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Quantitative analysis of major elements in igneous rocks with X-ray fluorescence spectrometer “ZSX primus II” using a 1:10 dilution glass bead

Yuki KUSANO^{1,*}, Susumu UMINO¹, Jinya KOBAYASHI²,
Tomoyuki MIZUKAMI¹, Masayuki OKUNO¹ and Shoji ARAI¹

¹ Division of Natural Systems, Graduate School of Natural Science and Technology,
Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

² Earth Science course, School of Natural Systems, College of Science and Engineering,
Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

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Abstract Detailed procedures of sample processing including preparation of a 1:10 dilution glass bead and evaluations of calibration lines of the X-ray fluorescence spectrometer for major element compositions of igneous rock samples are presented. We used 11 igneous rock standard samples of the Geological Survey of Japan and the synthetic material for the calibration. A powdered rock sample ignited at 900 °C for four hours and lithium tetraborate as an alkali flux ignited at 700 °C for four hours are weighed 0.4000 ± 0.0001 g and 4.0000 ± 0.0001 g, respectively. The mixture of rock powder sample and lithium tetraborate is put into a platinum crucible and fused to a glass bead. The calibration lines for basalts and andesites named “Major12” analyze 10 major elements such as Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P in 10 minutes. The result of repeated analyses of six standard materials shows that the relative standard deviations are less than 3% and relative errors are less than 1.2%. Therefore, the calibration lines “Major12” are sufficient to be applied to routine measurement of igneous rocks. For analysis of ultramafic rocks, another set of calibration lines “majorOl” was made based on standard samples including synthesized materials of SiO₂ and MgO reagents, and the calibration lines cover wider Si, Mg, Ni and Cr ranges than “Major12”. The calibration lines “majorOl” successfully reproduced concentrations of nine major element compositions (Si, Ti, Al, Fe, Mn, Mg, Ca, Ni, Cr) of the standard samples of ultramafic rocks.

Keywords: Quantitative analysis, Major element, X-ray fluorescence spectrometer (XRF), ZSX primus II, 1:10 dilution glass beads,

* *Corresponding author.*

Address after April 1, 2015: Volcanic Activity Research Group, Institute of Earthquake and Volcano Geology, Geological Survey of Japan/AIST, Central 7 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan
Email: f09j004e@alumni.niigata-u.ac.jp (Y. Kusano)

1 Introduction

A wavelength dispersive X-ray fluorescence spectrometer (XRF) ZSX primus II (Rigaku Corporation) has been launched in Earth Science Course, School of Natural Systems, College of Science and Engineering, Kanazawa University since November 2013. The instrument was used for scientific studies by researchers of Kanazawa University (Otsuka et al., 2014a; Hamada et al., 2014) and visitors, and for education of undergraduate students in the first year. Because sample preparation is handy and the original programs of qualitative and semi-quantitative analyses installed in the ZSX primus II are easy for a beginner to use, the instrument has been frequently used for researches in material engineering and archeology. However, the results of the semi-quantitative analyses of some ultramafic rock glass beads give twice as high Ni and Cr contents as the recommended values. Because these elements are critical in the field of earth sciences, the analytical procedures are required to be more accurate for geochemical studies.

Whole rock major element compositions give the fundamental geological information that characterizes rock samples. Recently, whole-rock powder samples are directly fused to a glass bead on an iridium foil (Ichiyama et al., 2013), and such a glass bead is utilized for major element analysis by an Electron Probe Micro Analyzer (EPMA) and for trace element analysis by a Laser-Abrasion Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Otsuka et al., 2014b). However, the reproducibility and precision of major element analyses of a doleritic sample are relatively low compared with those by XRF (data source from Otsuka et al., 2014a, b and Kusano unpublished data). In view of the ease of sample preparation, accuracy and precision of analyses, glass beads with 1:10 dilution or lower dilution (1:2 and 1:5) have been used for major element analyses of igneous and sedimentary rocks by many laboratories and institutes (e.g. Tsuchiya and Hasenaka, 1995; Kimura and Yamada, 1996; Goto et al., 2002; Seno and Motoyoshi, 2004; Shinjo and Miyamoto, 2007; Nakano et al., 2012; Yamasaki, 2014). Therefore, we have established quantitative analytical procedures of major elements of igneous rock samples using 1:10 dilution glass beads.

We present analytical procedures based on the calibration lines using 1:10 dilution glass beads, and the conditions and precision of the quantitative analysis of andesitic and basaltic rocks, and ultramafic rocks.

2 Sample preparation

2.1 Standard samples

Eleven geochemical reference materials of the igneous rocks (JA-2, JA-3, JB-1b, JB-2, JB-3, JG-1a, JG-2, JG-3, JGb-1, JP-1 and JR-1) provided by the Geological Survey of Japan (GSJ) and one synthetic material are used for the calibration lines. The synthetic material is a 1:1 mixture of JB-2 and JP-1. The U.S. Geological Survey (USGS) reference materials, BCR-2, BHVO-2, BIR-1 and DTS-2, are also used to evaluate the accuracy and precision of measurements by repeated analysis. Recommended values of these materials are taken from the GSJ Geochemical Reference samples DataBase (<https://gbank.gsj.jp/geostandards/>) and the USGS website (http://crystal.usgs.gov/geochemical_reference_standards/index.html). The recommended values are recalculated on an anhydrous basis and total Fe calculated as Fe₂O₃ (Table 1).

Table 1. Recommended values of geochemical standard samples on an anhydrous basis.

