

NEW INSIGHTS INTO THE PROVENANCE OF THE OBSIDIAN FRAGMENTS OF THE ISLAND OF USTICA (PALERMO, SICILY)*

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In this study we applied a multidisciplinary approach, coupling geophysical and geochemical measurements, to unveil the provenance of 170 obsidian flakes, collected on the volcanic island of Ustica (Sicily). On this island there are some prehistoric settlements dated from the Neolithic to the Middle Bronze Age. Despite not having geological outcrops of obsidian rocks, the countryside of Ustica is rich in fragments of this volcanic glass, imported from other source areas. The study of obsidian findings was carried out first through visual observations and density measurements. At least two different obsidian families have been distinguished, probably imported from Lipari and Pantelleria islands. Analysing the magnetic properties of the samples, these two main sources were confirmed, but the possibility of other provenances was inferred. Finally, we characterized the geochemical signature of the Ustica obsidians by performing microchemical analyses through electron microprobe (EMPA) and laser ablation (LA-ICP-MS). The results were compared with literature data, confirming the presence of the Lipari and Pantelleria sources (Sicily) and indicating for the first time in this part of Italy a third provenance from Palmarola island (Latium). Our results shed new light on the commercial exchanges in the peri-Tyrrhenian area during the prehistoric age.

KEYWORDS: OBSIDIAN, PROVENANCE STUDIES, GEOCHEMICAL AND PHYSICAL ANALYSES, PERI-TYRRHENIAN AREA, USTICA ISLAND, NEOLITHIC, BRONZE AGE

INTRODUCTION

In the Western and Central Mediterranean, there are four main geological sources of obsidian natural glasses. These are located on the Italian islands of Sardinia (Monte Arci), Lipari, Pantelleria and Palmarola (Fig. 1), and were widely exploited during the Neolithic and the Bronze Age (~6000–1000 BC) to obtain raw materials for the manufacture of tools. Obsidian was transferred to a large number of prehistoric villages from these geological sources, feeding trade and cultural exchanges between the ancient populations. In the past few decades, studies on the provenance of archaeological obsidian fragments have been based on their chemical and physical characterization, which proved to be powerful investigative tools to reconstruct the ancient trade routes and the relations between distant peoples (e.g., Cann and Renfrew

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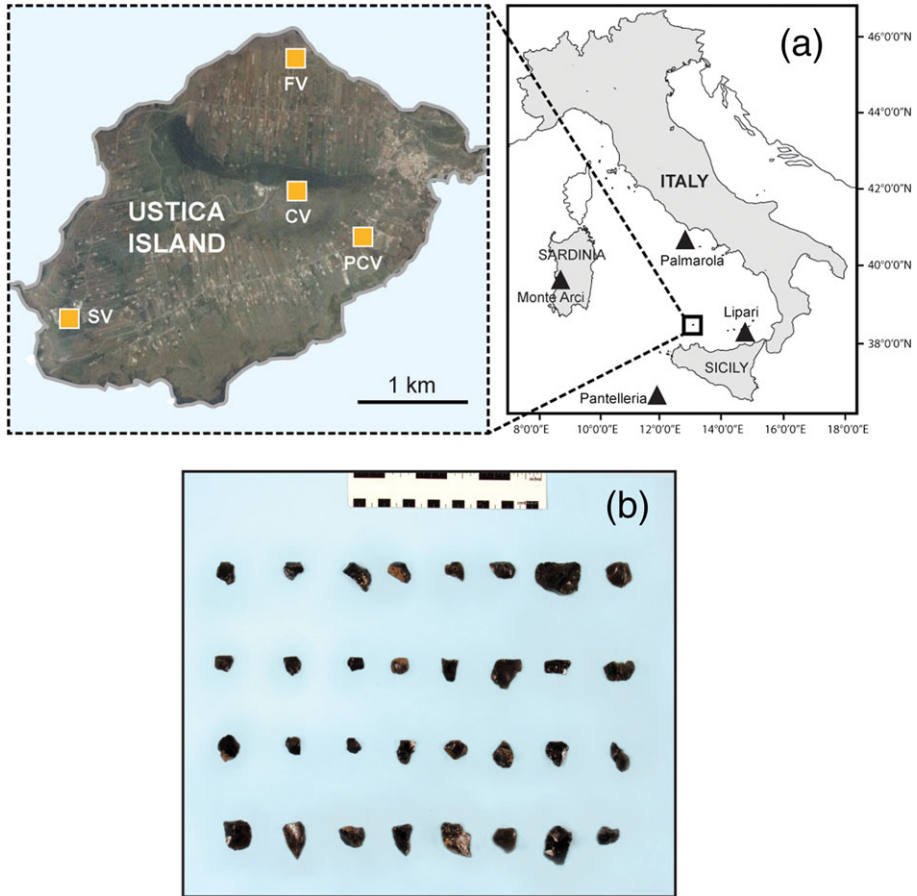


Figure 1 (a) The location of the island of Ustica, with indications of the main archaeological sites: SV, Spalmatore village; FV, Faraglioni village; CV, Culunnella village; PCV, Piano dei Cardoni village. (b) Obsidian fragments from the island of Ustica.

1964; McDougall *et al.* 1983; Francaviglia 1984; Francaviglia and Piperno 1987; Francaviglia 1988; Bigazzi *et al.* 1993; Williams-Thorpe 1995; Acquafredda *et al.* 1996, 1999; Tykot 1996; Tykot and Young 1996; Le Bourdonnec *et al.* 2010; Tykot *et al.* 2013). In particular, geochemical methods (e.g., electron microprobe analyser, EMPA; scanning electron microscopy, SEM-EDS; X-ray fluorescence, XRF; neutron activation analysis, NAA; proton-induced X-ray emission, PIXE; laser ablation, LA-ICP-MS) have proved to be the best techniques to correlate the obsidian fragments with their source of provenance (e.g., Acquafredda *et al.* 1996, 1999; Oddone *et al.* 1999; Le Bourdonnec *et al.* 2006; Barca *et al.* 2007; De Francesco *et al.* 2008; Tykot *et al.* 2013). The laser ablation offers the advantage of analysing a great number of trace elements and in particular rare earth elements (REE) with high precision and sensitivity, a rapid analytical time and minimal damage to the sample (e.g., Speakmann and Neff 2005; Barca *et al.* 2007). Also, previous rock magnetic studies indicated that the analysis of various magnetic properties can be effective for distinguishing the obsidians from different Central Mediterranean sources (e.g., McDougall *et al.* 1983; Weaver 2005; Weaver *et al.* 2005; Zanella *et al.* 2012).

This paper deals with the obsidian collected on the island of Ustica, located 70 km north of the coast of Palermo (Sicily; Fig. 1 (a)), which is the northernmost prehistoric settlement of western Sicily and an unexpected centre of ancient trade and cultural exchanges. As a matter of fact, Ustica has been inhabited since at least the Neolithic, as demonstrated by the Neolithic Spalmatore settlement (sixth to fifth millennia BC), the Piano dei Cardoni Eneolithic village (fourth to third millennia BC), the Colunnella Ancient Bronze Age village (third to second millennia BC) and the Faraglioni Middle Bronze Age village (14th–13th centuries BC) (Fig. 1 (a)) (e.g., Holloway and Lukesh 1995; Spatafora and Mannino 2008). These archaeological sites are rich in obsidian fragments, which derive exclusively from the importation of raw materials and artefacts from distant sources, as no obsidian natural outcrops are found on this volcanic island.

We used a multidisciplinary approach, coupling physical (density and magnetic properties) and geochemical analyses (major elements by EMPA and trace elements by LA-ICP-MS) to unravel the provenance of the archaeological obsidian fragments collected on the surface near to the archaeological sites previously mentioned.

