

The solution introduction ICP-MS technique to trace element analysis of rocks

Miki SHIRASAKA, Shoji ARAI, Satoko ISHIMARU,
Yoshito ISHIDA, Yohei SHIMIZU and Tomoaki MORISHITA

*Department of Earth Sciences, Faculty of Science, Kanazawa University, Kanazawa,
920-1192, Japan*

Abstract : The solution introduction ICP-MS technique for trace element analysis of rock samples was constructed at Kanazawa University. Trace element concentrations of geological standards (JB-2, JP-1, JA-1, and JGB-2) and Avacha peridotite xenoliths, Russia, which are strongly depleted in major elements and the hardest matter for analysis, were determined by the ICP-MS equipment. The values of concentration of middle to heavy masses (Rb-U) in geological standards coincide with those reported by other studies with ICP-MS techniques. The reproducibility is within 5 % of differences of values of Rb to Hf in JB-2 in response to the changes in dates, dilutions and calibration methods. In the case of peridotites (low trace elements concentrations in the order of ppb to sub-ppb), relative standard deviations and relative differences among the runs under the various conditions are larger than in basalt with trace element concentrations in the order of ppm. Especially, large relative standard deviations (> 10s %) for alkaline elements (Li, Rb, Cs), HFSE (Zr, Nb, Ta), Pb and Bi are shown in the refractory Avacha peridotite xenoliths with trace element concentrations in the order of sub-ppb. The solution introduction ICP-MS technique is a powerful tool for a precise insight into trace element characteristics of rocks of wide chemical compositions.

1. Introduction

Trace-elements characteristics of geological materials give us very important information about their constitutions, origins, histories and others. Because of the low concentrations as ppb-ppt orders of those elements in the geological material like peridotite, their precise determination is sometimes difficult and time consuming. Number of datasets of trace elements in peridotite has increased from 1990's due to improvement of technique of inductively coupled plasma mass spectrometry (ICP-MS) (cf. Ionov et al., 1992; Ionov et al., 1993; Ionov et al., 1995; Bedini et al., 1999; Takazawa et al., 2003), which enables us to measure trace elements with more than sub-ppb order concentrations.

ICP-MS, X7 (Thermo Electron Corporation, UK) was installed at the Department of Earth Sciences, Kanazawa University in March, 2003. In order to measure trace-element concentrations of rock samples, especially basalt and peridotite, we established the solution introduction ICP-MS technique and examined reproducibility of results and consistency

with other studies.

2. Analytical techniques

2.1. Samples

In order to compare ICP-MS techniques between this study and the previous studies, we analyzed the following geological standards prepared by the Geological Survey of Japan: JB-2, basalt from the Oshima volcano, Japan; JP-1, peridotite (dunite) from Horoman, Japan; JA-1, andesite from the Hakone volcano, Japan; JGb-2, gabbro from Mt. Tsukuba, Japan. In order to check to our ability to determine the trace element concentrations in refractory peridotite with low trace element contents, we analyzed 6 peridotite (harzburgite) xenoliths from Avacha (Avachinsky) volcano in Kamchatka, Russia (AX-10, -106, -159, -213, -629, -729). The Avacha peridotite is extremely refractory (Fo of olivine, 91-93; Cr# = Cr / (Cr + Al) of spinel, 0.5-0.8) (Arai et al., 2003) and may be the hardest material from trace element analysis.

2.2. Sample preparation

De-ionized water, further purified (18.2 M Ω resistivity) by a milli-Q Element A-10 system (Millipore, Japan), was used throughout the procedure. All acids are of Ultrapur grade (Kantokagaku, Japan).

Rock powders of 100 mg were weighted into screw-cap Savillex® Teflon® beakers, and 1 ml of HNO₃, 1 ml of HClO₄ and 1.5 ml of HF were added to each sample. This beaker was agitated in an ultrasonic bath in 10 minutes, and then the sample was heated to dissolve at 110° C in 3-7 days. The solution obtained was evaporated to achieve near dryness at 110° C in 9-12 hours. After evaporation, 1 ml of HNO₃ was added to the sample. The beaker was capped again and heated at 110° C in more than 2 hours. Moreover, 4 ml of water was added to the sample and heated again at 110° C in more than 4 hours. This solution was diluted with water to 100 ml by using a Teflon® PFA volumetric flask (VIT-LAB, Germany). In the case of the sample with dilution factor of more than 1000 times, the solution was further diluted with 1.2 % HNO₃ in a test tube. Three solution samples were produced for each rock sample

A rock blank was prepared as follows. Water was “grinded” in an agate mortar, and was poured into a screw-cap Savillex® Teflon® beaker. At 110° C, this beaker was dried up completely. Addition of acids to the rock blank and the subsequent preparations were similar to those for a rock sample.

2.3. Instrumentation and data acquisition

The ICP-MS used in this study is X7 (Thermo Electron corporation, UK) installed at Kanazawa University. Details of operating conditions are shown in Table 1. An autosampler was used to supply the ICP-MS with samples, standards and wash acid. The system is

optimized to give a sensitivity of approximately 120,000 cps for ^{115}In in a $1 \text{ ng} \cdot \text{ml}^{-1}$ tuning solution and a yield for CeO^+ formation of about 3 %.

Data were acquired using software supplied by the manufacturer in peak jumping mode: number of peak jump sweeps, 50; points per peak, 3; numbers of separation in atomic mass unit, 50; collector type, pulse counting; and dwell time shown in Table 2. Mixed standard solutions were prepared from ATX-1, -7, -8, and -13 (SPEX, USA).

Internal standardization

In order to correct for signal drift during each analytical run, 1ppb of ^{115}In was used for all masses. The internal standard, In 1 ppb, was added to standards, rock blanks and samples. The sensitivity of 1 ppb In in a solution represents R . We estimate intensity of an element in a solution by internal standard correction, I_{ci} , as follows:

$$I_{ci} = I / (R / R_b) \quad \text{---(1)}$$

where I is the present intensity of the element in the solution, and R_b is sensitivity of In in the standard blank.

Calibration methods

The sensitivities of all elements were examined by external calibration in standard solutions. Calibration lines for each element were drawn through three points of calibration (0.1, 1 and 10 ppb) and the point of origin. The corrections for intensities in standards, samples and rock blanks were accomplished prior to estimations of concentrations. Because the concentration of each element in the standard blank is defined as 0 ppm, an intensity of an element in a solution, I_{cb} , is subtracted by the intensity in the blank, I_b , from an intensity estimated by internal standard correction,

$$I_{cb} = I_{ci} - I_b \quad \text{---(2)}$$

The sample solution corrected by removal contamination during preparation is shown as

$$I_c = I_{cbi} - I_{cbrb} \quad \text{---(3)}$$

where I_{cbrb} is I_{cb} of the rock blank.

In some samples, quantitative determinations of element concentrations were performed by the standard addition method. Calibration lines for each element are drawn through the points of the addition standard (1 ppb) to the sample and the point of the zero addition standard to the sample. In the case of standard addition method, the I_b is an inten-

Table 1. X7 operating conditions.

Forward power	1300 W
Reflected power	< 5 W
Nebuliser gas flow rate	0.92 l/min
Cooling gas flow rate	13 l/min
Auxiliary gas flow rate	0.8 l/min
Sample uptake rate	0.6 ml/min
Water cooled single-pass spray chamber maintained at 3 °C	

Table 2. Data acquisition characteristics and detection limits (D.L.). Individual detection limits with dilution factors of rock blanks are shown in sub-columns.

element	mass	dwell time (s)	D.L. of standard blanks (ppt)				D.L. of rock blanks (ppb)			
			x 1,000	x 5,000	x 10,000	x 50,000	x 100,000	x 50,000	x 100,000	x 100,000
Li	7	0.02	0.20-0.84	0.41-0.71	1.8-3.9	2.9-6.7	12-16	23		
Be	9	0.1	0.23-0.55	0.47-0.57	1.5-2.5	3.9-5.5	17-20	37		
Sc	45	0.1	5.9-9.4	6.3-124	30-584	42-1200	273-433	589		
Rb	85	0.02, 0.1	0.26-0.49	0.7-1.5	2.0-5.6	3.5-10	16-49	102		
Sr	88	0.1	0.20-0.33	0.46-0.77	1.4-2.8	1.7-3.6	10	18		
Y	89	0.1	0.066-0.13	0.15-0.24	0.35-0.74	0.58-1.3	4.6-5.7	12		
Zr	90	0.1	0.15-0.22	0.43-0.52	0.73-1.3	1.3-2.5	6.7-8.1	14		
Nb	93	0.1	0.10-0.22	0.16-0.34	0.57-1.4	1.4-2.9	7.6-9.5	22		
Cs	133	0.02	0.09-0.19	0.10-0.17	0.43-0.59	0.86-1.7	4.3-6.3	13		
Ba	137	0.1	0.84-1.41	2.1-2.9	5.8-8.9	7.2-15	33-38	72		
La	139	0.1	0.044-0.10	0.12-0.20	0.33-0.50	0.42-0.96	2.1-2.8	6.1		
Ce	140	0.1	0.052-0.10	0.17-0.30	0.46-0.59	0.77-1.3	2.6	4.8		
Pr	141	0.1	0.037-0.065	0.064-0.092	0.20-0.33	0.29-0.64	2.2	5.0		
Nd	146	0.1	0.080-0.13	0.25-0.37	0.56-0.80	0.86-1.3	3.5-3.9	6.0		
Sm	147	0.1	0.065-0.19	0.15-0.21	0.50-1.0	0.64-1.7	5.2-6.2	13		
Eu	153	0.1	0.031-0.050	0.050-0.081	0.16-0.31	0.37-0.68	1.9-2.1	4.0		
Gd	157	0.1	0.077-0.17	0.12-0.21	0.32-0.78	0.72-1.8	3.5-5.0	12		
Tb	159	0.1	0.007-0.023	0.017-0.028	0.050-0.092	0.098-0.31	0.52-0.67	1.2		
Dy	163	0.1	0.033-0.072	0.082-0.11	0.19-0.31	0.36-0.95	1.7	5.4		
Ho	165	0.1	0.008-0.024	0.021-0.031	0.052-0.1	0.092-0.30	0.51-0.65	1.6		
Er	166	0.1	0.035-0.056	0.064-0.084	0.18-0.29	0.40-0.68	2.1-3.0	3.4		
Tm	169	0.1	0.009-0.020	0.015-0.024	0.050-0.10	0.11-0.27	0.63-0.66	1.3		
Yb	172	0.1	0.024-0.047	0.076-0.094	0.16-0.32	0.30-0.84	1.5-1.7	3.5		
Lu	175	0.1	0.006-0.016	0.017-0.024	0.045-0.083	0.090-0.26	0.33-0.41	0.6		
Hf	178	0.1	0.030-0.067	0.069-0.095	0.13-0.26	0.28-0.75	1.2-1.9	2.9		
Ta	181	0.1, 0.5	0.048-0.24	0.032-0.19	0.20-0.72	0.58-2.6	2.2-3.7	7.3		
Pb	208	0.1	0.25-0.50	0.76-1.2	1.9-2.9	2.6-4.9	11-14	24		
Bi	209	0.1	0.033-0.062	0.042-0.061	0.12-0.24	0.27-0.61	1.1	2.5		
Th	232	0.1	0.027-0.056	0.047-0.071	0.15-0.23	0.21-0.45	1.1-1.9	2.3		
U	238	0.1	0.019-0.036	0.035-0.049	0.068-0.12	0.090-0.31	0-0.64	1.1		

sity of an element in the rock blank. An intensity of an element in the zero addition standard to the sample or the addition standard to sample is corrected as follows:

$$I_c = I_{ci} - I_b \quad \text{---(4)}$$

The sequence of an analytical run

Analyses of the 3 % HNO₃ and the following blank proceeded to analyses of a group of sub-samples, standards or rock blanks. The 3 % HNO₃ was used to wash out memory effects. In order to examine signal drifts of elements through the run, the blank correction in a sample or a rock blank is generally as follows:

$$I_c = I_{ci} - I_{bi} \quad \text{---(5)}$$

where I_{bi} is the calculated intensity by internal standard correction in the preceding blank.

