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Title	XRF analysis of major and trace elements for silicate rocks using low dilution ratio fused glass
Author(s)	Tanaka, Ryoji; Orihashi, Yuji
Citation	HUEPS Technical Report, 2, 1-20
Issue Date	1997-12
Doc URL	http://hdl.handle.net/2115/62041
Type	report
File Information	HUEPS_TR_2.pdf

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December, 1997

XRF Analysis of Major and Trace Elements for Silicate Rocks Using Low Dilution Ratio Fused Glass

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An X-ray fluorescence spectrometry (XRF) method to determine 10 major and 18 trace elements in silicate rocks has been investigated . The analysis is carried out on fused glass beads, containing one part rock powder, two parts of lithium metaborate/tetraborate flux and 0.3 parts of lithium nitrate by weight. Calibration lines were established using international silicate rock reference materials. The low dilution fused glass technique effectively eliminates particle size effect, and allows accurate determination of both major and trace elements from single glass beads. Analyses of standard rocks agree well with the recommended values of Imai et al.(1995) for GSJ reference materials, and with those of Potts et al.(1992) for USGS standards.

1. INTRODUCTION

In resent years, X-ray fluorescence (XRF) techniques for analysis of silicate rock materials have been developed to eliminate matrix effects and sample heterogeneity, while retaining low detection limits. Although the fusion technique has established for major element analysis (Claisse, 1956; Norrish and Hutton, 1969; Norrish and Chappell, 1977), there are several sample preparation procedures for trace element analysis, including between powder pellets and fused glass beads. Both the pressed powder and fused glass methods have their own advantages and disadvantages when factors such as peak sensitivity, sample homogeneity, potential for contamination of samples and/or spectrometers, and sample preparation times and costs are considered   (e. g. Norrish and Chappell, 1977; Hutton and Elliot, 1980; Bower and Valentine, 1986; Chappell, 1991;

Enzweiler and Webb, 1996). Particle size effects include grain size, inter-mineral, and mineralogical effects. These effects increase when samples contains abundant sheet silicate minerals, quartz, and accessory minerals, and so can be a problem in some rock types when powder pellets are used. In techniques which utilize samples in solution, such as ICP-MS, sample preparation requires acid digestion. Fusion of samples with alkali flux is necessary to achieve complete decomposition (Jarvis, 1990 ; Hall and Pelchat, 1990; Itoh et al., 1992; Ujiie and Imai, 1996), especially in coarser grained samples such as granite. Sample heterogeneity and sampling errors also increase with the small quantities of sample aliquot utilized by such methods (Terashima et al., 1995). Low-dilution fused glass XRF methods have thus been developed to eliminate particle size effects, sample heterogeneity, and sampling errors for the analysis of silicate rock materials (Thomas and Haukka, 1978; Hutton and Elliot, 1980; Lee and McConchie, 1982; Eastell and Wills, 1990, 1993; Murata et al., 1994; Kimura and Yamada, 1996).

Since XRF analysis is a comparative method, the accuracy of calibration lines rely on homogeneity of the standards and reliability of their certified values. Compilations of data such as those of Gladney and Roelandts (1988a, b) and Imai et al. (1995) eliminate unacceptable data and are calculated statistically by each compiler considering analytical bias. The GSJ 'igneous rock series' of reference samples are widely used in Japan as calibration standards in XRF analysis of silicate rocks because (1) there are a large number of reference samples, which cover a wide range of compositions (e.g. from 42 to 77 wt.% SiO_2), (2) the standards are readily available, (3) data sets of recommended values have been compiled and proposed considering interanalytical bias (Itoh et al., 1992; Imai et al., 1995), and (4) bottle to bottle heterogeneity has been shown to be low, except for MgO in JA2 (Terashima et al., 1990). Recommended values proposed by the distributor (e.g. Ando et al., 1989, Imai et al., 1995) are used in many laboratories. However, it has been pointed out some uncertainty must exist in some compiled values for GSJ reference materials, caused by the particular application of individual methods (Goto et al., 1988; Hall and Pelchat, 1990; Goto and Tatsumi, 1991, 1992; Murata, 1993). Secondary reference compositions which previously determined by other analytical methods have used for calibration lines in XRF analysis in some laboratories. Consequently, systematic interlabolatory bias may have occurred by use of individual reference data for GSJ reference samples.

In this report, we describe the XRF analytical procedure in our laboratory using the 1:2 (sample to flux ratio) dilution fused glass method for 10 major and 18 trace elements in silicate rock samples, and evaluate the recommended values of Imai et al., (1995) by comparison with USGS reference samples. We also report analytical results of some international reference samples including the GSJ, the USGS, the South African

Bureau of Standards (SABS), the Institute of Geophysical and Geochemical Exploration China (IGGE) reference samples.

2. SAMPLE PREPARATION

Sample preparation procedure is essentially the same that as described by Murata et al. (1994); mixing 1.8g of rock powder with 3.6g of lithium metaborate/tetraborate flux (Johnson Matthey Materials Technology, Spectroflux 100B) and 0.54g of lithium nitrate (Wako Chemicals Co.). After samples and flux are dried at 110°C for more than two hours, these are weighted in a 95%Pt-5%Au crucible (inside diameter is 30mm and 1.5mm thick) to minimize contamination and scattering during weighing. Then weighted powder is mixed on the touch-mixer. Fusing and agitation is carried out automatically using a high frequency bead sampler (Tokyo Kagaku Co. Ltd. NT-2100), with 240 seconds fusion time and 400 seconds agitation, both at 1200°C. About 50mg of lithium iodide (solid form, Aldrich Chemical Company, Inc.) is added just after agitation to ease to removal after glass bead from the crucible. The fused glass beads produced are about 2.5mm thick, with a flat surface and slightly convex reverse side. When the inside diameter of crucibles is larger than 30mm, the fused glass beads are more prone to breakage easier to break especially for alkaline-earth metal-rich samples.

To examine fusion efficiency and homogeneity on the basis of JIS R2216 method, six fused glasses of the same sample (JB2) were weighted and the intensities of the major element $K\alpha$ lines are measured. The coefficient of variation of bead weight was 0.049 and the standard deviations (s) for intensities were less than 0.05. These results indicate the instrumental conditions for fusion were adequate (see JIS R2216).