THE ISLAND OF USTICA

The island of Ustica (Fig. 1 (a)) is the small subaerial part (~8.6 km²) of a large submarine volcanic complex (around 100 km²) that rises over 2200 m from the bottom of the Tyrrhenian Sea. The first volcanic activity was subaqueous (e.g., Romano and Sturiale 1971) and became subaerial at ~500 ka (De Vita *et al.* 1998). The most recent eruptive activity is related to the Falconiera tuff cone (~130 ka) and at the present time the volcano is considered inactive. Even if the eruptive activity of Ustica was almost contemporaneous with that of the nearby Aeolian volcanoes (Barberi and Innocenti 1980; De Vita *et al.* 1995), the petrological affinity of the eruptive products of the two volcanic systems is completely different. The volcanics of Ustica show Na-alkaline affinity, ranging in composition from basalts to trachytes, with the mafic products dominant by far over the felsic products (Romano and Sturiale 1971; Civetta *et al.* 1981; Cinque *et al.* 1988; De Vita 1993; Bellia *et al.* 2000) and suggesting an intraplate (i.e., anorogenic) affinity, whereas the magmas of the Aeolian islands have a clear island-arc signature, related to the subduction of the Ionian plate beneath the Tyrrhenian crust (Peccerillo 2003).

The most evolved trachytic products of Ustica belong to the volcanic unit of Grotte del Lapillo. The deposits consist of pumice and ash fall-out layers, without subaerial effusive products, which instead are found as submarine lavas in the Colombara shoal (Bellia *et al.* 2000). This unit represents the only silica-rich volcanic event that could have generated glassy/obsidianaceous rocks—which, however, have never been reported. The lack of obsidian natural outcrops on the island is confirmed by several studies that deal in detail with the volcanic history of Ustica (e.g., Romano and Sturiale 1971; Cinque *et al.* 1988; De Vita 1993).

MATERIALS AND METHODS

We analysed a set of 170 obsidian flakes (Fig. 1 (b)), collected on the surface of the island. These samples belong to the 'Museo della Parrocchia di San Ferdinando Re' of Ustica and were collected by the late C. G. Seminara, honorary inspector of the Soprintendenza BB.AA.CC. of Palermo, in the surroundings of the aforementioned four main archaeological settlements. Unfortunately, no specific information about the sampling location, and thus the age of each fragment, has been found. However, as inferred by the dating of the Ustica archaeological settlements (e.g., Spatafora and Mannino 2008), we can generally state that this collection spans

a time interval ranging from the Neolithic to the Bronze Age. In addition, we analysed a group of geological samples as representative of the main obsidian sources of the Central Mediterranean. These samples were collected *in situ* by the authors and are related to the following four obsidian natural outcrops: Lipari (eastern side of the island, Vallone del Gabellotto), Pantelleria (northern side of the island, close to Lago di Venere), Palmarola (eastern side of the island, near La Forcina) and Sardinia (western side of Monte Arci, near Marrubiu).

The samples were analysed at the laboratories of the INGV—Istituto Nazionale di Geofisica e Vulcanologia in Rome and Palermo. The obsidian flakes have the typical appearance of black to grey volcanic glasses, with some fragments that show green and brown shades, and are often marked by granular inclusions (microlites) or whitish pumiceous veins. In a few cases, the samples have the shape of tools, blades, scrapers, arrowheads and human artefacts; more frequently, they are processing waste, or processed objects then reduced into fragments. In any case, this study does not include the detailed morphological characterization of these obsidian samples. We can only observe that the presence of abundant waste flakes on the soil surface could indicate a local production of obsidian artefacts from the imported raw material.

The characterization of the physical properties of the obsidians includes density measurements and magnetism. The bulk density of the samples has been determined by immersion in distilled water, using an analytical balance; these measurements were carried out discarding the altered or inhomogeneous samples. Then rock magnetic properties were measured at the INGV palaeomagnetic laboratory in Rome; we first analysed 32 geological samples and 50 archaeological samples from Ustica. For these specimens, we measured, in order:

- The mass-specific magnetic susceptibility (χ).
- The natural remanent magnetization (NRM). The NRM was then stepwise demagnetized by the application of an alternating magnetic field (AF) up to a maximum peak value of 100 mT.
- The anhysteretic remanent magnetization (ARM), produced by simultaneous application of an AF of 100 mT and a direct current (DC) bias field of 0.05 mT. The ARM was then AF stepwise demagnetized as for the NRM.
- The isothermal remanent magnetization (IRM), produced stepwise with the application of pulse magnetic fields up to 0.9 T ($IRM_{0.9T}$). The IRM was then AF stepwise demagnetized as for the NRM and the ARM.

The magnetic susceptibility was measured using an AGICO MFK-1 kappabridge, while the remanent magnetizations (NRM, ARM and IRM) were measured on a 2G Enterprises superconducting rock magnetometer, with SQUID sensors and in-line AF and DC coils, installed within a magnetically shielded room.

We then systematically measured χ , NRM and $IRM_{0.9T}$, which were the parameters that displayed the most interesting variations, on additional 120 obsidian specimens collected in Ustica.

Samples were prepared for chemical point micro-analyses, cutting slices of $\sim 0.5\text{ cm}^2$ from each obsidian flake, which were then embedded in epoxy resin, abraded and polished (until they became $0.3\text{ }\mu\text{m}$ grain-sized polycrystalline diamond slurry). The resulting mounts were ultrasonically washed in bi-distilled water and carbon-coated before microprobe analysis.

The major elements composition of the glasses was measured at the INGV laboratory in Rome, using an electron microprobe (EMPA; JEOL JXA8200) combined with an energy- and five wavelength-dispersive spectrometer detectors. We used a slightly defocused beam with a size of $5\text{ }\mu\text{m}$, with a counting time of 5 s for the background and 15 s for the peak. The analytical error was less than 5%.

The trace elements composition of the obsidians was analysed at the INGV laboratory in Palermo using LA-ICP-MS. Due to the limited availability of the instrument, was applied a stricter selection and 33 representative archaeological obsidians were chosen from our collection, on the basis of the main differences that had arisen from the major element geochemistry and on the comparison between archeological flakes, geological samples and literature data. The instrument is equipped with a GeoLasPro 193 nm ArF Excimer laser ablation (LA) system, connected to an Agilent 7500ce quadrupole ICP-MS. Data acquisition was accomplished in peak-jumping mode, with one point per peak and 10 ms dwell. The plasma conditions were adjusted to oxide formation <1% and monitored using the 248/232 mass ratio. On each fragment, three spots with a diameter of 32 μm were realized, in order to monitor the compositional heterogeneity related to the eventual occurrence of microlites. The operating conditions of the laser device, for crater spots of 32 μm , were as follows: 10 Hz of repetition rate, 15 J cm^{-2} of fluence and 0.8 L min^{-1} of He flux in the ablation cell. Each spot analysis lasted for 2 min, including 1 min for background acquisition and 1 min for the analysis. NIST RM 612 was used as an external standard and was measured at the beginning and at end of each group of analyses (25 measurements). ^{29}Si was used as the internal standard, obtained by EMPA measurements. The data were processed using the Glitter program (Van Achterbergh *et al.* 2001) and the results were corrected for the fractionation index as suggested by Pearce *et al.* (2011) for rhyolitic compositions. The accuracy of the analyses (RSD%) was checked by repeated analyses of the USGS basaltic reference glass BCR-2G, and turned out to be between 2% and 5% for K, Sc, Ti, V, La, Ce, Eu and Th, between 6% and 10% for Li, Rb, Sr, Cs, Ba, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, Ta, Pb and U, and between 11% and 15% for Zn, Y, Zr, Tb, Lu and Hf.

RESULTS AND DISCUSSION

The 170 obsidian samples from the island of Ustica were analysed for both physical and chemical properties, in order to evaluate their provenance and eventually to find sources not previously mentioned in the literature.