A sample list in the run 031104 is given in Table 3 as an example. Blanks were analyzed in both before and after analyses of each group of sub-samples, standards and rock blanks to investigate signal variations of elements throughout the run 031104. Original intensities are shown in Figure 1. Intensities of all elements in the blank (the order 7 in Table 3) after analysis of standards increased in counts comparing with the blank in the order 2, i. e. before analysis of standards. The treatment of 3 % HNO₃ in the order 8 suppressed the increases of counts in REE, Hf, Ta, Pb, Bi, and Th afterward. Memory effects were partly washed out for Li, Rb and Cs, but the counts for these elements are higher than those in blank in the order 2 before analysis of standards. These intensities of rock blanks in the orders 10 to 12 are corrected as follows:

$$I_{cbrb} = I_{ci} (\text{rock blank}) - (I_{bi} (\text{the order 9}) + I_{bi'} (\text{the order 13})) / 2. \quad \text{---(7)}$$

The corrected intensities of other elements for rock blanks are as the equation (6).

The blank after analysis of sub-samples was in higher intensity of V than those before their analysis. The V intensity of sample is corrected as follows:

$$I_c = I_{ci} (\text{sample}) - I_{ci} (\text{the blank before sub-samples}). \quad \text{---(8)}$$

Memory effects of Sc appeared after analysis of peridotite xenoliths (x 5,000). Also the analysis of JB-2 (x 10,000) left memory effects of Rb, Sr, Y, Zr, Ba and Cs. Basically, the intensities of these elements are corrected by the equation (6). Because contents of Sr, Y, Zr and Ba were different between jars A and B, corrected intensities in the JB-2 are represented by ;

$$I_c = I_{ci} (\text{JB-2}) - I_{ci} (\text{the blank in the order 25}). \quad \text{---(9)}$$

Memory effects of Li, Be, Rb and Cs were related not only with analyses of standards in the run 031104 but also with former runs. The Li, Be, Rb and Cs in the blank decreased simply in counts from the highest intensities in the order 7 to 400, 7, 1200 and 600, respectively, with time through the run 031104. These intensities of samples are corrected as follows:

$$I_c = I_{ci} (\text{sample}) - (I_{ci} (\text{the blank before sub-samples}) - I_{ci} (\text{the blank after sub-samples})) / 2. \quad \text{---(10)}$$

Intensities in sub-samples that were kept constant with time between the blank analy-

Table 3. The sample list in the run 031104 for analysis of Avacha peridotite xenoliths (AX-106, -10 and -213). The blank was divided into two jars (A and B).

order	sample	dilution	remarks	order	sample	dilution	remarks
1	3 % HNO3			30	3 % HNO3		
2	blank		jar A	31	blank		jar B
3	standard blank			32	AX-106-1	1,000	
4	standard 0.1 ppb			33	AX-106-2	1,000	
5	standard 1 ppb			34	AX-106-3	1,000	
6	standard 10 ppb			35	blank		jar B
7	blank		jar A	36	3 % HNO3		
8	3 % HNO3			37	blank		jar A
9	blank		jar A	38	AX-10-1	1,000	
10	rock blank	10,000		39	AX-10-2	1,000	
11	rock blank	5,000		40	AX-10-3	1,000	
12	rock blank	1,000		41	blank		jar A
13	blank		jar A	42	3 % HNO3		
14	AX-106-1	5,000		43	blank		jar A
15	AX-106-2	5,000		44	AX-213-1	1,000	
16	AX-106-3	5,000		45	AX-213-2	1,000	
17	blank		jar A	46	AX-213-3	1,000	
18	3 % HNO3			47	blank		jar B
19	blank		jar A	48	3 % HNO3		
20	AX-10-1	5,000		49	blank		jar B
21	AX-10-2	5,000		50	JB2	10,000	
22	AX-10-3	5,000		51	blank		jar B
23	blank		jar A	52	3 % HNO3		
24	3 % HNO3			53	blank		jar B
25	blank		jar A	54	rock blank	10,000	same as 10
26	AX-213-1	5,000		55	rock blank	5,000	same as 11
27	AX-213-2	5,000		56	rock blank	1,000	
28	AX-213-3	5,000		57	rock blank	1,000	same as 12
29	blank		jar B	58	blank		jar B

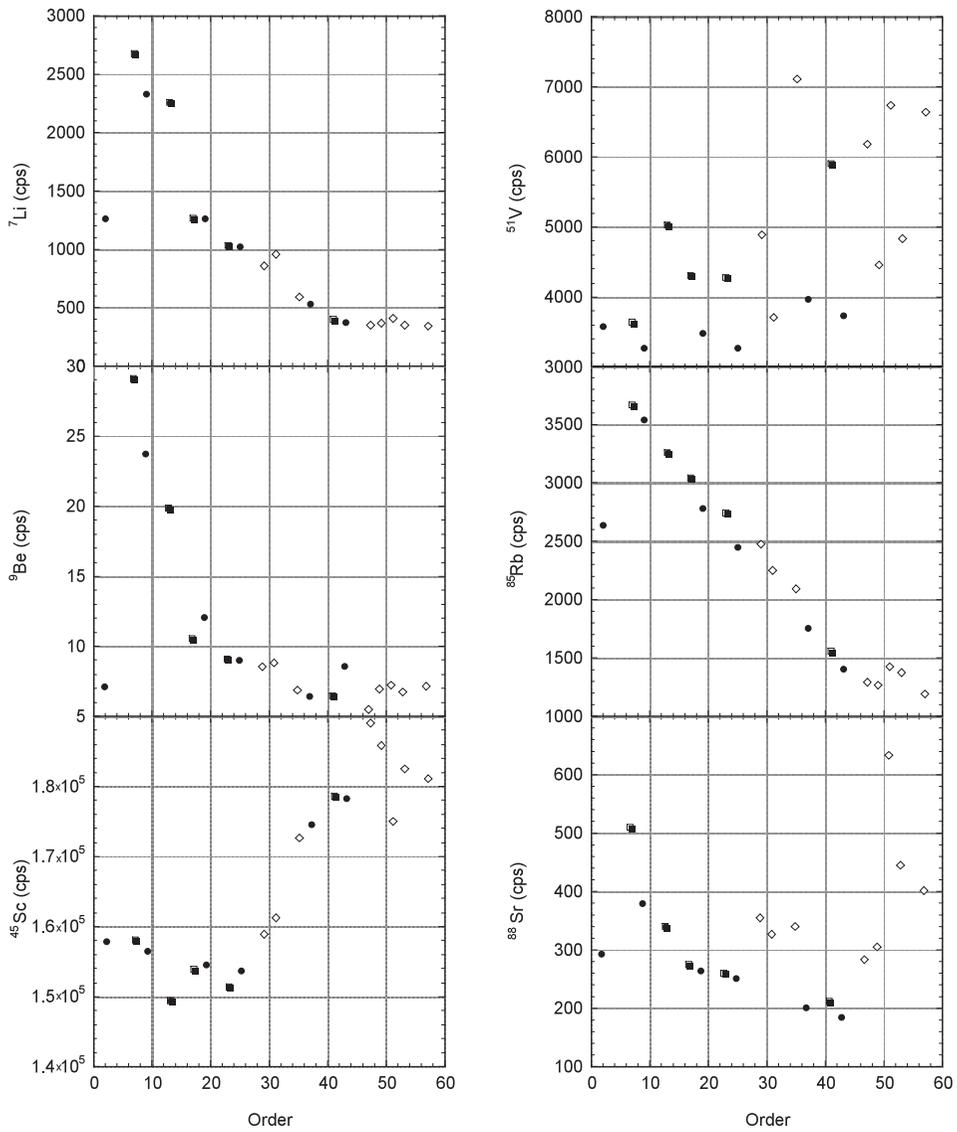


Figure 1 Profiles of intensities corrected for internal standard in blanks in the run 031104 (Table 3). *Filled circle*; the blanks in jar A analyzed before standards, rock blanks and samples. *Filled square*; the blanks in jar A analyzed after standards, rock blanks and samples. *Opened diamond*; the blanks in jar B. *cps*; counts per second

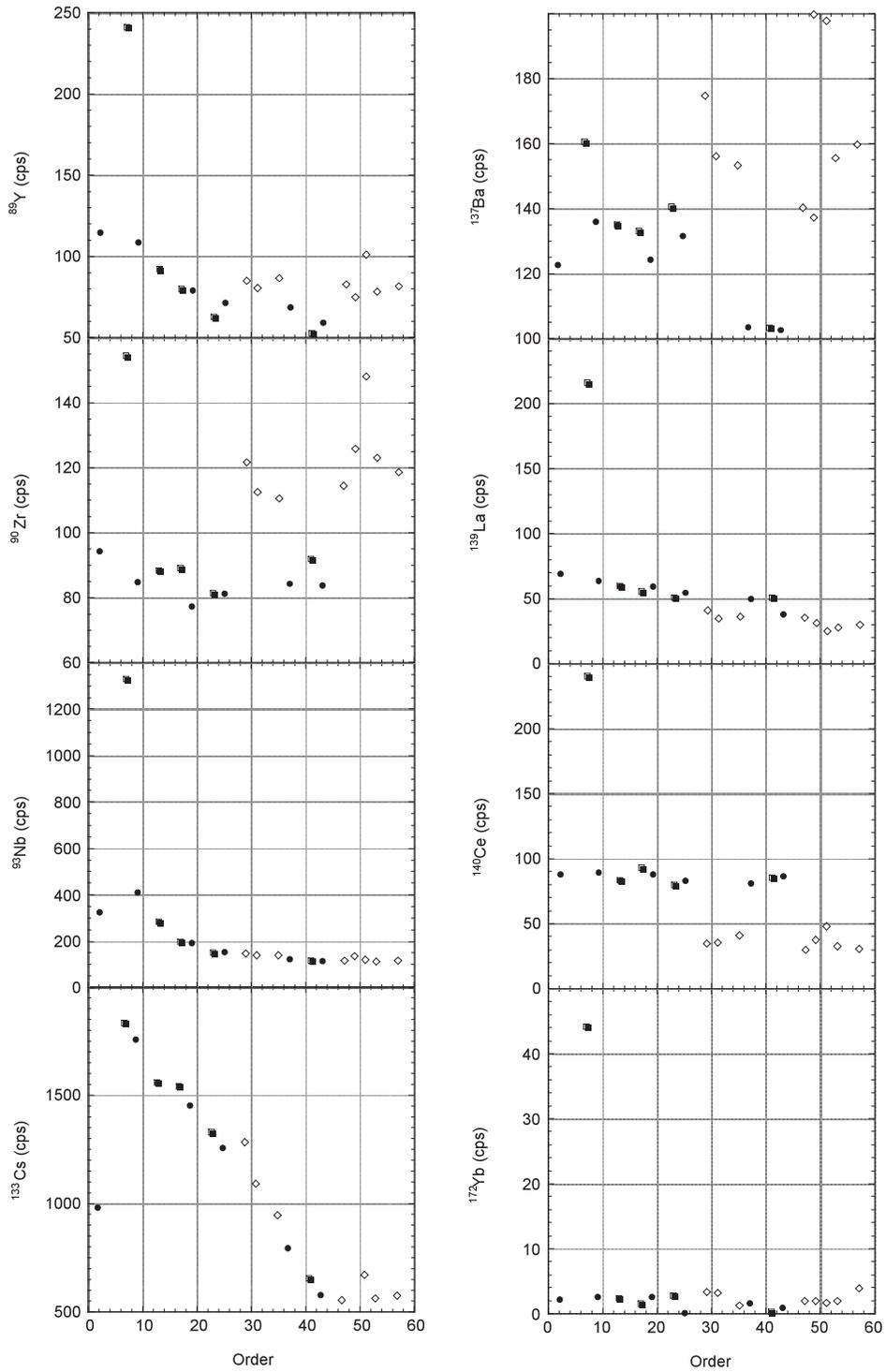


Figure 1 (continued)

