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## INDICE - CONTENTS

<p>F. ALQUINI, D. BERTONI, G. SARTI – Extreme erosion of a dune crest within a short timespan (January-September 2016): the recent case in the Migliarino - San Rossore - Massaciuccoli Regional Park (Tuscany, Italy). <i>Erosione molto accentuata della cresta di una duna frontale in un breve periodo di tempo (gennaio-settembre 2016): il recente caso nel Parco Regionale di Migliarino - San Rossore - Massaciuccoli (Toscana, Italia).</i></p>	pag. 5	<p>M. LEZZERINI, M. TAMPONI, G. D'AMATO AVANZI, S. IACCARINO, N. PERCHIAZZI – XRF analysis of major and minor elements in silicate rocks using fused glass discs at high dilution ratio. <i>Determinazione XRF degli elementi maggiori e minori in rocce silicatiche utilizzando dischi fusi con alti rapporti di diluizione.</i></p>	» 55
<p>M. BELGIORNO, P. MARIANELLI, G. PASQUINI, A. SBRANA – A contribution to the study of a Pisa alluvial plain sector for low temperature geothermal assessment. <i>Un contributo allo studio di un settore della piana alluvionale di Pisa ai fini di una valutazione geotermica a bassa temperatura.</i></p>	» 17	<p>S. MERLINO – OD character and polytypic features of the structure of the molecular crystal (1R,3S)-dimethyl 2-oxocyclohexane-1,3-dicarboxylate. <i>Carattere OD e aspetti politipici della struttura del cristallo molecolare (1R,3S)-dimethyl 2-oxocicloesano-1,3-dicarbossilato.</i></p>	» 61
<p>P. BILLI – Variation of the hydrological characteristics of rivers in Italy throughout the last 80 years. <i>Variazione delle caratteristiche idrologiche dei fiumi in Italia negli ultimi 80 anni.</i></p>	» 25	<p>C. MONTEMAGNI, P. FULIGNATI, S. IACCARINO, P. MARIANELLI, C. MONTOMOLI, A. SBRANA – Deformation and fluid flow in the Munsiri Thrust (NW India): a preliminary fluid inclusion study. <i>Deformazione e "fluid flow" lungo il Munsiri Thrust (India NW): studio preliminare su inclusioni fluide.</i></p>	» 67
<p>A. COLLARETA – Fossil turtle and whale barnacles (Crustacea: Cirripedia: Coronuloidea) kept at the Natural History Museum of Pisa University: an annotated catalogue. <i>Cirripedi fossili simbionti dei vertebrati marini (Crustacea: Cirripedia: Coronuloidea) nelle collezioni del Museo di Storia Naturale dell'Università di Pisa: un catalogo annotato.</i></p>	» 41	<p>N. PERCHIAZZI, P. ARMIENTI, S. IACCARINO, M. LEZZERINI – A contribution to the mineralogy of the Larderello geothermal field. X-ray crystallographic studies on borate minerals "bechilite" and "lagonite" and crystal structure determination of ginorite. <i>Contributo alla mineralogia del campo geotermico di Larderello. Studi cristallografici a raggi X dei borati "bechilite" e "lagonite" e determinazione strutturale della ginorite.</i></p>	» 79
<p>S. FARINA – Catalogue of the late Pleistocene-Holocene fossil mammalian collection from "Canale delle Acque Alte (Canale Mussolini)" (Natural History Museum, University of Pisa). <i>Catalogo della collezione a mammiferi fossili del Pleistocene Superiore - Olocene di "Canale delle Acque Alte (Canale Mussolini)" (Museo di Storia Naturale dell'Università di Pisa).</i></p>	» 47	<p>L. ROOK, Un ricordo di Augusto Azzaroli (1921-2015) <i>In memory of Augusto Azzaroli (1921-2015)</i></p>	» 89
		<p>Processi Verbali - <a href="http://www.stsn.it">http://www.stsn.it</a></p>	» 101



MARCO LEZZERINI (\*), MARCO TAMPONI (\*), GIACOMO D'AMATO AVANZI (\*),  
SALVATORE IACCARINO (\*), NATALE PERCHIAZZI (\*)

