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X-RAY FLUORESCENCE ANALYSIS OF MAJOR ELEMENTS IN SILICATE ROCKS USING FUSED GLASS DISCS

Abstract - XRF analysis of major elements in silicate rocks (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) was carried out using fused glass discs prepared by mixing 0.875 g of powdered rock samples with 6,125 g of lithium tetraborate. The method was calibrated on twenty two international rock standards and twelve additional samples prepared by mixing available standards. The margin of error was calculated to be between 4-7%, 2-4% and about 1% respectively for abundances ranging from 0 to 1%, 1 to 10% and 10 to 65%. Overall, the analytical data obtained via the proposed method are superior to those acquired by processing briquetted rock samples and comparable to those obtained using powdered rock samples dissolved in a lithium borate glass. However, applying the technique calls for great care during sample preparation.

Key words - X-ray fluorescence, major element analysis, silicate rocks, fused glass discs, reliability.

Riassunto - *Determinazione degli elementi maggiori in rocce silicatiche mediante fluorescenza-X su "perle" di fusione.* In questa nota viene proposta una metodologia analitica in fluorescenza-X per la determinazione degli elementi maggiori (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) in campioni di rocce silicatiche preparati secondo la tecnica della fusione. Le perle di fusione sono state preparate fondendo una miscela contenente 0,875 g di polvere e 6,125 g di fondente (tetraborato di litio). Per la messa a punto di questa metodologia sono stati utilizzati 22 standards internazionali più dodici campioni preparati mescolando tra di loro alcuni di questi standards. Gli errori inerenti la procedura analitica sono mediamente compresi tra 4-7% per concentrazioni dell'elemento < 1%, tra 2-4% per concentrazioni comprese tra 1 e 10% e intorno all'1% per concentrazioni > 10%. I risultati ottenuti indicano che la riproducibilità e l'accuratezza dei dati analitici sono per la maggior parte degli elementi superiori a quelle ottenibili mediante l'uso di polveri pressate. L'aspetto più delicato della metodologia impiegata è rappresentato dalla preparazione del campione, che richiede molta cura, buona manualità ed esperienza.

Parole chiave - Fluorescenza a raggi-X, analisi dei componenti maggiori, rocce silicatiche, «perle» di fusione, affidabilità.

INTRODUCTION

X-ray fluorescence (XRF) is well recognized as an accurate, rapid technique for major element determinations on rocks samples. The main problems encountered in XRF rock analysis concern the correction of matrix effects (absorption and enhancements) and the effects due to sample heterogeneity (grain size, different particle-absorption of minerals etc.) when rock powders are employed. Matrix effects can be overcome by using appropriate experimental or calculated coefficients to account for the influence of the major components on the analytical lines of the element being analysed. Rock powder heterogeneity effects, on the other hand, are mathematically difficult to handle owing to the different grain size distributions and wide variability in mineralogical composition.

The fusion method, which consists of dissolving the sample in a lithium tetraborate (or metaborate) removes most of the effects of powder heterogeneity, and if high sample/borate dilutions are used (1: > 10, sample to lithium borate), such techniques considerably reduce matrix effects as well. Many procedures for fusing samples into a borate glass are furnished in the literature (e.g., see Lachance & Claisse, 1995 and references therein). At present, the most widely adopted fusion procedures utilize 1:5 to 1:10 sample/borate dilutions, which represent a reasonable compromise between sensitivity and reduction of matrix effects. At such dilution levels, however, interelement corrections must still be applied for high-accuracy analysis.

This paper describes a fusion method which utilizes a sample-lithium tetraborate fusion mixture (1:7, sample to borate) to determine the major elements in silicate rocks. An evaluation of the techniques' precision and accuracy is also provided.