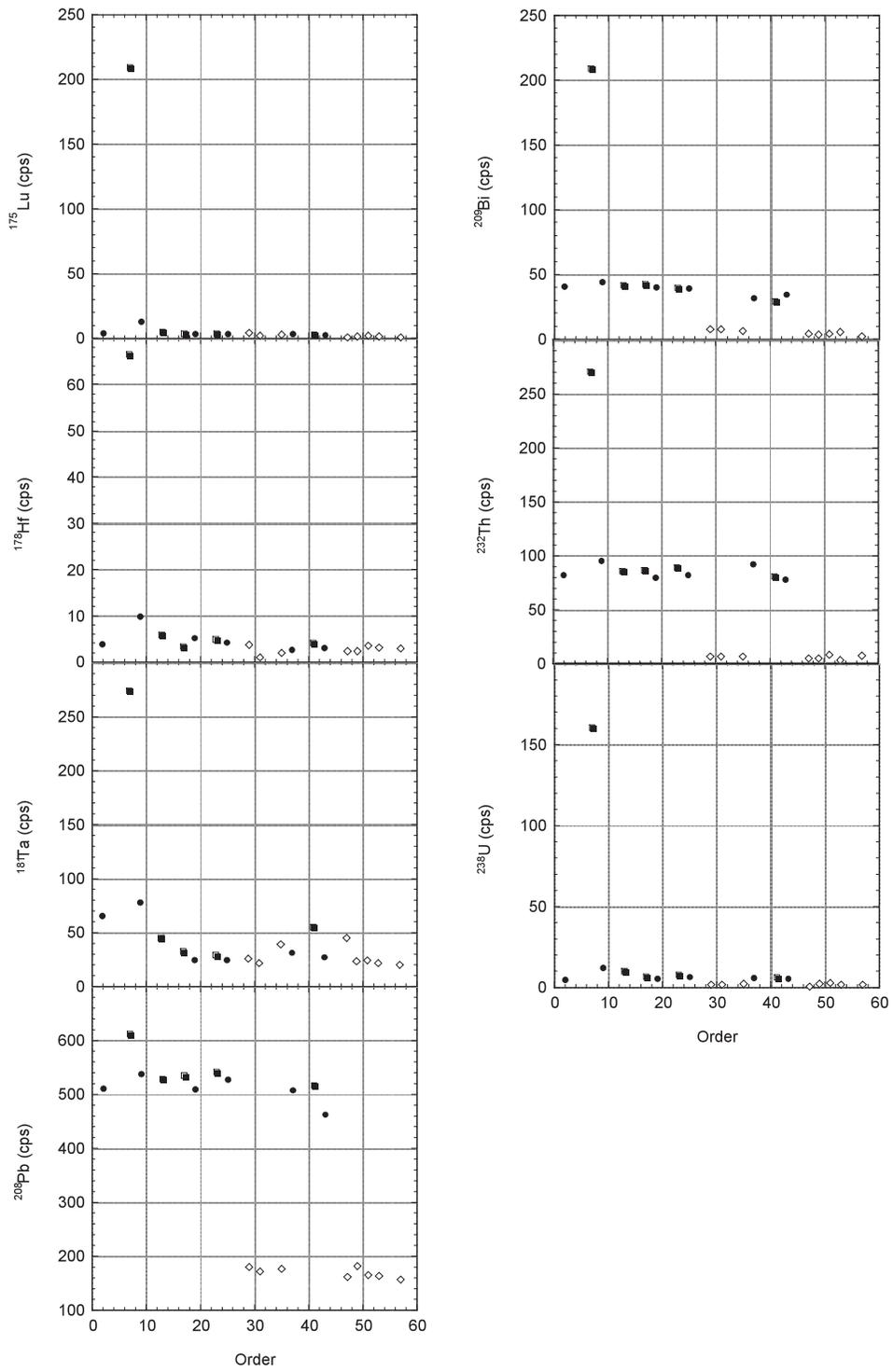


Figure 1 (continued)

Table 4. Measured trace element concentrations (ppm), precision estimates, reference values, and working values for JB-2. *ES* and *SA* mean external standard calibration method and standard addition calibration method, respectively. *Italic numbers* indicate values above higher limits of concentrations of calibration lines. *The values with asterisks* in reference denote preferable values.

run	30829		30902		30919	30924	31030	31105	30919	31003
calibration method	ES	RSD	ES	RSD	ES	ES	ES	ES	ES	SA
number of solutions	3	(%)	3	(%)	1	1	1	1	1	1
dilution	10,000		10,000		10,000	10,000	10,000	10,000	50,000	10,000
Li	8.3	3	8.43	2	8.41	6.8	7.26	7.16	9.39	7.73
Be	0.261	7	0.28	3	0.258	0.207	0.238	0.247	0.311	0.207
Sc	49.1	0.8	46.9	1	43.2	45.9	62.9		24.5	62.2
V	<i>521</i>	0.8	<i>521</i>	0.5	<i>477</i>	<i>453</i>	<i>577</i>	<i>482</i>	<i>534</i>	<i>454</i>
Cr	22.9	0.6	23.6	0.5	22	20.7	23.1	24.1	19.6	23.7
Ni	16.7	2	16.3	0.2	14.1	13			10.5	17.4
Rb	5.49	0.5	5.55	2	5.32	5.22	5.71	5.62	5.05	5.72
Sr	<i>165</i>	0.2	<i>166</i>	0.5	<i>164</i>	<i>157</i>	<i>170</i>	<i>168</i>	160	<i>158</i>
Y	20.2	0.2	20.2	0.4	19.8	19	20.6	20.5	19.6	20.2
Zr	43.3	0.3	44.2	0.7	43.1	41.1	44.5	44.5	42.3	<i>43</i>
Nb	0.443	3	0.456	4	0.411	0.423	0.455	0.471	0.441	0.462
Cs	0.762	3	0.753	1	0.748	0.727	0.743	0.774	0.738	0.756
Ba	<i>208</i>	0.2	<i>212</i>	0.5	<i>210</i>	<i>197</i>	<i>211</i>	<i>212</i>	208	<i>197</i>
La	2.12	0.3	2.1	0.7	2.1	1.96	2.12	2.13	2.08	2.11
Ce	6.02	0.3	6.03	0.7	6.02	5.63	6.08	6.04	5.95	6.06
Pr	1.04	0.3	1.05	0.8	1.04	0.98	1.05	1.05	1.04	1.06
Nd	5.92	0.5	5.93	0.4	5.99	5.52	5.84	5.86	5.99	5.86
Sm	2.13	1	2.13	0.6	2.16	2.01	2.08	2.13	2.1	2.15
Eu	0.851	0.5	0.852	0.6	0.866	0.797	0.846	0.841	0.858	0.846
Gd	2.82	0.5	2.81	0.3	2.85	2.68	2.79	2.79	2.78	2.75
Tb	0.553	0.2	0.551	0.5	0.563	0.52	0.546	0.543	0.555	0.553
Dy	3.73	0.4	3.7	0.8	3.82	3.49	3.63	3.7	3.72	3.67
Ho	0.792	0.6	0.787	0.6	0.814	0.746	0.789	0.785	0.794	0.785
Er	2.48	0.6	2.45	0.9	2.54	2.31	2.43	2.42	2.52	2.5
Tm	0.356	0.3	0.35	0.8	0.371	0.335	0.352	0.348	0.364	0.348
Yb	2.44	0.7	2.42	0.7	2.51	2.28	2.37	2.36	2.5	2.34
Lu	0.365	0.5	0.363	0.6	0.378	0.343	0.359	0.361	0.374	0.36
Hf	1.49	0.4	1.44	0.2	1.51	1.37	1.41	1.41	1.46	1.42
Ta	0.0756	13	0.0646	9	0.054	0.0458	0.0598	0.0649	0.072	0.0576
Pb	4.84	1	4.84	0.3	5.12	4.56	4.76	4.84	5.05	5.18
Bi	0.0271	3	0.0281	2	0.0301	0.0293	0.026	0.0278	0.0298	0.0328
Th	0.242	2	0.245	0.5	0.261	0.239	0.238	0.239	0.283	0.241
U	0.147	0.5	0.148	0.7	0.158	0.138		0.144	0.17	0.155

ses are corrected by the equation (6). The blank of the jar B had higher contents of Sr, Y, Zr and Ba and lower contents of Ce, Pb, Bi and Th than that of the jar A. These element intensities in the blank of the jar B are corrected as follows:

$$I_{ci} = I_{ci} \text{ (the blank of the jar B)} - (I_{ci} \text{ (the blank in the order 47)} - I_{ci} \text{ (the blank in the order 43)}). \quad \text{---(11)}$$

Detection limits

A detection limit (*DL*) of an element is calculated as follows:

$$DL = 3 \times (I_{cb} \times (\text{dwell time}))^{0.5} / A \quad \text{---(12)}$$

31003 SA 1 50,000	31003 SA 1 100,000	31010 SA 1 10,000	reference (Imai et al., 1995)	Working values by ICP-MS technique					
				et al. (1992)	Barrat (1996)	Makishima & Nakamura (1997)	Makishima et al. (1999)	Dulski (2001)	Makishima et al. (2002)
7.72	7.47		7.78	9.22					
0.25	0.241		0.26 *	0.22					
50.8	47.2		53.5	53.29					
424	420		575	546.9					
23	23		28.1	24.13					25
14.6	14.4		16.6	9.51					14.2
5.6	5.42		7.37	6.59		7.13		6.3	
143	114		178	176.8		177		179	
20.2	19.5		24.9	24.48		25.9		22.3	
41.8	38.6		51.2	44.8			45.9, 46	50	
0.453	0.446		1.58 *	0.8			0.43, 0.461		
0.756	0.751		0.85	0.78		0.794		0.78	
180	138		222	211.9		229		217	
2.15	2.08	2.13	2.35	2.41	2.18	2.19		2.22	
6.02	5.89	6.07	6.76	6.6	6.48	6.43		6.4	
1.06	1.04	1.05	1.01	1.11	1.14	1.13		1.13	
5.94	5.76	5.78	6.63	6.74	6.21	6.39		6.1	
2.13	2.05	2.12	2.31	2.38	2.26	2.27		2.11	
0.846	0.831	0.839	0.86	0.85	0.84	0.86		0.82	
2.74	2.72	2.76	3.28	3.01	3.24	3.12		3.2	
0.553	0.55	0.554	0.6	0.6	0.58	0.592		0.56	
3.77	3.56	3.68	3.73	3.85	3.8	4.13		3.8	
0.799	0.785	0.8	0.75	0.86	0.86	0.898		0.84	
2.42	2.39	2.47	2.6	2.5	2.47	2.47		2.48	
0.349	0.351	0.357	0.41	0.42		0.392		0.37	
2.39	2.31	2.42	2.62	2.63	2.45	2.6		2.46	
0.357	0.36	0.367	0.4	0.39	0.39	0.397		0.38	
1.38	1.37		1.49	1.4			1.47, 1.45	1.8	
0.0521	0.0551		0.13	0.19			0.0327		
4.81	4.67		5.36	4.95		5.28		5.1	
0.029	0.0283		0.033 *						
0.244	0.234		0.35	0.25		0.277		0.26	
0.15	0.144		0.18	0.1		0.166		0.148	

where A is sensitivity of the element. Datasets of detection limits in standard blanks and rock blanks are listed in Table 2. The standard blanks have detection limits of the order of ppt for Sc and Ba and of the order of sub-ppt for the other elements. Detection limits of all elements in rock blanks increase from the order of sub-ppb to ppb with increasing the dilution factor from 1,000 to 100,000 times.

