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Accuracy and reproducibility of trace and selected major element measurements in geological standard rocks using inductively coupled plasma mass spectrometry (ICP-MS)

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Abstract We report the accuracy and reproducibility of 37 trace and 9 selected major element concentrations in 12 geological standard rocks using an inductively coupled plasma mass spectrometer. The geological standard rocks of the Geological Survey of Japan reference materials (JB-1, JB-1a, JB-1b, JB-2, JB-3, JA-1, JA-2, JA-3, JR-2, JSd-1) and the United States Geological Survey reference materials (BIR-1a, BHVO-2), were digested using HF-$HClO_4$–HNO_3, diluted to appropriate levels, and analyzed. The reproducibility of replicate analyses (i.e., measurement of several different solutions of the same reference material) is better than 5% (1σ) for almost all elements. However, for Li, Sc, Ni and Zn, reproducibility is comparatively worse ($>$8%), likely caused by inhomogeneous distribution of the elements in the rock powder and/or interferences due to polyatomic ions. Our results are in agreement with reference values within 7% difference, except for Cr (up to 8% difference), Y and Zr (up to 10% difference) in some reference materials.

Key words: ICP-MS, volcanic rock, sediment, whole rock analysis

Introduction

Today, quantitative determinations of major and trace elements in rock samples are mostly performed by X-ray fluorescence spectrometry (XRF) and inductively coupled plasma mass spectrometry (ICP-MS). XRF measurements of rock samples provide relatively poor detection limits for some of the trace elements of interest and require correction of spectral overlaps for important elements such as Y, Zr and Nb (e.g., Sano *et al.*, 2020). Compared to XRF, the advantages of ICP-MS are its multi-element capability (e.g., applicable to all the naturally occurring rare-earth elements, REEs), low detection limits, and the simple spectra of the elements. Developments in analytical techniques have been made during the last two decades to obtain accurate and precise trace element abundances at ng/g (ppb) levels in rock samples using ICP-MS (e.g., Chang *et al.*, 2003; Nakamura and Chang, 2007; Senda *et al.*, 2014).

It is evident that when a method of analysis gains popularity, to guarantee the quality of the data produced, it is necessary to report the accuracy and reproducibility of analytical data in individual laboratories. We have published several papers to report trace element concentrations in rock digest solutions since 2016 (Sano *et al.*, 2016), however, major elements were not targeted. This paper, therefore, reports the establishment of a quantitative analytical routine for 37 trace and 9 major elements in volcanic rocks and sediment samples using ICP-MS. We also report the accuracy, reproducibility, and detection limits for each element based on several repeat analyses of 12 international reference materials and blank solutions during the last 7 years since 2014.

Analytical methods

Reagents, labware and calibration

The purified water (18.2 MQ cm) used throughout the present analysis was produced using a Milli-Q water purification system (Merck Millipore, Japan). Reagents used for sample digestion and dilution of standard solutions were TAMAPURE-AA grade 38% HF (AA-100), 70% $HClO_4$ (AA-100), and 68% HNO_3 (AA-100) (Tama Chemical Co, Ltd., Japan). 23-ml Teflon PFA vials with screw caps (Savillex, USA) were used for sample decomposition. Two-types of polyethylene bottles, 10 ml (Yamayu Co Ltd., Japan) and 15 ml (Thermo Scientific Nalgene, USA), were used to store the sample solutions after decomposition and dilution, prior to ICP-MS analysis. To avoid contamination and to achieve low blanks, new polyethylene bottles were filled with 0.5 M HNO_3 (EL 1.38, Kanto Chemical Co. Inc., Japan) for more than 2 weeks and washed twice with Milli-Q water prior to use. PFA vials were rinsed prior to each use by fluxing with 6 M HCl (EL, Kanto Chemical Co. Inc., Japan) on a hot plate at 100°C for 3 days, followed by cleaning on a hotplate for another day with 5–10% TMSC (Tama Chemicals Co, Ltd., Japan), followed by cleaning on a hotplate for 2 days with the 6 M HCl, followed by cleaning on a hotplate for 2 days with 6 M HNO_3 (EL 1.38, Kanto Chemical Co. Inc., Japan), and finally rinsed in Milli-Q water on a hotplate for another day. The vials were then filled with the 0.5 M HNO_3 and stored before the use.

The standard solutions for making calibration lines were prepared by gravimetric serial dilution from commercial standard solutions: a multi-element standard solution containing 10 μg/g (ppm) of REEs, Th and U (SPEX CertriPrep Int., USA); single element standard stock solutions containing 1,000 μg/g (ppm) for trace elements (Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, Ce, Hf, Ta, Tl, Pb; SPEX CertriPrep Int., USA); and single element standard stock solutions containing 1,000 μg/g (ppm) for major elements (Ti, Al, Fe, Mn, Mg, Ca, Na, K and P; FUJIFILM Wako Pure Chemical Industries Ltd., Japan). The standard solutions were diluted by 2% HNO_3 for all elements excluding high-field strength elements (HFSE: Zr, Nb, Hf, Ta), and by 2% HNO_3–0.1% HF for the HFSE. In order to reduce memory effects, multi-element standard solutions were prepared such that elements were present at levels no higher than those expected to occur in real samples after dilution. We prepared four or five diluted standard solutions including a reagent blank solution for each element (Table 1).

Sample digestion

Before sample digestion, 0.5 M HNO_3 was removed from the PFA vials and they were cleaned twice with Milli-Q water. Then, the vials were dried on a hot plate at 80°C for ~1 hour. Samples were digested using the method shown in the analytical flow chart in Fig. 1. We digested 16 samples in one cycle.

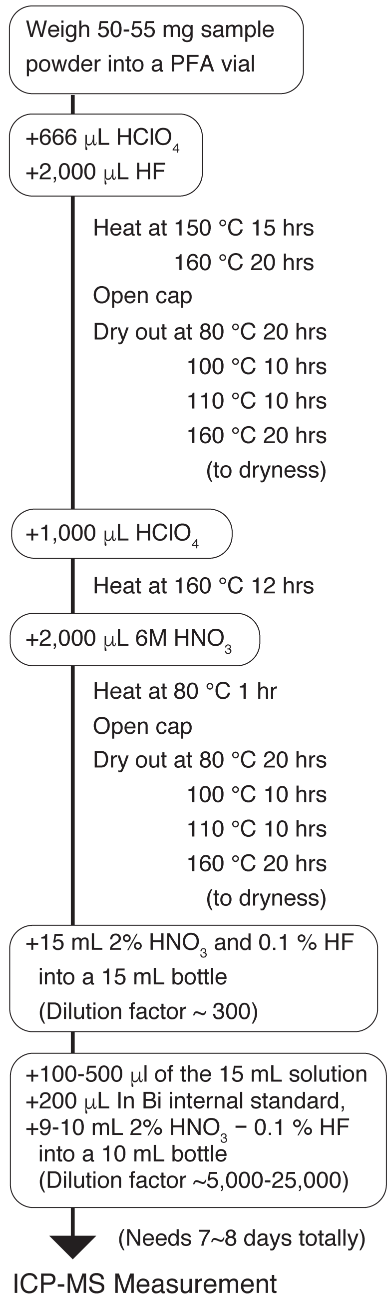

Fig. 1. Analytical protocol for the acid digestion method.

Powdered sample (50–55 mg) was weighed into the vial, followed by 666 μl $HClO_4$ and 2,000 μl HF. We note that $HClO_4$ was added prior to HF to avoid violent reactions and the formation of fluorides in acid digestion. The vial was tightly capped and the powdered sample dissolved using an ultrasonic cleaning machine for 20 minutes. The sample vial

Table 1. Isotopes, cell gas mode, potential interference, calibration solutions, and count time to determine each element concentration. Detection limit and blank for each element are also shown.

Isotope	Cell gas mode	Potential Interferences	Calibration solutions (ng/g)	Count time (sec)	*DL (pg/g)	**Blank (pg)
^{7}Li	no gas		0, 0.001, 0.01, 0.1, 1	0.3	85	20
^{9}Be	no gas		0, 0.001, 0.01, 0.1, 1	3.0	1.1	0.93
^{23}Na	no gas		0, 3, 30, 300, 3000	0.1	##n.d.	n.d.
^{24}Mg	no gas	^{23}Na^{1}H	0, 5, 50, 500, 5000	0.1	n.d.	n.d.
^{27}Al	no gas	^{14}N spread	0, 10, 100, 1000, 10000	0.1	n.d.	n.d.
^{31}P	no gas	^{14}N^{16}O^{1}H	0, 0.5, 5, 50, 500	0.3	n.d.	n.d.
^{39}K	no gas	^{38}Ar^{1}H	0, 1, 10, 100, 1000	0.1	n.d.	n.d.
^{44}Ca	no gas	^{14}N$_2$^{16}O	0, 10, 100, 1000, 10000	0.3	n.d.	n.d.
^{45}Sc	no gas	^{44}Ca^{1}H	0, 0.001, 0.01, 0.1, 1	0.1	67	110
^{45}Sc	He	^{44}Ca^{1}H	0, 0.001, 0.01, 0.1, 1		49	54
^{47}Ti	no gas	^{31}P^{16}O	0, 1, 10, 100, 1000	0.1	n.d.	n.d.
^{51}V	no gas		0, 0.2, 2, 20	0.3	**340**	**520**
^{52}Cr	no gas	^{36}Ar^{16}O	0, 0.2, 2, 20	0.1	26	44
^{53}Cr	no gas	^{36}Ar^{16}O^{1}H	0, 0.2, 2, 20	0.1	**610**	**330**
^{55}Mn	no gas	^{40}Ar^{14}N^{1}H, ^{39}K^{16}O	0, 0.5, 5, 50, 500	0.1	n.d.	n.d.
^{56}Fe	no gas	^{40}Ar^{16}O, ^{40}Ca^{16}O	0, 10, 100, 1000, 10000	0.1	n.d.	n.d.
^{59}Co	no gas	^{43}Ca^{16}O, ^{40}Ar^{18}O^{1}H	0, 0.3, 3, 30	0.3	**140**	**210**
^{60}Ni	no gas	^{44}Ca^{16}O	0, 0.1, 1, 10	0.3	**680**	**220**
^{63}Cu	no gas	^{49}Ti^{16}O, ^{25}Mg^{40}Ar	0, 0.1, 1, 10	0.1	**170**	**240**
^{66}Zn	no gas	^{26}Mg^{40}Ar, ^{50}Cr^{16}O, ^{50}Ti^{16}O	0, 0.1, 1, 10	0.3	**6200**	**3500**
^{66}Zn	He	^{26}Mg^{40}Ar, ^{50}Cr^{16}O, ^{50}Ti^{16}O	0, 0.1, 1, 10		**2272**	**440**
^{71}Ga	no gas		0, 0.001, 0.01, 0.1, 1	0.3	20	31
^{85}Rb	no gas		0, 0.1, 1, 10	0.1	36	48
^{88}Sr	no gas		0, 0.2, 2, 20	0.1	87	49
^{89}Y	no gas		0, 0.004, 0.04, 0.4, 4	0.3	9.3	12
^{90}Zr	no gas	^{50}Ti^{40}Ar, ^{50}Cr^{40}Ar, ^{51}V^{40}Ar	0, 0.1, 1, 10	0.1	**300**	**530**
^{93}Nb	no gas		0, 0.01, 0.1, 1	0.9	26	4.3
^{115}In#	no gas			0.1	n.d.	n.d.
^{115}In#	He				n.d.	n.d.
^{133}Cs	no gas		0, 0.001, 0.01, 0.1, 1	1.5	0.61	0.56
^{137}Ba	no gas		0, 0.2, 2, 20	0.3	43	50
^{139}La	no gas		0, 0.001, 0.01, 0.1, 1	0.9	1.2	0.99
^{140}Ce	no gas		0, 0.003, 0.03, 0.3, 3	0.9	3.1	3.4
^{141}Pr	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.80	0.48
^{146}Nd	no gas		0, 0.001, 0.01, 0.1, 1	2.1	1.3	1.5
^{147}Sm	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.89	0.61
^{153}Eu	no gas	^{137}Ba^{16}O	0, 0.001, 0.01, 0.1, 1	2.1	0.64	0.26
^{157}Gd	no gas	^{140}Ce^{16}O^{1}H, ^{141}Pr^{16}O	0, 0.001, 0.01, 0.1, 1	2.1	1.4	1.4
^{159}Tb	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.79	0.34
^{163}Dy	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.64	0.47
^{165}Ho	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.78	0.38
^{166}Er	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.60	0.44
^{169}Tm	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.66	0.38
^{172}Yb	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.72	0.51
^{175}Lu	no gas		0, 0.001, 0.01, 0.1, 1	2.1	0.88	0.35
^{178}Hf	no gas		0, 0.01, 0.1, 1	2.1	7.4	12
^{181}Ta	no gas	^{185}Ho^{16}O	0, 0.01, 0.1, 1	3.0	6.1	6.7
^{205}Tl	no gas		0, 0.001, 0.01, 0.1, 1	2.1	2.3	3.3
^{208}Pb	no gas		0, 0.001, 0.01, 0.1, 1	2.1	39	41
^{209}Bi#	no gas			0.3	n.d.	n.d.
^{209}Bi#	He				n.d.	n.d.
^{232}Th	no gas		0, 0.001, 0.01, 0.1, 1	2.1	3.3	2.9
^{238}U	no gas		0, 0.001, 0.01, 0.1, 1	2.1	2.4	1.9