## XRF ANALYSIS OF MAJOR AND MINOR ELEMENTS IN SILICATE ROCKS USING FUSED GLASS DISCS AT HIGH DILUTION RATIO

**Abstract** - XRF analysis of major and minor elements in silicate rocks using fused glass discs at high dilution ratio. X-ray fluorescence (XRF) is an accurate, rapid spectroscopic technique for chemical element determinations on rock samples. The aim of this research was to evaluate a calibration method for the determination of major and minor elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) in silicate rocks using fused glass discs with a 1:30 sample/borate dilution. The analytical method has been calibrated by using forty-two international rock standards. The accuracy appears acceptable for many mineralogical and petrographic purposes. A high dilution ratio makes possible the use of a small amount of sample (225 mg) to obtain good castings in high-melting materials. By contrast, the decrease of the analytical intensity makes not easy the determination of trace elements at the typical concentration levels of geological samples. doi: 10.2424/ASTSN.M.2016.20

**Keywords** - XRF; fused glass disc; major and minor elements; calibration; high dilution ratio

**Riassunto** - Determinazione XRF degli elementi maggiori e minori in rocce silicatiche utilizzando dischi fusi con alti rapporti di diluizione. La fluorescenza a raggi-X (XRF) è una tecnica spettroscopica accurata e rapida per la determinazione degli elementi chimici presenti in campioni di rocce. Lo scopo di questa ricerca è stato quello di valutare un metodo di calibrazione per la determinazione degli elementi maggiori e minori (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) in rocce silicatiche mediante utilizzo di dischi fusi con un rapporto campione/fondente di 1:30. Il metodo analitico è stato calibrato utilizzando quarantadue standard internazionali di rocce. L'accuratezza risulta accettabile per fini mineralogici e petrografici. Un alto rapporto di diluizione consente l'impiego di una piccola quantità di campione (225 mg) per ottenere più agevolmente buone fusioni in materiali altofondenti. Per contro, la diminuzione delle intensità analitiche non facilita la determinazione degli elementi in traccia ai livelli di concentrazione tipici dei campioni geologici. doi: 10.2424/ASTSN.M.2016.20

**Parole chiave** - XRF; disco di vetro fuso; elementi maggiori e minori; calibrazione; alto rapporto di diluizione.

### INTRODUCTION

X-Ray Fluorescence (XRF) is a fast and accurate spectroscopic technique for determining chemical composition of rock samples (Bower & Valentine, 1986; Chappell, 1991; Lachance & Claisse, 1995; Tamponi *et al.*, 2003; Beckhoff *et al.*, 2006; Lezzerini *et al.*, 2013, 2014; Lezzerini & Tamponi, 2015). Theoretical and empirical

approaches are available and used in quantitative XRF. The theoretical methods are based on mathematical models that involve fundamental parameter, i.e. basic physical parameters, such as attenuation coefficients, transition probabilities, and fluorescent yields (Sherman, 1955; Shiraiwa & Fujino, 1966). Alternatively, methods with empirical calibration curves can also be used for determining major, minor and trace elements of rock samples. The main problems encountered by using these methods in rock chemical analysis by XRF concern the matrix effects (absorption and enhancements) due to the heterogeneity of samples (grain size, absorption, etc.). Sample heterogeneity effects can be drastically reduced by preparing the sample in the form of fused disks, by dissolving the sample in a lithium borate mixture. However, this methodology is almost exclusively used for determining major and minor elements, since the dilution of the sample in a 'light' matrix causes a considerable decrease of the peak/background ratio in fluorescence intensities. Matrix effects can be corrected by using appropriate experimental or calculated coefficients that take into account the influence of the major components on the analytical lines of the elements to be analysed.

