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Chemical Characterization of Obsidians from Different Mediterranean Sources by Non-destructive SEM-EDS Analytical Method

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The aim of our research is to check the SEM-EDS non-destructive analytical method for discriminating and locating the possible sources of obsidian artefacts. Moreover, in order to obtain a significant discrimination of Mediterranean obsidians, we analysed samples collected from outcrops of the major sources: Monte Arci (Sardinia) and Palmarola, Lipari, Pantelleria, Gyali and Melos islands. All samples were analysed by both XRF (whole rock) and SEM-EDS (glass and microliths-microphenocrysts). The XRF analysis reveals that major elements discriminate obsidian. The discrimination using major elements is very useful because the amount of trace elements is lower than the detection limit of a Si(Li) ED Detector. The major elements, particularly SiO_2, Al_2O_3, CaO, Na_2O and K_2O, of obsidian glass discriminate the six main Mediterranean sources. Our work demonstrates, therefore, the possibility of discriminating different provenance of obsidian artefacts using SEM-EDS, by means of a relatively rapid, effective and above all non-destructive method.

Keywords: OBSIDIAN, METHODOLOGY, NON-DESTRUCTIVE ANALYSIS, SEM-EDS, MEDITERRANEAN BASIN.

Introduction

The identification of the source area of ancient obsidian artefacts provides valuable information on trade routes and cultural and social relationships in prehistoric times. To date, several physical and chemical methods have been proposed to locate the source area of obsidians. The main physical methods are: (i) refraction index and density (Wainwright, 1927), (ii) fission-track dating (Bigazzi *et al.*, 1971), (iii) thermoluminescence (Huntley & Bailey, 1973), (iv) Sr isotopes (Gale, 1981), (v) magnetic properties (McDougall *et al.*, 1983) and (vi) back-scattered petrography (Kayani & McDonnell, 1996). The main chemical methods are: (i) optical emission spectrography (Cann & Renfrew, 1964), (ii) neutron activation (Gordus, Wright & Griffin, 1968), (iii) X-ray fluorescence (Stevenson, Stross & Heizer, 1971), (iv) X-ray fluorescence using peak intensity ratios of various elements (Crisci *et al.*, 1994; Nelson, D'Auria & Bennett, 1975), (v) proton induced X-ray emission (PIXE) (Nielson *et al.*, 1976) and (vi) electron microprobe (Merrik & Brown, 1984). Most of these methods are destructive.

In the present paper, we check a method already preliminarly proposed (Acquafredda *et al.* 1995*b*, 1996*a*, *b*) to discriminate obsidians by non-destructive chemical analysis performed using an Energy Dispersive Spectrometer linked with a Scanning Electron Microscope. Obsidians from the main Mediterranean sources were collected and examined.

Main Geological Characters of the Major Obsidian Sources in the Mediterranean Basin

The six major obsidian source areas in the Mediterranean basin are Monte Arci (Sardinia), and Palmarola, Lipari, Pantelleria, Melos and Gyali islands (Figure 1).

Gyali

Gyali belongs to the southern Aegean volcanic arc. The south-western part of the islet is formed by pumice (Keller, 1980); the north-eastern part by obsidian domes and rhyolitic lava flows (Di Paola, 1974). Fission-track dating gave ages of 24 ka (Wagner, Storzes & Keller, 1976) and 30 ka (Bigazzi & Radi, 1981); anomalous values of 8·04 and 2·01 Ma are reported by Durrani *et al.* (1971)).

Gyali obsidians are grey in colour, with remarkable transparency and are particularly shiny, and fundamentally consist of glass with very scarce microliths.

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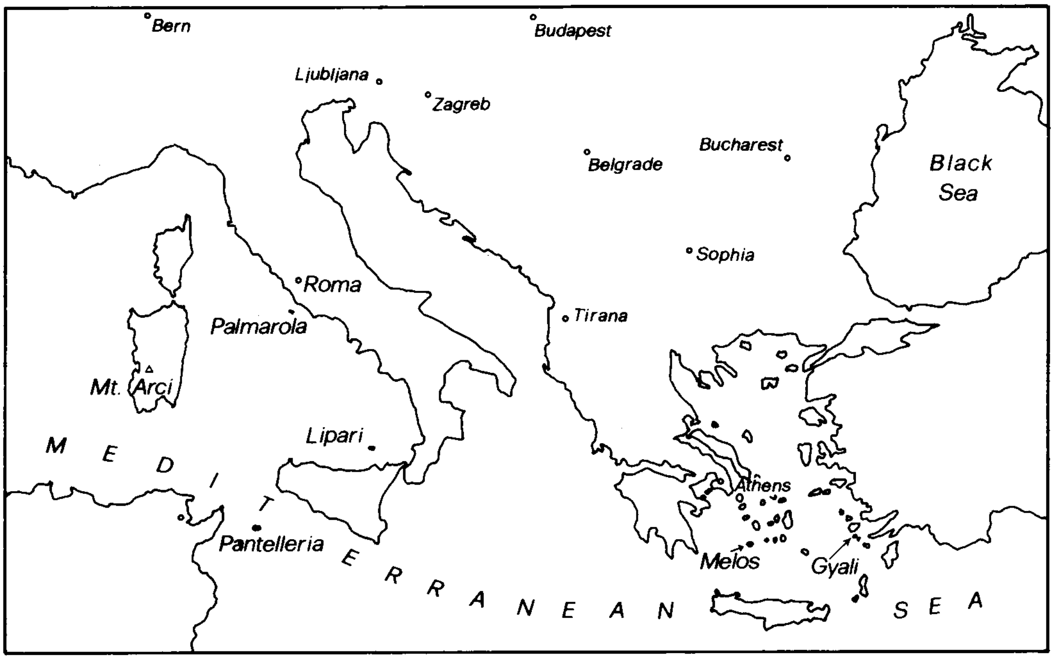

