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Non Destructive Sourcing of Obsidians by Two Different Home Made pXRF Devices: Analytical Capabilities for Provenance Studies

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Abstract

The main objective of this work was to characterize and test provenance discrimination of twenty two obsidian samples: twenty samples from Ecuador (Cotopaxi, Quiscatola, Mullumica, Rio Guambi e Oyacachi) and two from Italy. Two portable Home-MadeX-ray fluorescence spectroscopy (pXRF) devices were used, both with a SiPIN detector, one employing an Ag X-ray tube and another with a W X-ray tube. Elements K, Ca, Ti, Mn, Fe, Rb, Sr, Y, Zr and Nb were detected in all samples. The two-dimensional graphs of ratios Rb/Fe vs. Rb/Sr, Mn/Ca vs. Rb/Sr,Zr/Fe vs. Rb/Sr, Ti/Mn vs. Rb/Sr showed that four samples of obsidian from Cotopaxi are grouped to form a distinct group as well as two samples of obsidian from Quiscatola, while samples Mullumica, Rio Guambi and Oyacachi form a large group. Results were compared with those obtained by more robust techniques, for instance, INAA, ICP and PIXE. A good relative analytical capability was observed for the two systems used for elemental characterization and provenance studies.

Key-words: Home-made pXRF, portable X-ray fluorescence spectroscopy; obsidians, chemical characterization; provenance studies.

1. Introduction

Obsidian has been a precious raw material of the prehistoric lithic industries, and as such was the object of long-distance, direct procurement expeditions, and/or was integrated in somewhat structured exchanges networks. The sources of this 'glassy' volcanic rock are rare, and spatially limited. Hence the determination of the origin of those found in archaeological sites is an excellent index of cultural territories extensions and of their relationships at a regional scale. The chemical composition and physical properties of obsidians are in principle specific to each source, which therefore offer different possibilities of characterization for sourcing purposes (F.-X. Le BOURDONNEC et al., 2014). In southern America, where the obsidian sources are located in the Andean belt, almost all provenance studies were obtained by their elemental composition, using neutron activation (INAA) (Burger and Asaro, 1977; Yacobaccio et al., 2004), laboratory-based X-ray fluorescence (XRF) (Burger and Asaro, 1977; Asaro et al., 1994; Burger et al., 1994), particle induced X-ray emission (PIXE) (Bellot-Gurlet et al., 1999; Seelenfreund et al, 2002) and inductively coupled plasma emission mass spectrometry (ICP) (Pereira et al., 2001; Bellelli et al., 2006). Fission-track dating was essentially in use during the past century (Miller andWagnet, 1981; Bigazzi et al., 1992; Dorighel et al., 1998). In order to determine the 'sphere of influence' of any given source and its far away fringes, it is essential to source as many archaeological samples as possible, and when possible the totality of an obsidian assemblage (Carter et al., 2008). This is also demanded to establish the chaînesopératoires at work (Carter et al., 2006; Lugliè et al., 2008, 2009). Finally, the use of non-destructive methods is often required by the archaeologist in charge of the analyzed samples, or by local authorities. PIXE and XRF can be used in a non-destructive mode (Poupeau et al., 2010). However, a limiting factor about PIXE is the availability of particle beams. XRF is cheap and fast and corresponds to the above requirement. Thus, in an early phase of Andean obsidian provenances studies Burger and Asaro (1977) used XRF to characterize more than 800 obsidian artefacts. The museum specimens and some others which could not, whatever the reasons, be brought to analytical centers, could not be studied by such XRF laboratory-based apparatus.

However, since the late 2000 decade a number of portable XRF (pXRF) instruments became available and were applied to obsidian studies (Craig et al., 2007; Nazaroff et al., 2010; Elias et al., 2009; Forster et al., 2012;

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Speakman et al.,2013, Vázquez et al., 2012; Campbell and Healey, 2016; Frahm, 2013; Forster and Grave, 2012; Lynch et al., 2016;

Otero and Stern, 2005; Nicholas, 2001;Nicola and Grave, 2012; Stern et al., 2000; Smith et al., 2007; Nagy, 1999; Brown et al., 2004; F.-X. Le BOURDONNEC et al., 2012; Gurlet et al., 2005; F.-X. Le BOURDONNEC et al., 2011). Two portable EDXRF equipments (pXRF) devised at State University of Londrina for archaeometric applications (Lopes et al., 2008) were used in this work with the main objective of testing their potentialities for obsidians provenance purposes, by analyzing a set of 20 samples taken in various Ecuadorian sources and two samples from Italy.

2. Materials and Methods

2.1 Sampling

The Ecuadorian sources of obsidian were first described at the end of the 19th century, where it was also observed that they had been "worked…by the indians for the making of weapons and ornaments" (Reiss, 1874, 1902). Recent investigations have shown that these sources are all linked to a major, about 20 km diameter, volcanic structure, the Chacana caldera (Hall and Mothes, 1997). The major obsidian outcrops are, on the northern edge of the caldera the two nearby rhyolitic flows of Mullumica and Callejones, and in a more internal zone, the volcanic breccia deposits of Cerro Yanaurcu and Loma Quiscatola (Bigazzi et al., 1992; Dorighel, 2000). The Mullumica and Callejones flows having a concordant fission-track age of about 0.17-0.18 Ma and same elemental type of composition are considered as contemporaneous and forming a single obsidian source. The Mullumica samples analyzed in this work with prefixes CM and CSM come from its bottom and top flow units respectively, while the samples with a prefix OYA belong to the Callejones flow (Dorighel et al., 1998). In addition, two samples, with references GMB, were taken in a secondary Mullumica obsidian source, as pebbles lying on the riverbed and bank of the Rio Guambi. The Quiscatola (QSC) and Yanaurcu obsidians, which present ages of about 1.4 Ma and undistinguishable elemental compositions, are also considered as making a single, albeit somewhat more extended source. A last group of samples, CTX, was collected among the clastic deposits of the still active Cotopaxy volcano. More than 98% of the obsidian sourced, from prehispanic sites, were found to come from these two sources, the origin of the few remaining outliers being undetermined (Burger et al., 1994; Dorighel et al., 1998; Bartolomé et al., 1999; Dorighel, 2000). The various analytical approaches used in these early works, were all based on laboratory-linked techniques. Because of the importance of obsidian in the Ecuadorian prehistory, and of the need to proceed to analyses in situ, for archaeological purposes, we selected twenty samples to test the capabilities of PXRF analyses in source identification and elemental composition.

