3° CONVEGNO INTERNAZIONALE
L'ossidiana del Monte Arci
nel Mediterraneo

Le vie dell'Ossidiana nel Mediterraneo ed in Europa

Paesaggio naturale e paesaggio umano nelle aree interne:
strategie di sviluppo sostenibile e di conservazione dell'identità locale

Atti del Convegno
25 - 26 settembre 2004
Comune di Pau
Paese dell'ossidiana

PTM Editrice
Mogoro 2005

Volume pubblicato con i contributi
Comune di Pau
e
R.A.S. (L.R. 26/98)

Progetto grafico
PTM editrice di Claudio Pia

Via dei Mestieri, 14 - 09095 Mogoro (OR)
tel. / fax: 0783 991976
e-mail: info@ptmeditrice.com
web: www.ptmeditrice.com

Editing - Ing. Maurizio Manias
Fotocomposizione, allestimento e stampa - **PTM** Mogoro
Finito di stampare nel mese di marzo 2006

F.-X. Le Bourdonnec[1], C. Lugliè[2], S. Dubernet[1], M. Bohn[3] and G. Poupeau[1]

Monte Arci (Sardinia) obsidians: new geochemical data from electron microprobe and ion beam analysis

Riassunto

Si presentano in questo lavoro nuovi dati geochimici sulle ossidiane del Monte Arci (Sardegna) sulla base di analisi della composizione elementare effettuate alla microsonda (EMP) e per emissione di raggi X indotta da protoni (PIXE). Le ossidiane appartenenti ai gruppi geochimici SA, SB1, SB2 ed SC possono essere discriminate in base al loro contenuto in elementi maggiori mediante EMP ed in base al loro contenuto in tracce mediante PIXE. Mentre le analisi EMP richiedono un frammento lucidato di pochi milligrammi, PIXE è un metodo del tutto non distruttivo. Sono stati analizzati quaranta campioni prelevati nell'ambito di un programma finalizzato alla caratterizzazione dei depositi secondari del Monte Arci.

Abstract

We bring new geochemical data on Monte Arci (Sardinia) obsidians from elemental analyses by electron microprobe (EMP) and proton-induced X-ray emission (PIXE). Obsidians from the geochemical groups SA, SB1, SB2 and SC can be sorted out from their major element contents by EMP and from their trace element contents by PIXE. While EMP analysis requires for analysis a few milligrams polished fragment, PIXE is strictly non-destructive. Forty samples were part of a program aimed at the geochemical characterization of Monte Arci secondary sources.

1. Introduction

The Monte Arci volcanic complex was by far the most important origin of obsidians used by Neolithic men in the Ligurian area. Although up to seven discrete obsidian geochemical type-compositions were recognized among the Monte Arci sources (Tykot, 2002), for archaeological purposes -circulation and provenance of raw material studies-only four types, dubbed SA, SB1, SB2 and SC (Hallam et al., 1976; Mackey and Warren, 1983; Tykot, 1997) have to be discriminated. In preceding *Convegni Internazionali* on

[1] Institut de Recherche sur les Archéomatériaux, UMR 5060, CNRS-Université Bordeaux 3, 33607 Pessac, France. françois.lebourdonnec@etu.u-bordeaux3.fr, Gerard.Poupeau@u-bordeaux3.fr, Stephan.Dubernet@u-bordeaux3.fr.

[2] Dipartimento di Scienze Archeologiche e Storico-Artistiche, Università di Cagliari. luglie@unica.it

[3] Domaines Océaniques, UMR 6538, CNRS-Université de Bretagne Occidentale, Brest, France. Marcel.bohn@ifremer.fr

the Monte Arci obsidians, we showed that alternatives approaches based on structural properties could easily be used to discriminate these obsidians in quasi non-destructive to non-destructive conditions (Poupeau et al., 2004a, b). In the frame of a program aimed at the geochemical mapping of Monte Arci secondary obsidian sources (Meloni et al., 2004a, b; Tanda et al., 2004) and at Ligurian obsidian provenance studies (Luglié et al., 2004) we are also developing conventional elemental analyses. It is the purpose of this article to present new data on Monte Arci obsidians obtained by electron microprobe (EMP) and Particle-induced X-ray emission (PIXE).