THEORY

The basic relation between the intensity of a characteristic line and an element's concentration is:

$$I_i = \frac{C_i}{\sum\limits_{i,j=1}^{N} C_i \bullet K_{i,j}} \qquad (1)$$

where, for an element i, I_i represents the intensity of the characteristic line, C_i the concentration (expressed as wt.%), and $K_{i,j}$ coefficients that account for the matrix

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effects (absorption and enhancement) due to the abundance of the major chemical components (C_j), including component i. The values of the $K_{i,j}$ coefficients have the dimension of mass absorption coefficients, as in rock samples enhancement can be regarded as negative absorption (Franzini *et al.*, 1976).

The $K_{i,j}$ coefficients may be determined experimentally or calculated from a set of reference samples of known composition. A number of algorithms of varying sophistication are available in the literature for computing the $K_{i,j}$ values (Lachance & Claisse, 1995). Herein, the algorithm set forth by Lucas-Tooth & Price (1961) has been applied:

$$C_i = D_i + E_i + I_i \cdot \left\{ 1 + \sum_{i,j=1}^{N} K_{i,j} \cdot I_j \right\} \quad (2)$$

In equation (2), D_i and E_i represent the parameters of the linear regression line correlating the concentrations with the intensities of element i, and $K_{i,j}$ empirical coefficients which correct for matrix effects. The Lucas-Tooth and Price algorithm is particularly suitable for processing silicate rocks when samples are dissolved in moderately diluted lithium borate mixtures (sample/lithium borate dilutions from 1:5 to 1:10).

EXPERIMENTAL PROCEDURE

Calibration of the fusion method was carried out on twenty-two international reference standards of silicate rocks. In order to widen the range of major element concentrations, twelve additional standards were prepared by mixing some of the available standards in appropriate proportions. The list of the standards utilized for calibration is reported in Table 1.

The sample preparation technique and the fusion procedure followed are essentially the same as those described by Claisse (1957). The powder sample is ignited to about 1000°C for 1 hour to eliminate the volatile components. A mixture containing 0.875 g of rock powder and 6.125 g of lithium tetraborate (corresponding to a 1:7 sample/borate dilution) is carefully homogenized in a Pt (95%)-Au (3%)-Rh (2%) crucible. Of the many procedures available for fusing samples into borate glass, a 1:7 sample/borate dilution was chosen as a good compromise, providing relatively short fusion times (about 15 minutes) and good homogeneity and stability of the fused discs. Two drops of 4% aqueous Ammonium iodure solution are added to the fusion mixture as a non-wetting agent. Fusion of the well-mixed flux and sample is performed on a Pt-Au-Rh crucible using a CLAISSE FLUXER-BIS!® automatic apparatus. The mixture is fused at 1000°C for about 15 minutes while continuously stirring the melt. At the end of fusion, when the sample has completely dissolved and any reactions ceased, the melt is poured into a Pt-plate and slowly cooled. After cooling, the glass disc is used directly for analysis.

The intensities of the major elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) were measured utilizing an ARL 9400 XP+ sequential X-Ray spectrometer on line with a P.C. The selected instrument conditions are reported in Table 2. Intensities were corrected for background, and blank correction was also applied to account for flux impurities.

RESULTS

In order to evaluate the reproducibility of the adopted methodology, seven standard samples with different chemical and mineralogical composition were selected. For each sample, ten fused discs were prepared independently and measured in different runs. The results obtained are summarized in Table 3, where the reference concentrations of the analysed elements are also reported (Govindaraju, 1994), together with the relative statistical counting error (RSD_I) and total relative