Major12	1	2	3	4	5	6	7	8	9	10	11	12
	JA-2	JA-3	JB-1b	JB-2	JB-3	JG-1a	JG-2	JG-3	JGb-1	JP-1	JR-1	JB-2+JP-1 synthetic standard
(wt%) SiO ₂	57.71	62.33	52.23	52.96	50.77	72.91	77.36	67.82	43.99	43.82	76.51	48.48
TiO ₂	0.68	0.70	1.29	1.18	1.43	0.25	0.04	0.48	1.61	0.01	0.11	0.61
Al ₂ O ₃	15.76	15.57	14.69	14.56	17.13	14.42	12.56	15.60	17.62	0.68	13.01	7.76
Fe ₂ O ₃ *	6.35	6.61	9.22	14.17	11.78	2.02	0.98	3.72	15.17	8.65	0.90	11.47
MnO	0.11	0.10	0.15	0.22	0.18	0.06	0.02	0.07	0.19	0.13	0.10	0.17
MgO	7.77	3.72	8.32	4.59	5.17	0.70	0.04	1.80	7.91	46.12	0.12	24.95
CaO	6.43	6.25	9.81	9.77	9.75	2.15	0.70	3.72	11.99	0.57	0.68	5.26
Na ₂ O	3.18	3.19	2.69	2.03	2.72	3.42	3.56	3.99	1.21	0.02	4.08	1.04
K ₂ O	1.85	1.41	1.35	0.42	0.78	3.99	4.74	2.66	0.24	0.00	4.47	0.21
P ₂ O ₅	0.15	0.12	0.26	0.10	0.29	0.08	0.00	0.12	0.06	0.00	0.02	0.05
Total	100	100	100	100	100	100	100	100	100	100	100	100

majorOl	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
	JA-2	JA-3	JB-1b	JB-2	JB-3	JG-1a	JG-2	JG-3	JGb-1	JP-1	JR-1	JB-2+JP-1	MgO30	MgO40	MgO55	MgO70	
													synthetic standard	synthetic standard	synthetic standard	synthetic standard	synthetic standard
(wt%) SiO ₂	57.67	62.31	52.18	52.96	50.76	72.91	77.36	67.82	43.99	43.50	76.51	48.30	70.00	60.00	45.00	30.00	
TiO ₂	0.67	0.70	1.29	1.18	1.43	0.25	0.04	0.48	1.61	0.006	0.11	0.60	0.00	0.00	0.00	0.00	
Al ₂ O ₃	15.75	15.57	14.68	14.56	17.13	14.42	12.56	15.60	17.62	0.68	13.01	7.73	0.00	0.00	0.00	0.00	
Fe ₂ O ₃ *	6.35	6.60	9.21	14.17	11.77	2.02	0.98	3.72	15.17	8.59	0.90	11.42	0.00	0.00	0.00	0.00	
MnO	0.11	0.10	0.15	0.22	0.18	0.06	0.02	0.07	0.19	0.12	0.10	0.17	0.00	0.00	0.00	0.00	
MgO	7.77	3.72	8.31	4.59	5.17	0.70	0.04	1.80	7.91	45.77	0.12	24.86	0.00	0.00	0.00	0.00	
CaO	6.43	6.24	9.80	9.77	9.75	2.15	0.70	3.72	11.99	0.56	0.68	5.24	30.00	40.00	55.00	70.00	
Na ₂ O	3.18	3.19	2.69	2.03	2.72	3.42	3.56	3.99	1.21	0.02	4.08	1.04	0.00	0.00	0.00	0.00	
K ₂ O	1.85	1.41	1.35	0.42	0.78	3.99	4.74	2.66	0.24	0.003	4.47	0.21	0.00	0.00	0.00	0.00	
P ₂ O ₅	0.15	0.12	0.26	0.10	0.29	0.08	0.00	0.12	0.06	0.002	0.02	0.05	0.00	0.00	0.00	0.00	
NiO	0.000	0.017	0.019	0.002	0.005	0.001	0.001	0.002	0.003	0.321	0.000	0.159	0.00	0.00	0.00	0.00	
Cr ₂ O ₃	0.065	0.010	0.066	0.004	0.008	0.003	0.001	0.003	0.009	0.421	0.000	0.209	0.00	0.00	0.00	0.00	
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	

*All Fe is listed as Fe₂O₃.

2.2 Procedure of making a 1:10 glass bead

Type II lithium tetraborate (Li₂B₄O₇) of Wako Pure Chemical Industries Co. Ltd. is used

as an alkali flux in this study. Approximately 50 g of the flux is put into an alumina crucible and ignited in an electric furnace (Thermolyne FB1414B, Thermo Fisher Scientific, Inc.) at 700 °C for four hours before measuring weight to remove absorbed and constitution water. Finely ground powder of igneous rock samples are weighed in a ceramic crucible and ignited at 900 °C for four hours in the furnace to measure volatile content in the sample (ignition loss (%); see appendix, if necessary to evaluate) and to avoid the platinum crucible from making alloy with carbonaceous or sulfide materials included in the samples. These crucibles are usually dried in an oven at 110 °C to exclude moisture. The ignited samples and lithium tetraborate are cooled and placed in a glass desiccator before being weighed.