Visual observations

A first rough characterization of the obsidian flakes was possible through observations with the naked eye and under the optical microscope. On the basis of features such as colour, opacity and textural heterogeneity, two main populations of obsidians have been recognized: (i) transparent obsidians with grey to brownish coloration and either varying amounts of microlites or free of microlites, these possibly belonging to Lipari quarries; and (ii) dark obsidians, whose greenish to black colour is due to their high Fe content (chiefly Fe^{2+}), a unique feature of Pantelleria peralkaline rhyolites (pantellerite rocks). This effect could be enhanced in some samples by the occurrence of sparse Na-Fe-rich clinopyroxene microlites, the presence of which was confirmed by SEM observations (S. Rotolo pers. Comm.).

Density measurements

The density frequency histograms of the Ustica obsidian samples are plotted in Figure 2. The density distribution is mainly bimodal with two modes, at 2.35 g cm^{-3} and at 2.47 g cm^{-3} respectively. These two modes represent the mode density values expected for Lipari and Pantelleria

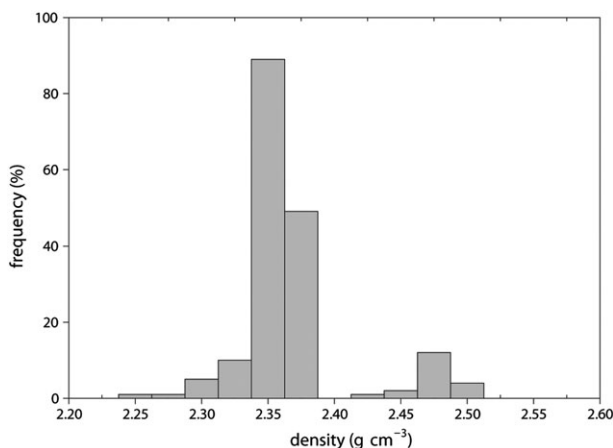


Figure 2 The frequency histogram of the density (g cm^{-3}) of 170 obsidian samples from Ustica.

obsidian specimens respectively (e.g., Vargo 2003). With this method, it is not possible to distinguish samples with densities typical of other sources, if they are statistically poorly represented.

Rock magnetic properties

The rock magnetic data show that high-coercivity minerals are the main magnetic carriers for all categories of samples, as indicated by the limited efficiency of the AF demagnetization treatment and by the observation that IRM is far from saturation at 0.9 T.

The prevalence of high-coercivity minerals implies that the ARM measurements have a low level of significance, so the analyses on the whole collection of specimens from Ustica were mostly based on the χ , NRM and $\text{IRM}_{0.9\text{T}}$ values. In fact, the data from the pilot samples indicate that samples of different origin have distinct magnetic properties and that the intensity of χ , NRM and $\text{IRM}_{0.9\text{T}}$ can potentially discriminate between the different sources (Figs 3 (a) and 3 (c)). The data collected on the 170 obsidian samples from Ustica indicate a mixing of different sources, with data spread along a main linear trend in the $\text{IRM}_{0.9\text{T}}$ versus NRM plot, stretching from values typical of Pantelleria obsidians to values typical of Monte Arci obsidians, and a main cluster on values typical of the Lipari obsidians (Fig. 3 (b)). The $\text{IRM}_{0.9\text{T}}$ versus χ plot allows easy identification of the obsidians of probable Pantelleria origin, since their data plot below the main linear trend defined by the other obsidian samples (Fig. 3 (d)).

The obsidian flakes recovered at Ustica are characterized by a larger range of variation of the magnetic properties with respect to those measured on the different geological obsidians (Fig. 3). We are confident in correlating some obsidian flakes to Pantelleria. On the other hand, with this method, it remains difficult to accurately distinguish in our data set, the Lipari, Palmarola and Monte Arci sources.

Geochemical composition

The chemical composition of the archaeological and geological samples, for both major and trace elements, is listed in Table 1 (the entire set of analyses performed using EMPA is available in Table S1). In the total alkali versus silica diagram (Le Bas *et al.* 1992), almost all the analysed

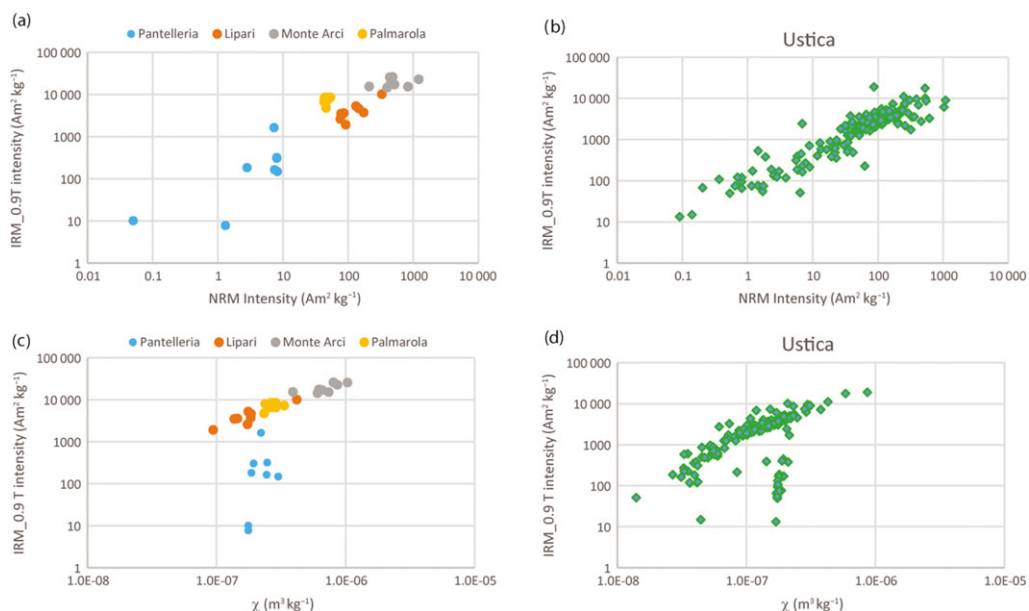


Figure 3 The rock magnetic parameters of pilot samples from four different sources (a,c) and from the whole collection of Ustica specimens (b,d). IRM versus NRM intensities are shown in (a) and (b), while IRM intensities versus mass-specific susceptibility values are shown in (c) and (d). Data from pilot samples indicate that different sources can be distinguished on the basis of the rock magnetic parameters and define a distribution similar to that reported by McDougall *et al.* (1983). The data from the Ustica obsidians indicate a distribution that is compatible with a mixture of fragments from different sources.

obsidians lie in the compositional field of rhyolites, with an SiO_2 content ranging between 71.7 wt% and 75.8 wt% and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ between 9.5 wt% and 12.2 wt% (see Fig. 4 (a) and inset). Only one sample (UST-10) plots in the field of trachytes (SiO_2 , 66.7 wt%; $\text{Na}_2\text{O} + \text{K}_2\text{O}$, 12.2 wt%).