2. Electron Microprobe analyses

Samples polished sections were analysed with the wavelength dispersive system (WDS) of an SX50 (CAMECA) electron microprobe at IFREMER (Brest). Using a five microns diameter electron beam of 15 keV and a beam intensity of 20 nA the counting times were limited to eight seconds. Elemental compositions (as % oxides) were computed from the average of five to ten spot measurements per sample using the PAP software (Pouchou and Pichoir, 1984). The composition of one Monte Arci SA-type sample (SA-66) used as an internal obsidian standard to insure consistency between analytical sessions was systematically determined from ~20 point measurements.

Forty four samples, mostly from primary but also sub-primary (down-warped blocks and pebbles) Monte Arci sources, were analyzed. Their glassy matrix appeared to be very homogeneous. Only exceptionally some point measurements, apparently due to the presence of feldspar crystals, had to be rejected. For all samples, standard deviation of spot measurements around the mean value for major element oxides were found to be <5% for Na, Al, Si, K, <10% for Ca and <30% for Fe. They reached higher values only for the four elements with oxides contents lower than 0.3%, as for Ti (<50%), Mg, P, and Mn (<80%). A discriminant analysis showed that four types of composition corresponding to the SA, SB1, SB2 and SC Monte Arci obsidians are clearly individualized (Fig. 1).

Within each geochemical type, the elemental EMP composition is remarkably constant, as shown in table 1, with coefficient correlations <3% for Na, Al, Si, K, <9% Ca, and <17% for Ti. We also reported in Table 1 the EMP microprobe data given by Tykot (1997). Although the number of samples analysed by Tykot is by far larger than in this work, the agreement between the two sets of data is very good, as exhibited in Fig. 2. The only systematic differences concern a slight 5 to 9% in K_2O contents and a factor of two in MnO contents. The large discrepancy in MnO contents might result from the fact this element is near to detection limit. This however has no influence on EMP geochemical type discrimination. Although a statistical analysis singles easily the four Monte Arci obsidian types (Fig. 1), binary diagrams as illustrated by Fig. 3 and 4 can also resolve the issue.

3. PIXE analyses

PIXE analyses were carried out using proton beams at *Centre d'Etude Nucléaire de*

Bordeaux-Gradignan (CENBG) and at *Centre de Recherche et de Restauration des Musées de France* (C2RMF, Paris). The samples were prepared as polished sections and the measures were taken on three point of their surface in order to minimize local element content variations effects. But rare exceptions, each sample PIXE composition was calculated as the average of these three measures. Data treatments were made with the 2000 version of the GUPIX software (Maxwell et al., 1989, Campbell et al., 2000). Fourteen elements, Na, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Zn, Ga, Rb, Sr, and Zr were systematically dosed. The only element content which was found to be highly variable inside a sample was Cl, which will not be considered in the following. Trace elements Y and Nb were found to be often near to detection level.

At CENBG we used the nuclear microprobe facility associated to a 4 MV Van de Graaff accelerator. The obsidians were fixed on the rotary sample holder of a vacuum chamber and exposed to a ~5 micrometers diameter beam operating in a scanning mode to cover a ~700x700 μm^2 surface area. As only one Si(Li) detector was available, element contents had to be determined in two steps. Light elements Na, Al, Si, K, Ca, Ti, Mn and Fe contents were dosed using a proton energy of 1.5 MeV, while Fe, Zn, Ga, Rb, Sr, and Zr required a higher 2.7 MeV energy.

At C2RMF we used the external micro-beam line of the AGLAE 2 MV accelerator tandem Van de Graaff. As two Si(Li) detectors were at disposal, light and heavy elements could be dosed in a single run (Calligaro et al., 1996, 2002). On this facility, the 3 MeV protons beam is operating in the room atmosphere after its exit from the accelerator vacuum through a thin silicon nitride foil. It impinges the sample with a diameter of about 30 microns. In order to minimize the free air absorption of low-energy X-rays, a lowering of the atmospheric mean atomic number was obtained through a flux of Helium between sample and detector. The high-energy X-ray detector was protected against low-energy X-rays by an aluminium filter. A motorized stage allowed one to move the samples during irradiation in order to average the analysis over a ~200x200 μm^2 surface. An internal obsidian standard systematically analysed in all PIXE sessions insured internal consistency between the measurements realized in vacuum (at CENBG) and in the room atmosphere (C2RMF), as shown in Poupeau et al. (2004b) and Le Bourdonnec et al. (2005).