Nowadays, XRF analysis is still the spectroscopic technique chosen by most geologists, petrologists and geochemists for obtaining rock chemical compositions (Thomas & Haukka, 1978; Enzweiler & Webb, 1996; Beckhoff *et al.*, 2006; Iaccarino *et al.*, 2017), and it is widely used for studies in the field of conservation and restoration of stones, marbles, ceramics, mortars and other interesting materials of cultural heritage (Franzini & Lezzerini, 2003; Franzini *et al.*, 2010; Mármol *et al.*, 2010; Tripathi *et al.*, 2010; Fiori *et al.*, 2011; Brown *et al.*, 2013; Miriello *et al.*, 2013; Theodoridou *et al.*, 2013; Villagran *et al.*, 2013; Gliozzo *et al.*, 2014; Lezzerini *et al.*, 2014; Rolett *et al.*, 2015).

The main purpose of this paper was to evaluate the accuracy of a calibration method for the determination of major and minor elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) in silicate rocks using fused glass discs at high sample/borate dilution ratio (1:30).

(\*) Dipartimento di Scienze della Terra, Università di Pisa (Italy), via S. Maria, 53 - 56126 Pisa. Email: marco.lezzerini@unipi.it

## MATERIALS AND METHODS

The calibration of the method for measuring the major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements of rocks was carried out on forty-two international standards of silicate rocks; the list of the reference materials utilized for the calibration is reported in Tab. 1.

Tab. 1 - List of rock international standards.

NAME	DESCRIPTION	NAME	DESCRIPTION
AC-E	0	MO-3	Gabbro
BIR-1	Basalt	MO-6	Anorthosite
DR-N	Diorite	MO-7	Orthoclase-gabbro
DT-N	Disthene	MO-13	Olivine-Basalt
DTS-1	Dunite	MRG-1	Gabbro
GS-N	Granite	MW-1	Miaskite
GSR-2	Andesite	MY-1	Peridotite
JA-2	Andesite	NIM-D	Dunite
JA-3	Andesite	NIM-P	Pyroxenite
JB-1a	Basalt	NIM-S	Syenite
JB-2	Basalt	OU-6	Slate
JB-3	Basalt	SGD-1a	Gabbro
JF-1	Feldspar	STM-1	Syenite
JF-2	Feldspar	SY-3	Syenite
JG-1a	Granodiorite	YG-1	Granite
JG-2	Granite	401	Limestone
JG-3	Granodiorite	402	Limestone
JGb-1	Gabbro	403	Limestone-dolomite blend
JP-1	Peridotite	1880a	Portland Cement
JR-1	Rhyolite	1882a	Calcium Aluminate cement
MA-N	Granite	1883a	Calcium Aluminate cement

The sample preparation technique and the fusion procedure are the same as those suggested by Claisse (1957). In particular, a mixture containing 0.225 g of sample powder and 6.775 g of flux (50% lithium tetraborate,  $\text{Li}_2\text{B}_4\text{O}_7$  and 50% lithium metaborate,  $\text{LiBO}_2$ , corresponding to a 1:30 sample/borate dilution), is carefully homogenized in a Pt<sub>95</sub>-Au<sub>5</sub> crucible using a Claisse Fluxer-Bis!® automatic apparatus. As a non-wetting agent, ammonium iodide is added. The mixture is fused at 1000 °C for about 20 minutes while continuously stirring the melt. When the sample has completely dissolved and any reactions ceased, the melt is poured into a Pt95-Au3-Rh2 plate and slowly cooled. After cooling, the glass disc (with a diameter  $\Phi = 32$  mm) is ready to be analyzed. The intensities of the major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements of the rocks were measured utilizing an ARL 9400 XP+ sequential X-ray spectrometer, hosted at the Dipartimento di Scienze della Terra (University of Pisa). The applied instrumental conditions are summarized in Tab. 2.

Tab. 2 - Instrumental conditions.

PARAMETER	NA, MG	AL, SI, P	K, CA, TI, MN, FE
$\lambda_E$	K <sub>a</sub>	K <sub>a</sub>	K <sub>a</sub>
Tube	Rh	Rh	Rh
kV	30	30	30
mA	80	80	80
AC	AX06	PET	LiF200
DET	FPC	FPC	FPC
COL	0.60°	0.60°	0.25°
CTP	20	20	20
CTB	20	20	20

$\lambda_E$  = analytical line; kV, mA = voltage and current of X-ray tube; AC = analysing crystal (AX06 = multilayer synthetic crystal, PET = penterythritol, LiF200 = lithium fluoride); DET = detector (FPC = flow proportional counter); COL = collimator (0.60°, 0.25° = angle divergences); CTP = counting time of peak (s); CTB = counting time of background (s).