The collection of samples from Ecuador consists of four different primary sources and a secondary source. These five sources are in the vicinity of Quito, in the graben interandean between the Cordillera Occidental and the Cordillera Real, as shown in Figure 1 (Gurlet et al, 2008), with the following areas: metamorphic punch of the Cordillera Real, undifferentiated volcanic material, volcano-clastic deposits of InterAndean graben, obsidian, silicic volcanic centers, andesitic lava flow, volcanic products, Antisana, normal faults and graben InterAndean craters and eruptive mouths. Table 1 shows a brief description of the obsidian samples analyzed by the pXRF systems employed in this study.

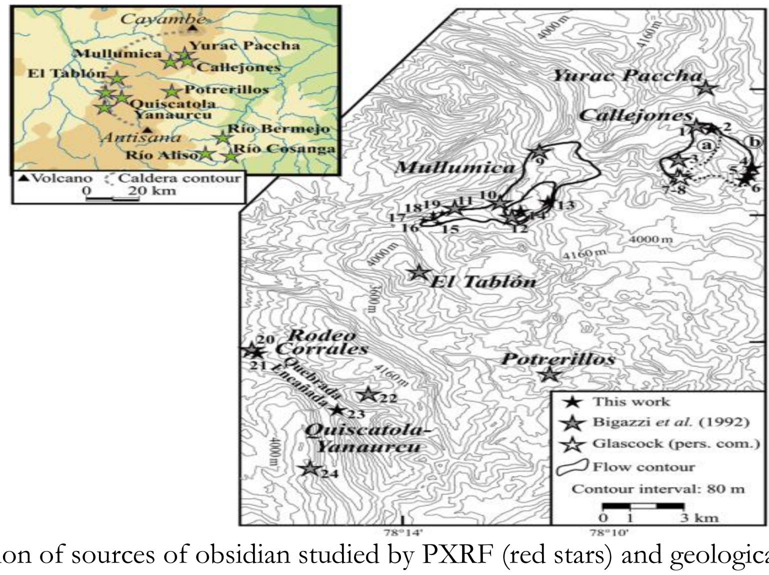

Figure 1 – Location of sources of obsidian studied by PXRF (red stars) and geological map of the Sierra de

Guanami (Gurlet et al, 2008).

According to data obtained from a fission track (FT) dating study, these sources may have been exploited by pre-Hispanic civilizations in their, socio-cultural and socio-economic systems (Duttine et al., 2007). These samples were kindly provided by Professors Dr. Rosa B. Scorzelli (CBPF-Brazil) and Dr. Gerard Poupeau (CNRS-France), which enabled this work. Also two obsidians samples from Sardinia (Italy) were measured (474 and BALT21), just for comparison purposes.

Table 1 – Occurrences and fission-track ages of the Ecuadorian obsidians analyzed by PXRF.

Source	Obsidian occurrence	FT age (Ma)	N	Ref
Callejones flow	Segregations in lava	0.17-0.18	4	1
		0.18-0.21	5	2
Cotopaxi	Pyroclastic deposits	0.02-0.54	4	2
Mullumica lower flow	Segregations in lava	0.17-0.20	6	1
		0.18-0.20	5	2
Mullumica upper flow	Segregations in lava	0.18	2	1
		0.18-0.20	1	2
Rio Guambi	Pebbles in mountain stream terrace	n.m		
Quiscatola	Blocks in volcanic breccia	1.30-1.64	2	1
		1.38-1.64	2	

FT, fission track age; N, number of samples dated; n.m., not measured.

(1) Bigazzi et al. (1992) and (2) Dorighel et al. (1998) FT plateau-ages. The precision on individual ages is of about ±10%.

2.2 Instrumental

. The pXRF-LFNA-02 system used for elements with atomic number greater than 26 is composed of a 4W X-ray tube with Ag (filter and target) and a Si-PIN detector model XR-100CR AmpetkInc., which has a resolution of 221 eV for the 5.9 keV line (25 µm-thickness Be window and Ag collimator) (Fig. 2). The pXRF-LFNA-03 system, used for elements with atomic number lower than 26, is composed of a 4W X-ray tube (with W target) and a Si-PIN detector model XR-100CR Amptek Inc., which has a resolution of 149 eV for the 5.9 keV line (12.7 µm-thickness Be window and Ag collimator).