Aliquots of twenty four Monte Arci obsidians of geochemical types otherwise determined (our unpublished ICP-AES and ICP-MS data, and P. Acquafredda, G. Bigazzi and A.M. de Francesco, pers. comm.) were analysed (Poupeau et al., 2004b, Le Bourdonnec et al., 2005). The average PIXE elemental composition for each group is reported in Table 2, where it appears that a clear-cut discrimination between Monte Arci obsidian types can be obtained from Ti, Zn, Sr, and Zr contents, as illustrated by f. i. the binary diagrams of figures 5 and 6. Obsidians from the SC group are also characterized by slightly higher Al, Ca, Fe and lower Si and Rb than those from types SA and SB.

Three samples were analysed by EMP and by PIXE. Eight major elements could be dosed by both methods. Taking into account the intrinsic lower precision of PIXE-determined element concentrations relative to EMP, the results obtained by these two approaches appear to be consistent, as shown in table 3.

4. Additional comments and perspectives

In provenance studies, the relative abundances of SA, SB (sometimes subdivided into SB1 and SB2) and SC obsidians present within a Neolithic site are often reported. The meaning of these mixed obsidian populations is not always clear. We believe that one step towards their interpretation would be to characterize the pebble populations which constitute the many secondary obsidian sources around the Monte Arci, notably in river beds and terraces. Forty of the samples analysed here by EMP were selected in the field specifically to be included in a program of geochemical fingerprinting of primary to secondary sources (Meloni et al., 2004b). The sampling localisation of these obsidians and their determined geochemical types are given in figure 7. These data are complementary to that given for more distant secondary sources by Meloni et al. (2004b). Their meaning will be discussed further with additional EMP data in a more comprehensive report in preparation.

Although "destructive" fingerprinting methods such as elemental analysis by EMP (Tykot, 1997 and this work) or structural analysis by electron spin resonance (Poupeau et al., 2004b; Duttine, 2005) require only a few milligrams fragment for Western Mediterranean obsidian sourcing studies, this is still too much for some samples. Methods are required which keep absolutely the integrity of the material submitted to analyses. We have shown (Le Bourdonnec et al., 2005 and in this work) that ion beam analysis by PIXE is one such method. It proved to be particularly useful for the study of early Neolithic obsidians as for the Su Carroppu Sardinian site (Lugliè et al., 2004).

5. Acknowledgements

We are very indebted to the colleagues who provided us with aliquotes of their Monte Arci obsidian samples, Pasquale Acquafredda (Bari), Giulio Bigazzi (Pisa) and Anna Maria de Francesco (Arcavata di Rende). The PIXE analyses would not have been possible without the generous collaboration of Philippe Moretto and Laurent Serani at CENBG (Gradignan) and Thomas Calligaro, Jean-Claude Dran, Brice Moignard and Laurent Pichon at C2RMF (Paris).

References

CALLIGARO T., MACARTHUR J.D., AND SALOMON J. 1996: An improved experimental setup for the simultaneous PIXE analysis of heavy and light elements with a 3 Mev proton external beam, *Nuclear Instruments and Methods in Physics Research B* 109/110: 125-128.

CALLIGARO T., DRAN J.C., MOIGNARD B., PICHON L., SALOMON J. AND WALTER PH. 2002: Ion beam analysis with external beams: Recent set-up improvements, *Nuclear Instruments and Methods in Physics Research B* 188: 135-140.

CAMPBELL J.L., HOPMAN T.L., MAXWELL J.A. AND NEJEDLY Z. 2000: The Guelph PIXE software package III: Alternative proton database, *Nuclear Instruments and Methods in Physics Research B* 170: 193-204.

DUTTINE M. 2005: *Recherche de provenance de quartz et d'obsidiennes préhistoriques en Europe occidentale. Apports de la résonance paramagnétique électronique*, Ph. D., Université Bordeaux 3, pp. 334.

