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INDICE - *CONTENTS*

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QUANTITATIVE SEM-EDS ANALYSIS OF REFERENCE SILICATE MINERAL AND GLASS SAMPLES

Abstract - P. Fulignati, P. Marianelli, A. Sbrana, *Quantitative SEM-EDS analysis of reference silicate mineral and glass samples.*

SEM-EDS microanalysis is an accurate technique for quantitative microchemical X-ray analyses of geological samples. The aim of this study was to set up the procedure for the determination of major, minor and volatile elements (Si, Al, Ti, Mg, Fe, Ni, Mn, Na, Ca, K, Ba, P, B, Cl, S, F) in reference silicate mineral and glass samples, by using the new SEM-EDS ThermoFisher® Quanta 400 Forensic with Pathfinder microanalysis installed at the Earth Sciences Department, University of Pisa. The obtained precision and accuracy are acceptable for many mineralogical, petrographic and geological purposes.

Key words - microanalysis, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS)

Riassunto - P. Fulignati, P. Marianelli, A. Sbrana, *Analisi quantitative SEM-EDS di campioni di riferimento di vetri e minerali silicatici.*

La microanalisi SEM-EDS è una tecnica accurata per le analisi microchimiche quantitative a Raggi X di campioni di materiali geologici. Lo scopo di questo studio era di mettere a punto una procedura per la determinazione degli elementi maggiori, minori e volatili (Si, Al, Ti, Mg, Fe, Ni, Mn, Na, Ca, K, Ba, P, B, Cl, S, F) in campioni di vetri e minerali silicatici di riferimento, usando il nuovo strumento SEM-EDS ThermoFisher® Quanta 400 Forensic con microanalisi Pathfinder installato al Dipartimento di Scienze della Terra dell'Università di Pisa. La precisione e l'accuratezza ottenute sono risultate soddisfacenti per finalità mineralogiche, petrografiche e geologiche.

Parole chiave - microanalisi, microscopio elettronico a scansione (SEM), spettroscopia a dispersione di energia (EDS)

Introduction

The composition of silicate minerals and glasses is particularly relevant in the study of geosciences. As a consequence, the possibility to carry out high quality, in situ and relatively fast analyses on these materials is pivoting for a lot of Earth Science scientists. This kind of analysis can be obtained by electron microprobe and scanning electron microscope using Wavelenght Dispersive Spectrometer (WDS), Energy Dispersive Specrometer (EDS) or an integration of both (WD/ED combined). Although detection limits (typically around 0.1%) of EDS apparatus are higher (about ten times higher, Goldstein *et al.*, 1981) and the resolution is lower (i.e. due to the interference between F/Fe Lα fluorine cannot be quantified in Fe-rich materials) than WDS apparatus, for many applications (e.g. major elements in rock-forming silicate and glasses) quantitative EDS analysis is perfectly satisfactory, and even has some advantages, including simpler setting up and compatibility with lower current density that minimize damage to feldspars, glasses, carbonates, etc. (Reed, 2005).

The main purpose of this paper is to evaluate the accuracy of calibration of the new SEM-EDS ThermoFisher® Quanta 400 Forensic with Pathfinder v. 1.3 microanalysis system recently installed at Dipartimento di Scienze della Terra, University of Pisa (Italy) as concern the quantitative determination of major and minor elements (Si, Al, Ti, Mg, Fe, Ni, Mn, Na, Ca, K, Ba, P, B, Cl, S, F) in silicate minerals and glasses.

The Pathfinder microanalysis is based on quantification in a 2-step process: 1) from spectrum to net peak intensities using the filter-fit method (McCarthy & Schamber, 1979); 2) from intensities to element concentration using the PROZA model for matrix correction (Bastin *et al.*, 1998 and references therein; Thermo Fisher Scientific Inc, 2016).

Materials and methods

The calibration of the method was carried out on five minerals, three natural glasses and one synthetic glass (Tab. 1). Samples were polished (down to 0.3 µm alumina powder) and carbon coated (25 nm thickness) before each analytical session.