* DL (Detection limit): Three-sigma standard deviation of measurements of blank solutions. DL ＞100 pg/g is shown in red.

** Blank: maximum values among 33 blank solutions. Blank ＞100 pg is shown in red.

\# In and Bi are analyzed for internal standards.

\## n.d.: not determined for major and internal standard elements.

was then placed in an oven for 15 hours at 150℃ and additional 20 hours at 160℃ to fully dissolve the sample. The vial cap was then opened to dry the sample solution by step heating at progressively increasing temperatures up to 160℃ (Fig. 1). After this, 1,000 μl of $HClO_4$ was added and the vial was

Table 2. Instrument operating parameters.

Instrument	Agilent 7700x
Plasma power	1550 W
Torch	Quartz glass torch with Pt injection
Nebliser	Micro Flow Nebliser with I-AS, made of PFA
Spray chamber	Scott (double-pass) type, made of PFA
Cones	Nickel-plated copper
Plasma Ar gas flow rate	15 L/min
Carrier gas flow rate	0.8 L/min
Make-up Ar gas flow rate	0.3-0.6 L/min
Sample uptake rate	0.1 mL/min
Sampling depth	8.0 mm
Reaction mode	no gas (all elements) / + He gas (Sc, Zn)
He gas flow rate	4.0 mL/min (reaction mode)
Scan mode	peak jump
Acuistition time	71 sec × 3
Wash time	60 sec 2% HNO_3 and 10 sec milli-Q water
Internal standard	^{115}In, ^{209}Bi
Oxiside ratio (156 : 140)	$<$1.5%

tightly capped and placed in an oven at 160°C for 12 hours. Next, the sample solution was refluxed with 2,000 μl of 6 M HNO_3 and heated at 80°C for 1 hour. At this stage, no visible undissolved residue or floccule remained in the solution. Once again, the cap was opened to dry the sample solution by step heating at progressively increasing temperatures up to 160°C (Fig. 1). Finally, the dried sample was refluxed with 2% HNO_3–0.1% HF in the 15 ml polyethylene bottle to make a 'mother sample solution'. Dilution factors at this stage were about 300.

Further dilution was undertaken with 2% HNO_3–0.1% HF in a 10 ml polyethylene bottle and ~100 ng/g (ppb) ^{115}In and ^{209}Bi solution was added as an internal standard before ICP-MS analysis. The internal standard was utilized to correct both instrumental drift and sensitivity drift during analysis of each sample solution. The drifts of low mass elements (Li to Nb) were normalized by In, those of high mass elements (Th and U) were normalized by Bi, and those of middle mass (Cs to Pb) were normalized by both In and Bi. Since volcanic rocks and sediments generally have no detectable In, this is the best element to use as an internal standard (Pretorius *et al.*, 2006). However, volcanic rocks and sediments sometimes have detectable Bi (e.g., JR-2). In this case, the drifts were normalized by only In. Total dilution factors were calculated for samples: 20,000–30,000 for JB-1, JB-1a, JB-1b, JB-3 and BHVO-2; 10,000–15,000 for JB-2, JA-1, JA-2, JA-3, JR-2 and JSd-1; 5,000–7,000 for BIR-1a.

A blank solution was also prepared in each cycle of sample digestion. The blank solution was analyzed after the sample solutions in order to monitor background memory effects during the course of the cycle. The above sample digestion procedure is itemized in the Appendix in detail.

Instrument

The ICP-MS used in this study is a quadrupole Agilent 7700x instrument (Agilent Technologies Japan, Ltd., Japan) at the National Museum of Nature and Science (NMNS). A HF-resistant spray chamber and PFA microflow nebulizer were employed to enable direct introduction of samples in diluted HNO_3–HF solution to the plasma since HFSE are unstable in simple HNO_3 solutions. All the solution introduction parts were carefully cleaned before use. Nickel-plated copper sample and skimmer cones were used throughout the study. The instrument parameters and operating conditions are shown in Table 2.

The instrument parameter was optimized daily using a 1 ng/g (ppb) tuning solution (Agilent Technologies Japan, Ltd., Japan) containing the whole mass range of the elements from Li to Tl (^{7}Li, ^{24}Mg, ^{59}Co, ^{89}Y, ^{140}Ce, ^{205}Tl) to obtain maximum signal intensity, minimum oxide formation rates and required counts ($>$10,000, $>$150,000, $>$15,000, $>$20,000, $>$20,000 and $>$10,000 counts/sec for Li, Mg, Co, Y, Ce and Tl, respectively). Signals of all elements were counted by pulse mode (for low count rates) and analog mode (for high count rates). Sensitivity differences of the two modes were optimized at least once per month using a 10 ng/g (ppb) tuning solution (Agilent Technologies Japan, Ltd., Japan) containing the whole mass range of elements. Oxide formation level was maintained at less than 1.5% of CeO relative to Ce, but we had to correct for overlaps between the spectra of oxides and hydroxides for some REEs (Table 1). To overcome this problem, we measured three separate solutions prepared by 1 ng/g (ppb) REEs solution, 5 ng/g (ppb) Ce, and 10 ng/g (ppb) Ba with 2 ng/g (ppb) Pt (SPEX CertriPrep Int., USA), and correction factors for the oxides and hydroxides were calculated ($<$1.5%) as follows.

^{157}Gd: $^{157}Gd - 0.00145 \times {}^{140}Ce - 0.0106 \times {}^{141}Pr$

^{153}Eu : $^{153}Eu - 0.00156 \times {}^{137}Ba$

^{181}Ta : $^{181}Ta - 0.0033 \times {}^{165}Ho$

These correction factors were applied to all measurements. The interference due to polyatomic ions affect measurements of trace elements as listed in Table 1 (May and Wiedmeyer, 1998; Pretorius *et al.*, 2006), but we did not conduct any correction for other trace elements in this study. Only Argon was used as makeup gas and carrier gas for the measurements of all elements (no gas mode), but we also tried to introduce Helium collision mode (He mode) for measurements of Sc and Zn that have high background to signal intensity (Table 1).

Results and Discussion

Detection limit and procedural blank

Detection limits (DLs) for trace elements were calculated using the results of analyses of 33 blank solutions that were separately digested over the last 7 years. The DLs are defined as three times the standard deviation of the analytical results. Table 1 shows that the DLs of most REEs are lower than 1 pg/g (ppt). These DLs theoretically allow the determination of sub ng/g (ppb) level elements in rock samples, even using a highly distributed sample solution in this study. Consequently, the procedural blank for a trace element is the main limitation in such highly sensitive ICP-MS analysis. In contrast to the REEs, some other trace elements (Cr, Co, Ni, Cu, Zn, Zr) have relatively high DLs ($>$100 pg/g: ppt), which were certainly caused by interference effects (Table 1). The slightly higher DLs of Rb, Sr, Ba and Pb ($>$30 pg/g: ppt) are probably due to contamination of these elements during preparation of blank solutions. The maximum blank for the trace elements is nanogram level (3.5 ng for Zn). We conclude that precise quantifications are possible for the analyzed elements in Table 1 because their concentrations in general volcanic rocks and sediments are usually at μg/g (ppm) level (Table 3). The high DLs for some elements suggest that the precise determinations of sub μg/g (ppm) level are sometimes difficult for these elements. For example, the procedural blank of Co (210 pg) is about 3% of the Co content (0.14 μg/g: ppm) in a 50 mg sample powder for JR-2 (Table 3). We should therefore consider the DLs and procedural blanks when we analyze elements with sub μg/g (ppm) levels (e.g., REEs in ultramafic rocks).

Reproducibility and Comparison to reference values

Over the last 7 years, we performed 26 separate digestions and trace element analyses for JB-1a (Table 3), and 16 solutions among them were selected for major element analysis by ICP-MS (Table 4). Multiple digestions and analyses were also conducted for another 11 geological standard rocks (Tables 3 and 4). The listed relative standard deviation (RSD) for each element in Tables 3 and 4 are likely to adequately account for uncertainties arising from weighing, digestion, and sample and calibration solution dilution and preparation, accounting for the fact that the replicated digestions were randomly performed over a period of 7 years by several scientists.

The reproducibility of replicated analyses (i.e., measurement of several different solutions of the same reference material) in the 12 geological standard rocks is better than 5% RSD for almost all elements (Table 3). However, the reproducibility for Li, Sc, Ni and Zn in many samples, is worse than 8% (red in Table 3). Interferences due to polyatomic ions for Sc, Ni and Zn (Table 1) are likely the cause of the relatively high RSD. The relatively high RSD for Li suggests this element may be affected by inhomogeneous distribution in the rock powders. We also note that the RSDs in sub μg/g (ppm) concentrations (e.g., Ta, Tl, Th and U in BIR-1a) are generally high caused by their high procedural blanks compared to their concentrations.

Measured concentrations of most major and trace elements in the 12 geological standard rocks agree with the reference (preferred, recommended, certi-

Table 3. Trace element concentrations (μg/g: ppm) in reference rocks.

