Provenance of obsidian artifacts from site of Colle Cera, Italy, by LA-ICP-MS method

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ABSTRACT. — This paper describes the chemical sourcing of 53 obsidian artefacts from Colle Cera, a large Neolithic village located in Loreto Aprutino (Abruzzo, Central Italy). Trace element analyses were carried out by the LA-ICP-MS method, an almost non-destructive analytical technique, capable of chemically characterising and establishing the definite origin and source area of archaeological artefacts. Twenty-seven trace and rare earth elements were analysed for each sample and their definite provenance was assigned: two sources in the peri-Tyrrhenian area, the islands of Lipari and Palmarola.

RIASSUNTO. — Nel presente lavoro viene determinata la provenienza di 53 reperti ossidianacei rinvenuti nel sito archeologico di Colle Cera, un importante villaggio Neolitico situato a Loreto Aprutino in Abruzzo (Italia Centrale). La concentrazione degli elementi in tracce e delle Terre Rare dei reperti è stata determinata utilizzando la metodologia analitica LA-ICP-MS, una tecnica che consente di caratterizzare chimicamente i reperti archeologici con minima distruttività. Le analisi puntuali hanno consentito di determinare per ciascun reperto la concentrazione (espressa in ppm) di ventisette elementi chimici e di attribuire una provenienza certa della materia prima.

Tra le varie sorgenti dell'area peri-Tirrenica, possibili fonti di sfruttamento in età neolitica, solo due di esse sono state rinvenute come fonte dei reperti analizzati, si tratta delle isole di Lipari e Palmarola.

KEY WORDS: *Obsidian; trace elements; LA-ICP-MS; Colle Cera site; peri-Tyrrhenian area; archaeological artefacts.*

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INTRODUCTION

In prehistoric ages, obsidian was a raw material commonly used for stone tools and weapons, therefore an enormous number of obsidian artefacts were recovered from archaeological sites. The chemical characterisation of archaeological obsidian is typically used for provenance studies and investigations into prehistoric exchange and other forms of cultural interaction.

Experimental research indicates that sources of obsidian in the peri-Tyrrhenian area are only found in a limited number of places: on the islands of Lipari, Pantelleria, Palmarola and Sardinia (Francaviglia, 1984; Tykot, 1996, 1997; Acquafredda *et al*., 1999; Bigazzi *et al*., 2005).

All these obsidian sources show, using TAS classification diagram (Le Bas *et al*., 1986), rhyolitic composition on the basis of major elements concentrations determined by XRF methodology (De Francesco *et al*., in press).

The Pantelleria obsidians are typically peralkaline (Civetta *et al*., 1984) while the other ones (Lipari, Palmarola and Sardinia-M.te Arci) are calc-alkaline rhyolites (Carmassi *et al*., 1985; De Rita *et al*., 1986; Crisci *et al*., 1991; Montanini *et al.*, 1994; Macciotta *et al.*, 2003) and all are chemically identifiable according to their trace element composition.

In the peri-Tyrrhenian area trachytic obsidian was discovered, as juvenile fragments and clasts, in the pyroclastic deposits of the Campi Flegrei district (Astroni volcano) (Isaia *et al*., 2004) or as glass in unit "Breccia Museo" trachytic deposit (Mastrolorenzo and Pappalardo, 2006); however these obsidians, probably for the scarce quality, were not exploited for the manufacturing of artefacts in the neolithic time.

Monte Arci, in western Sardinia, was the most important source of glassy, black, top-quality obsidian in prehistoric times (Assorgia *et al*., 1976; Montanini and Villa, 1993; Montanini *et al.*, 1994; Macciotta *et al.*, 2003; Bigazzi *et al*., 2005). Much research has led to the characterisation of the obsidian sources in the volcanic complex of Monte Arci, and various authors, adopting several analytical methods (Hallam *et al.*, 1976; Machey and Warren, 1982; Thorpe *et al.*, 1984; Crisci *et al*. 1994; Tykot, 1997, 2002; Acquafredda *et al*., 1999; De Francesco *et al.*, in press), have geochemically distinguished different groups. In particular, Hallam *et al.*(1976) and Mackey and Warren (1982) have identified four sources: Conca Cannas (SA), Santa Maria Zuarbara (SB), Perdas Urias (SC) and Sonnixeddu (SD). Thorpe *et al*. (1984) found only three groups: SA, SB and SC. Tykot (1997) and De Francesco *et al*. (in press) using various methods, distinguished the obsidian of Monte Arci into four main groups, called SA, SB1, SB2 and SC.