The SEM-EDS Quanta 400 is equipped with a Thermo Scientific Pathfinder EDS UltraDry 10 (129 eV) detector working under high-vacuum mode (<10^{-4} Pa). The active area is 10 mm^2 and 129 eV energy resolution at Mn k-alpha. Norvar window with proprietary evacuated tube design for detection sensitivity to Be. The instrumental conditions were set in order to obtain the optimization of analytical results considering the materials commonly investigated by the users of

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the Laboratory. Spectra collection has been performed at 20 kV accelerating voltage, 10^{-10} A beam current. This is not the optimal condition for the determination of elements lighter than fluorine, however 20 kV accelerating voltage minimizes the migration of alkalies (Goodhew & Gulley, 1975) and improves the statistics of heavy elements. Spot diameter was tuned before each analytical session in order to obtain 32000 cps on pure Au sample with 500X magnification. In order to minimize thermal decomposition effects each analysis was performed with a scanning window of about 900 μm^2 and an acquisition time of 50 seconds live time (preliminary analyses on reference minerals and glasses with different acquisition live times were performed and 50 seconds live time resulted the best choice).

Repeated analyses were performed on each sample of reference material in different analytical sessions in order to check the reproducibility of analyses. For the calibration we adopted a selection of international reference samples (CFA47, ALV981R23, KE12, Scapolite Zabargad, Metrich, 1985; Metrich & Clocchiatti, 1989; Metrich & Rutherford, 1992; Vaggelli *et al*., 1999), minerals supplied by C.M. Taylor Corporation (Multi-Element Standard No. 214-30, Albite, Ortose, Olivine, Diopside), and one B-bearing synthetic glass appositely prepared (Flint glass, Kimble Italia).

The PROZA correction factors (PCF) for matrix correction (Bastin *et al*., 1998) were tuned in order to minimize the discrepancies between the measured and the expected values of B_2O_3, Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, S, Cl, K_2O, CaO, TiO_2, MnO, FeO, NiO (expressed as wt.%) in reference material. The analyses were normalized to 100 wt. % due to the Thermo Scientific Pathfinder software used; obviously this must be taken into account during quantification processes of analysis performed on hydrous phases (i.e., water-rich natural and experimental glasses, hydrous minerals, etc), as normalization to 100% may disguise the effect of water content (Reed, 2005).

Results and discussion

After the afore-mentioned accurate calibration, the huge number of analysis collected on reference minerals and glasses testifies the good precision obtained with the new SEM-EDS apparatus at Dipartimento di Scienze della Terra di Pisa (Tab. 1). Collected data on reference minerals and glasses indicate that the analytical precision reached with the new SEM EDS instrument is good. For concentrations higher than 10 wt.% the percent deviation is within 2%, and the percent deviation is generally within 5% also for concentration down to around 0.5 wt.% (Tab. 1). Box plots of reference mineral and glass analyses (Fig. 1) provide a medium to show both the homogeneity of reference samples and the reproducibility of analyses performed with Quanta 400 apparatus. The narrow spread of the box plots (Fig. 1) indicates a good reproducibility of the data and a general compositional homogeneity of the reference samples. Only Olivine and ALV981R23 show wider spread of the FeO boxplot that can be ascribed to a slightly higher compositional heterogeneity of the sample, and not to the analytical procedure.

We also determined the equations representing the absolute deviation as function of concentration of elements. The equations have been calculated through a linear regression from data reported in Tab. 1 for MgO, Al_2O_3, SiO_2, K_2O, CaO, FeO, TiO_2 and Cl (Fig. 2).

Tab. 2 provides a comparison of the chemical concentrations determined with SEM EDS Quanta 400 with values recommended from either WDS data of literature or provided by supplying companies. Because of normalization to 100%, due to the Pathfinder software used, the composition of reference material determined by WDS are normalized to 100 for comparison. The average percentage error for EDS systems is considered around 5% for all elements (Krusemann, 1995); as a consequence, the results obtained in this study are particularly encouraging as the average percentage error is generally below 3% with the exception of low concentration elements (such as CaO in Albite, Na_2O in Diopside, MgO in CFA47 glass, Tab. 2). However, these errors may still be considered acceptable for many mineralogical and petrographic purposes. The obtained results are well in agreement with those obtained by WDS apparatus. Indeed, several papers, based on EDS data performed with SEM-EDS instrument of Dipartimento di Scienze della Terra, University of Pisa, demonstrated the reliability of EDS data on reference standards in comparison with WDS analyses performed on the same standards (Cioni *et al*., 1998; Marianelli & Sbrana, 1998; Fourmentraux *et al*., 2012; Gatti *et al*., 2018).

