The accuracy and determination limits of rock chemical analysis by X-ray fluorescence spectrometry at Mineral Resources Research Group, Geological Survey of Japan

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1. Introduction

Mineral Resources Research Group installed an X-ray fluorescence spectrometer (XRF) at the 7-6-1110 room of Geological Survey of Japan in March 2013. Since the installation, we have created calibration lines for various compositional rocks. In this report, we have shown the accuracy and determination limits of rock chemical analysis using the calibration lines as of January 2016.

The XRF is RIGAKU ZSX Primus III+, a wavelength dispersive spectrometer with an Rh tube of 3 kW. The tube irradiates X-ray to a sample obliquely downward. The software provided by RIGAKU on PC can control all machinery setting. A sample autoloader enables us continuous analysis up to 39 samples.

2. Standard samples and sample preparation

2.1 Quantitative analysis of major elements using fused disks

We created calibration lines of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5 using the GSJ standard samples JA-1, JA-2, JA-3, JA-1a, JB-2, JB-3, JB-1a, JG-2, JG-3, JGb-1, JGb-2, JR-1, JR-2, and JR-3. We adopted the recommended analytical values of the standard samples by Imai et al. (1995) and Terashima et al. (1998) for creating calibration lines. To minimize matrix and mineral effects, we used the fused disk method, and set the dilution ratio of sample by flux 1:10. In practice, we weighed sample 0.5 g and flux (Spectromelt A10: $Li_2B_4O_7$) 5 g, and mixed them completely with an agate mortar. We usually added two drops of remover (LiBr 33% aqueous solution) to the mixture of sample and flux. Fused disks were produced by a microwave bead sampler (Herzog HAG-M-HF) using crucibles of Pt 95% and Au 5% alloy at 1250°C. We temporarily named the quantitative analytical program "GB (2014_06)".

2.2 Quantitative analysis of SiO_2, Al_2O_3, TiO_2, and Fe_2O_3 in high-silica rocks

For the analysis of high-silica rocks, we used the standard samples Silicon dioxide (Spec pure) made by Johnson Matthey (JM) and JG-2. The mixing samples of JM and JG-2 (five steps) were produced to create calibration lines. The chemical compositions of the standard samples are listed in Table 1. The specification of fused disks is the same as in the former section. We temporarily named the quantitative analytical program "high_SiAlTiFe".

2.3 Quantitative analysis of major and minor elements using powder pellets

We created calibration lines of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5 (major elements) and Ba, Cu, Nb, Co, Ni, Rb, Sr, V, Zn, Zr, La, Ce, Nd, Sm, Yb, Ga, Th, U, Y, Sn, and Ta (minor elements) using the GSJ standard samples JA-1, JA-2, JB-2, JB-3, JG-2, JG-3, JGb-1, JP-1, JR-1, JR-2 and JR-3. Due to the higher contents of Cr in JP-1 and Zr in JR-3, we produced mixing samples of JP-1 with silicon dioxide (three steps) and JR-3 with silicon dioxide (two steps). The chemical compositions of the standard samples are listed in Table 2. Powder pellets were formed by a hydraulic molding press machine (TYPE-BRE-33, Maekawa) using aluminum rings 20 mm in inner diameter. The pressure and time of molding were 20 MPa and 30 seconds, respectively. We adopted the recommended values of the standard samples by Imai et al. (1995), and temporarily named the quantitative analytical program "REE (GIS)".

3. Analytical procedure

We set voltage and current of the Rh tube 50 kV and 50 mA, respectively. The condition of the sample chamber was in vacuum. A sample holder with mask 20 mm in inner diameter is made of stainless steel, and is rotated during analysis. We referred analytical conditions and times to Johnson et al (1999), Seno et al. (2002), and Kawano (2010). The analytical time of GB(2014_06) was 11 minutes/sample, high_SiAlTiFe 4 minutes/sample, and REE(GIS) 225 minutes/sample. The detailed analytical conditions of GB(2014_06), high_SiAlTiFe, and REE(GIS) are listed in Tables 3, 4 and 5, respectively.

In the analysis using REE(GIS), we applied the matrix correction (JIS model) for all elements except for Si. We also applied the overlap correction for interfered specific X-ray. In the analysis, the overlapped X-ray peaks were identified as follows: Cu-Kα and Th-Lβ, Nb-Kα and Y-Kβ, Co-Kα and Nd-Lγ, Ni-Kα and Rb-Kβ, Sm-Lα and La-Lγ, Yb-Lα and Ni-Kα and Rb-Kβ and Co-Kβ, Ga-Kα and Nb-Kβ, Ta-Lα and U-Lβ, Y-Kα and Rb-Kβ and Th-Lβ. The software provided by RIGAKU automatically calculated all of the matrix and overlap corrections. The correction coefficients are listed in Tables 6 and 7.

The accuracy (ACR) of calibration lines were calculated by the following equation:

$$\mathrm{ACR}=\sqrt{\frac{\sum(Cm-Cr)^2}{n-2}}$$

Cm= analysis of each element, Cr= analysis of each standard value

n= number of standard samples for the calibration line

The 95% confidence interval of each calibration line was calculated using the predict function based on the linear regression model. We used Statistic free software R (R core team, 2014, ver. 3.1.1) for the predict function. To verify the accuracy of each analytical program, we analyzed the standard samples issued by GSJ and Natural Resources Canada.

4. Analytical results and discussions

4.1 GB(2014_06) program

The calibration lines are shown in Figure 1. The correlation factors of SiO_2, MgO, K_2O, CaO, TiO_2 and Fe_2O_3 are greater than 0.999, and Al_2O_3, P_2O_5, MnO and Na_2O greater than 0.99. The relative errors for each element were less than 0.4%. Thus, the accuracy of quantitative analysis using GB(2014_06) is enough high. To determine hypothetical determination limit, we calculated the 95% confidence interval and relative errors for each calibration line. In this program, we defined that the compositional range of which it is within the 95% confidence interval and has less relative error than 10% from the recommended value is the hypothetical determination limit (Table 8).

To verify the applicability of the calibration lines, we analyzed the following standard samples, which were not used for creating the calibration line: JF-1, JZn-1, JP-1, JMs-2, JDo-1, JCh-1, JSd-1 and JH-1 (Table 9). When the rock analyses are lower than the hypothetical determination limit, most of the analyses were divergent from the recommended values. Thus, we cannot extrapolate the calibration lines for lower concentration side from the hypothetical determination limit. In contrast, when the rock analyses are higher than the hypothetical determination limit, even if the rocks are not only silicate but also carbonate, most of the analyses were within the relative error limit. However, the rocks of extreme compositions such as JCh-1, JMs-1 and JP-1, some elements showed divergent compositions from the recommended values. On the basis of the results above, we practically defined the determination limit of the calibration lines as shown in Table 10.

4.2 high_SiAlTiFe program

The calibration lines for quantitative analysis of SiO_2, Al_2O_3, TiO_2 and Fe_2O_3 are shown in Figure 2. All elements showed high correlation factors greater than 0.99, and the relative errors were 0.55, 0.062, 0.002 and 0.006 %, respectively. When we use the same definition as the former section, the hypothetical determination limit is shown in Table 11. To verify the applicability of the calibration lines, we analyzed the following standard samples, which were not used for creating the calibration lines: JF-1, JCh-1, JP-1, JDo-1, and the mixture samples JG2M3, JG2M4 and JG2M5 (Table 12). On the basis of the results above, we practically defined the determination limit of the calibration lines as shown in Table 13.

4.3 REE(GIS) program

The calibration line for each element and the analyses after the matrix correction are shown in Figure 3. Though, most of the elements showed the correlation factors greater than 0.97, those of Sm, Yb, Ga, U and Sn were 0.88, 0.57, 0.82, 0.73, and 0.89, respectively. The specific X-ray of Ta cannot be enough detected (only 2 of 19 points). Thus, the accuracy of the analysis Sm, Yb, Ga, U, Sn and Ta using this calibration lines is not sufficient. In this program, we defined that the ranges of which the divergent rate from the recommended values is less than 30% are the hypothetical determination limit (Table 14). To verify the applicability of the calibration lines, we analyzed the following standard samples, which were not used for creating the calibration lines: JLs-1, JLk-1, JDo-1, JMs-1, JMn-1, JZn-1, JCu-1, SY-4 (Certificate of analysis by Canadian Certified Reference Material Project (CCRMP), 1993) and WPR-1a (Certificate analysis by CCRMP, 2012) (Table 15). When the rock analyses are lower than the hypothetical determination limit, most of the analyses were divergent from the recommended values. When the analyses are within the hypothetical determination limit, the accuracy is enough high in general. Though, the analyses are within the hypothetical determination limit, some elements of extreme compositional rocks (e.g., Fe_2O_3 and Na_2O in JZn-1, Ba in JLs-1, Rb in SY-4, Sr in JLs-1 and JDo-1, Y and Zn in JDo-1 and Ce in JLk-1) occasionally showed divergent compositions from the recommended values. Thus, when the rocks are different types from the standard samples used for creating calibration lines, the accuracy of their analyses would not be enough. On the basis of the results above, we practically defined the determination limit of the calibration lines as shown in Table 16.

In the analysis using powder pellets, we cannot ignore the grain-size and mineral effects for analyses. However, the calculation of the effects was only valid for the standard samples for creating the calibration lines, and thus we cannot apply REE(GIS) for different type of rocks from the standard samples. To enhance the accuracy of analysis using powder pellets, we should create specific calibration lines for each rock types.

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Table 1. Standard samples in high_SiAl

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3
JG-2	76.830	12.470	0.044	0.970
JM+JG2(1/2)	88.420	6.235	0.022	0.485
JM+JG2(1/3)	92.277	4.157	0.015	0.323
JM+JG2(1/4)	94.200	3.118	0.011	0.243
JM+JG2(1/10)	97.683	1.247	0.004	0.097
JM+JG2(1/56)	99.594	0.222	0.001	0.017
JM	100.000	0.000	0.000	0.000

Table 2. Standard samples in REE(GIS)

	SiO_2	Al_2O_3	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	MnO	Na_2O	MgO
JA-1	63.97	15.22	0.17	0.77	5.70	0.85	7.07	0.16	3.84	1.57
JA-2	56.42	15.41	0.15	1.81	6.29	0.66	6.21	0.11	3.11	7.60
JB-2	53.25	14.64	0.10	0.42	9.82	1.19	14.25	0.22	2.04	4.62
JB-3	50.96	17.20	0.29	0.78	9.79	1.44	11.82	0.18	2.73	5.19
JG-2	76.83	12.47	0.00	4.71	0.70	0.04	0.97	0.02	3.54	0.04
JG-3	67.29	15.48	0.12	2.64	3.69	0.48	3.69	0.07	3.96	1.79
JGb-1	43.66	17.49	0.06	0.24	11.90	1.60	15.06	0.19	1.20	7.85
JP-1	42.38	0.66	0.00	0.00	0.55	0.01	8.37	0.12	0.02	44.60
JP-1(1/2)	71.19	0.33	0.00	0.00	0.28	0.00	4.19	0.06	0.01	22.30
JP-1(1/4)	85.60	0.17	0.00	0.00	0.14	0.00	2.09	0.03	0.01	11.15
JP-1(1/8)	92.80	0.08	0.00	0.00	0.07	0.00	1.05	0.02	0.00	5.58
JR-1	75.45	12.83	0.02	4.41	0.67	0.11	0.89	0.10	4.02	0.12
JR-1 (1/2)	87.73	6.42	0.01	2.21	0.34	0.06	0.45	0.05	2.01	0.06
JR-1 (1/4)	93.86	3.21	0.01	1.10	0.17	0.03	0.22	0.02	1.01	0.03
JR-1 (1/8)	96.93	1.60	0.00	0.55	0.08	0.01	0.11	0.01	0.50	0.02
JR-3	72.76	11.90	0.02	4.29	0.09	0.21	4.72	0.08	4.69	0.05
JR-3(1/2)	86.38	5.95	0.01	2.15	0.05	0.11	2.36	0.04	2.35	0.03
JR-3 (1/4)	93.19	2.98	0.00	1.07	0.02	0.05	1.18	0.02	1.17	0.01
JR-3 (1/8)	96.60	1.49	0.00	0.54	0.01	0.03	0.59	0.01	0.59	0.01

