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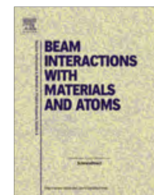

Chemical analysis of obsidian by a SIMS/EDX combined system

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ABSTRACT

A recently built combined EDX–SIMS system was used for a quantitative standardless analysis of obsidians. By using the novel scheme of analysis described in the paper, concentrations of 47 elements were measured. The range of concentrations analyzed varied by up to 8 orders of magnitude, from 10^{15} atoms/cm^3 to 10^{23} atoms/cm^3, which cannot be attained by any other analytical method based on electron or X-ray irradiations. The experimentally measured concentrations were compared with the data of XRF analysis: the data proved to differ in less than a factor of two for the majority of elements. The technique we suggest can be used to analyze almost any solid material.

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1. Introduction

Archaeologists and geologists analyze in their studies a great variety of materials: different organic materials, metals and alloys, ceramics, natural and human-made glasses, concrete, etc. A detailed chemical analysis of geo- and archaeological artifacts is typically supplemented by a special analysis. For example, a chemical composition analysis of any obsidian artifact is accompanied by the so-called Obsidian Hydration Dating analysis (OHD) [1].

The chemical analysis of such complex materials as natural glasses is carried out by X-ray Fluorescence Spectroscopy (XRF), Electron Microprobe analysis (EDX/WDX), or by Particle Induced X-ray Emission Spectroscopy (PIXE). The techniques mentioned above have advantages, as well as some limitations. First of all, none of the above techniques offers OHD which is highly necessary for the archaeological dating of obsidian artifacts.

It has recently been suggested that Secondary Ion Mass Spectrometry (SIMS) be used to perform the OHD analysis [2,3]. As compared with other techniques, the SIMS technique demonstrates an extremely high sensitivity (to 10^{-7} atomic %), a unique opportunity to analyze any element of the Periodic Table from Hydrogen to Uranium, and an opportunity to carry out analysis of the isotope ratio for any element with stable isotopes [4]. The critical disadvantage of SIMS which strongly limits its application in practical analytical work is a poor quantification [4,5]. Quite pure materials, such as semiconductor crystals, can be quantitatively analyzed by SIMS with an experimental error of about 10% by using special implanted standards. At the same time, the SIMS analysis of basic elements (a concentrations range of 1–100 at.%) is performed with an appreciably lower accuracy and needs a set of standards. In practice, the quantitative analysis of a complex material is done by using another analytical technique, and then the sample analyzed is used as a standard for the subsequent SIMS analysis. The EDX technique is widely used for this purpose.

We have recently modified our Cameca ims-6f ion microprobe available at Cinvestav – IPN (Mexico, DF) by installing an energy dispersive X-ray detector [6,7]. The principal idea of the modification was to use the EDX technique as an internal calibrating tool for the SIMS technique. In this paper we report on the application of this combined SIMS–EDX system for quantitative standardless analysis of obsidians.

The methodology of our analysis was as follows:

(1) A non-destructive standardless EDX quantitative analysis of basic elements (concentration >0.1 atomic %) by using the P/B ZAF method [8].
(2) SIMS quantification of the basic elements already quantified by EDX. The analysis included acquisition of Relative Sensitivity Factors (RSFs) for these elements and an extrapolation of RSFs for other elements by using the well known exponential relation between the secondary ion formation probability and the ionization potential of the element [4].

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(3) The use of the calibration curve to quantify other elements of interest detected in the mass spectrum.

It is important to note that we did not use any standards during this analysis.

2. Experimental

All experiments were performed with a Cameca ims-6f ion micro-probe. A negative oxygen ion beam was focused by a three-lens optical system and scanned over a 150 × 150 μm surface area. The secondary ions emitted from the central area of the experimental crater (approximately 40 microns) were focused onto the entrance of a double focusing mass spectrometer with a 90° magnetic sector. The secondary ions that had passed through the mass-spectrometer were detected by a Faraday Cup or by an Electron Multiplier, depending on the analytical signal. To avoid charging effect, i.e., formation of a strong surface electrical potential during the ion irradiation of the dielectrics, we deposited a 100 nm gold film on the experimental sample surface by the thermal evaporation method.