On the basis of the silica and alkali composition, the archaeological obsidian flakes tend to gather in two main groups, which correspond to glasses with different peralkalinity indexes (P. I. = molar $[(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3]$). The largest group, which consists of 149 samples, occupies the compositional range with higher silica (74.4–75.8 wt%) and lower alkali (8.9–9.8 wt%) contents (Fig. 4 (a)). These flakes have a P.I. between 0.86 and 0.99. Comparison with geological obsidians and literature data (Le Bourdonnec *et al.* 2010) suggests that most of them probably belong to Lipari. The smaller group, which comprises 20 samples, shows a slightly lower silica content (66.7–72.7 wt%) and a significantly higher content of total alkali (11.0–12.2 wt%) (Fig. 4 (a)), and has a P.I. > 1.5. These are typical features of pantellerite rocks, rhyolites characterized by an excess of alkali with respect to aluminium, low Al and high Fe. We can assign to these obsidians a provenance from the Pantelleria source. The observed compositional differences between Pantelleria archaeological and geological samples could be due to a different source sampling, given the variety of obsidian quarry candidates, and the consideration that differences among peralkaline rocks (strongly peralkaline pantellerites to slightly peralkaline comendites) consist in subtle variations of Na and Al contents. One sample (UST-49) is characterized by a higher alkali content with respect to the Lipari group (Fig. 4 (a)), also displaying a slightly higher peralkalinity (P.I. = 1.04; Table 1); these are geochemical features that could be attributed to the

Table 1 *The chemical data of a selected suite of the studied samples, where both major elements (in wt%, determined by electron microprobe) and trace elements (in ppm, analysed by LA-ICP-MS) have been performed*

Sample	UST-1	UST-6	UST-7	UST-10	UST-11	UST-14	UST-20
Number of analyses	2	3	2	2	2	2	2
Provenance	Lipari	Pant.	Lipari	Pant.	Lipari	Lipari	Lipari
SiO ₂	75.20	72.22	75.03	66.75	75.52	74.61	74.98
TiO ₂	0.06	0.15	0.10	0.67	0.01	0.08	0.11
Al ₂ O ₃	13.21	7.68	13.05	11.16	13.13	13.29	12.95
FeO	1.54	8.14	1.34	8.10	1.19	1.52	1.57
MnO	0.04	0.32	0.02	0.35	0.02	0.05	0.07
MgO	0.05	0.05	0.06	0.17	0.04	0.03	0.02
CaO	0.77	0.23	0.77	0.51	0.68	0.76	0.69
Na ₂ O	3.91	6.82	4.19	7.35	3.96	4.12	3.58
K ₂ O	5.20	4.35	5.42	4.84	5.41	5.50	6.02
P ₂ O ₅	0.02	0.03	0.02	0.10	0.02	0.03	0.01
P.I.	0.91	2.07	0.98	1.55	0.94	0.96	0.96
Na ₂ O/K ₂ O	0.75	1.57	0.77	1.52	0.73	0.75	0.60
Na ₂ O + K ₂ O	9.11	11.18	9.61	12.19	9.38	9.62	9.60
⁷ Li	88	52	89	25	86	93	84
⁹ Be	7	11	7	6	7	8	7
¹¹ B	213	23	214	11	210	218	182
³⁹ K	36 807	31 271	37 280	34 854	44 499	38 665	36 287
⁴⁵ Sc	2	3	2	5	3	2	3
⁴⁷ Ti	466	1397	465	3879	474	477	435
⁵¹ V	0	0	0	0	1	0	0
⁵⁹ Co	0	0	0	0	0	0	0
⁶³ Cu	7	3	7	3	9	6	6
⁶⁶ Zn	50	456	49	272	45	49	45
⁸⁵ Rb	284	184	287	109	288	296	256
⁸⁸ Sr	13	3	14	1	15	14	12
⁸⁹ Y	40	194	45	107	43	50	44
⁹⁰ Zr	162	1 807	180	1 061	172	195	175
⁹³ Nb	37	436	38	235	37	39	33
¹³³ Cs	15	3	16	1	15	16	13
¹³⁷ Ba	15	25	15	27	14	15	12
¹³⁹ La	51	241	55	129	51	58	48
¹⁴⁰ Ce	96	429	99	223	104	101	83
¹⁴¹ Pr	10	45	10	24	11	11	9
¹⁴⁶ Nd	39	188	41	105	39	44	34
¹⁴⁷ Sm	7	31	7	17	7	8	6
¹⁵³ Eu	0	4	0	3	0	0	0
¹⁵⁷ Gd	6	33	7	18	7	7	6
¹⁵⁹ Tb	1	5	1	3	1	1	1
¹⁶³ Dy	5	30	6	17	7	7	5
¹⁶⁵ Ho	1	7	1	4	1	2	1
¹⁶⁶ Er	4	19	4	11	4	5	4
¹⁶⁹ Tm	0	2	1	1	1	1	0
¹⁷² Yb	4	15	4	8	4	5	4
¹⁷⁵ Lu	1	2	1	1	1	1	1
¹⁷⁸ Hf	5	36	5	20	6	6	5
¹⁸¹ Ta	2	22	2	12	2	2	2
²⁰⁸ Pb	31	16	32	8	32	32	24
²³² Th	41	31	45	16	47	50	37
²³⁸ U	14	11	15	5	14	15	11

*P.I., percalcinity index.

The samples named 'UST-' are the archaeological samples, while those named 'LIP-', 'PANT-', 'PALM-' and 'MARCI-' are the geological samples analysed in this study.

[Correction added on 20 February 2017, after first online publication: The data for rows 14 to 49 (⁷Li to ²³⁸U) of samples UST-20 and UST-56 have been interchanged.]

Table 1 (Continued)

Sample	UST-29	UST-31	UST-33	UST-35	UST-42	UST-43	UST-49
Number of analyses	2	2	2	2	2	2	2
Provenance	Lipari	Lipari	Pant.	Lipari	Lipari	Lipari	Palm.
SiO ₂	74.87	75.61	72.02	74.87	75.23	74.90	75.09
TiO ₂	0.06	0.04	0.21	0.07	0.06	0.15	0.08
Al ₂ O ₃	13.17	12.66	7.60	13.32	12.82	13.04	12.98
FeO	1.58	1.39	8.08	1.52	1.32	1.46	1.36
MnO	0.11	0.00	0.31	0.09	0.10	0.01	0.03
MgO	0.04	0.03	0.04	0.01	0.01	0.03	0.06
CaO	0.69	0.77	0.36	0.67	0.64	0.73	0.38
Na ₂ O	4.04	4.16	6.94	3.85	4.09	3.89	4.66
K ₂ O	5.43	5.32	4.41	5.55	5.68	5.77	5.35
P ₂ O ₅	0.00	0.02	0.01	0.06	0.05	0.01	0.00
P.I.	0.95	0.99	2.13	0.93	1.00	0.97	1.04
Na ₂ O/K ₂ O	0.74	0.78	1.57	0.69	0.72	0.67	0.87
Na ₂ O + K ₂ O	9.47	9.48	11.36	9.40	9.78	9.66	10.01
⁷ Li	27	83	48	116	96	95	57
⁹ Be	8	6	10	7	8	6	9
¹¹ B	220	210	19	186	211	192	69
³⁹ K	42 213	43 521	31 997	38 793	38 644	40 887	37 119
⁴⁵ Sc	2	3	6	5	3	5	5
⁴⁷ Ti	482	470	1343	451	483	449	584
⁵¹ V	1	1	0	0	1	1	0
⁵⁹ Co	0	0	0	0	0	0	0
⁶³ Cu	5	9	3	6	10	5	3
⁶⁶ Zn	50	46	512	50	48	49	45
⁸⁵ Rb	298	284	172	270	298	276	443
⁸⁸ Sr	14	13	3	12	15	12	5
⁸⁹ Y	49	31	196	43	46	35	49
⁹⁰ Zr	189	133	1 791	171	184	145	246
⁹³ Nb	39	37	391	34	37	35	70
¹³³ Cs	16	15	2	14	16	15	45
¹³⁷ Ba	15	14	20	13	14	13	8
¹³⁹ La	58	43	212	48	53	45	73
¹⁴⁰ Ce	103	102	364	85	105	88	142
¹⁴¹ Pr	11	10	39	9	11	9	14
¹⁴⁶ Nd	44	33	166	35	39	34	50
¹⁴⁷ Sm	8	6	27	6	8	6	8
¹⁵³ Eu	0	0	3	0	0	0	0
¹⁵⁷ Gd	7	5	33	7	7	6	9
¹⁵⁹ Tb	1	1	4	1	1	1	1
¹⁶³ Dy	6	5	27	5	7	5	6
¹⁶⁵ Ho	2	1	6	1	1	1	2
¹⁶⁶ Er	5	3	18	4	4	4	5
¹⁶⁹ Tm	1	0	2	1	1	0	1
¹⁷² Yb	5	4	14	4	4	3	5
¹⁷⁵ Lu	1	0	2	1	1	0	1
¹⁷⁸ Hf	6	5	32	5	7	4	7
¹⁸¹ Ta	3	2	18	2	2	2	4
²⁰⁸ Pb	33	33	13	26	34	28	44
²³² Th	49	38	26	38	47	35	55
²³⁸ U	15	15	8	12	14	13	18