Table 2. (Continued)

	Ba	Cu	Nb	Co	Ni	Rb	Sr	V	Y	Zn
JA-1	311.00	43.00	1.85	12.30	3.49	12.30	263.00	105.00	30.60	90.90
JA-2	321.00	29.70	9.47	29.50	130.00	72.90	248.00	126.00	18.30	64.70
JB-2	222.00	225.00	1.58	38.00	16.60	7.37	178.00	575.00	24.90	108.00
JB-3	245.00	194.00	2.47	34.30	36.20	15.10	403.00	372.00	26.90	100.00
JG-2	81.00	0.49	14.70	3.62	4.35	301.00	17.90	3.78	86.50	13.60
JG-3	466.00	6.81	5.88	11.70	14.30	67.30	379.00	70.10	17.30	46.50
JGb-1	64.30	85.70	3.34	60.10	25.40	6.87	327.00	635.00	10.40	109.00
JP-1	19.50	6.72	1.48	116.00	2460.00	0.80	3.32	27.60	1.54	41.80
JP-1(1/2)	9.75	3.36	0.74	58.00	1230.00	0.40	1.66	13.80	0.77	20.90
JP-1(1/4)	4.88	1.68	0.37	29.00	615.00	0.20	0.83	6.90	0.39	10.45
JP-1(1/8)	2.44	0.84	0.19	14.50	307.50	0.10	0.42	3.45	0.19	5.23
JR-1	50.30	2.68	15.20	0.83	1.67	257.00	29.10	7.00	45.10	30.60
JR-1 (1/2)	9.75	3.36	7.60	0.42	0.84	128.50	14.55	3.50	22.55	15.30
JR-1 (1/4)	4.88	1.68	3.80	0.21	0.42	64.25	7.28	1.75	11.28	7.65
JR-1 (1/8)	2.44	0.84	1.90	0.10	0.21	32.13	3.64	0.88	5.64	3.83
JR-3	65.80	2.90	510.00	0.98	1.60	453.00	10.40	4.20	166.00	209.00
JR-3(1/2)	32.90	1.45	255.00	0.49	0.80	226.50	5.20	2.10	83.00	104.50
JR-3 (1/4)	16.45	0.73	127.50	0.25	0.40	113.25	2.60	1.05	41.50	52.25
JR-3 (1/8)	8.23	0.36	63.75	0.12	0.20	56.63	1.30	0.53	20.75	26.13

Table 2. (Continued)

	Zr	La	Ce	Nd	Sm	Yb	Ga	Th	U	Sn	Ta
JA-1	88.30	5.24	13.30	10.90	3.52	3.03	16.70	0.82	0.34	1.16	0.13
JA-2	116.00	15.80	32.70	13.90	3.11	1.62	16.90	5.03	2.21	1.68	0.80
JB-2	51.20	2.35	6.76	6.63	2.31	2.62	17.00	0.35	0.18	0.95	0.13
JB-3	97.80	8.81	21.50	15.60	4.27	2.55	19.80	1.27	0.48	0.94	0.15
JG-2	97.60	19.90	48.30	26.40	7.78	6.85	18.60	31.60	11.30	3.00	2.76
JG-3	144.00	20.60	40.30	17.20	3.39	1.77	17.10	8.28	2.21	1.40	0.70
JGb-1	32.80	3.60	8.17	5.47	1.49	1.06	17.90	0.48	0.13	0.48	0.18
JP-1	5.92	0.08	0.19	0.07	0.02	0.02	0.70	0.19	0.04	0.05	0.02
JP-1(1/2)	2.96	0.04	0.10	0.04	0.01	0.01	0.35	0.10	0.02	0.03	0.01
JP-1(1/4)	1.48	0.02	0.05	0.02	0.00	0.01	0.18	0.05	0.01	0.01	0.01
JP-1(1/8)	0.74	0.01	0.02	0.01	0.00	0.00	0.09	0.02	0.00	0.01	0.00
JR-1	99.90	19.70	47.20	23.30	6.03	4.55	16.10	26.70	8.88	2.86	1.86
JR-1 (1/2)	49.95	9.85	23.60	11.65	3.02	2.28	8.05	13.35	4.44	1.43	0.93
JR-1 (1/4)	24.98	4.93	11.80	5.83	1.51	1.14	4.03	6.68	2.22	0.72	0.47
JR-1 (1/8)	12.49	2.46	5.90	2.91	0.75	0.57	2.01	3.34	1.11	0.36	0.23
JR-3	1494.00	179.00	327.00	107.00	21.30	20.30	36.60	112.00	21.10	17.40	36.80
JR-3(1/2)	747.00	89.50	163.50	53.50	10.65	10.15	18.30	56.00	10.55	8.70	18.40
JR-3 (1/4)	373.50	44.75	81.75	26.75	5.33	5.08	9.15	28.00	5.28	4.35	9.20
JR-3 (1/8)	186.75	22.38	40.88	13.38	2.66	2.54	4.58	14.00	2.64	2.18	4.60

Table 3. Analysis condition for each element in GB(2014_06)

Element	Line	Target	Filter	Slit	Analyzing Crystal	Counter	PHA	2θ			Time		
								Peak	B.G.1	B.G.2	Peak	B.G.1	B.G.2
Si	Kα	Rh	out	S4	PET	PC	100-300	109.09	107.00	110.60	40	10	10
Ti	Kα	Rh	out	S2	LiF (200)	SC	100-300	86.14	85.26	86.80	20	10	10
Al	Kα	Rh	out	S4	PET	PC	100-300	144.84	140.60	147.15	40	10	10
Fe	Kα	Rh	out	S2	LiF (200)	SC	100-300	57.51	56.54	58.20	20	10	10
Mn	Kα	Rh	out	S2	LiF (200)	SC	100-300	62.97	62.42	63.48	20	10	10
Mg	Kα	Rh	out	S4	RX25	PC	100-250	37.89	36.00	39.45	40	10	10
Ca	Kα	Rh	out	S4	LiF (200)	PC	100-300	113.13	111.00	114.80	40	10	10
Na	Kα	Rh	out	S4	RX25	PC	100-250	46.04	44.60	47.45	40	10	10
K	Kα	Rh	out	S4	LiF (200)	PC	100-300	136.71	134.50	138.45	40	10	10
P	Kα	Rh	out	S4	Ge	PC	100-300	141.14	138.60	142.70	40	10	10

Table 4. Analytical condition for each element in high_SiAlTiFe2.

Element	Line	Target	Filter	Slit	Analyzing Crystal	Counter	PHA	2θ			Time		
								Peak	B.G.1	B.G.2	Peak	B.G.1	B.G.2
Si	Kα	Rh	out	S4	PET	PC	100-300	109.09	106.85	110.55	40	10	10
Al	Kα	Rh	out	S4	PET	PC	100-300	144.83	140.70	147.50	40	10	10
Ti	Kα	Rh	out	S2	LiF1	SC	100-300	86.12	84.94	86.90	20	10	10
Fe	Kα	Rh	out	S2	LiF1	SC	100-300	57.51	56.34	58.16	20	10	10

Table 5. Analytical condition for each element in REE (JIS)

Element	Line	Target	Filter	Slit	Analyzing Crystal	Counter	PHA	2θ			Time		
								Peak	B.G.1	B.G.2	Peak	B.G.1	B.G.2
Si	Kα	Rh	out	S4	PET	PC	100-300	109.03	107.25	110.40	20	10	10
Al	Kα	Rh	out	S4	PET	PC	100-300	144.77	141.30	147.00	20	10	10
P	Kα	Rh	out	S4	Ge	PC	100-300	141.05	138.10	146.65	40	20	20
K	Kα	Rh	out	S4	LiF(200)	PC	100-300	136.68	135.00	138.20	40	20	20
Ca	Kα	Rh	out	S4	LiF(200)	PC	100-300	113.12	111.60	114.35	20	10	10
Ti	Kα	Rh	out	S2	LiF(200)	SC	100-300	86.11	85.24	86.82	40	20	20
Fe	Kα	Rh	out	S2	LiF(200)	SC	100-300	57.50	57.02	57.98	20	10	10
Mn	Kα	Rh	out	S2	LiF(200)	SC	100-300	62.95	62.44	63.54	20	10	10
Na	Kα	Rh	out	S4	RX25	PC	100-300	46.04	44.65	47.15	40	20	20
Mg	Kα	Rh	out	S4	RX25	PC	100-300	37.91	36.25	39.20	40	20	20

Table 5. (Continued)

Element	Line	Target	Filter	Slit	Analyzing Crystal	Counter	PHA	2θ			Time (s)		
								Peak	B.G.1	B.G.2	Peak	B.G.1	B.G.2
Ba	Lα	Rh	out	S2	LiF(200)	SC	100-300	87.13	86.66	87.70	320	160	160
Cu	Kα	Rh	out	S2	LiF(200)	SC	100-300	45.01	44.54	45.54	100	50	50
Nb	Kα	Rh	out	S2	LiF(200)	SC	100-300	21.39	21.01	21.74	200	100	100
Co	Kα	Rh	out	S2	LiF(200)	SC	100-300	52.77	52.46	53.00	100	50	50
Ni	Kα	Rh	out	S2	LiF(200)	SC	100-300	48.65	47.98	49.50	160	80	80
Rb	Kα	Rh	out	S2	LiF(200)	SC	100-300	26.60	26.14	27.08	100	50	50
Sr	Kα	Rh	out	S2	LiF(200)	SC	100-300	25.13	24.48	25.76	100	50	50
V	Kα	Rh	out	S2	LiF(200)	SC	100-300	76.91	76.66	77.04	160	80	80
Y	Kα	Rh	out	S2	LiF(200)	SC	100-300	23.78	23.44	24.24	160	80	80
Zn	Kα	Rh	out	S2	LiF(200)	SC	100-300	41.78	41.40	42.20	100	50	50
Zr	Kα	Rh	out	S2	LiF(200)	SC	100-300	22.54	22.04	22.96	60	30	30
La	Lα	Rh	out	S2	LiF(200)	SC	100-300	82.88	82.30	84.00	160	80	80
Ce	Lα	Rh	out	S2	LiF(200)	SC	100-300	78.98	77.50	79.90	200	100	100
Nd	Lα	Rh	out	S2	LiF(200)	SC	100-300	72.10	71.74	72.52	200	100	100
Sm	Lα	Rh	out	S2	LiF(200)	SC	100-300	66.20	65.90	-	600	600	-
Yb	Lα	Rh	out	S2	LiF(200)	SC	100-300	49.04	49.52	-	900	900	-
Ga	Kα	Rh	out	S2	LiF(200)	SC	100-300	39.90	38.30	39.60	100	50	50
Th	Lα	Rh	out	S2	LiF(200)	SC	100-300	27.45	27.10	27.78	200	100	100
U	Lα	Rh	out	S2	LiF(200)	SC	100-300	26.13	25.78	26.26	900	900	10
Sn	Kα	Rh	out	S2	LiF(200)	SC	100-300	14.03	13.50	14.50	900	450	450
Ta	Lα	Rh	out	S2	LiF(200)	SC	100-300	44.4	43.90	45.00	600	300	300