Palmarola is the smallest of the five islands of the Pontine archipelago (Carmassi *et al*., 1985; De Rita *et al*., 1986), and its most important obsidian flow is found on the southern flank of Monte Tramontana. Detritic deposits containing abundant obsidian blocks occur along the coastline, mainly at Punta Vardella, at the south-east end of the island, and on the top of the cliff of Cala Brigantina (Bigazzi *et al*., 2005; Tykot *et al*., 2005).

The volcanic island of Pantelleria, located in the Channel of Sicily, is composed of peralkaline rocks, and its obsidian, characteristically greenish in colour, is known as pantellerite (Civetta *et al*., 1984). Obsidian outcrops in three localities: Balata dei Turchi, Gelkhamar, and the lake of Venere, and geochemical differences led Francaviglia (1988) to identify five deposits.

Lipari, the main island of the Aeolian Archipelago, lies about 30 km off the north-east coast of Sicily. Three main outcrops of high-quality, transparent black obsidian occur, in flows deriving from eruptions of historic age (Forgia Vecchia, Rocche Rosse), i.e., not quarried previously. Only the obsidian from Pomiciazzo and Canneto (Crisci *et al*., 1991; Acquafredda *et al*., 1999; Bigazzi *et al.*, 2005) was exploited in Neolithic times.

The numerous characterisation studies on the Tyrrhenian obsidians demonstrate that trace element chemical compositions are typically differentiated, and their variations identify their sources. These differences also mean that provenance can be assigned to artefacts found at archaeological sites in the peri-Tyrrhenian area (Crisci *et al*., 1994; Acqufredda *et al*., 1999; De Francesco and Crisci, 1999; De Francesco *et al*. , 2000, 2004, 2006; Barca *et al*., 2007).

LA-ICP-MS, used in this work, is an excellent method for analysing obsidian artefacts, and the micro-holes left by the laser (about 40 μm in diameter) make this technique almost non-destructive. In addition, LA-ICP-MS can analyse a great number of trace and REE with high sensitivity in a very short time. All these characteristics make it capable of assigning the provenance of raw materials to archaeological obsidian (Gratuze, 1999; Carter *et al*., 2006; Barca *et al*., 2007).

Characteristics of the site

The Colle Cera site comprises a large Neolithic settlement, almost completely occupying the top of a hill at 237 m a.s.l. (coordinates: lat. 42° 26' 30,066''; long. 14° 00' 16,948'') in the town of Loreto Aprutino (Abruzzo). Sampling carried out until now has revealed the exceptionally

good state of conservation and the complexity of the structures of this settlement (Fig. 1) (Tozzi and Colombo, 2006).

Excavations were carried out starting in 2004 by the Department of Archaeological Sciences, University of Pisa, in collaboration with the *Soprintendenza ai Beni Archeologici* of the Abruzzo Region, with grants from the Municipality and *Archeoclub* of Loreto Aprutino.

The settlement belongs to the cultural setting known as *Cultura di Catignano – Scaloria Bassa,* a transitional phase between the ancient Neolithic (*Cultura della Ceramica Impressa*) and the middle Neolithic (Tozzi, 1998, 2001; Tozzi and Zamagni, 2003).

The *Cultura di Catignano – Scaloria Bassa* covers Abruzzo, Molise and northern Apulia, as far as the Gargano promontory. Its distinctive feature is the occurrence of the so-called *"figulina" ware*, with complex motifs painted in red, sometimes bordered by fringes/friezes, dots and geometric patterns obtained with the "negative" technique. The shapes of the fine brown ceramic ware and the coarse ceramic type clearly derive from that of the *Ceramica impressa*, although it has lost its characteristic decoration.