3. ANALYTICAL METHOD

3.1 Analytical conditions and standard materials

XRF analysis was carried out using a Philips PW1404 spectrometer at Hokkaido University. A Rh anode X-ray tube was used for both major and trace element analysis. Other reports of analysis using this equipment include analysis of 10 major element in silicate rocks using 1:5 fused glass and a Sc anode tube (Tsuchiya et al., 1989); 15 trace elements in silicate rocks using powder pellets with Rh-anode tube (Nakagawa et al., 1994); and 10 major and 6 trace elements in manganese ore using powder pellets with a Rh anode tube (Miyajima and Miura, 1996).

Spectrometer conditions for 10 major elements and 18 trace elements (Nb, Zr, Y, Sr, Rb, U, Th, Pb, Ga, Zn, Ni, Co, Cr, Ce, V, La, Ba, Sc) are given in Table 1. International silicate rock and mineral reference materials provided by the GSJ (JA1, JA2, JA3, JB1a, JB2, JB3, JG1a, JG2, JG3, JGb1, JP1, JR1, JR2, JF1) and the USGS (BIR1, DNC1, DTS1, QLO1, RGM1, STM1, W2) were used to set up the calibration lines.   Recommended values were taken from Imai et al. (1995) for the GSJ samples and Potts et al. (1992) for the USGS samples.

Analytical spectral angles were determined using the silicate monitor glass produced by Dr. K. Norrish, which contains high concentrations of the analytical elements (about 2000ppm of each trace elements). Pulse-height selections were used to reduce interference from higher order spectral line and backgrounds. Line overlap corrections ($YK\beta$ on $NbK\alpha$, $SrK\beta$ on $ZrK\alpha$, $RbK\beta$ on $Yk\alpha$, $VK\beta$ on $CrK\alpha$, $TiK\beta$ on $Vk\alpha$, and $TiK\alpha$ on $BaL\alpha$) are applied using multiple regression analysis after measurement of reference materials. Drift correction was performed daily using the Norrish silicate monitor glass.

3.2 Matrix corrections and calibration

Major elements : Calibration lines for major elements from basaltic to rhyolitic compositions (SiO_2 = 43.9 ~ 76.8wt.%) were made using all the reference materials except peridotite (JP1 and DTS1). Multiple regression analysis for matrix correction was based on the de Jongh model of the on-line Philips X40 program. The correction factors are selected as to maximize the accuracy of the each calibration lines.   The analytical lines and background positions measured are listed in Table 1, and calibration standard compositional ranges, accuracy, correlation coefficients and line overlap corrections are given in Table 2.

Eastell and Willis (1993) emphasized the necessity of careful matrix corrections for major element analysis when using 1:2 dilution fused glass, by analysis of a wide variety of rock types in which SiO_2 contents ranged from 33 to 99 wt.%. Tsuchiya et al. (1989) successfully made matrix corrections for 1:5 dilution fused glass with standard samples ranging from 29 to 93wt., SiO_2 using the same equipment, program, and Sc-anode tube as in this study. In this present work, the result of accuracy of calibration lines suggests that the de Jongh model of the X40 program gives adequate matrix correction for 1:2 dilution fused glass within the compositional range of the calibration standards. The relationships between recommended and calculated values for major elements are shown in Figure 1.

Trace elements : Matrix effect for trace elements have been corrected using

Compton-scattered tube line intensities. This method is widely used in many laboratories, but care must be taken at wavelengths longer than the FeK absorption edge. Wills (1991) determined mass absorption coefficients using Compton scattered tube line intensities, and found that $MoK\alpha$ and $RhK\alpha$ Compton peaks ($MoK\alpha C$ and $RhK\alpha C$) gave the best results for common silicate rocks.

The relationship between $RhK\alpha C$ intensity (RRhC) and calculated mass absorption coefficients from the major element compositions and the flux components at the 1.0 ($\mu_{1.0}$) wavelength is:

(1) $\mu 1.0 = 23061 RRhC^{-1.02}$

the correlation coefficient (r^2) is 0.997. Thus the relation between concentration of a given element i (Ci) and net intensity of i (Ii) for wavelengths shorter than FeK absorption edge is expressed as:

(2) $Ci=Di+EiIi/R^{1.02}$

where Di and Ei are constant. This equation can be approximated to

(3) $Ci=Di'+EiIi'/R$

It is well known that mass absorption coefficients for wavelengths longer than the FeK absorption edge are correlated with concentration of Fe_2O_3 (Sugisaki et al., 1981). The relationship between the ratio of mass absorption coefficients on the short and long wavelength sides of the Fe K edge ($\mu_{1.0}/\mu_{1.8}$) and Fe_2O_3 concentration (C_{Fe2O3}) is expressed by

(4) $\mu_{1.0}/\mu_{1.8}=0.0068 (C_{Fe2O3})+0.1869$ $r^2=0.999$

Using equation (4), matrix correction for wavelengths longer than the FeK absorption edge are corrected from RRhC and the concentration of Fe_2O_3 using the de Jongh model. For wavelengths longer than TiK absorption edge, concentration of TiO_2 is also used for correction. These can be represented as below.

(5) $Ci=Di+(1+ \Sigma j\alpha i,jCj/100)EiIiR^{-1}$

where ai,j is constant representing the matrix correction for element j on element i. Using this method, de Jongh model matrix correction incorporating both $FeK\alpha$ and Compton scattered $RhK\alpha$ tube line intensities were used for $CoK\alpha$, $CrK\alpha$, and $CeL\alpha$. In addition, matrix correction using TiKa is also carried out for $VL\alpha$, $BaL\alpha$, $LaL\alpha$, and $ScL\alpha$.

Accuracy and correlation coefficients for calibration lines corrected by these methods are mostly better, or in a few cases, of equal accuracy to these corrected by background intensities. Concentrations of Nb and Zr in STM1, and Cr and Ni in both JP1 and DTS1 are significantly higher than in the other calibration standards. Since the slope of calibration lines strongly depends on the higher concentrations, we have examined the effect of the higher concentration reference materials. Analytical results for the extreme elements in the above standards were derived from extrapolated calibration curves which

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included only standards with more normal compositions. Relative errors compared to published recommended values are then calculated by:

(6)   error(%)=100 (Xr-Xc)/Xr

where Xr is the recommended value and Xc is the calculated value from the extrapolated calibration line. The calculated errors are 0.9% (Nb, STM1), 2.0% (Zr, STM1), 4.5% (Cr, JP1), 4.4% (Cr, DTS1), 5.2% (Ni, JP1), and 5.1% (Ni, DTS1). As a result of this, JP1 and DTS1 were excluded from the Cr and Ni calibration lines, as their inclusion would cause relatively large errors at lower concentrations. The relationships between recommended and calculated values for the trace elements are shown in Figure 2.