Table 1 (Continued)

Sample	UST-51	UST-56	UST-62	UST-64	UST-65	UST-71	UST-78
Number of analyses	2	2	2	2	2	2	2
Provenance	Lipari	Pant.	Lipari	Lipari	Lipari	Lipari	Pant.
SiO ₂	75.62	72.34	74.40	75.30	75.24	75.27	72.14
TiO ₂	0.02	0.22	0.08	0.10	0.08	0.06	0.33
Al ₂ O ₃	12.56	7.68	13.63	12.67	12.92	12.94	7.63
FeO	1.49	8.02	1.45	1.63	1.34	1.53	7.66
MnO	0.13	0.40	0.11	0.10	0.10	0.08	0.31
MgO	0.03	0.04	0.05	0.09	0.02	0.06	0.04
CaO	0.76	0.26	1.02	0.74	0.71	0.70	0.29
Na ₂ O	3.77	6.65	4.61	4.05	3.83	4.05	7.19
K ₂ O	5.60	4.38	4.63	5.29	5.76	5.28	4.41
P ₂ O ₅	0.01	0.01	0.03	0.02	0.01	0.03	0.00
P.I.	0.98	2.04	0.92	0.98	0.97	0.96	2.18
Na ₂ O/K ₂ O	0.67	1.52	0.99	0.77	0.67	0.77	1.63
Na ₂ O + K ₂ O	9.38	11.03	9.24	9.34	9.59	9.33	11.60
⁷ Li	102	54	88	88	96	86	51
⁹ Be	7	12	7	6	6	7	11
¹¹ B	225	25	185	188	187	190	21
³⁹ K	40 378	35 473	41 417	41 611	40 549	41 996	33 544
⁴⁵ Sc	3	3	3	3	3	3	3
⁴⁷ Ti	481	1495	493	488	483	511	1473
⁵¹ V	1	0	1	1	1	1	0
⁵⁹ Co	0	0	0	0	0	0	0
⁶³ Cu	6	3	7	6	7	7	3
⁶⁶ Zn	46	483	53	52	52	54	462
⁸⁵ Rb	298	199	320	318	299	328	190
⁸⁸ Sr	14	4	15	14	14	16	4
⁸⁹ Y	50	229	53	45	45	55	214
⁹⁰ Zr	193	2 071	211	183	184	217	1 932
⁹³ Nb	38	470	41	40	38	42	447
¹³³ Cs	16	3	17	17	16	18	3
¹³⁷ Ba	15	27	16	16	15	17	24
¹³⁹ La	57	275	62	56	54	64	249
¹⁴⁰ Ce	101	472	108	105	98	110	432
¹⁴¹ Pr	11	50	11	11	10	12	46
¹⁴⁶ Nd	43	215	46	42	40	47	192
¹⁴⁷ Sm	7	36	8	7	7	8	32
¹⁵³ Eu	0	4	0	0	0	0	4
¹⁵⁷ Gd	7	37	8	7	7	9	34
¹⁵⁹ Tb	1	5	1	1	1	1	5
¹⁶³ Dy	6	35	7	6	6	7	31
¹⁶⁵ Ho	2	8	2	2	1	2	7
¹⁶⁶ Er	5	23	5	4	4	5	20
¹⁶⁹ Tm	1	3	1	1	1	1	2
¹⁷² Yb	4	18	5	4	4	5	16
¹⁷⁵ Lu	1	2	1	1	1	1	2
¹⁷⁸ Hf	6	43	6	5	5	7	37
¹⁸¹ Ta	2	24	3	3	2	3	22
²⁰⁸ Pb	31	18	34	34	31	35	15
²³² Th	47	36	53	47	43	54	31
²³⁸ U	15	12	16	16	14	16	10

Table 1 (Continued)

Sample	UST-81	UST-84	UST-90	UST-95	UST-96	UST-98	UST-102
Number of analyses	2	2	2	2	2	2	2
Provenance	Lipari	Lipari	Lipari	Lipari	Pant.	Lipari	Lipari
SiO ₂	75.82	74.74	75.30	75.40	72.72	75.12	75.07
TiO ₂	0.01	0.13	0.00	0.07	0.21	0.13	0.03
Al ₂ O ₃	13.10	13.44	12.86	12.94	7.28	13.59	12.90
FeO	1.43	1.64	1.68	1.54	7.89	1.16	1.40
MnO	0.01	0.09	0.06	0.11	0.28	0.11	0.14
MgO	0.03	0.07	0.09	0.03	0.02	0.03	0.06
CaO	0.63	0.70	0.72	0.75	0.28	0.71	0.66
Na ₂ O	3.62	3.90	4.10	3.97	6.88	4.21	3.64
K ₂ O	5.31	5.26	5.19	5.18	4.43	4.92	6.08
P ₂ O ₅	0.03	0.03	0.00	0.01	0.01	0.02	0.01
P.I.	0.89	0.90	0.96	0.94	2.21	0.90	0.97
Na ₂ O/K ₂ O	0.68	0.74	0.79	0.77	1.55	0.86	0.60
Na ₂ O + K ₂ O	8.94	9.16	9.28	9.16	11.30	9.14	9.72
⁷ Li	88	85	91	86	53	92	99
⁹ Be	7	7	7	7	11	8	6
¹¹ B	196	210	198	209	21	197	200
³⁹ K	39 136	44 479	39 904	45 447	33 345	41 231	46 497
⁴⁵ Sc	2	3	2	4	2	2	2
⁴⁷ Ti	482	469	491	473	1460	495	486
⁵¹ V	0	1	1	1	0	0	0
⁵⁹ Co	0	0	0	0	0	0	0
⁶³ Cu	6	9	7	9	3	7	4
⁶⁶ Zn	48	47	50	48	457	50	47
⁸⁵ Rb	293	290	294	292	187	305	329
⁸⁸ Sr	11	14	14	15	4	14	14
⁸⁹ Y	47	37	49	40	206	51	48
⁹⁰ Zr	172	155	192	162	1 895	196	189
⁹³ Nb	38	38	38	38	444	39	39
¹³³ Cs	15	15	16	15	3	16	16
¹³⁷ Ba	11	14	15	14	24	15	15
¹³⁹ La	50	49	56	49	247	58	56
¹⁴⁰ Ce	91	105	99	105	434	102	102
¹⁴¹ Pr	9	11	10	11	46	11	11
¹⁴⁶ Nd	38	36	42	37	192	43	42
¹⁴⁷ Sm	7	7	7	7	32	7	7
¹⁵³ Eu	0	0	0	0	4	0	0
¹⁵⁷ Gd	7	6	7	7	32	7	7
¹⁵⁹ Tb	1	1	1	1	5	1	1
¹⁶³ Dy	6	6	6	6	31	7	6
¹⁶⁵ Ho	1	1	2	1	7	2	2
¹⁶⁶ Er	4	4	5	4	20	5	5
¹⁶⁹ Tm	1	1	1	1	2	1	1
¹⁷² Yb	4	4	4	4	16	5	4
¹⁷⁵ Lu	1	1	1	1	2	1	1
¹⁷⁸ Hf	5	6	5	6	37	6	6
¹⁸¹ Ta	2	2	2	2	22	2	3
²⁰⁸ Pb	29	34	30	32	15	31	30
²³² Th	42	43	45	44	32	48	48
²³⁸ U	14	15	14	15	10	15	15