Extensive relations with contemporary cultures have been documented by the findings of Catignano ceramic ware in Latium, the Marches, Umbria and Tuscany. High-pressure green stone (eclogite and jadeite) from the north-western Alpine arc was brought to Abruzzo, cinnabar from Monte Amiata in Tuscany, and obsidian from Lipari and Palmarola (Tozzi and Zamagni, 2003; Colombo, 2006; Pessina and Radi, 2006).

The chronology of the Catignano culture has been well established by means of 26 datings of various structures in the settlement. Radio-carbon ages (traditional method and AMS) have supplied ages of between 6585±85 BP (Rome 1148, calibrated to 1σ : 5560-5470 BC) and 5865±50 BP (R 1100, calibrated to 1σ : 4800-4680 BC). The two Colle Cera samples dated so far, from structures 8A and 8B (Fig.2), gave dates
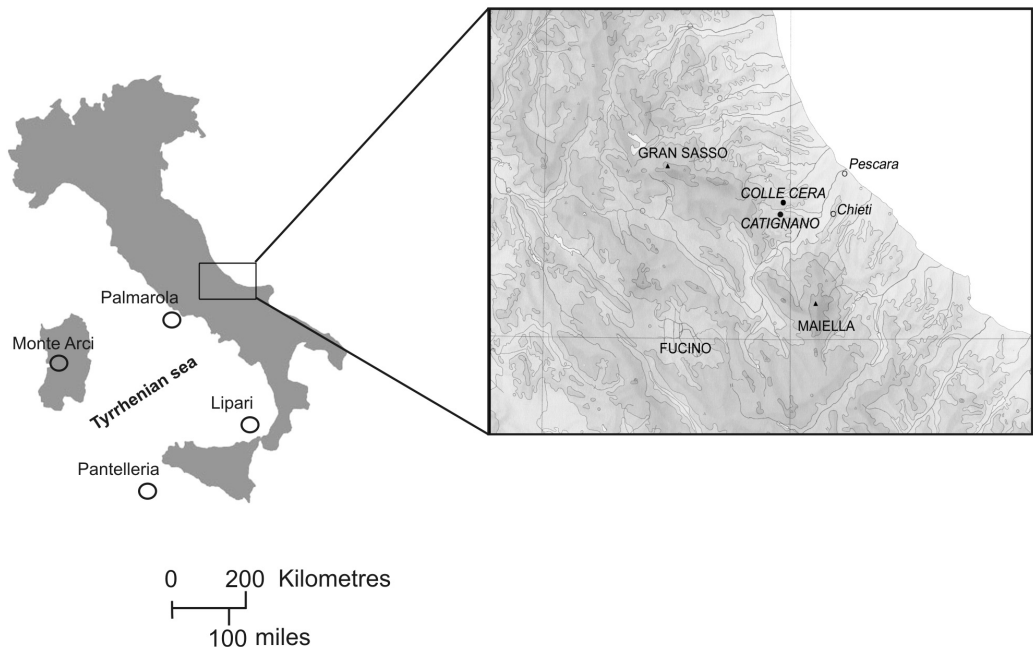

Fig. 1 – Locations of obsidian outcrops (circles) in peri-Tyrrhenian area and archaeological site (square) of Colle Cera.

Fig. 2 – Structures 8A and 8B of Colle Cera settlement.

of 6154±55 BP (LTL 1157A, calibrated to 1σ: 5210-5040 BC) and 6136±55 BP (LTL 1156A, calibrated to 1σ: 5210-5090 BC), respectively.

Analytical methods

Analyses were carried out at the Department of Earth Sciences, University of Calabria, Italy, using a combination of Laser Ablation (LA) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The equipment was an Elan DRCe (Perkin Elmer/SCIEX), operating either in normal mode as a standard ICP-MS instrument or in a dynamic reaction cell (DRC), connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 nm). Samples were ablated by laser beam in a cell, and the vaporised material was then flushed (Gunther and Heinrich, 1999) to the ICP, where it was quantified. The constant laser repetition rate was 10 Hz and fluence about 20 J/cm². Each ablation crater was generally 40 μm in diameter and nearly invisible to the naked eye. The above instrumentation can rapidly analyse solid samples and determine trace and REE concentrations to ppm and ppb levels, with very low detection limits and without any sample manipulation.