The EDX measurements were performed with a Bruker Quantax Energy Dispersive X-ray detector installed at the mass spectrometer, as demonstrated in Fig. 1. The experimental sample was irradiated by a normally incident 10 keV electron beam. The beam diameter was about 0.5 mm, and the registration take-off angle of characteristic X-rays was 60° with respect to the sample surface. We determined the optimal electron beam current during the experiment; all the measurements reported here were performed with the electron beam current as high as 0.2 μA. To avoid the charging effect in the EDX analysis discussed above, we covered the obsidian samples being analyzed by a thin carbon film of about 30-nm thickness prepared by the ion sputtering deposition technique. The EDX data were quantified by using the P/B ZAF method recommended by the provider of the EDX system [8].

The experimental obsidian samples were cut from a big rock from the Pachuca district (Central Mexico). The samples were polished by the standard technique; we used sequentially meshes of 400 grits, 800 grits, 1200 grits, and 1600 grits, and then finished with a cloth and a 1-micron diamond paste.

To estimate the accuracy of the experimental technique suggested, we compared our quantitative analysis with the independent analysis carried out at the Geoarchaeological XRF Laboratory, NM, USA, by the XRF method.

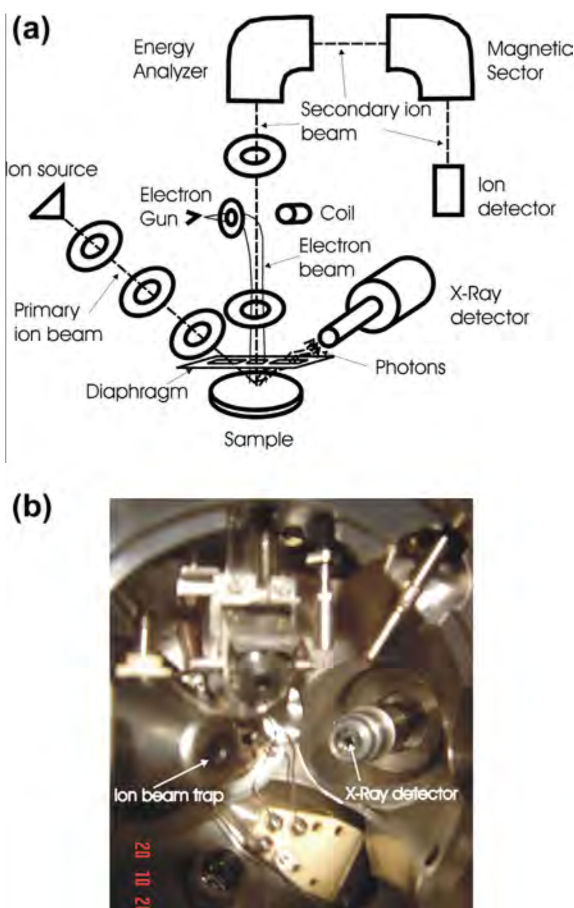


Fig. 1. Scheme of the combined SIMS–EDX instrument based on a commercial ims-6f Cameca ion microprobe (a) and photo of the main chamber with installed EDD (b) (the photo taken with dismounted immersion lens).

3. Experimental results and discussion

Fig. 2 shows the experimental EDX spectrum with identified elements. The Table below Fig. 2 shows the calculated compositions. The elements corresponding to the materials of the sample holder and diaphragms, i.e., tungsten and copper, were excluded from the list of elements analyzed.