Figure 1. Major obsidian source areas in the Mediterranean basin.

Melos

Melos is also an island of the southern Aegean volcanic arc. According to Fytikas *et al*. (1976, 1986), two distinct stages characterize its volcanic activity. The former (Middle–Upper Pliocene) is represented by a basal mainly submarine pyroclastic series (3·50–3·08 Ma); the latter is Lower Pleistocene in age (1·85–0·97 Ma) and produced submarine pyroclastic sequences and rhyolitic domes; ryolitic lavas with obsidian rise up in the Demenegaki and Nihia areas. Conglomerates, unknown in age, outcrop near Adamas, Nihia, Plaka, Phylakopi, Plakota; at Nihia and Adamas beaches contain large obsidian pebbles. We also found obsidians between Sarakiniko and Pollonia in Lower Pleistocene pyroclastites and at Agia Sophia in Middle-Upper Pliocene pyroclastites.

Melos obsidians contain relatively abundant microliths and are grey in colour, shiny and with moderate transparency.

Pantelleria

Pantelleria lies on the Sicilian Channel continental rift. Six sialic eruptive cycles ranging in age between 50 ka and 8 ka have been recognized (Civetta *et al.*, 1988). Large nodules and lenses of obsidian are interbedded only in the Green Tuff Formation of the first cycle, dated 49·6 ka by Cornette *et al*. (1983) and 50–45 ka by Mahood & Hildreth (1986). The main primary obsidian sources are three: Balata dei Turchi, Saltò La Vecchia and Bagno di Venere.

Pantelleria obsidians contain scarce but relatively developed microliths: their colour is often grey-greenish, and moderately shiny and transparent.

Lipari

Lipari belongs to the Eolian Islands Archipelago, which is generally considered a volcanic arc (Barberi *et al.*, 1973, 1974). Only the volcanic activity of the last 10,000 years has given obsidian. The volcanic centres of this period may be attributed (Cortese *et al.*, 1986) to two groups: the Canneto Dentro-Vallone Gabellotto and the Forgia Vecchia-Monte Pilato. The older activity formed small explosion breccia cones and was followed by a final obsidian flow at Canneto Dentro, and by widespread obsidian-rich pumice at Gabellotto (11·4 and 8·6 ka according to fission-track dating by Bigazzi & Bonadonna, 1973; and Wagner, Storzes & Keller, 1976, respectively). Pumices with obsidian blocks of the second group lay on a palaeosoil containing Neolithic ceramic, obsidian artefacts and coins dated 580 AD (Buchner, 1949; Pichler, 1968). Only the older obsidians can have provided raw material for Neolithic artefacts.

Lipari obsidians are fundamentally composed of glass and are black in colour, very shiny and often perlitic.

Monte Arci

Remarkable Tertiary–Quaternary volcanic activity formed widespread volcanic products attributable to two magmatic cycles in western Sardinia. The first cycle, Oligo-Miocene in age, has calc-alkaline affinity. The second cycle, connected with the extensional tectonic processes which originated the Campidano *Graben*, is characterized by within-plate volcanism. The Monte Arci complex lies along the north-eastern border of this *Graben*. Age determinations give different values: K-Ar method indicates an age comprised between 3·8 and 2·7 Ma (Belluomini *et al.*, 1970; Di Paola *et al.*, 1975; Savelli, 1975; Beccaluva *et al.*, 1983), while $^{40}Ar/^{39}Ar$ values indicate a shorter period of volcanic activity, comprised between 3·24 and 3·16 Ma (Montanini & Villa, 1993). Even older ages (5·7–4·9 Ma) have been determined by fission-track for rhyolitic obsidians (Bigazzi *et al.*, 1976).

According to Montanini (1992) and Montanini, Barbieri & Castorina, (1994), Monte Arci volcanic activity consists of four main episodes. The first generated large quantities of two types of sub-alkaline rhyolites: mafic inclusion free (IFR) and mafic inclusion bearing (MIBR) rhyolites. The obsidians belong to the IFR rhyolites.