We would like to remark that the new SEM-EDS system has been tested and set up in the present work for quantitative routine microchemical analyses of B (very light element) in silicate glass. We obtained very good results showing a percentage deviation of 1.60 and a percentage error of 0.75 (Tabs 1 and 2).

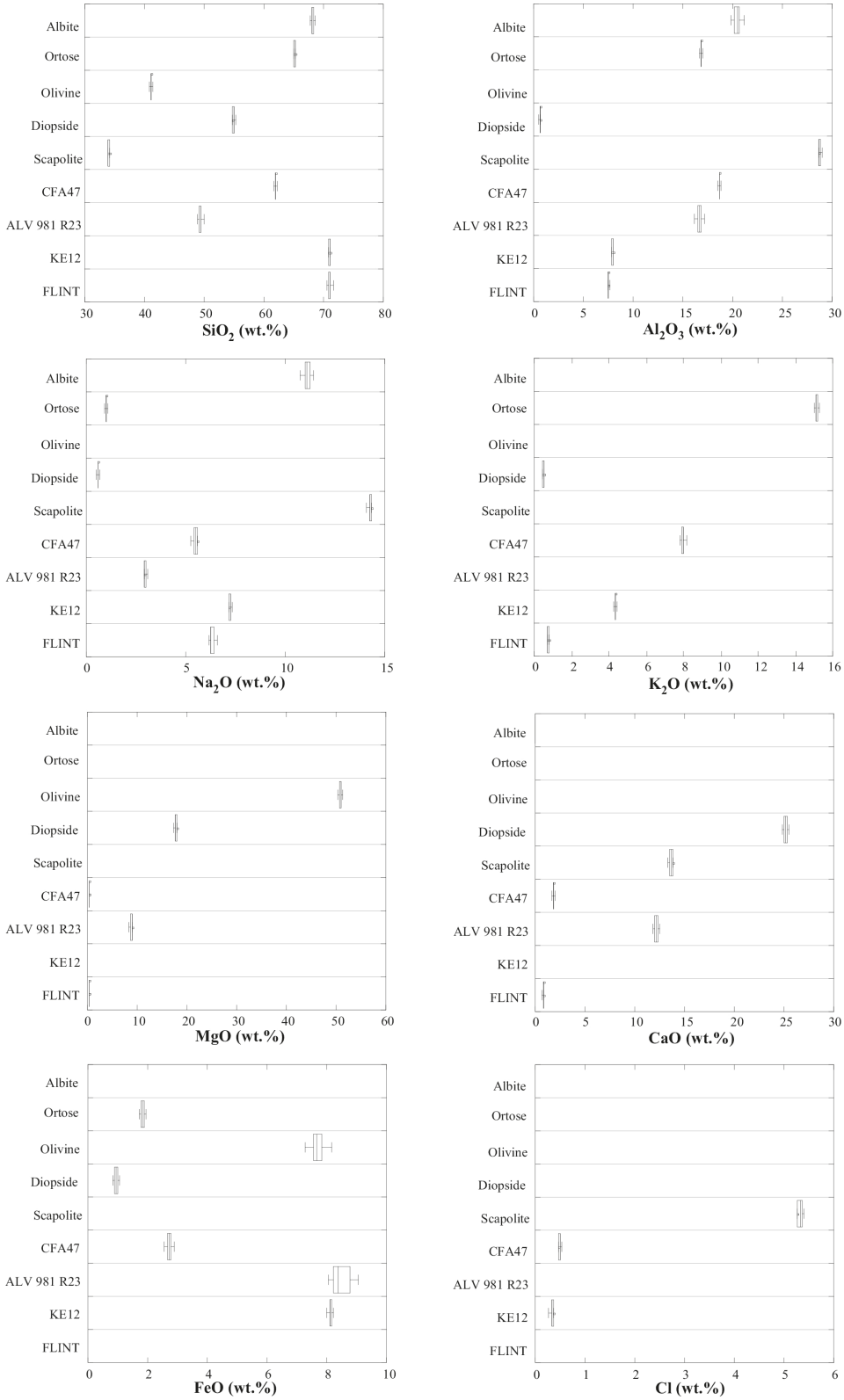

Figure 1. Box plots summarizing the whole set of EDS reference mineral and glass analyses. Each box encloses 50% of the data (the median value of the variable is displayed as a line). The lines extending from each box mark the minimum and maximum values of the data set, outliers are not displayed.