Glass beads are made from a mixture of 0.4 g of a powdered rock sample and 4.0 g of lithium tetraborate. First, 4.0000 ± 0.0001 g of lithium tetraborate is precisely weighed on a sheet of powder paper with an analytical balance. Second, 0.4000 ± 0.0001 g of a powdered rock sample is weighed by placing it carefully on the weighed lithium tetraborate on the powder paper sheet in the balance, until the balance measures accurately 4.4000 ± 0.0002 g. Because powdered rock samples tend to stick to the powder paper by their static electricity, we weigh the lithium tetraborate first, and then the sample. The weighed sample and lithium tetraborate on the powder paper are placed on a larger sheet of powder paper (with five by five inches) and are folded with care by bringing a corner of the sheet gently to the diagonal corner, and then bringing the corner back to the original position. Then, switch the corners and repeat folding several times.

The mixed sample and lithium tetraborate are put into a platinum crucible (an alloy of 95% Pt and 5% Au). Small grains stuck on the powder paper and edge of the platinum crucible are scraped off by the edge of a powder paper into the platinum crucible. Finally, 4% lithium bromide aqueous solution (2.2 g LiBr solution with 50 g pure water) are added by two drops from the container, which reduces viscosity and enhances surface energy of the melted sample to help homogenization of the melt and exfoliation of the quenched glass bead from the crucible.

The weighed sample mixture is fused with an automatic high-frequency bead sampler (TK-4100, Tokyo Kagaku Co. Ltd.) by placing at 900 °C for 120 seconds for pre-fusion (fuse 1), at 1100 °C for 240 seconds for fusion (fuse 2) and for 240 seconds during agitation (Table 2). In case that the melt does not evenly cover the bottom of the crucible and sticks to one side of the crucible at the end of an automated fusing run, we adjust the shape of the melt to a flat, circular disk by inclining the crucible with a platinum coated tong. When the color of fused sample changes from red to yellowish, the platinum crucible is moved over a cooling fan for five minutes. If the cooled disk is heterogeneous due to incomplete mixing of the sample and lithium tetraborate, or contains remnants of unfused sample or crystallites grown during quenching, we run a shortened program to remelt the glass bead under the same temperatures for 120

seconds in fuse 1, for 180 seconds in fuse 2 and for 180 seconds in agitation (Table 2).

Table 2: Heating and melting settings of the bead sampler TK-4100.

	Prefusion (Fuse 1)		Fusion (Fuse 2)		Agitation	
	Time (s)	Temperature(°C)	Time (s)	Temperature(°C)	Time (s)	Temperature(°C)
Usual program	120	900	240	1100	240	1100
Ultra mafick rock	120	900	240	1150	240	1150
Remelting	120	900	180	1100	180	1100

The cooled glass bead can be retrieved from the platinum crucible by using a sucker. Care must be taken not to touch the measurement surface of the glass bead, which will be the one in contact with the bottom of the crucible. A label denoting the sample ID is put on the upper side of the bead (not on the measurement surface). The sample ID includes the sample name, dilution rate and the date of fusion. The glass bead wrapped in a sheet of powder paper is stored in a desiccator.

Dews of lithium tetraborate and remnants of glass bead adhered to the platinum crucible and the cap are resolved by putting the crucible and the cap in dilute hydrochloric acid solution overnight.

Table 3: Instrumental settings of ZSX primus II.

MajorID	Element	Line	Angle (2θ)			Counting time (s)			PHA	Detector	Slit	Crystal
			Peak	BG1	BG2	Peak	BG1	BG2				
	Si	Kα	109.056	—	—	40	—	—	100–300	PC	S4	PET
	Ti	Kα	86.158	86.78	85.66	40	10	10	100–340	SC	S2	LiF(200)
	Al	Kα	144.78	148	140.55	40	10	10	100–320	PC	S4	PET
	Fe	Kα	57.514	—	—	40	—	—	100–450	SC	S2	LiF(200)
	Mn	Kα	62.968	62.5	63.5	40	10	10	100–330	SC	S2	LiF(200)
	Mg	Kα	38.508	—	—	40	—	—	100–400	PC	S4	RX25
	Ca	Kα	113.13	—	—	40	—	—	100–290	PC	S4	LiF(200)
	Na	Kα	46.796	45.2	48.9	40	10	10	95–300	PC	S4	RX25
	K	Kα	136.692	—	—	40	—	—	100–300	PC	S4	LiF(200)
	P	Kα	141.066	139.6	142.95	40	10	10	140–300	PC	S4	Ge

majorOI	Element	Line	Angle (2θ)			Counting time (s)			PHA	Detector	Slit	Crystal
			Peak	BG1	BG2	Peak	BG1	BG2				
	Si	Kα	109.052	—	—	40	—	—	100–300	PC	S4	PET
	Ti	Kα	86.110	—	—	20	—	—	100–300	SC	S2	LiF(200)
	Al	Kα	144.768	—	—	40	—	—	100–300	PC	S4	PET
	Fe	Kα	57.512	—	—	20	—	—	100–300	SC	S2	LiF(200)
	Mn	Kα	62.964	—	—	20	—	—	100–300	SC	S2	LiF(200)
	Mg	Kα	38.504	—	—	40	—	—	100–250	PC	S4	RX25
	Ca	Kα	113.128	—	—	40	—	—	100–300	PC	S4	LiF(200)
	Na	Kα	46.802	—	—	40	—	—	100–250	PC	S4	RX25
	K	Kα	136.688	—	—	40	—	—	100–300	PC	S4	LiF(200)
	P	Kα	141.070	—	—	40	—	—	150–300	PC	S4	Ge
	Ni	Kα	48.650	—	—	20	—	—	100–300	SC	S2	LiF(200)
	Cr	Kα	69.348	—	—	20	—	—	100–300	SC	S2	LiF(200)

PC: proportional counter, SC: scintillation counter.