Tab. 1 - List of rock standards.	
Name	**Description**
DNC-1	Dolerite
GSR-2	Andesite
JB-2	Basalt
JP-1	Peridotite
MO-12	Andesite-Basalt
MO-13	Olivine-Basalt
MO-2	Basalt
MO-3	Gabbro
MO-6	Anorthosite
MO-7	Orthoclase-gabbro
MRG-1	Gabbro
MW-1	Miaskite
MY-1	Peridotite
NIM-D	Dunite
NIM-G	Granite
NIM-P	Pyroxenite
NIM-S	Syenite
SDC-1	Mica Schist
SGD-1a	Gabbro
SGD-2	Gabbro
STM-1	Syenite
SY-3	Syenite
BT1	50% NIM-D + 50% NIM-S
BT2	40% NIM-D + 60% NIM-S
BT3	29% NIM-D + 71% NIM-S
BT14	50% DNC-1 + 50% NIM-D
BT15	50% GSR-2 + 50% SGD-1a
BT16	35% MO-7 + 65% MW-1
BT17	50% MO-7 + 50% MW-1
BT18	65% MO-7 + 35% MW-1
BT19	50% NIM-S + 50% SDC-1
BT20	50% NIM-S + 50% SY-3
BT21	25% SGD-1a + 75% SY-3
BT22	50% SGD-1a + 50% SY-3

For the identification of standards see Govindaraju (1994), App. 3.

Tab. 2 - Instrument conditions.

	Na	**Mg**	**Al**	**Si**	**P**	**K**	**Ca**	**Ti**	**Mn**	**Fe**
λE	Ka	Ka	Ka	Ka	Ka	Ka	Ka	Ka	Ka	Ka
Tube	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh	Rh
kV	40	40	40	40	40	40	40	40	40	40
mA	80	80	80	80	80	80	80	80	80	80
AC	AX06	AX06	PET	PET	PET	PET	LiF200	LiF200	LiF200	LiF200
DET	FPC	FPC	FPC	FPC	FPC	FPC	FPC	FPC	FPC	FPC
COL	0.60°	0.60°	0.60°	0.60°	0.60°	0.25°	0.25°	0.25°	0.25°	0.25°
CTP	5	5	5	5	5	5	5	5	5	5
CTB	5	5	5	5	5	5	5	5	5	5

λE: analytical line; kV: (voltage); mA: (current) of X-ray tube; CA: analysing crystal; DET: detector; FPC: flow proportional counter; COL: collimator (°); CTP: counting time of peak (s); CTB: counting time of background (s).

standard deviation (RSD_{P+I}) consequent to counting standard error (I) and sample preparation (P).

The data obtained indicate that the reproducibility of the analytical method is determined essentially by sample preparation (sample ignition, sample and flux weighing, sample-flux homogenisation, melting procedure). The relative statistical counting errors are generally negligible (less than 1%) if we exclude light elements such as Mg and Na when present at concentrations below 1%, as well as minor elements such as P, Mn and Ti. However, in general, these latter elements never yield RSD_I values greater than 1.7%, except for P which exhibits $RSD_I = 4.3\%$ at a concentration of 0.05% (Table 3). In the set of standards used, some elements exhibited high RSD_{P+I} compared to the RSD_I values. Higher RSD_{P+I} values were obtained sporadically for sodium, magnesium (samples SGD-1a, MW-1, and IC1, where, however, MgO is < 1%), aluminium (samples SGD-1a and MRG-1) and silicon (sample MRG-1). Such relatively low precision is probably related to imperfect homogeneity of the fused discs, which mainly reflects on the intensities of light elements such as Na and Si, for which the infinite thickness is very small (about 5 μm for Na and about 20 μm for Si). Nevertheless, the precision attained in preparation of the fused disks is quite good, greater than ± 3-4% for concentrations ranging from 1 to 10 wt% (except HE-1 for Na$_2$O), and greater than ± 1.5% for concentrations between 10 and 65 wt% (except SGD-1a for Al$_2$O$_3$).

Given the relatively high degree of dilution adopted, the first step in processing the experimental data collected on the standards was to obtain linear calibration curves for all the elements by correlating the intensities and concentrations reported in the literature. Table 4 lists the parameters of the regression line for each element measured and the relative standard deviation (RSD) calculated for the thirty-four standards according to the relation:

$$RSD = \pm\, 100 \cdot \sqrt{\frac{\Sigma\,(C_{OSS} - C_{REF})^2}{n-1}} \Bigg/ X_m \qquad (3)$$

where C_{OSS} and C_{REF} respectively represent the observed and reference concentrations of each element (wt%), and X_m the average concentration for the interval of interest.

