The Monte Arci (Sardinia, western Mediterranean) obsidians: characterization by multivariate analysis from SEM-EDS, EMP-WDS and PIXE elemental compositions

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L'ossidiana del Monte Arci nel Mediterraneo

Nuovi apporti sulla diffusione,
sui sistemi di produzione e sulla loro cronologia

Atti del 5° Convegno internazionale
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The Monte Arci (Sardinia, western Mediterranean) obsidians: characterization by multivariate analysis from SEM-EDS, EMP-WDS and PIXE elemental compositions

François-Xavier Le Bourdonnec[1], Gérard Poupeau[1, 2] and Carlo Lugliè[3]

Riassunto
Viene indagata la potenzialità relativa di EMP-WDS, SEM-EDS e PIXE per la discriminazione dei quattro tipi di ossidiana del Monte Arci sulla base della composizione elementare, ai fini degli studi di provenienza. Si pone in evidenza il fatto che tale discriminazione possa essere ottenuta per mezzo della EMP-WDS (determinando il contenuto di dieci elementi maggiori e minori) e della SEM-EDS (sei elementi maggiori), particolarmente qualora vengano utilizzate delle analisi multivariate. Mediante la PIXE (quindici elementi) tale obiettivo può essere conseguito solo a partire dal contenuto di elementi in tracce, soprattutto Zn, Sr e Zr, e senza la necessità di ricorrere all'analisi multivariata. L'interesse di simili approcci viene illustrato mediante i risultati ottenuti su oltre 300 manufatti neolitici provenienti dalla Francia meridionale, dalla Corsica e dalla Sardegna. Se le misurazioni PIXE sono state fatte in modo non distruttivo, i dati in EMP-WDS sono stati ricavati a partire da sezioni lucide. Sebbene sia possibile realizzare analisi SEM-EDS in modo non distruttivo, anche queste sono state effettuate a partire da sezioni lucide, in modo da escludere ogni possibile disturbo generato da un'alterazione delle superfici dell'ossidiana.

Abstract
The relative capability of EMP-WDS, SEM-EDS and PIXE for the distinction by their elemental compositions of the four Monte Arci obsidian types to be considered in provenance studies is examined. It is shown that this distinction can be reached by EMP-WDS (10 major and minor elements contents

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determined) and SEM-EDS (six major elements) especially when multivariate analyses are used. With PIXE (fifteen elements) this goal can be reached only from trace elements contents, especially Zn, Sr and Zr, and without the need of a multivariate analysis. The interest of these approaches is illustrated by the results obtained on more than 300 Neolithic artifacts from southeastern France, Corsica and Sardinia. While PIXE measurements were made on a non-destructive mode, EMP-WDS data were obtained from polished sections. Although SEM-EDS analyses can be performed non-destructively, they were also made from polished sections in order to eliminate any possible influence of superficial obsidian alteration.

Introduction

Due to their importance as a raw material during the Neolithic in western Mediterranean (e. g. Tykot 1996; Lugliè 2009), obsidians of the Monte Arci volcanic complex (centre-west of Sardinia) were during the last thirty years the subject of many characterization studies. It was estimated more than ten years ago from electron microprobe analyses by wavelength dispersion spectrometry (EMP-WDS) (Tykot 1997), and later on confirmed (Tykot 2002a), that for provenance studies of obsidians from archaeological sites only four types of Monte Arci obsidian elemental compositions, SA, SB1, SB2 and SC had to be considered. Since then, no less than eight other techniques were proposed to distinguish these obsidian types (Table 1), among which the easily accessible and cheap technique of scanning electron microscopy coupled with energy dispersion spectroscopy (SEM-EDS) (Le Bourdonnec et al. 2006).

Table 1: Analytical techniques in use for the distinction of the four Monte Arci obsidian types

Technique	Reference
Electron microprobe	Tykot 1997
ICP-MS	Tykot 1997
Neutron activation analysis	Tykot 2002c, Oddone et al. 2010
X-Ray fluorescence	de Francesco et al. 2004
PIXE	Poupeau et al. 2004
MicroRaman spectroscopy	Bellot-Gurlet et al. 2004
Electron spin resonance	Duttine 2005, Duttine et al. in prep.
Scanning electron microscope	Le Bourdonnec et al. 2006
Laser ablation ICP-MS	Barca et al. 2007