Table 6. Theoretical matrix correction coefficients in REE(GIS)

	Analytical elements									
	SiO_2	Al_2O_3	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	MnO	Na_2O	MgO
SiO_2	-	-	-	-	-	-	-	-	-	-
Al_2O_3	-	-	-8.65×10^{-4}	-1.02×10^{-3}	-1.07×10^{-3}	-1.13×10^{-3}	-1.25×10^{-3}	-1.23×10^{-3}	-7.94×10^{-4}	-7.41×10^{-4}
P_2O_5	-5.40×10^{-3}	9.51×10^{-4}	-	9.61×10^{-4}	9.71×10^{-4}	7.36×10^{-4}	9.05×10^{-4}	8.69×10^{-4}	9.73×10^{-4}	9.51×10^{-4}
K_2O	-5.52×10^{-3}	1.47×10^{-3}	-5.93×10^{-3}	-	2.21×10^{-2}	2.05×10^{-2}	2.33×10^{-2}	2.27×10^{-2}	2.38×10^{-3}	2.04×10^{-3}
CaO	-5.08×10^{-3}	2.67×10^{-3}	-5.54×10^{-3}	-4.75×10^{-3}	-	2.14×10^{-2}	2.37×10^{-2}	2.31×10^{-2}	3.94×10^{-3}	3.39×10^{-3}
TiO_2	-4.44×10^{-3}	4.31×10^{-3}	-4.93×10^{-3}	-5.16×10^{-3}	-4.92×10^{-3}	-	2.33×10^{-2}	2.26×10^{-2}	5.61×10^{-3}	5.08×10^{-3}
Fe_2O_3	-1.55×10^{-3}	1.16×10^{-2}	-2.23×10^{-3}	-3.65×10^{-3}	-3.92×10^{-3}	-4.38×10^{-3}	-	3.73×10^{-3}	1.28×10^{-2}	1.24×10^{-2}
MnO	-2.12×10^{-3}	1.02×10^{-2}	-2.78×10^{-3}	-4.18×10^{-3}	-4.39×10^{-3}	-4.59×10^{-3}	6.83×10^{-3}	-	1.14×10^{-2}	1.10×10^{-2}
Na_2O	-1.50×10^{-3}	1.19×10^{-2}	-2.19×10^{-3}	-2.59×10^{-3}	-2.67×10^{-3}	-2.70×10^{-3}	-2.96×10^{-3}	-2.91×10^{-3}	-	1.30×10^{-2}
MgO	-4.17×10^{-4}	1.43×10^{-2}	-1.11×10^{-3}	-1.46×10^{-3}	-1.55×10^{-3}	-1.76×10^{-3}	-1.96×10^{-3}	-1.92×10^{-3}	-1.92×10^{-3}	-
Ba	5.04×10^{-7}	2.62×10^{-6}	4.74×10^{-7}	8.53×10^{-7}	9.97×10^{-7}	1.68×10^{-6}	7.91×10^{-6}	6.75×10^{-6}	1.87×10^{-6}	2.35×10^{-6}
Cu	3.54×10^{-7}	2.44×10^{-6}	2.64×10^{-7}	1.17×10^{-7}	8.20×10^{-8}	-2.72×10^{-8}	-3.01×10^{-7}	-2.34×10^{-7}	2.21×10^{-6}	2.53×10^{-6}
Nb	-5.64×10^{-8}	1.07×10^{-6}	2.48×10^{-8}	2.38×10^{-6}	2.43×10^{-6}	2.46×10^{-6}	2.34×10^{-6}	2.43×10^{-6}	7.16×10^{-7}	8.95×10^{-7}
Co	1.06×10^{-7}	1.81×10^{-6}	2.32×10^{-8}	-1.72×10^{-7}	-2.13×10^{-7}	-2.94×10^{-7}	1.09×10^{-6}	-4.38×10^{-7}	1.88×10^{-6}	1.88×10^{-6}
Ni	2.65×10^{-7}	2.21×10^{-6}	1.79×10^{-7}	2.38×10^{-8}	-1.13×10^{-8}	-1.11×10^{-7}	-2.56×10^{-7}	-2.47×10^{-7}	2.35×10^{-6}	2.31×10^{-6}
Rb	-2.61×10^{-7}	5.29×10^{-7}	1.08×10^{-6}	1.40×10^{-6}	1.41×10^{-6}	1.41×10^{-6}	1.12×10^{-6}	1.26×10^{-6}	2.28×10^{-7}	3.75×10^{-7}
Sr	-1.89×10^{-7}	6.83×10^{-7}	1.27×10^{-6}	1.65×10^{-6}	1.67×10^{-6}	1.65×10^{-6}	1.39×10^{-6}	1.53×10^{-6}	3.43×10^{-7}	5.07×10^{-7}
V	-3.05×10^{-7}	7.74×10^{-7}	-3.61×10^{-7}	-4.28×10^{-7}	-4.08×10^{-7}	3.11×10^{-7}	4.94×10^{-6}	4.82×10^{-6}	8.79×10^{-7}	8.45×10^{-7}
Y	-1.70×10^{-7}	7.68×10^{-7}	-4.16×10^{-8}	1.83×10^{-6}	1.85×10^{-6}	1.91×10^{-6}	1.96×10^{-6}	1.81×10^{-6}	4.09×10^{-7}	5.75×10^{-7}
Zn	5.03×10^{-7}	2.80×10^{-6}	4.10×10^{-7}	2.72×10^{-7}	2.36×10^{-7}	8.64×10^{-8}	-2.33×10^{-7}	-1.33×10^{-7}	2.49×10^{-6}	2.88×10^{-6}
Zr	-8.08×10^{-8}	9.84×10^{-7}	5.37×10^{-8}	2.13×10^{-6}	2.16×10^{-6}	2.18×10^{-6}	2.00×10^{-6}	2.11×10^{-6}	5.97×10^{-7}	7.87×10^{-7}
La	5.89×10^{-7}	2.84×10^{-6}	5.60×10^{-7}	9.48×10^{-7}	1.08×10^{-6}	1.58×10^{-6}	8.24×10^{-6}	6.99×10^{-6}	1.78×10^{-6}	2.44×10^{-6}
Ce	6.97×10^{-7}	3.12×10^{-6}	6.48×10^{-7}	9.73×10^{-7}	1.09×10^{-6}	1.65×10^{-6}	7.87×10^{-6}	5.71×10^{-6}	2.76×10^{-6}	2.99×10^{-6}
Nd	8.32×10^{-7}	3.23×10^{-6}	7.69×10^{-7}	1.07×10^{-6}	1.18×10^{-6}	1.58×10^{-6}	6.57×10^{-6}	2.98×10^{-6}	1.91×10^{-6}	2.34×10^{-6}
Sm	1.07×10^{-6}	3.60×10^{-6}	1.01×10^{-6}	1.28×10^{-6}	1.37×10^{-6}	1.62×10^{-6}	3.40×10^{-6}	2.97×10^{-6}	7.05×10^{-8}	2.83×10^{-6}
Yb	1.28×10^{-6}	9.84×10^{-7}	1.50×10^{-6}	2.03×10^{-6}	2.13×10^{-6}	2.39×10^{-6}	2.83×10^{-6}	2.65×10^{-6}	4.51×10^{-7}	6.96×10^{-7}
Ga	5.88×10^{-7}	3.01×10^{-6}	4.92×10^{-7}	3.87×10^{-7}	3.60×10^{-7}	2.68×10^{-7}	-1.28×10^{-7}	7.64×10^{-9}	-2.24×10^{-7}	2.63×10^{-6}
Th	1.97×10^{-7}	1.80×10^{-6}	1.92×10^{-7}	1.17×10^{-6}	4.23×10^{-6}	4.93×10^{-6}	6.53×10^{-6}	6.42×10^{-6}	1.19×10^{-6}	1.48×10^{-6}
U	1.51×10^{-7}	1.69×10^{-6}	1.36×10^{-7}	1.01×10^{-6}	2.70×10^{-6}	4.87×10^{-6}	6.61×10^{-6}	6.46×10^{-6}	1.11×10^{-6}	1.48×10^{-6}
Sn	7.91×10^{-8}	1.62×10^{-6}	4.89×10^{-8}	7.28×10^{-7}	9.90×10^{-7}	4.98×10^{-6}	5.62×10^{-6}	5.46×10^{-6}	1.53×10^{-6}	1.59×10^{-6}
Ta	5.72×10^{-7}	1.17×10^{-6}	1.52×10^{-6}	2.51×10^{-6}	2.66×10^{-6}	3.01×10^{-6}	3.80×10^{-6}	3.51×10^{-6}	6.26×10^{-7}	8.95×10^{-7}

Table 6. (Continued)