3.3 Detection limits

The lower limit of detection (LLD) is given by :

(7) $LLD(3\%) = 6\sqrt{(Cb/T)}/mi$

where Cb is background in net counts per second (cps), T is the total counting time for peak plus background, and mi is cps/ppm (Chappell, 1991). A given LLD is calculated by measurement of peak and background intensities with counting time T for all the reference materials included in the calibration lines. Averages of the LLDs so derived are given in Table 2. Most of the counting times were set at levels designed to produce LLDs of about 1 ppm for the $K\alpha$ and $L\alpha$ spectra. Relatively higher LLDs for $VK\alpha$, $LaL\alpha$, $BaL\alpha$, and $ScK\alpha$ are caused by lower excitation of the Rh tube at longer wavelengths.

X-ray tube impurities are checked using a teflon sample in an aluminum holder. This shows that the tube is contaminated with Fe, Cu, Cr, and W. From the relationship between ranges of concentration and intensity, the impurities of Cu and Cr are significant. For Cr, the intensity of impurity is constant for samples, and this does not affect the accuracy of calibration lines. It could be contamination originates from the instrument itself. The Cr LLD in Table 3 is thus corrected for this impurity by subtraction. However, the impurities of Cu are not constant, and are affected by sample mass absorption.

3.4 Precision

Several reference materials were analyzed 10 times each to estimate analytical precision (Table 3). Coefficients of variation (C.V.) for the major elements are mostly below ±1%, except for 5.9% of P_2O_5 for JG1a. The C.Vs. of the trace elements analysis is higher for lower concentrations. Consequently, when determining trace elements in unknown samples, we use the average of three repeat analyze with 1/3 counting times, and check the C.V. for each element.

4. CONFORMITY BETWEEN USGS AND GSJ REFERENCE MATERIALS

Systematic heterogeneity between bottles has been reported for some GSJ reference materials by some authors (Goto et al., 1988; Goto and Tatsumi, 1991, 1992; Kimura et al., 1996). In contrast Orihashi et al. (1993a, b) found that no systematic heterogeneity can be seen in the recommended values of Ando et al. (1989) compared with USGS reference materials. Murata (1993) adopted secondary reference compositions for Ba, Nb, Pb, Rb, Sr, Th, Y, and Zr in GSJ reference materials analyzed by XRF. For this reference compositions of Ba and Y had been determined previously by ICP-AES (Goto et al., 1988). Compared with the recommended values of Imai et al.(1995), the reference compositions of Y, Zr, Nb, and Ba (>200ppm) of Murata (1993) and Goto et al., (1988) are systematically low. Therefore, since we use only international reference materials to set up the calibration lines, we have examined conformity between GSJ and USGS reference materials. Calibration lines were set up using seven USGS reference materials (Fig. 3). We also plot data determined for GSJ reference materials in relation to the recommended values of Imai et al. (1995). The average differences of the above elements between the recommended values of Imai et al. (1995) and the results in fourteen GSJ reference materials determined using calibration lines from eight USGS reference materials are 102% for Y, 104% for Zr, 99% for Nb, and 100% for Ba (Fig. 3). These data suggest that there is no major systematic heterogeneity between the two sets of reference materials, except perhaps for the relatively large difference in Zr, which is strongly affected by G2. Since both sets of recommended values are summarized by the same procedure; i.e. calculating mean values as a function of analytical procedure, after eliminating aberrant data (e.g. Gladney and Roelandts, 1988a) and the recommended values thus do not necessarily represent the true value of each reference material, we cannot evaluate systematic heterogeneity in the GSJ reference materials.

5. ANALYSIS OF REFERENCE MATERIALS

Results of routine analysis of 10 additional international silicate rock and mineral reference materials available from the USGS, the SABS, the IGGE, and the GSJ are listed in Table 4. Most of the data conform well with the published values, even in the extrapolated ranges, except for Ni content in JH1. This could be caused heterogeneity between bottles, or by an incorrect preferable value.

6. CONCLUSION

Ten major and 18 trace elements in silicate rock materials have been determined by XRF using a Philips PW1404 spectrometer equipped with an Rh-anode tube. Both major and trace elements are determined in a single low-dilution fused glass bead to eliminate particle size effects. Matrix corrections for major elements are carried out by multiple regression analysis, and for trace elements by utilization of Compton scattered Rh-tube line intensities. International reference materials were used to set up the calibration lines. No systematic heterogeneity is evident between the GSJ and USGS standards.