Dilution factors

We determined the extent of dilution from values of concentration of calibration standards, intensities below 2×10^6 cps (counts per seconds) under the pulse counting of detec-

Table 5. Measured trace element concentrations (ppm), precision estimates, reference values, and working values for JP-1. *ES* and *SA* mean external standard calibration method and standard addition calibration method, respectively. *Italic numbers* indicate values above higher limits of concentrations of calibration lines. *The values with asterisks* in reference denote preferable values.

run	030829		031106		reference (Imai et al., 1995)	Working values by ICP-MS technique				
	calibration method number of solutions dilution	ES 3 1,000	RSD (%) 6	SA 3 5,000		RSD (%) 10	Ionov et al. (1992)	Dulski (2001)	Takazawa et al. (2003)	Makishima & Nakamura (1997)
Li		1.59	8	1.38	4	1.79 *				
Be		0.0068	9	0.005	12	< 0.1 *				
Sc				7.72	12	7.24	7.6		7.6	
V		<i>38.6</i>	6	<i>26.7</i>	10	27.6		22		
Rb		0.223	8	0.229	1	0.80 *	0.34	0.5	0.32	0.34
Sr		0.502	2	0.502	2	3.32 *	0.6	0.63	0.59	0.57
Y		0.0843	3	0.0832	3	1.54		0.097	0.108	0.1
Zr		4.88	3	4.82	3	5.92	5	5.5	5.59	5.34
Nb		0.0521	29	0.0442	27	1.48	0.067		0.052	0.036
Cs		0.0291	22	0.0323	12	0.15 *			0.04	0.035
Ba		9.47	1	<i>9.16</i>	6	19.5	10.3	9.2	10.1	9.8
La		0.0252	2	0.0249	7	0.084	0.038	0.034	0.028	0.03
Ce		0.0531	2	0.0511	3	0.19 *	0.067	0.063	0.063	0.054
Pr		0.00722	2	0.0068	10	0.020 *	0.012	0.0089	0.0089	0.0071
Nd		0.0286	5	0.0272	4	0.072 *	0.039	0.033	0.034	0.033
Sm		0.00853	4	0.0077	4	0.019	0.019	0.009	0.1	0.013
Eu		0.00596	4	0.0058	10	0.004 *	0.0046	0.0021	0.003	0.0031
Gd		0.00955	6	0.0090	16	0.015 *	0.016	0.0092	0.012	0.013
Tb		0.00179	5	0.0018	7	0.003 *	0.0027	0.0016	0.0026	0.0026
Dy		0.0132	6	0.0118	10	0.022 *	0.02	0.0132	0.015	0.018
Ho		0.00302	3	0.0030	5	0.018 *	0.0052	0.003	0.0039	0.0043
Er		0.0119	1	0.0109	5	0.016 *	0.016	0.0112	0.012	0.014
Tm		0.00224	4	0.0021	5	< 0.041 *	0.0033	0.0023		
Yb		0.0190	2	0.0170	8	0.022	0.023	0.0209	0.019	0.021
Lu		0.00382	2	0.0034	3	0.0044 *	0.005	0.004	0.0042	0.0047
Hf		0.120	3	0.105	3	0.2	0.126	0.127	0.116	0.12
Ta		0.0095	92	0.0050	26	0.02 *	0.0048		0.006	0.0036
Pb		0.0918	53	0.086	61	0.12 *	0.18	0.18	0.08	0.09
Bi		0.00218	6	0.0022	7					
Th		0.0113	2	0.0097	3	0.19	0.013	0.012	0.014	0.012
U		0.0113	2	0.0102	4	0.036	0.013		0.012	0.012

tor and detection limits. Generally, the dilution factor grows larger as the sample has higher trace element contents. In this study, basically, we adopted the dilution factor of 1,000 or 5,000 times for peridotites and of 10,000 for basalt, gabbro and andesite.

3. Results and discussion

The values of trace-element concentrations for all rock samples are listed in Tables 4 to 8. In the case of basalt (JB-2), gabbro (JGb-2) and andesite (JA-1), the relative standard deviation (RSD) is lower than 5 % for Rb, Sr, Y, Cs, REE, Pb, Bi, Th and U. The RSD is up to several tens percent for HFSE (Zr, Nb, Hf and Ta). The RSD of all elements examined are larger in peridotite (JP-1 and AX) than in basalt, gabbro and andesite.

Table 6. Measured trace element concentrations (ppm), precision estimates, reference values, and working values for JA-1. *ES* and *SA* mean external standard calibration method and standard addition calibration method, respectively. *Italic numbers* indicate values above higher limits of concentrations of calibration lines. *The values with asterisks* in reference denote preferable values.

run	030829		reference (Imai et al., 1995)	Working values by ICP-MS technique					
	calibration method number of solutions dilution	ES 3 10,000		RSD (%) 3	Yoshida et al. (1992)	Barrat (1996)	Makishima & Nakamura (1997)	Moriguchi & Nakamura (1998)	Makishima et al. (1999)
Li		11.2	3	10.8	13.92				
Be		0.524	4	0.5	0.51				
Sc		26.9	2	28.5	33.83				
V		97.2	3	105	131.7				
Cr		5.62	11	7.83	4.14				
Ni		3.88	9	3.49 *	1.36				4.65
Rb		9.74	0.4	12.3	13.76		12.4		1.9
Sr	247		1	263	263.2		270		
Y		25.1	1	30.6	30.79		32.7		
Zr		77.2	1	88.3	83.47			81.2	
Nb		1.16	2	1.85	1.51			1.18, 1.22	
Cs		0.611	3	0.62	0.7		0.652		
Ba	293		2	311	313.5		318		
La		4.75	1	5.24	5	4.64	5.13		
Ce		12.5	1	13.3	12.97	13.06	14.1		
Pr		1.99	2	1.71	2.02	2.04	2.19		
Nd		10.6	1	10.9	10.76	10.29	11.5		
Sm		3.32	0.9	3.52	3.45	3.22	3.49		
Eu		1.19	2	1.2	1.08	1.06	1.2		
Gd		4.02	2	4.36	4.06	3.99	4.37		
Tb		0.734	2	0.75	0.75	0.69	0.754		
Dy		4.73	2	4.55	4.64	4.73	5		
Ho		0.979	2	0.95	0.97	0.99	1.13		
Er		3.05	2	3.04	3	2.89	3.04		
Tm		0.430	1	0.47	0.46		0.473		
Yb		2.96	2	3.03	2.91	2.87	3.13		
Lu		0.445	2	0.47	0.43	0.45	0.481		
Hf		2.57	3	2.42	2.39			2.51, 2.47	
Ta		0.122	5	0.13	0.19			0.107	
Pb		5.61	2	6.55			5.99		
Bi		0.0049	5	0.0091					
Th		0.738	2	0.82	0.82		0.808		
U		0.355	3	0.34	0.34		0.392		

3. 1. Reproducibility

In order to investigate reproducibility in response to differences of date, calibration method and dilution factor, we analyzed the same samples, JB-2 and JP-1, under the various conditions.

Difference in date

The JB-2 solution with dilution factor of 10,000 was analyzed through 5 analytical runs using the external standard calibration method. The differences of concentration among analytical runs are shown in Figure 2. While the relative differences of light-mass elements (Li-Ni) range from 0.7 to 1.3, the concentrations of middle- to heavy-mass ele-

Table 7. Measured trace element concentrations (ppm), precision estimates, reference values, and working values for JGb-2. *ES* and *SA* mean external standard calibration method and standard addition calibration method, respectively. *Italic numbers* indicate values above higher limits of concentrations of calibration lines.

run	030829		reference (Imai et al., 1995)	Working values by ICP-MS technique (Dulski, 2001)
calibration method	ES	RSD		
number of solutions	3	(%)		
dilution	10000			
Li	15.4	6	15.7	
Be	0.142	11		
Sc	18.9	7	24.7	
V	<i>170</i>	3	174	
Cr	<i>119</i>	3	125	
Ni	17.1	3	13.6	
Rb	1.85	4	2.9	2.35
Sr	<i>400</i>	3	438	447
Y	3.13	2	4.5	3.43
Zr	5.82	4	11.6	7.66
Nb	0.642	6	1.9	
Cs	0.527	1	0.51	0.560
Ba	32.1	3	36.5	34.1
La	1.43	3	1.5	1.47
Ce	2.98	2	3.0	3.06
Pr	0.385	3	0.39	0.415
Nd	1.81	3	1.8	1.81
Sm	0.493	2	0.51	0.49
Eu	0.596	3	0.59	0.610
Gd	0.579	4	0.48	0.612
Tb	0.101	2	0.15	0.097
Dy	0.635	3	0.60	0.640
Ho	0.129	2	0.15	0.134
Er	0.393	4	0.36	0.389
Tm	0.0575	2	0.059	0.056
Yb	0.390	3	0.39	0.384
Lu	0.0590	2	0.062	0.058
Hf	0.230	6	0.25	0.3
Ta	0.119	30	0.29	
Pb	0.880	2	1.5	1.07
Bi	0.0208	2	0.022	
Th	0.143	5	0.19	0.1
U	0.0231	7	0.041	0.026

ments except Ta are stable within 10 % of relative differences. The analysis of JB-2 in the run 030924 is inferred to fail in the last sample preparation, because it yielded clearly lower concentrations of REE than in the other runs.

In the runs 030829, 030902 and 030919, dwell time of Ta was 0.1 seconds, whereas the other runs were performed under the condition of 0.5 seconds of the Ta dwell time. In the following discussion, the concentration of Ta in the run 031030 is a representative value for JB-2 using the external calibration method under the dilution factor of 10,000.

Difference in dilution factor

In the case of using external standard calibration method, the JB-2 solution prepared with a dilution factor of 50,000 in the run 030919 resulted in concentrations in Li, Be, Ni, Cr, Ta, Th and U showing > 10 % differences to the solution with a lower dilution factor (x 10,000). The REE concentrations show the differences within 3 %. The large differences for the former elements are due not to an error of sample dilution but to the difference of concentration between blanks.

The limits of determinations of values depend on the dilution factors in the case of using standard addition calibration method in this study. Analyses of JB-2 solutions with various dilution factors (x 10,000, 50,000, 100,000) yield various Sc, V, Sr, Ba concentrations in the run 031003 (Table 4). However, most of the elements concentration determined below higher limits of concentration in calibration lines show < 5 % of relative differences among solutions in this run. These results indicate that a value without a calibration line is possibly doubtful.

Difference in calibration method

Comparing two types of calibration method in the JB-2 solution with dilution factor of 10,000, the concentrations of elements from Cr to Ta have relative differences within 5 %.

Summary of the reproducibility of JB-2 analysis

The concentrations of middle-mass elements (Rb-Hf) without one outer calibration line can be reproduced even if we change date of analysis, dilution factor (x 10,000 or 50,000), and calibration method. Light-and heavy-mass elements concentrations, however, show various values within 50 % of relative differences.