In provenance studies, the attribution of an obsidian artifact to one of the four Monte Arci types can be obtained by bivariate, ternary or 3D plots comparing trace element contents (Bressy et al. 2003: fig. 3; Tykot 2007:

fig. 3; Lugliè et al. 2007, 2009; Barca et al. 2007), element ratios (de Francesco et al. 2004; Barca et al. 2007), structural parameters obtained by ESR (Duttine 2005; Duttine et al. in prep.) or Raman microspectroscopy (Bellot-Gurlet et al. 2004: fig. 8). Multivariate analyses for the data treatment were introduced by Tykot (1997) for EMP-WDS, de Francesco et al. (2004) for XRF and Le Bourdonnec et al. (2006) for SEM-EDS.

We summarize here the results obtained so far by our group on Monte Arci geological obsidians and on western Mediterranean Neolithic obsidians by EMP-WDS, SEM-EDS and particle induced X-ray emission (PIXE) and discuss the relative potentialities and interest of multivariate analyses in sourcing studies. As far as possible, each sample was analyzed by the three techniques, and eventually from the same microprobe-quality polished section.

1. Sourcing from EMP-WDS

This technique provided the Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe contents of 101 Monte Arci geological samples and of 41 obsidian artifacts from the middle Neolithic site of Vasculacciu (southern Corsica). All measurements were made with the CAMECA SX50 microprobe of IFREMER (Brest) operating at 15 kV and delivering a 20 nA defocused (5 μm dia.) electron beam with a counting time of eight seconds (Le Bourdonnec et al. 2005a). Elemental compositions (as wt% by mass) were computed from the average of 10 to 20 spot measurements per sample using the PAP routine (Pouchou and Pichoir 1984). The overall stability of the analytical system was controlled by repeated analyses of the SA type Sardinian obsidian SA-66 internal standard (see Le Bourdonnec 2007).

The obsidian glassy matrix elemental composition of any single sample appeared to be very homogeneous. Thus for the four elements with the highest concentrations, Na, Al, Si and K, the relative standard deviation of spot-measured contents around their mean value were found to be <5% in all samples. Slightly higher dispersions affect two elements with an about one per cent oxide content, Ca and Fe, with values still <10% and <30% respectively. The relative standard deviations become important only for the four elements with oxide contents lower than 0.3% and may reach nearly 50% for Ti and 80% for Mg, P, and Mn (Le Bourdonnec et al. 2005a; Le Bourdonnec 2007). Over a total of more than 2330 'spot' analyses, only 338 (14.5% of spectra) had to be rejected as 'anomalous', apparently due in many instances to the presence of micro- to pheno-crystals of feldspar, mafic crystals, oxides, etc. (see f.i. Kayani and McDonnell 1996).

The contents of Al, K, Ca and Ti are among the most important to characterize the four Monte Arci obsidian types. However due to the internal variability of each type, one must use at least one couple of bivariate plots of element contents to separate them, such as the K-Ca and K-Al one used by Tykot (1997: fig. 4). It is shown here that the same result can be reached through the Ti-Al and Ti-K plots (Figure 1).