Comparing the results reported in Tables 3 and 4, it can be seen that for Na and K, as well as P, no significant differences exist between the precision (sample preparation and instrumental measurement) and the RSD values calculated from the regression line. Thus, for these elements determinations was carried out directly, using the linear equation reported in Table 4. The linear equations in Table 4 were also used for the Ti and Mn analysis; for these elements an RSD of ± 5% can, in fact, be considered acceptable given their low concentrations.

By contrast, for Mg, Al, Si, Ca and Fe, the RSD values calculated from the calibration line are significantly greater than the precision of the fusion method adopted (see Table 4). This is probably a consequence of incomplete attenuation of matrix effects due to sample dilution. Therefore, for this subset of elements, the measured intensities were processed by application of the Lucas-Tooth and Price (1961) algorithm. Table 4 reports the resulting RSD values for Al, Si, Ca and Fe after matrix-effect corrections were applied.

Table 5 provides a comparison of the concentrations determined following the described procedure with the values recommended in the literature (Govindaraju, 1994). The observed experimental values refer to samples ignited at T~1000°C. The total concentration values (wt%) for the major elements analysed (Na$_2$O, MgO, Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, K$_2$O, CaO, TiO$_2$, MnO, Fe$_2$O$_3$) range between 99.12 (sample BT19) and 101.40 (sample NIM-D), if we exclude samples NIM-P and MO-2, which display relatively low oxide totals (96.28 and 97.77, respectively). As far as sample NIM-P is concerned, the low total is certainly due to the high Cr$_2$O$_3$ content (2.52 wt%), whereas for the MO-2 sample, the low-quality of the glass disc is thought to be the cause.

The good accuracy of the analytical data can be verified in Table 6, which reports the relative standard deviations (RSD) calculated via equation 3 for different concentrations. The table also provides a compar-

Tab. 3 - Reproducibility on ten replicate glass discs of seven selected rock standards.

SiO₂

	C_{REF}	RSD_I	RSD_{P+I}
MRG-1	39.63	0.1	1.5
SGD-1a	46.60	0.1	0.9
HE-1	47.47	0.1	0.6
MW-1	58.34	0.1	0.7
SY-3	60.76	0.1	0.6
IC-1	60.95	0.1	0.6
GSR-2	63.67	0.1	0.6

TiO₂

	C_{REF}	RSD_I	RSD_{P+I}
SY-3	0.15	1.3	7.7
MW-1	0.40	0.8	2.0
IC-1	0.43	0.7	3.1
GSR-2	0.55	0.6	1.9
HE-1	1.70	0.4	0.6
SGD-1a	1.72	0.4	2.2
MRG-1	3.82	0.2	0.9

Al₂O₃

	C_{REF}	RSD_I	RSD_{P+I}
MRG-1	8.58	0.2	0.7
SY-3	11.97	0.2	0.5
SGD-1a	14.94	0.2	3.7
HE-1	16.99	0.2	0.6
GSR-2	0.55	0.2	0.6
IC-1	18.71	0.2	0.6
MW-1	21.85	0.2	0.7

MnO

	C_{REF}	RSD_I	RSD_{P+I}
GSR-2	0.08	1.3	1.6
MW-1	0.13	0.8	0.9
MRG-1	0.17	0.7	0.8
SGD-1a	0.17	0.7	1.4
HE-1	0.19	0.8	1.4
IC-1	0.20	0.7	1.8
SY-3	0.33	0.6	1.0

MgO

	C_{REF}	RSD_I	RSD_{P+I}
MW-1	0.35	1.6	7.7
IC-1	0.56	1.3	6.7
GSR-2	1.81	0.7	2.0
SY-3	2.72	0.6	1.0
HE-1	5.59	0.4	1.0
SGD-1a	7.03	0.3	3.4
MRG-1	13.73	0.2	0.7