The measured intensities have been corrected for background, and correction with a blank sample was also applied to account for flux impurities. In order to determine concentration of major and minor elements, the simple algorithm proposed by Lucas-Tooth and Price (1961) was used:

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

where  $D_i$  and  $E_i$  are the parameters of the linear regression correlating the concentrations  $C_i$  (expressed as weight percentage, wt%) with the intensities  $I_i$  of the element 'i', and  $K_{i,j}$  are empirical coefficients correcting for matrix effects. The coefficients ( $D_i$ ,  $E_i$ ,  $K_{i,j}$ ) may be calculated from a set of reference samples using multivariate regression methods.

## RESULTS AND DISCUSSION

Tab. 3 provides a comparison of the chemical concentrations determined following the described procedure with the values recommended in the literature. In Fig. 1, the observed ( $C_{obs}$ ) and reference ( $C_{ref}$ ) concentration values (expressed as oxide wt%) of each determined element, together with  $RSEE$  values and the average concentration of the interval ( $C_a$ ), are graphically reported. The  $RSEE$  values, i.e. the accuracy achieved in the determination of major and minor elements, were calculated according to the following equation:

$$RSEE = \frac{100}{C_a} \cdot \sqrt{\frac{\sum (C_{obs} - C_{ref})^2}{(n-1)}}$$

In addition, data of Fig. 1 shows that *RSEE* values vary from 1.6% ( $\text{SiO}_2$ ) to 3.5% ( $\text{Fe}_2\text{O}_3$ ) for major elements and from 5.3% ( $\text{P}_2\text{O}_5$ ) to 8.1 (MnO) for minor elements, and results significantly higher than those observed by Lezzerini *et al.* (2013) on fused glass discs with a sample/borate ratio of 1:9. This behavior is not surprising and it is easily explained by the increase of statistical counting errors due to the higher dilution ratio.

## CONCLUSIONS

Within the compositional range of the studied reference materials, the XRF determinations of major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements by using calibration parameters on fused glass disks prepared with high sample/borate ratio (1:30) yield accuracies of measurement significantly worse than those obtained using a lower sample/borate ratio (1:9) (Tamponi *et al.*, 2003; Lezzerini *et al.*, 2013).

The accuracy is better than 4% for major elements and better than about 8% for minor elements. However, these errors may still be considered acceptable for many mineralogical and petrographic purposes.

Tab. 3 - Accuracy in the determination of major and minor elements.