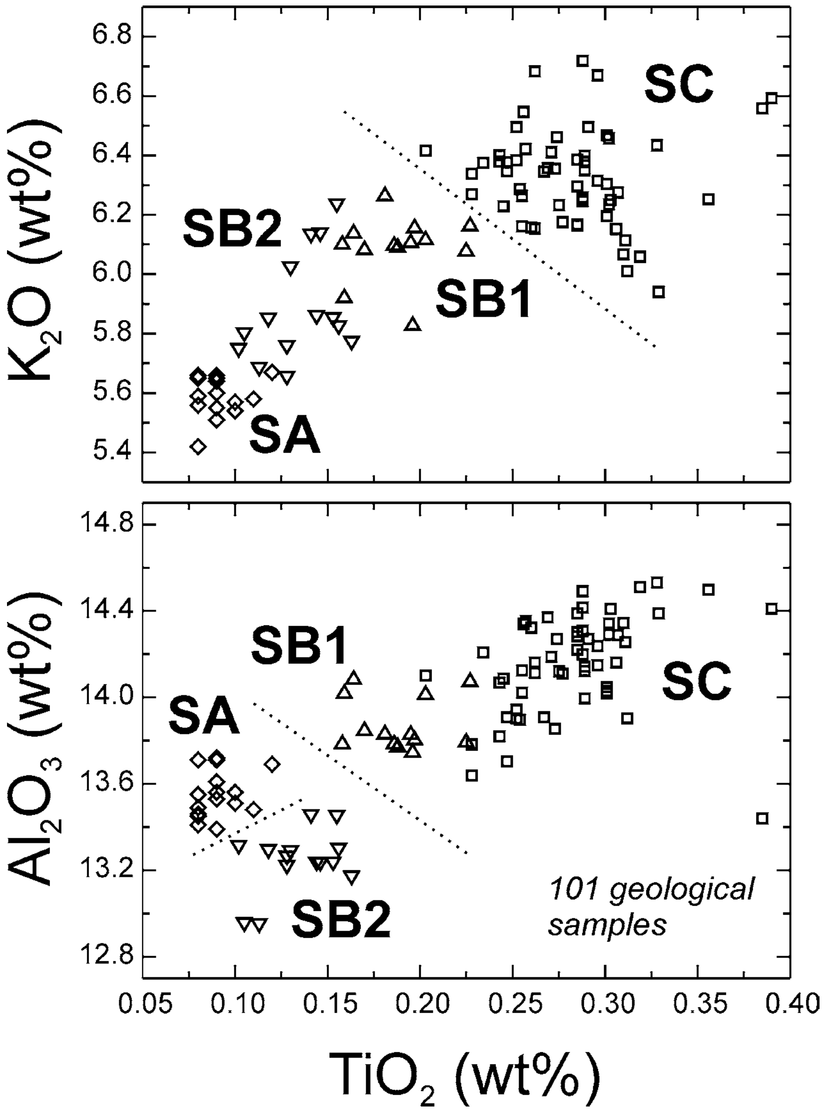

Fig. 1: Bivariate plots of major element oxides contents as determined by EMP-WDS for geological samples from the Monte Arci. Top, K_2O *vs*. TiO_2; bottom, Al_2O_3 *vs*. TiO_2.

However in both cases the distinctions between obsidian types remain subtle. Hence the interest of a multivariate analysis, taking into account all the elements determined (Tykot 1997). A discriminant analysis with the XLSTAT software (Addinsoft 2007) allowed a better individualization of the Monte Arci obsidian types (Figure 2, top). For archaeological obsidian provenance studies, a classificatory analysis taking into account this first step provides directly, through the 'prediction' option of XLSTAT a type attribution, as for the Vasculacciu artifacts (Figure 2, bottom). Previously to this analysis, made on millimeter-sized polished sections, other possible (western Mediterranean) origins for these obsidians had been excluded principally from their Na content (Bressy et al. 2008).

2. Sourcing from SEM-EDS

The content of elements Na, Al, Si, K, Ca and Fe can be routinely determined with scanning electron microscopes equipped with an energy dispersion spectrometer (SEM-EDS).The JEOL JMS 6460 LV apparatus of CRP2A-IRAMAT (Bordeaux) used in this work allowed also to eventually detect in Monte Arci obsidians or sometimes measure quantitatively in other western Mediterranean obsidians other elements like Mg, Ti and Mn (Le Bourdonnec et al. 2010). Eighty of the samples previously analyzed by EMP-WDS were treated by SEM-EDS. All measurements were made with an accelerating voltage of 20 kV and a micrometer-sized electron beam scanned over a sample surface area of approximately 1 mm^2. All spectra were obtained with the same (170,000) total number of counts, corresponding to acquisition times of about 70 seconds. The INCAx-sight energy dispersive spectrometer software (Oxford Industries) uses a Phi-Rho-Z approach to calculate element contents as percent oxides. For each polished section 10 to 17 such measurements were made. In only five cases over a total of 1000 'spot' analyses (i.e. 0.5% of the spectra) had an 'anomalous' spectrum to be rejected. One Monte Arci SA-type sample (ARC-URS) was used as an internal obsidian standard. Its elemental composition was checked from 10 to 20 point measurements at least twice in each run from the same polished section. As for the internal obsidian standard used in EMP-WDS analyses, this reference thick section was systematically re-polished before each run to obtain a new clean surface. For each sample, whatever the element to be considered, the relative standard error about the mean of 'point' measurements was always <3% around the average content (Le Bourdonnec et al. 2006; Le Bourdonnec 2007). The most discriminating elements are Al, Ca and Fe. However as for EMP-WDS data, in spite of the very homogeneous composition of each