Table 1 (Continued)

Sample	UST-104	UST-146	UST-148	UST-159	UST-165	LIP-1	LIP-2
Number of analyses	2	2	2	2	2	3	3
Provenance	Pant.	Lipari	Lipari	Lipari	Pant.	Lipari	Lipari
SiO ₂	71.82	74.48	74.97	75.12	71.71	75.20	75.19
TiO ₂	0.28	0.08	0.11	0.10	0.20	0.10	0.12
Al ₂ O ₃	7.93	13.52	13.32	13.37	7.73	13.46	13.47
FeO	7.89	1.48	1.41	1.63	8.00	1.47	1.46
MnO	0.31	0.10	0.07	0.01	0.33	0.09	0.10
MgO	0.02	0.04	0.02	0.04	0.01	0.06	0.06
CaO	0.31	0.73	0.73	0.64	0.29	0.73	0.74
Na ₂ O	6.93	3.72	3.46	4.90	7.09	3.70	3.73
K ₂ O	4.49	5.87	5.89	4.17	4.64	5.18	5.10
P ₂ O ₅	0.02	0.00	0.03	0.02	0.00	0.01	0.02
P.I.	2.05	0.92	0.91	0.94	2.16	0.87	0.87
Na ₂ O/K ₂ O	1.54	0.63	0.59	1.18	1.53	0.71	0.73
Na ₂ O + K ₂ O	11.41	9.58	9.35	9.06	11.73	8.88	8.83
⁷ Li	51	89	60	91	52	93	90
⁹ Be	11	7	6	7	10	7	8
¹¹ B	21	197	198	211	21	206	205
³⁹ K	33 483	43 347	41 301	42 488	33 298	41 370	39 745
⁴⁵ Sc	3	2	2	3	3	4	4
⁴⁷ Ti	1461	479	476	466	1438	504	485
⁵¹ V	0	1	1	1	0	1	1
⁵⁹ Co	0	0	0	0	0	0	0
⁶³ Cu	3	5	7	8	3	8	7
⁶⁶ Zn	450	51	49	46	447	51	49
⁸⁵ Rb	189	297	292	288	187	308	297
⁸⁸ Sr	4	14	13	15	3	14	14
⁸⁹ Y	230	48	43	43	204	52	50
⁹⁰ Zr	2 094	189	175	172	1 866	204	198
⁹³ Nb	455	39	39	36	438	40	39
¹³³ Cs	3	16	16	15	3	17	16
¹³⁷ Ba	25	15	15	14	24	16	15
¹³⁹ La	267	57	54	52	242	59	56
¹⁴⁰ Ce	450	102	100	105	424	104	101
¹⁴¹ Pr	48	10	10	11	45	11	10
¹⁴⁶ Nd	209	43	41	38	188	43	42
¹⁴⁷ Sm	35	8	7	8	32	8	7
¹⁵³ Eu	4	0	0	0	4	0	0
¹⁵⁷ Gd	36	7	6	7	33	8	8
¹⁵⁹ Tb	5	1	1	1	5	1	1
¹⁶³ Dy	35	6	6	7	30	7	6
¹⁶⁵ Ho	8	2	1	1	7	2	2
¹⁶⁶ Er	23	5	4	4	20	5	5
¹⁶⁹ Tm	3	1	1	1	2	1	1
¹⁷² Yb	17	4	4	5	16	5	4
¹⁷⁵ Lu	2	1	1	1	2	1	1
¹⁷⁸ Hf	42	6	5	7	37	6	6
¹⁸¹ Ta	24	2	2	2	22	3	3
²⁰⁸ Pb	16	31	31	36	15	32	32
²³² Th	35	47	45	47	31	50	48
²³⁸ U	11	15	15	15	10	15	14

Table 1 (Continued)

Sample	LIP-3	PALM-1	PALM-2	PALM-3	PANT-1	PANT-2
Number of analyses	3	3	3	3	3	3
Provenance	Lipari	Palmarola	Palmarola	Palmarola	Pantelleria	Pantelleria
SiO ₂	75.12	74.22	74.14	74.24	70.78	70.57
TiO ₂	0.10	0.09	0.07	0.10	0.53	0.56
Al ₂ O ₃	13.57	13.86	14.14	14.06	11.34	11.60
FeO	1.44	1.08	1.35	0.55	5.97	5.79
MnO	0.07	0.05	0.04	0.04	0.30	0.34
MgO	0.09	0.17	0.17	0.08	0.23	0.23
CaO	0.73	0.35	0.43	0.53	0.41	0.37
Na ₂ O	3.70	5.03	5.02	5.38	5.62	5.73
K ₂ O	5.16	5.20	4.99	5.19	4.76	4.78
P ₂ O ₅	0.03	0.07	0.06	0.06	0.06	0.03
P.I.	0.86	1.00	0.97	1.03	1.27	1.26
Na ₂ O/K ₂ O	0.72	0.97	1.01	1.04	1.18	1.20
Na ₂ O + K ₂ O	8.86	10.23	10.01	10.57	10.38	10.50
⁷ Li	96	57	57	55	36	35
⁹ Be	8	9	9	10	10	9
¹¹ B	229	69	73	71	11	10
³⁹ K	43 317	40 244	40 757	40 323	39 589	39 756
⁴⁵ Sc	4	3	3	3	9	9
⁴⁷ Ti	528	626	641	632	3 657	3 587
⁵¹ V	1	1	1	1	0	0
⁵⁹ Co	0	0	0	0	0	0
⁶³ Cu	9	3	3	3	2	2
⁶⁶ Zn	59	46	49	48	330	328
⁸⁵ Rb	352	485	497	483	145	146
⁸⁸ Sr	17	5	5	6	2	2
⁸⁹ Y	50	58	59	62	158	159
⁹⁰ Zr	217	296	299	310	1 708	1 694
⁹³ Nb	45	77	79	77	351	353
¹³³ Cs	20	49	51	49	1	1
¹³⁷ Ba	21	8	9	10	59	60
¹³⁹ La	77	87	89	91	182	186
¹⁴⁰ Ce	139	160	165	164	309	319
¹⁴¹ Pr	14	16	16	16	32	33
¹⁴⁶ Nd	53	59	62	62	135	139
¹⁴⁷ Sm	9	9	9	10	23	23
¹⁵³ Eu	0	0	0	0	3	4
¹⁵⁷ Gd	9	8	8	9	26	26
¹⁵⁹ Tb	1	1	1	1	4	4
¹⁶³ Dy	7	8	8	8	23	23
¹⁶⁵ Ho	2	2	2	2	5	6
¹⁶⁶ Er	5	6	6	6	16	16
¹⁶⁹ Tm	1	1	1	1	2	2
¹⁷² Yb	5	5	6	6	13	13
¹⁷⁵ Lu	1	1	1	1	2	2
¹⁷⁸ Hf	7	8	8	9	33	34
¹⁸¹ Ta	3	5	5	5	18	19
²⁰⁸ Pb	41	46	48	49	12	12
²³² Th	61	66	69	70	27	28
²³⁸ U	21	19	20	20	8	8

Table 1 (Continued)