Monte Arci obsidians are very rich in relatively large microliths-microphenocrysts (up to 0·3 mm, visible even to the naked eye) and grey in colour, remarkably shiny and perlitic.

Palmarola

Palmarola is the westernmost island of the Pontine Islands Archipelago (Gaeta Goulf). It consists of calc-alkaline volcanic rocks laying on Pliocene sediments. The Palmarola volcanic products comprise obsidian dykes crossing a microbreccia composed of glassy rhyolitic clasts in a glassy matrix. The volcanic activity is related to the stretching of the Thyrrenian Sea and began in the Upper Pliocene and Pleistocene (De Rita *et al.*, 1989). Geochronological data by fission-track method indicate $1{\cdot}7 \pm 0{\cdot}3$ Ma for the obsidians (Bigazzi *et al.*, 1971).

Palmarola obsidians are fundamentally glassy, black in colour, poorly shiny and semi-opaque.

The occurrence, geodynamic setting, petrographic and geochemical characteristics and age of the Monte Arci, Palmarola, Lipari, Pantelleria, Melos, Gyali obsidians are reported in Table 1.

Sample Location

In each of the six islands, the samples analysed were collected mostly from outcrops, and partly from artefacts collected over wide areas. The sampling is also statistically representative of every geological-archaeological source area.

Monte Arci obsidians were sampled from several lava flows outcropping at Riu Cannas, Canale Perdera-Riu Solacera and in the Perdas Urias area.

At Palmarola, the obsidians were collected from dykes of the southern slope of Mt. Tramontana or constitute artefacts found on the beaches of the western coast.

The Lipari samples come from blocks included in pumices and from flows of the Canneto-Vallone Gabellotto-Papesca area; one sample comes from the Neolithic quarry at the fifth hairpin-bend of the Canneto–Lami road (AGIP, 1984); one comes from works refuse found at Contrada Diana (near Lipari town).

The Pantelleria obsidians analysed belong to the Green Tuff Formation and were collected at Fossa della Perrace (near Bagno di Venere), and at Balata dei Turchi and Saltò La Vecchia.

At Gyali, the samples were collected from the lava flows and domes of the north-eastern part of the islet.

The Melos samples come from the volcanic domes of the Nihia area, the lava flows of the Demenegaki area, the Lower Pleistocene pyroclastites of Mandrakia headland, Paxaina, Adamas, Prophet Ilias (near Kato Konia), the conglomerates of Adamas beach, Nihia, Tripiti and from works refuse found at Phylakopi and Sarakiniko.

Analytical Methods

All obsidian samples were analysed by both XRF and SEM-EDS methods.

XRF method

Major and trace element determinations of the whole rock were performed by XRF using a Philips PW1480/10 automatic spectrometer and following the analytical techniques outlined by Franzini, Leoni & Saitta (1972, 1975) and Leoni & Saitta (1976). Two reference standards (AGV-1 of USGS-U.S.A. and NIM-G of NIM-South Africa) were used: the precision is better than 5% for all elements with the exception of Ce, La and Ba for which the precision is better than 10%. Loss on ignition was not determined to permit a better comparison with SEM-EDS analyses.

SEM-EDS method

The chemical composition of the obsidian glass is fairly homogeneous: more than 200 microanalyses on different samples of obsidians always indicate the monotony of the glass composition in the same lava flow (Table 3). Therefore the chemical analysis, performed in several (3–4) points of the same sample, gives its average composition. Glass composition, as well as the nature of phenocrysts, varies among obsidians originated from different volcanoes and can also vary in different bodies of the same volcano.

SEM-EDS offers a well investigated analytical method which gives reliable results in analysing both glass and microphenocrysts. Samples may range in size from a few μm to more than 15 cm; before being analysed, they are cleaned by ultrasonic bath in absolute ethylic alcohol and coated with a carbon film. The microanalyses were performed with a S 360 Cambridge Scanning Electron Microscope coupled with a LINK AN 10,000 Energy Dispersive Spectrometer. X-ray intensities were converted in wt% oxides by ZAF4/FLS quantitative analyses software support of Oxford-Link

Table 1. Geodynamic setting, petrographic and geochemical characteristics and age of Mediterranean obsidian sources