Only two point analyses were carried out on portions of archaeological fragments without roughnesses or alterations, and were sufficient to assign provenance. In order to remove any trace of soil, each find was cleaned by ultrasound in Millipore water. Each analytical sequence was executed on two or three obsidian shards in turn, in association with the standard material used to calibrate the equipment (Barca et al., 2007). Data were transmitted to a PC and processed by the GLITTER program; calibration was performed on glass reference material produced by the National Institute of Standards and Technology NIST SRM 612 at nominal concentrations of trace elements of 50 ppm in conjunction with internal standardisation, applying SiO_2 concentrations (Fryer et al., 1995; Longerich et al., 1996) to each archaeological find determined independently of SEM-EDS analyses. In order to evaluate possible errors within each analytical sequence, determinations were also made on glass reference material NIST SRM 610, with nominal concentrations of trace elements of 500 ppm, as unknown sample, and element concentrations were compared with reference values. Since the National Institute of Standards and Technology (NIST) certifies only eight elements in

this glass, the mean values of measurements carried out in the various analytical sequences in this study were compared with those published in the literature (Pearce *et al.*, 1997; Dulski, 2001; Gao *et al.*, 2002) and were included in Table 1. Accuracies, expressed as the relative difference from reference values, was

TABLE 1

*Analyses of NIST SRM 610 standard glass. Comparison between literature data (*Pearce *et al. 1997;* Dulski, *2001;* Gao *et al., 2002) and results from present study*

Elements	[1] Present study	1s	[2] Pearce *et al.* (1997)	1s	[3] Dulski (2001)	1s	[4] Gao *et al.* (2002)	1s
Sc	482	4	441.1	9.6			442	10
V	453	17	441.7	42.7			442	5
Zn	501	67	456.3	19.2			455	20
Rb	425	19	431.1	11.4	411	5	431	6
Sr	526	5	497.4	18.3	505	6	497	5
Y	494	11	449.9	19.3	454	8	450	7
Zr	464	20	439.9	7.8	456	6	439	7
Nb	460	5	419.4	57.6			420	5
Cs	363	28	360.9	67.5	372	6	360	7
Ba	450	16	424.1	29.3	452	5	425	6
La	480	23	457.4	72.4	440	7	457	6
Ce	468	22	447.8	16.8	456	8	448	6
Pr	467	24	429.8	30	472	8	430	5
Nd	440	15	430.8	37.5	430	5	430	5
Sm	486	28	450.5	20.6	446	5	449	10
Eu	462	26	461.1	52.1	459	7	460	5
Gd	461	27	419.9	25.2	466	4	420	6
Tb	446	29	442.8	22.4	457	6	442	6
Dy	468	21	426.5	18	438	3.9	426	7
Ho	482	25	449.4	24.6	451	9	448	8
Er	462	23	426.0	23.9	455	8	426	7
Tm	462	18	420.1	19.2	453	6.8	420	8
Yb	490	18	461.5	30.6	452	2	460	9
Lu	476	17	434.7	31	451	11	435	9
Hf	446	28	417.7	28.2	443	12	418	9
Ta	408	12	376.6	77.6			376	8
Pb	455	22	413.3	15.4	430	11	413	7
Th	487	14	450.6	27.8	472	10	451	7
U	448	17	457.1	13.6	464	11	457	8

1) Mean values of 18 determinations
2) Preferred averages of results from various authors and by different methods
3) Values determined by solution ICP-MS
4) Values determined by LA-ICP-MS

always better than 10%, and most elements plotted in the range +/-5%.