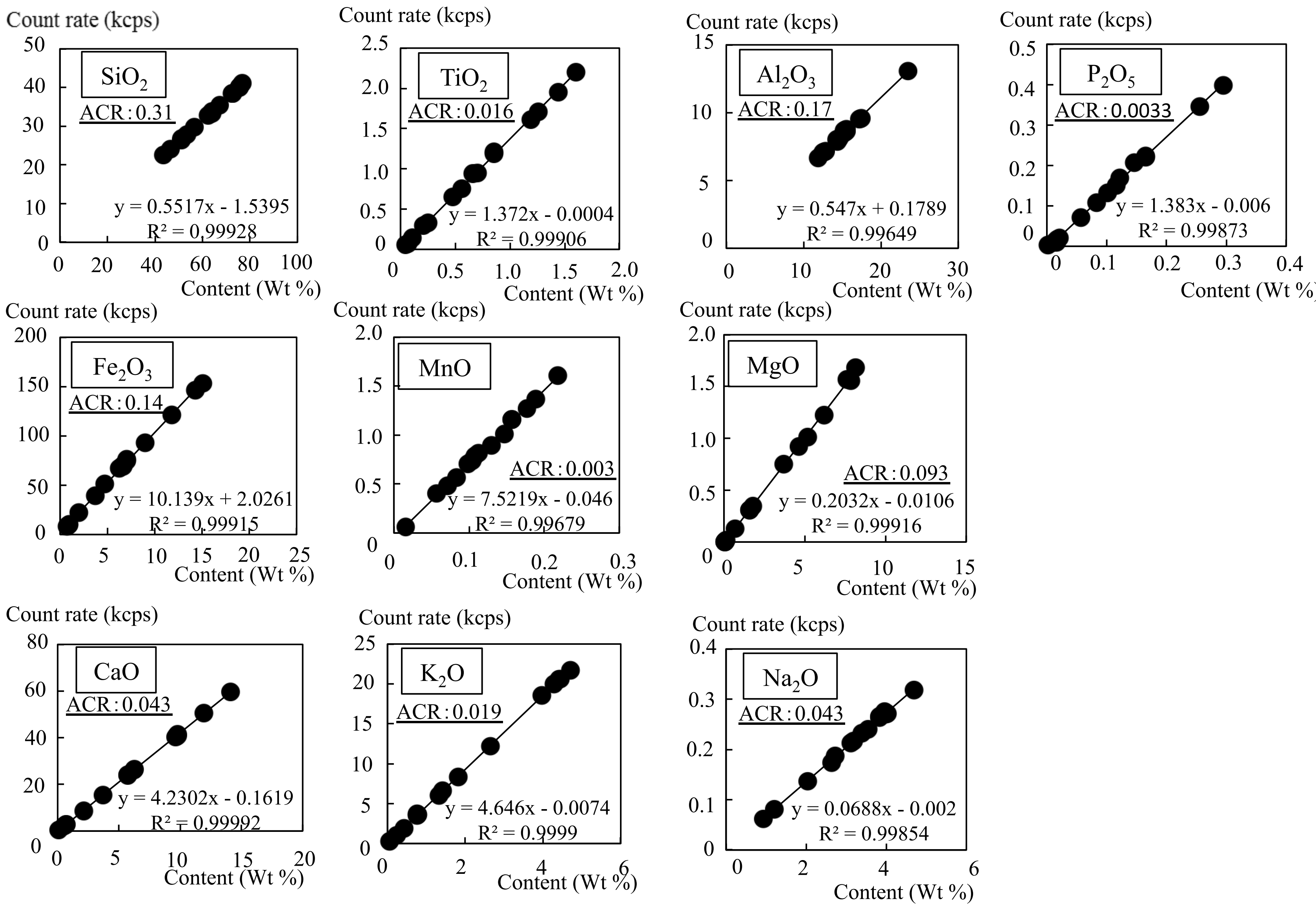
	Analytical elements									
	Ba	Cu	Nb	Co	Ni	Rb	Sr	V	Y	Zn
SiO_2	-	-	-	-	-	-	-	-	-	-
Al_2O_3	-1.15×10^{-3}	-1.31×10^{-3}	-1.37×10^{-3}	-1.28×10^{-3}	-1.30×10^{-3}	-1.36×10^{-3}	-1.36×10^{-3}	-1.18×10^{-3}	-1.36×10^{-3}	-1.32×10^{-3}
P_2O_5	7.45×10^{-4}	1.01×10^{-3}	1.25×10^{-3}	9.47×10^{-4}	9.82×10^{-4}	1.19×10^{-3}	1.20×10^{-3}	7.88×10^{-4}	1.22×10^{-3}	1.04×10^{-3}
K_2O	2.08×10^{-2}	2.53×10^{-2}	3.01×10^{-2}	2.41×10^{-2}	2.47×10^{-2}	2.87×10^{-2}	2.90×10^{-2}	2.14×10^{-2}	2.94×10^{-2}	2.58×10^{-2}
CaO	2.17×10^{-2}	2.54×10^{-2}	3.09×10^{-2}	2.44×10^{-2}	2.49×10^{-2}	2.91×10^{-2}	2.95×10^{-2}	2.21×10^{-2}	3.00×10^{-2}	2.60×10^{-2}
TiO_2	-3.91×10^{-4}	2.56×10^{-2}	3.24×10^{-2}	2.42×10^{-2}	2.49×10^{-2}	3.03×10^{-2}	3.08×10^{-2}	4.04×10^{-4}	3.14×10^{-2}	2.63×10^{-2}
Fe_2O_3	-4.66×10^{-3}	5.19×10^{-2}	7.00×10^{-2}	8.07×10^{-3}	5.01×10^{-2}	6.44×10^{-2}	6.57×10^{-2}	-4.58×10^{-3}	6.73×10^{-2}	5.38×10^{-2}
MnO	-4.79×10^{-3}	5.07×10^{-2}	6.44×10^{-2}	4.81×10^{-2}	4.95×10^{-2}	5.99×10^{-2}	6.09×10^{-2}	-4.42×10^{-3}	6.22×10^{-2}	5.20×10^{-2}
Na_2O	-2.74×10^{-3}	-3.15×10^{-3}	-3.58×10^{-3}	-3.04×10^{-3}	-3.10×10^{-3}	-3.44×10^{-3}	-3.47×10^{-3}	-2.79×10^{-3}	-3.51×10^{-3}	-3.20×10^{-3}
MgO	-1.79×10^{-3}	-2.10×10^{-3}	-2.44×10^{-3}	-2.02×10^{-3}	-2.06×10^{-3}	-2.33×10^{-3}	-2.35×10^{-3}	-1.83×10^{-3}	-2.39×10^{-3}	-2.14×10^{-3}
Ba	-	8.59×10^{-6}	1.15×10^{-5}	8.16×10^{-6}	8.38×10^{-6}	1.05×10^{-5}	1.07×10^{-5}	2.11×10^{-6}	1.10×10^{-5}	8.83×10^{-6}
Cu	-4.98×10^{-8}	-	1.39×10^{-5}	-3.72×10^{-7}	1.57×10^{-6}	1.27×10^{-5}	1.30×10^{-5}	-8.16×10^{-8}	1.33×10^{-5}	2.46×10^{-6}
Nb	2.46×10^{-6}	1.84×10^{-6}	-	2.28×10^{-6}	2.03×10^{-6}	-7.36×10^{-7}	-1.11×10^{-6}	2.49×10^{-6}	7.34×10^{-6}	1.60×10^{-6}
Co	-3.21×10^{-7}	8.69×10^{-6}	1.13×10^{-5}	-	1.80×10^{-6}	1.05×10^{-5}	1.07×10^{-5}	-3.28×10^{-7}	1.09×10^{-5}	8.96×10^{-6}
Ni	-1.35×10^{-7}	2.24×10^{-6}	1.32×10^{-5}	1.42×10^{-6}	-	1.21×10^{-5}	1.24×10^{-5}	-1.51×10^{-7}	1.27×10^{-5}	9.92×10^{-6}
Rb	1.40×10^{-6}	4.60×10^{-7}	2.43×10^{-5}	1.01×10^{-6}	6.93×10^{-7}	-	7.05×10^{-6}	1.40×10^{-6}	7.50×10^{-6}	1.80×10^{-7}
Sr	1.65×10^{-6}	7.52×10^{-7}	2.58×10^{-5}	1.29×10^{-6}	9.83×10^{-7}	5.24×10^{-6}	-	1.65×10^{-6}	7.95×10^{-6}	4.70×10^{-7}
V	3.61×10^{-7}	5.31×10^{-6}	6.52×10^{-6}	5.08×10^{-6}	5.21×10^{-6}	6.12×10^{-6}	6.21×10^{-6}	-	6.32×10^{-6}	5.43×10^{-6}
Y	1.90×10^{-6}	1.11×10^{-6}	1.04×10^{-5}	1.61×10^{-6}	1.32×10^{-6}	5.48×10^{-6}	6.29×10^{-6}	1.91×10^{-6}	-	8.37×10^{-7}
Zn	6.30×10^{-8}	1.95×10^{-6}	1.58×10^{-5}	-3.37×10^{-7}	-5.74×10^{-7}	1.43×10^{-5}	1.47×10^{-5}	3.59×10^{-8}	1.51×10^{-5}	-
Zr	2.18×10^{-6}	1.46×10^{-6}	1.09×10^{-5}	1.93×10^{-6}	1.66×10^{-6}	-1.03×10^{-6}	6.25×10^{-6}	2.19×10^{-6}	7.06×10^{-6}	1.22×10^{-6}
La	1.78×10^{-6}	9.12×10^{-6}	1.24×10^{-5}	8.56×10^{-6}	8.85×10^{-6}	1.13×10^{-5}	1.16×10^{-5}	2.13×10^{-6}	1.19×10^{-5}	9.42×10^{-6}
Ce	1.72×10^{-6}	9.85×10^{-6}	1.35×10^{-5}	9.29×10^{-6}	9.58×10^{-6}	1.22×10^{-5}	1.25×10^{-5}	2.08×10^{-6}	1.29×10^{-5}	1.02×10^{-5}
Nd	1.81×10^{-6}	1.10×10^{-5}	1.50×10^{-5}	9.10×10^{-6}	1.07×10^{-5}	1.36×10^{-5}	1.40×10^{-5}	2.04×10^{-6}	1.43×10^{-5}	1.13×10^{-5}
Sm	1.66×10^{-6}	1.20×10^{-5}	1.65×10^{-5}	7.52×10^{-6}	1.03×10^{-5}	1.49×10^{-5}	1.53×10^{-5}	1.81×10^{-6}	1.57×10^{-5}	1.24×10^{-5}
Yb	2.42×10^{-6}	5.16×10^{-6}	2.34×10^{-5}	3.56×10^{-6}	3.96×10^{-6}	2.08×10^{-5}	2.14×10^{-5}	2.46×10^{-6}	2.21×10^{-5}	5.61×10^{-6}
Ga	2.44×10^{-7}	-7.05×10^{-7}	1.62×10^{-5}	-2.64×10^{-7}	-5.46×10^{-7}	1.45×10^{-5}	1.49×10^{-5}	2.05×10^{-7}	1.54×10^{-5}	2.05×10^{-6}
Th	4.97×10^{-6}	6.86×10^{-6}	3.28×10^{-5}	6.71×10^{-6}	6.76×10^{-6}	1.17×10^{-5}	1.36×10^{-5}	5.75×10^{-6}	1.69×10^{-5}	6.94×10^{-6}
U	4.94×10^{-6}	7.09×10^{-6}	1.79×10^{-5}	6.83×10^{-6}	6.94×10^{-6}	1.18×10^{-5}	1.27×10^{-5}	5.09×10^{-6}	1.49×10^{-5}	7.25×10^{-6}
Sn	5.06×10^{-6}	6.12×10^{-6}	7.38×10^{-6}	5.82×10^{-6}	5.98×10^{-6}	7.07×10^{-6}	7.15×10^{-6}	5.17×10^{-6}	7.24×10^{-6}	6.28×10^{-6}
Ta	3.07×10^{-6}	5.23×10^{-6}	2.63×10^{-6}	4.18×10^{-6}	4.65×10^{-6}	2.33×10^{-5}	2.40×10^{-5}	3.15×10^{-6}	2.48×10^{-5}	5.98×10^{-6}

Table 6. (Continued)