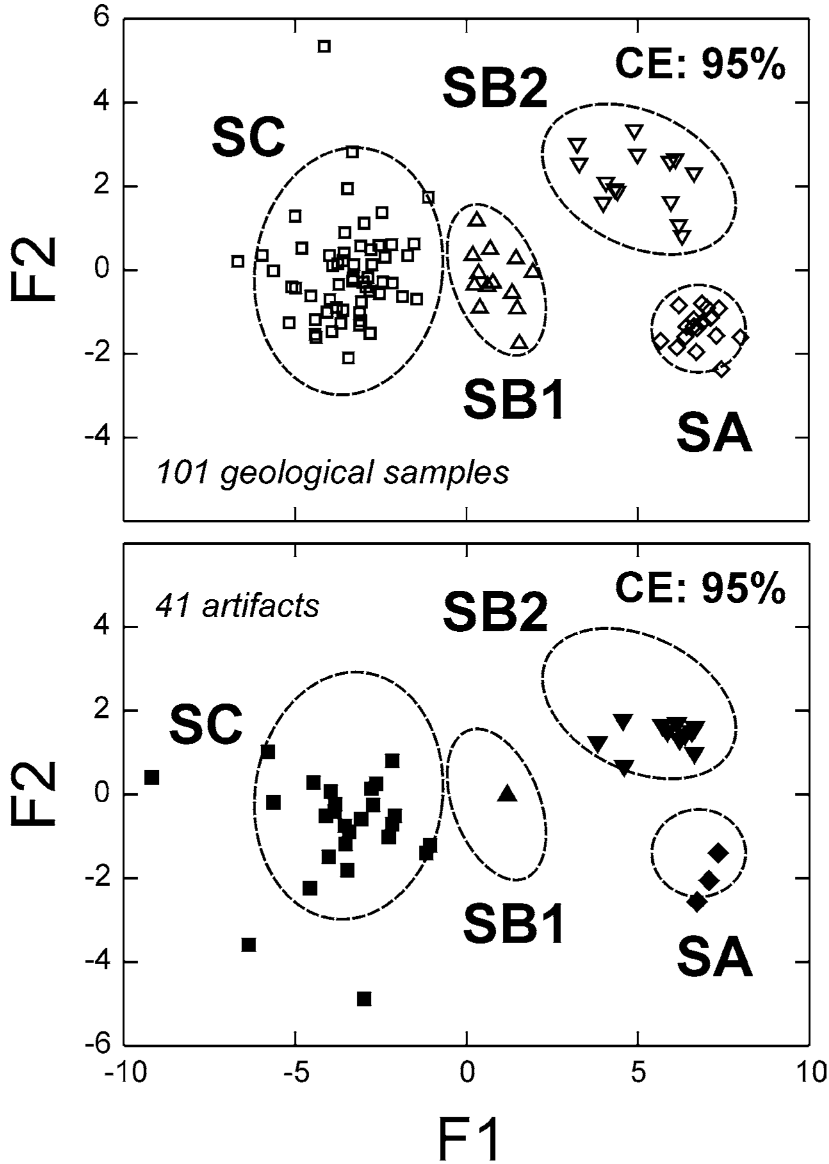

Fig. 2: Discriminant analysis of Monte Arci obsidians from element contents as determined by EMP-WDS.
Top: geological samples. The ellipses defining the obsidian types are calculated at a 95% confidence level. CE: confidence ellipses.
F1 = 3.603Na_2O - 1.246MgO + 1.982Al_2O_3 + 2.375SiO_2 - 12.909P_2O_5 - 3.422K_2O - 5.227CaO - 11.806TiO_2 + 1.178Fe_2O_3 - 188.318.
F2 = 1.099Na_2O + 14.181MgO - 2.287Al_2O_3 + 1.838SiO_2 - 3.752P_2O_5 + 3.614K_2O + 0.136CaO + 12.017TiO_2 - 0.815Fe_2O_3 - 133.539.
Bottom: determination of the Monte Arci obsidian types for 41 Corsican artifacts from the Vasculacciu Corsican Neolithic site.

sample, the Monte Arci source obsidians exhibit internal variations in composition which might seriously limit the use of bivariate diagrams in sourcing studies (see f.i. how the SA and SB2 obsidian fields are close to each other in Figure 3). To the contrary, again a discriminant analysis