HALLAM B. R., WARREN S. E. AND RENFREW C. 1976: Obsidian in the western Mediterranean: characterisation by neutron activation analysis and optical emission spectroscopy, *Proceedings of the Prehistoric Society* 42: 85-110.

LE BOURDONNEC F.-X., DELERUE S., DUBERNET S., MORETTO PH., CALLIGARO T., DRAN J.C. AND POUPEAU G. 2005: PIXE characterization of Western Mediterranean and Anatolian obsidians and Neolithic provenance studies, *Nuclear Instruments and Methods in Physics Research B*, Accepted.

LUGLIÈ C., ATZENI E., POUPEAU G., LE BOURDONNEC F.-X., DUBERNET S. AND TOURNIÉ A. 2004: Circolazione dell'ossidiana nel Neolitico a ceramica cardiale della Sardegna: il caso del riparo di Su Carroppu di Sirri (Carbonia, CA), XXXIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria, Firenze, 25-27 novembre 2004, Abstract and in press.

MACKEY M. P. AND WARREN S. E. 1982: The identification of obsidian sources in the Monte Arci region of Sardinia, *Proceedings of the 22nd Symposium on Archaeometry*, University of Bradford, UK: 420-431.

MAXWELL J. A., CAMPBELL J. L. AND TEESDALE W. J. 1989: The Guelph PIXE software package, Nuclear Instruments and Methods in Physics Research B, 43: 218-230.

MELONI S., LUGLIÈ C., ODDONE M. AND GIORDANI L. 2004a: Characterization of Obsidian Samples from Monte Arci (Sardinia, Italy): implications for provenance investigations on obsidian artifacts, in CASTELLI P., CAULI B., DI GREGORIO F., LUGLIÈ C., TANDA G., USAI C. (a cura di), *L'ossidiana del Monte Arci nel Mediterraneo: recupero dei valori di un territorio*, Atti del convegno, Oristano, 29 novembre -1 dicembre 2002: 77-92.

MELONI S., LUGLIÈ C., ODDONE M. AND GIORDANI L. 2004b, Ossidiana di Monte Arci: nuovi dati sulla composizione delle diverse fonti, *2° Convegno internazionale L'ossidiana del Monte Arci nel Mediterraneo, Atti del convegno*, Pau, 28-30 novembre 2003: 311-322.

POUCHOU J. L. AND PICHOIR F. 1984: A new model for quantitative X-ray-microanalysis. 1. Application to the analysis of homogeneous samples. *La Recherche Aérospatiale*, 1984 3: 167-192.

POUPEAU G., SCORZELLI R. B., VILLENEUVE G., DUTTINE M., DUBERNET S., STEWART S., BELLOT-GURLET L., FRÖHLICH F., LE BOURDONNEC F.-X. AND DELERUE S. 2004a: Obsidian characterization from structural properties and provenance studies. The case of the Monte Arci (Sardinia, Italia) obsidians, in CASTELLI P., CAULI B., DI GREGORIO F., LUGLIÈ C., TANDA G., USAI C. (a cura di), *L'ossidiana del Monte Arci nel Mediterraneo: recupero dei valori di un territorio*, Atti del convegno, Oristano, 29 novembre -1 dicembre 2002: 98-106.

POUPEAU G., LE BOURDONNEC F.-X., DUTTINE M., VILLENEUVE G., DUBERNET S., LUGLIÈ C., MORETTO PH., BELLOT-GURLET L., FRÖHLICH, F., SCORZELLI R. B., SOUZA AZEVEDO I., LÓPEZ A., AND STEWART S. 2004b: The Monte Arci obsidian: new fingerprinting approaches in provenance studies, *2° Convegno internazionale L'ossidiana del Monte Arci nel Mediterraneo, Atti del convegno*, Pau, 28-30 novembre 2003: 323-332.

TANDA G., LUGLIÈ C., MELONI S., ODDONE M., POUPEAU G. AND LE BOURDONNEC F.-X. 2004: *L'ossidiana del Monte Arci: nuove acquisizioni sullo sfruttamento e sulla circolazione alla luce dei dati archeometrici,* XXXIX Riunione Scientifica dell'Istuto Italiano di Preistoria e Protostoria, Firenze, 25-27 novembre 2004, Abstract.