Acknowledgments

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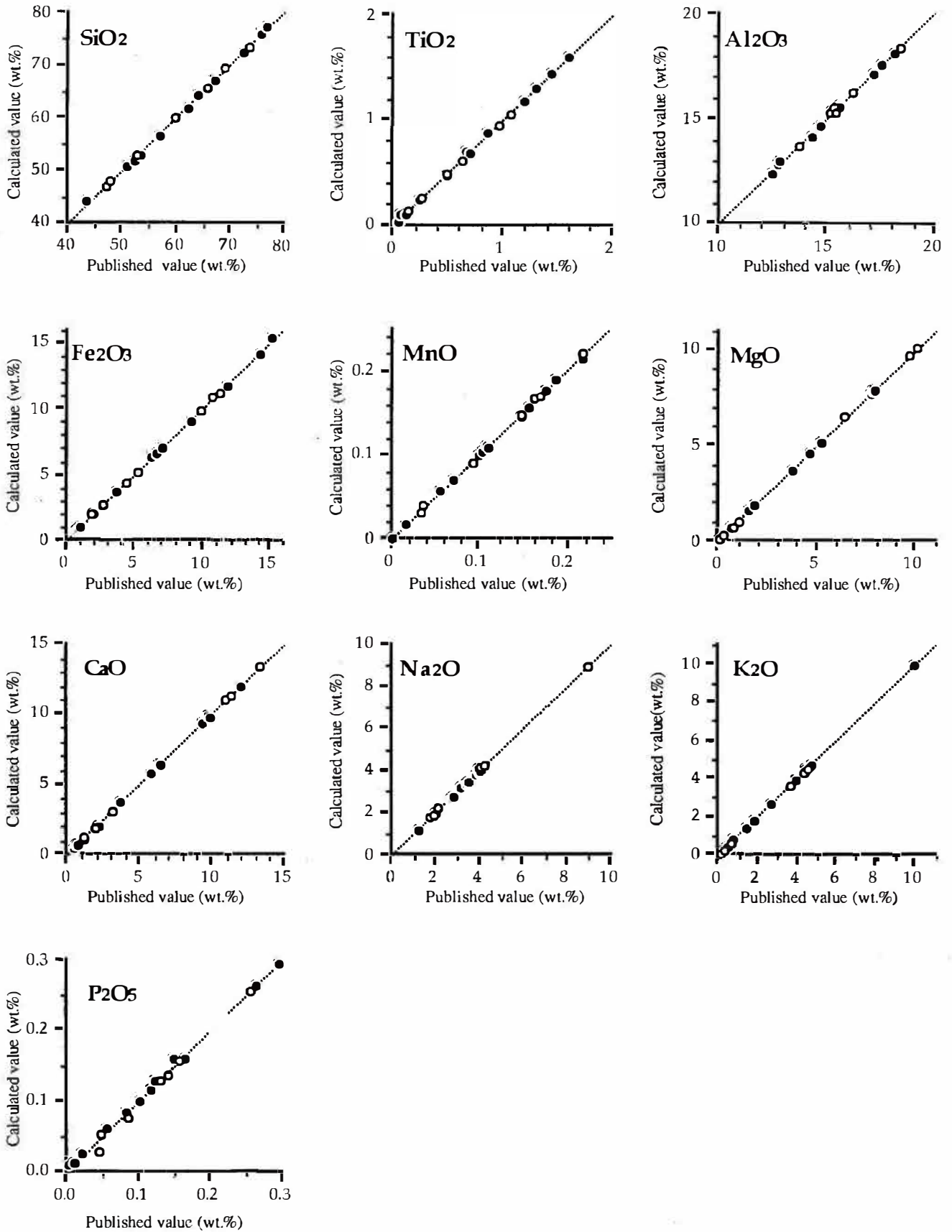
Figure 1 Results of analyzed versus expected recommended values for calibration reference samples for major elements. Black circle = GSJ; open circle=USGS; cross = USGS, SABS, IGGE, and GSJ which do not used to set up the calibration lines (data are shown in Table 4).
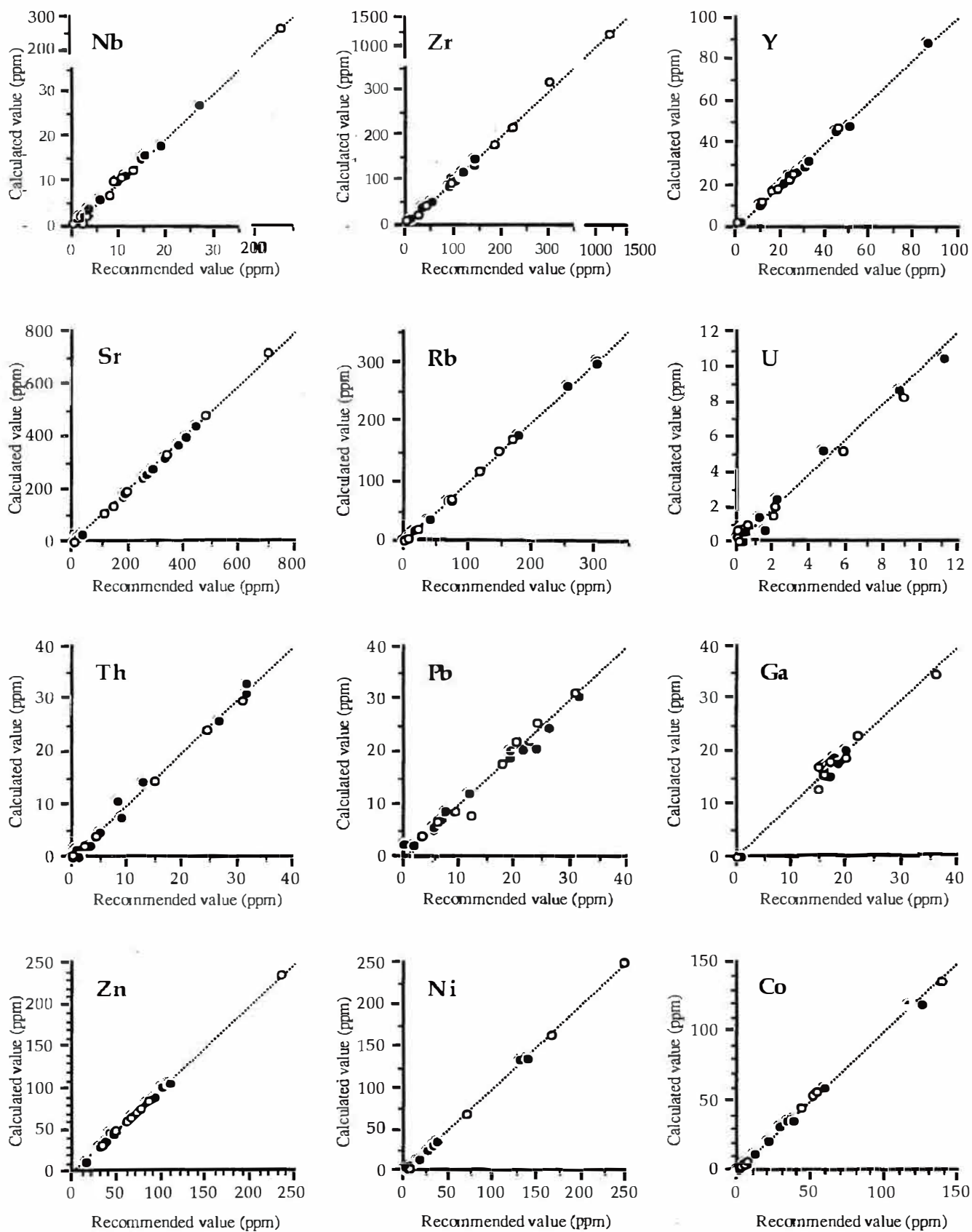
Figure 2 Results of analyzed versus expected recommended values for calibration reference samples for trace elements. Symbols as in Figure 1.