Sample	Run No.	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	La	Ce
JB-1	EG11	9.4	1.20	26.0	206	$	35.0	128	51		17.0	37.3	437	19.5	126	33.1	1.33	482	35.39	63.37
	AF11	10.7	1.38	28.0	220		37.5	136	56	82	17.8	37.4	441	20.0	126	36.5	1.37	492	37.22	66.30
	AF23	10.5	1.28	26.3	216		36.3	135	53	79	17.2	36.5	429	19.5	124	31.9	1.31	470	35.56	63.18
	KH34	10.3	1.30	26.0	193	461	35.8	132	54	88	17.4	37.3	430	20.1	130	31.0	1.29	487	35.43	63.44
	KH58	10.5	1.38	27.3	225		38.7	143	57	77	18.6	38.9	449	21.6	137	37.6	1.38	507	37.82	67.60
	KH70	10.1	1.27	25.4	194	451	35.4	131	53	60	17.1	37.5	427	20.2	129	34.5	1.31	473	35.65	63.98
	OR22	10.4	1.27	26.0	196	448	34.7	124	53	77	17.2	33.1	405	18.0	111	31.7	1.28	455	34.72	61.90
	KM14-2	12.0	1.48	27.2	200	462	36.8	126	48	68	17.7	37.8	426	20.8	128	33.9	1.36	482	36.58	65.10
	ES16	10.2	1.27	27.8	221	464	37.2	139	54	98	17.9	38.7	446	22.0	134	36.7	1.34	498	42.37	74.32
	ET48	8.6	1.13	27.5	221	465	35.4	130	49	87	17.3	38.0	430	22.3	141	36.6	1.35	498	45.59	78.23
JB-1	**average**	**10.3**	**1.30**	**26.8**	**209**	**459**	**36.3**	**132**	**53**	**80**	**17.5**	**37.2**	**432**	**20.4**	**129**	**34.4**	**1.33**	**484**	**37.63**	**66.74**
	RSD*	0.9	0.10	0.9	13	7	1.2	6	3	11	0.5	1.6	12	1.3	8	2.4	0.04	15	3.55	5.36
	RSD (%)**	**8.3**	7.6	3.4	6.1	1.6	3.4	4.6	5.4	**14.3**	2.8	4.3	2.9	6.4	6.4	7.0	2.6	3.2	**9.4**	**8.0**
JB-1	**pref.#**	**11.5**	**1.33**	**29**	**211**	**430**	**38.1**	**140**	**56.7**	**85.2**	**17.9**	**39**	**444**	**24**	**142**	**28**	**1.2**	**489**	**38**	**66**
JB-1a	EG23	10.3	1.32	28.3	203		37.0	129	56	80	17.4	38.4	443	21.6	137	26.0	1.23	495	36.99	65.89
	KF36	11.8	1.52	34.1	241	407	39.6	150	60	69	18.7	42.8	465	21.5	158	26.5	1.16	460	34.56	61.45
	PP11	11.6	1.51	30.2	234	409	38.8	146	57	83	18.5	43.0	462	21.4	134	26.3	1.16	459	34.47	61.05
	OJ47	7.7	1.33	28.2	208	453	36.1	151	54	77	17.4	37.4	438	21.2	135	25.5	1.18	482	35.60	62.92
	OJ75	10.6	1.31	27.9	202		37.0	141	55	87	17.7	37.4	459	20.9	137	25.6	1.19	486	35.05	62.72
	E15	13.1	1.47	31.6	222		39.7	144	59	86	18.7	39.4	421	21.9	136	25.8	1.21	478	35.29	62.77
	OJ90	11.1	1.34	28.1	220	424	37.4	139	54	67	17.7	37.3	446	20.8	135	25.6	1.18	476	34.92	62.24
	PP27	11.7	1.38	26.8	194	417	36.1	131	49	71	17.4	35.9	435	20.5	130	23.9	1.15	473	34.84	62.18
	M23	10.7	1.41	28.4	198		36.4	133	46		17.3	37.3	450	21.5	137	25.8	1.26	500	36.65	65.19
	KI14	11.6	1.44	29.2	232	432	39.0	146	56	88	18.7	39.1	458	21.4	142	26.9	1.22	495	36.81	64.62
	MG07	11.4	1.40	29.1	235		39.0	148	57	111	18.5	38.6	460	21.4	139	26.5	1.17	475	35.31	63.00
	OJ90m	11.2	1.36	27.5	192		37.2	135	53	89	17.5	36.5	449	21.1	135	25.4	1.21	489	36.58	64.82
	PA14	11.3	1.43	31.0	239	421	40.3	148	58	85	19.2	39.7	456	22.1	144	27.2	1.23	490	36.49	63.88
	A14	10.5	1.29	27.2	211	412	36.3	133	53	79	17.5	36.4	435	20.5	133	25.0	1.20	488	36.67	64.14
	AM14	11.5	1.42	28.5	216	416	37.4	178	56	75	18.0	35.7	448	20.9	137	25.6	1.19	488	36.43	64.23
	SA6	11.1	1.39	29.2	210	414	38.4	150	57		18.4	38.6	468	21.2	142	26.7	1.18	472	35.38	62.96
	A30	11.5	1.41	30.4	217	416	39.3	165	59		18.9	40.0	480	21.8	143	27.0	1.22	477	36.25	64.19
	SA16	11.1	1.33	28.9	218	414	36.8	140	54		18.0	36.4	453	19.7	132	25.8	1.19	497	36.71	65.29
	SA32	11.7	1.46	27.5	202		37.9	137	53	86	17.9	35.1	442	20.8	133	25.5	1.19	479	35.69	63.85
	A46	11.8	1.38	27.3	218	430	37.6	137	51	86	17.9	35.6	444	19.6	123	24.9	1.19	486	35.79	63.62
	PI14	8.7	1.08	22.1	168	419	32.4	117	45	85	16.0	33.5	423	18.7	117	23.5	1.21	499	36.55	65.16
	P30	10.7	1.29	25.7	206		36.0	134	50	78	17.4	35.6	432	19.7	125	23.8	1.17	479	35.67	63.55
	SA48	11.1	1.42	27.3	205	425	38.0	141	54	79	18.2	36.7	443	21.0	131	25.1	1.19	482	36.13	63.97
	SA64	12.0	1.47	27.9	208	414	38.3	140	55	79	18.3	36.7	450	21.1	131	25.4	1.18	483	36.20	64.32
	KM14	11.5	1.39	26.8	206	421	37.0	136	53	80	17.7	35.6	437	20.7	132	24.8	1.18	472	34.90	62.15
	EG51	12.4	1.45	29.9	234	433	38.3	144	56	87	17.7	37.9	444	20.7	133	25.4	1.17	473	34.66	61.78
JB-1a	**average**	**11.1**	**1.38**	**28.4**	**213**	**421**	**37.6**	**142**	**54**	**82**	**18.0**	**37.6**	**448**	**20.9**	**135**	**25.6**	**1.19**	**482**	**35.79**	**63.54**
	RSD	1.1	0.09	2.2	17	11	1.6	12	4	9	0.7	2.2	14	0.8	8	0.9	0.02	11	0.79	1.27
	RSD (%)	**9.5**	6.4	7.7	7.9	2.6	4.3	**8.3**	6.8	**10.9**	3.7	5.9	3.0	3.7	5.7	3.7	2.1	2.2	2.2	2.0
JB-1a	**pref.**	**10.8**	**1.44**	**27.81**	**200.3**	**408**	**38.53**	**139.5**	**54.5**	**88.5**	**18.13**	**38.15**	**443.4**	**22.91**	**140.1**	**27.57**	**1.216**	**495.1**	**37.74**	**65.93**
JB-1b	ET14	10.3	1.21	30.6	239	457	39.9	153	53	76	18.1	35.0	443	20.8	129	25.7	0.84	492	38.10	65.85
	ET27	9.2	1.12	28.9	215	455	36.2	138	48	74	16.9	34.1	431	20.2	125	24.2	0.85	504	39.39	67.76
	IZ11	11.7	1.37	28.7	229	448	38.7	150	51	84	17.5	33.7	436	19.2	118	24.7	0.80	479	36.95	64.95
	EG52	11.9	1.31	30.8	241	466	39.5	152	55	85	17.4	35.0	444	20.0	125	24.7	0.82	487	36.77	64.31
JB-1b	**average**	**10.8**	**1.25**	**29.8**	**231**	**456**	**38.6**	**148**	**52**	**80**	**17.5**	**34.5**	**439**	**20.1**	**124**	**24.8**	**0.83**	**490**	**37.80**	**65.72**
	RSD	1.3	0.11	1.1	12	7	1.6	7	3	5	0.5	0.6	6	0.7	4	0.6	0.02	10	1.21	1.50
	RSD (%)	**12.1**	**8.7**	3.7	5.1	1.6	4.3	4.8	6.0	6.8	2.8	1.9	1.4	3.4	3.6	2.6	3.0	2.1	3.2	2.3
JB-1b	**recom.##**	**10.8**	**1.3**		**214**	**439**	**40.3**	**148**	**55.5**	**80**		**39.1**	**439**				**1.21**			
JB-2	KH02B	8.4	0.26	49.3	597		36.5	14.9	219	98	16.1	6.2	181	21.6	46.4	0.48	0.75	215	2.17	6.30
	EG24	7.4	0.24	54.1	571		36.2	11.0	219	114	16.1	6.4	171	22.2	46.1	0.44	0.78	214	2.17	6.38
	EG36	8.6	0.25	61.3			37.5	21.0	222	123	16.4	6.5	180	22.4	48.0	0.46	0.78	215	2.15	6.27
	OJ35	6.2	0.22	61.3	554	26.3	33.4	12.0	185	102	15.0	5.9	163	20.4	47.8	0.42	0.71	190	1.93	5.70
	KF37	8.4	0.27	64.9			38.2	14.3	200	121	16.7	7.1	186	22.6	53.4	0.48	0.76	201	2.07	6.04
	PP12	8.2	0.26	64.0		29.9	37.9	14.0	196	122	16.5	7.0	184	22.3	47.0	0.49	0.75	200	2.05	5.97
	OJ48	6.5	0.22	55.8	574	30.4	34.8	12.3	192	112	15.8	6.1	174	21.8	45.6	0.48	0.76	210	2.09	6.15
	OJ59	6.0	0.21	55.8	578	28.8	35.0	13.0	189	111	15.9	6.2	175	21.9	46.1	0.44	0.77	212	2.12	6.20
JB-2	**average**	**7.5**	**0.24**	**58.3**	**575**	**28.9**	**36.2**	**14.1**	**203**	**113**	**16.1**	**6.4**	**177**	**21.9**	**47.6**	**0.46**	**0.76**	**207**	**2.10**	**6.13**
	RSD	1.1	0.02	5.4	15	1.8	1.7	3.1	15	9	0.5	0.4	8	0.7	2.5	0.02	0.02	9	0.08	0.22
	RSD (%)	**14.7**	**9.7**	**9.3**	2.7	6.2	4.7	**22.0**	7.4	**8.1**	3.2	6.7	4.4	3.1	5.3	5.3	3.0	4.4	3.9	3.6
JB-2	**pref.**	**8.08**	**0.273**	**54.08**	**572.4**	**26.65**	**37.57**	**14.77**	**222.1**	**110.4**	**16.62**	**6.4**	**178.2**	**23.56**	**48.25**	**0.565**	**0.8**	**218.1**	**2.281**	**6.552**
JB-3	KH03B	8.2	0.73	32.8			37.9	43.2	206	99	21.5	15.0	433	25.4	100.2	1.83	0.95	250	8.61	21.98
	OJ76	7.0	0.62	33.9	412	61	34.6	37.0	191	105	19.5	14.1	422	23.9	92.9	1.87	0.90	231	7.85	20.21
	OJ91	7.2	0.62	33.8	412	60	34.9	37.7	187	91	19.9	14.3	408	23.6	91.8	1.82	0.90	224	7.83	19.99
	OJ91m	7.5	0.64	34.4	398		35.2	35.9	190	117	20.1	13.9	413	24.1	92.1	1.89	0.92	233	8.25	21.01
	IZ12	8.4	0.70	34.3	431		36.6	38.8	193	115	20.5	14.2	416	23.0	88.5	1.87	0.90	228	7.91	20.32
	EG53	8.3	0.71	36.3		60	36.7	39.1	202	114	20.1	14.7	414	24.0	93.1	1.88	0.92	231	7.92	20.18
JB-3	**average**	**7.8**	**0.67**	**34.3**	**413**	**60.7**	**36.0**	**38.6**	**195**	**107**	**20.3**	**14.4**	**418**	**24.0**	**93.1**	**1.86**	**0.91**	**233**	**8.06**	**20.61**
	RSD	0.6	0.05	1.1	13	0.6	1.3	2.5	7	10	0.7	0.4	9	0.8	3.9	0.03	0.02	9	0.31	0.76
	RSD (%)	**8.0**	7.1	3.3	3.2	0.9	3.6	6.5	3.8	**9.7**	3.4	3.0	2.1	3.3	4.1	1.4	2.1	3.8	3.9	3.7
JB-3	**recom.**	**7.212**	**0.81**	**33.8**	**372**	**58.1**	**34.3**	**36.3**	**194.0**	**100**	**19.8**	**15.1**	**403.0**	**26.9**	**97.8**	**2.5**	**0.94**	**245**	**8.81**	**21.50**

Table 3 (continued). Trace element concentrations (μg/g: ppm) in reference rocks.