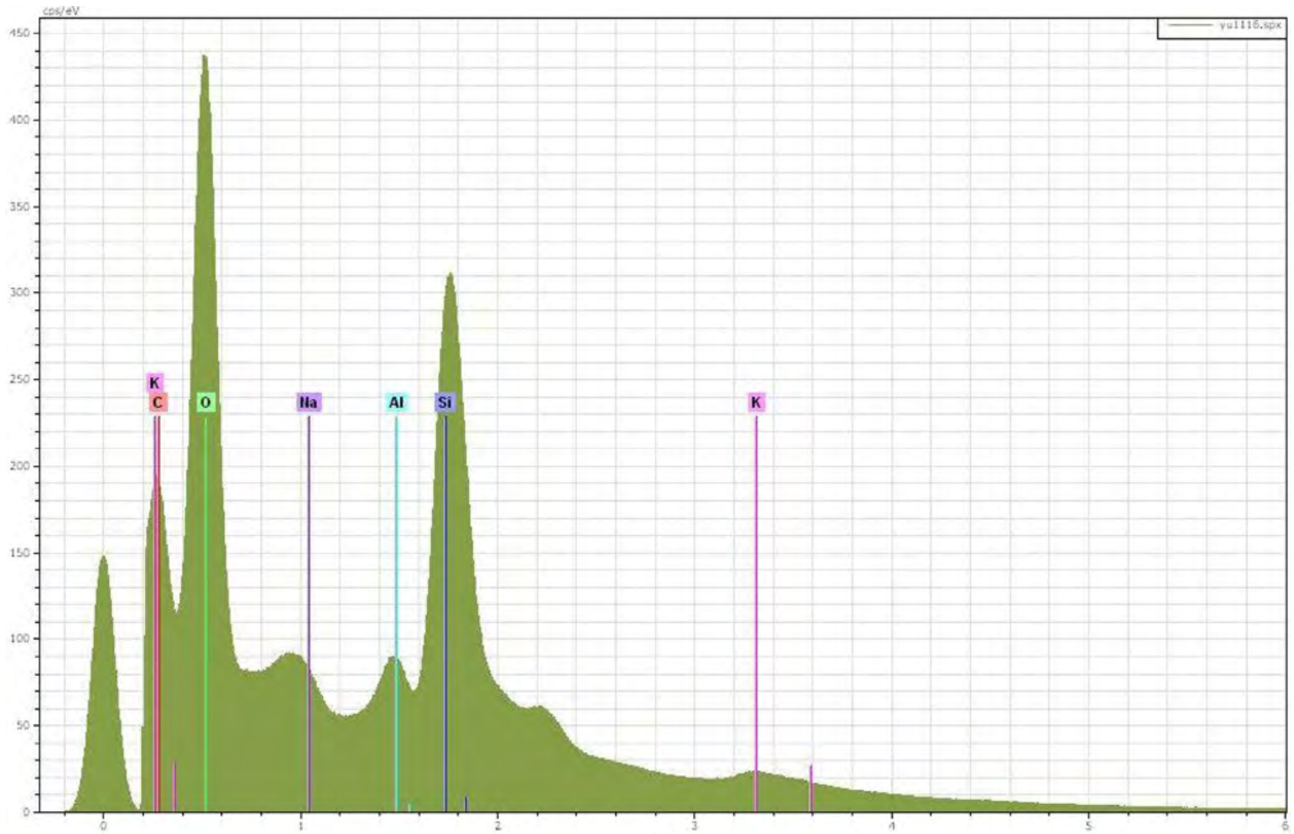
Fig. 3a–c shows the SIMS mass spectrum of secondary positive ions measured for the obsidian sample. Because of the dynamic range of the analysis of more than 8 orders of magnitude, almost all elements of the Periodic Table were identified in the mass spectrum. This considerably complicated the quantitative analysis because of the existence of many mass interferences between atomic and cluster secondary ions. To avoid the interferences, we applied a voltage offset of −80 V to the sample potential biased at +5 kV [5].

First of all, we calculated RSFs for the elements quantified with EDX and plotted them as a function of the ionization potential of the element. To this end, we used the well known exponential relation between the ion yield of the element analyzed and its ionization potential I_p measured experimentally and confirmed by the existing theoretical models [4,5]:

$$P^{+} \propto \exp\left[-\frac{I_p - \Phi}{\varepsilon_n}\right], \tag{1}$$

where Φ is the work function of the emitting surface, and ε_n is the constant characterizing the ionization process.