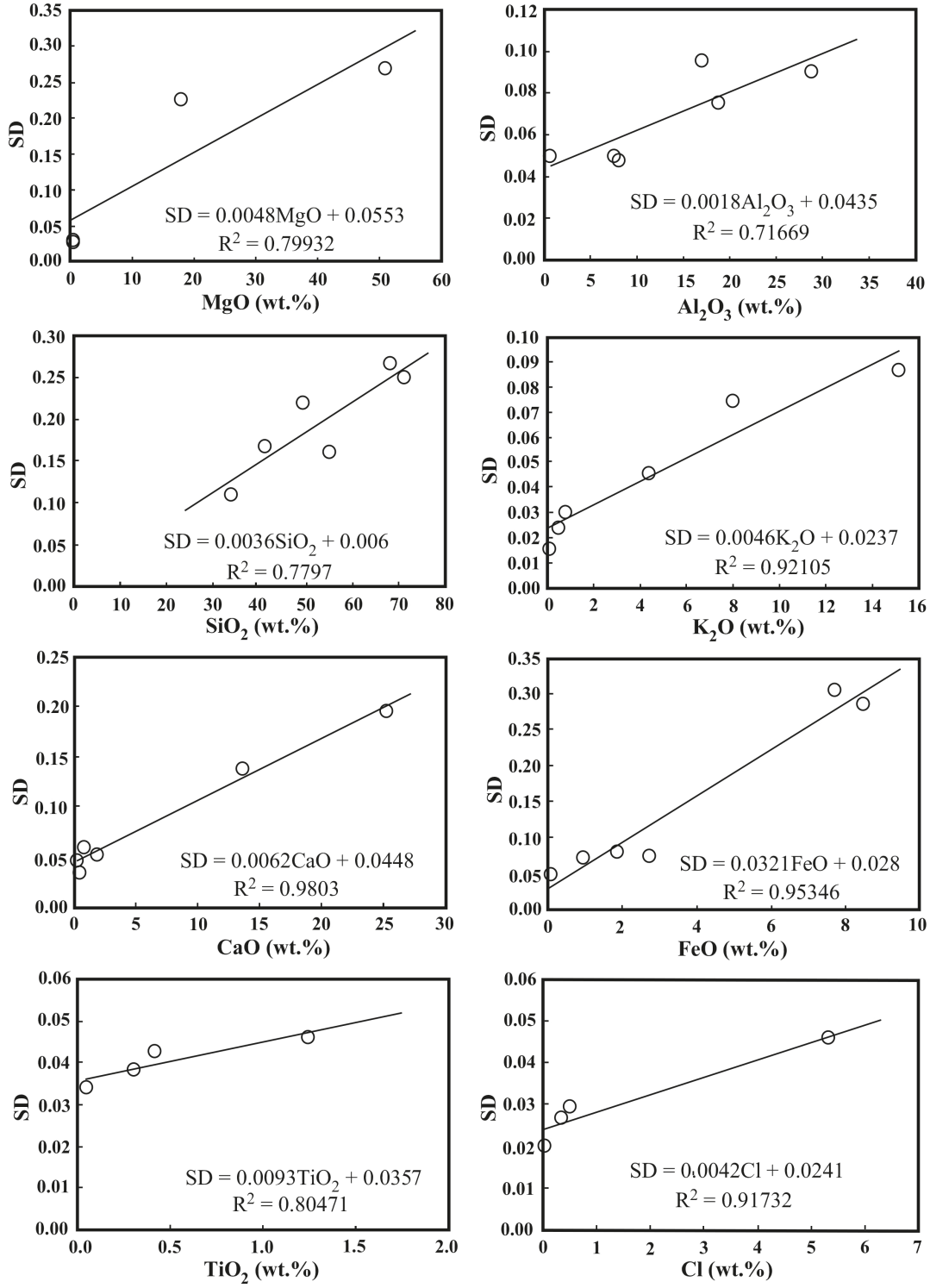

Figure 2. Diagrams showing the chemical concentration in wt.% analyzed on reference minerals and glasses in respect to the standard deviation (1σ). Regression lines and R^2 are calculated on the basis of the concentrations analyzed in following minerals and glasses. MgO: Olivine, Diopside, CFA47, Flint glass; Al_2O_3: Ortose, Diopside, Scapolite Zabargad, CFA47, KE12, Flint glass; SiO_2: Albite, Olivine, Diopside, Scapolite Zabargad, ALV 981 R23, Flint glass; K_2O: Ortose, Scapolite Zabargad, CFA47, KE12, ALV 981 R23, Flint glass; CaO: Albite, Diopside, Scapolite Zabargad, CFA47, KE12, Flint glass; FeO: Ortose, Olivine, Diopside, Scapolite Zabargad, CFA47, ALV 981 R23; TiO_2: Scapolite Zabargad, CFA47, ALV 981 R23, KE12; Cl: Scapolite Zabargad, CFA47, KE12, Flint glass.

Table 1. EDS analyses of reference minerals and glasses.

	Albite			Ortose			Olivine			Diopside			Scapolite Zabargad		
	(49 an.)	*SD*	*%SD*	*(20 an.)*	*SD*	*%SD*	*(80 an.)*	*SD*	*%SD*	*(35 an.)*	*SD*	*%SD*	*(30 an.)*	*SD*	*%SD*
SiO_2	68.18	0.27	0.39	65.17	0.10	0.15	41.10	0.17	0.41	54.91	0.16	0.29	33.98	0.11	0.33
Al_2O_3	20.49	0.34	1.65	16.85	0.10	0.57				0.60	0.05	8.30	28.74	0.09	0.31
FeO				1.83	0.08	4.39	7.71	0.30	3.95	0.94	0.07	7.66	0.07	0.05	71.00
MnO													0.02	0.01	52.63
MgO							50.86	0.27	0.53	17.80	0.23	1.27			
