Major element analysis of silicate rocks using electron probe microanalyzer.

Takeshi MORI, Petr JAKEŠ* and Masatoshi NAGAOKA

*Department of Earth Sciences, Kanazawa University,
Kanazawa, Japan*

Abstract Results of the electron probe analysis of USGS and other standards of silicate rocks are reported. GULSON and LOVERING's method (GULSON and LOVERING, 1968) was slightly modified for obtaining higher X-ray intensities and better reproducibility. The results show good agreement with the recommended values of the standard rocks.

INTRODUCTION

Need for fast and reliable major element analysis of heterogeneous geological materials is urgent. NORRISH and CHAPPELL (1967) proposed a method of X-ray fluorescence analysis using fused samples. GULSON and LOVERING (1968) applied the fusion technique to electron probe microanalysis. Their method has been recently used by some authors (e.g. MEDARIS and DOTT, 1970). We have also adopted basically the same technique as used by GULSON and LOVERING, but some modifications were made for increasing the sensitivities of the analysis. The X-ray intensities were increased by the use of higher sample concentration in the fusion mixture than in the case of GULSON and LOVERING's method, but this procedure in turn requires to crush and melt the sample twice and also to correct for the matrix effect in SiO_2 and MgO determinations. In the following, we intend to describe the results of our attempt on standards of USGS (W-1, G-1, G-2, AGV-1, BCR-1, GSP-1, PCC-1, DTS-1), Geological Survey of Japan (JB-1, JG-1), Spectroscopic Society of Canada (SY-2) and Queen Mary College (QMC-II).

SAMPLE PREPARATION

Finely crushed rock sample (100-200 mesh) was precisely weighed (0.280 gr.) into

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* Present address
    Geological Institute, Czechoslovak Acad. Sci. Praha, Czechoslovakia.

a glass bottle and mixed with 0.750 gr. of fusion mixture, i.e. the reagents, composed of Lithium tetraborate(anhyd.) 38.0 gr. Lithium carbonate 29.6 gr. Lanthanum oxide 13.2 gr (Norrish and Hutton 1969, or Norrish and Chappell 1967). The sample was transferred into a platinum crucible and fused above a Mekker burner at about 950-1000°C for a few minutes being stirred. The melt was continuously stirred by gentle shaking of the crucible. After the macroscopic heterogeneities (usually black spots on the surface of melt) were completely eliminated the melt was poured into a brass ring on a graphite plate and pressed into disk using an aluminium plunger. The disk shape was most suitable for crushing of the glass in a mortar. The glass remaining on the wall was removed as much as possible by quenching the hot crucible in water. The glass disk and the loose material thus obtained were crushed again in an agate mortar. The powder was transferred into the platinum crucible and remelted. After thorough mixing, the melt was poured onto the graphite plate to produce small "beads" of 1-4 mm in diameter. Usually 5-10 such beads were produced and of these two for each sample were mounted in plastic. The mount was polished (with 0.25μ diamond paste at the final stage), carbon coated, then used for analysis.

ANALYTICAL CONDITIONS

Hitachi electron probe microanalyzer, Model XMA-5A (3 channels with 38° take off angle), was used in this work. Accelerating voltage was kept at 15 KV, and specimen current at about 0.03 μA. The accelerating voltage was calibrated against the critical excitation voltages of Zn, Zr and Mo. First order $K\alpha$ lines were measured. The diffraction crystals LiF, ADP and KAP were used for, Fe, Ti, Mn; Si, Ca, K; and Mg, Al, Na, respectively. The beam stability was checked at every 30 minutes on one of the standard crystals periclase, albite and corundum.

After measuring the intensity of a peak for an element, values of the background intensity were measured on both sides of the peak. Then the intensity of background was

Table 1.   Background intensity of Mg (FM : fusion mixture).