The reproducibility of peridotite

Incompatible trace-element concentrations are generally lower in peridotite than in basalt. In order to examine the reproducibility for trace-element analysis of peridotite, JP-1 and Avacha peridotite xenoliths were analyzed with various calibration methods and dilution factors (x 1,000 or 5,000). The relative differences among the runs are plotted in Figures 3 and 4. Most of the values of concentrations determined in the peridotite solutions are in < 15 % of relative differences to those obtained with a dilution factor of 1,000 by using external standard calibration method. In some cases, the values of alkaline elements (Li, Rb, Cs), HFSE (Zr, Nb, Hf, Ta), Pb, Bi, Th and U are dispersed among the runs under the various conditions. The dispersion for alkaline elements and HFSE is different in manner from JB-2, and possibly being due either to memory effects or to contamination of blanks.

Table 8. Measured trace element concentrations (ppm) for Avach peridotite xenoliths (AX-10, -106, -159, -213, -629 and -729). ES and SA mean external standard calibration method and standard addition calibration method, respectively.

sample calibration method number of solutions dilution	AX-10						AX-106					
	ES		RSD		SA		ES		RSD		SA	
	3	(%)	3	(%)	3	(%)	3	(%)	3	(%)	3	(%)
	1000		5000		5000		1000		5000		5000	
Li	1.13	3	1.19	5	1.10	2	1.18	1	1.18	5	1.26	6
Be	0.0035	10	< D.L.		< D.L.		0.0018	17	0.004	77	< D.L.	
Rb	< D.L.		< D.L.		< D.L.		< D.L.		< D.L.		< D.L.	
Sr	1.43	3	1.42	1	1.40	3	0.435	0.2	0.438	1	0.423	4
Y	0.0919	4	0.0906	3	0.088	3	0.0507	4	0.0512	3	0.050	2
Zr	0.316	4	0.322	5	0.309	4	0.0911	2	0.0982	5	0.093	5
Nb	0.0137	8	0.0178	33	0.010	28	0.0092	13	0.0212	33	0.0069	59
Cs	0.0036	18	0.0086	59	< D.L.		0.0040	21	0.0072	59	< D.L.	
Ba	< D.L.	4	0.7	3	0.634	7	< D.L.	5	< D.L.	3	0.22	4
La	0.0218	7	0.0212	10	0.021	5	0.0123	10	0.0123	10	0.0120	10
Ce	0.0600	3	0.0574	7	0.059	5	0.0332	6	0.0325	7	0.0317	8
Pr	0.00953	3	0.0095	3	0.0097	5	0.0054	4	0.0057	3	0.0051	7
Nd	0.0470	4	0.0459	1	0.046	5	0.0253	4	0.0265	1	0.0246	6
Sm	0.0133	2	0.0121	9	0.011	14	0.0073	3	0.0073	9	0.007	18
Eu	0.00444	9	0.0047	11	0.0044	2	0.00208	9	0.0024	11	0.0021	20
Gd	0.0122	3	0.0126	2	0.011	1	0.0071	1	0.0067	2	0.007	5
Tb	0.00202	6	0.00204	1	0.0019	12	0.00128	3	0.00150	1	0.0013	8
Dy	0.0138	2	0.0136	9	0.0138	5	0.00819	2	0.0079	9	0.0080	8
Ho	0.00323	6	0.00349	6	0.0035	3	0.00189	6	0.00215	6	0.0019	17
Er	0.0142	4	0.0141	8	0.0137	5	0.00782	2	0.0082	8	0.0077	2
Tm	0.00270	5	0.00290	14	0.0028	6	0.00156	1	0.00181	14	0.0016	4
Yb	0.0260	1	0.0260	3	0.0257	7	0.0152	1	0.0155	3	0.0152	4
Lu	0.00513	1	0.00534	3	0.0049	8	0.00329	3	0.00359	3	0.0033	8
Hf	0.00748	5	0.00772	26	0.0076	0	0.0027	9	0.00409	26	0.0030	19
Ta	0.00754	102	0.0228	99	0.0144	76	0.00551	151	0.0225	99	0.0069	87
Pb	0.0755	65	0.057	127	< D.L.		0.351	123	0.348	127	0.337	120
Bi	0.00020	20	< D.L.		0.0004	55	0.00034	17	0.0003	41	< D.L.	
Th	0.00278	8	< D.L.		0.0030	14	0.00164	3	0.0016	30	0.0011	13
U	0.00125	9	0.00147	4	0.0013	5	0.00065	10	0.00087	4	0.0008	12

3. 2. Comparisons with other working values of geological standards

The relative differences of values of concentration in the run 030829 (external standard calibration method; dilution factor of 10,000 for JB-2, JA-1 and JGb-2 and of 1,000 for JP-1) of this study and previous studies using ICP-MS technique from the reference values (Imai, 1995), which were mainly determined to be mean values of reviewed datasets until 1991, are shown in Figures 5 to 8. In the case of JB-2 and JA-1, the relative differences in most of middle- to heavy-mass element concentrations determined by ICP-MS techniques including this study are confined within 20 % from the reference values (Figs. 5 and 7). Although the values of middle- to heavy-masses are different from reference values for JP-1 and JGb-2 (Figs. 6 and 8), the results in this study coincide well with other studies by ICP-MS technique.

The Nb values of all geological standards are commonly much lower than the reference values (Figs. 5 to 8). The values of Nb of JB-2 by various techniques are shown in

AX-159						AX-213					
ES	RSD	ES	RSD	SA	RSD	ES	RSD	ES	RSD	SA	RSD
3	(%)	3	(%)	3	(%)	3	(%)	3	(%)	3	(%)
1000		5000		5000		1000		5000		5000	
1.25	3	1.15	3	1.09	3	1.15	2	1.14	1	1.13	3
0.0035	18	0.001	66	<D.L.		0.0013	26	0.00499	16	<D.L.	
<D.L.		<D.L.		<D.L.		<D.L.		<D.L.		<D.L.	
0.363	2	0.360	2	0.350	2	0.117	2	0.119	4	0.108	1
0.0765	2	0.0740	2	0.074	1	0.0528	3	0.0536	2	0.0510	1
0.0620	2	0.058	2	0.064	5	0.0890	4	0.0979	5	0.0849	4
0.0307	44	0.0217	52	0.072	74	0.0101	21	0.0166	12	0.0096	13
0.0011	158	<D.L.		<D.L.		0.0015	46	0.0025	54	<D.L.	
0.274	4	0.263	4	0.20	5	<D.L.	3	0.2	7	0.128	2
0.0097	6	0.0093	4	0.009	7	0.0087	11	0.0085	10	0.008	3
0.0336	4	0.0336	4	0.031	5	0.0183	11	0.0189	10	0.016	4
0.00614	3	0.0058	10	0.006	11	0.00281	6	0.0031	6	0.002	5
0.0285	2	0.0288	4	0.026	2	0.0122	9	0.0145	12	0.012	2
0.0095	3	0.0108	0	0.009	4	0.0037	5	0.0037	4	<D.L.	
0.0029	2	0.0029	2	0.0026	4	0.00106	6	0.0012	6	0.0010	32
0.0096	5	0.0094	5	0.0082	6	0.00414	6	0.0046	12	0.0047	11
0.00174	1	0.00163	6	0.0016	3	0.00092	5	0.00117	7	0.0009	14
0.0125	4	0.0116	8	0.0111	7	0.00703	1	0.0071	7	0.0062	1
0.00327	2	0.00311	6	0.0029	3	0.00181	3	0.00210	5	0.0017	4
0.0141	3	0.0133	4	0.0127	2	0.00835	10	0.0092	9	0.008	11
0.00290	3	0.00312	3	0.0027	9	0.00162	3	0.00170	5	0.0016	11
0.0279	3	0.0278	4	0.0256	2	0.0153	4	0.0164	1	0.0140	1
0.00566	1	0.00554	3	0.0051	3	0.00313	4	0.00338	3	0.0029	1
0.00247	12	0.0026	28	0.0022	2	0.00240	8	0.0031	11	0.0023	3
0.0176	72	0.0179	78	0.120	65	0.00511	56	0.0173	31	0.0115	63
0.0278	25	0.024	20	<D.L.		0.063	8	0.073	7	0.019	75
0.00066	6	0.0007	32	<D.L.		0.00013	45	0.0011	7	<D.L.	
0.00202	35	0.0025	33	0.0013	75	0.00134	31	0.00309	17	0.0008	5
0.00184	1	0.00174	14	0.0017	6	0.00069	13	0.00110	5	0.0006	0

Figure 9 for comparison. The values determined by ICP-MS techniques are confined within narrow range from 0.43 to 0.8 ppm. In contrast the values determined by XRF are scattered from 0.2 to 3.8 ppm encompassing the range of ICP-MS data.

In JP-1, the values determined by ICP-MS techniques are lower than reference values. The values of La for JP-1 by various techniques are shown in Figure 10 as an example. They range widely from 0.025 to 27 ppm. The La values determined by ICP-MS techniques range narrowly again from 0.025 to 0.043 ppm, that is nearly the lowest of all ranges obtained by various techniques (Fig. 10). This indicates that the values of trace elements in JP-1 can be reproduced well under the various conditions (laboratory, machine and user), whereas they have been overestimated in some previous studies using other techniques because of their low concentrations (< 10s ppb).

Table 8
(continued)

sample calibration method number of solutions dilution	AX-629						AX-729			
	ES	RSD	ES	RSD	SA	RSD	ES	RSD	SA	RSD
	3	(%)	3	(%)	3	(%)	3	(%)	3	(%)
	1000		5000		5000		1000		5000	
Li	1.31	4	1.41	2	1.16	1	1.30	5	1.13	4
Be	0.0133	6	0.012	9	0.010	2	0.0030	8	<D.L.	
Rb	0.130	40	0.030	97	0.03	11	0.0181	95	<D.L.	
Sr	9.55	4	9.44	5	9.23	2	1.28	1	1.24	2
Y	0.459	4	0.449	4	0.473	0	0.130	1	0.124	3
Zr	1.52	5	1.48	4	1.55	1	0.218	2	0.215	3
Nb	0.0286	9	0.0157	12	0.0295	9	0.0172	7	0.0249	74
Cs	0.0107	3	0.0069	11	0.010	22	0.0018	55	<D.L.	
Ba	3.93	4	3.87	5	3.86	1	0.445	2	0.36	1
La	0.0959	5	0.0954	5	0.0991	0	0.0143	3	0.013	6
Ce	0.271	5	0.271	5	0.281	0	0.0391	1	0.035	4
Pr	0.0450	4	0.0439	4	0.0453	0	0.00766	1	0.0066	5
Nd	0.233	4	0.233	5	0.225	3	0.0381	3	0.0361	3
Sm	0.0701	3	0.0696	6	0.066	7	0.0146	1	0.013	13
Eu	0.0281	4	0.0282	6	0.0270	6	0.00582	2	0.0052	16
Gd	0.0751	3	0.0753	4	0.0714	2	0.0174	1	0.015	4
Tb	0.0136	4	0.0134	6	0.0137	5	0.00321	0.1	0.0031	13
Dy	0.0856	5	0.0855	3	0.0813	2	0.0233	1	0.021	2
Ho	0.0183	5	0.0180	5	0.0181	3	0.00514	1	0.00466	5
Er	0.0618	5	0.0609	4	0.0603	1	0.0177	1	0.0169	5
Tm	0.00973	3	0.00963	9	0.00938	3	0.00298	3	0.0028	6
Yb	0.0747	4	0.0755	4	0.0691	3	0.0250	0.1	0.0231	2
Lu	0.0128	2	0.0126	5	0.0120	0	0.00455	2	0.0042	3
Hf	0.0440	6	0.0447	7	0.0435	1	0.00731	4	0.0066	7
Ta	0.00226	17	0.0024	12	0.0197	9	0.0140	50	0.0882	115
Pb	0.0835	16	0.081	19	0.057	22	0.0190	31	<D.L.	
Bi	0.00109	22	0.0012	12	0.00	27	0.00061	23	0.00055	9
Th	0.0139	5	0.0142	3	0.0123	1	0.00249	21	0.0013	41
U	0.00511	5	0.00546	7	0.00478	7	0.00825	8	0.0007	22

4. Summary and conclusions

We have constructed the solution introduction ICP-MS technique at Kanazawa University, and determined the trace element concentrations in geological standards and peridotite xenoliths by this technique. The values of Rb to Hf in JB-2 in this study show reproducibility within 5 % of differences under the various conditions for changes in date of analysis, dilution factor and calibration method. In the case of peridotite with low trace-element concentrations, relative standard deviations and relative differences among the runs under the various conditions are larger than in basalt. The lowest detection limits are in the order of sub-ppb for rock blanks, but alkaline elements (Li, Rb, Cs), HFSE (Zr, Nb, Ta), Pb and Bi show dispersed values of concentration in the order of ppb.