3 Analytical Conditions

3.1 Instrument condition

A glass bead is set on a stainless steel sample holder with the measurement surface up. The bead is screwed up to be in contact with a sample mask with a hole 30 mm in diameter in the center. After passing through the height checker, the sample holder is set on the sample stage. 48 sample holders can be set on the stage. We usually set a sample used for calibration of the Pulse Height Analyzer (PHA) on the stage no. H-1. Unknown samples are set on other 47 stages.

The ZSX primus II is equipped with an end-window X-ray tube and a rhodium anode, and is controlled by ZSX software run on a windows 7 personal computer. As ZSX is run and X-ray is turned on, ZSX automatically sets the acceleration voltage and electric current to 50 kV and 50mA, respectively and adjusts the X-ray counter by measuring the calibration sample on the stage no. H-1.

3.2 Measuring basalt and andesite with “Major12”

3.2.1 Calibration lines

Ten major elements Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P are analyzed by an application program “Major12” in 10 minutes. The instrument conditions of each element are listed in Table 3.

Eleven GSJ standard and one synthetic samples are used to make calibration lines. A regression calculation was done by the ZSX software. $K\alpha$ lines of Si, Fe, Mg, Ca and K are measured for 40 seconds at peak positions only because peak to background X-ray count ratios are large so that the differences of the gross and net peak counts are negligible. Both peak and background X-ray intensities are measured for $K\alpha$ lines of Ti, Al, Mn, Na and P, based on which background corrections are made. The gross and net count rates are linearly correlated with the mass fraction of oxides, yielding linear calibration lines of all major elements (Figure 1). However, JG-2 shows higher P $K\alpha$ intensity than that expected for the P_2O_5 concentration of the recommended value. Since repeated measurements of JG-2 show higher P intensities, JG-2 was excluded from P_2O_5 calibration in this report. Correlation coefficients (R^2) of X-ray intensities and mass fractions of major element oxides are better than 0.99 for all elements. As shown in the enlarged plots of Al_2O_3 and MgO, X-ray intensities and the mass fractions of oxides are well correlated around the range of a large number of standard samples.

The calibration ranges and accuracy of each element are shown in Table 4. The accuracy of a calibration line is given by