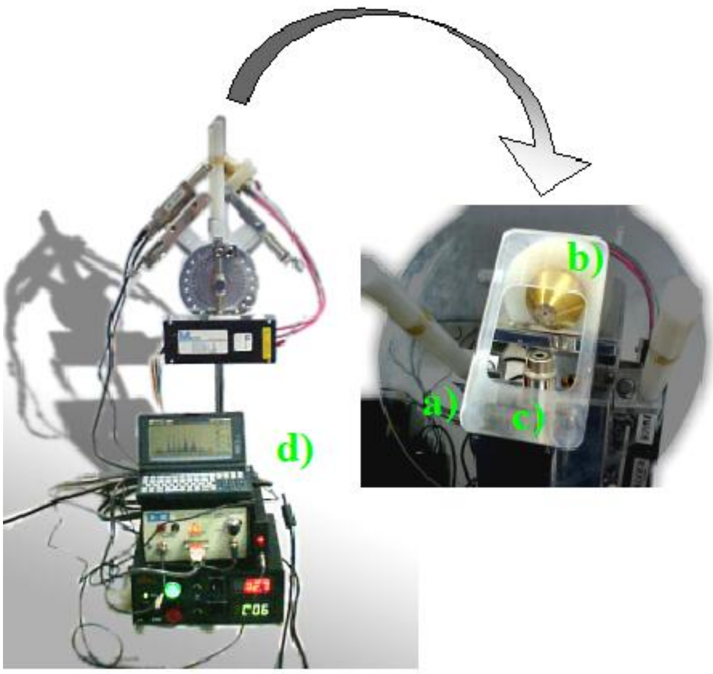

Figure 2- Portable X-Ray Fluorescence-PXRF-LFNA-02: a) sample port, b) mini X-ray tube,c) X-ray detector,d) standard electronic andlaptop computer.

3 Results and discussion

3.1 Optimization of the mobile devices

The analytical sensitivity of the two mobile devices was optimized for obsidian matrix using a factorial design 2^4 on current and voltage applied to the X-ray tube and distances tube-sample and detector-sample. The samples were measured without any previous preparation with a 1000 s excitation-detection time.The samples were not broken, the flattest area possible was used for the measurements, although some samples were very irregular, without flatland. The thickness of the samples ranged from 2 to 10 mm, for purposes of XRF, any sample of the order of 1 mm already attenuates all the X-rays lines of interest, making all equivalent samples from this point of view. The intensities of characteristics$K\alpha$ and $L\alpha$ X-rays were employed for the elements detection. The spectra were analyzed bytheWinQ-XAS software. Only net areas greater than three standard deviations above the mean background level were accepted. The WinQxas data were transposed under Excel for Windows for their analyses. For elemental and cluster analysis were usedabsolute concentrationdetermined through calibration curves obtained from standard obsidian samples. Statistical analyses used SPSS for Windows (Negash, 2006). Elements K, Ca, Ti, Mn, Fe, Rb, Sr, Y, Zr and Nb were detected in all obsidian samples. Figure 3 and 4show, respectively,the spectrum measured for a reference sample (Sierra de Pachuca) with the equipment pXRF-LFNA-02 (Ag anode) and pXRF-LFNA-03 (W anode).

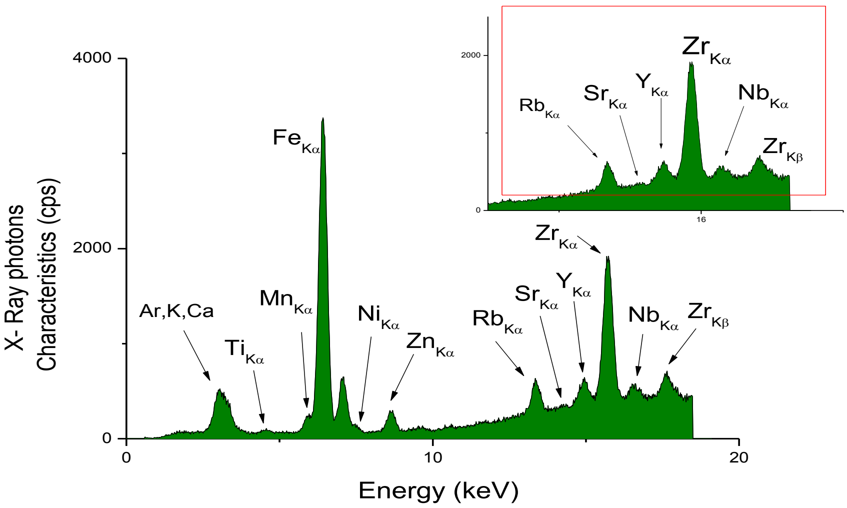

Figure 3 – Energy spectrum of the measurement performed withthe reference sample Sierra de Pachuca with the equipment pXRF-LFNA-02, Ag anode X-ray tube.

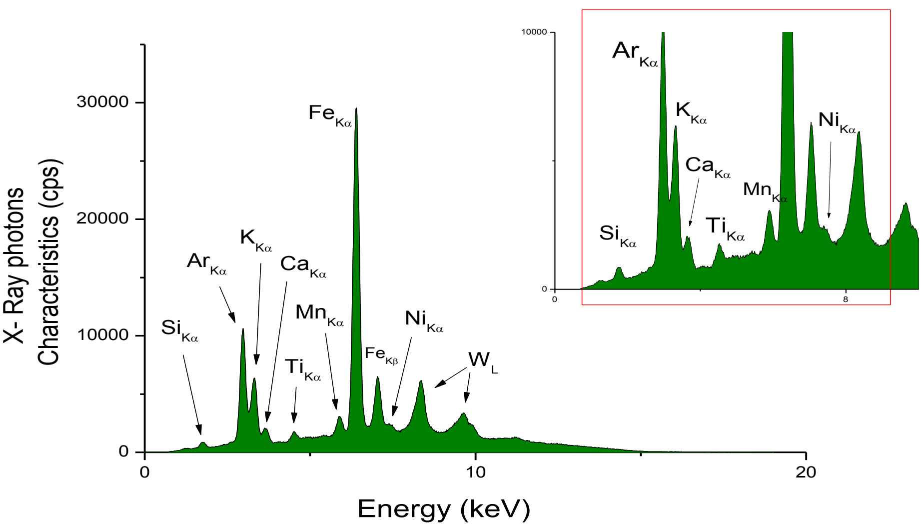

Figure4 – Energy spectrum of the measurement performed with the reference sample Sierra de Pachuca with the equipment pXRF-LFNA-03, W anode X-ray tube.