Estimated values of B. G. intensities at the peak position of Mg		B. G. intensities measured at Mg peak position for MgO free sample	
Sample	Intensity (CPS)	Sample (gram)	Intensity (CPS)
W-1	3.5	$0.14\ SiO_2 + 0.14\ Fe_2O_3 + 0.75\ FM$	5.4
AGV-1	3.2	$0.14\ SiO_2 + 0.75\ FM$	7.5
JG-1	3.6	$0.14\ SiO_2 + 0.89\ FM$	4.5
PCC-1	3.1	$0.14\ Al_2O_3 + 0.89\ FM$	4.2
DTS-1	3.8		
BCR-1	3.6		
G-2	3.1		
GSP-1	3.3		

estimated by averaging the above two values. The estimated values thus obtained at the peak position of Mg are shown in Table 1, together with the intensities of the background measured at the same peak position on fused oxide samples free from Mg. The merit of fusion with heavy absorber is that the background intensity remains nearly constant among different rock samples. A slight difference in background intensity existed between glass samples prepared from pure oxides and those from rock samples. For this reason we did not use oxide glass for background measurment.

The electron beam was adjusted to about 40μ in diameter and sample was continuously moved under it. GULSON and LOVERING (1968) reported relatively good stability of glass against the beam bombardment. Also in our experiment no appreciable change in count rate was observed even when the driving speed of sample was as low as 10μ/min. We preferred a higher driving speed (50μ/min) for eliminating an effect of heterogeneity of sample which can exist in some cases.

Values of detection limit for various element under the condition of our analysis

Table 2. Detection limit in wt.%.

SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O
0.42	0.15	0.11	0.19	0.03	0.15	0.12	0.19	0.05

are shown in Table 2. Here, the values were calculated according to the following formula given by NORRISH and CHAPPELL (1967):

$$\text{Detection Limit} = \frac{6}{m}\sqrt{\frac{Cb}{T}}$$

m : the number of counts per second obtained per unit concentration for the element in the sample

T : total analytical time

Cb: the number of counts per second in the background position

RESULTS AND DISCUSSION

Generally, X-ray intensity, I, of i-th element is related to its content, Ci by the following equations (BENCE and ALBEE 1968):

$$C_i = \beta_i \times I_i \times K \qquad (1)$$

here K is a constant that depends on instrumental conditions; β is a correction term, being expressed as:

$$\beta_i = \alpha_i^{\text{FM}} \times C_{\text{FM}} + \sum_j \alpha_i^j \times C_j \qquad (2)$$

in which α_i^j is a correction factor to evaluate the effect of concentration of element "j" on the count rate of element i, and is considered to be constant within certain compositional range of "j". C_{FM} and α_i^{FM} denote concentration of fusion mixture and correction factor for the effect of fusion mixture on "i", respectively.

Then we get

$$\frac{C_{unk}}{C_{std}} = \frac{\beta_{unk}}{\beta_{std}} \times \frac{I_{unk}}{I_{std}} \qquad (3)$$

where subscripts *unk* and *std* refer to unknown and standard samples respectively. The value $\alpha_i^{FM} \times C_{FM}$ is far larger than the value $\sum_j \alpha_i^j \times C_j$, so that the difference in β among various samples becomes negligibly small. The value of $\frac{\beta_{unk}}{\beta_{std}}$ is very close to unity, when that of dilution factor $\left(\frac{C_{rock}+C_{FM}}{C_{rock}}\right)$ is sufficiently high as 6.36 as preferred by Gulson and Lovering (1968). The relationship between the concentration and X-ray intensity for three elements of nine standard rocks are shown in Figure 1. The results of regression analyses are summarized in Table 3. Except for SiO_2 and MgO,

Table 3.　Linear regression analyses for elements.

oxide	equation	error in wt.%
SiO_2	$C = 0.3554 \times I + 2.4$	1.3
TiO_2	$C = 0.2546 \times I - 0.59$	0.071
Al_2O_3	$C = 0.1121 \times I - 0.33$	0.32
Fe_2O_3	$C = 0.1282 \times I - 0.95$	0.29
MnO	$C = 0.0973 \times I - 0.437$	0.021
MgO	$C = 0.1503 \times I - 0.47$	0.48
CaO	$C = 0.0743 \times I - 0.65$	0.10
Na_2O	$C = 0.2701 \times I - 0.66$	0.17
K_2O	$C = 0.0678 \times I - 0.296$	0.088

C : Concentration of oxide in wt.%
I : X-ray intensity in c.p.s.

good linear relations between C and I can be seen in the Figure and Table. The observed discrepancy from the linear relation in SiO_2 and MgO is due to the approximation $\left(\frac{\beta_{unk}}{\beta_{std}} = 1.0\right)$. Then, for increasing the accuracy of the analyses of the two elements, the correction factors α_{Si}^{FM} and α_{Mg}^{FM} were measured on the glasses made from pure oxides and fusion mixture. The values thus obtained are 1.12 and 1.29 respectively. For all other α_{Si}^j and α_{Mg}^j the values given by Albee and Ray (1970) were used (Table 4).