CaO

	C_{REF}	RSD_I	RSD_{P+I}
MW-1	1.11	0.5	0.6
IC-1	2.53	0.3	0.9
GSR-2	5.46	0.2	0.6
SY-3	8.40	0.2	0.6
HE-1	10.36	0.1	0.5
SGD-1a	11.02	0.1	1.0
MRG-1	14.89	0.1	0.4

Fe₂O₃

	C_{REF}	RSD_I	RSD_{P+I}
GSR-2	2.15	0.1	1.0
MW-1	3.06	0.2	2.1
IC-1	3.57	0.1	1.4
SY-3	6.61	0.1	0.9
HE-1	11.40	0.1	0.7
SGD-1a	11.71	0.1	1.4
MRG-1	18.17	0.1	0.4

Na₂O

	C_{REF}	RSD_I	RSD_{P+I}
MRG-1	0.75	1.6	2.7
SGD-1a	2.83	0.8	1.5
HE-1	3.80	0.6	6.0
GSR-2	4.05	0.6	3.8
SY-3	4.20	0.6	3.9
IC-1	5.63	0.5	2.5
MW-1	8.55	0.4	0.5

K₂O

	C_{REF}	RSD_I	RSD_{P+I}
MRG-1	0.18	1.2	1.5
HE-1	1.93	0.3	0.4
GSR-2	1.99	0.3	0.7
SGD-1a	2.97	0.3	1.6
SY-3	4.31	0.2	0.8
MW-1	6.16	0.2	0.9
IC-1	7.33	0.2	0.7

P₂O₅

	C_{REF}	RSD_I	RSD_{P+I}
MW-1	0.05	4.3	4.1
MRG-1	0.08	3.0	3.0
IC-1	0.09	1.6	5.4
GSR-2	0.25	1.6	3.0
SY-3	0.55	1.0	3.4
HE-1	0.57	1.6	4.4
SGD-1a	1.01	0.7	3.3

C_{REF}: reference concentration (wt%) (Govindaraju, 1994); RSD_I: relative statistical counting error; RSD_{P+I}: total relative standard deviation due to glass disc preparation and statistical counting error. HE-1 (Etna basalt) and IC-1 (Campanian ignimbrite) are working standards.

Tab. 4 - Calibration line parameters, detection limits and relative standard errors.

	A_1	A_0	L.R.	RSD_{LIN}	RSD_{P+I}	RSD_{CORR}
SiO₂	0.274	2.868	0.01	1.3	0.8	0.9
TiO₂	0.110	-0.031	0.002	3.8	1.5	3.8
Al₂O₃	0.263	0.171	0.02	1.9	1.1	1.3
Fe₂O₃ T	0.033	-0.102	0.001	6.9	1.1	2.0
MnO	0.033	-0.026	0.001	6.9	1.2	6.9
MgO	0.313	-0.307	0.02	2.0	1.6	1.4
CaO	0.107	0.087	0.003	3.8	0.6	1.4
Na₂O	0.675	-0.642	0.02	2.6	2.7	2.6
K₂O	0.108	-0.036	0.002	1.6	1.0	1.6
P₂O₅	0.230	-0.012	0.02	5.2	3.5	5.2

A_1 and A_0: angular coefficient and intercept of the regression line, respectively; L.R.: detection limit (wt%); RSD_{LIN}: relative standard deviation of the concentrations determined from the regression line; RSD_{P+I}: total relative standard deviation.

Tab. 5 - Comparison between XRF analyses and reference literature data.