3.2 Application to Ecuadorian obsidian sources

Figures 5 and 6 show typical spectra of anobsidian sample from Mullumica sourcemeasured with the pXRF-LFNA-03 system and pXRF-LFNA-02, respectively.The samples measured by different techniques are not the same but are part of the same population as were taken from the same block of obsidian.

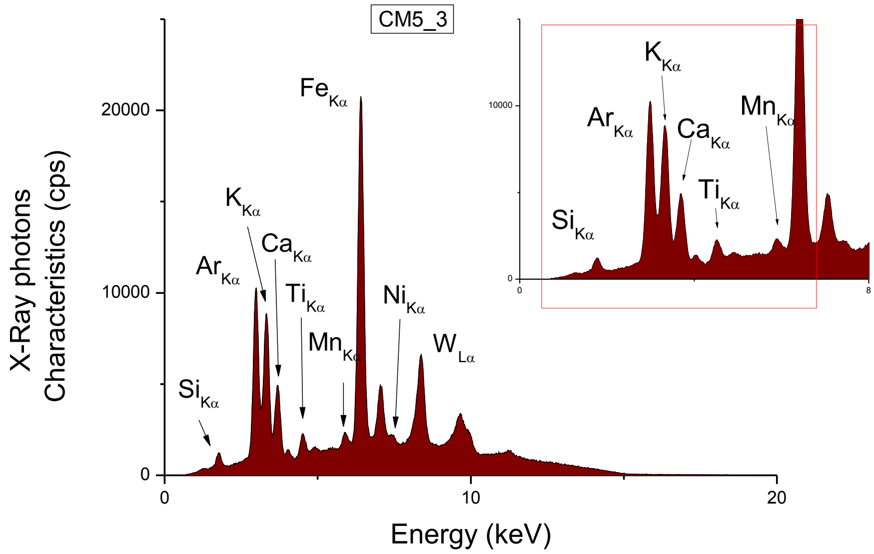

Figure5 – Energy spectrum of the measurement performed for CM5 sample with the equipment pXRF-LFNA-03, W anode X-ray tube.

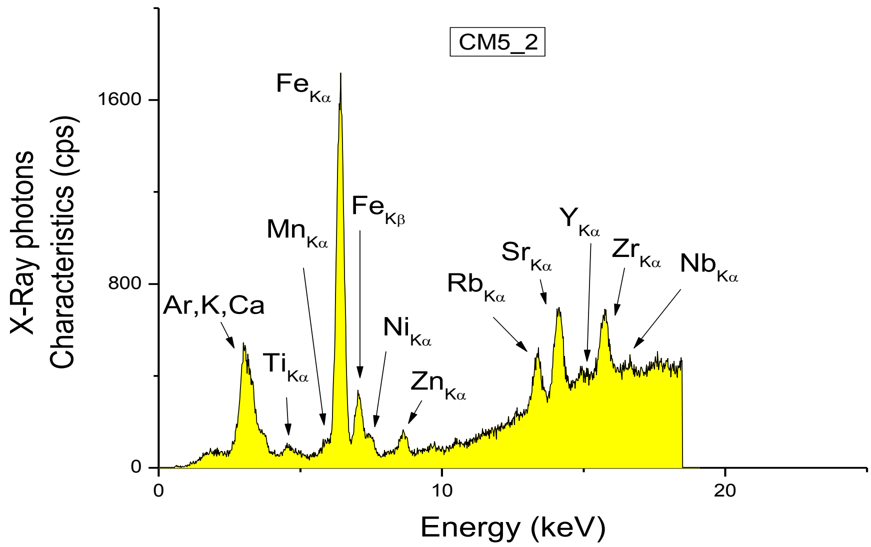

Figure 6 – Energy spectrum of the measurement performed for CM5 sample with the equipment pXRF-LFNA-02, Ag anode X-ray tube.

3.2 Provenance Studies

The measured K, Ca, Ti, Mn, Fe, Rb, Sr, Y, Zr and Nbintensities were used to construct discriminant diagrams (Seelenfreund, 2002). The Figures 7, 8, 9 and 10 show plots of Zr/Fe vs Rb/Sr, Mn/Ca vs Rb/Sr, Rb/Fe vs Rb/Sr and Ti/Mn vs Rb/Sr intensities values, respectively.It can be seen that the three obsidian geochemical types are very well discriminated.Figure 13 shows the dendrogram obtained by cluster analysis employing the Ward Method.

That is to say, both instruments pXRF-LFNA-02 and pXRF-LFNA-03 provided geochemical data for elements K, Ca, Ti, Mn, Fe, Rb, Sr, Y, Zr and Nb demonstrate significant analytical capabilities for obsidian provenance studies (Nazaroff, 2010). Literature reports that Rb, Sr, and Zrtrace-elements were able to distinguish among different obsidian geochemical source groups (Cecil, 2007).

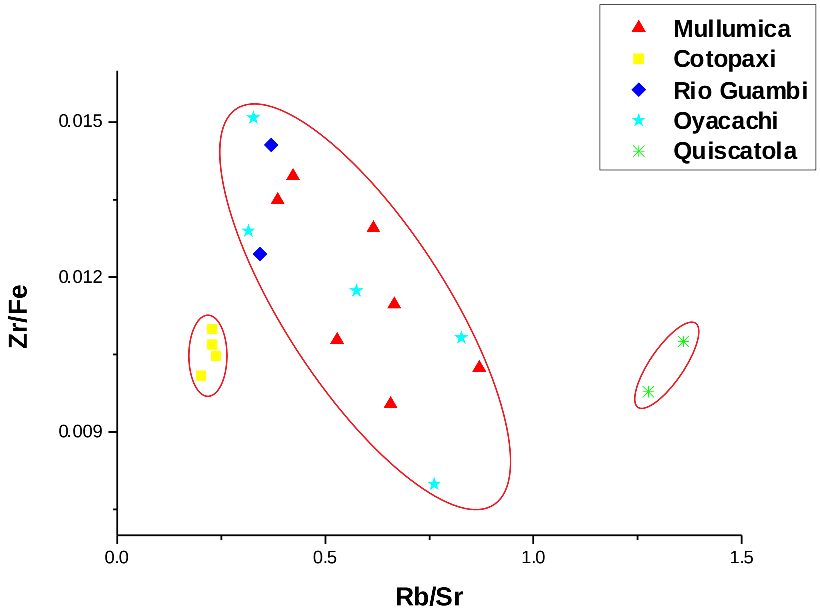

Figure 7 – Two-dimensional plot of the intensities values (Zr/Fe versus Rb/Sr) for the Ecuadorian samples.