Figure 1. The relationship between the concentration and X-ray
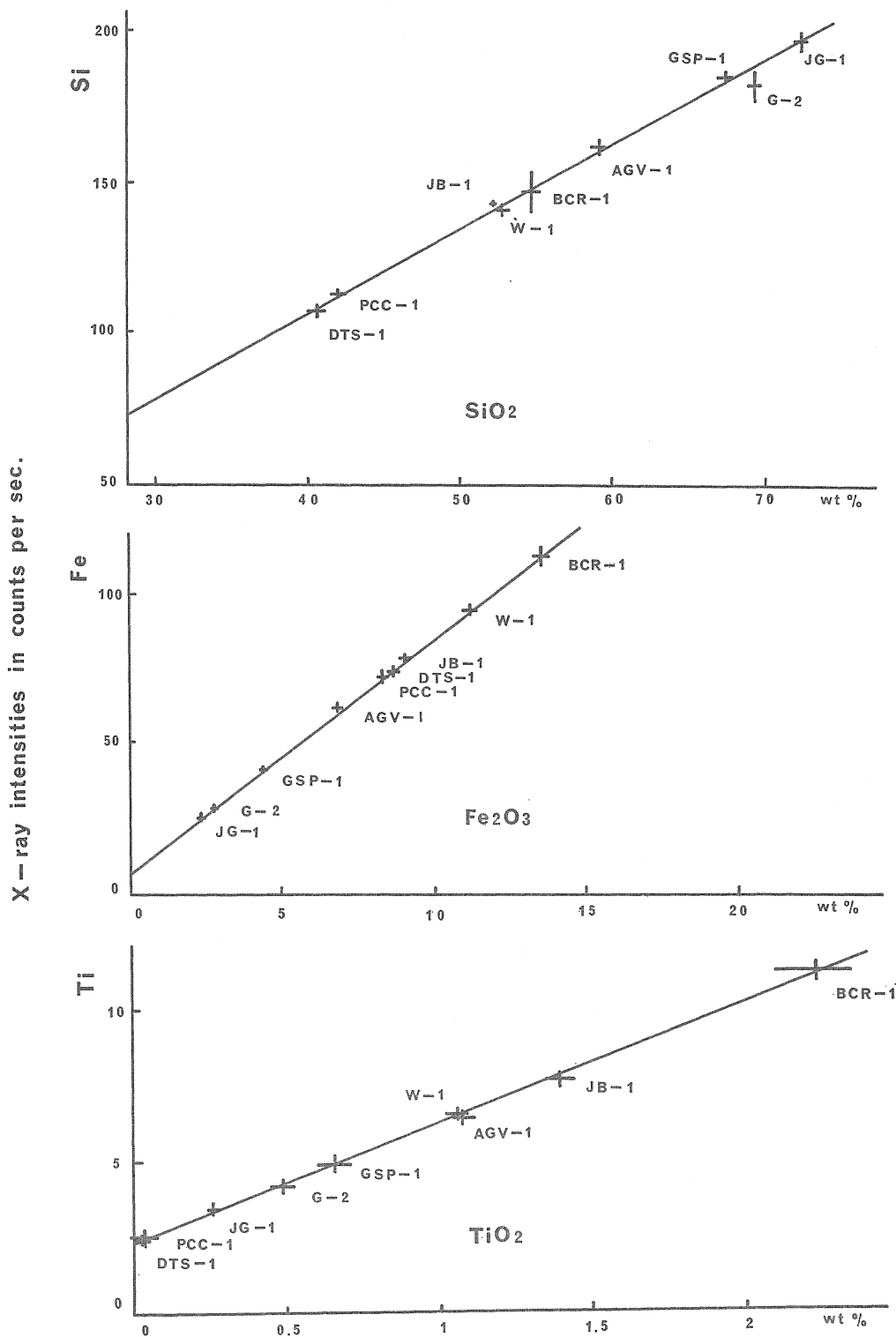intensity for three elements of nine standard rocks.