The values of concentration of middle- to heavy-masses (Rb-U) in geological standards of this study coincide with those from other studies with ICP-MS techniques. The advantages of ICP-MS technique in comparison with other techniques are the excellent re-

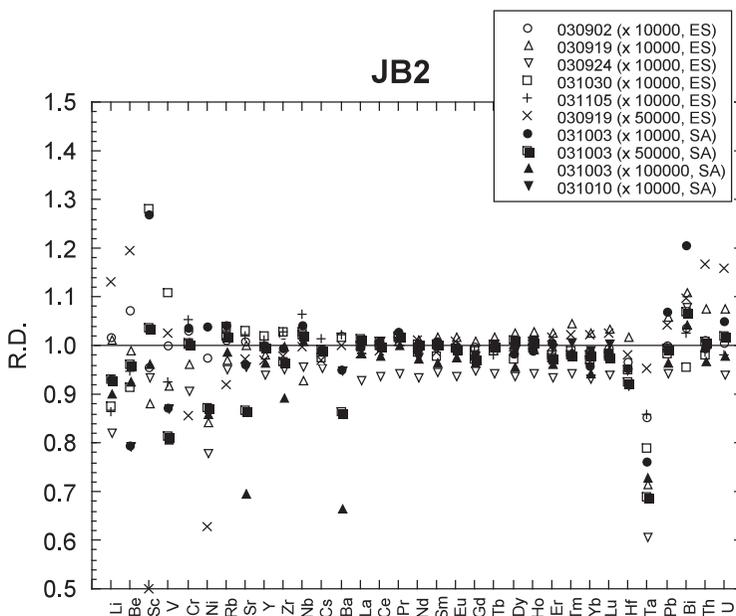


Figure 2 Relative differences (R.D.s) of the trace-element concentration in JB-2 under various conditions from the values determined by the run 030829: the external standard calibration method with a dilution factor of 10,000.

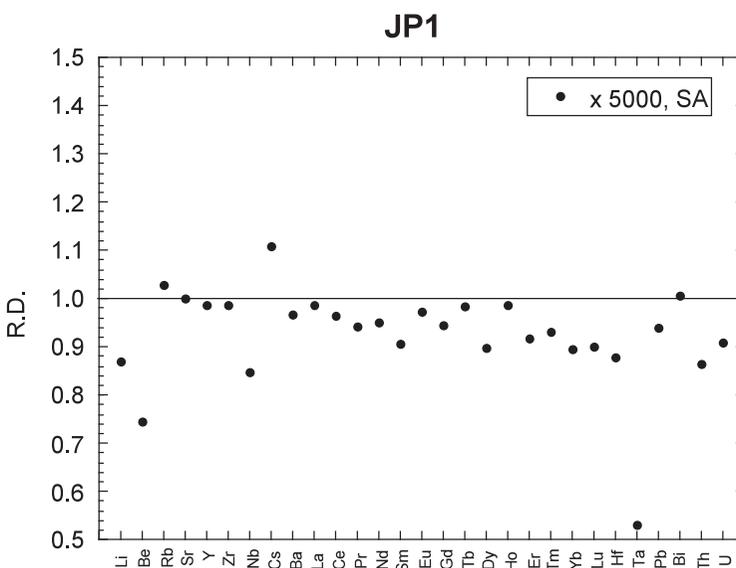


Figure 3 Relative differences (R.D.s) of the trace-element concentration in JP-1 under various conditions from the values determined by the run 030829: the external standard calibration method with a dilution factor of 1,000.

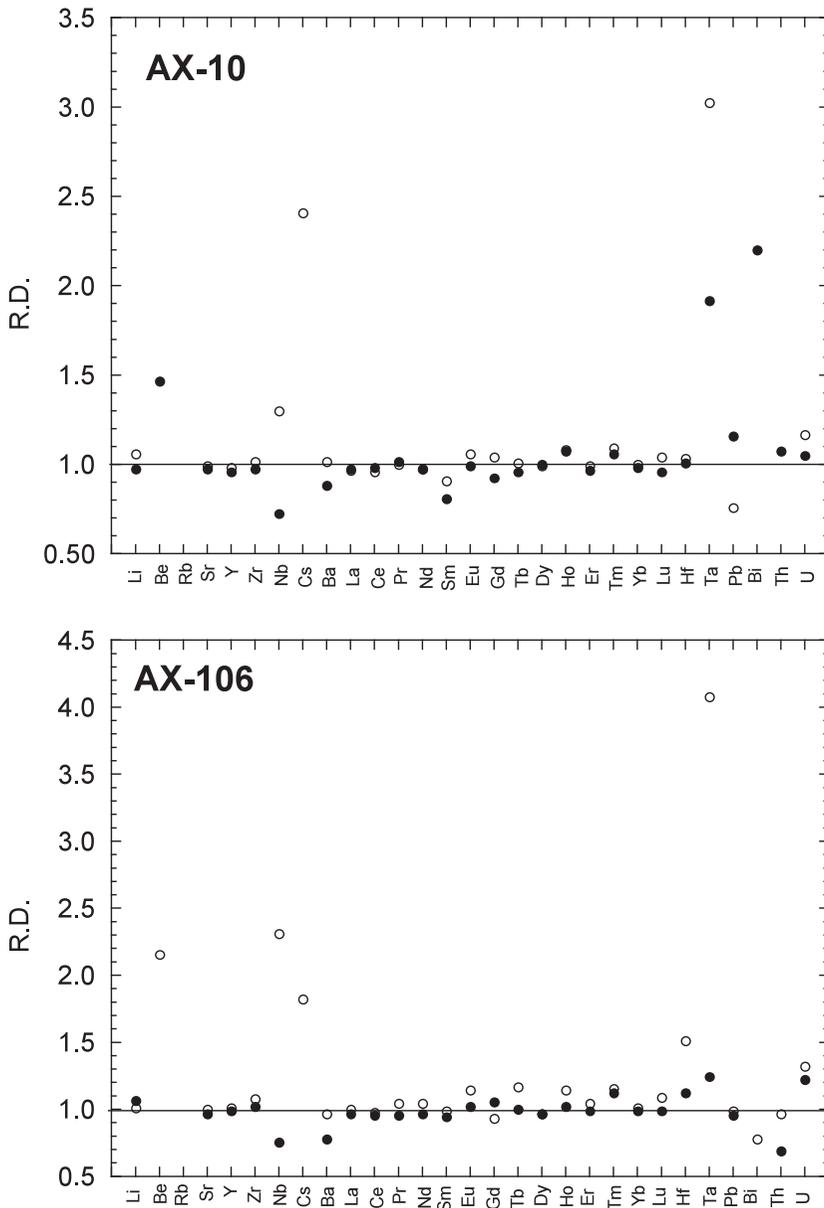


Figure 4 Relative differences (R.D.s) of the trace-element concentration in Avacha peridotite xenoliths under various conditions from the values determined by the external standard calibration method with a dilution factor of 1,000. *Opened circle*; the external standard calibration method, dilution factor of 5,000. *Filled circle*; the standard addition calibration method with a dilution factor of 5,000.

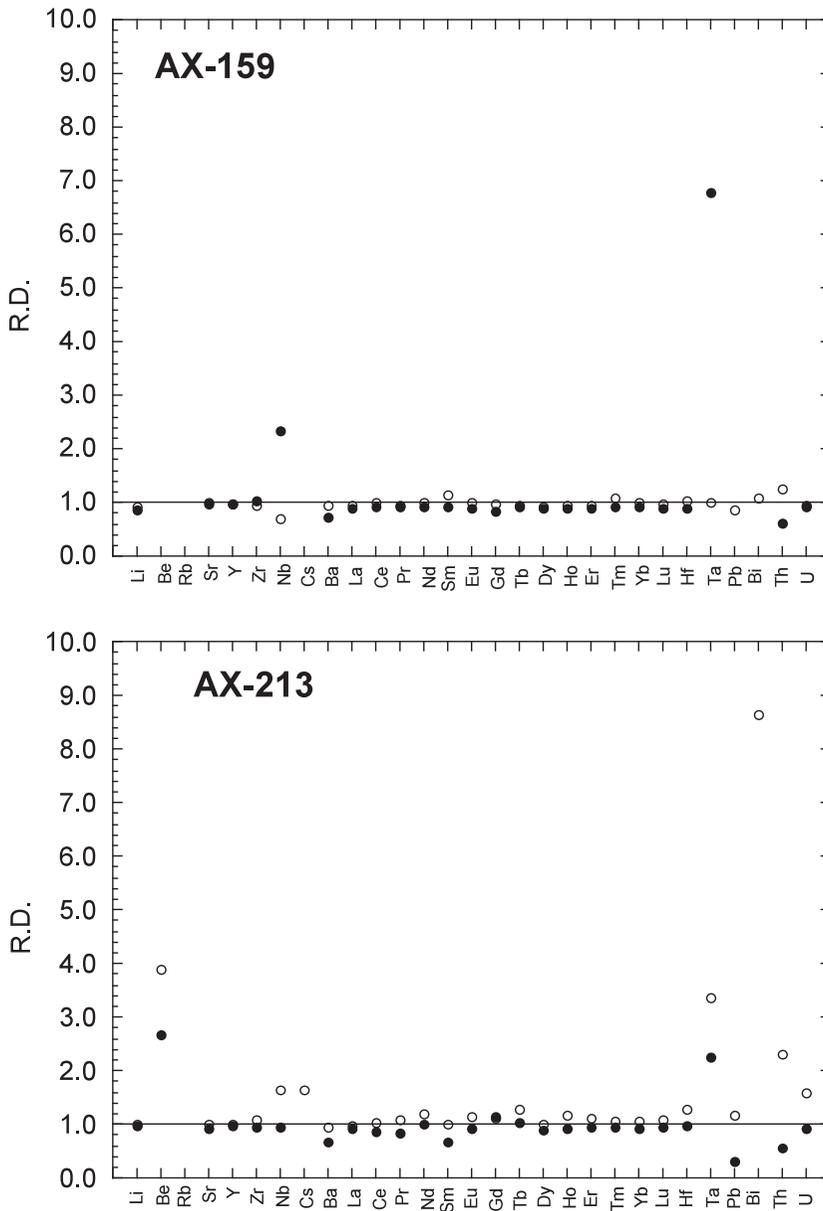


Figure 4 (continued)