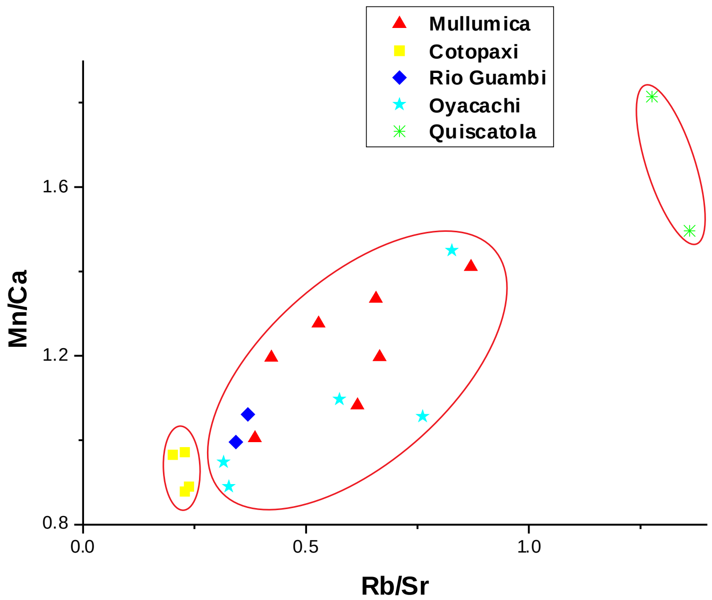

Figure 8 – Two-dimensional plot of the intensitiesvalues(Mn/Ca versus Rb/Sr) for the Ecuadorian samples.

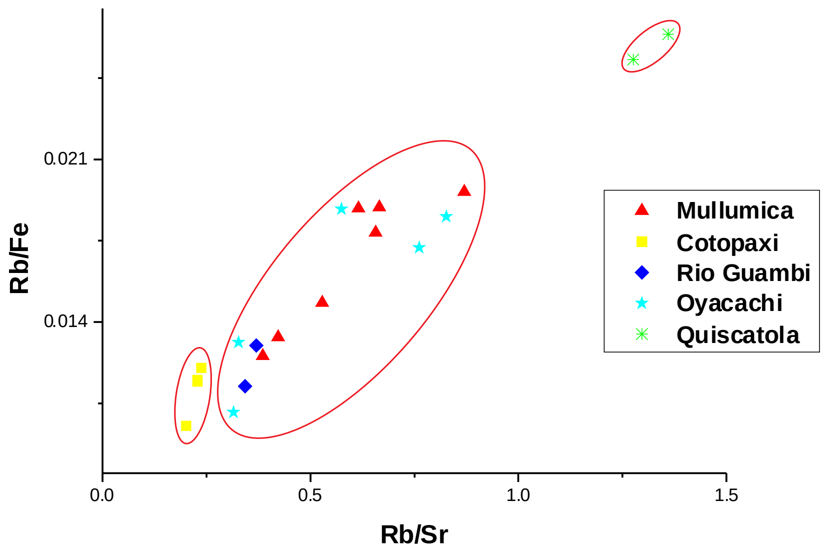

Figure 9 – Two-dimensional plot of the intensities values (Rb/Fe versus Rb/Sr) for the Ecuadorian samples.

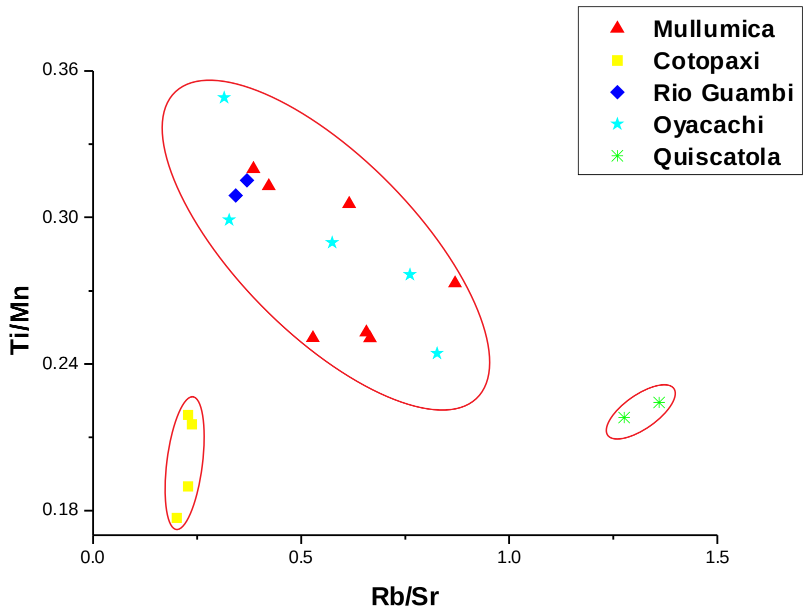

Figure 10 – Two-dimensional plot of the intensities values (Ti/Mn versus Rb/Sr) for the Ecuadorian samples.

Two-dimensional plotsemploying concentration valuesof ICP and PIXEdata for the same obsidians are showed in Figures 11 and 12.Samples are best grouped in Figure 8, pXRF intensities data of this work, than in the chart shown in Figure 11 (ICP concentrationsdata).