Sample	Run No.	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	La	Ce
JA-1	KH04B	11.3	0.51	26.8	106		11.5	5.6	45	80	17.6	11.1	265	27.4	84.5	1.29	0.60	305	5.02	13.25
	PP28	10.8	0.46	27.2	99	11.7	10.3	1.8	37	85	16.4	10.4	250	25.6	77.3	1.09	0.59	285	4.55	12.30
	PA15	10.8	0.49	32.7	129	11.6	11.9	2.0	45	108	19.2	12.1	277	29.1	89.4	1.35	0.66	308	5.01	13.31
	A15	9.6	0.43	27.1	105	10.2	10.2	2.0	39	92	16.5	10.6	247	26.0	79.4	1.17	0.62	294	4.85	12.88
	ET28	9.2	0.42	27.9	107	9.3	10.8	3.0	39	90	16.7	10.8	253	26.5	79.7	1.16	0.63	302	4.96	13.04
	A47	11.0	0.47	28.0	110	9.9	10.7	2.0	40	98	17.1	10.3	261	24.7	77.3	1.22	0.62	293	4.75	12.79
JA-1	**average**	**10.4**	**0.46**	**28.3**	**109**	**10.5**	**10.9**	**2.7**	**41**	**92**	**17.2**	**10.9**	**259**	**26.6**	**81.3**	**1.21**	**0.62**	**298**	**4.86**	**12.93**
	RSD	0.8	0.03	2.2	10	1.1	0.7	1.5	3	10	1.1	0.7	11	1.6	4.8	0.09	0.03	9	0.18	0.37
JA-1	**pref.**	**10.43**	**0.53**	**27.9**	**106.2**	**7.5**	**11.51**	**2.2**	**42.5**	**88.3**	**16.7**	**11.02**	**259.3**	**28**	**83.7**	**1.333**	**0.627**	**304**	**4.88**	**13.15**
JA-2	MG08	31.0	2.27	19.4	136		28.7	137	31		17.3	73.5	257	16.3	118	8.8	4.88	304	15.27	32.20
	ET29	26.2	1.94	17.6	119	430	26.1	121	28	64	16.3	69.9	238	15.6	120	8.3	5.03	316	15.89	32.88
	ET30	26.4	1.95	17.6	120	423	26.3	120	29	63	16.4	70.6	243	15.6	112	8.3	5.12	318	16.14	33.33
	IZ13	32.9	2.40	18.0	131	422	28.3	130	30	69	17.2	71.0	252	15.1	116	8.6	4.92	308	15.29	32.22
JA-2	**average**	**29.1**	**2.14**	**18.1**	**127**	**425**	**27.3**	**127**	**29**	**65**	**16.8**	**71.2**	**248**	**15.7**	**117**	**8.5**	**4.99**	**312**	**15.65**	**32.66**
	RSD	3.4	0.23	0.9	9	4	1.3	8	2	3	0.5	1.6	8	0.5	3	0.3	0.11	7	0.44	0.55
JA-2	**pref.**	**29.18**	**2.26**	**18.93**	**119.7**	**425**	**28.33**	**136**	**29**	**64.5**	**16.85**	**69.8**	**245.8**	**16.89**	**108.5**	**9.3**	**4.78**	**308.4**	**15.46**	**32.86**
JA-3	KH05B	15.0	0.79	20.7	176		22.3	37.7	49	66	17.9	37.8	302	19.5	122	3.08	2.17	333	9.64	22.54
	ET15	13.8	0.70	23.1	199	67	22.4	34.5	48	77	18.4	37.9	293	19.8	130	3.17	2.19	325	9.48	22.01
	ET31	12.1	0.61	19.7	168	69	19.4	30.5	42	65	16.1	34.3	273	18.0	111	2.82	2.11	316	9.35	21.54
	AM15	13.9	0.69	20.6	178		20.0		45	57	16.4	33.7	289	18.0	112	2.90	2.05	310	9.00	21.05
	A31	13.7	0.68	21.8	194	71	21.1	39.5	46	51	17.3	36.9	296	18.8	117	3.00	2.08	299	8.86	20.76
JA-3	**average**	**13.7**	**0.70**	**21.2**	**183**	**69**	**21.0**	**35.6**	**46**	**63**	**17.2**	**36.1**	**290**	**18.8**	**118**	**2.99**	**2.12**	**316**	**9.26**	**21.58**
	RSD	1.0	0.06	1.3	13	2	1.3	3.9	3	10	1.0	1.9	11	0.8	8	0.14	0.06	13	0.33	0.72
JA-3	**pref.**	**14.5**	**0.80**	**22.0**	**169**	**66.2**	**21.1**	**32.2**	**43.4**	**68**	**16.3**	**36.7**	**287.0**	**21.1**	**118**	**3.4**	**2.08**	**323.0**	**9.33**	**22.80**
JR-2	KH06B	86.2	3.81	5.5	4.1		0.18		5.4	23	18.4	316	9.1	46.6	94.3	18.2	26.4	31.1	15.34	38.36
	IZ14	92.7	4.08	5.8	1.4	5.8	0.12	0.8	1.0	32	18.0	303	7.9	42.9	83.6	17.3	24.8	27.2	14.22	35.71
	P31	77.3	3.43	5.0	1.3	6.5	0.11	0.8	0.9	23	17.0	283	7.7	41.3	79.7	16.4	24.6	26.9	14.17	35.76
	EG54	96.5	3.95	6.1	1.5	3.7	0.14	0.7	1.3	28	17.9	308	8.1	44.6	87.7	17.0	24.5	27.4	14.01	35.46
JR-2	**average**	**88.2**	**3.82**	**5.6**	**2.1**	**5.3**	**0.14**	**0.8**	**2.2**	**27**	**17.8**	**303**	**8.2**	**43.8**	**86.3**	**17.2**	**25.1**	**28.2**	**14.44**	**36.32**
	RSD	8.4	0.28	0.4	1.3	1.4	0.03	0.1	2.2	4	0.6	14	0.6	2.3	6.2	0.7	0.9	2.0	0.61	1.36
JR-2	**recom.**	**79.2**	**3.75**	**5.6**	**3.0**	**3.1**	**0.46**	**2.0**	**1.4**	**28**	**17.9**	**303.0**	**8.1**	**51.5**	**96.3**	**18.7**	**25.0**	**39.5**	**16.30**	**38.80**
BIR-1a	KH07B	3.36	0.109	41.5	362		54.8	183	128	67	16.1	0.18	113	15.1	15.7	0.50		7.02	0.63	1.97
	KH33	3.00	0.097	38.2	316		49.1	162	114	60	14.3	0.20	103	13.6	13.5	0.44		5.90	0.56	1.74
	KH59	2.79	0.088	45.9	326	425	54.6	169	120	78	15.7	0.16	107	14.7	14.4	0.47	0.0062	6.47	0.60	1.91
	KH71	2.90	0.089	40.5	325	414	50.9	167	118	63	14.9	0.21	104	14.0	13.9	0.47	0.0029	6.42	0.58	1.84
	KH83	2.82	0.081	38.8	317		48.3	161	113		14.1	0.40	105	13.3	13.1	0.45	0.0076	5.78	0.55	1.72
	OR11	2.68	0.085	45.0	293		49.7	154	104	62	13.8	0.25	97	12.8	11.8	0.20	0.0043	5.68	0.54	1.73
	OR23	2.79	0.082	44.8	292	427	51.0	166	112	67	14.0	0.30	98	12.1	11.5	0.34	0.0038	5.80	0.55	1.74
	AF12	2.75	0.085	45.7	311		50.1	162	110	71	14.2	0.23	99	12.8	12.4	0.39	0.0054	5.87	0.55	1.74
	AF24	2.82	0.084	46.0	325	409	52.5	168	110	70	14.6	0.27	104	13.5	13.2	0.47	0.0044	6.14	0.58	1.82
	EG12	2.76	0.090	44.0	332		52.0	171	114	77	15.0	0.29	110	14.0	13.9	0.49	0.0072	6.44	0.59	1.85
	KI15	3.14	0.094	51.5	357	400	54.8	177	119	86	15.8	0.23	111	15.0	15.2	0.51	0.0065	6.38	0.60	1.86
BIR-1a	**average**	**2.89**	**0.089**	**43.8**	**323**	**415**	**51.6**	**167**	**115**	**70**	**14.8**	**0.25**	**104**	**13.7**	**13.5**	**0.43**	**0.0054**	**6.17**	**0.57**	**1.81**
	RSD	0.20	0.008	3.8	22	11	2.3	8	6	8	0.8	0.07	5	0.9	1.3	0.09	0.0016	0.41	0.03	0.08
	RSD (%)	7.0	**9.1**	**8.7**	6.8	2.7	4.5	4.7	5.6	**11.4**	5.4	**27.3**	5.0	6.9	**9.8**	**21.3**	**29.7**	6.6	4.8	4.6
BIR-1	**pref.**	**3.203**	**0.102**	**43.21**	**320.6**	**392.9**	**52.22**	**168.9**	**120.7**	**70.4**	**15.46**	**0.21**	**108.6**	**15.6**	**14.8**	**0.553**	**0.00646**	**6.75**	**0.627**	**1.92**
BHVO-2	SA7	4.6	1.01	34.3		304	47.0	134	139		22.5	9.68	425	24.7	179	17.0	0.090	124	14.47	36.36
	SA33	4.4	1.06	30.3	330	292	43.3	116	124	109	20.3	8.48	382	22.9	160	16.2	0.094	120	13.97	34.66
	IZ15	5.0	1.07	31.9	353	306	45.9	123	133	116	21.6	8.80	404	22.9	160	16.3	0.091	124	14.13	35.49
	SA49	4.4	1.01	31.1	326	307	44.6	119	130	103	21.4	9.04	390	23.8	162	15.9	0.089	126	14.46	36.25
	SA65	4.7	1.09	31.9	345		45.6	120	131	105	21.7	8.95	400	24.1	165	16.7	0.096	125	14.60	36.62
BHVO-2	**average**	**4.6**	**1.05**	**31.9**	**339**	**302**	**45.3**	**122**	**132**	**108**	**21.5**	**8.99**	**400**	**23.7**	**165**	**16.4**	**0.092**	**124**	**14.33**	**35.88**
	RSD	0.2	0.04	1.5	13	7	1.4	7	5	6	0.8	0.44	16	0.8	8	0.5	0.003	2	0.27	0.80
	RSD (%)	4.9	3.7	4.7	3.7	2.2	3.1	5.9	4.1	5.4	3.7	4.9	4.0	3.4	4.8	2.8	3.3	1.9	1.9	2.2
BHVO-2	**pref.**	**4.5**	**1.076**	**31.83**	**318.2**	**287.2**	**44.89**	**119.8**	**129.3**	**103.9**	**21.37**	**9.261**	**394.1**	**25.91**	**171.2**	**18.1**	**0.0996**	**130.9**	**15.2**	**37.53**
JSd-1	E16	26.7	1.40	11.6	81		10.8	6.9	22	94	17.5	67.2	316	13.0	21.9	10.1	1.96	507	15.49	31.08
	SA17	22.4	1.20	10.3	72		9.9	9.4	21	77	16.2	61.9	328	12.5	23.6	9.8	1.96	513	15.13	30.23
	PI15	19.2	1.06	8.7	64		9.2	6.4	20	93	15.0	58.7	322	11.5	20.1	9.3	1.98	531	15.84	31.54
	KM15	23.9	1.29	9.8	76		10.1	7.0	37	90	16.1	61.6	327	12.4	22.1	9.8	1.90	503	15.37	30.67
JSd-1	**average**	**23.0**	**1.23**	**10.1**	**73**		**10.0**	**7.4**	**25**	**89**	**16.2**	**62.4**	**323**	**12.3**	**21.9**	**9.7**	**1.95**	**514**	**15.46**	**30.88**
	RSD	3.1	0.14	1.2	7		0.7	1.3	8	8	1.0	3.5	6	0.6	1.4	0.3	0.03	13	0.30	0.56
JSd-1	**recom.**	**22.80**	**1.4**	**10.9**	**76**		**11.2**	**7.04**	**22**	**96.5**	**17.2**	**67.4**	**340**	**14.8**	**132**	**11.1**	**1.89**	**520**	**18.1**	**34.4**

* RSD (relative standard deviation): One sigma standard deviation of the replicated measurements.