Fig. 4 shows the calibration curve built by extrapolating the SIMS data for the high-concentration elements. Fig. 4 also demonstrates the RSFs obtained for some elements implanted in a SiO_2 crystal and measured by a quadruple SIMS instrument [5]. These RSFs lie surprisingly close to the extrapolation curve plotted for our experimental results in spite of the fact that the mass spectrometer of another type was used. This leads to the conclusion that such implanted standards can be used for the quantitative SIMS analysis of the elements of interest in natural glasses. Another important observation from Fig. 4 is a relatively high deviation of the experimental RSFs from the fitting curve: they differ in more than two times. We suppose that this is the experimental error of our standardless technique because this is a typical situation for any SIMS analysis. The estimated RSFs were used to quantify the depth profiles obtained for 48 elements (see Fig. 5, as an example). To obtain the profile, 17 elements were measured during approximately 12 min to get a good statistics and to avoid transient and surface contamination effects. The atomic density of obsidian was chosen to be equal to the silicon oxide density: 7.8E22 atoms/cm^3. The ion intensity of silicon was used as a matrix



Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	[wt.%]	Error in wt.%	K fact.	Z corr.	A corr.	F corr.
Oxygen	K-series	46.078149	46.07814948	60.65515288	46.078149	1.335154304	1	0.842771	0.72911	1.000489
Silicon	K-series	37.036009	37.03600931	27.77272016	37.036009	0.955698689	1	0.051608	0.94903	1.000526
Aluminium	K-series	7.3580706	7.35807056	5.743459813	7.3580706	0.210448681	1	0.075413	0.936083	1.013946
Sodium	K-series	2.6850283	2.685028328	2.459748031	2.6850283	0.095226823	1	0.181832	0.84627	1.004138
Potassium	K-series	4.0864781	4.086478107	2.201241411	4.0864781	0.127189327	1	0.007287	0.988425	1.001711
Magnesium	K-series	0.0280998	0.028099849	0.024349203	0.0280998	0.000717052	1	0.118989	0.897691	1.009154
Calcium	K-series	1.346732	1.346731972	0.707703746	1.346732	0.058670826	1	0.00509	0.993875	1.000404
Iron	K-series	0.9682187	0.968218724	0.365132079	0.9682187	0.049234747	1	0.000313	1.0246	1
Barium	L-series	0.3822464	0.382246401	0.058621154	0.3822464	0.034557608	1	0.000645	1.008706	1.001091
Titanium	K-series	0	0	0	0	0	1	1	1.005041	1.000739
Manganese	K-series	0.0309673	0.030967272	0.011871525	0.0309673	0.000774735	1	0.000534	1.018903	1.000417
	Sum:	100	100	100						

Fig. 2. EDX spectrum obtained for the obsidian sample (see details in the text). The Table below the figure shows the composition calculated.

signal in all measurements. Then the concentration of the element x was calculated as:

$$C_x = \frac{I_x^+}{I_m^+} \cdot RSF_x, \quad (2)$$

where I_i is the secondary ion intensity of the element of interest (x) and of the matrix element (m). We used atoms/cm^3 in our calculations to compare the EDX, XRF, and SIMS data.

Table 1 summarizes all the data obtained in the quantitative SIMS analysis. Here we also compare the SIMS measurements with the data of external XRF measurements. We do not compare the EDX and XRF data, because these two techniques are really similar and any difference in the quantitative analysis performed by these techniques can be explained by an operator's error or a sample inhomogeneity.

As mentioned above, the interference between atomic and cluster ions gives rise to a special problem in the SIMS quantification. For example, the interference between $^{14}N^+$ and $^{28}Si^{++}$ complicates a nitrogen analysis. The High Mass Resolution SIMS regime should be applied to resolve the problems encountered in this and similar cases. We did not perform such an analysis in this study.

The experimental data obtained in our studies and the calculations which we carried out demonstrate some important benefits of the quantitative SIMS–EDX analysis:

(1) Almost all elements of the Periodic Table can be analyzed quantitatively quite effectively.