Table 4.   Correction factors, α_{Si}^{j} and α_{Mg}^{j}.

i \ j	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO
Si	1.38	1.48	1.54	1.00	1.01	1.07	1.10	1.24	1.31
Mg	2.05	1.00	1.04	1.11	1.20	1.32	1.43	1.80	1.97

Among the standard samples here used, we took W-1 as reference and calculated the compositions of others assuming the linearity between the X-ray intensities and concentrations. For SiO_2 and MgO, the correction mentioned above was made. The K_2O content of W-1, 0.65 wt. %, is too low, then in the case of K_2O determination, GSP-1 or G-1 was used as a standard.

Chemical compositions thus obtained are given in Table 5a. The differences between our results and the recommended values (FLEISCHER, 1969; FLANAGAN, 1969; TIBA, 1970) are shown in parentheses. Table 5b lists the results of additional works, in which analyses of some independently prepared duplicates are also included. The recommended values for SY-2 and QMC-Il were taken from the circulars of the Spectroscopic Society of Canada and of Dept. Geology, Queen Mary College. The counting time for the data listed in Table 5a and 5b is 500 sec. and 100 sec. respectively. As there is no significant difference between the duplicates counting time of 100 sec. seems appropriate for routine analysis.

The results are good for Al_2O_3, Fe_2O_3 (total iron), CaO, Na_2O, K_2O, TiO_2 and MgO. Only SiO_2 has error up to 2 wt. %, which may partly be caused by error of weighing. Because of the smaller dilution factor, MnO was determined with satisfactory figures.

The error in SiO_2 determination by GULSON and LOVERING appears to be about 0.8 wt. %, while our error after correction is about 0.9 wt. %. Therefore our smaller dilution factor did not substantialy influence the accuracy. The error for other elements are also similar between two alternative dilution factors. On the other hand, smaller dilution factor makes it possible to determine MnO with reasonable accuracy.