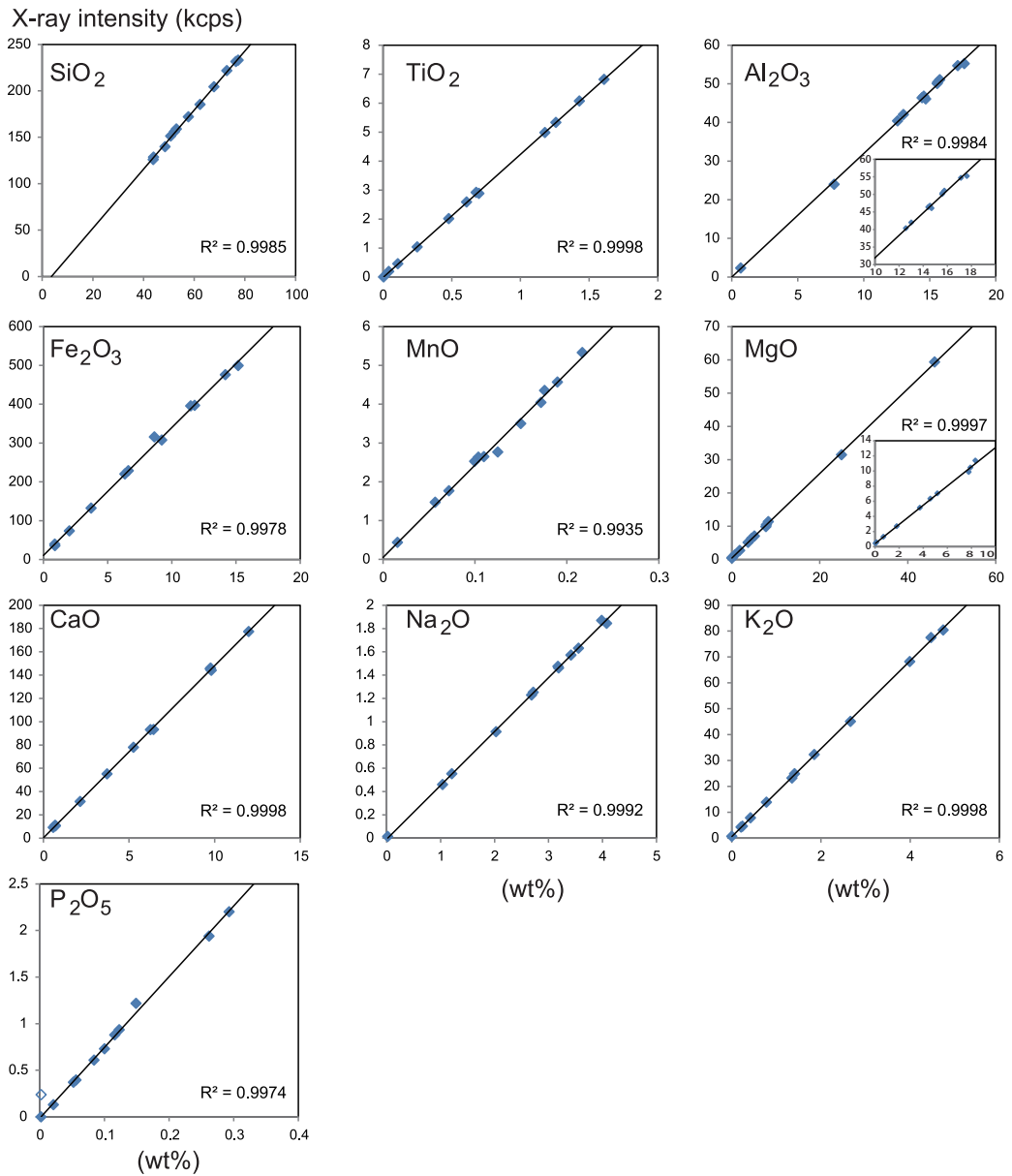


Figure 1: Calibration lines “Major12” for major elements. X-ray intensity (kcps) and concentrations (wt %) of 12 reference materials are plotted in each oxides. The enlarged insets are ranges of Al₂O₃ and MgO with a large number of reference materials. Filled symbols are standard samples used for the calibration and an open symbol is excluded sample from the calibration lines.

$$\text{Accuracy} = \sqrt{\frac{\sum (C_m - C_r)^2}{n - 2}} \dots\dots\dots(1)$$

where C_m is a mass fraction of oxide of a standard determined by the calibration line for the element, C_r is a recommended value, n is number of samples. Accuracies of calibration lines are less than 0.5 wt% in measured elements and are comparable to those of previous studies (Shinjo and Miyamoto, 2007; Goto et al., 2002; Nakano et al., 2012; Yamasaki, 2014).

To facilitate routine analyses, a protocol for correcting the drifts in the X-ray count rates was made. Using this method (alpha method), drift corrections are made to compensate the drop of X-ray count rates of the same sample (JB-1b) between the day of a routine analysis and the day when the calibration line is made using standard samples. The corrected X-ray count rate I_c is given by

$$I_c = I \times \alpha; \alpha = I_i/M_i \dots\dots\dots(2)$$

where I is a measured X-ray count rate on the day of routine analysis and α is the correction coefficient defined as the ratio of the X-ray count rate of the sample measured on the day of the calibration using standard samples (I_i) to that on the day of routine analysis (M_i). We use a GSJ standard sample JB-1b for drift correction, which is also used for the calibration lines. The JB-1b glass bead for the X-ray count rate correction is different from the one used for the calibration. A routine measurement of unknown sample is made after drift correction.

Table 4: Ranges of major element oxide compositions used for the calibration lines and accuracies of the calibration lines.

Oxides (wt%)	Major12		majorOl	
	Calibration range (wt%)	Accuracy	Calibration range (wt%)	Accuracy
SiO ₂	77.36 – 43.82	0.52	77.36 – 30.00	0.39
TiO ₂	1.61 – 0.01	0.007	1.61 – 0.01	0.012
Al ₂ O ₃	17.62 – 0.68	0.2	14.64 – 0.68	0.13
Fe ₂ O ₃ *	15.17 – 0.90	0.23	15.17 – 0.90	0.15
MnO	0.22 – 0.02	0.005	0.22 – 0.02	0.003
MgO	46.12 – 0.04	0.23	70.00 – 0.04	0.33
CaO	11.99 – 0.57	0.065	11.99 – 0.57	0.032
Na ₂ O	4.08 – 0.02	0.037	4.08 – 0.02	0.054
K ₂ O	4.74 – 0.003	0.027	4.74 – 0.003	0.03
P ₂ O ₅	0.29 – 0.002	0.005	0.29 – 0.002	0.006
NiO	—	—	0.32 – 0.00	0.011
Cr ₂ O ₃	—	—	0.42 – 0.00	0.005

*Total Fe calculated as Fe₂O₃.

3.2.2 Evaluation of the calibration lines and the results of repeated analyses

Results of repeated measurements of standard and reference samples are listed in Table 5. Three samples, JA-2, JA-3 and JB-1b, used for the calculation of the calibration lines and three additional samples, BHVO-2, BCR-2 and BIR-1 were analyzed. Repeated measurements were made in several days together with drift corrections.

Relative standard deviations (RSDs) of the repeated measurements are less than the following ratios: 0.28% for SiO₂, 0.59% for TiO₂, 0.35% for Al₂O₃, 0.14% for Fe₂O₃, 0.94% for MnO, 0.34% for MgO, 0.26% for CaO, 0.74% for Na₂O, 1.76% for K₂O and 2.46% for P₂O₅. RSDs are less than 3% for all major elements, indicating that the calibration lines have more than 97% reproducibility.

Relative differences between the measured and the recommended mass fraction oxides are represented by a Diff. value (= [(average value of measured standard samples / recommended value) - 1] × 100) (Shinjo and Miyamoto, 2007). Diff. values of BHVO-2, BCR-2 and BIR-1 are less than 1.2% in almost all major elements. Although some elements show more than 2.5% in Diff. values, there are no constant and systematic differences in any unique element. Therefore, the calibration lines “Major12” give

Table 5: Reproducibility of standard rock samples on Major12 calibration lines.