Sample	PANT-3	MARCI-1	MARCI-2	MARCI-3
Number of analyses	3	3	3	3
Provenance	Pantelleria	M. Arci	M. Arci	M. Arci
SiO ₂	70.80	75.37	75.04	74.77
TiO ₂	0.53	0.18	0.24	0.20
Al ₂ O ₃	11.35	13.77	13.95	14.14
FeO	5.81	0.99	0.51	1.12
MnO	0.30	0.02	0.03	0.07
MgO	0.24	0.17	0.04	0.15
CaO	0.40	0.70	0.74	0.84
Na ₂ O	5.74	3.18	3.14	3.27
K ₂ O	4.78	5.55	6.19	5.38
P ₂ O ₅	0.03	0.08	0.11	0.09
P.I.	1.29	0.82	0.85	0.79
Na ₂ O/K ₂ O	1.20	0.57	0.51	0.61
Na ₂ O + K ₂ O	10.52	8.73	9.33	8.65
⁷ Li	35	63	59	54
⁹ Be	9	3	3	5
¹¹ B	11	20	18	16
³⁹ K	40 443	43 358	45 442	39 869
⁴⁵ Sc	8	6	6	6
⁴⁷ Ti	3 547	1 007	1 343	958
⁵¹ V	0	2	4	3
⁵⁹ Co	0	1	1	1
⁶³ Cu	3	2	1	1
⁶⁶ Zn	362	46	44	71
⁸⁵ Rb	158	244	234	244
⁸⁸ Sr	2	41	68	56
⁸⁹ Y	149	23	24	32
⁹⁰ Zr	1 668	127	184	136
⁹³ Nb	368	31	30	45
¹³³ Cs	1	7	6	4
¹³⁷ Ba	67	271	514	327
¹³⁹ La	193	33	41	32
¹⁴⁰ Ce	348	65	77	66
¹⁴¹ Pr	36	7	8	8
¹⁴⁶ Nd	145	29	35	32
¹⁴⁷ Sm	24	5	6	7
¹⁵³ Eu	4	1	1	1
¹⁵⁷ Gd	27	5	6	6
¹⁵⁹ Tb	4	1	1	1
¹⁶³ Dy	24	4	4	5
¹⁶⁵ Ho	6	1	1	1
¹⁶⁶ Er	16	2	2	3
¹⁶⁹ Tm	2	0	0	0
¹⁷² Yb	14	1	2	2
¹⁷⁵ Lu	2	0	0	0
¹⁷⁸ Hf	34	3	4	4
¹⁸¹ Ta	20	2	2	3
²⁰⁸ Pb	15	28	27	36
²³² Th	30	18	19	20
²³⁸ U	10	5	5	6

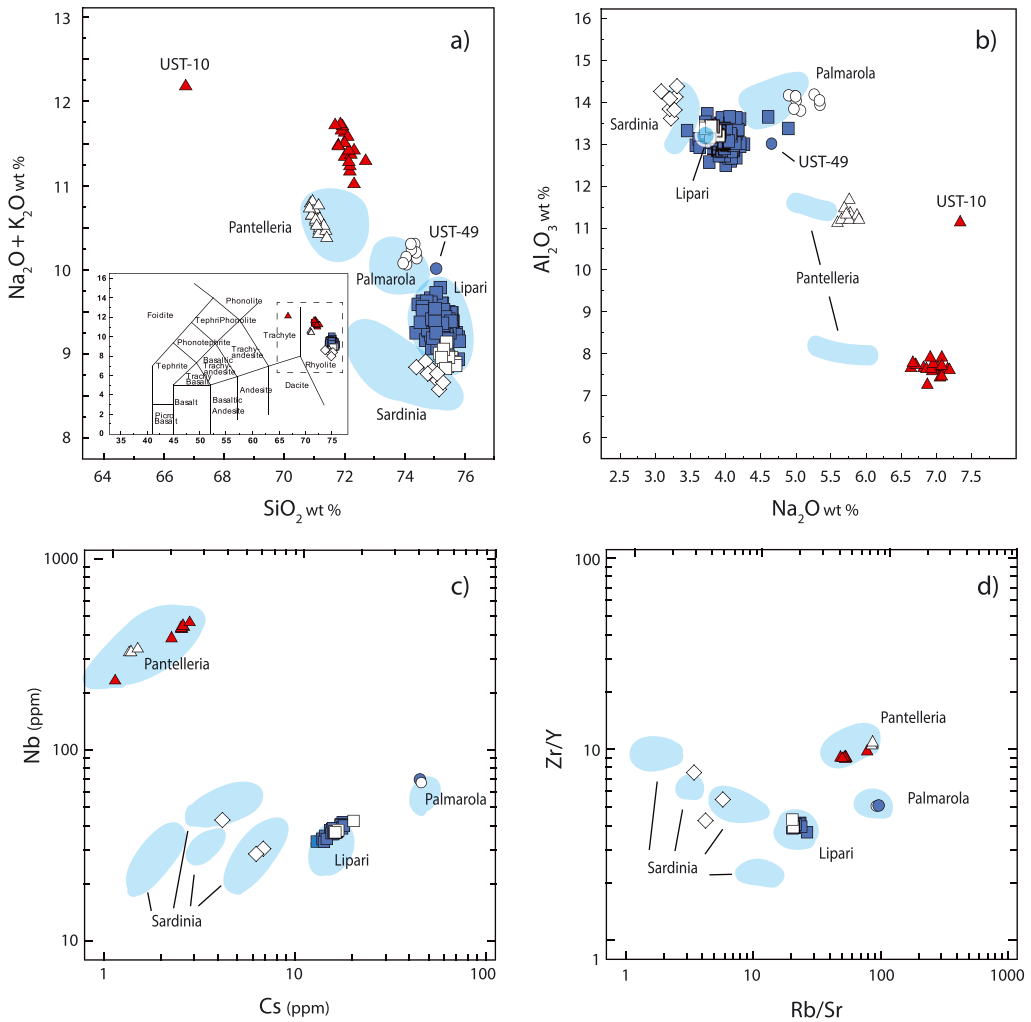


Figure 4 (a) The total alkali versus silica diagram (after Le Bas et al. 1992). The Ustica archaeological samples are represented in blue (those with P.I. < 1.5) and red (those with P.I. > 1.5); the open symbols are the geological samples, representing the provenance of Monte Arci (diamonds), Lipari (squares), Palmarola (circles) and Pantelleria (triangles); the light blue areas are from Le Bourdonnec et al. (2010). (b) The Al₂O₃ versus Na₂O diagram. (c,d) The Cs versus Nb (ppm) (c) and Rb/Sr versus Zr/Y (d) plots: the light blue areas are the compositional fields of Lipari, Palmarola, Pantelleria and Sardinia, from Barca et al. (2007). [Correction added on 20 February 2017, after first online publication: An old version of Figure 4 was accidentally published in the paper, and this has been replaced with the correct version.]

Palmarola source. As shown in the Al₂O₃ versus Na₂O plot (Fig. 4 (b)), the group previously attributed to Lipari tend to be scattered, also overlapping the Palmarola and Sardinia (Monte Arci) compositional fields. In particular, three samples seem to show compositional affinities with the Palmarola field.

The major element geochemistry, and in particular the observed variations in SiO₂, Al₂O₃ and Na₂O composition, helped us to distinguish various obsidian sources with some ambiguities. In order to refine these results, we performed a trace elements investigation through LA-ICP-MS. Thirty-eight chemical elements were determined on the selected 33 samples (already mentioned

in the 'Materials and Methods' section) and the results are listed in Table 1. The selected samples are as follows: 19 flakes representative of the compositional field of Lipari (e.g., UST-1, UST-11 and UST-84); eight samples representative of Pantelleria (e.g., UST-21, UST-33 and UST-78); three samples that display compositional affinities with both Lipari and Monte Arci (UST-81, UST-146, UST-148); and three samples that display a Na-affinity with Palmarola (UST-49, UST-62 and UST-159) (Fig. 4 (b)).