TYKOT R. H. 1997: Characterization of the Monte-Arci (Sardinia) obsidian sources, *Journal of Archaeological Science* 24: 467-479.

TYKOT R.H. 2002: Chemical Fingerprinting and Source Tracing of Obsidian: The Central Mediterranean Trade in Black Gold, *Acc. Chem. Res.* 35: 618-627.

Table 1

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO
SA type											
This study											
ave	3.43	0.08	13.32	74.45	0.08	5.52	0.58	0.08	0.06	1.31	nd
sd	0.09	0.01	0.10	0.47	0.01	0.06	0.03	0.01	0.01	0.07	-
N	13	13	13	13	13	13	13	13	11	13	-
Tykot, 1997											
ave	3.45	0.08	13.40	74.72	0.06	5.25	0.59	0.09	0.08	1.25	0.02
sd	0.11	0.01	0.15	0.25	0.01	0.13	0.03	0.01	0.01	0.09	0.02
N	204	206	205	204	60	204	205	206	60	206	201
SB1 type											
This study											
ave	3.35	0.10	13.72	74.08	0.12	6.08	0.74	0.19	0.05	1.01	nd
sd	0.03	0.04	0.02	0.19	0.01	0.06	0.01	0.02	0.02	0.18	-
N	8	8	8	8	8	8	8	8	4	8	-
Tykot, 1997											
ave	3.38	0.13	13.62	73.84	0.04	5.56	0.75	0.17	0.10	1.35	0.05
sd	0.10	0.04	0.10	0.35	0.01	0.20	0.06	0.03	0.02	0.17	0.02
N	28	28	28	28	21	28	28	28	21	28	28
SB2 type											
This study											
ave	3.41	0.13	13.16	75.57	0.07	5.81	0.59	0.14	0.06	1.16	nd
sd	0.05	0.03	0.14	0.47	0.01	0.06	0.03	0.02	0.02	0.12	-
N	6	6	6	6	6	6	6	6	5	6	-
Tykot, 1997											
ave	3.36	0.11	12.97	75.08	0.04	5.46	0.57	0.13	0.08	1.15	0.02
sd	0.06	0.02	0.14	0.27	0.01	0.11	0.02	0.02	0.01	0.09	0.02
N	128	130	129	127	81	81	130	130	81	129	130
SC type											
This study											
ave	3.30	0.14	13.92	73.70	0.11	6.33	0.84	0.27	0.04	1.25	nd
sd	0.07	0.07	0.14	0.43	0.02	0.10	0.08	0.03	0.01	0.31	-
N	17	17	17	17	17	17	17	17	11	17	-
Tykot, 1997											
ave	3.31	0.20	13.92	72.71	0.03	5.90	0.87	0.27	0.14	1.52	0.11
sd	0.11	0.06	0.18	0.34	0.01	0.18	0.08	0.03	0.01	0.19	0.02
N	336	335	337	336	120	336	337	338	120	330	336

Table 1: Mean electron microprobe (EMP) compositions of SA, SB1, SB2 and SC types of Monte Arci obsidians as determined in this work and by Tykot (1997). Ave, average values (oxides %); sd, standard deviations; N, number of samples analyzed.

Table 2

Type		Na_2O	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Zn	Ga	Rb	Sr	Zr
SA	ave	3.40	13.65	75.72	4.92	0.60	0.09	0.05	1.27	76	23	250	28	77
(N=7)	sd	0.06	0.12	0.14	0.12	0.01	0.01	0.01	0.04	3	1	14	4	7
SB1	ave	3.43	13.89	74.93	5.03	0.73	0.14	0.05	1.44	72	24	250	65	121
(N=6)	sd	0.05	0.11	0.15	0.08	0.02	0.01	0.01	0.06	2	1	10	4	6
SB2	ave	3.23	13.26	75.88	5.27	0.61	0.13	0.03	1.24	44	19	237	42	108
(N=7)	sd	0.12	0.13	0.24	0.20	0.06	0.02	0.01	0.08	3	2	16	8	14
SC	ave	3.29	14.23	73.69	5.45	0.87	0.27	0.03	1.72	58	21	178	127	238
(N=4)	sd	0.07	0.13	0.17	0.11	0.03	0.02	0.01	0.14	5	2	18	20	17

Table 2: Mean particle induced X-ray emission (PIXE) compositions of SA, SB1, SB2 and SC types of Monte Arci obsidians as determined in this work. Na to Fe contents are given in oxides %, Zn to Zr in ppm. Legends as in table 1.