Calibration standard samples															
JA-2 (n=11)						JA-3 (n=7)					JB-1b (n=7)				
Andesite						Andesite					Basalt				
(wt%)	Average	Stdev.(σ)	RSD (%)	R.V.	Diff. (%)	Average	Stdev.(σ)	RSD (%)	R.V.	Diff. (%)	Average	Stdev.(σ)	RSD (%)	R.V.	Diff. (%)
SiO ₂	57.79	0.16	0.28	57.71	0.1	62.14	0.11	0.17	62.33	-0.3	52.62	0.09	0.18	52.23	0.7
TiO ₂	0.70	0.00	0.56	0.68	2.9	0.69	0.00	0.59	0.70	-1.4	1.26	0.01	0.42	1.29	-2.3
Al ₂ O ₃	16.03	0.04	0.23	15.76	1.7	15.71	0.03	0.17	15.57	0.9	14.41	0.04	0.26	14.69	-1.9
Fe ₂ O ₃ *	6.39	0.01	0.14	6.35	0.6	6.62	0.00	0.04	6.61	0.2	9.03	0.01	0.09	9.22	-2.1
MnO	0.11	0.001	0.94	0.11	0.0	0.11	0.001	0.71	0.10	10.0	0.14	0.001	0.77	0.15	-6.7
MgO	7.47	0.01	0.19	7.77	-3.9	3.78	0.01	0.34	3.72	1.6	8.62	0.01	0.13	8.32	3.6
CaO	6.27	0.01	0.10	6.43	-2.5	6.26	0.00	0.03	6.25	0.2	9.67	0.00	0.02	9.81	-1.4
Na ₂ O	3.22	0.02	0.49	3.18	1.3	3.16	0.01	0.20	3.19	-0.9	2.67	0.01	0.42	2.69	-0.7
K ₂ O	1.86	0.003	0.14	1.85	0.5	1.42	0.001	0.04	1.41	0.7	1.33	0.001	0.11	1.35	-1.5
P ₂ O ₅	0.16	0.001	0.66	0.15	6.7	0.11	0.001	0.81	0.12	-8.3	0.26	0.001	0.44	0.26	0.0
Total	100.00			100.00		100.00			100.00		100.00			100.00	

Standard samples without calibration lines															
BHVO-2 (n=7)						BCR-2 (n=7)					BIR-1 (n=4)				
Basalt						Basalt					Basalt				
(wt%)	Average	Stdev.(σ)	RSD (%)	R.V.	Diff. (%)	Average	Stdev.(σ)	RSD (%)	R.V.	Diff. (%)	Average	Stdev.(σ)	RSD (%)	R.V.	Diff. (%)
SiO ₂	50.12	0.10	0.20	49.78	0.7	54.40	0.12	0.21	54.17	0.4	48.01	0.02	0.03	47.60	0.9
TiO ₂	2.74	0.00	0.17	2.72	0.7	2.32	0.01	0.26	2.26	2.7	0.95	0.01	0.56	0.95	0.0
Al ₂ O ₃	13.36	0.02	0.15	13.47	-0.8	13.36	0.05	0.35	13.52	-1.2	15.01	0.01	0.09	15.38	-2.4
Fe ₂ O ₃ *	11.96	0.01	0.06	12.27	-2.5	13.76	0.01	0.11	13.82	-0.4	11.12	0.01	0.07	11.21	-0.8
MnO	0.17	0.001	0.59	0.17	0.0	0.20	0.002	0.77	0.20	0.0	0.17	0.001	0.58	0.17	0.0
MgO	7.27	0.01	0.09	7.21	0.8	3.63	0.01	0.32	3.59	1.1	9.58	0.01	0.13	9.63	-0.5
CaO	11.42	0.01	0.04	11.37	0.4	7.06	0.02	0.26	7.13	-1.0	13.33	0.00	0.04	13.20	1.0
Na ₂ O	2.20	0.01	0.45	2.21	-0.5	3.11	0.01	0.42	3.16	-1.6	1.79	0.01	0.74	1.81	-1.1
K ₂ O	0.52	0.001	0.18	0.52	0.0	1.80	0.003	0.19	1.79	0.6	0.03	0.001	1.76	0.03	0.0
P ₂ O ₅	0.26	0.001	0.40	0.27	-3.7	0.35	0.001	0.37	0.35	0.0	0.02	0.001	2.46	0.02	0.0
Total	100.00			100.00		100.00			100.00		100.00			100.00	

Stdev.: standard deviation; RSD: relative standard deviation; R.V.: recommended value; Diff.: Difference from the recommended value.

*Total Fe calculated as Fe₂O₃.

X-ray intensity (kcps)