Results and Discussion

Fifty-three archaeological fragments of worked obsidian recovered from the Colle Cera site, mainly from structures 8A and 8B (Fig. 2) and including all obsidian finds collected so far, were analysed to determine provenance. Each fragment was generally of millimetric thickness, less than one centimeter across, variably transparent or opaque, and black in colour.

Twenty-seven chemical elements, including REE, were determined in each artefact. Table 2 lists the analytical results in ppm; each data represents the mean value of two point analyses.

To determine the provenance of each find the resulting data were compared with those from obsidian samples of various geological sources, analysed by Barca *et al.* (2007) with the same method.

In particular the variations among trace element concentrations of the four geological sources of the peri-Thyrrenian area allowed to distinguish seven compositional groups: three of these can be attributed respectively to the Lipari, Palmarola and Pantelleria islands, the other four groups belong to the Monte Arci complex in Sardinia (subgroups called SA, SB1, SB2 and SC (De Francesco *et al.* (in press) and reference therein).

The obsidians of Lipari and Palmarola show trace elements composition extremely homogeneous inside the group but easily distinguishable from the other ones; on the contrary the obsidian from Pantelleria shows great variability inside the group but trace element concentrations are tipically different from the other groups. The four Monte Arci sub-groups sometimes show similar trace element compositions but the differences are sufficient to separate them.

The best discriminating trace elements are Cs, Y, Zr, Nb and Ba, and most of the REE; in particular the binary plots of simple two-element (Fig. 3a, 3b) (Ba *vs.* Ho and Zr *vs.* Yb) or element ratio *vs.* element (Fig. 3c, 3d) (Zr/Y *vs.* La; Zr/Y *vs.* Er), applied to distinguish the sources of the peri-Tyrrhenian area in previous study (Barca *et al.*, 2007), were used in this paper to assign each

fragment its correct provenance. The analysed artefacts plot in two distinct areas and indicate a double provenance, i.e. from Lipari or Palmarola.

In particular, the composition of the largest group – 46 artefacts – indicates an Aeolian origin, and the remaining seven were from Palmarola. No doubtful cases were discovered and, although minimal compositional dishomogeneity was found in some cases, variations were always compatible with possible heterogeneneity within the same source.

Conclusions

Our research demonstrates that the LA-ICP-MS tecnique used in this work is a very powerful tool for characterization and determination of the source areas of archaeological obsidian artefacts. This method produced data of great analytical precision on a high number of trace elements, including REE, for all the studied archaeological finds from Colle Cera, in a very short time, without any sample manipulation.

Comparison of the geochemical characteristics of all the obsidian artefacts and the characteristics of their raw materials allowed us to establish the provenance of each find with certainty. Data revealed that the raw materials came exclusively from the islands of Lipari and Palmarola and, in particular, that the obsidian from Lipari was much more widely used than that from Palmarola.

In the Neolithic sites of central-eastern Italy, many analyses of provenance of obsidian carried out by means of traditional methods (fission-track and X-ray fluorescence) and sources supplying the central-Adriatic flank of Italy were, again, Lipari and Palmarola. However frequency varies in time in a significant manner, and Palmarola was clearly the main source of supply in the case of *Ceramica impressa*, e.g., 80-90% in the site of Colle Santo Stefano. Later, material from Palmarola diminished in favour of that from Lipari where, in the Catignano settlement, it reached about 90% (Bigazzi and Radi, 1998; 2003; Pessina and Radi, 2006).

The situation found at Colle Cera follows this trend perfectly, on a total number of fifty-three artefacts analysed about the 87% indicate an Aeolian origin, showing a relationship between the

TABLE 2

Analyses of obsidian artefacts by LA-ICP-MS. Each datum (in ppm) is the mean values of two determinations