	SiO$_2$		TiO$_2$		Al$_2$O$_3$		Fe$_2$O$_{3T}$		MnO		MgO		CaO		Na$_2$O		K$_2$O		P$_2$O$_5$		sum
	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	C$_{REF}$	C$_{OBS}$	
DNC-1	47.32	46.87	0.48	0.48	18.41	18.67	9.99	10.48	0.15	0.14	10.11	10.39	11.34	11.35	1.88	1.92	0.23	0.22	0.09	0.08	100.60
GSR-2	63.67	63.74	0.55	0.56	16.99	17.11	5.15	5.33	0.08	0.08	1.81	1.84	5.46	5.48	4.05	4.08	1.99	1.94	0.25	0.24	100.40
JB-2	52.82	53.22	1.18	1.23	14.57	14.97	14.24	14.38	0.20	0.21	4.63	4.88	9.82	9.69	2.02	2.01	0.42	0.41	0.10	0.11	101.11
JP-1	44.34	44.36	0.00	0.00	0.63	0.86	8.54	8.73	0.12	0.13	45.78	45.92	0.57	0.55	0.02	0.17	0.00	0.00	0.00	0.01	100.73
MO-2	49.59	48.56	1.66	1.60	16.68	16.47	11.17	10.75	0.17	0.17	6.62	6.24	8.95	8.80	3.77	3.81	0.99	0.99	0.40	0.38	97.77
MO-3	38.00	37.86	1.47	1.43	13.81	13.75	18.73	18.93	0.22	0.22	8.75	8.44	15.91	15.96	0.73	0.72	0.21	0.18	2.17	2.13	99.62
MO-6	51.85	52.22	1.87	1.85	22.81	23.00	6.27	6.48	0.08	0.08	2.10	2.16	10.07	10.29	4.05	4.19	0.76	0.73	0.14	0.15	101.15
MO-7	41.10	41.28	3.42	3.37	17.73	17.43	12.44	12.22	0.15	0.15	6.51	6.31	14.73	14.56	2.07	2.02	0.76	0.78	1.09	1.06	99.18
MO-12	49.66	49.87	1.60	1.60	16.67	16.77	10.49	10.44	0.14	0.16	7.35	7.40	8.69	8.77	3.83	3.92	1.12	1.11	0.45	0.47	100.51
MO-13	49.57	49.96	1.66	1.70	17.94	17.63	10.48	10.70	0.14	0.16	5.86	5.91	9.09	9.16	3.91	3.97	0.95	0.97	0.40	0.42	100.58
MRG-1	39.63	40.17	3.82	3.85	8.58	8.71	18.17	18.37	0.17	0.16	13.73	13.93	14.89	15.03	0.75	0.74	0.18	0.18	0.08	0.09	101.23
MW-1	58.34	58.47	0.40	0.41	21.85	21.95	3.06	3.09	0.13	0.13	0.35	0.31	1.11	1.08	8.55	8.64	6.16	6.12	0.05	0.05	100.25
MY-1	46.55	46.00	0.11	0.08	1.88	1.75	11.84	11.79	0.19	0.20	37.95	37.61	1.29	1.44	0.11	0.20	0.04	0.01	0.04	0.02	99.10
NIM-D	38.84	40.04	0.02	0.02	0.30	0.45	16.91	16.75	0.22	0.24	43.37	43.48	0.28	0.26	0.04	0.15	0.01	0.00	0.01	0.01	101.40
NIM-G	76.38	77.46	0.09	0.10	12.19	12.08	2.04	2.15	0.02	0.02	0.06	0.00	0.79	0.77	3.39	3.29	5.03	4.94	0.01	0.01	100.82
NIM-P*	51.80	50.68	0.20	0.20	4.23	4.17	12.18	12.20	0.22	0.24	25.67	25.71	2.70	2.58	0.37	0.41	0.09	0.07	0.02	0.02	96.28