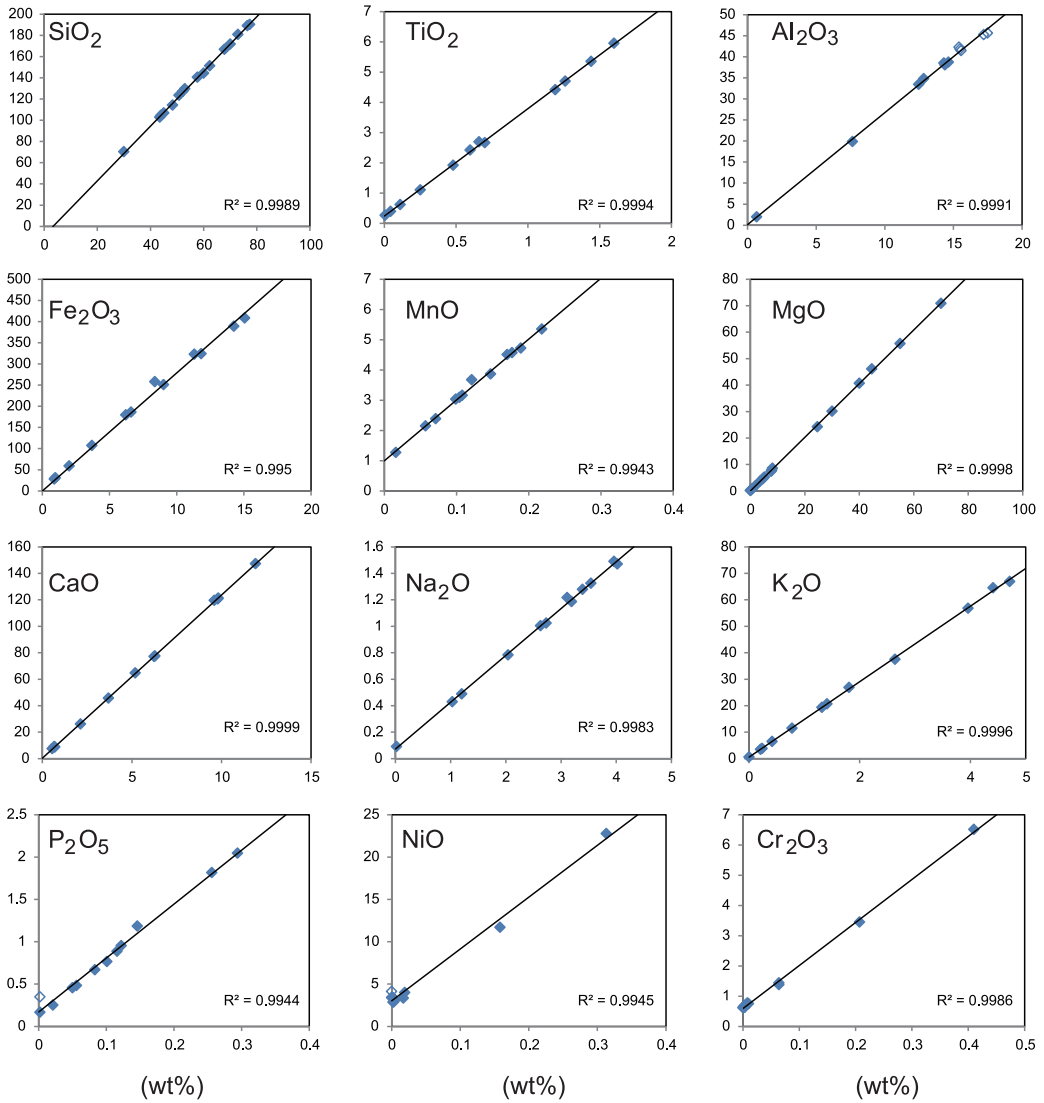


Figure 2: Calibration lines “majorOI” for major elements plotted on X-ray intensity (kcps) and concentrations (wt%) of 16 standard samples. Legend of symbols is the same as Figure 1.

sufficiently precise and accurate results for rock samples of andesitic to basaltic compositions.

Table 6: Reproducibility of standard rock samples on majorOI calibration lines.

	Calibration standard samples			Standard samples without calibration lines										
	JP-1			DTS-2 (n=3)			BCR-2			BIR-1				
	Dunite			Dunite			Basalt			Basalt				
(wt%)	Measured	R.V.	Diff (%)	Measured	Stdev.(σ)	RSD (%)	R.V.	Diff (%)	Measured	R.V.	Diff (%)	Measured	R.V.	Diff (%)
SiO ₂	43.15	43.50	-0.8	39.42	0.01	0.03	39.40	0.1	54.35	54.17	0.3	47.63	47.56	0.1
TiO ₂	0.006	0.006	0.0	0.013	0.000	0.00	—	—	2.31	2.26	2.2	0.95	0.95	0.0
Al ₂ O ₃	0.69	0.68	1.5	0.42	0.004	0.83	0.45	-6.7	13.27	13.52	-1.8	15.12	15.37	-1.6
Fe ₂ O ₃ *	8.72	8.59	1.5	8.00	0.003	0.04	7.76	3.1	13.81	13.82	-0.1	11.28	11.21	0.6
MnO	0.13	0.12	8.3	0.12	0.001	1.00	0.11	9.1	0.20	0.20	0.0	0.17	0.17	0.0
MgO	45.94	45.77	0.4	49.19	0.08	0.16	49.40	-0.4	3.64	3.59	1.4	9.60	9.62	-0.2
CaO	0.57	0.56	1.8	0.13	0.001	0.43	0.12	8.3	7.10	7.13	-0.4	13.29	13.19	0.8
Na ₂ O	0.05	0.02	150.0	0.06	0.002	3.48	0.03	100.0	3.17	3.16	0.3	1.82	1.80	1.1
K ₂ O	0.007	0.003	133.3	0.007	0.001	7.28	—	—	1.80	1.79	0.6	0.02	0.03	-33.3
P ₂ O ₅	0.006	0.002	200.0	0.004	0.001	14.56	—	—	0.35	0.35	0.0	0.02	0.02	0.0
NiO	0.32	0.32	0.0	0.46	0.001	0.12	0.48	-4.2	0.009	0.00	—	0.03	0.02	50.0
Cr ₂ O ₃	0.41	0.42	-2.4	2.17	0.003	0.15	2.27	-4.4	0.006	0.003	100.0	0.05	0.05	0.0
Total	100.00	99.99		99.99			100.02		100.02	99.99		99.98		

Stdev.: standard deviation; RSD: relative standard deviation; R.V.: recommended value; Diff.: Difference from the recommended value.