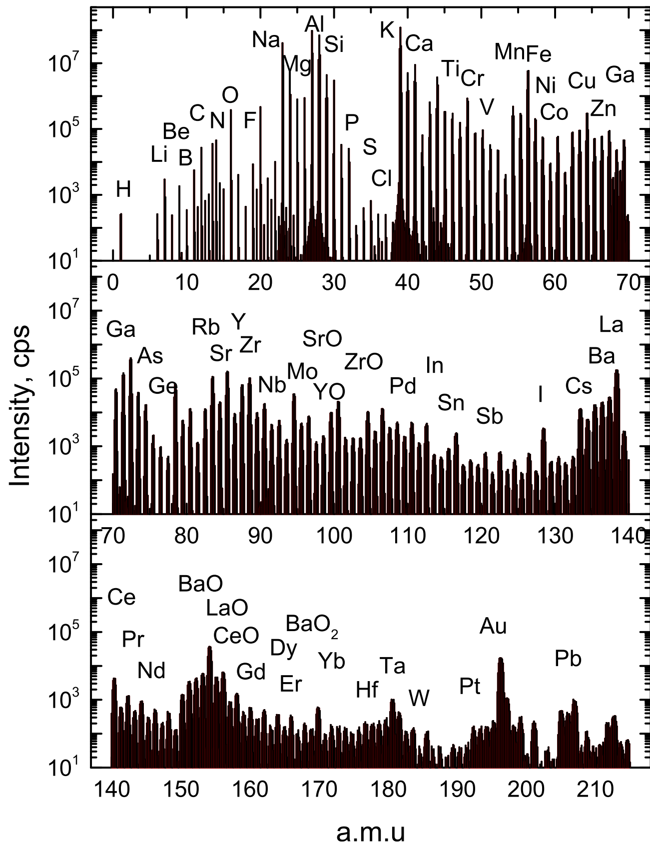


Fig. 3. SIMS mass-spectrum obtained for the obsidian sample. The majority of the elements of the Periodic Table are identified.

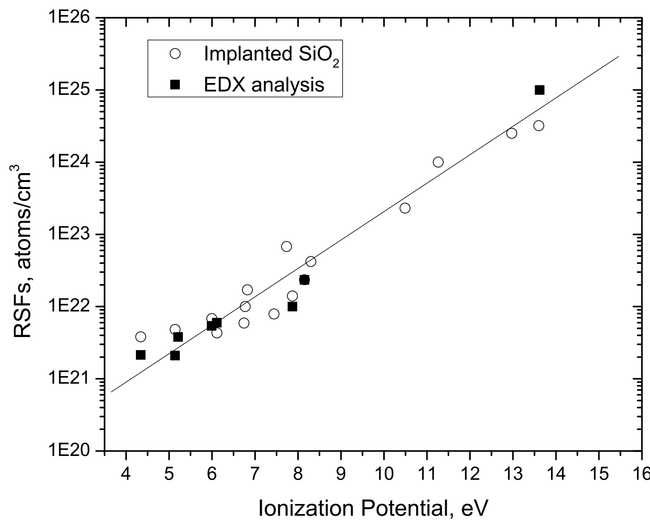


Fig. 4. SIMS Relative Sensitivity Factors calculated for the composition determined by EDX as a function of the ionization potential of the element. The RSFs for a set of elements implanted in SiO_2 are shown for comparison [4].

(2) The dynamic range of the analysis is as high as 8 orders of magnitude, from 10^{15} to 10^{23} atoms/cm^3.
(3) Light elements, such as H, Li, Be, and C, are analyzed efficiently. This cannot be attained by the EDX, PIXE or XRF techniques.
(4) The experimental error in the quantitative SIMS analysis of the majority of elements is relatively low; the high experimental error for a number of elements can be decreased by using the implanted standards prepared with a SiO_2 crystal.
(5) The absolute experimental error of the SIMS analysis looks relatively high; on the other hand, the relative error of such an analysis (i.e., the experimental error for a set of similar samples measured under the same experimental conditions) does not exceed 10%.
(6) The combined SIMS–EDX technique we have developed can be efficiently applied to any unknown solid material with a complex chemical composition.
(7) Almost all modern SIMS instruments with an electron gun installed can be equipped with an additional Energy Dispersive X-ray Detector.
(8) If necessary, the analysis of the isotope ratio and the OHD analysis can be carried out in addition to the chemical analysis.