Table 3

Sample			Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
SA type												
ARC-URS	EMP	ave	3.65	0.06	13.45	75.38	0.07	5.42	0.64	0.08	0.06	1.22
		sd	0.29	0.02	0.29	0.22	0.05	0.23	0.07	0.03	0.03	0.15
		n	5	5	5	5	3	5	5	5	3	5
	PIXE	ave	3.38	nd	13.77	75.66	nd	4.83	0.59	0.09	0.05	1.28
		sd	0.04	-	0.10	0.10	-	0.05	0.01	0.01	0.01	0.08
		n	7	-	7	7	-	7	7	7	7	7
SA-66	EMP	ave	3.52	0.07	13.34	74.64	0.08	5.51	0.59	0.08	0.07	1.24
		sd	0.34	0.02	0.23	0.38	0.04	0.27	0.11	0.03	0.05	0.12
		n	17	17	17	17	16	17	17	16	11	17
	PIXE	ave	3.43	nd	13.55	75.75	nd	4.94	0.62	0.08	0.05	1.31
		sd	0.09	-	0.05	0.14	-	0.06	0.03	0.01	0.01	0.10
		n	3	-	3	3	-	3	3	3	3	3
SB2 type												
SB2-74B	EMP	ave	3.47	0.15	13.17	75.51	0.08	5.78	0.58	0.16	nd	1.08
		sd	0.05	0.01	0.09	0.11	0.04	0.06	0.04	0.03	-	0.08
		n	5	5	5	5	5	5	5	5	-	5
	PIXE	ave	3.35	nd	13.21	75.65	nd	5.09	0.74	0.14	0.03	1.33
		sd	0.06	-	0.13	0.39	-	0.05	0.27	0.01	0.01	0.02
		n	3	-	3	3	-	3	3	3	3	3

Table 3: Comparison between the elemental compositions determined respectively by EMP and PIXE for three Monte Arci obsidians. Legends as in table 1; n, number of spot measures per sample.

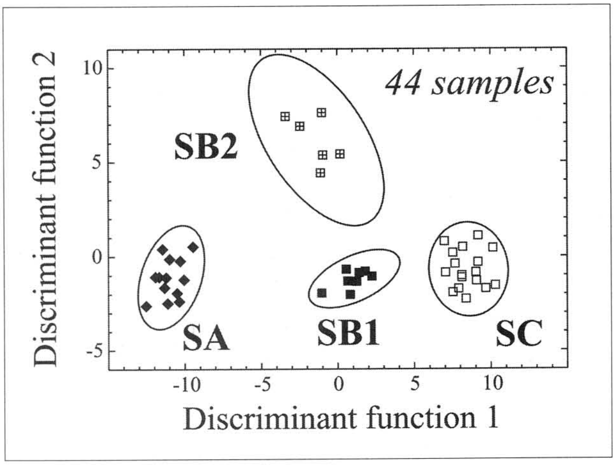

Fig. 1.
Discriminant analysis of EMP data for 44 Monte Arci obsidians. Ellipses represent the 90% confidence level for the four Monte Arci geochemical types.

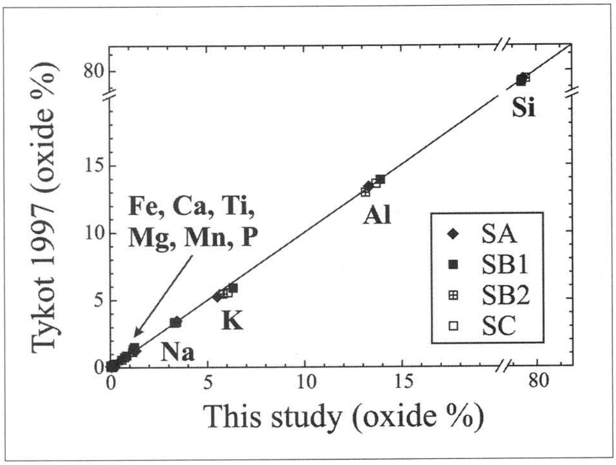

Fig. 2.
Comparison between oxides contents determined by EMP on Monte Arci obsidians in this work and by Tykot (1997).