	Analytical elements										
	Zr	La	Ce	Nd	Sm	Yb	Ga	Th	U	Sn	Ta
SiO_2	-	-	-	-	-	-	-	-	-	-	-
Al_2O_3	-1.36×10^{-3}	-1.17×10^{-3}	-1.18×10^{-3}	-1.22×10^{-3}	-1.24×10^{-3}	-1.33×10^{-3}	-1.33×10^{-3}	-1.45×10^{-3}	-1.43×10^{-3}	-1.25×10^{-3}	-1.35×10^{-3}
P_2O_5	1.24×10^{-3}	7.66×10^{-4}	7.89×10^{-4}	8.31×10^{-4}	8.67×10^{-4}	1.00×10^{-3}	1.07×10^{-3}	1.27×10^{-3}	1.26×10^{-3}	1.21×10^{-3}	1.05×10^{-3}
K_2O	2.97×10^{-2}	2.12×10^{-2}	2.16×10^{-2}	2.23×10^{-2}	2.29×10^{-2}	2.53×10^{-2}	2.62×10^{-2}	3.06×10^{-2}	3.05×10^{-2}	2.93×10^{-2}	2.62×10^{-2}
CaO	3.04×10^{-2}	2.20×10^{-2}	2.23×10^{-2}	2.29×10^{-2}	2.34×10^{-2}	2.55×10^{-2}	2.64×10^{-2}	3.11×10^{-2}	3.10×10^{-2}	3.10×10^{-2}	2.64×10^{-2}
TiO_2	3.18×10^{-2}	-3.35×10^{-4}	-2.69×10^{-4}	2.20×10^{-2}	2.27×10^{-2}	2.55×10^{-2}	2.69×10^{-2}	3.23×10^{-2}	3.22×10^{-2}	3.29×10^{-2}	2.65×10^{-2}
Fe_2O_3	6.85×10^{-2}	-4.65×10^{-3}	-4.78×10^{-3}	-4.89×10^{-3}	3.29×10^{-3}	5.12×10^{-2}	5.53×10^{-2}	6.86×10^{-2}	6.88×10^{-2}	7.23×10^{-2}	5.39×10^{-2}
MnO	6.32×10^{-2}	-4.61×10^{-3}	-4.61×10^{-3}	2.87×10^{-3}	5.58×10^{-3}	5.06×10^{-2}	5.31×10^{-2}	6.39×10^{-2}	6.38×10^{-2}	6.61×10^{-2}	5.26×10^{-2}
Na_2O	-3.54×10^{-3}	-2.77×10^{-3}	-2.81×10^{-3}	-2.88×10^{-3}	-2.94×10^{-3}	-3.17×10^{-3}	-3.23×10^{-3}	-3.68×10^{-3}	-3.65×10^{-3}	-3.47×10^{-3}	-3.25×10^{-3}
MgO	-2.41×10^{-3}	-1.81×10^{-3}	-1.84×10^{-3}	-1.89×10^{-3}	-1.94×10^{-3}	-2.11×10^{-3}	-2.17×10^{-3}	-2.49×10^{-3}	-2.48×10^{-3}	-2.37×10^{-3}	-2.17×10^{-3}
Ba	1.12×10^{-5}	1.89×10^{-6}	2.01×10^{-6}	2.13×10^{-6}	6.79×10^{-6}	8.58×10^{-6}	9.04×10^{-6}	1.11×10^{-5}	1.11×10^{-5}	8.95×10^{-6}	8.92×10^{-6}
Cu	1.36×10^{-5}	-7.81×10^{-8}	-1.12×10^{-7}	-1.86×10^{-7}	-2.90×10^{-7}	2.04×10^{-6}	1.07×10^{-5}	1.35×10^{-5}	1.36×10^{-5}	1.46×10^{-5}	2.18×10^{-6}
Nb	8.38×10^{-6}	2.46×10^{-6}	2.46×10^{-6}	2.44×10^{-6}	2.40×10^{-6}	1.83×10^{-6}	1.30×10^{-6}	-1.77×10^{-6}	6.63×10^{-6}	3.81×10^{-5}	1.56×10^{-6}
Co	1.11×10^{-5}	-3.32×10^{-7}	-3.57×10^{-7}	-4.07×10^{-7}	-5.22×10^{-7}	1.57×10^{-6}	9.18×10^{-6}	1.12×10^{-5}	1.12×10^{-5}	1.16×10^{-5}	9.02×10^{-6}
Ni	1.30×10^{-5}	-1.53×10^{-7}	-1.81×10^{-7}	-2.33×10^{-7}	-3.12×10^{-7}	1.93×10^{-6}	1.02×10^{-5}	1.29×10^{-5}	1.30×10^{-5}	1.38×10^{-5}	2.04×10^{-6}
Rb	2.35×10^{-5}	1.38×10^{-6}	1.37×10^{-6}	1.31×10^{-6}	1.23×10^{-6}	4.76×10^{-7}	-1.04×10^{-7}	6.54×10^{-6}	6.70×10^{-6}	2.82×10^{-5}	1.49×10^{-7}
Sr	8.48×10^{-6}	1.63×10^{-6}	1.62×10^{-6}	1.57×10^{-6}	1.50×10^{-6}	7.69×10^{-7}	1.64×10^{-7}	7.01×10^{-6}	7.17×10^{-6}	2.99×10^{-5}	4.44×10^{-7}
V	6.41×10^{-6}	5.43×10^{-7}	5.70×10^{-7}	6.05×10^{-7}	4.87×10^{-6}	5.33×10^{-6}	5.52×10^{-6}	6.54×10^{-6}	6.52×10^{-6}	6.59×10^{-6}	5.51×10^{-6}
Y	9.64×10^{-6}	1.89×10^{-6}	1.88×10^{-6}	1.84×10^{-6}	1.78×10^{-6}	1.10×10^{-6}	5.30×10^{-7}	5.85×10^{-6}	8.17×10^{-6}	3.32×10^{-5}	8.00×10^{-7}
Zn	1.54×10^{-5}	3.28×10^{-8}	-5.56×10^{-10}	-7.94×10^{-8}	-1.92×10^{-7}	1.64×10^{-6}	2.99×10^{-6}	1.53×10^{-5}	1.53×10^{-5}	1.66×10^{-5}	2.61×10^{-6}
Zr	-	2.17×10^{-6}	2.16×10^{-6}	2.14×10^{-6}	2.08×10^{-6}	1.46×10^{-6}	9.15×10^{-7}	5.87×10^{-6}	6.33×10^{-6}	3.51×10^{-5}	1.18×10^{-6}
La	1.21×10^{-5}	-	2.08×10^{-6}	2.29×10^{-6}	5.14×10^{-6}	9.06×10^{-6}	9.67×10^{-6}	1.20×10^{-5}	1.21×10^{-5}	1.06×10^{-5}	9.48×10^{-6}
Ce	1.32×10^{-5}	2.00×10^{-6}	-	2.49×10^{-6}	2.52×10^{-6}	9.80×10^{-6}	1.04×10^{-5}	1.30×10^{-5}	1.30×10^{-5}	1.28×10^{-5}	1.02×10^{-5}
Nd	1.47×10^{-5}	1.94×10^{-6}	2.20×10^{-6}	-	2.87×10^{-6}	1.09×10^{-5}	1.16×10^{-5}	1.45×10^{-5}	1.46×10^{-5}	1.57×10^{-5}	1.14×10^{-5}
Sm	1.61×10^{-5}	1.75×10^{-6}	2.06×10^{-6}	2.49×10^{-6}	-	1.05×10^{-5}	1.27×10^{-6}	1.59×10^{-5}	1.60×10^{-5}	1.80×10^{-5}	1.25×10^{-5}
Yb	2.27×10^{-5}	2.45×10^{-6}	2.48×10^{-6}	2.56×10^{-6}	2.66×10^{-6}	-	1.15×10^{-5}	2.21×10^{-5}	2.23×10^{-5}	2.68×10^{-5}	5.49×10^{-6}
Ga	1.58×10^{-5}	2.09×10^{-7}	1.73×10^{-7}	8.45×10^{-8}	-2.65×10^{-8}	-7.70×10^{-7}	-	1.53×10^{-5}	1.55×10^{-5}	1.76×10^{-5}	1.95×10^{-6}
Th	1.81×10^{-5}	5.02×10^{-6}	5.76×10^{-6}	6.34×10^{-6}	6.43×10^{-6}	6.76×10^{-6}	7.02×10^{-6}	-	1.59×10^{-6}	5.56×10^{-5}	6.90×10^{-6}
U	$1.68.\times10^{-5}$	5.01×10^{-6}	5.08×10^{-6}	5.89×10^{-6}	6.48×10^{-6}	6.99×10^{-6}	7.38×10^{-6}	1.25×10^{-5}	-	5.75×10^{-5}	7.23×10^{-6}
Sn	7.30×10^{-6}	5.13×10^{-6}	5.21×10^{-6}	5.36×10^{-6}	5.50×10^{-6}	6.09×10^{-6}	6.40×10^{-6}	7.46×10^{-6}	7.37×10^{-6}	-	6.32×10^{-6}
Ta	2.55×10^{-5}	3.13×10^{-6}	3.20×10^{-6}	3.35×10^{-6}	3.54×10^{-6}	4.92×10^{-6}	6.56×10^{-6}	2.48×10^{-5}	2.51×10^{-5}	3.02×10^{-5}	-

Table 7. Overlap correcting coefficient in REE(GIS)

	Analytical elements									
	Cu	Nb	Co	Ni	Y	Zr	Sm	Yb	Ga	Ta
Nb	–	–	–	–	–	–	–	–	−0.064	–
Co	–	–	–	–	–	–	–	−0.005	–	–
Ni	–	–	–	–	–	–	–	−0.011	–	–
Rb	–	–	–	−0.085	−0.159	–	–	−0.007	–	–
Sr	–	–	–	–	–	−0.073	–	–	–	–
Y	–	−0.034	–	–	–	–	–	–	–	–
La	–	–	–	–	–	–	−1.040	–	–	–
Nd	–	–	−0.014	–	–	–	–	–	–	–
Th	−0.066	–	–	–	−0.183	–	–	–	–	–
U	–	–	–	–	–	–	–	–	–	−1.532



ACR: Accuracy R^2: coefficient of determination

Figure 1. Calibration lines in GB(2014_06) analyses file

Table 8. The hypothetical determination limits indicating each calibration line in GB(2014_06)

element	Hypothetical determination limit			relative error(%)
SiO_2	43.320	-	77.705	<1
Al_2O_3	11.720	-	23.802	<3
MgO	0.626	-	8.411	<3
Na_2O	0.885	-	4.688	<3
P_2O_5	0.054	-	0.297	<5
K_2O	0.040	-	4.698	<5
CaO	0.658	-	14.163	<3
TiO_2	0.091	-	1.620	<6
Fe_2O_3	1.850	-	15.059	<4
MnO	0.068	-	0.223	<5

Table 9. The result of quantitative analysis method in GB(2014_06)