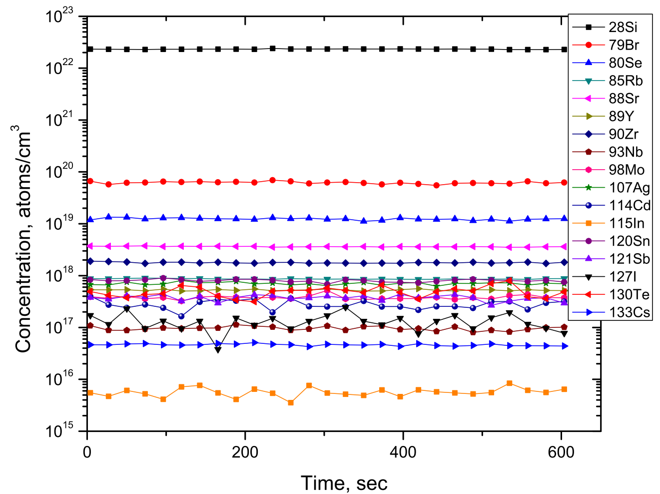


Fig. 5. Concentrations of 17 elements in the obsidian sample. A silicon ion signal was used as a reference signal for all measurements.

Table 1
The elemental composition of the obsidian sample defined by EDX-SIMS in a comparison with independent XRF data.

Element	SIMS	XRF*	Error	Element	SIMS	XRF	Error
H	1.1E21	–		Y	7.6E17	1.5E18	
Li	4.7E18	–		Zr	1.7E19	1E19	
Be	1E18	–		Nb	9.6E17	1E18	
B	2.6E18	–		Mo	3.8E17	–	
C	1E19	–		Ag	7E17	–	
F	5.7E19	–		Cd	2.5E17	–	
P	1.3E19	–		In	5.6E15	–	
S	6.8E17	–		Sn	7.8E17	–	
Cl	1.3E19	–		Sb	4E17	–	
Ca	5E20	1E21	x2	I	1.2E17	–	
Ti	8E19	3E20	x4	Te	4.8E17	–	
V	2.7e18	–		Cs	4.6E16	–	
Cr	<1.6E20	–		Ba	6.3E19	7.4E19	
Mn	5.6E19	8.6E19	x2	La	7.3E16	–	
Fe	7.5E20	9.3E20		Ce	1.2E17	–	
Ni	<4.4E18	1E18		Ta	4.4E16	–	
Co	1.3E18	–		W	<1E17	–	
Cu	<3.8E18	2.8E17		Pt	<1E17	–	
Ga	4.2E18	1.4E18	x3	Au	<1E17	–	
Ge	9.7E18	–		Hg	<6E16	–	
As	2.7E18	–		Tl	7E14	–	
Se	6.1E18	–		Pb	2.4E18	1.5E18	x2
Rb	8.7E18	9.1E18		Bi	2.6E16	–	
Sr	5.6E18	1E19	x2	Zn	<1E20		

* XRF measurements were carried out at the Geoarchaeological XRF Laboratory, NM, USA.

4. Conclusion

We have demonstrated an efficient quantitative standardless analysis of an obsidian sample by the combined EDX–SIMS technique. Almost 50 elements of the Periodic Table with the concentrations ranging from 10^{15} atoms/cm^3 to 10^{23} atoms/cm^3 were quantified with a reasonable accuracy. In principle, both analyses, i.e., SIMS and EDX, can be carried out under the same vacuum conditions, the same limited area of the sample surface can be analyzed successively. The EDX–SIMS combined instrument represents a useful tool for 3-D chemical and isotope analysis of geological and archaeological samples.

Acknowledgments

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