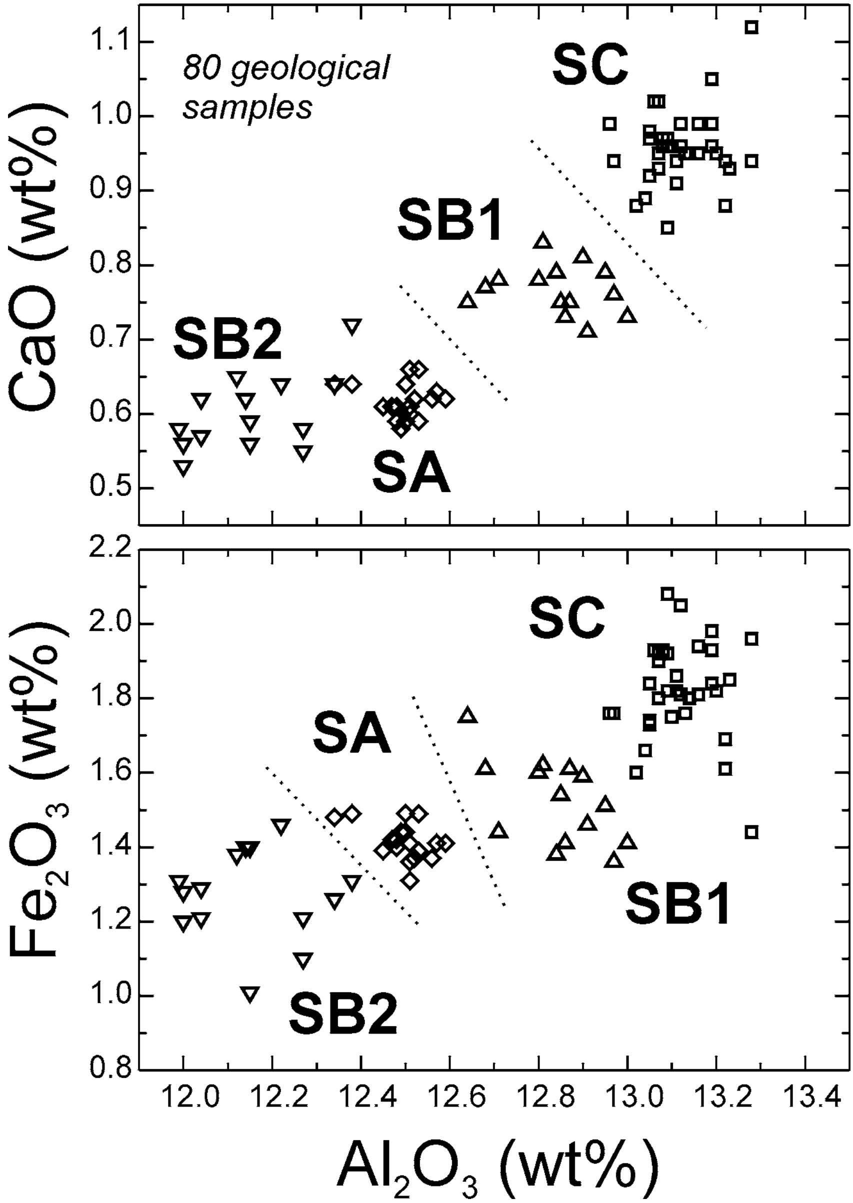

Fig. 3: Bivariate plots of major element oxides contents as determined from EMP-WDS for Sardinian obsidian sources. Top, CaO vs. Al_2O_3; bottom, Fe_2O_3 vs. Al_2O_3.

(based on the only six elements always determined) offers a much favourable situation (Figure 4, top).

