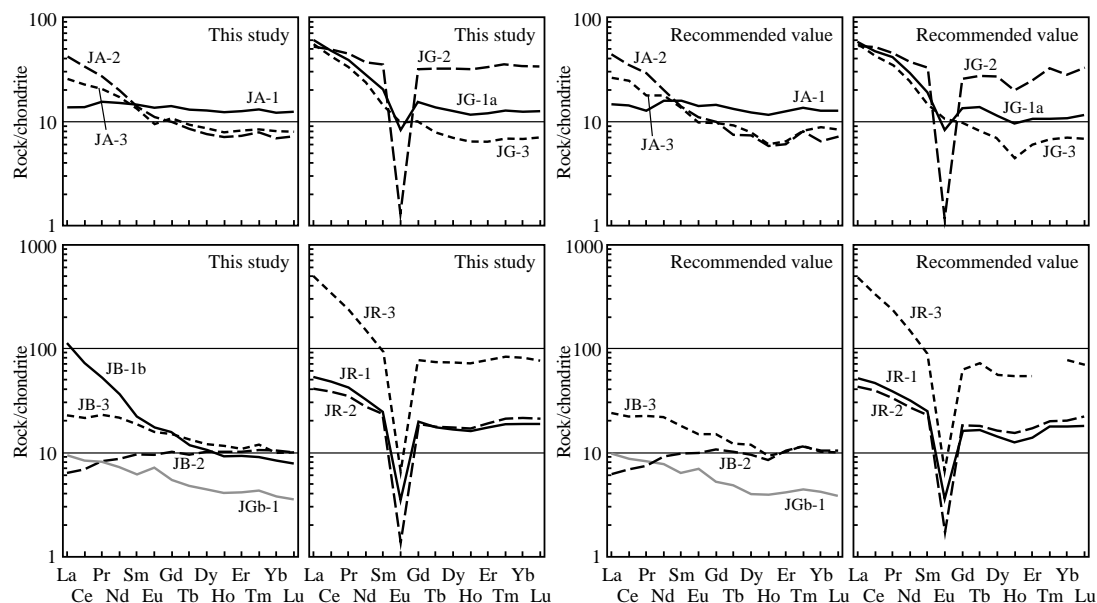
where X is the concentration of the target ion in the unknown sample, and Y is the measured value detected by ICP-MS. The coefficients “a” and “b” respectively are the slope and intercept of the calibration curve, which is given by the analytical results for the 0.005, 0.05, 0.5, 5, and 50 ppb reference solutions.

The software provided by the instrument manufacture adopts the following measured value for Y :

$$Y = y_{\sigma} \times \frac{x_i}{y_i} \quad (2)$$

where  $y_{\sigma}$  and  $y_i$  are the signal counts of the target ion and of the internal standard ion, respectively, and  $x_i$  denotes the concentration of the internal standard of the first level in the calibration curve. Therefore, for the quantitative analysis the same internal standard content was required in all references and samples.

The proportion of internal standard solution against the sample solution was taken into account, to control the homogeneity of the internal standard content within  $\pm 1\%$ . Both the reference and sample solutions were prepared to



**Fig. 3.** Chondrite-normalized REEs diagrams for GSJ Reference Materials from this study and the recommended values. Chondrite values are from Taylor and McLennan (1985).

9 ml before the addition of the internal standard. Repeated test reweighing of the reference and sample solutions resulted in average weights of  $9.0356 \pm 0.0292$  g ( $3\sigma$ ,  $n=25$ ) and  $9.0344 \pm 0.0163$  g ( $3\sigma$ ,  $n=31$ ), respectively. A 100 ppb indium solution was prepared as a stock internal standard. Similar tests and weighing of 1ml pipetted aliquots of the stock internal standard gave an average of  $1.0238 \pm 0.0031$  g ( $3\sigma$ ,  $n=31$ ). Based on these results, pipetting of the 1 ml stock internal standard into the 9 ml solutions of both the references and samples leads to internal standard contents of  $10.18 \pm 0.06$  ppb in each solution. Since the stock internal standard in this study contained 109.1 ppb indium, the final indium contents of all the reference and sample solutions were within  $11.10 \pm 0.02$  ppb.

### Conclusions

This study established a quantitative method of trace element analysis by  $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$  fused solutions and inductively coupled plasma mass spectrometry. The method involves the dissolution of fused samples with mixed acids such as HF,  $\text{HClO}_4$ ,  $\text{HNO}_3$ , and HCl. To avoid matrix effects arising from the alkali fused solution, the following procedure was incorporated into the measurement: (1) the fused glass samples had a sample:alkali flux ratio of 1:2; (2) the final dilution factor of the analyzed solutions was 6000-8000 times; and (3) the internal standard method was adopted. The acidity of the final analyzed solutions was adjusted with 5%  $\text{HNO}_3$ -0.1% HF. 10 ppb indium was selected as the internal standard. Homogeneity of the internal standard content was controlled within  $\pm 1\%$  by pipetting 1 ml stock of the internal standard (100 ppb) into the 9 ml sample solutions. Data for GSJ reference materials were used for

method validation, and the experimental results obtained agreed well with recommended values.

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(要 旨)

亀井淳志, 2016. LiBO<sub>2</sub>-Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 融解/誘導結合プラズマ質量分析法による GSJ 標準岩石試料の微量元素分析. 島根大学地球資源環境学研究報告, 34, 41-49.

本研究では岩石の微量元素分析を行うにあたり, LiBO<sub>2</sub>-Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> で融解した試料を酸分解して ICP-MS 分析する手法を確立した. アルカリ融解法は難溶解性鉱物の分解に有効であるが, 分析中にマトリクス効果が大いことも知られている. そこで本研究では次の手順を考慮した. (1) 岩石粉: アルカリ融剤の量比を 1 : 2 とする. (2) アルカリ融解ガラスを 5% HNO<sub>3</sub>-0.1% HF で 6000~8000 倍に希釈する. (3) 検量線作成に内部標準法を用いる. さらに, 検量線用溶液および試料溶液の内部標準元素 (インジウム) の濃度差を 1% 未満に抑えた. 地質調査総合センターの 13 種の標準岩石試料を用いて 31 種の微量元素 (Sc, V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Cs, Ba, 14 REEs, Hf, Ta, Pb, Th および U) を分析した. その結果, 全てに良好な分析値が得られた.