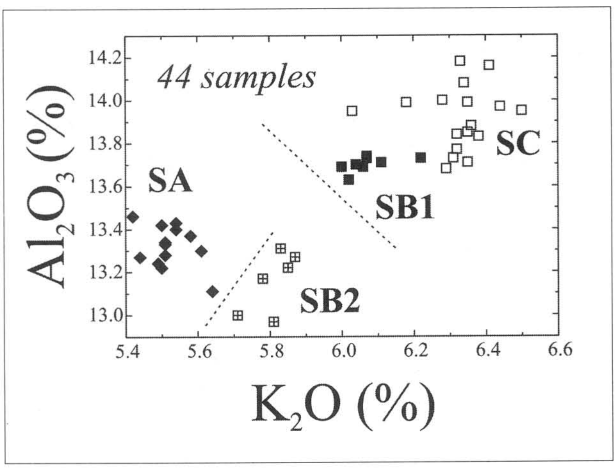

Fig. 3.
Comparison between the Al_2O_3 and K_2O contents as determined by EMP on Monte Arci obsidians.

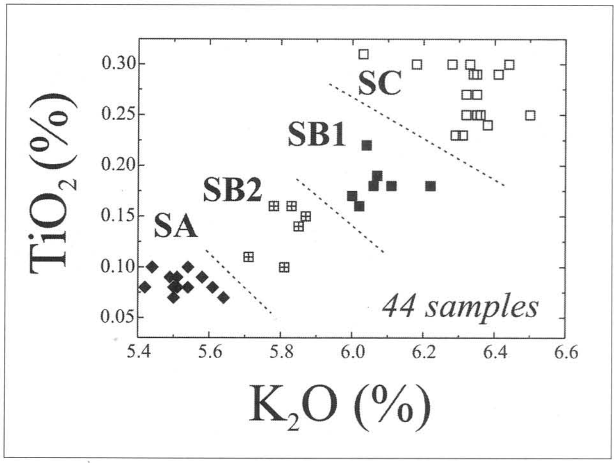

Fig. 4.
Comparison between the TiO_2 and K_2O contents as determined by EMP on Monte Arci obsidians.

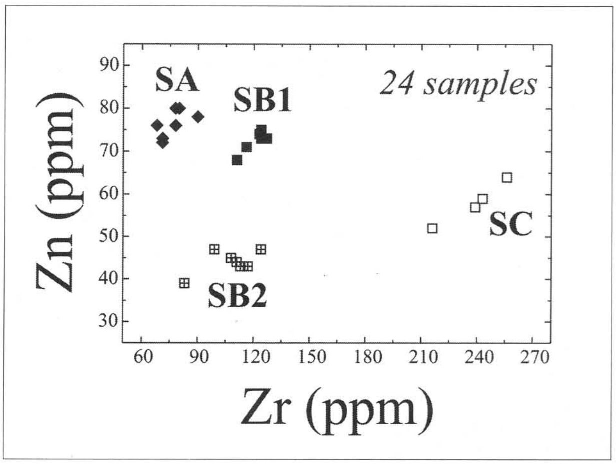

Fig. 5.
Comparison between the Zn and Zr contents as determined by PIXE on Monte Arci obsidians.

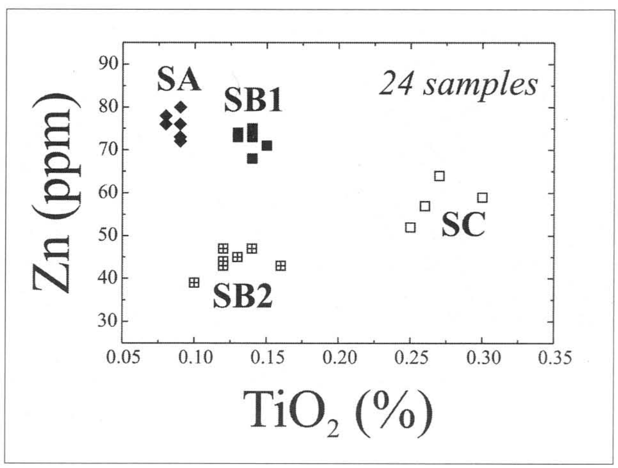

Fig. 6.
Comparison between the Zn and TiO_2 contents as determined by PIXE on Monte Arci obsidians.