*Total Fe calculated as Fe₂O₃.

3.3 Measuring ultramafic rocks with “majorOI”

For quantitative analyses of ultramafic rocks, we used four synthetic samples in addition to 12 standard samples used for “Major12”. The synthetic samples are made from MgO and SiO₂ reagents (“Magnesium Oxide (Heavy)” and “Quartz Granular for Elemental Analysis”, of Wako Pure Chemical Industries, Ltd.). The “Quartz Granular” was ground for 60 minutes in an automatic agate mortar. Four standard samples were synthesized by mixing MgO and SiO₂ reagents at ratios of 3:7, 4:6, 5.5:4.5, and 7:3 in mass. The synthesized samples were melted at a high temperature (1150 °C) (Table 2) to avoid unmelted remains at lower temperatures used by the melting program for basalt and andesite samples. However, melting at the high temperature resulted in recrystallization of the bottom of the platinum crucible. Therefore, we recommend using the high-temperature fusion program only for ultramafic rock samples.

3.3.1 Calibration lines

Sixteen GSJ reference standard and synthetic samples are used to make the calibration lines “majorOI” for ultramafic samples. K α lines of 12 elements, Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Cr and Ni, are measured for 40 seconds at an acceleration voltage of 50 kV and with an electric current of 50 mA. The measurement conditions are shown in Table 3.

Theoretical matrix corrections were made for Si, Ti, Fe and Mn on the basis of the measured X-ray intensity and fundamental parameter (RIGAKU Denki, Co. Ltd., 1982) by the ZSX software. The calibration lines “majorOI” were calculated by fitting linear expressions to the plots of X-ray count rates and the mass fractions of oxides (Figure 2). The compositional ranges and the accuracy of analyzed elements are listed in Table 4.

The calibration ranges of SiO_2 and MgO are wider and Al_2O_3 is narrower than those of “Major12”. Four industrial standard samples are used only for calibrations of SiO_2 and MgO . To obtain high precisions in low Al_2O_3 and high Ni and Cr concentration ranges, high Al_2O_3 and low NiO and Cr_2O_3 standard samples are excluded from the calibration lines. Fitting of calibration lines by quadratic expressions was also attempted, but the precisions of the calibration curves were similar to those by linear expressions. Accuracies of the calibration lines are less than 0.4 wt%. The correlation coefficients between the X-ray intensities and mass concentrations are more than 0.99 in all elements.

3.3.2 Evaluation of the calibration lines and the result of repeated analyses

The results of repeated analyses are listed in Table 6. We measured two ultramafic rock and two basalt samples. JP-1 is included in the standard samples for the calibration lines. DTS-2, BCR-2 and BIR-1a are not used for the calibration.

RSDs of repeated analyses of DTS-2 are less than the following ratios: 0.03% for SiO_2 , 0.00% for TiO_2 , 0.83% for Al_2O_3 , 0.04% for Fe_2O_3 , 1.00% for MnO , 0.16% for MgO , 0.43% for CaO , 3.48% for Na_2O , 7.28% for K_2O , 14.56% for P_2O_5 , 0.12% for NiO and 0.15% for Cr_2O_3 . Na, K and P present large RSDs.

Although Al_2O_3 and CaO of DTS-2 show more than 5% Diff. values, they are still within the recommended values. Na_2O , K_2O , P_2O_5 of JP-1 and DTS-2 are significantly different from the recommended values, while the Diff. values of these elements of BCR-2 and BIR-1a are almost negligible. Therefore, the large differences from the recommended values and the wide RSD variations in Na_2O , K_2O , P_2O_5 of JP-1 and DTS-2 are ascribed to the low accuracy of the calibration lines at low concentrations. As shown in NiO and Cr_2O_3 contents in ultramafic rocks and basalts, “majorOl” cannot reproduce low Ni and Cr concentrations in basalts.

4 Summary

We established the procedures of sample preparation and instrument conditions for quantitative analyses by ZSX primus II with 1:10 dilution glass beads. After ignited in an electric furnace, mixtures of 0.4000 g of powdered rock samples and 4.0000 g of lithium tetraborate are fused to glass beads. Calibration lines for basalt and andesite (application “Major12”) are made by 11 GSJ reference samples and a 1:1 mixture of JB-2 and JP-1 for analyses of Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P. A routine measurement is done with X-ray drift correction by measuring JB-1b, followed by

measurements of unknown samples. Standard samples used for making calibration lines are not measured every time. The calibration lines well reproduce the recommended values of the GSJ and USGS reference materials with less than 3% in RSDs and less than 1.2% in relative errors of analyses.

Another application named “majorOI” was also designed for analyzing ultramafic rocks, and was calibrated with 12 standard samples used for “Major12”, and four synthetic samples made from industrial SiO₂ and MgO reagents at ratios of 3:7, 4:6, 5.5:4.5, and 7:3 in mass. The “majorOI” analyzes Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Ni and Cr. The calibration lines have low precision in Na, K, P due to their low concentrations in the ultramafic standard samples. However, Si, Ti, Al, Fe, Mn, Mg, Ca, Ni and Cr are achieved with sufficient accuracies in major element compositions of dunite samples.

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Appendix

Ignition loss (%) is calculated by $[(\text{the lost weight}/\text{the raw sample weight}) \times 100]$ to evaluate absorbance and magmatic water content. The weight loss at more than 900 °C is considered to be volatile content of the sample such as H₂O and CO₂.

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