Standard	Na <sub>2</sub> O		MgO		Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		P <sub>2</sub> O <sub>5</sub>		K <sub>2</sub> O		CaO		TiO <sub>2</sub>		MnO		Fe <sub>2</sub> O <sub>3</sub>	
	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>	C <sub>ref</sub>	C <sub>obs</sub>
AC-E	6.60	6.57	0.03	0.14	14.82	14.85	70.95	71.48	0.01	0.01	4.53	4.60	0.34	0.05	0.11	0.12	0.06	0.06	2.55	2.42
BIR-1	1.75	1.82	9.66	9.72	15.31	15.46	47.63	47.35	0.05	0.03	0.03	0.01	13.21	13.37	0.96	0.95	0.17	0.17	11.23	11.50
DR-N	3.06	3.04	4.50	4.41	17.92	18.03	54.05	54.54	0.26	0.24	1.74	1.75	7.21	7.11	1.11	1.10	0.23	0.20	9.92	10.06
DT-N	0.04	0.11	0.04	<0.01	60.38	60.57	37.18	36.81	0.09	0.07	0.12	0.13	0.04	<0.01	1.43	1.40	0.01	<0.01	0.67	0.54
DTS-1	0.02	<0.01	50.00	49.26	0.19	<0.01	40.74	40.40	<0.01	<0.01	<0.01	<0.01	0.17	<0.01	0.01	0.01	0.12	0.12	8.75	8.36
GS-N	3.83	3.76	2.34	2.38	14.90	14.74	66.85	66.75	0.28	0.28	4.70	4.75	2.54	2.19	0.69	0.68	0.06	0.04	3.81	3.75
GSR-2	4.05	4.05	1.81	1.89	16.99	16.94	63.67	63.70	0.25	0.26	1.99	1.94	5.46	5.45	0.55	0.54	0.08	0.07	5.15	5.16
JA-2	3.16	3.19	7.87	7.39	15.70	16.33	57.55	57.71	0.15	0.16	1.84	1.90	6.64	6.25	0.69	0.65	0.11	0.10	6.29	6.31
JA-3	3.18	3.01	3.66	3.73	15.60	15.13	62.36	60.24	0.11	0.12	1.41	1.35	6.29	5.94	0.68	0.65	0.11	0.09	6.60	6.18
JB-1a	2.78	2.75	7.86	8.04	14.71	14.98	52.89	53.50	0.26	0.26	1.44	1.44	9.36	9.54	1.32	1.32	0.15	0.14	9.23	9.12
JB-2	2.02	1.98	4.63	4.50	14.57	13.71	52.82	50.45	0.10	0.10	0.42	0.37	9.82	9.08	1.18	1.21	0.20	0.20	14.24	13.95
JB-3	2.81	2.71	5.18	5.12	16.83	17.53	50.85	51.70	0.29	0.29	0.78	0.77	9.82	9.87	1.44	1.47	0.16	0.17	11.84	12.20
JF-1	3.57	3.42	0.01	0.31	18.12	18.60	67.13	68.66	0.01	0.01	10.14	10.07	0.93	0.87	0.01	0.06	<0.01	<0.01	0.08	0.94
JF-2	2.48	2.46	<0.01	0.10	18.55	18.52	65.63	64.50	<0.01	<0.01	13.19	13.08	0.09	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.03
JG-1a	3.44	3.40	0.70	0.80	14.35	13.94	72.85	72.68	0.08	0.08	4.05	4.02	2.15	1.78	0.25	0.23	0.06	0.05	2.07	2.04
JG-2	3.57	3.64	0.04	0.21	12.48	12.38	77.37	77.98	<0.01	<0.01	4.75	4.73	0.80	0.41	0.04	0.06	0.02	0.01	0.93	1.09
JG-3	4.06	4.10	1.80	1.94	15.64	15.91	67.63	68.50	0.12	0.13	2.65	2.65	3.79	3.57	0.48	0.49	0.07	0.07	3.76	3.64
JGb-1	1.24	1.23	7.88	7.69	17.77	17.78	43.72	43.51	0.05	0.06	0.24	0.24	12.05	11.71	1.63	1.62	0.17	0.16	15.25	15.21
JP-1	0.02	<0.01	45.78	45.70	0.63	0.41	44.34	43.37	<0.01	<0.01	<0.01	0.03	0.57	0.20	<0.01	0.01	0.12	0.11	8.54	8.38
JR-1	4.15	4.18	0.09	0.29	13.06	12.90	76.40	76.90	0.02	0.01	4.47	4.56	6.04	0.35	0.10	0.08	0.10	0.10	0.97	0.83