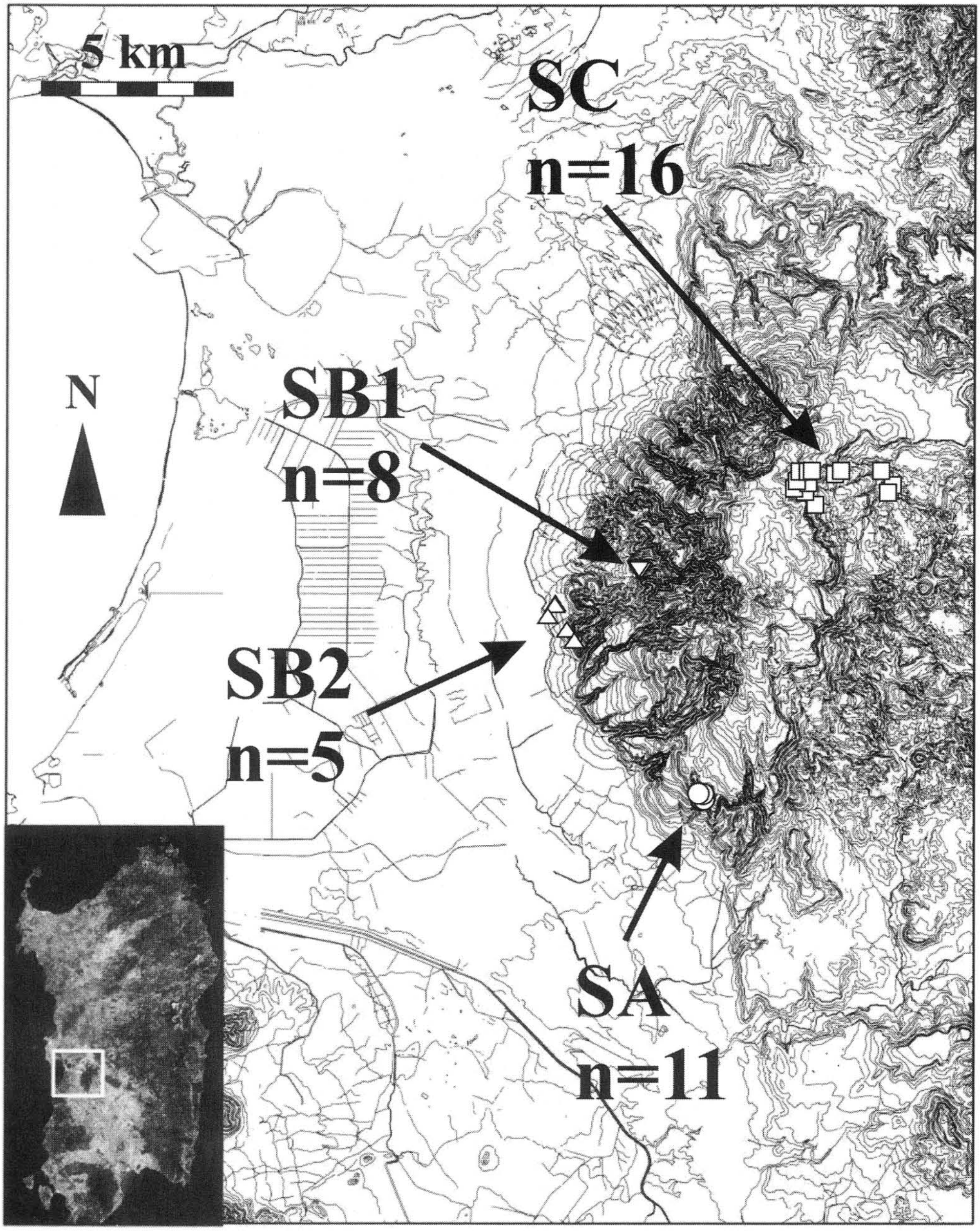

Fig. 7 Localisation and geochemical types of 40 obsidians analyzed by EMP.