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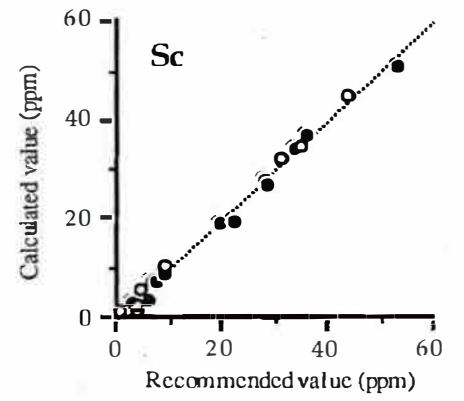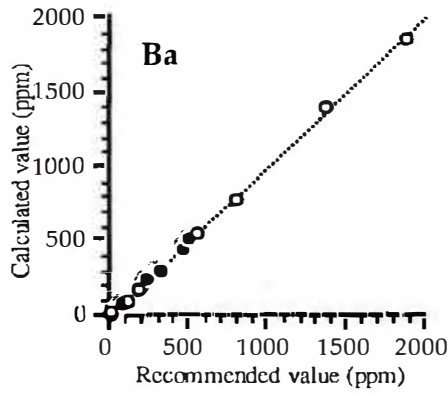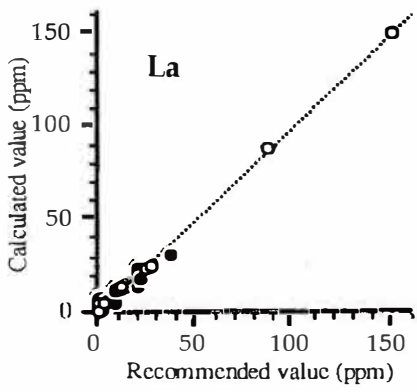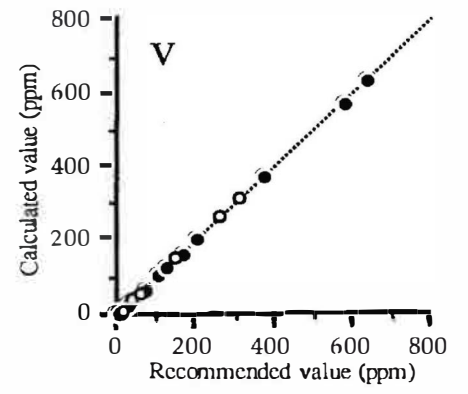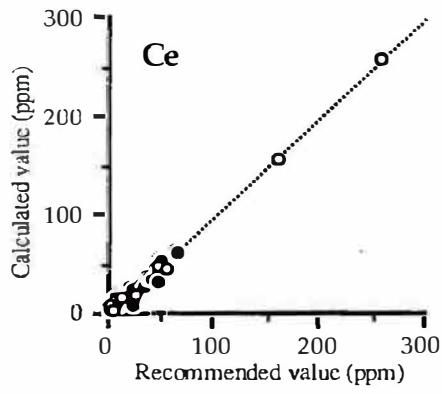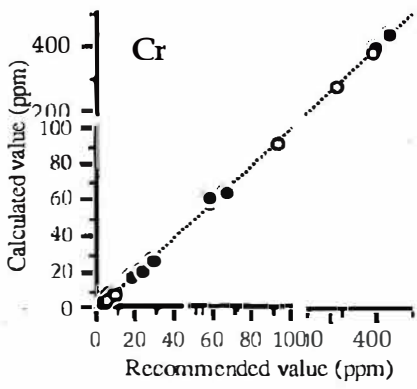
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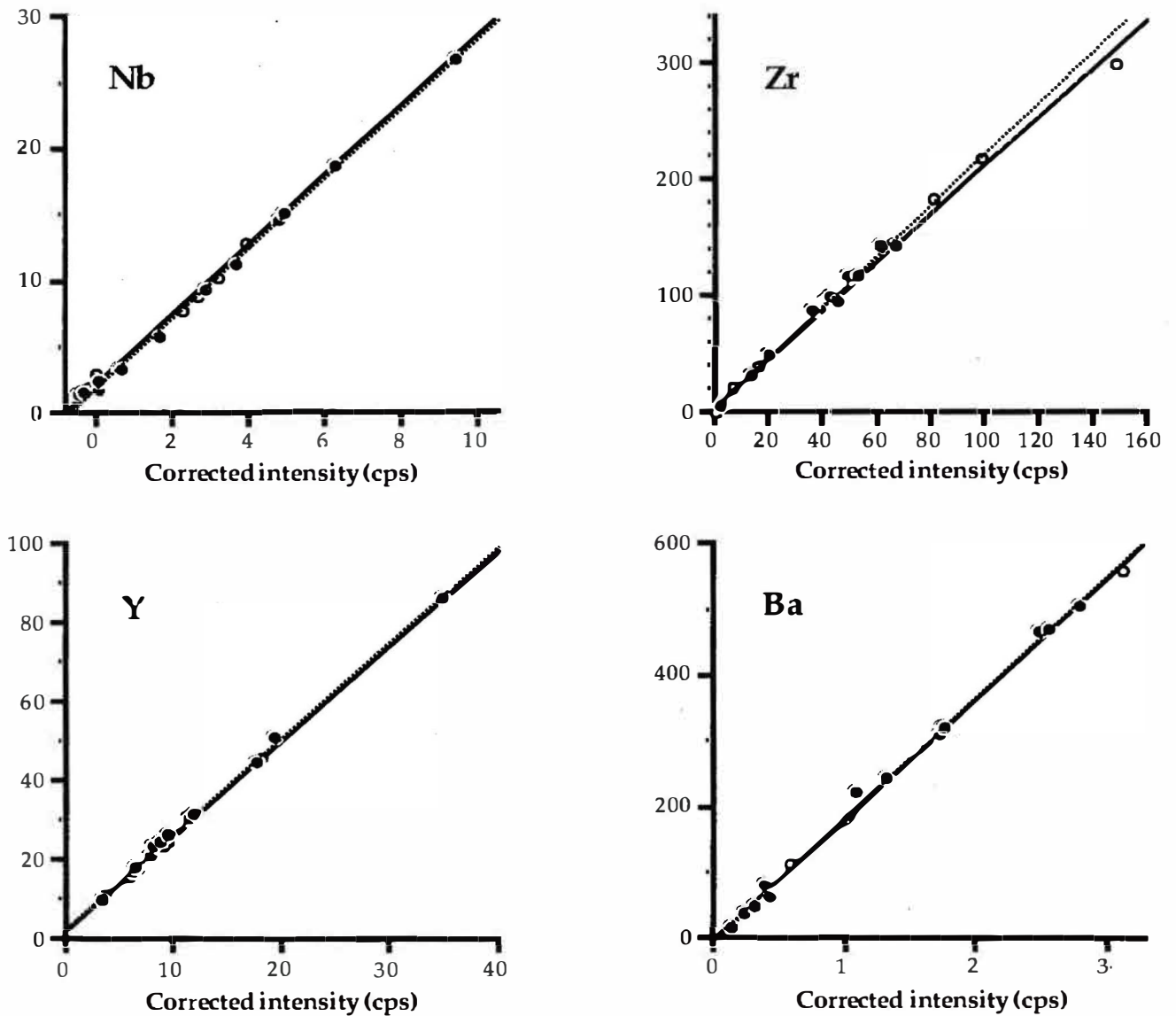
Figure 3 Comparison of separate Nb, Zr, Y and Ba calibrations for GSJ (solid circles) and USGS standards (open circles). The solid lines represent the calibrations made with the USGS reference samples, and the broken lines are the GSJ calibrations. Recommended values used are those of Imai et al. (1995) for the GSJ standards, and Potts et al. (1992) for the USGS suite.