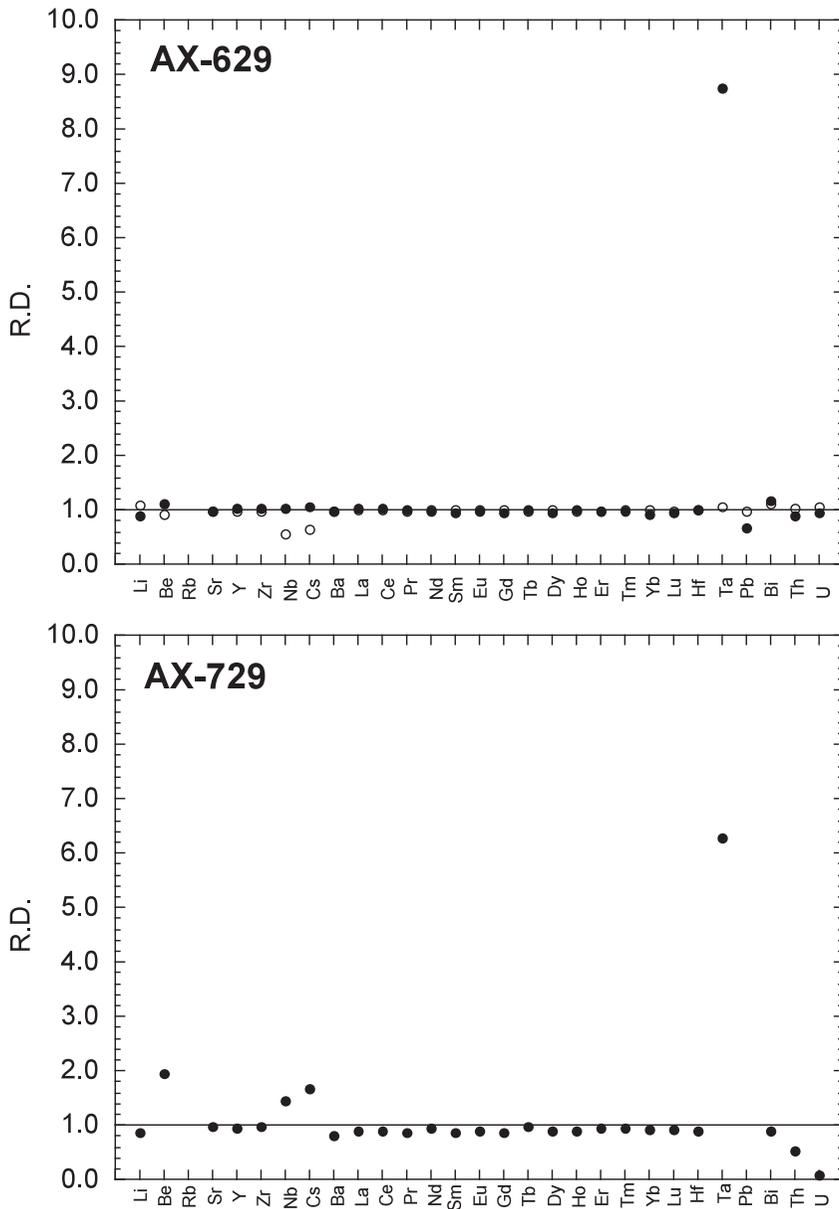


Figure 4 (continued)

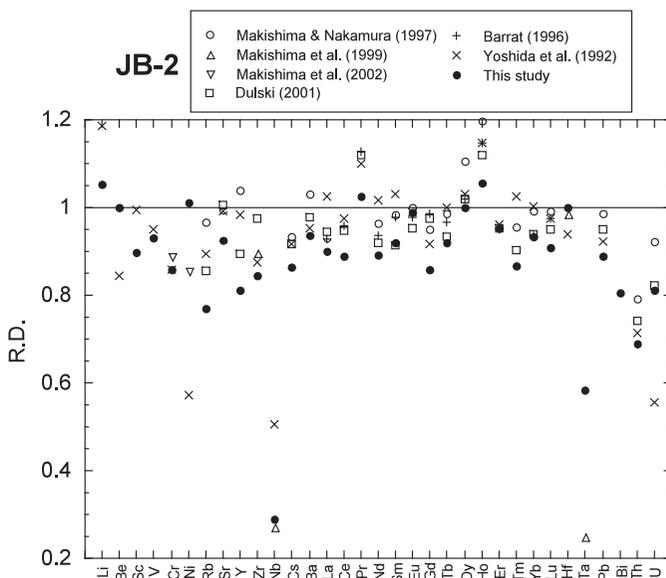


Figure 5 Relative differences (R.D.s) of working values including the run 030829 (the external standard calibration method with a dilution factor of 10,000) in this study to the reference values of Imai et al. (1995) for JB-2.

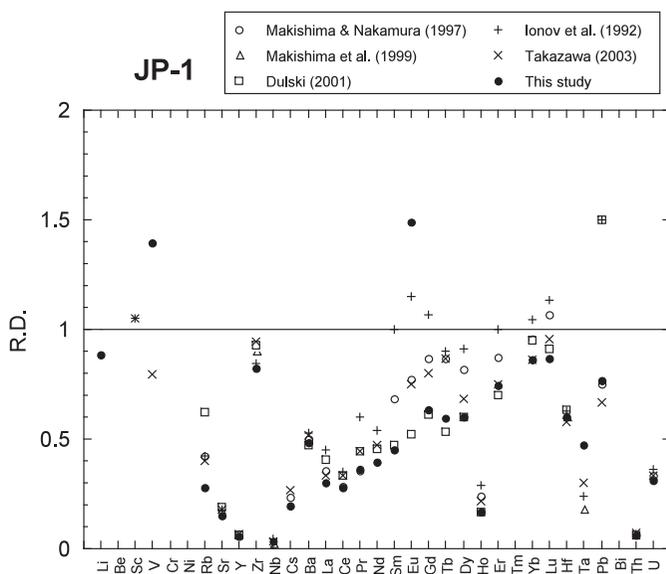


Figure 6 Relative differences (R.D.s) of working values including the run 030829 (the external standard calibration method with a dilution factor of 1,000) in this study to the reference values of Imai et al. (1995) for JP-1.

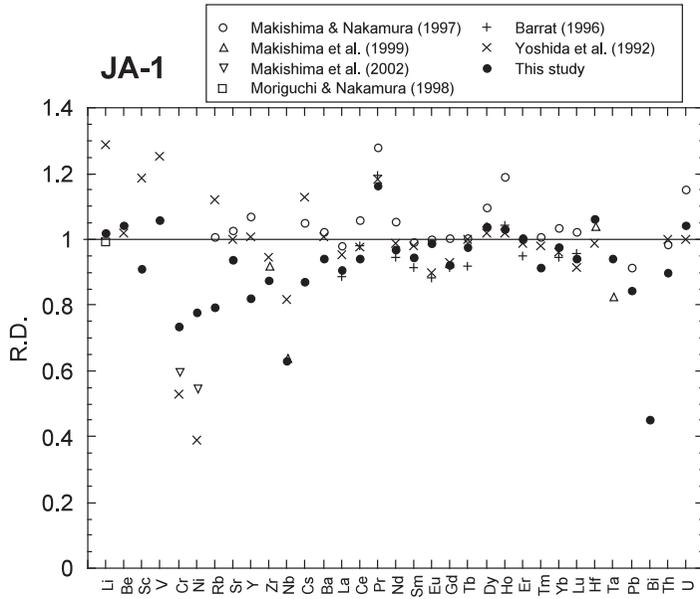


Figure 7 Relative differences (R.D.s) of working values including the run 030829 (the external standard calibration method with a dilution factor of 10,000) in this study to the reference values of Imai et al. (1995) for JA-1.

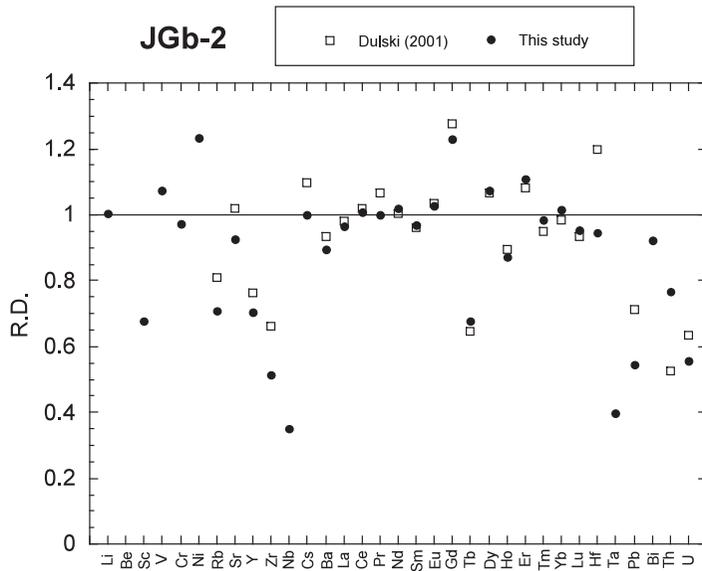


Figure 8 Relative differences (R.D.s) of working values including the run 030829 (the external standard calibration method with a dilution factor of 10,000) in this study to the reference values of Imai et al. (1995) for JGb-2.

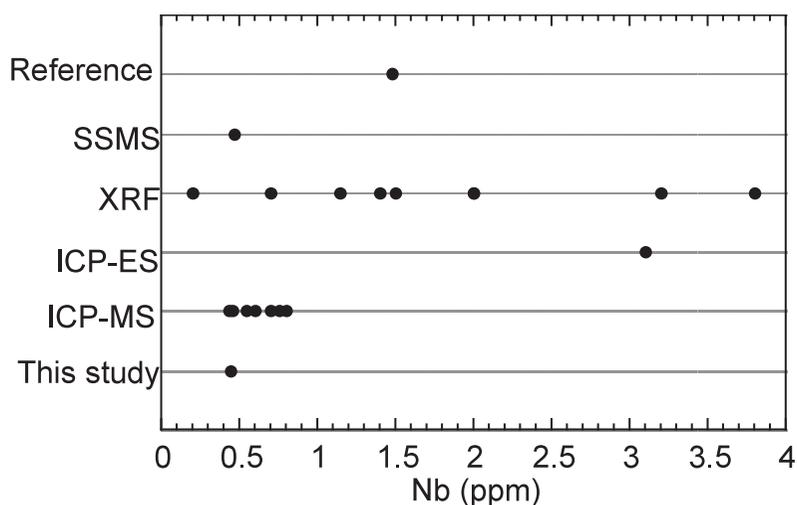


Figure 9 A comparison of the values of Nb concentration in JB-2 by various techniques. The list of working values from literature is given in Table 9. The reference value is from Imai et al. (1995)

Table 9. A list of values of Nb in JB-2 by previous studies and the present study.

value	technique	reference
0.44	ICP-MS	This study (the run 030829: external standard calibration method; a dilution factor of 10,000)
0.7	ICP-MS	Hall and Pelchat (1990)
0.8	ICP-MS	Yoshida et al. (1992)
0.76	ICP-MS	Garbe-Schonberg (1993)
0.6	ICP-MS	Tanaka (1993)
0.55	ICP-MS	Jochum and Jenner (1994)
0.46	ICP-MS	Makishima et al. (1999)
0.43	ICP-MS	Makishima et al. (1999)
3.1	ICP-ES	Tagiri and Fujinawa (1988)
0.47	SSMS	Jochum and Jenner (1994)
1.4	XRF	Tamura et al. (1989)
3.2	XRF	Kawano et al. (1992)
1.5	XRF	Verma and Besch (1992)
3.8	XRF	R.B.Hallett and (1993)
0.2	XRF	Sparks (1994)
0.7	XRF	Longerich (1995)
2	XRF	Tsuchiya and Hasenaka (1995)
2	XRF	Kakubuchi et al. (1999)
1.14	XRF	Umemoto et al. (2000)