MA-N	6.00	6.02	0.04	0.13	18.07	18.26	68.36	68.26	1.43	1.43	3.26	3.31	0.61	0.29	0.01	0.01	0.04	0.03	0.48	0.53
MO-3	0.73	0.79	8.75	8.38	13.81	13.54	38.00	38.46	2.17	2.16	0.21	0.22	15.91	16.03	1.47	1.42	0.22	0.22	18.73	18.71
MO-6	4.05	3.99	2.10	2.08	22.81	22.71	51.85	51.72	0.14	0.13	0.76	0.72	10.07	10.47	1.87	1.84	0.08	0.07	6.27	5.98
MO-7	2.07	2.02	6.51	6.52	17.73	17.58	41.10	41.54	1.09	1.09	0.76	0.76	14.73	14.83	3.42	3.52	0.15	0.15	12.44	12.26
MO-13	3.91	3.99	5.86	5.98	17.94	17.86	49.57	50.35	0.40	0.41	0.95	0.97	9.09	9.58	1.66	1.66	0.14	0.16	10.48	10.82
MRG-1	0.75	0.78	13.73	13.69	8.58	8.57	39.63	39.88	0.08	0.07	0.18	0.17	14.89	14.99	3.82	3.78	0.17	0.17	18.17	18.34
MW-1	8.55	8.62	0.35	0.42	21.85	21.88	58.34	58.19	0.05	0.03	6.16	6.22	1.11	0.79	0.40	0.39	0.13	0.12	3.06	2.87
MY-1	0.11	0.07	37.95	38.83	1.88	1.47	46.55	47.65	0.04	0.00	0.04	0.01	1.29	1.17	0.11	0.04	0.19	0.20	11.84	12.12
NIM-D	0.04	<0.01	43.38	43.27	0.30	<0.01	38.83	39.02	0.01	<0.01	0.01	<0.01	0.28	<0.01	0.02	0.17	0.22	0.22	16.91	17.05
NIM-P	0.37	0.33	25.35	25.67	4.18	4.15	51.14	51.21	0.02	0.02	0.09	0.08	2.66	2.35	0.20	0.18	0.22	0.23	12.77	12.54
NIM-S	0.43	0.51	0.46	0.49	17.43	17.35	63.99	63.86	0.12	0.11	15.43	15.54	0.68	0.30	0.04	0.05	0.01	<0.01	1.41	1.40
OU-6	1.84	1.94	2.49	2.51	21.27	21.23	59.67	60.58	0.12	0.13	3.17	3.14	0.77	0.43	1.04	1.10	0.29	0.31	9.34	9.52
SGD-1a	2.83	2.85	7.03	6.95	14.94	14.77	46.60	46.22	1.01	1.03	2.97	2.94	11.02	10.96	1.72	1.65	0.17	0.15	11.71	11.58
STM-1	9.11	9.11	0.10	0.16	18.73	18.70	60.75	60.15	0.16	0.13	4.36	4.35	1.11	0.93	0.14	0.12	0.22	0.24	5.32	5.38
SY-3	4.20	4.25	2.72	2.91	11.97	11.63	60.76	59.99	0.55	0.54	4.31	4.26	8.40	8.41	0.15	0.16	0.33	0.32	6.61	6.55
YG-1	3.62	3.67	0.13	0.24	13.14	12.72	73.80	72.99	0.03	0.02	5.09	5.02	1.11	0.71	0.20	0.24	0.05	0.04	2.83	2.65
401	0.04	0.10	6.39	6.83	0.39	0.17	3.71	4.01	0.06	0.07	0.11	0.10	88.89	88.41	0.04	0.01	0.02	0.02	0.35	0.74
402	0.04	0.10	10.21	10.35	0.94	0.54	4.68	4.63	0.09	0.10	0.28	0.25	83.01	81.80	0.06	0.01	0.03	0.02	0.66	0.41
403	0.05	0.04	25.25	25.01	0.79	0.53	3.32	3.41	0.08	0.06	0.26	0.24	69.61	70.31	0.05	<0.01	0.03	0.02	0.56	0.61
1880a	0.20	0.30	1.79	2.12	5.38	5.41	21.11	21.21	0.23	0.22	0.96	1.01	66.34	66.87	0.26	0.24	0.81	0.81	2.92	2.81
1882a	0.02	0.13	0.51	0.53	39.31	39.54	4.03	4.79	0.07	0.08	0.05	0.07	39.45	39.42	1.79	1.80	0.04	0.02	14.73	14.68
1883a	0.30	0.25	0.19	<0.01	69.76	69.63	0.24	0.77	<0.01	0.01	0.01	0.01	29.40	29.37	0.02	0.07	<0.01	<0.01	0.08	0.11