CaO	0.20	0.05	24.05							25.18	0.19	0.77	13.65	0.14	1.01
Na_2O	11.12	0.17	1.56	1.00	0.03	3.49				0.57	0.04	6.73	14.25	0.06	0.43
K_2O	bdl			15.15	0.09	0.57							0.49	0.02	4.83
NiO							0.33	0.04	11.58						
S													3.43	0.03	1.02
Cl													5.33	0.05	0.86

	CFA47			ALV 981 R23			KE12			Flint glass		
	(60 an.)	*SD*	*%SD*	*(30 an.)*	*SD*	*%SD*	*(25 an.)*	*SD*	*%SD*	*(20 an.)*	*SD*	*%SD*
SiO_2	61.91	0.13	0.21	49.38	0.22	0.44	70.97	0.10	0.13	71.07	0.25	0.35
TiO_2	0.42	0.04	10.32	1.25	0.05	3.71	0.30	0.04	12.76			
Al_2O_3	18.70	0.08	0.40	16.69	0.22	1.33	7.91	0.05	0.60	7.53	0.05	0.66
FeO	2.70	0.07	2.75	8.47	0.29	3.37	8.12	0.08	0.98			
MnO	0.21	0.03	16.70	0.21	0.04	21.12	0.34	0.03	9.57			
MgO	0.28	0.03	10.08	8.81	0.21	2.43				0.40	0.03	7.50
CaO	1.83	0.05	2.90	12.15	0.19	1.55	0.43	0.03	7.93	0.78	0.06	7.69
Na_2O	5.47	0.10	1.85	2.95	0.04	1.40	7.23	0.04	0.56	6.29	0.18	2.86
K_2O	7.99	0.07	0.93	0.03	0.02	60.27	4.37	0.05	1.05	0.75	0.03	4.00
BaO										2.20	0.10	4.55
P_2O_5				0.04	0.03	68.43						
B_2O_3										10.62	0.17	1.60
S				0.02	0.01	43.48						
Cl	0.50	0.03	5.91				0.33	0.03	8.05	bdl		
F										0.19	0.09	26.47

Averaged analyses of mineral and glass fragments normalized to 100; all Fe as FeO.
(an.) = number of averaged analyses; SD = standard deviation (1σ); %SD = percent deviation; bdl = below detection limit.