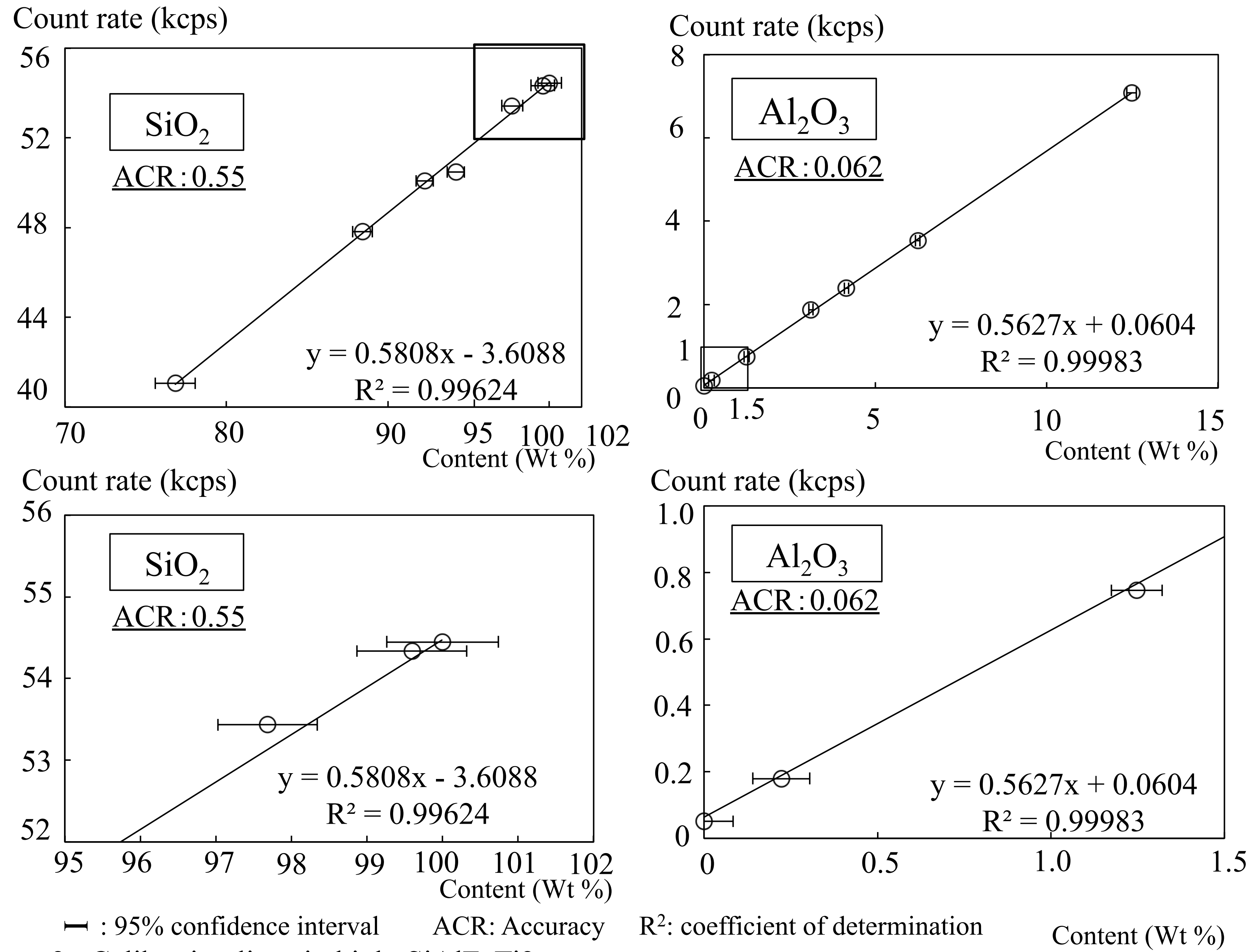
	JF-1			JZn-1			JP-1			JMs-2		
mass%	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.
SiO_2	67.686	66.690	1.471	44.441	43.950	1.105	42.684	42.380	0.713	40.177	41.780	3.989
Al_2O_3	18.809	18.080	3.877	6.190	6.320	2.108	0.654	0.660	0.887	13.067	14.180	8.514
MgO	0.029	0.006	79.167	1.827	1.940	6.208	45.542	44.600	2.068	2.902	3.240	11.657
Na_2O	3.327	3.370	1.305	0.402	0.450	11.885	0.249	0.021	91.580	5.202	5.790	11.302
P_2O_5	0.015	0.010	34.211	0.061	0.005	91.857	0.011	0.002	81.481	1.258	1.260	0.196
K_2O	10.239	9.990	2.428	0.845	0.830	1.829	0.014	0.003	78.261	2.570	2.700	5.053
CaO	0.901	0.930	3.196	18.494	18.100	2.132	0.609	0.550	9.658	4.492	4.680	4.190
TiO_2	-0.003	0.005	247.059	0.194	0.200	2.881	-0.005	0.006	230.435	1.384	1.400	1.146
Fe_2O_3	-0.052	0.080	255.039	15.882	16.860	6.348	9.330	8.370	10.289	10.551	10.960	3.872
MnO	-0.025	0.001	104.065	1.464	1.490	1.767	0.093	0.121	30.108	2.275	2.260	0.671

	JDo-1			JCh-1			JSd-1			JH-1		
mass%	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.
SiO_2	3.036	0.216	92.885	99.082	97.810	1.284	63.540	66.550	4.737	46.386	48.180	3.867
Al_2O_3	0.001	0.017	1142.857	0.769	0.734	4.527	14.320	14.650	2.303	5.457	5.660	3.717
MgO	18.562	18.470	0.495	0.093	0.075	19.099	1.753	1.813	3.399	16.156	16.730	3.552
Na_2O	0.170	0.013	92.412	0.187	0.031	83.672	2.709	2.727	0.657	0.725	0.710	2.001
P_2O_5	0.046	0.034	25.758	0.019	0.017	11.170	0.119	0.122	2.867	0.098	0.099	1.538
K_2O	-0.001	0.002	332.000	0.214	0.221	3.175	2.136	2.183	2.191	0.526	0.530	0.697
CaO	37.730	33.960	9.992	0.075	0.045	39.812	2.947	3.034	2.938	14.721	15.020	2.032
TiO_2	-0.008	0.001	115.833	0.016	0.032	92.683	0.663	0.643	3.046	0.648	0.670	3.475
Fe_2O_3	-0.113	0.021	118.440	0.248	0.356	43.780	5.197	5.059	2.652	9.954	10.270	3.171
MnO	-0.009	0.007	169.894	0.008	0.017	105.952	0.093	0.092	0.645	0.175	0.190	8.883

m.v; measured value,   r.v.; recommended value,   r.e; relative error

Table 10. The determination limits indicating each calibration line in GB(2014_06)

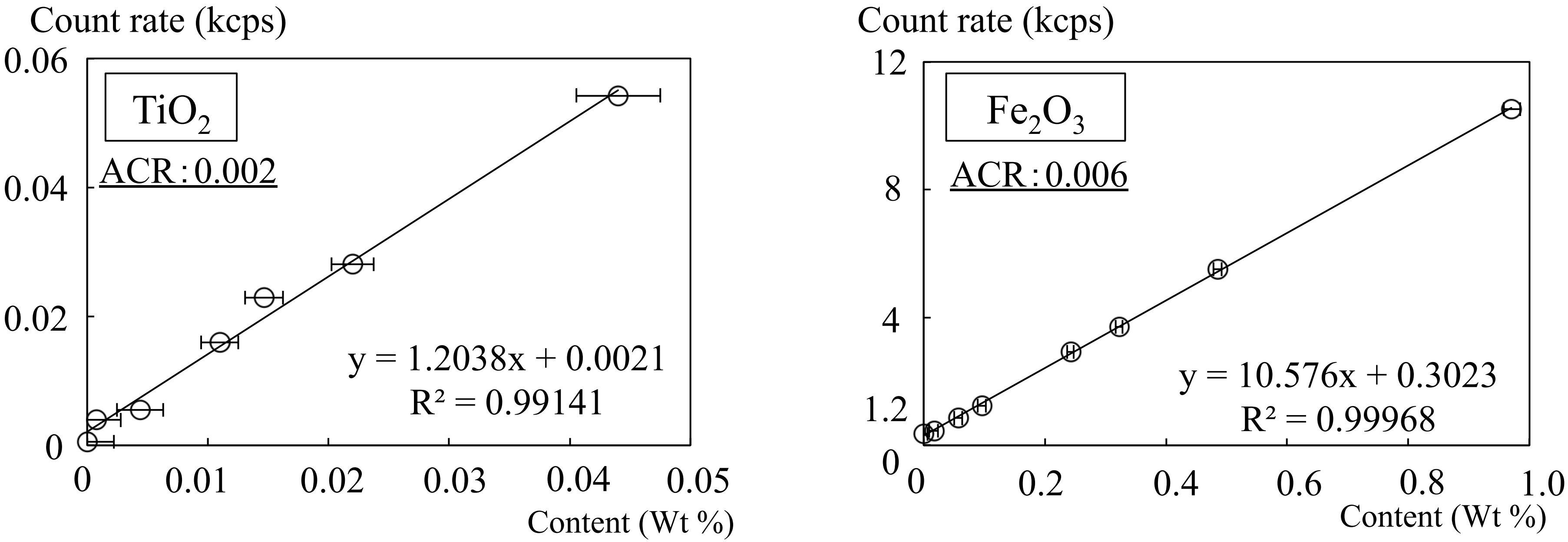
element	determination limit	relative error(%)
SiO_2	41.780 - 97.810	<4
Al_2O_3	0.660 - 23.802	<9
MgO	0.626 - 44.600	<12
Na_2O	0.450 - 5.790	<12
P_2O_5	0.054 - 0.297	<5
K_2O	0.040 - 9.990	<6
CaO	0.550 - 33.960	<10
TiO_2	0.091 - 1.620	<6
Fe_2O_3	1.850 - 16.860	<11
MnO	0.068 - 2.260	<9



I : 95% confidence interval   ACR: Accuracy R^2: coefficient of determination

Figure 2. Calibration lines in high_SiAlFeTi2

The both upper figures show whole of calibration lines in high_SiAlTiFe. The lower figures indicates the extended parts surrounded into a square at each upper figure.



: 95% confidence interval   ACR: Accuracy R^2: coefficient of determination

Figure 2. Calibration lines in high_SiAlFeTi2 (Continued)

The both upper figures show whole of calibration lines in high_SiAlTiFe2. The lower figures indicates the extended parts surrounded into a square at each upper figure.

Table 11. The hypothetical determination limits indicating each calibration curve in high_SiAlTiFe2

element	Hypothetical determination limit (%)			relative error(%)
SiO_2	75.740	-	98.850	<2
Al_2O_3	0.130	-	12.600	<5
TiO_2	0.020	-	0.047	<3
Fe_2O_3	0.081	-	0.240	<10
	0.241	-	0.981	<2

Table 12. The result of quantitative analysis method in high_SiAlTiFe

	JDo-1			JCh-1			JP-1			JF-1		
mass%	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.
SiO2	6.801	0.216	96.824	97.110	97.810	0.721	43.977	42.380	3.631	67.567	66.690	1.297
Al2O3	0.048	0.017	63.750	0.762	0.734	3.717	0.701	0.660	5.782	18.688	18.080	3.253
TiO2	0.001	0.001	33.000	0.026	0.032	23.117	0.006	0.006	9.091	0.004	0.005	38.675
Fe2O3	0.035	0.021	40.571	0.387	0.356	7.931	9.142	8.370	8.442	0.095	0.080	16.084

	JG2M3			JG2M4			JG2M5		
mass%	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.	m. v.	r.v.	r.e.
SiO_2	98.480	98.701	0.224	98.944	99.202	0.248	99.489	99.897	0.410
Al_2O_3	0.704	0.741	5.240	0.471	0.445	5.799	0.036	0.056	54.167
TiO_2	0.003	0.003	-	0.003	0.002	33.333	-0.001	0.000	100.000
Fe_2O_3	0.052	0.058	9.615	0.030	0.035	17.978	0.001	0.004	500.000