Table 1 Spectrometer conditions used in XRF analysis.

| Element	Line	kV	mA	Counting time(s)	Detector	Collimator	Crystal	Angle(2θ)			Discriminator level(%)	
								Peak	+Back	-Back	Lower	Upper
Si	Kα	40	75	30	FL	coarse	PE	109.16	4.00	-	22	82
Ti	Kα	40	75	50	FL	fine	LiF200	86.21	-	1.32	30	70
Al	Kα	40	75	30	FL	coarse	PE	144.90	-	5.10	25	80
Fe	Kα	40	75	30	FL	fine	LiF200	57.56	-	0.88	37	68
Mn	Kα	40	75	60	SC	coarse	LiF200	63.07	2.00	-	20	75
Mg	Kα	40	75	50	FL	coarse	TlAP	45.29	3.00	-	20	85
Ca	Kα	40	75	30	FL	coarse	LiF200	113.26	-	4.00	30	74
Na	Kα	40	75	50	FL	coarse	TlAP	55.21	-	2.62	20	80
K	Kα	40	75	40	FL	coarse	LiF200	136.82	4.00	-	28	72
P	Kα	40	75	60	FL	coarse	GE	141.16	3.00	-	20	80
Rh	Kα-compton	80	30	60	SC	fine	LiF200	18.34	-	-	30	70
Nb	Kα	80	30	200	SC	fine	LiF200	21.39	0.30	0.36	20	76
Zr	Kα	80	30	120	FS	fine	LiF200	22.55	0.46	0.32	18	75
Y	Kα	80	30	160	FS	fine	LiF200	23.80	0.42	0.56	16	78
Sr	Kα	80	30	120	SC	coarse	LiF200	25.14	0.86	0.64	20	70
Rb	Kα	80	30	100	FS	fine	LiF200	26.63	0.50	0.70	20	70
U	Lα	75	40	500	SC	fine	LiF200	26.13	0.20	0.32	20	68
Th	Lα	80	30	300	FS	fine	LiF200	27.45	0.28	0.28	18	69
Pb	Lβ	80	30	300	FS	fine	LiF200	28.27	0.22	0.28	20	70
Ga	Kα	80	30	180	FS	fine	LiF200	38.93	0.38	0.32	18	74
Zn	Kα	80	30	120	FS	coarse	LiF200	41.84	0.78	0.64	20	72
Ni	Kα	50	60	120	FS	coarse	LiF200	48.75	0.88	0.88	20	72
Co	Kα	50	60	300	FS	fine	LiF200	52.83	0.60	-	20	76
Cr	Kα	40	75	150	FL	coarse	LiF200	69.47	1.16	1.04	12	80
Ce	Lα	40	75	600	FL	fine	LiF200	71.70	0.24	-	33	66
V	Lα	40	75	180	FL	fine	LiF200	77.01	-	0.82	34	80
La	Lα	40	75	600	FL	fine	LiF200	92.97	0.50	-	25	68
Ba	Lα	40	75	300	FL	fine	LiF200	87.18	1.20	-	30	73
Sc	Lα	40	75	300	FL	fine	LiF200	97.77	-	0.6	35	74

An Rh-anode tube was used for an analysis. FL = flow counter; SC = scintillation counter; FS = flow and scintillation counters used in tandem. Flow counter gas used is ArCH4. Collimator spacing: fine, 0.15mm, coarse 0.55mm.
A small diameter (24mm) collimator mask was used for all elements. Sample spinning was used for all samples.

Table 2 Data for the range of calibration, accuracy, lower limits of detection, elements used for matrix corrections, and lineoverlaps.

Element	Range for calibration line (wt.%)		Accuracy (wt.%)	LLD (ppm)	Correlation coefficient (r^2)	Matrix correction	Line overlap Correction
SiO_2	43.93 ~	76.79	0.30	-	1.000	Al,Fe,Ca	-
TiO_2	0.044 ~	1.61	0.02	-	1.000	Mg	-
Al_2O_3	12.90 ~	18.70	0.08	-	0.999	Si,Fe,Mn,Mg,K	-
Fe_2O_3	0.78 ~	15.15	0.12	-	1.000	Si,Mg,Ca	-
MnO	0.016 ~	0.224	0.002	-	0.999	Si,Ti,Al,Fe,Mg,Na	-
MgO	0.04 ~	10.08	0.04	-	1.000	Si,Ti,Al,Fe,Mn,Ca	-
CaO	0.51 ~	13.20	0.03	-	1.000	Si,Ti,Fe,Mn	-
Na_2O	1.21 ~	9.08	0.04	-	1.000	Si,Ti	-
K_2O	0.03 ~	10.06	0.02	-	1.000	Ti,Fe	-
P_2O_5	0.002 ~	0.294	0.007	-	0.997	-	-
	(ppm)		(ppm)	(ppm)			
Nb	1.48 ~	268	0.5	1.1	1.000	-	$YK\beta$
Zr	5.92 ~	300	6.3	1.0	1.000	-	$SrK\beta$
Y	1.54 ~	86.5	0.9	0.9	0.999	-	$RbK\beta$
Sr	8.11 ~	478	5.8	1.3	0.999	-	-
Rb	0.27 ~	303	1.1	1.3	1.000	-	-
U	0.13 ~	11.3	0.6	1.9	0.980	-	$RbK\alpha$
Th	0.03 ~	31.6	1.6	0.9	0.996	-	-
Pb	1.92 ~	31.5	1.4	3.0	0.991	-	-
Ga	0.15 ~	36	1.1	1.4	0.988	-	-
Zn	13.6 ~	109	1.6	1.4	0.999	-	-
Ni	1.67 ~	247	2.2	1.1	1.000	-	-
Co	0.46 ~	139	1.1	2.4	1.000	Fe	$FeK\beta$
Cr	2.83 ~	436	3.4	2.2	1.000	Fe	$VK\beta$
Ce	6.76 ~	259	3.9	8.7	0.998	Fe	-
V	3.00 ~	635	3.4	2.6	1.000	Fe,Ti	$TiK\beta$
La	2.35 ~	150	1.9	5.6	0.998	Fe,Ti	-
Ba	19.5 ~	1880	9.8	7.5	1.000	Fe,Ti	$TiK\alpha$
Sc	0.61 ~	53.5	1.2	3.8	0.997	Fe,Ti	-

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Table 3 Precision (N=10) of major and trace elements in selected reference materials.