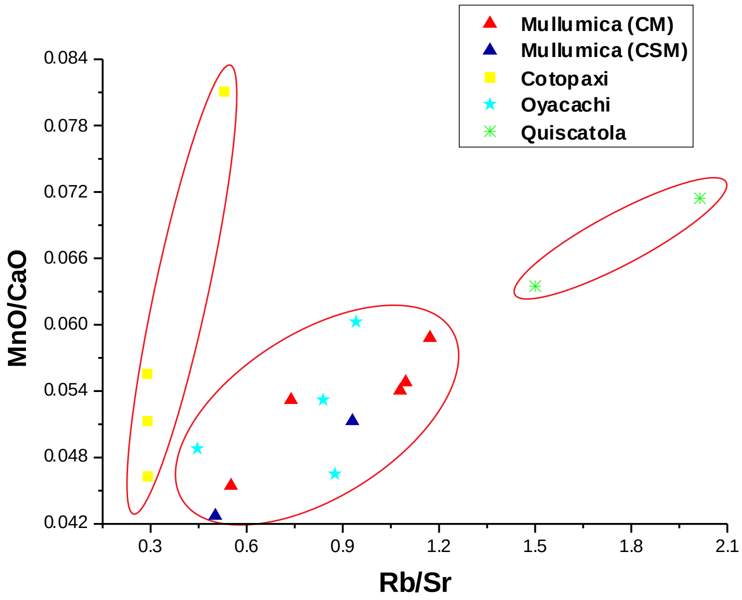

Figure 11 – Two-dimensional graph of the ratios between the concentrations, MnO/CaO and Rb/Sr for the Ecuadorian samples, measured by ICP.

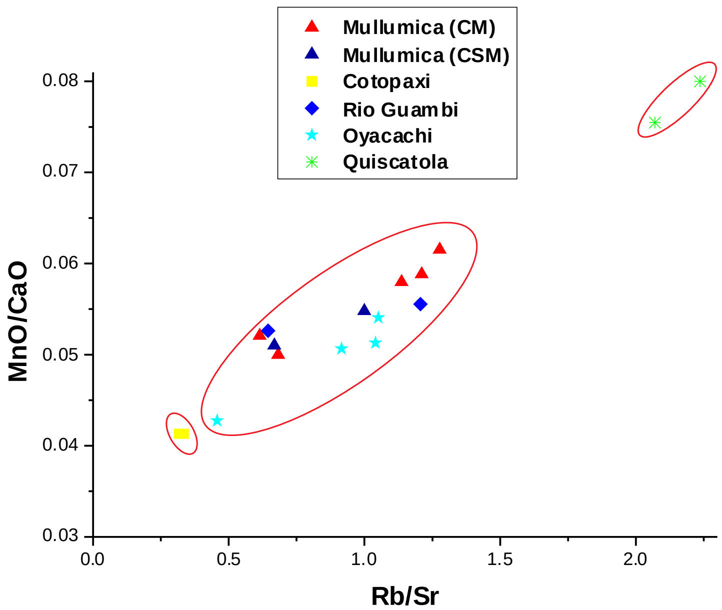

Figure12 – Two-dimensional graph of the ratios between the concentrations, MnO/CaO and Rb/Sr for the Ecuadorian samples, measured by PIXE.

The results of grouping shown in two-dimensional graphics are in agreement with cluster analysis of the Ward Method type using the intensities values, as can be seen at Figure 13. Multivariate analysis resulted in three groups of Ecuadorian samples, one formed by the four samples from the region of Cotopaxi, another formed by the two samples from Quiscatola and a large group formed by all other Ecuadorian samples, which clearly show clustering of the samples from the different sources. Mullumica and Callejones flows are composed of the incomplete mixing of two magmas just before the eruption to the surface. If one of these groups is not too different from the Cotopaxi group, and considering the limited number of samples employed, they could mix wrongly in one large group in the multivariate analysis.

Figure 14 shows the dendrogram obtained by cluster analysis employing the Ward Method for results of concentrations of the elements obtained by PIXE, ICP and intensities values obtained by pXRF for Ecuadorian samples.

Samples from Sardinia, Italy didn't group together. One mixed with the large Mullumica-Oyacachi-Rio Guambi group, and the other separated from all samples.

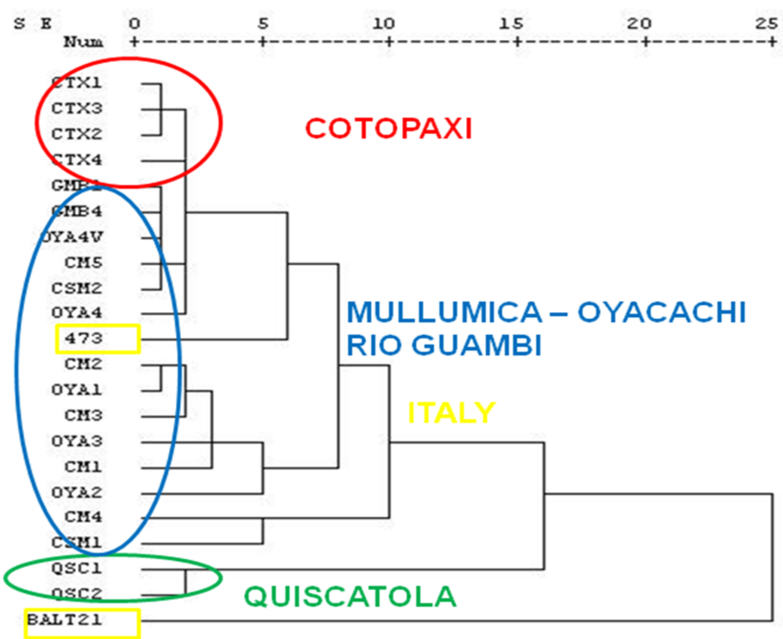

Figure 13 – Dendrogram obtained by cluster analysis of the Ward Method.