** RSDs (%) of only basaltic samples are shown because other samples have small number of a replicated analyses. ＞8% RSD values are shown in red.

\# GeoRem preferred values (http://georem.mpch-mainz.gwdg.de/) are shown in green.

\#\# Recommended, certified, or information values (https://gbank.gsj.jp/geostandards/welcome.html) are also shown in green.

$ Blank means we did not analyze the elements.

$$ Note that Zr and Hf values of this study (in blue) are distinctly lower than recommended values.

Table 3 (continued). Trace element concentrations (μg/g: ppm) in reference rocks.

Sample	Run No.	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Th	U
JB-1	EG11	6.76	25.28	4.88	1.40	4.56	0.73	3.98	0.78	2.24	0.32	2.02	0.30	3.48	2.36	0.095	6.47	7.99	1.39
	AF11	7.04	26.09	5.04	1.42	4.66	0.74	4.11	0.81	2.31	0.31	2.04	0.30	3.47	2.45	0.084	6.81	9.11	1.51
	AF23	6.68	24.88	4.83	1.38	4.48	0.71	3.89	0.77	2.19	0.30	1.94	0.29	3.40	2.16	0.086	6.75	7.91	1.39
	KH34	6.67	25.10	4.77	1.39	4.45	0.72	3.95	0.78	2.22	0.30	1.97	0.30	3.51	2.07	0.089	6.53	8.42	1.52
	KH58	7.13	26.44	5.11	1.54	5.13	0.77	4.18	0.81	2.32	0.31	2.10	0.30	3.65	2.65	0.086	6.51	8.33	1.51
	KH70	6.75	24.95	4.88	1.48	4.94	0.71	3.96	0.77	2.21	0.30	1.97	0.28	3.44	2.44	0.083	6.45	8.18	1.50
	OR22	6.54	24.51	4.71	1.39	4.61	0.71	3.92	0.76	2.14	0.31	1.97	0.29	3.27	2.18	0.095	7.15	10.36	1.69
	KM14-2	6.86	25.31	4.77	1.44	4.74	0.74	4.01	0.77	2.23	0.31	1.99	0.28	3.61	2.53	0.086	6.51	8.96	1.59
	ES16	7.36	26.32	5.01	1.47	4.40	0.80	4.00	0.81	2.34	0.31	2.01	0.31	3.61	2.55	0.094	6.13	9.34	1.66
	ET48	7.57	26.73	5.00	1.46	3.97	0.80	4.09	0.81	2.33	0.32	2.03	0.31	3.83	2.72	0.092	6.09	9.99	1.68
JB-1	**average**	**6.93**	**25.56**	**4.90**	**1.44**	**4.59**	**0.74**	**4.01**	**0.79**	**2.25**	**0.31**	**2.00**	**0.30**	**3.53**	**2.41**	**0.089**	**6.54**	**8.86**	**1.54**
	RSD	0.33	0.77	0.13	0.05	0.31	0.04	0.09	0.02	0.07	0.01	0.05	0.01	0.16	0.22	0.005	0.31	0.85	0.11
	RSD (%)	4.8	3.0	2.7	3.6	6.8	4.9	2.3	2.6	3.0	2.0	2.2	3.4	4.4	9.0	5.2	4.8	9.6	7.2
JB-1	**pref.**	**7.2**	**26.3**	**5.1**	**1.46**	**4.7**	**0.72**	**4.1**	**0.83**	**2.2**	**0.3**	**2.16**	**0.31**	**3.5**	**1.8**	**0.087**	**6.3**	**9.2**	**1.6**
JB-1a	EG23	6.87	25.43	4.91	1.40	4.35	0.71	3.93	0.77	2.19	0.31	1.97	0.29	3.51	1.57	0.079	5.61	7.87	1.41
	KF36	6.51	24.11	4.68	1.31	4.17	0.66	3.71	0.73	2.06	0.28	1.85	0.27	3.54	1.41	0.071	5.73	8.03	1.48
	PP11	6.47	23.78	4.58	1.29	4.09	0.65	3.68	0.72	2.04	0.28	1.80	0.27	3.13	1.38	0.073	5.70	8.12	1.46
	OJ47	6.70	24.78	4.79	1.35	4.18	0.68	3.89	0.76	2.14	0.30	1.92	0.29	3.45	1.53	0.081	6.20	8.93	1.55
	OJ75	6.69	24.81	4.83	1.35	4.29	0.69	3.89	0.76	2.15	0.30	1.94	0.29	3.44	1.52	0.076	6.04	8.62	1.55
	E15	6.69	24.65	4.81	1.34	4.52	0.67	3.91	0.74	2.11	0.28	1.91	0.26	3.23	1.45	0.063	6.35	8.46	1.55
	OJ90	6.63	24.51	4.77	1.37	4.49	0.71	3.88	0.77	2.18	0.30	1.94	0.29	3.37	1.49	0.084	6.00	8.68	1.55
	PP27	6.69	24.72	4.85	1.41	4.63	0.71	3.99	0.78	2.21	0.31	2.00	0.30	3.54	1.55	0.085	5.71	8.39	1.51
	M23	6.89	25.52	4.99	1.44	4.35	0.73	4.03	0.82	2.34	0.29	1.97	0.34	3.79	1.70	0.106	4.60	8.97	1.46
	KI14	6.83	25.23	4.87	1.36	4.36	0.71	3.94	0.79	2.18	0.31	2.00	0.30	3.45	1.54	0.086	5.86	9.02	1.58
	MG07	6.60	24.40	4.67	1.33	4.31	0.68	3.80	0.75	2.14	0.29	1.86	0.27	3.26	1.44	0.092	5.84	8.07	1.50
	OJ90 m	6.85	25.49	5.03	1.37	4.44	0.71	4.09	0.79	2.25	0.32	2.11	0.31	3.58	1.60	0.089	6.12	8.79	1.58
	PA14	6.77	24.92	4.79	1.36	4.38	0.69	3.79	0.76	2.11	0.29	1.92	0.29	3.33	1.49	0.082	5.78	8.63	1.52
	A14	6.84	25.31	4.92	1.43	4.62	0.74	4.04	0.81	2.24	0.32	2.07	0.32	3.70	1.64	0.103	5.76	9.18	1.62
	AM14	6.84	25.30	4.92	1.40	4.49	0.73	4.03	0.80	2.26	0.31	2.03	0.30	3.68	1.64	0.092	5.46	8.24	1.48
	SA6	6.61	24.48	4.67	1.30	4.15	0.66	3.76	0.73	2.10	0.28	1.89	0.26	3.09	1.38	0.060	6.12	9.02	1.62
	A30	6.77	25.03	4.75	1.31	4.09	0.66	3.85	0.75	2.11	0.28	1.89	0.27	3.12	1.41	0.067	6.11	9.09	1.60
	SA16	6.95	25.78	5.00	1.45	4.79	0.75	4.13	0.82	2.31	0.32	2.11	0.31	3.78	1.69	0.089	5.93	8.87	1.59
	SA32	6.73	24.99	4.81	1.37	4.49	0.72	3.97	0.78	2.22	0.31	2.00	0.30	3.48	1.57	0.088	5.55	8.12	1.48
	A46	6.75	25.24	4.87	1.39	4.60	0.72	4.02	0.78	2.24	0.31	2.01	0.29	3.47	1.59	0.090	5.82	8.37	1.54
	PI14	7.00	26.20	5.05	1.48	4.92	0.77	4.31	0.85	2.42	0.34	2.17	0.33	3.94	1.75	0.108	6.18	9.21	1.70
	P30	6.72	25.06	4.82	1.37	4.38	0.71	4.02	0.78	2.21	0.31	1.99	0.29	3.48	1.42	0.083	5.69	8.48	1.53
	SA48	6.79	25.35	4.86	1.39	4.43	0.70	4.00	0.77	2.23	0.31	2.00	0.28	3.47	1.53	0.079	5.76	8.48	1.51
	SA64	6.79	25.35	4.87	1.38	4.42	0.70	4.02	0.77	2.21	0.30	1.99	0.29	3.47	1.58	0.078	5.81	8.61	1.53
	KM14	6.61	24.52	4.82	1.38	4.38	0.70	3.91	0.77	2.19	0.29	1.97	0.29	3.42	1.55	0.085	5.98	8.83	1.59
	EG51	6.54	24.34	4.70	1.32	4.28	0.69	3.80	0.75	2.10	0.31	1.90	0.28	3.31	1.49	0.086	5.80	8.20	1.50
JB-1a	**average**	**6.74**	**24.97**	**4.83**	**1.37**	**4.41**	**0.70**	**3.94**	**0.77**	**2.19**	**0.30**	**1.97**	**0.29**	**3.46**	**1.53**	**0.084**	**5.83**	**8.59**	**1.54**
	RSD	0.13	0.54	0.12	0.05	0.20	0.03	0.14	0.03	0.09	0.01	0.09	0.02	0.21	0.10	0.012	0.33	0.39	0.06
	RSD (%)	2.0	2.2	2.4	3.4	4.5	4.2	3.5	3.9	4.0	4.8	4.3	6.9	6.0	6.5	14.0	5.7	4.5	4.0
JB-1a	**pref.**	**7.1**	**26.15**	**5.099**	**1.484**	**4.7**	**0.699**	**4.07**	**0.805**	**2.232**	**0.3197**	**2.1**	**0.3147**	**3.47**	**1.738**	**0.072**	**6.44**	**8.97**	**1.615**
JB-1b	ET14	6.84	24.90	4.73	1.34	4.25	0.67	3.70	0.72	2.04	0.28	1.85	0.27	3.09	1.34	0.058	5.31	8.83	1.47
	ET27	7.21	26.08	5.04	1.43	4.64	0.73	3.97	0.81	2.18	0.32	2.11	0.31	3.51	1.55	0.080	5.10	9.52	1.53
	IZ11	6.75	24.89	4.67	1.33	4.25	0.67	3.75	0.72	2.08	0.28	1.81	0.26	3.15	1.35	0.054	5.33	8.67	1.50
	EG52	6.74	24.93	4.63	1.33	4.21	0.67	3.69	0.73	2.05	0.29	1.83	0.28	3.07	1.36	0.071	5.51	8.76	1.53
JB-1b	**average**	**6.88**	**25.20**	**4.77**	**1.36**	**4.34**	**0.69**	**3.78**	**0.75**	**2.09**	**0.29**	**1.90**	**0.28**	**3.21**	**1.40**	**0.07**	**5.31**	**8.94**	**1.51**
	RSD	0.22	0.59	0.18	0.05	0.20	0.03	0.13	0.04	0.06	0.02	0.14	0.02	0.21	0.10	0.01	0.17	0.39	0.03
	RSD (%)	3.2	2.3	3.9	3.5	4.6	4.5	3.5	5.8	3.1	7.0	7.5	8.5	6.5	7.2	18.1	3.1	4.3	1.8
JB-1b	**recom.**																**6.8**		
JB-2	KH02B	1.07	5.92	2.17	0.76	2.98	0.55	3.66	0.80	2.40	0.35	2.31	0.36	1.46	0.029	0.034	4.93	0.26	0.13
	EG24	1.09	6.03	2.17	0.76	2.99	0.55	3.71	0.81	2.46	0.36	2.36	0.36	1.46	0.035	0.032	4.20	0.21	0.12
	EG36	1.07	5.95	2.13	0.77	2.98	0.55	3.68	0.81	2.43	0.35	2.32	0.35	1.40	0.031	0.031	3.66	0.19	0.11
	OJ35	0.98	5.42	1.96	0.70	2.82	0.50	3.39	0.74	2.23	0.32	2.14	0.33	1.40	0.034	0.022	4.05	0.21	0.12
	KF37	1.04	5.77	2.09	0.73	2.86	0.53	3.54	0.77	2.32	0.33	2.24	0.34	1.46	0.031	0.029	4.19	0.23	0.14
	PP12	1.04	5.72	2.05	0.72	2.82	0.52	3.49	0.76	2.29	0.33	2.20	0.33	1.32	0.030	0.029	4.37	0.23	0.14
	OJ48	1.06	5.90	2.13	0.75	3.00	0.54	3.67	0.81	2.42	0.35	2.34	0.36	1.44	0.035	0.033	4.60	0.22	0.12
	OJ59	1.07	5.96	2.14	0.75	3.02	0.55	3.69	0.81	2.44	0.35	2.36	0.36	1.45	0.032	0.030	4.46	0.22	0.12
JB-2	**average**	**1.05**	**5.83**	**2.10**	**0.74**	**2.93**	**0.54**	**3.60**	**0.79**	**2.37**	**0.34**	**2.28**	**0.35**	**1.42**	**0.03**	**0.03**	**4.31**	**0.22**	**0.12**
	RSD	0.03	0.20	0.07	0.03	0.09	0.02	0.12	0.03	0.08	0.01	0.08	0.01	0.05	0.00	0.00	0.38	0.02	0.01
	RSD (%)	3.2	3.4	3.4	3.4	3.0	3.4	3.2	3.4	3.5	3.6	3.6	4.1	3.4	7.3	12.7	8.8	9.4	7.2
JB-2	**pref.**	**1.129**	**6.392**	**2.266**	**0.836**	**3.123**	**0.5863**	**3.868**	**0.863**	**2.537**	**0.393**	**2.529**	**0.3894**	**1.487**	**0.0396**	**0.034**	**5.25**	**0.2576**	**0.1528**
JB-3	KH03B	3.27	15.88	4.29	1.30	4.64	0.76	4.54	0.94	2.74	0.38	2.44	0.38	2.86	0.10	0.051	5.44	1.23	0.42
	OJ76	3.03	14.85	4.00	1.21	4.37	0.70	4.36	0.88	2.54	0.36	2.35	0.35	2.71	0.10	0.039	4.81	1.22	0.43
	OJ91	3.02	14.66	3.99	1.21	4.38	0.71	4.30	0.88	2.55	0.36	2.34	0.35	2.59	0.11	0.046	4.79	1.24	0.45
	OJ91 m	3.15	15.43	4.18	1.27	4.61	0.75	4.58	0.93	2.69	0.39	2.47	0.37	2.73	0.12	0.044	4.86	1.21	0.43
	IZ12	3.02	14.82	3.99	1.22	4.34	0.71	4.33	0.88	2.56	0.34	2.32	0.34	2.63	0.11	0.039	4.76	1.22	0.45
	EG53	3.01	14.74	3.96	1.20	4.30	0.71	4.23	0.87	2.51	0.36	2.30	0.35	2.55	0.12	0.053	4.94	1.27	0.47
JB-3	**average**	**3.08**	**15.06**	**4.07**	**1.24**	**4.44**	**0.72**	**4.39**	**0.90**	**2.60**	**0.37**	**2.37**	**0.36**	**2.68**	**0.11**	**0.05**	**4.94**	**1.23**	**0.44**
	RSD	0.10	0.49	0.13	0.04	0.15	0.03	0.14	0.03	0.09	0.02	0.07	0.02	0.11	0.01	0.01	0.26	0.02	0.02
	RSD (%)	3.4	3.2	3.3	3.3	3.3	3.5	3.2	3.4	3.5	4.2	3.0	4.6	4.3	9.6	12.7	5.2	1.7	4.0
JB-3	**recom.**	**3.11**	**15.60**	**4.27**	**1.32**	**4.67**	**0.73**	**4.54**	**0.80**	**2.49**	**0.42**	**2.55**	**0.31**	**2.67**	**0.15**	**0.048**	**5.58**	**1.27**	**0.48**