Table 2. Calculated percentage errors of EDS analyses of reference minerals and glasses.

	Albite		Ortose		Olivine		Diopside		Scapolite Zabargad	
	(49 an.)	*%error*	*(20 an.)*	*%error*	*(80 an.)*	*%error*	*(35 an.)*	*%error*	*(30 an.)*	*%error*
SiO2	68.18	0.04	65.17	0.52	41.10	0.28	54.91	0.40	33.98	2.06
Al2O3	20.49	3.64	16.85	1.40			0.60	28.61	28.74	0.80
FeO			1.83	7.52	7.71	1.03	0.94	54.00	0.07	3.45
MnO									0.02	5.26
MgO					50.86	0.01	17.80	0.66		
CaO	0.20	48.23					25.18	0.33	13.65	0.25
Na2O	11.12	2.93	1.00	6.14			0.57	33.50	14.25	3.62
K2O			15.15	1.88					0.49	13.59
NiO					0.33	12.58				
S									3.43	0.42
Cl									5.33	2.40

	CFA47		ALV 981 R23		KE12		Flint glass	
	(60 an.)	*%error*	*(30 an.)*	*%error*	*(25 an.)*	*%error*	*(20 an.)*	*%error*
SiO2	61.91	0.05	49.38	0.75	70.97	0.20	71.07	0.03
TiO2	0.42	1.04	1.25	2.60	0.30	6.91		
Al2O3	18.70	0.44	16.69	0.18	7.91	1.12	7.53	2.26
FeO	2.70	1.40	8.47	0.27	8.12	6.82		
MnO	0.21	12.83	0.21	31.82	0.34	16.41		
MgO	0.28	51.72	8.81	0.97			0.40	15.00
CaO	1.83	0.89	12.15	2.42	0.43	19.35	0.78	5.13
Na2O	5.47	1.36	2.95	1.83	7.23	0.05	6.29	3.82
K2O	7.99	0.43	0.03	48.00	4.37	4.03	0.75	13.33
BaO							2.20	2.27
P2O5			0.04	37.62				
B2O3							10.62	0.75
S			0.02	80.83				
Cl	0.50	1.61			0.33	0.36		
F							0.19	21.05

(an.) = number of averaged analyses, present study; %error = percentage error, estimated from EDS analyses (this paper) and reference values from literature. Albite, Ortose, Olivine and Diopside: Marianelli & Sbrana (1998); Scapolite: Metrich 1985; CFA47: Metrich & Clocchiatti (1989), Metrich (1985), Vaggelli *et al.* (1999); ALV 981 R23: Fine & Stolper (1986), Metrich & Clocchiatti (1989), Vaggelli *et al.* (1999); KE12: Metrich & Rutherford (1992); Flint glass: Kimble Italia.

Conclusions

The new SEM-EDS ThermoFisher® Quanta 400 Forensic with Pathfinder v. 1.3 X-ray microanalysis system allows quantitative microchemical analyses of silicate minerals and glasses. This apparatus, equipped with the Norvar window and an analyzer electronics with up to 1,000,000 X-ray input counts per second and 300,000 X-ray output counts per second, dramatically improves the counting statistics allowing reducing the collecting time (50 sec live time) with respect to older liquid N_2-cooled SEM-EDS apparatus. This also minimizes thermal decomposition, which affects the quantification of light elements.

Precision and accuracy of quantitative EDS analysis can be considered comparable to that of WDS analysis for concentrations above 1%, provided that proper standards are used (Reed, 2005). In the present work, the microanalytical routine developed for this SEM-EDS apparatus testifies that the estimated analytical precision and accuracy (Tabs 1 and 2, Figs 1 and 2) result to be appropriate for analyzing the major and some minor elements of silicate minerals and glasses

and the volatile elements (Si, Al, Ti, Mg, Fe, Ni, Mn, Na, Ca, K, Ba, P, B, Cl, S, F).

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