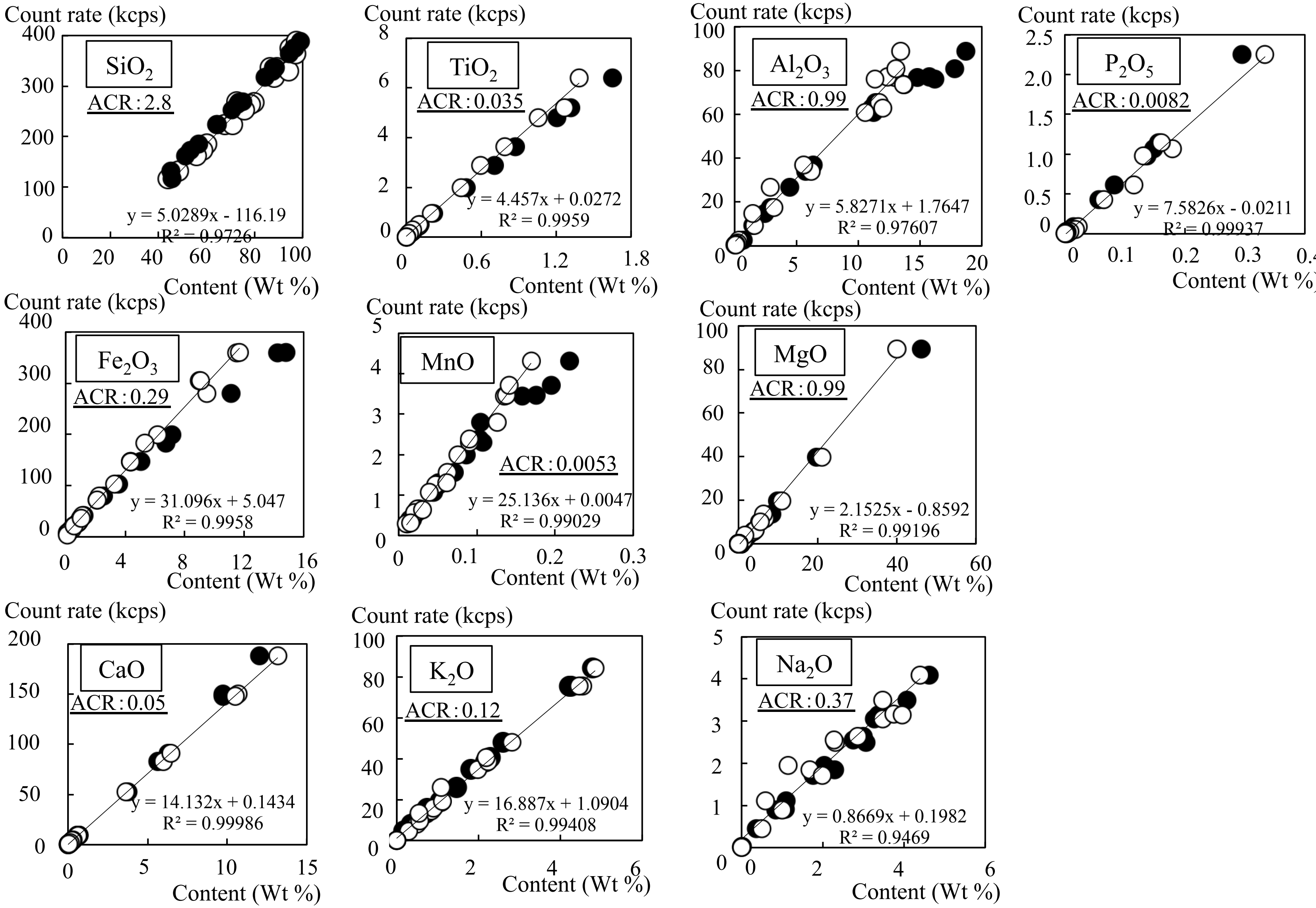
m.v; measured value, r.v.; recommended value, r.e; relative error

Table 13. The determination limits indicating each calibration curve in high_SiAlTiFe2

element	determination limit (%)			relative error(%)
SiO_2	42.380	-	75.739	<4
	75.740	-	98.850	<2
Al_2O_3	0.130	-	12.600	<5
TiO_2	0.020	-	0.047	<3
	0.020	-	0.047	<25*
Fe_2O_3	0.241	-	0.981	<2
	0.241	-	0.981	<8*

*:the rocks excepting Granite and Quartz

non *:all rocks



ACR: accuracy R^2: coefficient of determination

○: estimated value (Xi^); It was calculated in following equation. $Xi\hat{}=(C_i - \Sigma B_j F_j) / (1+\Sigma A_j F_j)$

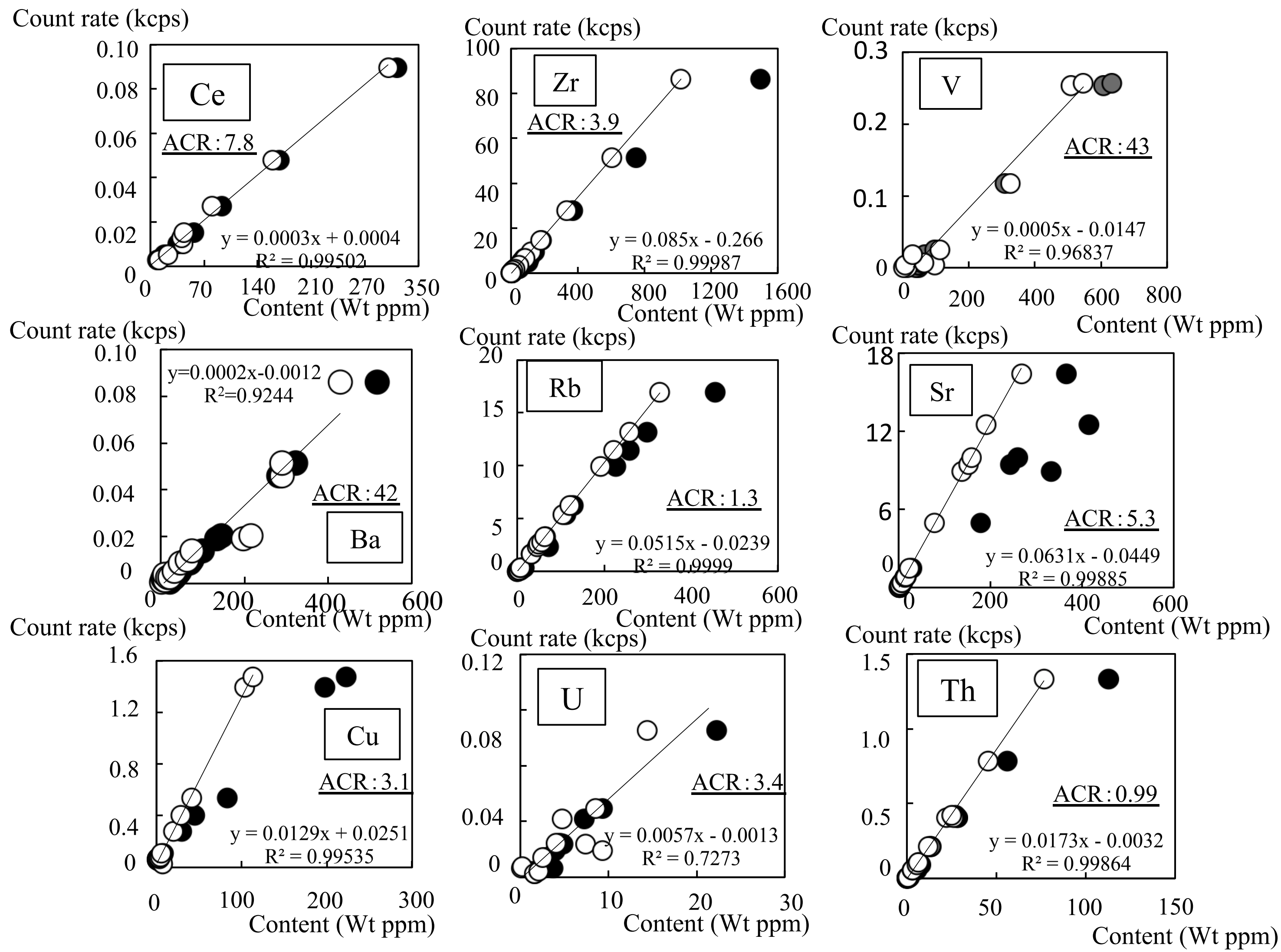
A: matrix correction constants (shown to Table 7) , B: overlap correction constants (shown to Table 8)

C: standard value of the target element, F: standard value of measurement elements excepting Si or Al

●: quantitative value (Wi); $W_i = X_i(1+\Sigma A_j F_j) + \Sigma B_j F_j$

Xi: each of calibration line

Figure 3. Calibration lines in REE(GIS)



ACR: accuracy R^2: coefficient of determination

○: estimated value (Xi^); It was calculated in following equation. Xi^=(C i - Σ B j F j) / (1+ Σ A j F j)

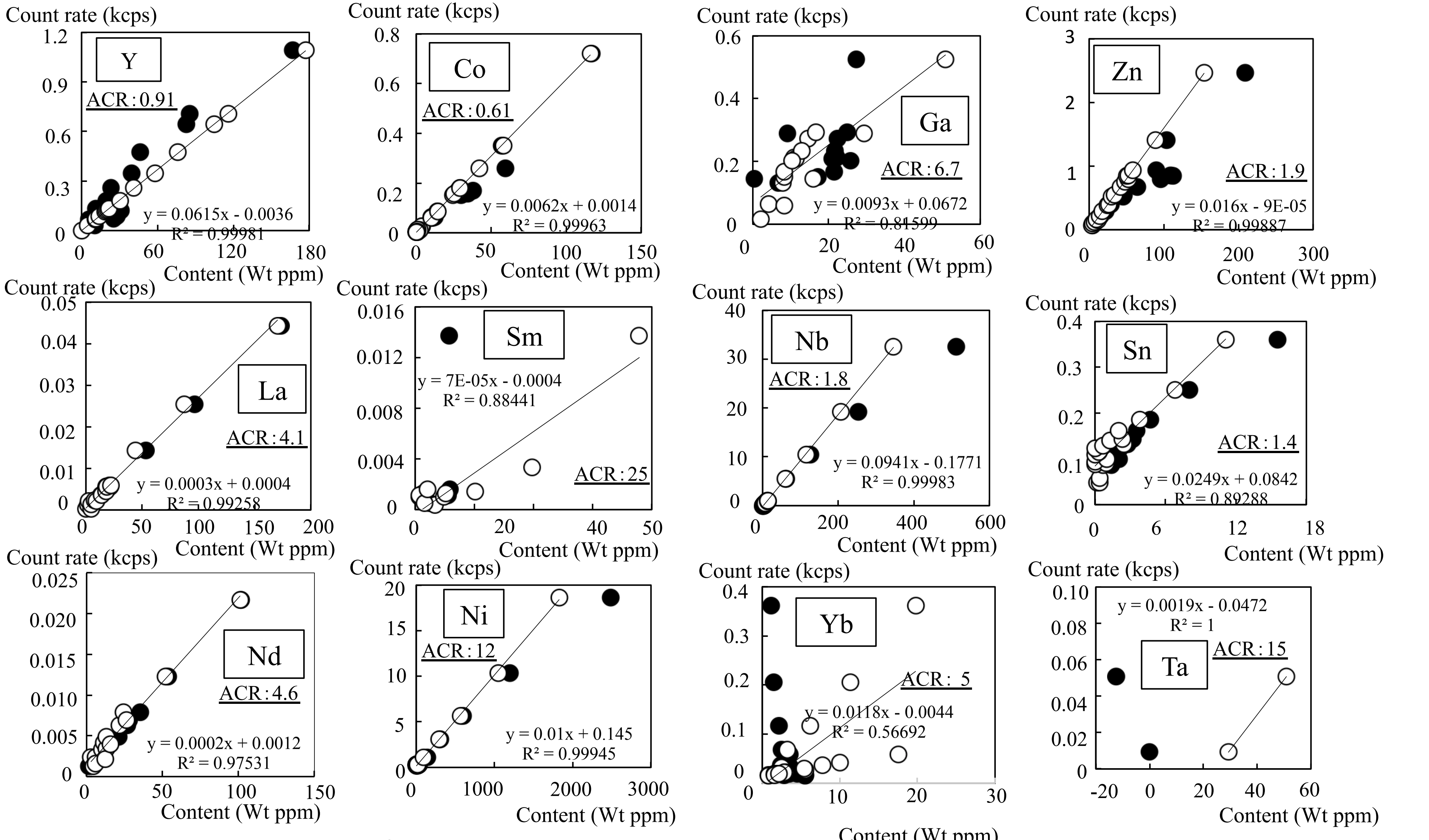
A: matrix correction constants (shown to Table 7) , B: overlap correction constants (shown to Table 8)