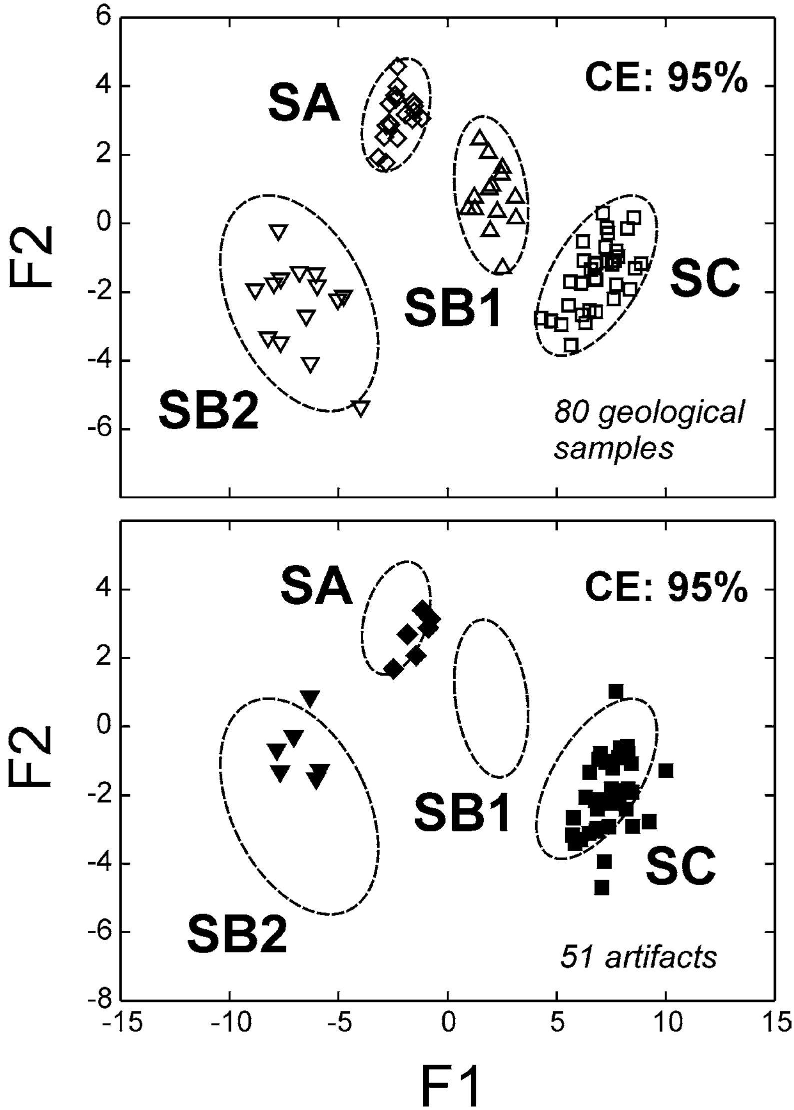

Fig. 4: Discriminant analysis of Monte Arci obsidians from element contents as determined by SEM-EDS.
Top: geological samples. The ellipses defining the obsidian types are calculated at a 95% confidence level. CE: confidence ellipses.
$F1 = 1.579Na_2O + 14.432Al_2O_3 + 5.292SiO_2 + 2.385K_2O + 15.364CaO + 9.372Fe_2O_3 - 625.748$
$F2 = -16.718Na_2O + 8.747Al_2O_3 + 0.229SiO_2 - 12.840K_2O - 14.694CaO + 4.333Fe_2O_3 - 1.914$.
Bottom: determination of the Monte Arci obsidian types for 51 Corsican artifacts from the A Fuata and Vasculacciu Corsican Neolithic sites.

The attribution of any prehistoric obsidian can then be accomplished following the same procedure as for EMP-WDS data. Thus it appears that three Monte Arci obsidian types are represented among the 51 Corsican artifacts analyzed so far, of which 43 come from the middle to late Neolithic A Fuata site of northern Corsica (Le Bourdonnec et al., 2008) and the remaining from Vasculacciu (Le Bourdonnec et al., 2006). As for EMP-WDS, all measurements were made from polished sections (Figure 4, bottom).

It may also be noted that, as previously shown by Acquafredda et al. (1999), it is possible by SEM-EDS to distinguish between each other the obsidians of the western Mediterranean island-sources, notably by their Na content. It is also possible to distinguish from SEM-EDS data at least two types of Pantellerian obsidians.

3. Sourcing from PIXE

PIXE is a very attractive technique as it is the only one which can provide the content of both major and trace elements in a strictly non-destructive mode, and whatever the size of the artifacts to be analyzed. In obsidians, depending on experimental conditions, from thirteen to fifteen elements, Na, Al, Si, Ca, K, Ti, Mn, Fe, Zn, Ga, Rb, Sr, Zr, ±Y, ±Nb, can be routinely determined (Le Bourdonnec et al. 2005a; Le Bourdonnec 2007). A set of 44 Monte Arci obsidians, most of which not analyzed by EMP-WDS or SEM-EDS in this work, were analyzed. The measurements were performed at the AGLAE extracted beam PIXE facility of the *Centre de Recherche et de Restauration des Musées de France* (C2RMF, Paris) (Luglié et al. 2007; 2008a; 2008c; Bressy et al. 2008) or with a nuclear microprobe at *Centre d'Etude Nucléaire de Bordeaux-Gradignan* (CENBG). At CENBG we used successively a 4 MV HVEE Van de Graaff accelerator (Luglié et al. 2007) and the new AIFIRA 3.5 MV HVEE Singletron accelerator (Luglié et al. 2008b). It was shown elsewhere that the results obtained from these facilities are similar (Le Bourdonnec et al. 2005b).