Area	Occurrence	Petrographic Classification	Chemical Affinity	Geological Setting*	Geological Age Range	Radiometric Age: Age (Ma)	Radiometric Age: Method	Radiometric Age: References	Radiometric Age: Dated rock
Gyali	domes	rhyolites	calcalkaline	VIA	Quaternary	0·024	FT**	Wagner, Storzer & Keller, 1976	obsidian
	lava flows					2·01–8·04	FT	Durrani *et al.*, 1971	obsidian
						0·0314	FT	Bigazzi & Radi, 1981	obsidian
Melos	domes	rhyolites	calcalkaline	VIA	Middle–Upper Plioc.	0·88–1·47	K-Ar	Fytikias *et al.*, 1976	obsidian
	lava flows				Quaternary	1·71	K-Ar	Fytikias *et al.*, 1976	rhyolite
	pyrocl. deposits					1·50–1·91	FT	Bigazzi & Radi, 1981	obsidian
	conglomerates					2·15–0·95	K-Ar	Angelier *et al.*, 1977	rhyolite
						8·95–2·36	FT	Durrani *et al.*, 1971	obsidian
Pantelleria	domes	pantellerites	alkaline	CE	Quaternary	0·135	FT	Bigazzi *et al.*, 1971	obsidian
	lava flows	alkali-rhyolites				0·0508			
	pyrocl. deposits	trackites				0·0500	K-Ar	Cornette *et al.*, 1983	alkali-rhyolite
						0·0470			
Lipari	lava flows	alkali-rhyolites	calcalkaline	VIA	Quaternary	0·0114	FT	Bigazzi & Bonadonna, 1973	obsidian
	pyrocl. deposits	to rhyolites				0·0086	FT	Wagner, Storzer & Keller, 1976	obsidian
Monte Arci	lava flows	rhyolites	subalkaline	WP	Plioc.–Pleistoc.	2·8–3·2	K-Ar	Belluomini *et al.*, 1970	obsidian
			and			2·9–3·2	FT	Bigazzi *et al.*, 1971	obsidian
			middle-alkaline			3·2–3·3	K-Ar	Di Paola, Puxeddu & Santacroce, 1975	obsidian
						3·1	FT	Bigazzi *et al.*, 1976	obsidian
						3·26–3·24	^{40}Ar-^{39}Ar	Montanini & Villa, 1993	rhyolite, dacite, trachyte, basalt
Palmarola	domes	rhyolites	calcalkaline	CE	Upper Plioc.–Pleistoc.	1·6–1·7	Rb-Sr	Barberi *et al.*, 1967	obsidian, rhyolite
	lava flows					1·6	K-Ar	Belluomini *et al.*, 1970	obsidian
						1·7	FT	Bigazzi *et al.* 1971	obsidian

* VIA=volcanic island arc; WP=within-plate rifting; CE=crustal extension.
** FT=fission-track dating.

Analytical (U.K.). After analyses, the carbon film may be removed by ultrasonic bath in acetone or in ethylic alcohol and by brushing.

The analyses of many obsidians, carried out on both raw surface and polished section, give quite comparable data. In fact, the error due to different geometry between the standardization of the spectrometer and the microanalyses of obsidian are negligible because of the very small and therefore pratically flat surface of the analysed sample. The analyses of microcrystals are qualitative if they are smaller than 5 μm, semi-quantitative or quantitative if they are larger. The accuracy of the microanalytical data is checked by many reference materials (standards from Micro-Analysis Consultants Ltd.), taking into particular account the crystallochemical formula.

The Contribution of XRF Analyses

To date (Cann & Renfrew, 1964; Belluomini & Taddeucci, 1971; Ammermann *et al*. 1990; Crisci *et al.*, 1994; Williams-Thorpe, 1995), the chemical discrimination of the above mentioned six major obsidian sources in the Mediterranean area has been performed mainly on the basis of trace elements. Instead, Francaviglia (1984, 1995) suggests a discrimination by major elements also. Therefore, we determined major elements to verify the possibility of discriminating obsidians on their basis. The possibility of distinguishing obsidians on the basis of major elements is fundamental, because the amount of trace elements is lower than the detection limit of a Si(Li) ED Detector.

XRF analyses of obsidians from Palmarola, Lipari and Melos have already been published in part (Acquafredda *et al.*, 1995*a*). We now give the results of chemical analyses of Monte Arci, Pantelleria and Gyali obsidian as well. The mean values of the chemical analyses are listed in Table 2.

The XRF analysis confirms, in agreement with other authors:

(a) the good discrimination among the analytical data of the six obsidian sources on the basis of both trace and major elements;
(b) the presence of a sole chemical population at Palmarola, Lipari and Gyali, of two chemical populations at Monte Arci (Cann & Renfrew, 1964; Hallam & Warren, 1976; Montanini, 1992; Tykot, 1992), Pantelleria (Francaviglia, 1988) and Melos (Francaviglia, 1984).

Among major elements, SiO_2, CaO, Na_2O and K_2O chiefly discriminate obsidian; CaO versus SiO_2 and Na_2O/K_2O versus Al_2O_3 diagrams (Figure 2) are very useful. The chemical data point out that:

(1) SiO_2 content of Pantelleria obsidians is lower (<72%) than that of the other obsidians, whereas Na_2O (>5·6%) and MnO (>0·3%) are higher. Moreover, two populations are distinguishable: (a) Fossa della Perrace (near Bagno di Venere) obsidians (B.V.) and (b) Saltò la Vecchia and Balata dei Turchi obsidians (S.V.). A comparison between the two populations shows that Na_2O and Fe_2O_3 of B.V. obsidians are lower than those of S.V. obsidians (respectively, <5·6%, <7·6% and >6·2%, >9·6%) whereas TiO_2 is higher in B.V. (>0·5%) than in S.V. (<0·4%).
(2) Melos obsidian has a higher CaO percentage (>1·2%) than the other obsidians. Two obsidian populations are present: Melos 1 formed by obsidians from volcanic domes of the Nihia area, from pyroclastites of Mandrakie headland, Adamas, Prophet Ilias and from conglomerates of Adamas beach, Nihia, Tripiti; Melos 2 formed by obsidians from Demenegaki lava flows. Melos 1 contains more SiO_2 (>77·4%) and less CaO(<1·5%) than Melos 2 (SiO_2 <76·8% and CaO >1·5%) (Figure 2(a)).
(3) Gyali obsidian is characterized by the highest SiO_2 percentage (>78·5%) (Figure 2(a)).
(4) Obsidians of Monte Arci, Palmarola and Lipari can not be discriminated by the CaO versus SiO_2 diagram, but by the Na_2O/K_2O versus Al_2O_3; this diagram (Figure 2(b)) discriminates Lipari from Monte Arci obsidians well and points out two populations of Sardinia obsidians: (a) Western Arci: formed by obsidians outcropping at Riu Cannas and in the Canale Perdera-Riu Solacera area; and (b) Eastern Arci formed by obsidians outcropping in the Perdas Urias area.

Therefore, our research confirms that obsidians can be distinguished on the basis of major elements.

Results of the SEM-EDS Analyses

After having analysed obsidian by XRF, our aim was to determine the major elements of glass and, in addition, the nature of the microphenocrysts recognizable by SEM-EDS (sialic microphenocrysts are usually more recognizable under optical microscope, femic ones under BSD SEM image). The microanalyses of obsidian glasses, divided into two groups, are reported in Table 3: group A comprises the microanalyses of thin sections, group B those on raw surface. Both Table 3 and Figure 3 show that the results of the two types of analyses are comparable.

A comparison between Table 2 and Table 3 points out that the values of the main oxides are different; this is due to the fact that Table 2 gives the whole-rock chemical composition, while Table 3 gives the glass chemical composition. A comparison between the diagrams of Figure 2 and 3 emphasizes that the fields of the different obsidian populations have the same distribution.

Chemical data of Table 3 reveal the following discrimination features:

Table 2. XRF analyses of obsidians

	Gyali (N=7)		Melos 1 (N=18)		Melos 2 (N=3)		Pant.(B.V.) (N=2)	Pant.(S.V.) (N=4)		Lipari (N=10)		W-Monte Arci (N=23)		E-Monte Arci (N=2)	Palmarola (N=10)	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	$\bar{x}$	σ
SiO_2	78·61	0·04	77·74	0·16	76·77	0·06	70·46	71·71	0·08	76·05	0·15	76·05	0·06	73·78	75·62	0·35
TiO_2	0·14	0·00	0·18	0·01	0·21	0·00	0·54	0·25	0·02	0·08	0·00	0·11	0·00	0·35	0·11	0·01
Al_2O_3	11·95	0·02	12·60	0·08	12·92	0·03	10·71	7·64	0·20	12·70	0·04	13·35	0·07	13·93	12·74	0·12
Fe_2O_3	1·19	0·01	1·31	0·05	1·64	0·02	7·51	9·83	0·11	1·91	0·06	1·69	0·03	2·23	2·02	0·09
MnO	0·03	0·00	0·07	0·01	0·06	0·00	0·30	0·34	0·01	0·06	0·00	0·06	0·00	0·03	0·08	0·00
MgO	0·00		0·10	0·02	0·17	0·03	0·15	0·00		0·00		0·01	0·01	0·22	0·00	
CaO	0·64	0·01	1·28	0·05	1·56	0·01	0·49	0·28	0·01	0·70	0·02	0·60	0·01	0·94	0·49	0·03
Na_2O	3·43	0·02	3·57	0·04	3·70	0·01	5·61	6·22	0·05	3·80	0·02	3·14	0·03	3·00	4·36	0·07
K_2O	4·00	0·02	3·13	0·08	2·93	0·00	4·21	3·73	0·02	4·71	0·06	4·92	0·05	5·44	4·58	0·18
P_2O_5	0·01	0·00	0·02	0·00	0·02	0·00	0·03	0·01	0·00	0·00		0·06	0·00	0·10	0·01	0·00
Ba	681	2·79	408	4·99	402	3·79	78	50	3·83	34	2·12	111	2·90	759	28	2·70
Rb	146	0·69	116	3·36	108	1·73	138	188	1·70	300	3·72	259	1·64	178·5	466	12·22
Sr	61	1·90	93	3·71	103	3·46	0	0		13	0·79	24	0·47	121·5	4	0·42
Y	16	0·49	15	1·56	14	1·00	128	191	3·42	46	2·16	40	0·71	26	64	3·78
Zr	113	0·49	110	6·05	118	5·86	1507	1942	16·68	184	7·05	98	1·90	266	310	11·46
Nb	18	0·49	10	0·43	9	0·00	302	405	3·70	38	0·97	55	0·90	30	70	3·27
V	1	0·53	4	0·99	10	0·00	0	0		1	0·00	1	0·34	9·5	1	0·67
Cr	13	2·79	33	12·04	32	15·72	17	12	1·41	20	7·29	13	3·94	15·5	13	3·75
Ni	3	0·53	2	0·46	2	0·58	3	4	0·58	5	2·80	2	0·42	5	2	0·42
La	42	0·58	27	0·59	26	0·58	174	255	4·79	61	5·01	24	0·60	53	93	1·52
Ce	65	2·06	45	2·32	44	1·15	318	476	6·81	115	8·58	51	2·06	130	175	3·08