C: standard value of the target element, F: standard value of measurement elements excepting Si or Al

●: quantitative value (Wi); $W_i = X_i\,(1+\Sigma A\,j\,F\,j) + \Sigma B\,j\,F\,j$

Xi: each of calibration line

Figure 3. (Continued)



ACR: accuracy R^2: coefficient of determination

○: estimated value (Xi^); It was calculated in following equation. Xi^=(C i - Σ B j F j) / (1+ Σ A j F j)

A: matrix correction constants (shown to Table 7) , B: overlap correction constants (shown to Table 8)

C: standard value of the target element, F: standard value of measurement elements excepting base element and measurement element

●: quantitative value (Wi); $W_i = X_i(1+\Sigma A_j F_j) + \Sigma B_j F_j$ Xi: each of calibration line

Figure 3. (Continued)

Table 14. The hypothetical determination limits indicating each calibration line in the REE(GIS)

element	Hypothetical determination limit (%)	relative error(%)
SiO2	42.38 - 96.93	<8
Al2O3	3.21 - 17.49	<17
P2O5	0.056 - 0.294	<22
K2O	1.10 - 4.71	<27
CaO	0.023 - 0.137	<17
	0.138 - 11.09	<9
TiO2	0.026 - 1.60	<14
Na2O	1.20 - 4.69	<20
MgO	4.62 - 44.6	<27
MnO	0.071 - 0.218	<15
Fe2O3	0.59 - 15.06	<12

Table 14. (Continued)

element	Hypothetical determination limit (%)			relative error(%)
Ba	311	-	466	<11
Cu	6.72	-	225	<20
Nb	15.2	-	510	<17
Co	3.62	-	12.2	<13
	12.3	-	116	<4
Ni	16.6	-	2460	<9
Rb	6.87	-	453	<6
Sr	1.3	-	403	<14
V	372	-	635	<21
Y	5.64	-	166	<6
Zn	15.3	-	209	<8
Zr	12.5	-	1494	<15
La	15.8	-	179	<18
Ce	48.3	-	327	<14
Nd	10.9	-	107	<27
Th	3.34	-	112	<11

Table 15. The result of quantitative analysis method in REE(GIS)

element	JLs-1			JLk-1			JDo-1			JMs-1			JMn-1		
	m.v	r.v	r.e	m.v	r.v	r.e	m.v	r.v	r.e	m.v	r.v	r.e	m.v	r.v	r.e
SiO2	13.76	0.12	99.13	60.28	57.16	5.18	18.34	0.22	98.82	56.59	53.74	5.03	29.91	14.11	52.83
Al2O3	-0.05	0.02	140.59	16.32	16.73	2.50	-0.07	0.02	125.97	15.27	15.82	3.63	4.09	4.30	5.15
P2O5	0.03	0.03	2.75	0.20	0.21	5.05	0.04	0.03	22.63	0.16	0.18	9.31	0.49	0.54	10.05
K2O	-0.03	0.00	109.79	2.99	2.81	6.07	-0.04	0.00	105.52	2.18	2.24	2.72	0.88	0.94	7.43
CaO	91.03	55.09	39.48	0.72	0.69	5.20	55.39	33.96	38.69	1.99	2.13	6.89	3.13	2.91	6.90
TiO2	-0.02	0.00	112.77	0.79	0.67	14.90	-0.01	0.00	113.30	0.73	0.70	4.24	1.23	1.06	13.82
Fe2O3	-0.47	0.02	103.57	8.07	6.93	14.11	-0.32	0.02	106.54	7.14	6.90	3.35	17.09	14.40	15.72
MnO	0.01	0.00	58.20	0.30	0.27	11.14	0.01	0.01	45.25	0.10	0.10	0.33	30.95	33.09	6.91
Na2O	-0.16	0.00	101.22	0.68	1.05	53.58	-0.13	0.01	109.85	3.30	4.07	23.42	1.32	2.80	112.01
MgO	1.18	0.61	48.85	2.40	1.74	27.54	20.68	18.47	10.70	3.82	2.87	24.89	3.98	3.12	21.56
Ba	829.33	476.00	42.60	691.33	574.00	16.97	46.33	6.14	86.75	295.00	307.00	4.07	1975.67	1714.00	13.24
Cu	4.00	0.27	93.30	71.00	62.90	11.41	5.00	1.41	71.80	87.67	88.00	0.38	9787.67	11132.00	13.73
Nb	5.00	1.00	80.00	16.00	15.80	1.25	3.00	0.40	86.67	9.00		-	33.00	27.60	16.36
Co	0.00	0.08	0.00	20.67	18.00	12.90	0.33	0.17	49.60	16.67	18.10	8.60	1740.33	1732.00	0.48
Ni	-2.00	0.36	118.10	38.00	35.00	7.89	10.00	2.90	71.00	55.33	53.00	4.22	12747.67	12632.00	0.91
Rb	-2.67	0.18	106.75	171.67	147.00	14.37	6.00	1.75	70.83	95.67	88.00	8.01	14.67	10.90	25.68
Sr	462.67	295.00	36.24	76.67	67.50	11.96	185.67	116.00	37.52	151.00	154.00	1.99	813.00	792.00	2.58
V	111.33	3.59	96.78	85.33	117.00	37.11	85.00	3.14	96.31	88.67	127.00	43.23	452.67	424.00	6.33
Y	0.67	0.22	66.55	50.00	40.00	20.00	18.00	10.30	42.78	23.00	24.30	5.65	119.00	111.00	6.72
Zn	2.33	3.19	36.71	170.00	152.00	10.59	56.33	35.40	37.16	268.00	264.00	1.49	1109.00	1068.00	3.70
Zr	16.33	4.19	74.35	149.33	137.00	8.26	9.33	6.21	33.46	119.00	132.00	10.92	383.33	344.00	10.26
La	-23.33	0.15	100.66	41.67	40.60	2.56	6.00	7.93	32.17	17.67		-	149.67	122.00	18.49
Ce	64.67	0.52	99.19	-12.67	87.90	793.95	1.33	2.49	86.75	-101.00		-	243.33	277.00	13.84
Nd	-23.00	0.14	100.59	49.33	35.70	27.64	-5.33	5.25	198.44	16.33		-	213.00	137.00	35.68
Th	-2.00	0.03	101.44	22.00	19.50	11.36	-2.00	-	-	7.00		-	13.33	11.70	12.25

m.v; measured value, r.v.; recommended value, r.e; relative error

Table 15. (Continued)

element	JZn-1			JCu-1			SY-4			WPR-1a		
	m.v	r.v	r.e	m.v	r.v	r.e	m.v	r.v	r.e	m.v	r.v	r.e
SiO2	44.63	43.95	1.52	31.85	28.68	9.96	49.33	49.90	1.16	44.87	36.64	18.34
Al2O3	5.80	6.32	8.97	0.11	0.29	168.52	18.53	20.69	11.66	4.91	4.95	0.73
P2O5	0.07	0.01	92.42	0.08	0.01	93.51	0.12	0.13	9.17	0.06	0.07	8.38
K2O	0.87	0.83	5.11	-0.03	0.02	143.69	1.78	1.66	6.64	0.16	0.19	17.99
CaO	18.49	18.10	2.12	23.93	23.50	1.80	8.91	8.05	9.61	3.52	3.54	0.63
TiO2	0.21	0.20	5.21	0.01	0.01	85.71	0.34	0.29	16.08	0.58	0.59	2.08
Fe2O3	17.52	11.80	32.65	23.32	17.50	24.95	5.78	6.21	7.51	15.67	16.21	3.43
MnO	1.54	1.49	3.35	0.57	0.59	2.67	0.11	0.11	3.57	0.16	0.18	10.56
Na2O	0.02	0.45	2077.42	-0.18	0.05	128.62	6.24	7.10	13.72	-0.10	0.08	182.19
MgO	2.66	1.94	26.99	2.00	2.13	6.34	1.25	0.54	56.71	30.84	25.24	18.16
Ba	282.33	208.00	26.33	-394.00	3.50	100.89	433.00	340.00	21.48	-10.67	70.60	761.88
Cu	30.33	29.00	4.40	36133.67	37300.00	3.23	7.67	7.00	8.70	2429.67	2990.00	23.06
Nb	9.33		-	5.00		-	11.33	13.00	14.71	6.00	3.88	35.33
Co	28.00	24.00	14.29	299.67	324.00	8.12	3.33	2.80	16.00	181.67	213.00	17.25
Ni	2.00	6.00	200.00	396.33	425.00	7.23	12.67	9.00	28.95	3517.00	4390.00	24.82
Rb	50.67	42.00	17.11	8.00	1.90	76.25	79.33	55.00	30.67	8.33	7.06	15.28
Sr	362.67	358.00	1.29	72.67	75.00	3.21	1233.00	1191.00	3.41	19.67	19.50	0.85
V	40.33	24.00	40.50	57.00	9.00	84.21	-0.33	8.00	2500.00	113.67	135.00	18.77
Y	-18.67		-	-1.00		-	137.33	119.00	13.35	8.67	8.39	3.19
Zn	23649.67	22200.00	6.13	657.00		-	95.33	93.00	2.45	159.00	160.00	0.63
Zr	63.33		-	16.00		-	486.67	517.00	6.23	44.00	41.80	5.00
La	8.00		-	-6.33		-	56.67	58.00	2.35	-4.33	4.04	193.23
Ce	-176.67		-	-9.33		-	104.00	122.00	17.31	-133.33	9.69	107.27
Nd	-2.00		-	-22.00		-	83.67	57.00	31.87	6.67	6.26	6.10
Th	9.67		-	-1.33		-	-1.00	1.40	240.00	-0.33	0.64	292.00

m.v; measured value, r.v.; recommended value, r.e; relative error

Table 16. The determination limits indicating each calibration line in the REE(GIS)

element	determination limit (ppm)			relative error(%)
SiO_2	42.38	-	96.93	<8
Al_2O_3	3.21	-	20.69	<17
P_2O_5	0.056	-	0.540	<22
K_2O	1.1	-	4.71	<27
CaO	0.023	-	0.137	<17
	0.138	-	23.5	<9
TiO_2	0.026	-	1.6	<14
*Na_2O	1.2	-	4.69	<20
MgO	4.62	-	44.6	<27
MnO	0.071	-	33.09	<15
*Fe_2O_3	0.59	-	15.06	<12

*: This limitation range can apply only the type of rocks used in Calibration lines.

Table 16. (Continued)

element	determination limit (ppm)			relative error(%)
*Ba	311	-	466	<11
Cu	6.72	-	37300	<20
Nb	15.2	-	510	<17
Co	3.62	-	12.2	<13
	12.3	-	116	<4
Ni	16.6	-	12632	<9
*Rb	6.87	-	453	<6
*Sr	1.3	-	403	<14
V	372	-	635	<21
*Y	5.64	-	166	<6
*Zn	15.3	-	209	<8
Zr	12.5	-	1494	<15
La	15.8	-	179	<18
*Ce	48.3	-	327	<14
Nd	10.9	-	107	<27
Th	3.34	-	112	<11

*: This limitation range can apply only the type of rocks used in Calibration lines.