JB1a	Recommended value (wt.%)	Average (N=10) mean σ	C.V. (%)	JG1a Recommended value (wt.%)	Average (N=10) mean σ	C.V. (%)
SiO2	52.90	52.62 ± 0.04	0.07	72.39	72.36 ± 0.04	0.06
TiO2	1.29	1.29 ± 0.00	0.35	0.25	0.25 ± 0.00	0.00
Al2O3	14.58	14.55 ± 0.01	0.05	14.32	14.14 ± 0.01	0.07
Fe2O3	9.13	8.90 ± 0.00	0.05	2.00	1.97 ± 0.00	0.00
MnO	0.149	0.150 ± 0.002	1.011	0.057	0.060 ± 0.001	0.993
MgO	7.90	7.82 ± 0.01	0.16	0.69	0.69 ± 0.00	0.58
CaO	9.40	9.35 ± 0.00	0.03	2.13	2.12 ± 0.01	0.24
Na2O	2.76	2.73 ± 0.02	0.62	3.39	3.37 ± 0.02	0.68
K2O	1.41	1.43 ± 0.00	0.32	3.96	3.97 ± 0.00	0.12
P2O5	0.262	0.263 ± 0.000	0.000	0.083	0.085 ± 0.005	5.891
Total	99.79	99.10 ± 0.03	0.03	99.28	99.00 ± 0.06	0.06

JR1	Recommended value (ppm)	Average (N=10) mean σ	C.V. (%)	W2 Recommended value (ppm)	Average (N=10) mean σ	C.V. (%)
Nb	15.2	15.6 ± 0.49	3.1	7.9	7.6 ± 0.74	9.7
Zr	99.9	97.3 ± 0.88	0.9	94	92.1 ± 1.02	1.1
Y	45.1	43.8 ± 0.58	1.3	24	22.0 ± 0.67	3.0
Sr	29.1	29.1 ± 0.67	2.3	194	192.1 ± 1.33	0.7
Rb	257	258 ± 1.60	0.6	20	21.5 ± 0.72	3.3
U	8.88	8.75 ± 0.68	7.8	0.53	n.d.	-
Th	26.7	24.8 ± 0.86	3.5	2.2	1.87 ± 0.88	46.9
Pb	19.3	18.8 ± 1.15	6.1	9.3	8.5 ± 1.15	13.5
Ga	16.1	17.4 ± 0.68	3.9	20	17.8 ± 0.75	4.2
Zn	30.6	29.7 ± 0.60	2.0	77	76.8 ± 1.07	1.4
Ni	1.67	5.58 ± 1.01	18.1	70	68.7 ± 1.32	1.9
Co	0.83	0.74 ± 0.67	90.5	44	43.6 ± 1.32	3.0
Cr	2.83	1.88 ± 0.97	51.4	93	89.1 ± 1.45	1.6
Ce	47.2	51.7 ± 4.64	9.0	24	21.3 ± 3.51	16.5
V	7.0	11.0 ± 1.71	15.6	262	261.4 ± 2.97	1.1
La	19.7	21.9 ± 2.56	11.7	11.4	11.3 ± 2.61	23.1
Ba	50.3	59.6 ± 5.97	10.0	182	177.1 ± 6.78	3.8
Sc	5.07	5.12 ± 0.97	18.9	35	35.1 ± 1.86	5.3

σ : standard deviation, C.V. : coefficient of variation, n.d. : no detection

Table 4 Major and trace elements data obtained by XRF analysis compared with recommended and preferred values (in parentheses) in additional SABS, USGS, IGGE, and GSJ silicate rock reference samples.