Gyali=North-eastern area of the island; Melos 1=Nihia, Adamas, Sarakiniko; Melos 2=Demenegaki; Pant. (B.V.)=Pantelleria Bagno di Venere; Pant. (S.V.)=Pantelleria Saltò la Vecchia and Balata dei Turchi; W-Monte Arci=Conca Cannas, Canale Perdera, Riu Solacera; E-Monte Arci=Perda Urias.

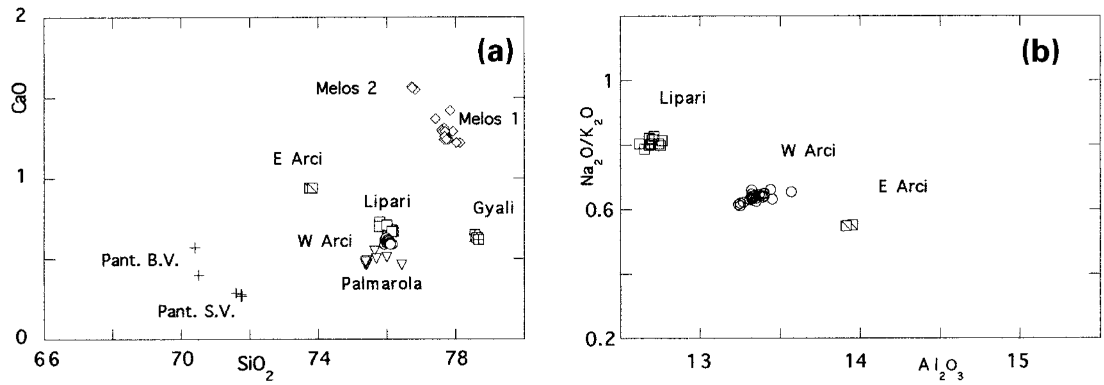

Figure 2. XRF chemical data plots. Gyali: ⊞; Melos: ◇; Pantelleria: +; Lipari: □; Western Monte Arci: ○; Eastern Monte Arci: ⧅; Palmarola: ▽.

(1) Pantelleria obsidian glass contains less SiO_2 (<73·3%) and CaO (<0·2%) than the other samples (Figure 3(a)). The main feature of Pantelleria obsidian glass is the highest contents of FeO (>7·0%) and Na_2O (>4·3%). Besides, the MnO content ranges from 0·17 to 0·47%, whereas the Mn values of the other obsidians are below the detection limit.
SEM-EDS analyses point out two populations (B.V. and S.V.), mainly on the grounds of SiO_2 and TiO_2 percentages (Figure 4(a)). Moreover, in B.V. obsidian glass SiO_2 is <69·0%, TiO_2 >0·5%; whilst in S.V. obsidian glass SiO_2 is >71·0%, TiO_2<0·4%.

(2) Melos and Gyali obsidian glasses are the richest in SiO_2 (>75·5%); CaO percentage allows the glasses of the two islands to be distinguished (Gyali: CaO<0·70; Melos: CaO>0·70, see Figure 3(a)). Moreover, at Melos, CaO content discriminates two different populations: the obsidians outcropping in the Domenegaki area (Melos 2, with CaO>1·40%) and the other (Melos 1, with CaO <1·40%) (Figure 3(a)).

(3) SiO_2 content of Palmarola, Lipari and Monte Arci obsidian glasses vary in the same range (73·0–76·0%); however, Palmarola has a lower CaO content (<0·20%) (Figure 3(a)). A CaO versus Na_2O diagram also plainly discriminates Palmarola from Lipari and Monte Arci obsidians (Figure 4(b)).

(4) Lipari and Monte Arci obsidian glasses have similar chemical compositions; nevertheless, a Na_2O/K_2O versus Al_2O_3 diagram (Figure 3(b)) allows a good discrimination between the two sources and reveals the existence of two populations at Monte Arci; the obsidians outcropping on its eastern slope (E-Arci) are richer in Al_2O_3, although they have the same Na_2O/K_2O ratio, than those outcropping on the western slope (W-Arci).

(5) The nature of microphenocrysts contributes to discriminate obsidians from different sources; in fact, obsidians outcropping in the six Mediterranean islands contain different microphenocrysts (Table 4). Femic minerals are more recognizable by Back Scattered Detector, on row surfaces such as artefacts, than are sialic minerals, since the mass absorption coefficient of the latter is similar to that of glass. Therefore pyroxenes, amphiboles and biotite microphenocrysts allow the best discrimination.