Table 3 (continued). Trace element concentrations (μg/g: ppm) in reference rocks.

Sample	Run No.	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Th	U
JA-1	KH04B	2.09	10.69	3.36	1.07	4.14	0.72	4.62	0.99	3.00	0.43	2.81	0.45	2.54	0.086	0.082	6.12	0.71	0.30
	PP28	1.98	10.22	3.23	1.05	4.12	0.71	4.62	0.98	2.94	0.42	2.83	0.43	2.47	0.090	0.079	5.60	0.75	0.35
	PA15	2.11	10.80	3.38	1.06	4.27	0.73	4.62	0.99	2.93	0.43	2.85	0.43	2.46	0.086	0.080	5.16	0.70	0.33
	A15	2.04	10.53	3.33	1.06	4.25	0.74	4.67	1.02	2.96	0.44	2.98	0.45	2.61	0.202	0.093	5.21	0.76	0.35
	ET28	2.11	10.76	3.43	1.09	4.45	0.76	4.81	1.05	3.05	0.46	3.11	0.48	2.71	0.098	0.097	5.47	0.82	0.37
	A47	2.04	10.49	3.30	1.06	4.16	0.72	4.65	0.99	2.96	0.43	2.81	0.43	2.52	0.091	0.081	5.20	0.71	0.34
JA-1	**average**	**2.06**	**10.58**	**3.34**	**1.07**	**4.23**	**0.73**	**4.67**	**1.01**	**2.97**	**0.44**	**2.90**	**0.45**	**2.55**	**0.11**	**0.085**	**5.46**	**0.74**	**0.34**
	RSD	0.05	0.22	0.07	0.01	0.12	0.02	0.08	0.03	0.04	0.02	0.12	0.02	0.10	0.05	0.008	0.37	0.04	0.02
JA-1	**pref.**	**2.082**	**10.69**	**3.396**	**1.112**	**4.15**	**0.727**	**4.75**	**1.032**	**2.959**	**0.445**	**2.949**	**0.454**	**2.51**	**0.0979**	**0.106**	**5.86**	**0.761**	**0.34**
JA-2	MG08	3.54	13.67	2.90	0.82	2.79	0.46	2.77	0.56	1.64	0.23	1.54	0.23	2.80	0.57	0.30	14.24	3.41	1.57
	ET29	3.72	14.17	3.08	0.88	3.04	0.51	2.94	0.62	1.76	0.27	1.77	0.27	3.21	0.67	0.38	13.37	3.76	1.66
	ET30	3.78	14.36	3.13	0.89	3.10	0.51	2.94	0.63	1.75	0.27	1.77	0.27	3.25	0.68	0.38	13.14	3.71	1.63
	IZ13	3.56	13.86	2.95	0.83	2.88	0.47	2.81	0.57	1.69	0.23	1.56	0.23	2.92	0.60	0.33	18.38	4.58	2.11
JA-2	**average**	**3.65**	**14.01**	**3.02**	**0.85**	**2.96**	**0.49**	**2.87**	**0.59**	**1.71**	**0.25**	**1.66**	**0.25**	**3.04**	**0.63**	**0.35**	**14.78**	**3.86**	**1.74**
	RSD	0.12	0.31	0.11	0.04	0.14	0.02	0.09	0.04	0.06	0.02	0.13	0.02	0.22	0.06	0.04	2.45	0.50	0.25
JA-2	**pref.**	**3.691**	**14.04**	**3.032**	**0.893**	**3.013**	**0.4786**	**2.851**	**0.591**	**1.676**	**0.2546**	**1.645**	**0.2549**	**2.838**	**0.652**	**0.33**	**18.88**	**4.8**	**2.182**
JA-3	KH05B	2.86	12.63	3.22	0.80	3.23	0.54	3.34	0.69	2.08	0.30	1.98	0.32	3.41	0.23	0.20	9.97	3.02	0.88
	ET15	2.84	12.32	3.10	0.76	3.25	0.54	3.25	0.68	2.01	0.29	1.98	0.30	3.26	0.23	0.19	7.18	3.07	0.92
	ET31	2.82	12.28	3.11	0.78	3.38	0.56	3.34	0.73	2.09	0.32	2.14	0.33	3.58	0.25	0.23	6.50	3.08	0.89
	AM15	2.72	11.95	3.03	0.73	3.16	0.53	3.22	0.68	2.01	0.30	1.96	0.29	3.41	0.25	0.20	6.19	2.73	0.83
	A31	2.69	11.63	2.89	0.69	2.95	0.50	3.05	0.63	1.87	0.27	1.82	0.27	2.89	0.20	0.18	6.30	2.69	0.80
JA-3	**average**	**2.78**	**12.16**	**3.07**	**0.75**	**3.20**	**0.53**	**3.24**	**0.68**	**2.01**	**0.30**	**1.97**	**0.30**	**3.31**	**0.23**	**0.20**	**7.23**	**2.92**	**0.86**
	RSD	0.08	0.38	0.12	0.04	0.16	0.02	0.12	0.03	0.09	0.02	0.11	0.02	0.26	0.02	0.02	1.58	0.19	0.05
JA-3	**pref.**	**2.40**	**12.30**	**3.05**	**0.82**	**2.96**	**0.52**	**3.01**	**0.51**	**1.57**	**0.28**	**2.16**	**0.32**	**3.42**	**0.27**	**0.230**	**7.7**	**3.25**	**1.18**
JR-2	KH06B	4.91	19.40	5.42	0.11	5.80	1.06	6.72	1.44	4.70	0.75	5.23	0.85	5.35	2.00	1.86	22.2	28.9	9.65
	IZ14	4.57	18.20	5.02	0.09	5.26	0.98	6.32	1.35	4.33	0.68	4.93	0.76	4.89	1.85	1.69	19.4	28.1	9.82
	P31	4.60	18.39	5.09	0.09	5.38	1.00	6.49	1.39	4.43	0.71	5.09	0.78	5.01	1.91	1.77	20.3	29.9	10.44
	EG54	4.54	18.13	4.98	0.09	5.30	0.98	6.29	1.37	4.31	0.69	4.95	0.77	4.88	1.87	1.70	19.6	28.5	9.96
JR-2	**average**	**4.66**	**18.53**	**5.13**	**0.09**	**5.44**	**1.01**	**6.46**	**1.39**	**4.45**	**0.71**	**5.05**	**0.79**	**5.03**	**1.91**	**1.75**	**20.34**	**28.83**	**9.97**
	RSD	0.17	0.59	0.20	0.01	0.25	0.04	0.20	0.04	0.18	0.03	0.14	0.04	0.22	0.07	0.08	1.27	0.77	0.34
JR-2	**recom.**	**4.75**	**20.40**	**5.63**	**0.14**	**5.83**	**1.10**	**6.63**	**1.39**	**4.36**	**0.74**	**5.33**	**0.88**	**5.14**	**2.29**	**1.850**	**21.5**	**31.4**	**10.90**
BIR-1a	KH07B	0.37	2.37	1.11	0.52	1.83	0.35	2.51	0.56	1.66	0.24	1.59	0.25	0.62	0.027	0.0050	2.97	0.070	0.014
	KH33	0.34	2.14	0.99	0.46	1.64	0.32	2.27	0.51	1.51	0.22	1.44	0.22	0.54	0.026	0.0026	2.54	0.042	0.009
	KH59	0.37	2.38	1.12	0.52	1.84	0.37	2.59	0.58	1.74	0.25	1.67	0.25	0.63	0.033		2.68	0.024	0.006
	KH71	0.35	2.29	1.06	0.50	1.76	0.35	2.52	0.55	1.67	0.24	1.57	0.24	0.59	0.037		3.04	0.029	0.010
	KH83	0.33	2.14	0.99	0.46	1.67	0.33	2.29	0.51	1.53	0.22	1.47	0.22	0.53	0.032	0.0011	2.59	0.056	0.027
	OR11	0.33	2.16	1.00	0.48	1.70	0.34	2.36	0.53	1.60	0.23	1.51	0.23	0.53		0.0001	2.62	0.060	0.004
	OR23	0.34	2.18	1.02	0.48	1.71	0.34	2.43	0.54	1.63	0.24	1.57	0.24	0.55	0.020	0.0021	2.75	0.054	0.011
	AF12	0.34	2.16	1.01	0.47	1.70	0.33	2.37	0.53	1.59	0.23	1.52	0.23	0.55	0.025		2.75	0.031	0.002
	AF24	0.36	2.27	1.07	0.50	1.78	0.35	2.49	0.56	1.68	0.24	1.59	0.24	0.59	0.035	0.0006	2.70	0.029	0.005
	EG12	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	2.83	0.030	0.010
	KI15	0.36	2.29	1.06	0.51	1.85	0.35	2.49	0.56	1.67	0.24	1.62	0.25	0.60	0.032	0.0021	3.23	0.029	0.008
BIR-1a	**average**	**0.35**	**2.25**	**1.05**	**0.49**	**1.75**	**0.35**	**2.44**	**0.54**	**1.64**	**0.24**	**1.56**	**0.24**	**0.58**	**0.03**	**0.0019**	**2.79**	**0.041**	**0.010**
	RSD	0.01	0.09	0.05	0.02	0.07	0.01	0.11	0.02	0.07	0.01	0.07	0.01	0.04	0.01	0.0015	0.21	0.016	0.007
	RSD (%)	4.1	4.2	4.7	4.3	4.2	4.2	4.3	4.4	4.4	4.7	4.5	4.5	6.2	**20.1**	**76.5**	7.5	**38.5**	**69.4**
BIR-1	**pref.**	**0.3723**	**2.397**	**1.113**	**0.5201**	**1.809**	**0.3623**	**2.544**	**0.5718**	**1.68**	**0.2558**	**1.631**	**0.2484**	**0.5822**	**0.0414**	**0.0021**	**3.037**	**0.0328**	**0.01051**
BHVO-2	SA7	5.02	23.11	5.69	1.90	5.69	0.87	4.88	0.88	2.32	0.29	1.79	0.24	3.92	0.87		1.38	1.14	0.38
	SA33	4.82	22.37	5.46	1.87	5.67	0.88	4.79	0.91	2.34	0.31	1.82	0.26	4.18	1.02	0.025	1.21	1.07	0.38
	IZ15	4.96	22.87	5.66	1.89	5.78	0.89	4.96	0.91	2.39	0.29	1.83	0.25	4.25	0.97	0.015	1.47	1.15	0.39
	SA49	5.06	23.46	5.85	1.94	5.89	0.91	5.05	0.92	2.45	0.31	1.92	0.26	4.32	1.01	0.010	1.33	1.10	0.36
	SA65	5.09	23.65	5.86	1.96	5.90	0.90	5.08	0.93	2.47	0.30	1.90	0.26	4.33	1.06	0.014	1.51	1.16	0.38
BHVO-2	**average**	**4.99**	**23.09**	**5.71**	**1.91**	**5.79**	**0.89**	**4.95**	**0.91**	**2.39**	**0.30**	**1.85**	**0.25**	**4.20**	**0.99**	**0.016**	**1.38**	**1.12**	**0.38**
	RSD	0.11	0.50	0.16	0.04	0.11	0.02	0.12	0.02	0.07	0.01	0.05	0.01	0.17	0.07	0.006	0.12	0.04	0.01
	RSD (%)	2.1	2.2	2.9	1.9	1.9	1.7	2.4	2.2	2.8	3.6	2.9	4.1	4.0	7.4	**39.7**	**8.5**	3.4	3.2
BHVO-2	**pref.**	**5.339**	**24.27**	**6.023**	**2.043**	**6.207**	**0.9392**	**5.28**	**0.9887**	**2.511**	**0.3349**	**1.994**	**0.2754**	**4.47**	**1.154**	**0.0224**	**1.653**	**1.224**	**0.412**
JSd-1	E16	3.95	15.45	3.26	0.83	2.86	0.42	2.33	0.44	1.24	0.16	1.08	0.15	0.74	0.64	0.29	8.97	2.87	0.58
	SA17	3.87	15.58	3.30	0.87	2.94	0.46	2.48	0.48	1.32	0.18	1.17	0.18	0.91	0.70	0.34	9.19	2.98	0.61
	PI15	4.03	16.26	3.41	0.91	3.14	0.48	2.60	0.50	1.38	0.19	1.22	0.19	0.92	0.75	0.36	9.60	3.11	0.66
	KM15	3.89	15.49	3.26	0.86	2.90	0.44	2.41	0.47	1.29	0.18	1.14	0.16	0.82	0.70	0.31	9.60	2.99	0.63
JSd-1	**average**	**3.93**	**15.69**	**3.31**	**0.87**	**2.96**	**0.45**	**2.45**	**0.47**	**1.31**	**0.18**	**1.15**	**0.17**	**0.85**	**0.70**	**0.32**	**9.34**	**2.99**	**0.62**
	RSD	0.07	0.38	0.07	0.03	0.12	0.02	0.11	0.03	0.06	0.01	0.06	0.02	0.09	0.05	0.03	0.32	0.10	0.03
JSd-1	**recom.**	**4.05**	**17.6**	**3.48**	**0.925**	**2.71**	**0.431**	**2.23**	**0.318**	**0.906**	**0.13**	**1.18**	**0.186**	**3.55**	**0.893**	**0.407**	**12.9**	**4.44**	**1**