But rare exceptions, each sample composition was calculated as the average of three 'point' analyses. Whereas at AGLAE a 3 MeV protons beam impinged a sample surface of about 30 μm^2, in the CENBG nuclear probes proton beams of the same energy and 5 µm diameter were scanned over a surface sample of nearly 700x700 μm^2. In some instances at CENBG a proton energy of only 1.5 MeV was used for the determination of major element contents (Luglié et al. 2007). Data treatments were made with the 2000 version of the GUPIX software (Maxwell et al. 1995; Campbell et al. 2000).

Due to an intrinsically lower precision in PIXE relatively to EMP-WDS and SEM-EDS analyses it is not possible to obtain a good separation of the Monte Arci obsidian types from their major elements contents, in spite of some Ti and Mn significant variations. It is only from major elements possible to distinguish SC obsidians from the three other types. To the contrary, an XLSTAT principal component analysis reveals the high separating power of trace elements Zn, Sr and Zr (Figure 5).

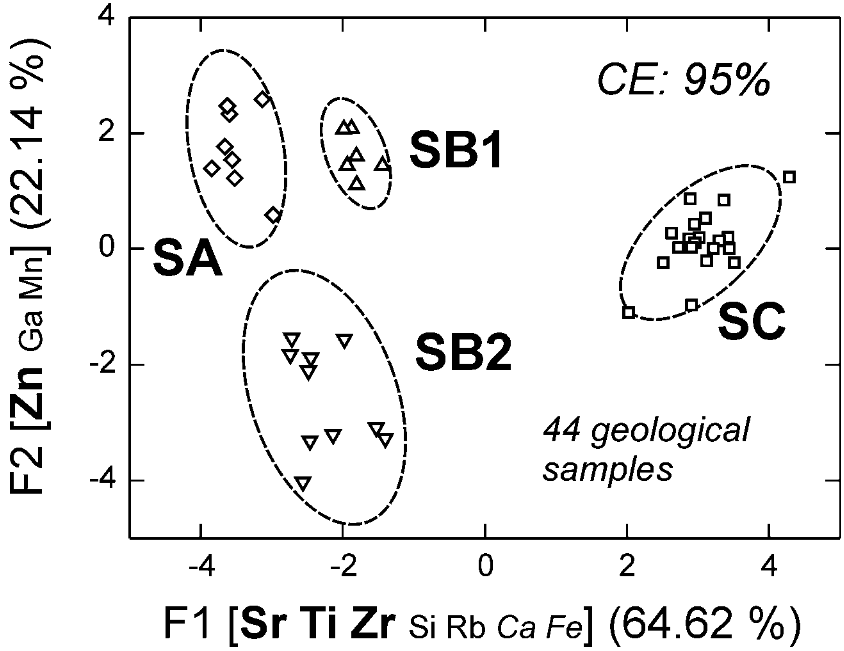

Fig. 5: Principal-component diagram for 44 obsidian samples from the Monte Arci as calculated from all element contents determined by PIXE. The most discriminating elements are indicated in bold characters. The confidence interval for ellipses is 95%. CE: confidence ellipses.

Their contents are different enough between the Monte Arci obsidian types to make 3D diagrams potentially more interesting in sourcing studies (Figure 6). Since 2000, 329 Neolithic obsidians collected from 25 Neolithic sites in southeastern France and in the Tyrrhenian islands of Corsica and Sardinia were sourced by PIXE (Poupeau et al. 2000; Salotti et al. 2000; Lugliè et al. 2007; 2008a; 2009; Bressy et al. 2008). Except one (Salotti et al. 2000), all these obsidians were found to come from Sardinia. When the data for the Sardinian-sourced obsidians are reported in a Zn/Sr/Zr diagram, it is clear that their belonging to one of the Monte Arci types is determined without any ambiguity.