C<sub>ref</sub> = reference concentration value; C<sub>obs</sub> = observed concentration value.

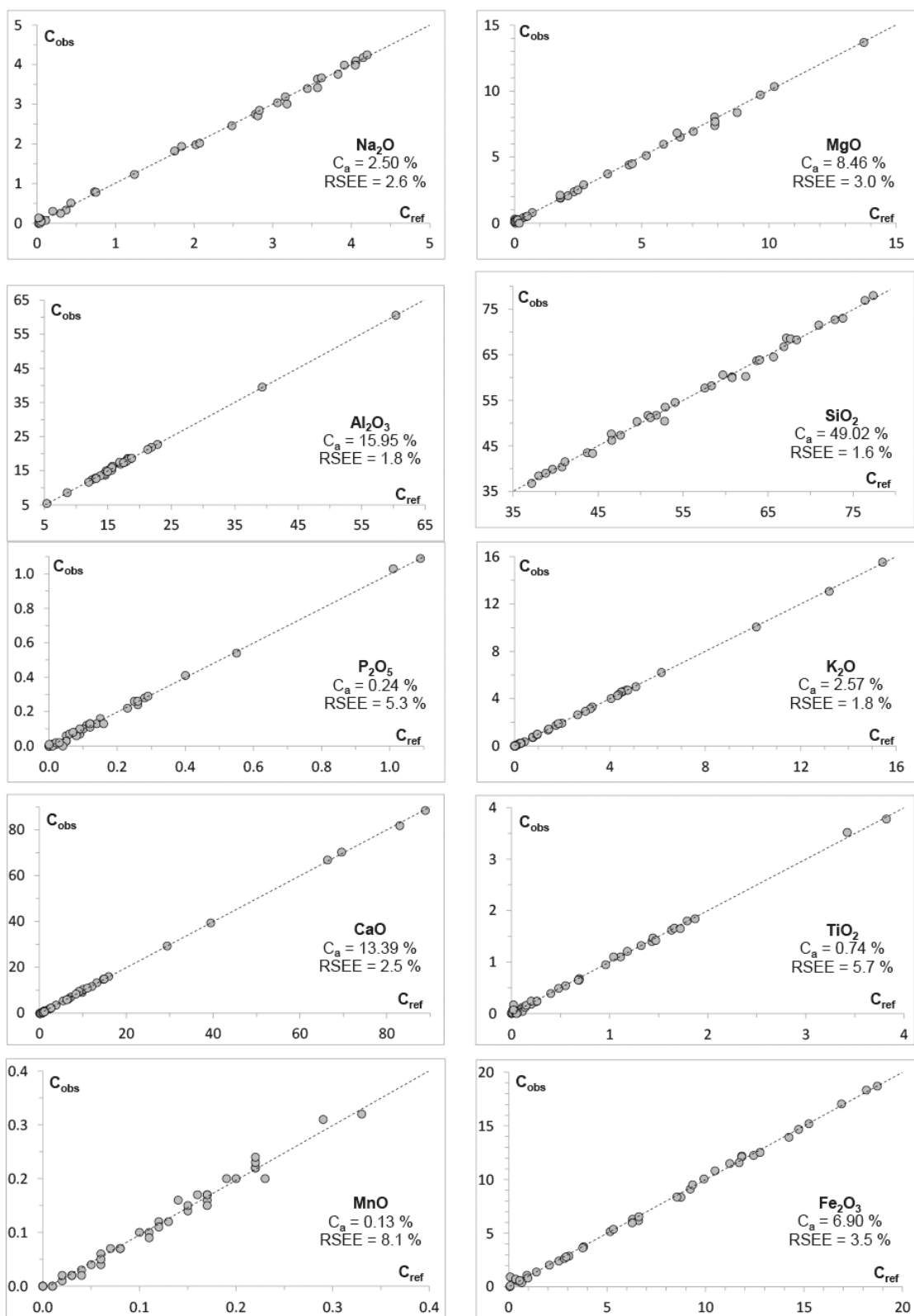


Fig. 1 - Accuracy in the determination of major and minor elements.



The main advantages offered by a high dilution ratio are the possibility of the use small amount of sample (a quite common case in cultural heritage studies) and the improvement of the quality of the fusion in high-melting materials. By contrast, the decrease of the analytical intensity makes less easy the determination of trace elements at the typical concentration levels of geological samples.

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