Pantelleria obsidians are poor in microphenocrysts, which are constituted by relatively big crystals of anorthoclase (50–150 μm) and apatite; clinopyroxene, magnetite and olivine are also present.

All Melos obsidians are rich in microphenocrysts of clinopyroxene (5–20 μm) and magnetite. Sometimes present are biotite, amphibole (with spinifex-like texture) and orthopyroxene microphenocrysts.

The microphenocrysts characteristic of Gyali are quartz (150 μm) and biotite (60–80 μm); scarse pyrite and apatite and rare clinopyroxene, sometimes in synneusis with magnetite, are present.

Palmarola microphenocrysts are mainly of very small clinopyroxenes (5–20 μm) and biotite.

Lipari obsidians contain clinopyroxene microphenocrysts (10–50 μm), almost always in synneusis with magnetite and olivine microphenocrysts.

Both Monte Arci populations are characterized by large biotite microphenocrysts (50–200 μm) with spinifex-like texture, by many crystals of feldspars (plagioclase and alkali feldspars, 50 μm in size), orthopiroxenes, magnetite, monazite and ilmenite.

Conclusions

Our research demonstrates that the proposed SEM-EDS analytical method has a potential for wide use in discriminating and discovering the source areas of archaeological obsidian artefacts, being relatively rapid, effective and above all non-destructive. Samples ranging from a few μm to 15 cm in size can be analysed. The only treatment of the artefact is a

Table 3. SEM-EDS microanalyses on (a) thin sections and (b) raw surfaces of obsidian glass

	Gyali		Melos 1		Melos 2		Pant.(B.V.)		Pant.(S.V.)		Lipari		W-Monte Arci		E-Monte Arci		Palmarola	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
(a)	(*N*=30)		(*N*=19)		(*N*=5)		(*N*=0)		(*N*=6)		(*N*=25)		(*N*=38)		(*N*=7)		(*N*=26)	
SiO_2	77·61	0·21	77·14	0·28	76·25	0·22			71·97	0·32	75·03	0·23	75·12	0·30	73·76	0·52	74·79	0·34
TiO_2	0·19	0·08	0·17	0·07	0·24	0·04			0·21	0·06	0·07	0·08	0·10	0·07	0·32	0·07	0·11	0·07
Al_2O_3	12·50	0·18	13·57	0·14	13·59	0·13			8·00	0·15	13·51	0·22	14·33	0·19	14·78	0·21	13·92	0·21
FeO	0·81	0·10	0·59	0·12	1·10	0·19			7·62	0·20	1·40	0·15	1·10	0·12	0·99	0·24	0·88	0·10
CaO	0·43	0·04	1·02	0·08	1·49	0·06			0·10	0·03	0·52	0·07	0·36	0·05	0·60	0·14	0·06	0·05
Na_2O	3·88	0·14	4·09	0·24	4·01	0·24			7·55	0·30	4·34	0·36	3·97	0·20	3·50	0·54	5·25	0·35
K_2O	4·58	0·11	3·41	0·08	3·31	0·04			4·22	0·07	5·11	0·30	5·03	0·10	6·05	0·60	4·97	0·16
(b)	(*N*=32)		(*N*=23)		(*N*=3)		(*N*=8)		(*N*=11)		(*N*=24)		(*N*=35)		(*N*=0)		(*N*=11)	
SiO_2	77·43	0·25	76·69	0·38	75·95	0·33	68·10	0·47	72·45	0·66	74·99	0·28	75·41	0·37			74·94	0·31
TiO_2	0·18	0·06	0·16	0·07	0·17	0·02	0·69	0·09	0·22	0·06	0·07	0·06	0·11	0·06			0·13	0·07
Al_2O_3	12·53	0·50	13·75	0·24	13·56	0·30	10·89	0·80	8·20	0·20	13·45	0·16	14·13	0·20			13·82	0·19
FeO	0·84	0·11	0·59	0·14	1·29	0·13	8·35	1·19	7·67	0·35	1·41	0·13	1·12	0·10			0·91	0·09
CaO	0·44	0·06	0·99	0·08	1·56	0·06	0·13	0·06	0·10	0·04	0·51	0·05	0·39	0·06			0·05	0·05
Na_2O	4·00	0·34	4·60	0·51	4·12	0·16	6·48	1·02	6·85	0·76	4·39	0·33	3·67	0·39			5·09	0·29
K_2O	4·56	0·18	3·27	0·12	3·35	0·07	4·98	0·40	4·19	0·04	5·17	0·22	5·18	0·17			5·07	0·13

For samples locality see Table 2; for all samples, MnO is below the detection limit except for Pantelleria samples containing MnO ranging from 0·17 to 0·47.