wt.%	GSR1	GSR2	GSR3	SDC1	SARM1	SARM48	JR3	JGb2	JH1	JSy1
SiO_2	73.21 (72.83)	61.97 (60.62)	45.25 (44.64)	65.76 (65.85)	76.24 (75.50)	68.08 (67.11)	72.95 (72.48)	46.56 (46.68)	49.44 (48.48)	59.56 (60.14)
TiO_2	0.29 (0.29)	0.53 (0.52)	2.42 (2.36)	1.06 (1.01)	0.083 (-)	0.086 (0.10)	0.22 (0.21)	0.53 (0.58)	0.64 (0.67)	n.d. (<0.005)
Al_2O_3	13.59 (13.40)	16.66 (16.17)	13.95 (13.83)	15.95 (15.75)	12.19 (12.08)	11.61 (11.24)	11.93 (12.10)	*24.07 (23.32)	6.13 (5.56)	*22.88 (23.45)
Fe_2O_3	2.15 (2.14)	5.09 (4.90)	13.90 (13.40)	7.27 (6.90)	1.95 (2.00)	0.60 (0.58)	4.78 (4.75)	6.51 (6.85)	10.15 (10.33)	0.10 (0.09)
MnO	0.060 (0.06)	0.080 (0.08)	0.18 (0.17)	0.12 (0.11)	0.015 (0.02)	0.008 (0.02)	0.083 (0.085)	0.120 (0.127)	0.189 (0.186)	0.001 (0.002)
MgO	0.41 (0.42)	1.69 (1.72)	7.79 (7.77)	1.72 (1.69)	0.022 (0.06)	0.09 (0.18)	0.053 (0.05)	6.42 (6.24)	17.18 (17.12)	0.012 (0.02)
CaO	1.52 (1.55)	5.39 (5.20)	9.12 (8.81)	1.44 (1.40)	0.78 (0.78)	8.78 (8.90)	0.120 (0.09)	14.07 (14.20)	14.82 (15.02)	0.28 (0.24)
Na_2O	3.18 (3.13)	4.04 (3.86)	3.43 (3.38)	2.09 (2.05)	3.39 (3.36)	3.27 (3.22)	4.68 (4.68)	0.97 (0.92)	0.72 (0.72)	11.16 (10.74)
K_2O	5.02 (5.01)	1.93 (1.89)	2.34 (2.32)	3.27 (3.28)	4.98 (4.99)	4.42 (4.26)	4.29 (4.33)	0.061 (0.06)	0.56 (0.52)	4.84 (4.83)
P_2O_5	0.093 (0.093)	0.24 (0.24)	1.00 (0.95)	0.15 (0.16)	0.010 (0.01)	0.075 (0.09)	0.018 (0.01)	0.018 (0.007)	0.105 (0.11)	0.013 (<0.01)
Total	99.52 (98.92)	97.62 (95.20)	99.37 (97.63)	98.82 (98.20)	99.66 (98.80)	97.01 (95.70)	99.12 (98.78)	99.32 (98.98)	99.93 (98.72)	98.85 (99.51)
ppm										
Nb	42 (40)	6.7 (6.8)	74 (68)	19 (18)	55 (53)	209 (202)	*557 ( )	1.6 ( )	4.6 ( )	1.3 (0.03)
Zr	166 (167)	108 (99)	273 (277)	300 (290)	271 (300)	297 (300)	*1468 ( )	21 ( )	51 ( )	71 (71.08)
Y	68 (62)	10 (9.3)	24 (22)	39 (40)	*135 (143)	*447 (436)	*170 ( )	5.2 ( )	15 ( )	4.7 (2.43)
Sr	112 (106)	*851 (790)	*1170 (1100)	182 (183)	11 (10)	30 (29)	11 (9)	435 (435)	153 (155)	25 (16.14)
Rb	*477 (466)	43 (37.6)	44 (37)	128 (127)	*324 (325)	286 (291)	*462 (458)	2.7 (<3)	15 (12)	67 (67.18)
U	*19 (18.8)	n.d. (0.9)	2.9 (1.4)	3.7 (3.1)	*17 (15)	*24 (-)	*22 ( )	n.d. ( )	n.d. ( )	n.d. (0.4)
Th	*52 (54)	2.4 (2.6)	6.3 (6.0)	11 (12.1)	*48 (51)	*105 (113)	*112 (116)	n.d. ( )	1.6 ( )	1.1 (0.36)
Pb	32 (31)	11 (11.3)	6.4 (7.2)	22 (25)	*38 (40)	*166 (135)	*39 (34.5)	1.9 (<3)	3.9 (<3)	5.2 (5.34)
Ga	20 (19)	19 (18.1)	25 (24.8)	22 (21.2)	30 (27)	29 (27.8)	35 ( )	17 ( )	7.2 ( )	23 (24.24)
Zn	27 (28)	70 (71)	153 (150)	101 (103)	51 (50)	55 (53)	201 (204)	48 (48)	62 (62)	3.8 (2.57)
Ni	2.0 (2.3)	18 (17)	148 (140)	36 (38)	3.7 (8)	1.8 (2.7)	6.4 ( )	14 (13.8)	160 (56)	2.4 (0.64)
Co	3.6 (3.4)	13 (13.2)	46 (46.5)	17 (17.9)	0.4 (0.36)	4.3 (0.51)	4.2 (1)	26 (28)	52 (53)	n.d. (0.04)
Cr	2.5 (5)	32 (32.4)	146 (134)	60 (64)	11 (12)	20 (23)	5.8 (2.5)	121 (130)	*794 (630)	2.2 (1.34)
Ce	108 (108)	39 (40)	72 (105)	85 (93)	208 (195)	*1127 (1115)	*329 (340)	11 ( )	22 (9)	9.0 (2.44)
V	27 (24)	96 (94.5)	206 (167)	109 (102)	8.8 (2?)	7.9 (8?)	6.5 (<10)	166 (175)	223 (231)	3.1 (0.4)
La	58 (54)	24 (21.8)	54 (56)	45 (42)	109 (109)	*635 (662)	*179 (177)	<1.7 ( )	10 ( )	2.8 (1.24)
Ba	330 (343)	1004 (1020)	566 (527)	664 (630)	123 (120)	328 (290)	74 ( )	49 ( )	125 ( )	23 (13.74)
Sc	5.4 (6.1)	8.8 (9.5)	17 (15.2)	15 (17)	1.7 (0.9)	4.2 (-)	n.d. ( )	26 ( )	77 ( )	3.0 ( )

Recommended and preferred values for GSR1, GSR2, GSR3, SDC1, SARM1, and SARM48 are from Potts et al. (1992); JR3, JGb2, and JH1 from Terashima et al. (1993); JSy1 from Terashima et al. (1995) for major elements and Govindaraju (1995) for trace elements. Extrapolated data are marked with asterisks. n.d. : no detection

Appendix   List of split and position of international reference samples used in this study.

Name	Rock type	Distributor	Split	Position
JB1a	alkali basalt	GSJ	1	44
JB2	tholeiitic basalt	GSJ	5	43
JB3	high-alumina basalt	GSJ	7	121
JA1	andesite	GSJ	5	43
JA2	andesite	GSJ	6	31
JA3	andesite	GSJ	1	68
JR1	rhyolite	GSJ	5	43
JR2	rhyolite	GSJ	5	101
JG1a	granodiorite	GSJ	7	106
JG2	granite	GSJ	2	48
JG3	granodiorite	GSJ	10	63
JGb1	gabbro	GSJ	1	64
JP1	dunite	GSJ	10	83
JF1	feldspar	GSJ	7	33
BIR1	basalt	USGS	No.1512	
DNC1	diabase	USGS	No.1131	
W2	diabase	USGS	No.192	
RGM1	rhyolite	USGS	35	31
QLO1	quartz latite	USGS	18	11
G2	granite	USGS	9	31
STM1	syenite	USGS	8	23
DTS1	dunite	USGS	46	28
GSR1	granite	IGGE	48	23
GSR2	andesite	IGGE	No.525110	
GSR3	basalt	IGGE	No.214103	
SDC1	mica schist	USGS	104	32
SARM1	granite	SABS	1	3
SARM48	fluorspar granite	SABS	47	24
JR3	peralkaline rhyolite	GSJ	4	84
JGb2	leucogabbro	GSJ	3	67
JH1	pyroxene hornblendite	GSJ	6	1
JSy1	syenite	GSJ	7	81

GSJ : Geological Survey of Japan; USGS : US Geological Survey ; IGGE : Institute of Geophysical and Geochemical Prospecting, People's Republic China; SABS : South African Breau of Standards