Table 4. Selected major element concentrations (wt%) in reference rocks.

Sample	Run No.	TiO_2	Al_2O_3	Fe_2O_3*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
JB-1	KH34 m	1.383	14.11	8.55	0.149	7.70	9.10	2.74	1.40	0.267
	KH70 m	1.384	14.78	8.72	0.153	7.61	9.10	2.73	1.39	0.269
	OR22 m	1.384	14.51	8.73	0.148	7.68	9.11	2.74	1.34	0.269
	ES16	1.378	15.28	9.10	0.153	8.31	8.99	2.77	1.41	0.287
	ET48	1.381	15.29	8.90	0.162	8.16	8.85	2.79	1.41	0.279
	KM14-2	1.359	14.77	8.80	0.153	7.66	9.03	2.66	1.39	0.305
JB-1	**average**	**1.378**	**14.79**	**8.80**	**0.153**	**7.85**	**9.03**	**2.74**	**1.39**	**0.279**
	RSD**	0.009	0.42	0.17	0.004	0.27	0.09	0.04	0.02	0.013
	RSD (%)#	0.7	2.8	2.0	2.8	3.5	1.0	1.5	1.8	4.8
JB-1	**pref.#**	**1.299**	**14.53**	**8.99**	**0.149**	**7.807**	**9.33**	**2.749**	**1.42**	**0.263**
JB-1a	KF36 m	1.368	14.32	8.98	0.146	7.68	9.27	2.71	1.38	0.264
	PP11 m	1.370	14.18	8.89	0.149	7.64	9.24	2.70	1.38	0.266
	OJ47 m	1.515	15.51	9.85	0.162	8.46	10.22	3.00	1.52	0.289
	OJ90 m	1.365	14.15	8.96	0.147	7.72	9.21	2.72	1.39	0.263
	PP27 m	1.385	14.36	8.95	0.147	7.82	9.30	2.77	1.40	0.271
	KI14 m	1.395	14.37	8.98	0.149	7.89	9.36	2.76	1.40	0.274
	PA14 m	1.386	14.14	8.98	0.148	7.73	9.24	2.73	1.40	0.262
	A14 m	1.336	13.67	8.71	0.145	7.37	9.10	2.64	1.35	0.255
	A30 m	1.331	13.73	8.79	0.145	7.35	9.13	2.66	1.35	0.253
	Sa6 m	1.338	13.76	8.81	0.145	7.51	9.03	2.65	1.35	0.258
	Sa16 m	1.325	13.66	8.73	0.144	7.52	9.00	2.65	1.35	0.252
	AM14 m	1.354	13.87	8.89	0.146	7.62	9.17	2.66	1.37	0.259
	PI14	1.358	14.72	8.90	0.148	7.81	9.03	2.70	1.37	0.299
	SA64	1.357	14.78	8.96	0.149	7.86	9.09	2.72	1.39	0.309
	KM14	1.354	14.78	8.90	0.149	7.82	9.13	2.65	1.39	0.306
	EG51	1.393	15.32	9.17	0.152	8.23	9.45	2.77	1.42	0.266
JB-1a	**average**	**1.371**	**14.33**	**8.97**	**0.148**	**7.75**	**9.25**	**2.72**	**1.39**	**0.272**
	RSD	0.044	0.57	0.26	0.004	0.29	0.29	0.09	0.04	0.019
	RSD (%)	3.2	4.0	2.9	2.9	3.7	3.1	3.3	3.0	6.9
JB-1a	**pref.**	**1.29**	**14.51**	**8.996**	**0.1419**	**7.81**	**9.314**	**2.738**	**1.407**	**0.261**
JB-1b	IZ11	1.352	14.96	9.12	0.148	8.78	9.77		1.34	0.261
	ET14 m	1.287	13.51	8.64	0.141	8.07	9.26	2.53	1.24	0.255
	ET27 m	1.279	13.45	8.72	0.141	7.97	9.29	2.51	1.24	0.250
	IZ11 m	1.322	14.51	9.00	0.146	8.22	9.54	2.57	1.29	0.249
	EG52	1.335	15.04	9.12	0.147	8.66	9.56	2.66	1.32	0.264
JB-1b	**average**	**1.315**	**14.29**	**8.92**	**0.145**	**8.34**	**9.48**	**2.57**	**1.29**	**0.26**
	RSD	0.031	0.77	0.23	0.003	0.36	0.21	0.07	0.05	0.01
	RSD (%)	2.4	5.4	2.5	2.2	4.3	2.2	2.6	3.6	2.6
JB-1b	**recom.##**	**1.26**	**14.38**	**9.02**	**0.147**	**8.14**	**9.60**	**2.63**	**1.32**	**0.256**
JB-2	OJ35 m	1.106	13.37	12.82	0.197	3.98	8.73	1.78	0.366	0.088
JB-2	PP12 m	1.203	14.49	13.96	0.215	4.37	9.49	1.94	0.398	0.095
JB-2	OJ48 m	1.220	14.64	14.00	0.217	4.41	9.51	1.95	0.401	0.095
JB-2	OJ59 m	1.235	14.86	14.14	0.217	4.51	9.64	1.99	0.408	0.095
JB-2	**average**	**1.191**	**14.341**	**13.729**	**0.212**	**4.32**	**9.34**	**1.92**	**0.393**	**0.093**
	RSD	0.058	0.663	0.613	0.010	0.23	0.42	0.09	0.019	0.004
	RSD (%)	4.9	4.6	4.5	4.6	5.3	4.4	4.8	4.7	3.8
JB-2	**pref.**	**1.167**	**14.62**	**14.28**	**0.213**	**4.43**	**9.852**	**2.054**	**0.4224**	**0.097**
JB-3	OJ76 m	1.521	17.63	11.81	0.181	5.10	9.69	2.69	0.77	0.304
JB-3	OJ91 m	1.504	17.40	11.70	0.180	5.01	9.64	2.67	0.76	0.294
JB-3	EG53	1.536	18.40	12.06	0.186	5.34	9.94	2.81	0.79	0.312
JB-3	**average**	**1.520**	**17.81**	**11.86**	**0.182**	**5.15**	**9.76**	**2.72**	**0.77**	**0.30**
	RSD	0.016	0.52	0.18	0.003	0.17	0.16	0.08	0.02	0.01
	RSD (%)	1.0	2.9	1.5	1.8	3.3	1.7	2.8	2.3	2.9
JB-3	**recom.**	**1.44**	**17.20**	**11.82**	**0.177**	**5.19**	**9.79**	**2.73**	**0.78**	**0.294**