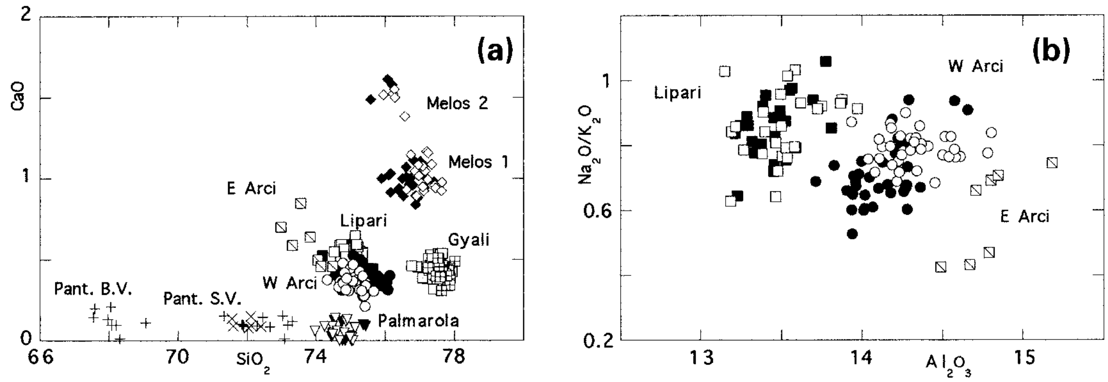

Figure 3. SEM-EDS chemical data plots. rs=raw surfaces; ts=thin sections. Gyali (rs): ⊡; Gyali (ts): ⊞; Melos (rs): ◆; Melos (ts): ◇; Pantelleria (rs): +; Pantelleria (ts): × ; Lipari (rs): ■; Lipari (ts): □; Western Monte Arci (rs): ●; Western Monte Arci (ts): ○; Eastern Monte Arci (ts): ⧅; Palmarola (rs): ▼; Palmarola (ts): ▽.

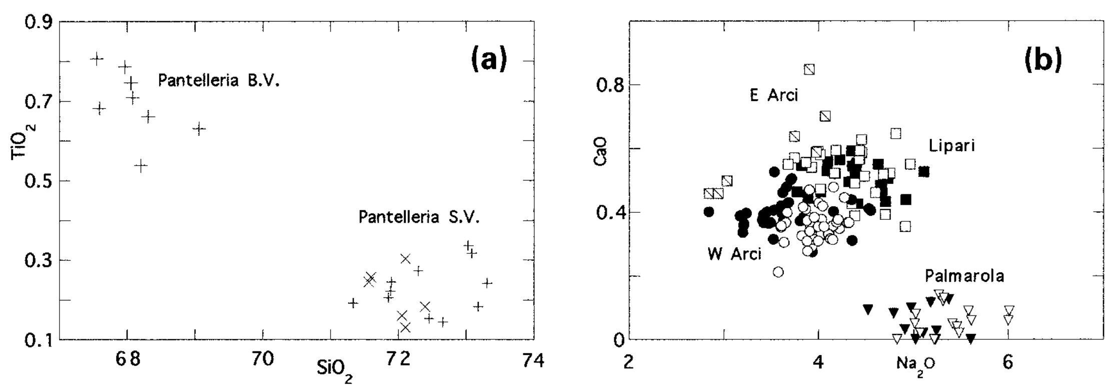

Figure 4. SEM-EDS chemical data plots. Symbols as in Figure 3.

coating with a carbon film which can be removed by either ethilic alcohol or acetone.

Moreover, our research allows the obsidian artefacts of the main Mediterranean sources to be discriminated by means of four diagrams only: the CaO versus SiO_2 diagram discriminates two populations at Melos, two at Pantelleria and discriminates Gyali and Palmarola obsidians; the same diagram does not allow Lipari obsidians to be distinguished from those of Arci. Also, Lipari obsidians and two populations of Arci obsidians are well discriminated by the Na_2O/K_2O versus Al_2O_3 diagram. The TiO_2 versus SiO_2 diagram discriminates the two populations of Pantelleria, whereas the CaO versus Na_2O diagram discriminates Palmarola from Lipari and Arci obsidians.

Microchemical investigation on the microphenocrysts present in the obsidian samples stress the discrimination among their different source areas.

Table 4. Microphenocrists recognized in the obsidians

Gyali	Qtz+Bt ± Py ± Ap ± Cpx ± Mag
Melos	Cpx ± Bt ± Amph ± Opx
Pantelleria	Anrt+Ap ± Cpx ± Mag ± Ol
Lipari	Cpx+Mag+Ol
Monte Arci	Bt+Pl+AlkFeld+Opx+Mag ± Mnz ± Ilm
Palmarola	Cpx+Bt

Amph=Amphibole; Anrt=Anorthoclase; AlkFeld=alkali Feldspar; Ap=Apatite; Bt=Biotite; Cpx=Clinopyroxene; Ilm=Ilmenite; Mag=Magnetite; Mnz=Monazite; Ol=Olivine; Opx=Orthopyroxene; Pl=Plagioclase Py=Pyrite; Qtz=Quartz; Zrn=Zircon.

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