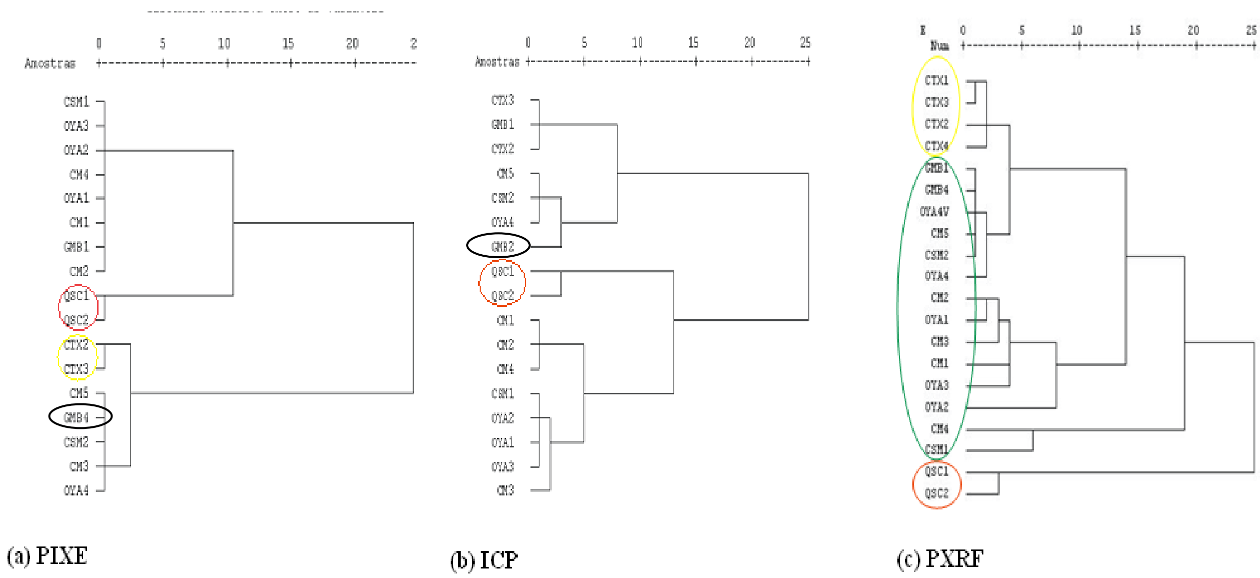

Figure 14 – Comparison among dendrograms obtained by cluster analysis of the Ward Method for (a) concentrations obtained for PIXE (b) concentrations obtained for ICP and (c) intensities values obtained for pXRF.

One important issue when pXRF systems are employed for obsidian sourcing is the consistency of the results obtained with different X-rays tubes or equipments (Speakman and Shackley, 2013). In order to verify this question, as some elements were measured both with Ag and W X-rays tubes, the correlation between them are show at Fig. 15, 16 and 17, which present the comparison of all data results for Ecuadorian obsidians between systems pXRF-LFNA-02 and pXRF-LFNA-03.At these pXRF comparison figures, it is observed a high correlationbetweenboth pXRF systems. There are only three systematic offsets for Ti between pXRF-LFNA-02 and pXRF-LFNA-03 data, but these points are the ones which have the greatest errors among the samples data.

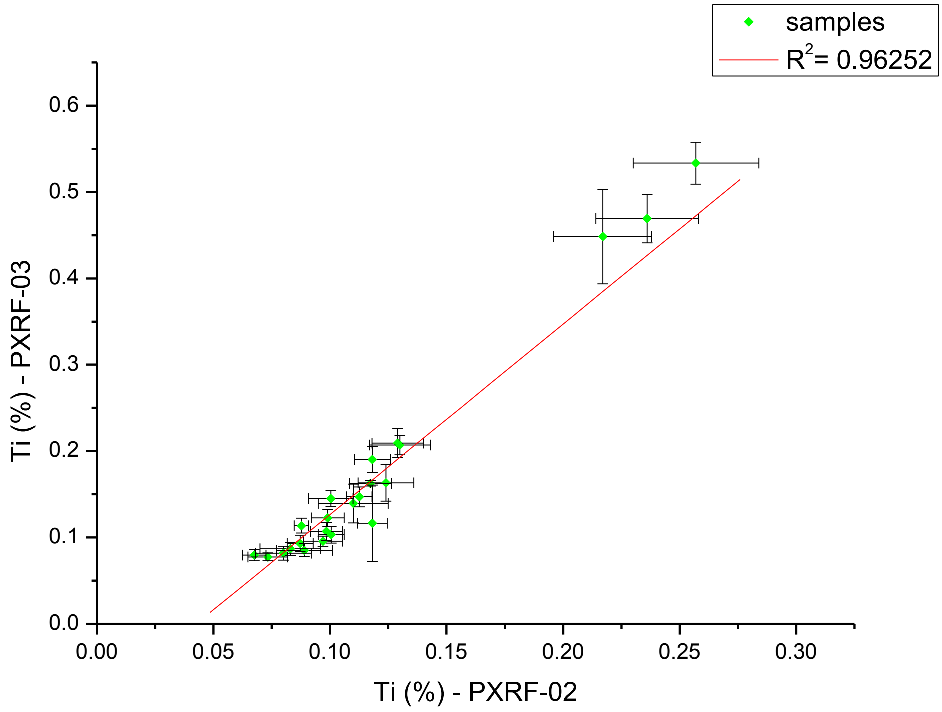

Figure 15 – Comparison of values (expressed as values %) obtained for obsidians samples using the pXRF-LFNA-02 (x-axis) and pXRF-LFNA-03 (y-axis) systems for Ti.