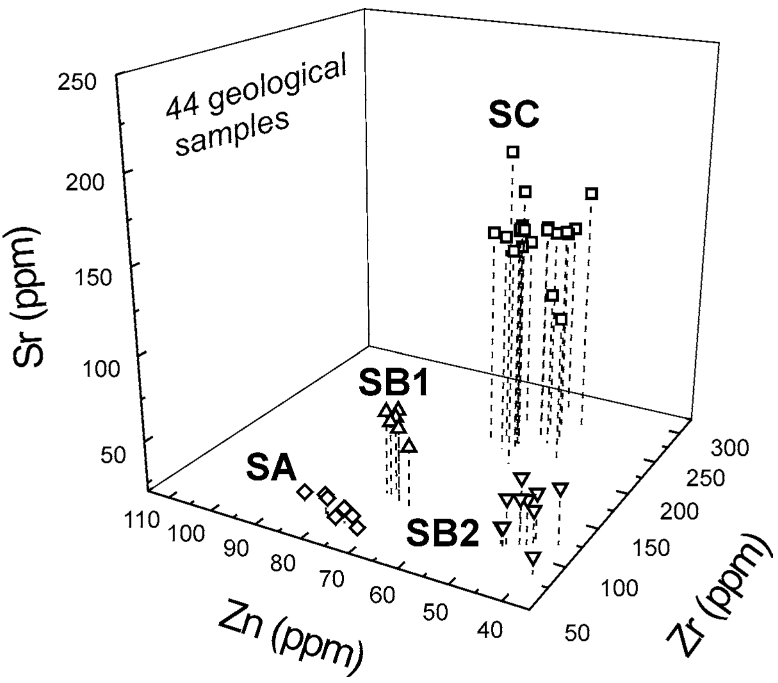

Fig. 6: 3D diagram showing the Zn, Sr and Zr contents in Monte Arci obsidians as determined by PIXE.

Final comments and conclusion

The present tendency in obsidian provenance studies to source as far as possible all elements of a prehistoric assemblage may involve the characterization of artifacts by the thousands. The sourcing of archaeological obsidians from their visual appearance is known to be possible only for 75 to 85% of an artifacts collection, depending on the size, shape, surface alteration, etc., of its individual components (Tykot and Ammerman 1997; Tykot 2002b; Lugliè et al. 2007; 2008b). To determine the origin of the remaining artifacts raw materials the mediation of an analytical technique is necessary. We have shown that, as far as a polished section can be made from a small artifact fragment, the determination of only six major elements by SEM-EDS is sufficient to determine from which of the four Monte Arci obsidian type it was made. Although the more expensive and less easily available EMP-WDS technique gives access to the content of ten elements, the distinction of the Monte Arci obsidian type is best realized, as for SEM-EDS, by a multivariate analysis. It must also be noted that the slight but significant differences observed in the determination of most major elements and especially Na, Al and Si, when determined by EMP-WDS and by SEM-EDS, have for consequence that the data obtained by these two techniques cannot be mixed in provenance studies (Le Bourdonnec et al. 2010).

It was once proposed to use SEM-EDS for non-destructive distinctions of “East” and “West” Monte Arci obsidians (Acquafredda et al. 1999). However prolonged artifacts residence times in soils may induce, according to local conditions and obsidians chemical compositions, a more or less pronounced superficial alteration revealed by Na oxide contents lowered sometimes by as much as 40%. This results in significantly distorted SEM-EDS compositions, which might limit in certain contexts the use of this sourcing technique in non-destructive mode (Poupeau et al. in prep). When non-destructive characterizations are required by the archaeological importance of an artifact and/or by administrative authorities, then PIXE is required. Superficial alterations of the chemical composition can here also be detected by a lowering of the Na content, but the contents of other major element is only negligibly affected because of the deeper thickness of the analyzed layer and no effect is observed in the trace elements used in provenance studies.

In conclusion, in provenance studies, multivariate analyses are required for the distinction of the Monte Arci obsidian types by destructive analysis from EMP-WDS and SEM-EDS, due to their major element compositions similarities and of internal source variations. They are not needed for the non-destructive PIXE analyses, due to the large differences between sources in certain trace element contents. Sourcing programmes involving large Sardinian obsidian assemblages can therefore be easily fulfilled by the coupling of non-destructive visual and PIXE determinations with SEM-EDS (or EMP-WDS, which requires same polished sample preparation) analyses.

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