NIM-S	63.99	64.18	0.04	0.04	17.43	17.64	1.41	1.53	0.01	0.01	0.46	0.41	0.68	0.72	0.43	0.34	15.43	15.33	0.12	0.11	100.31
SDC-1	67.04	66.94	1.03	1.05	16.04	15.96	7.03	6.96	0.12	0.12	1.72	1.79	1.43	1.42	2.09	2.06	3.34	3.32	0.16	0.15	99.77
SGD-1a	46.60	46.64	1.72	1.64	14.94	14.93	11.71	11.64	0.17	0.16	7.03	6.99	11.02	10.95	2.83	2.79	2.97	3.04	1.01	1.05	99.83
SGD-2	47.05	47.43	1.74	1.68	15.06	15.38	11.43	11.46	0.17	0.16	6.87	6.94	10.78	10.87	2.74	2.67	3.12	3.28	1.04	1.03	100.90
STM-1	60.75	60.37	0.14	0.15	18.73	18.72	5.32	5.43	0.22	0.23	0.10	0.10	1.11	1.15	9.11	9.12	4.36	4.31	0.16	0.16	99.74
SY-3	60.76	60.72	0.15	0.14	11.97	11.76	6.61	6.66	0.33	0.31	2.72	2.77	8.40	8.42	4.20	4.06	4.31	4.29	0.55	0.53	99.66
BT1	51.33	51.35	0.03	0.03	8.83	8.76	9.20	8.92	0.12	0.11	22.01	21.99	0.48	0.47	0.24	0.23	7.69	7.80	0.07	0.06	99.72
BT2	53.89	53.95	0.03	0.03	10.54	10.50	7.64	7.44	0.09	0.09	17.71	17.66	0.52	0.52	0.27	0.29	9.23	9.35	0.08	0.07	99.90
BT3	56.64	56.93	0.04	0.04	12.43	12.44	5.93	5.79	0.07	0.07	12.98	13.06	0.57	0.57	0.32	0.29	10.93	10.96	0.09	0.08	100.23
BT14	43.05	42.96	0.25	0.28	9.31	9.31	13.49	13.61	0.18	0.19	26.81	26.78	5.78	5.68	0.96	1.04	0.12	0.11	0.05	0.05	100.01
BT15	54.95	54.73	1.14	1.13	15.94	15.87	8.50	8.51	0.13	0.12	4.48	4.47	8.30	8.18	3.43	3.39	2.49	2.46	0.64	0.67	99.53
BT16	52.32	52.50	1.46	1.56	20.41	20.56	6.34	6.20	0.14	0.14	2.50	2.51	5.87	5.86	6.28	6.30	4.27	4.28	0.41	0.41	100.32
BT17	49.73	49.69	1.91	1.97	19.79	19.68	7.75	7.64	0.14	0.14	3.43	3.41	7.91	7.88	5.31	5.29	3.46	3.51	0.57	0.57	99.78
BT18	47.14	47.24	2.36	2.41	19.18	19.08	9.16	8.95	0.14	0.14	4.35	4.28	9.96	9.94	4.34	4.29	2.65	2.69	0.72	0.74	99.76
BT19	65.49	64.79	0.53	0.55	16.73	16.62	4.24	4.17	0.06	0.06	1.09	1.12	1.05	1.09	1.25	1.22	9.42	9.37	0.14	0.13	99.12
BT20	62.36	61.88	0.10	0.09	14.72	14.55	4.02	4.02	0.17	0.16	1.58	1.56	4.52	4.58	2.30	2.26	9.90	9.87	0.33	0.33	99.30
BT21	57.14	56.74	0.55	0.53	12.72	12.56	7.94	7.88	0.29	0.27	3.81	3.87	9.06	9.08	3.85	3.76	3.97	3.96	0.67	0.67	99.32
BT22	53.62	53.51	0.94	0.91	13.46	13.40	9.21	9.10	0.25	0.24	4.89	4.98	9.71	9.70	3.51	3.44	3.63	3.67	0.78	0.84	99.79