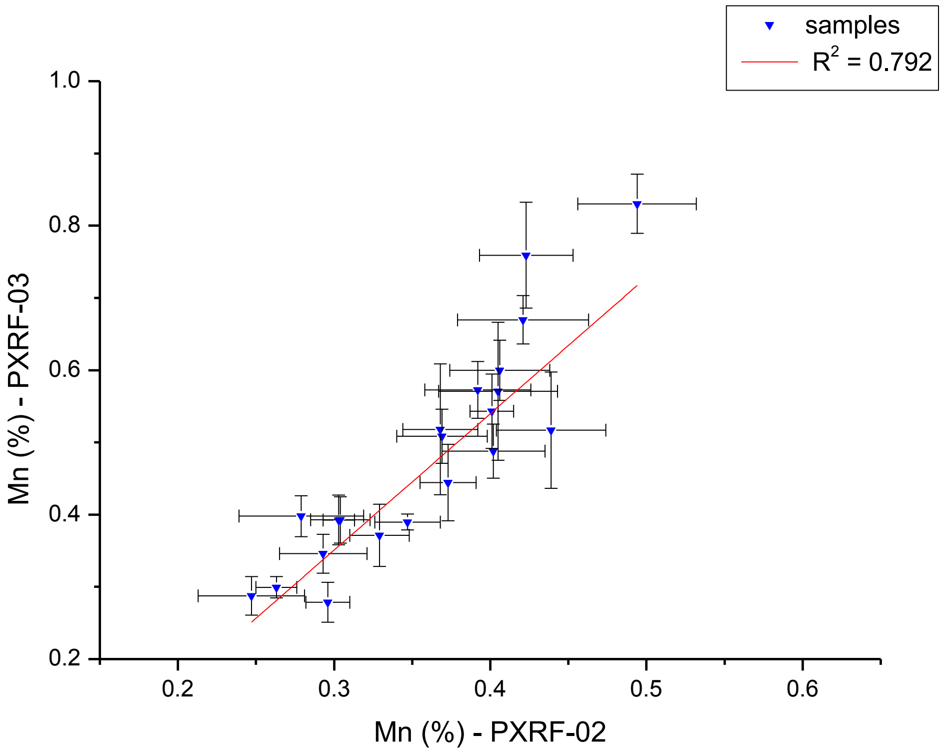

Figure 16 –Comparison of values (expressed as values %) obtained for obsidians samples using the pXRF-LFNA-02 (x-axis) and pXRF-LFNA-03 (y-axis) systems for Mn.

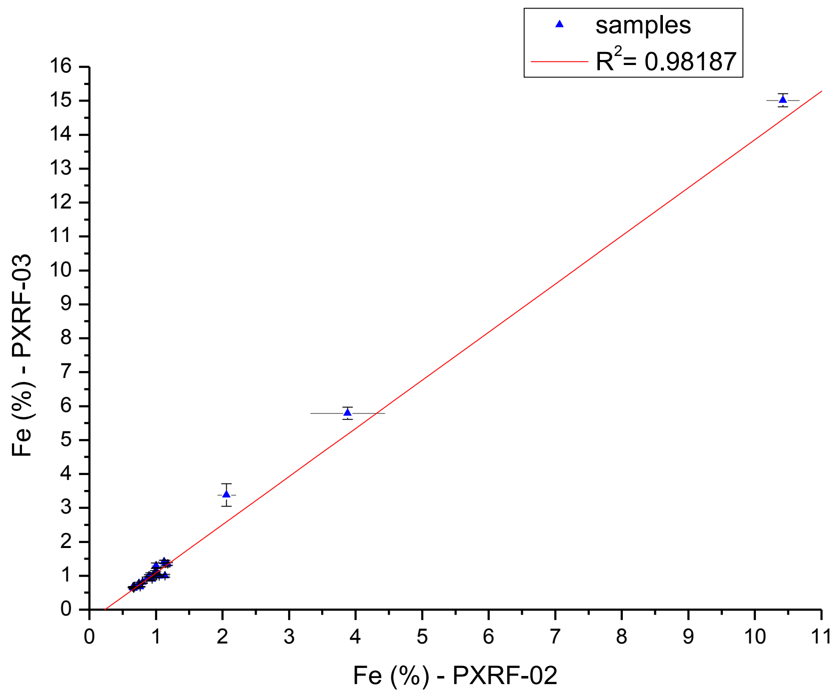

Figure 17 – Comparison of values (expressed as values %) obtained for obsidians samples using the pXRF-LFNA-02 (x-axis) and pXRF-LFNA-03 (y-axis) systems forFe.

5.Conclusions

The results of grouping shown in two-dimensional graphics are in agreement with cluster analysis of the Ward Method type using the intensities values. Multivariate analysis resulted in three groups of samples, one formed by the four samples from the region of Cotopaxi, another formed by the two samples from Quiscatola and a large group formed by all other Ecuadorian samples. Mullumica and Callejones flows are composed of the incomplete mixing of two magmas just before the eruption to the surface. Samples from Sardinia, Italy formed a group apart from others. Overall, this study showed that pXRF LFNA-02and pXRF-LFNA-03 portable devices used in this work have the ability to make quick measurements adapting to any environment, ideal for preliminary in situ measurements with simultaneous multielemental analysis without any sample preparation. Coupled with these advantages there is a loss of accuracy compared to the more robust bench top equipment which need preparation of the samples, leading to their partial or total destruction. Considering that the measurements were performed with very small samples, with irregular surfaces and without any preparation process, the grouping results can be considered excellent when compared with the reference techniques ICP, INAA and PIXE. The results obtained by the two PXRF systems used in this work had a good correlation, which along the grouping results highlight the analytical capabilities of this methodology for nondestructive provenance studies of sourcing of obsidians.

6. Acknowledgments

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