To distinguish the different sources, we considered the trace elements displaying the greatest variation, such as Cs versus Nb and Zr/Y versus Rb/Sr; our results and literature data (Barca *et al.* 2007) are plotted in Figures 4 (c) and 4 (d). These graphs confirm that it is possible to attribute the provenance of the Ustica obsidian fragments to at least three different sources: Lipari, Pantelleria and Palmarola. The group of samples belonging to Lipari is the most abundant, and displays a homogeneous trace element composition. The samples belonging to Pantelleria display the highest content of high field strength trace elements (i.e., Nb and Zr) and at least two different sources can be recognized on the basis of their major and trace element chemistry. In detail, sample UST-10, the one displaying the lowest SiO₂, the highest alkali content and the lowest Nb and Y content, should be assigned to the Gelkhamar quarry rather than to the Lago di Venere obsidian flow (S. Rotolo pers. Comm.; Francaviglia 1988; Tykot 1995; De Francesco *et al.* 2008). The other group of samples, characterized by the highest enrichment in trace elements (e.g., Zr > 1791 ppm; Nb > 390 ppm), should come from the Balata dei Turchi quarries (De Francesco *et al.* 2008). Finally, sample UST-49, which we assign to Palmarola, is easily distinguishable because of its high content of Rb and Cs.

Moreover, these data suggest the absence of fragments from Sardinian sources in our collection of Ustica obsidians.

Multivariate statistical elaboration

Principal component analysis (PCA) is a technique used to emphasize variations and show strong patterns in a data set, making data easy to explore and visualize. Starting from the awareness that the chemical composition of a magmatic system has a specific fingerprint, and that groups of variables need to move together, this analysis permits a multivariate statistical elaboration of this system that is characterized by many variables. The result is a simplification of the system by replacing a group of variables with a single new variable. The new set of variables, called the principal components, is a linear combination of the original variables. All the principal components are orthogonal to each other, so there is no redundant information. The first principal component is a single axis in space. When each observation is projected on that axis, the resulting values form a new variable, and the variance of this variable is the maximum among all possible choices of the first axis. The second principal component is another axis in space, perpendicular to the first. Projecting the observations on this axis generates another new variable. The variance of this variable is the maximum among all possible choices of this second axis.

Some selected major oxides (SiO₂, Al₂O₃, FeO, CaO and Na₂O, in wt%), as well as trace elements (Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ho, Ta, Pb and Th, in ppm), trace element ratios (Zr/Rb, Zr/Y, Ta/Th, Rb/Sr, Rn/Nb and Sr/Nb) and some magnetic properties (Mass sus, NRM intensity and IRM_{0.9T}) have been considered as input variables. A set of 69 samples—33 archaeological samples (the same samples on which we performed both major and trace element geochemistry) and 36 geological samples (12 samples analysed in this work and 24 from the literature)—were considered for this purpose (Fig. 5). The major and trace element compositions and the magnetic properties have been analysed in this work. As a result, a set of principal

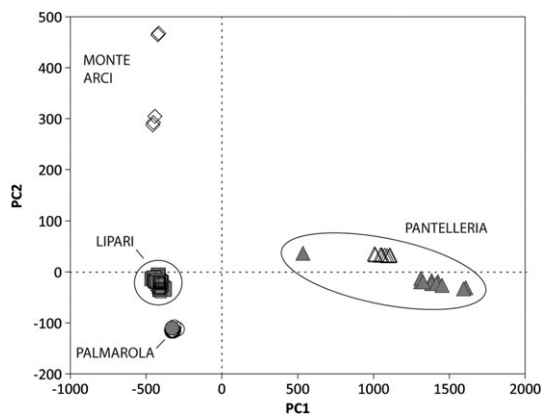


Figure 5 A binary plot of the component scores produced by the principal component analysis using MATLAB© software for the Ustica obsidian flakes (in grey). The open symbols are the geological obsidians from Monte Arci (diamonds), Pantelleria (triangles), Lipari (squares) and Palmarola (circles). The geological obsidians considered for the PCA are the 12 analysed samples (considering both physical and chemical data) and 24 samples from the literature of Lipari, Pantelleria, Palmarola and Monte Arci sources (for the major element geochemistry, Le Bourdonnec *et al.* 2010—for the trace element composition, Tykot, 1997; Barca *et al.* 2007). The ellipses enclose samples with a compositional affinity.

components was obtained, as large as the original set of variables, in which the sum of the variances of the first two principal components represents 98.5% of the total variance of the original data. In a binary diagram (Fig. 5), where the horizontal and vertical axes represent the first principal component and the second principal component, respectively, the differences between samples from the Lipari and Pantelleria sources are emphasized, and it is clear that no obsidians collected on Ustica fall in the field of variation typical of Monte Arci obsidians. On the other hand, sample UST-49 shows a close correspondence with the field defined by the samples from Palmarola.

CONCLUSIONS

Since the mid-1990s, it had been believed that the obsidian fragments found on Ustica were all imported from the neighbouring island of Lipari, located about 160 km eastward (Dixon *et al.* 1968). Tykot (1995), studying the chemical composition of 12 obsidian fragments collected on the surface out of the Faraglioni village archaeological site (Middle Bronze Age), attributed the provenance of one of them to the island of Pantelleria, situated about 230 km to the SSW. This single finding paved the way for further confirmation of the presence on Ustica of obsidians from the island of Pantelleria (Foresta Martin and Ailara 2004; Pappalardo *et al.* 2013).

The primary goal of this multidisciplinary study (coupling physical and chemical analyses) was to perform an investigation on the provenance of a representative population of Ustica obsidians (170 flakes), collected close to the Neolithic and Middle Bronze Age archaeological sites on the island.

The study of the physical characteristics of these samples indicated the presence of two main sources, Lipari and Pantelleria. In addition, rock magnetic properties suggested the possibility of other provenances, notably from Palmarola (Latium) and Monte Arci (Sardinia). To verify this hypothesis, we performed major and trace element characterization, discovering that one of them

can be reliably attributed to the source of Palmarola, an island situated ~250 km to the north of Ustica. At the same time, the trace element composition indicates the absence of fragments from Sardinian sources. As confirmation of our geochemical results, principal component analysis strengthened the three above-mentioned sources for the Ustica obsidian flakes analysed in this study. We thus came to the conclusion that about 87.6% of the analysed Ustica obsidian fragments come from Lipari, 11.8% come from Pantelleria and only 0.6% come from Palmarola. In any event, there is no specific chronological control applicable to the obtained percentages, due to the unavailability of dating on our obsidians.

By means of this study, through the comparison of different analytical methodologies, we can confirm that the analysis of trace elements using laser ablation ICP–MS is the most effective way to discriminate among different sources of provenance for obsidian fragments.

Our study confirms the significant presence of obsidians from Pantelleria on the island of Ustica, as already inferred by Tykot (1995). Indeed, Ustica seems to have been inserted in a network of trade with the island of Pantelleria, which involved more the western part of Sicily (Grotta dell’Uzzo and Monte Cofano sites: Francaviglia and Piperno 1987; Francaviglia 1988) rather than the eastern part (e.g., Tykot *et al.* 2013).

In addition, we have presented here the first occurrence of a Palmarola obsidian flake in Ustica samples. This result extends the known diffusion area of obsidians southward from Palmarola island: until now, it was limited to northern and central Italy (Barca *et al.* 2008; Freund 2014). Thus our result represents the first finding from this island reported for the whole of Sicily.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Table S1. Complete chemical analysis performed on archaeological obsidians (Major elements, wt. %; trace element, ppm). [Correction added on 20 February 2017, after first online publication: The file for Table S1 has been replaced with a corrected version. The data for ^7Li to ^{238}U of samples UST-20 and UST-56 have been interchanged.]