Sample	Run No.	TiO_2	Al_2O_3	Fe_2O_3*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
JA-1	PP28 m	0.89	14.65	6.96	0.156	1.41	5.61	3.75	0.755	0.158
	PA15 m	0.89	14.59	6.90	0.156	1.39	5.63	3.74	0.754	0.155
	A15 m	0.87	14.44	6.82	0.153	1.37	5.49	3.68	0.738	0.154
	ET28 m	0.88	14.54	6.85	0.154	1.37	5.56	3.73	0.745	0.164
	A47	0.88	15.78	6.95	0.156	1.58	5.55	3.86	0.758	0.177
JA-1	**average**	**0.882**	**14.80**	**6.90**	**0.155**	**1.42**	**5.57**	**3.75**	**0.750**	**0.161**
	RSD	0.009	0.55	0.06	0.002	0.09	0.06	0.07	0.009	0.009
JA-1	**pref.**	**0.85**	**15.19**	**7.05**	**0.1543**	**1.54**	**5.72**	**3.91**	**0.779**	**0.1595**
JA-2	IZ13	0.74	16.90	6.41	0.110	7.60	6.47		1.94	0.163
	ET29 m	0.701	14.92	6.140	0.107	6.53	6.09	3.050	1.76	0.159
	ET30 m	0.704	15.00	6.095	0.105	6.45	6.09	3.069	1.76	0.154
	IZ13 m	0.720	16.43	6.312	0.108	7.15	6.30	3.148	1.84	0.151
JA-2	**average**	**0.716**	**15.81**	**6.24**	**0.11**	**6.93**	**6.24**	**3.09**	**1.83**	**0.157**
	RSD	0.017	1.00	0.15	0.00	0.54	0.18	0.05	0.09	0.005
JA-2	**pref.**	**0.670**	**15.51**	**6.289**	**0.109**	**7.84**	**6.26**	**3.072**	**1.779**	**0.152**
JA-3	ET15 m	0.71	15.43	6.51	0.105	3.43	6.15	3.06	1.36	0.112
JA-3	ET31 m	0.71	15.23	6.48	0.105	3.39	6.22	3.10	1.37	0.109
JA-3	A31 m	0.74	16.21	6.62	0.107	3.65	6.37	3.15	1.40	0.115
JA-3	**average**	**0.720**	**15.62**	**6.53**	**0.106**	**3.49**	**6.25**	**3.10**	**1.38**	**0.112**
	RSD	0.015	0.52	0.07	0.001	0.14	0.11	0.04	0.03	0.003
JA-3	**recom.**	**0.70**	**15.56**	**6.60**	**0.104**	**3.72**	**6.24**	**3.19**	**1.41**	**0.116**
JR-2	IZ14	0.063	13.94	0.78	0.117	0.042	0.56		4.909	0.004
JR-2	IZ14 m	0.056	13.19	0.76	0.113	0.038	0.53	4.02	4.648	0.003
JR-2	EG54	0.064	13.29	0.76	0.112	0.043	0.56	4.05	4.481	0.007
JR-2	**average**	**0.061**	**13.47**	**0.77**	**0.114**	**0.041**	**0.55**	**4.03**	**4.679**	**0.005**
	RSD	0.005	0.41	0.02	0.003	0.002	0.02		0.216	0.002
JR-2	**recom.**	**0.07**	**12.72**	**0.77**	**0.112**	**0.04**	**0.50**	**3.99**	**4.45**	**0.012**
BIR-1a	KH59 m	1.077	15.80	11.78	0.181	9.925	13.64	1.894	0.023	0.026
BIR-1a	KH71 m	1.024	15.07	11.36	0.173	9.528	13.05	1.788	0.021	0.025
BIR-1a	OR23 m	1.071	15.69	11.97	0.184	10.017	13.75	1.873	0.022	0.026
BIR-1a	AF24 m	1.038	15.05	11.35	0.174	9.477	13.10	1.796	0.022	0.025
BIR-1a	KI15 m	1.011	14.84	11.34	0.174	9.338	12.91	1.767	0.021	0.025
BIR-1a	**average**	**1.044**	**15.29**	**11.56**	**0.177**	**9.66**	**13.29**	**1.824**	**0.022**	**0.025**
	RSD	0.029	0.43	0.30	0.005	0.30	0.38	0.056	0.001	0.001
	RSD (%)	2.8	2.8	2.6	2.8	3.1	2.8	3.1	4.9	2.8
BIR-1	**pref.**	**0.959**	**15.51**	**11.40**	**0.173**	**9.689**	**13.29**	**1.832**	**0.029**	**0.03**
BHVO-2	IZ15	3.042	14.74	13.11	0.181	7.80	11.98		0.563	0.282
BHVO-2	SA7	2.888	13.97	12.46	0.174	7.38	11.28	2.22	0.528	0.333
BHVO-2	SA49	2.866	14.32	12.61	0.175	7.44	11.46	2.21	0.530	0.321
BHVO-2	SA65	2.986	14.38	12.74	0.176	7.53	11.49	2.25	0.532	0.332
BHVO-2	SA33	2.782	13.47	12.23	0.166	7.09	10.76	2.12	0.502	0.298
BHVO-2	**average**	**2.913**	**14.18**	**12.63**	**0.174**	**7.45**	**11.39**	**2.20**	**0.531**	**0.313**
	RSD	0.102	0.48	0.33	0.005	0.26	0.44	0.05	0.022	0.022
	RSD (%)	3.5	3.4	2.6	3.1	3.4	3.9	2.5	4.1	7.1
BHVO-2	**pref.**	**2.731**	**13.44**	**12.39**	**0.169**	**7.527**	**11.4**	**2.219**	**0.513**	**0.269**
JSd-1	PI15	0.681	15.22	5.06	0.092	1.79	3.03	2.73	2.162	0.135
JSd-1	KM15	0.663	14.91	4.94	0.089	1.76	2.94	2.69	2.105	0.136
JSd-1	**average**	**0.672**	**15.06**	**5.00**	**0.090**	**1.77**	**2.98**	**2.71**	**2.133**	**0.136**
JSd-1	**recom.**	**0.643**	**14.65**	**5.059**	**0.092**	**1.813**	**3.034**	**2.727**	**2.183**	**0.122**

* Total iron as Fe_2O_3.
** One sigma standard deviation of the replicated measurements.
\# RSD (%) of only basaltic samples are shown because other samples have small number of a replicated analyses.
\# GeoRem preferred values (http://georem.mpch-mainz.gwdg.de/) are shown in green.
\## Recommended, certified, or information values (https://gbank.gsj.jp/geostandards/welcome.html) are also shown in green.

fied, or information) values as shown in Tables 3 and 4. Concentrations for Cr in basaltic samples are slightly (7%) higher than the reference values, however, this could be the result of interference from polyatomic ions (Table 1). For most geological standard rocks, Y and Zr concentrations were ~10% lower than the reference values, and this has been reported by previous studies for ICP-MS analysis (Quing *et al.*, 2003; Pretorius *et al.*, 2005; Senda *et al.*, 2014). The likely reason for the higher Y and Zr estimates is that these values are mainly based on early XRF data, where these measurements may have been overestimated due to large Rb (to Y) and Sr (to Zr) corrections and the use of rock reference materials for calibration (e.g., Sano *et al.*, 2020). In contrast, the low Y and Zr ICP-MS values may suggest that these refractory elements were not fully dissolved during sample digestion. Table 3 also shows that our Zr and Hf concentrations in JSd-1 (shown in blue) are distinctly lower than their reference values. This fact certainly indicates that zircon, a refractory mineral with high Zr and Hf concentrations, was present in the sedimentary material. If zircon is present in a sample rock, we cannot use Zr and Hf data obtained from acid digested solutions for geological discussion. Finally, we note that REE concentrations analyzed in this study are slightly (1–7%) lower than the reference values for basaltic rocks, but the slight differences would not affect our geological discussion.

Summary

We established routine sample digestion procedures suitable for ICP-MS measurements of volcanic rocks and sediments, and we quantitatively analyzed 37 trace and 9 selected major element concentrations in 12 geological standard rocks. The reproducibility of replicated analyses (i.e., measurement of several different solutions of the same reference material) in the 12 geological standard rocks is better than 5% RSD for almost of all elements. Our measured concentrations of most major and trace elements in the 12 geological standard rocks agree with the reference values.

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Appendix: A procedure for acid digestion of rock powder

1. Left 0.5M HNO_3 out of PFA vial and clean the vial and cap with Milli-Q water (twice).
2. Dry on a heater (P-4: 80°C, ~1 h)
3. Write run number on the PFA vial and cap
4. Weigh (0.0500–0.0550 g) sample powder and put in the PFA vial
5. Add 666 ml $HClO_4$ [blue pipette scale = 0.666]
6. Add 2,000 ml HF in draft chamber [blue pipette scale = 1.000 × 2] and close cap tightly
7. Ultrasonic cleaning (20 min)
8. Heat (P-1: 150°C 15 h, 160°C 20 h) and wait 1 day 8 h
9. Tap the PHA vial to dislodge droplets
10. Dryness: Open cap and dry on a heater (P2: 80°C 20 h, 110°C 10 h, 150°C 15 h, 160°C 20–30 h) and wait 2 days 17 h~3 days 3 h
11. Close cap (during T = 160°C) and switch off the heater and wait until T decreases (＜40°C)
12. Add 1,000 ml $HClO_4$ (blue pipette scale = 1.000) and close cap tightly
13. Heat (P-3: 160°C 12 h)
14. Add 2,000 ml 6 M HNO_3 (blue pipette scale = 1.000 × 2) and close cap tightly
15. Heat (P-4: 80°C ~1 h)
16. Dryness: Open cap and dry on a heater (P2: 80°C 20 h, 110°C 10 h, 150°C 15 h, 160°C 20–30 h) and wait 2 days 17 h~3 days 3 h
(Left Milli-Q water out of 15 ml and 10 ml bottles and dry in clean booth)
17. Close cap (during T = 160°C) and switch off the heater and wait until T decreases (＜40°C)
18. Write run number on 15 ml bottle and weigh (~7.3 g)
19. Add ~7.5 ml of 2% HNO_3 + 0.1% HF in PFA jar and close cap, and shake well, and pour the solution into the 15 ml bottle [two times]
20. Weigh the solution in the 15 ml bottle (~20–23 g) [dilution factor: ~300]
21. Write run number on 10 ml bottle and weigh (~2.8 g)
22. Add 100-500 μl of the solution [by using blue pipette] in the 10 ml bottle and weigh
(e.g., JB-1a = 100 μl, BIR-1a = 500 μl, BHVO = 100 μl, JB-2 = 200 μl, JB-3 = 100 μl, blank = 1,000 μl)
23. Add 200 μl Internal standard (In & Bi~100 ppb) [by using yellow pipette] and weigh
24. Add 2% HNO_3 + 0.1% HF up to 10 ml and weigh