ACKNOWLEDGMENTS

	a								b					
	JG-1	JB-1	G-2	GSP-1	AGV-1 (a)	PCC-1	DTS-1	BCR-1 (a)	G-1 (a)	G-1 (b)	BCR-1 (b)	SY-2	AGV-1 (b)	QMC-I1
SiO_2	72.98	53.34	67.70	68.58	60.20	42.70	40.64	54.64	73.28	72.63	55.16	60.15	59.89	76.71
	(0.88)	(1.33)	(−1.49)	(1.30)	(1.20)	(0.83)	(0.17)	(0.15)	(0.76)	(0.11)	(0.67)	(−0.58)	(0.89)	(1.26)
TiO_2	0.28	1.36	0.47	0.64	1.04	0.02	0.02	2.26	0.23	0.29	2.09	0.12	1.07	0.02
	(0.02)	(0.05)	(−0.06)	(−0.06)	(−0.04)	(0.00)	(0.00)	(0.03)	(−0.03)	(0.03)	(−0.14)	(−0.02)	(−0.01)	(−0.02)
Al_2O_3	14.49	14.34	15.19	15.16	16.91	0.93	0.55	13.26	14.54	14.77	13.76	12.32	17.43	14.45
	(0.27)	(−0.08)	(−0.16)	(0.04)	(−0.10)	(0.07)	(0.00)	(−0.40)	(0.41)	(0.64)	(0.10)	(0.98)	(0.42)	(0.51)
Total Fe as Fe_2O_3	2.34	9.08	2.74	4.39	6.99	8.25	8.57	13.40	2.01	2.07	13.49	6.39	6.92	0.78
	(−0.01)	(0.02)	(−0.03)	(0.06)	(0.19)	(−0.29)	(−0.28)	(−0.11)	(0.07)	(0.13)	(−0.02)	(−0.76)	(0.12)	(0.25)
MnO	0.05	0.17*	0.05	0.04	0.08	0.09	0.11	0.19	0.01	0.00	0.18	0.25	0.05	0.01
	(−0.02)		(0.01)	(0.00)	(−0.02)	(−0.03)	(−0.02)	(0.01)	(−0.02)	(−0.03)	(0.00)	(−0.08)	(−0.05)	(−0.02)
MgO	0.95	7.79	0.90	1.14	1.64	45.08	50.94	3.34	0.25	0.22	3.47	2.66	1.54	0.10
	(0.25)	(0.08)	(0.12)	(0.18)	(0.15)	(1.52)	(1.13)	(0.06)	(−0.14)	(−0.17)	(0.19)	(0.67)	(0.05)	(0.00)
CaO	2.26	9.29	2.00	2.16	4.91	0.55	0.15	7.03	1.38	1.44	7.13	8.13	4.98	0.99
	(0.10)	(0.09)	(0.01)	(0.13)	(−0.07)	(0.02)	(−0.01)	(0.08)	(0.00)	(0.06)	(0.18)	(−1.52)	(0.00)	(0.19)
Na_2O	3.54	2.78*	3.96	2.79	4.17	0.02	0.08	3.20	3.24	3.47	3.27	4.34	4.13	4.60
	(0.12)		(−0.20)	(−0.04)	(−0.16)	(−0.03)	(0.03)	(−0.11)	(−0.07)	(0.16)	(−0.04)	(0.12)	(−0.20)	(0.00)
K_2O	3.92	1.42*	4.38	5.49*	2.95	0.04	0.09	1.87	5.47*	5.47*	1.77	4.75	3.08	3.97
	(−0.02)		(−0.13)		(0.05)	(0.02)	(0.07)	(0.19)			(0.09)	(0.06)	(0.18)	(−0.35)
H_2O+*	0.66	1.10	0.55	0.57	0.81	4.70	0.47	0.77	0.39	0.39	0.77	0.21	0.81	0.23
total**	101.47	100.67	97.94	100.96	99.70	102.38	101.62	99.96	100.80	100.75	101.09	99.32	99.90	101.86

Table 5. Comparison between the probe-analysis and published values of standard rocks. The figures in the parentheses are the difference from the published values.
* Quoted from literatures
** Excess total is partly due to the conversion of FeO to Fe_2O_3

REFERENCES

ALBEE, A. L. and RAY, L. (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulfates. *Anal. Chem.* 42, 1480-1414.

BENCE, A. E. and ALBEE, A. L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* 76, 382-403.

FLANAGAN, F. J. (1969) U. S. Geological Survey standards-II. First compilation of data for the new U.S.G.S. rocks. *Geochim. Cosmochim. Acta,* 33, 81-120.

FLEISCHER, M. (1969) U. S. Geological Survey standards-I. Additional data on rocks G-1 and W-1, 1965-1967. *Geochim. Cosmochim. Acta,* 33, 65-79.

GULSON, B. L. and LOVERING, J. F. (1968) Rock analysis using the electron probe. *Geochim. Cosmochim. Acta,* 32, 119-122.

MEDARIS, L. G. Jr. and DOTT, R. H. Jr. (1970) Mantle-derived peridotites in southwestern Oregon : relation to plate tectonics. *Science,* 169, 971-974.

NORRISH, K. N. and CHAPPELL, B. W. (1967) X-ray fluorescence spectrography in J. Zussman editor *"Physical methods in determinative mineralogy"* Academic Press 161-214.

NORRISH, K. and HUTTON, J. T. (1969) An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta,* 33, 431-453.

TIBA, T. (1970) JB-1 and JG-1···Geological Survey of Japan silicate rock standards···. *Jour. Geol. Soc. Japan.* 76,441-447.

POSTSCRIPT

We have determined SiO_2 of a few standards using KAP diffraction crystal instead of ADP and have obtained better results as follows :

JB-1	AGV-1	G-1	PCC-1	G-2	JG-1
52.48	59.09	72.30	41.57	67.80	72.40
(0.47)	(0.09)	(−0.22)	(−0.30)	(−1.39)	(0.30)