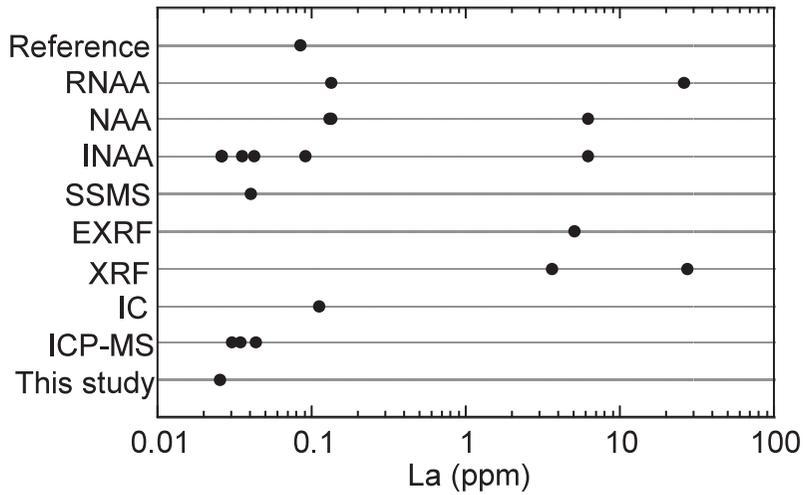


Figure 10 A comparison of the values of La concentration in JP-1 by various techniques. The list of working values with references is given in Table 10. The reference value is from Imai et al. (1995)

Table 10. A list of the values of La in JP-1 by previous studies and the present study. Details of references are given in GSJ homepage.

value	technique	reference	remarks
	ICP-MS	This study (the run 030829: external standard calibration method; a	
0.043	ICP-MS	Jochum and Jenner (1994)	
0.03	ICP-MS	Makishima and Nakamura	
0.034	ICP-MS	Dulski (2001)	
0.11	IC	Watkins and (1992)	
0.111	IC	Watkins (1993)	unpublished data
6.1	INAA	Wakabayashi and Shima	unpublished data
0.042	INAA	Sims et al. (1988)	
0.026	INAA	Hirai and Suzuki (1989)	unpublished data
0.035	INAA	Hallett and (1993)	
0.09	INAA	Stix et al. (1996)	
0.026	INAA	Korotev (1996)	
0.13	NAA	Miyamoto (1988)	unpublished data
6.1	NAA	Wakabayashi (1988)	
0.131	NAA	Aota et al. (1994)	
0.131	RNAA	Oura et al. (1991)	1991 Annual Meet. Japan Geochem. Soc.
26	RNAA	Ebihara et al. (1995)	
0.04	SSMS	Jochum and Jenner (1994)	
5	EXRF	Uto (1991)	unpublished data
3.6	XRF	Olszowy (1985)	unpublished data
27	XRF	Wolf (1998)	unpublished data

producibility despite of various analytical conditions and the sensitivity to determine trace-element concentrations as low as in the order of sub ppt to ppb. The solution introduction ICP-MS technique established in this study is powerful tool for analysis of geological and environmental processes and materials based on trace-element geochemistry.

Acknowledgments

We acknowledge Associate Prof. J. Kimura of Shimane University, Associate Prof. E. Takazawa of Niigata University and Dr. Y. Orihashi of University of Tokyo for their advice about the solution introduction ICP-MS technique to geological samples. We are also grateful to Ms. T. Takahashi, Mr. T. Iyama and Mr. S. Simon of Thermo Electron Corporation for their supplying basic information about the solution introduction ICP-MS technique with us. The ICP-MS system was installed in the course of research by the 21st-Century COE project "Environmental Monitoring and projection of Long-and Short-Term Dynamics of Pan-Japan Sea Area: Construction of Monitoring Network and Assessment of Human Effects" led by Prof. K. Hayakawa, Kanazawa University. We express our deepest appreciation to Prof. K. Hayakawa for his leadership.

References

- Aota, N., Y. Miyamoto, S. Kosanda, Y. Oura, and K. Sakamoto (1994). Neutron Activation analysis of fifteen GSJ igneous rock reference samples. *Geost. Newsletter*, **18**, 65-84.
- Arai S., S. Ishimaru, and V.M. Okrugin (2003) Metasomatized harzburgite xenoliths from Avacha volcano as fragments of mantle wedge of the Kamchatka arc: implication for the metasomatic agent. *The Island Arc*, **12**, 233-246.
- Barrat, J.A., F. Keller, J. Amosse, R.N. Taylor, and R.W. Nesbit (1996). Determination of rare earth elements in sixteen silicate reference samples by ICP-MS after Tm addition and ion exchange separation. *Geost. Newsletter*, **20**, 133-139.
- Bedini R.M., and J. -L. Bodinier (1999) Distribution of incompatible trace elements between the constitution of spinel peridotite xenoliths: ICP-MS data from the East African Rift. *Geochim. Cosmochim.*, **63**, 3883-3990.
- Dulski P., (2001). Reference Materials for Geochemical Studies: New analytical data by ICP. . -MS and critical discussion of reference values: *Geost. Newsletter*, **25**, 87-125.
- Ebihara, M., S. Kimura, and H. Akaiwa (1995). Radiochemical neutron activation analysis of trace lanthanoids in geological and cosmochemical samples. *Fresenius' J. Anal. Chem.*, **351**, 514-520.
- Garbe-Schonberg, C. (1993). Simultaneous determination of thirty-seven trace elements in twenty-eight international rock standards by ICP-MS. *Geost. Newsletter*, **17**, 81-97.
- Hall, G.E.M., and J.C. Pelchat (1990). Analysis of standard reference materials for Zr, Nb, Hf and Ta by ICP-MS after lithium metaborate fusion and cupferron separation: *Geost. Newsletter*, **14**, 197-206.
- Hallett, R.B., and P.R. Kyle (1993). XRF and INAA determinations of major and trace elements in geo-

- logical survey of Japan igneous and sedimentary rock standards. *Geost. Newsletter*, **17**, 127-133.
- Imai, N., S. Terashima, S. Itoh, and A. Ando (1995). Compilation of analytical data for minor and trace elements in seventeen GSJ geochemical reference samples, "Igneous Rock Series". *Geost. Newsletter*, **19**, 135-213.
- Ionov, D.A., L. Savoyant, and C. Dupuy (1992). Application of the ICP-MS technique to trace element analysis of peridotites and their minerals. *Geost. Newsletter*, **16**, 311-315.
- , C. Dupuy, S.Y. O'Reilly, M.G. Kopylova, and Y.S. Genshft (1993) Carbonated peridotite xenoliths from Spitsbergen: implications for trace element signature of mantle carbonate metasomatism. *Earth Planet. Sci. Lett.*, **119**, 283-297.
- , V.S. Prikhod'ko, and S.Y. O'Reilly (1995) Peridotite xenoliths in alkali basalts from the Sikhote-Alin, southeastern Siberia, Russia: trace-element signatures of mantle beneath a convergent continental margin. *Chem. Geol.*, **120**, 275-294.
- Jochum, K.P., and G. Jenner (1994). Trace element analysis of GSJ silicate reference materials: Comparison of SSMS with ICP-MS data and a critical discussion: comparison of SSMS with ICP-MS data and a critical discussion of compiled values, *Fresenius' J. Anal. Chem.*, **350**, 310-318.
- Kakubuchi, S., T. Ishisaka, and Y. Kawano (1999). X-ray fluorescence analysis of major and trace elements in silicate rocks using fused disk samples. *J. Fac. Cul. Edu. Saga Univ.*, **3**, 133-140.
- Korotev, R.L. (1996). A self-consistent compilation of elemental concentration data for 93 geochemical reference samples. *Geost. Newsletter*, **20**, 217-245.
- Longerich, H.P. (1995). Analysis of pressed pellets of geological samples using wavelength-dispersive X-Ray fluorescence spectrometry. *X-ray Spectrometry*, **24**, 123-136.
- Makishima, A., K. Kobayashi, and E. Nakamura (2002). Determination of Cr, Ni, Cu and Zn in milligram samples of geological materials using isotope dilution high resolution ICP-MS. *Geost. Newsletter*, **26**, 41-51.
- , and E. Nakamura (1997). Suppression of matrix effects in ICP-MS by high power operation of ICP: application to precise determination of Rb, Sr, Y, Cs, Ba, REE, Pb, Th and U at ng /g level in a few milligram silicate sample. *Geost. Newsletter*, **21**, 307-319.
- , -----, and T. Nakano (1999). Determination of zirconium, niobium, hafnium and tantalum at ng g⁻¹ levels in geological materials by direct nebulisation. *Geost. Newsletter*, **23**, 7-20.
- Moriguti, T. and E. Nakamura (1998). High-yield lithium separation and precise isotopic analysis for natural and aqueous samples. *Chem. Geol.*, **145**, 91-104.
- Sims, K.W., E.S. Gladney, C. Lundstrom, and N.W. Bower (1988). Elemental concentrations in Japanese silicate rock standards: a comparison with the literature. *Geost. Newsletter*, **12**, 379-389.
- Stix, J., M.P. Gorton, and E. Fontaine (1996). Major and trace element analysis of fifteen Japanese igneous reference rocks by XRFS and INAA. *Geost. Newsletter*, **20**, 87-94.
- Tagiri, M., and A. Fujinawa (1988). Chemical analysis of REE and trace metals in GSJ rock reference samples by ICP. *J. Mineral. Petrol. Econ. Geol.*, **83**, 102-108.
- Takazawa, E., T. Okayasu, and K. Satoh (2003). Geochemistry and origin of the basal lherzolites from the northern Oman ophiolite (northern Fizeh Block). *Geochm. Geophys. Geosyst.*, **4**, 1021, doi: 10.1029/2001GC000232.

- Tamura, S., Y. Kobayashi, and K. Shuto (1989). Quantitative analysis of the trace elements in silicate rocks by X-ray fluorescence method. *Earth Science*, **43**, 180-185. (in Japanese with English abst)
- Tanaka, M. (1993). Inorganic analysis of global environmental samples. *The TRC News*, **44**, 20-27.
- Tsuchiya, N., and T. Hasenaka (1995). Major and trace element analyses of rock samples by X-ray fluorescence spectrometry using Rh anode tube. *Ann, Rep. Fac. Edu., Univ. Iwate*, **55**, 89-110.
- Umemoto, K., T. Imaoka, T. Yamasaki, and M. Owada (2000). Quantitative chemical analyses of rocks by X-ray fluorescence spectrometry using a mixed alkali flux. *Rep. Center of Instrumental Analysis, Yamaguchi Univ.*, **8**, 16-23.
- Verma, S.P., and T. Besch (1992). Determination of twelve trace elements in twenty-seven and ten major elements in twenty-three geochemical reference samples. *Geost. Newsletter*, **16**, 301-309.
- Watkins, R.T., and A.P.L. Roex (1992). The rare-earth element content of GSJ rock reference samples determined by gradient ion chromatography. *Geochem. J.*, **26**, 241-249.
- Yoshida, T., S. Yamasaki, and A. Tsumura (1992). Determination of trace and ultra-trace elements in 32 international geostandards by ICP-MS. *J. Min. Pet. Econ. Geol.*, **87**, 107-122.