* includes Cr2O3 = 2.52%
C$_{REF}$: reference concentration (wt%) (Govindaraju, 1994); C$_{OBS}$: observed concentration (wt%).

Tab. 6 - Absolute and relative standard deviation obtained via the proposed method. Literature values are also reported for the sake of comparison.

			1			**2**		**3**			**4**	
	C	N	Average	SD	RSD	RSD	C	SD	RSD	C	SD	RSD
SiO$_2$	38-52	18	46.29	0.51	**1.1**	0.7	11-70	0.29	0.7	5-94	0.32	0.6
	52-77	16	60.01	0.42	**0.7**							
TiO$_2$	0-1	19	0.24	0.02	**8.3**	4.4	0-19	0.02	0.2	0-2.7	0.03	2.2
	1-4	15	1.87	0.06	**3.2**							
Al$_2$O$_3$	0.3-2	3	0.94	0.11	**11.7**	1.2	2-65	0.15	0.4	1-18	0.14	1.5
	4-15	14	11.59	0.16	**1.4**							
	15-23	17	18.14	0.19	**1.0**							
Fe$_2$O$_{3\,T}$	1-5	5	2.95	0.03	**1.0**	1.7	0-33	0.12	0.7	1-15	0.07	0.9
	5-10	15	7.37	0.14	**1.9**							
	10-19	14	13.09	0.23	**1.8**							
MnO	0-0.30	34	0.15	0.01	**6.7**	4.0	0-0.2	0.01	7.0	0-0.2	0.01	8.0
MgO	1-2	4	1.55	0.04	**2.6**	2.1	0-9	0.08	1.8	0-14	0.06	0.9
	2-10	16	5.12	0.14	**2.7**							
	10-46	10	25.61	0.17	**0.7**							
CaO	0.5-5	12	1.36	0.07	**5.1**	1.0	0-15	0.11	1.5	0.5-90	0.12	0.3
	5-16	20	9.79	0.10	**1.0**							
Na$_2$O	0.2-2	10	0.72	0.05	**6.9**	2.5	0-6	0.09	3.0	0-4	0.09	4.5
	2-9	21	4.08	0.07	**1.7**							
K$_2$O	0-1	13	0.37	0.02	**5.4**	2.3	0-5	0.04	1.6	0-4.5	0.01	0.4
	1-5	14	3.34	0.06	**1.8**							
	5-17	7	9.82	0.08	**0.8**							
P$_2$O$_5$	0-1	30	0.25	0.01	**4.0**	2.3	0-1.3	0.02	2.6	0-1.1	0.01	1.8
	1-3	4	1.33	0.03	**2.3**							

C: range of concentrations (wt%); X: average concentration of the interval; N: number of analysed samples; SD: absolute standard deviation; RSD: relative standard deviation; 1: this work; 2: Bower & Valentine (1986) (dilution 1:10); 3: Couture *et al.* (1993) (dilution 1:9); 4: El Maghraoui *et al.* (1998) (dilution 1:7).

ison of the resulting RSD values with those obtained by other laboratories via XRF analysis on fused glass discs (Bower & Valentine, 1986; Couture *et al.*, 1993; El Maghraoui *et al.*, 1998). Of course, the RSD values vary with concentration. On the whole, all the elements except Al exhibit RSDs ranging from 5% (Ca) to 7% (Mn) at concentrations of < 1%. Aluminium yields a higher RSD (11.4%), though such an error can hardly be considered meaningful, as it refers to a low number of samples (N = 3). The measured RSD decreases with increasing concentration, and its values align with those obtained in other laboratories (Tab. 6). Lastly, it is worthwhile noting that the RSD values for Na, K and Mg are quite similar to those determined via Atomic Absorption Spectroscopy (Van Loon, 1988).

CONCLUDING REMARKS

The precision obtainable in major element analysis of silicate materials via the XRF procedure described in this work depends heavily on preparation of the glass discs (sample and flux weighing, ignition before fusion, powder grain size, degree of homogenisation of the melt during the fusion process, etc.), whereas statistical counting is generally negligible except for minor (P, Ti and Mn) and light elements at low concentration levels (< 1 wt%). Within the studied range of composition the proposed XRF analytical procedure yields precision and accuracy which can be considered acceptable for petrological and geochemical purposes (Tables 4, 5 and 6). Finally, independent determination of the abundance of each element also enables evaluating the quality of the analytical data obtained through assessment of the totals for the ten major elements determined.

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