Provenance	Palmarola							Lipari									
Samples	465	470	471	482	484	508	510	462	463	464	466	467	469	472	473	474	475
Sc	2.04	2.87	3.56	2.84	2.28	4.12	3.46	2.27	1.19	1.72	2.46	1.88	2.36	1.88	2.05	2.05	2.41
Zn	56.3	47.3	60.4	44.1	44.9	60.8	46.8	49.0	50.6	57.3	52.4	47.5	43.5	45.2	44.1	44.2	44.1
Rb	436	475	510	425	457	553	453	251	257	254	245	235	232	237	249	242	251
Sr	4.67	5.41	8.93	4.63	4.34	5.65	4.92	13.60	13.34	14.15	11.30	12.14	11.43	12.37	12.27	12.14	12.48
Y	45.4	51.6	51.8	46.8	50.7	57.8	48.0	35.8	36.4	36.3	29.0	33.5	31.2	32.2	30.6	30.7	33.1
Zr	232	262	269	243	258	286	243	145	144	149	120	135	129	130	125	125	135
Nb	63.5	68.8	73.3	61.0	66.8	73.1	61.9	32.6	30.4	30.6	27.7	28.3	27.5	28.7	27.8	28.0	30.1
Cs	44.7	49.9	53.1	47.0	46.5	54.5	46.9	12.6	13.8	14.5	13.2	12.5	12.6	13.2	13.1	13.2	14.2
Ba	9.6	8.6	8.8	7.7	9.0	9.3	7.6	11.9	12.1	12.8	11.3	10.9	12.0	11.0	11.9	11.9	14.8
La	75.5	84.8	87.0	81.6	80.7	89.7	77.3	47.0	47.6	50.5	39.8	42.8	42.6	43.1	43.0	43.4	47.1
Ce	151	175	189	156	156	182	158	99	92	95	85	84	84	88	90	89	96
Pr	15.2	17.5	17.9	14.5	15.9	18.3	15.5	10.5	9.8	10.3	8.5	8.7	9.0	9.1	9.4	9.4	9.7
Nd	48.6	55.1	59.4	53.2	52.2	62.3	49.3	36.2	35.6	37.4	28.7	30.5	30.3	32.5	31.4	31.1	34.6
Sm	9.8	10.7	11.0	10.2	10.8	11.8	10.2	8.7	6.5	7.9	5.5	6.7	6.0	6.4	5.9	7.1	7.1
Gd	6.8	9.2	8.7	7.0	7.8	10.1	8.0	6.1	5.9	6.6	5.0	5.9	5.2	4.9	5.1	5.2	5.9
Tb	1.13	1.34	1.35	1.19	1.20	1.59	1.20	1.06	0.85	1.08	0.75	0.74	0.77	0.87	0.83	0.68	0.93
Dy	7.98	8.76	9.69	7.33	8.46	9.75	8.03	5.77	5.80	6.28	4.74	6.04	5.38	5.45	5.71	5.36	5.51
Ho	1.41	1.84	1.75	1.65	1.76	1.86	1.69	1.33	1.16	1.36	0.98	1.10	1.04	1.16	1.15	1.02	1.14
Er	4.06	5.28	5.88	4.59	5.03	7.08	5.74	4.15	3.45	4.11	3.03	3.10	3.20	3.22	3.76	3.72	3.18
Tm	0.75	0.91	0.81	0.7	0.89	1.14	0.84	0.63	0.50	0.59	0.41	0.49	0.54	0.54	0.42	0.53	0.55
Yb	5.59	6.20	6.82	6.39	5.90	7.05	6.03	5.23	4.28	4.10	3.61	3.99	4.16	3.50	4.34	4.15	4.16
Lu	0.69	0.84	1.08	0.75	0.84	0.96	0.93	0.65	0.63	0.59	0.53	0.69	0.59	0.53	0.64	0.63	0.43
Hf	7.97	9.22	9.42	8.57	8.71	9.76	8.14	5.84	6.01	5.61	4.89	5.26	5.03	5.31	5.18	4.44	5.25
Ta	4.75	5.47	5.56	4.66	5.13	5.57	5.15	2.77	2.20	2.52	2.04	2.06	2.21	2.20	2.18	2.11	2.27
Pb	42.0	47.0	51.3	41.8	46.8	49.4	45.3	29.0	26.1	26.6	24.5	23.6	23.9	24.8	28.1	25.6	25.6
Th	67.2	72.4	74.4	69.6	72.8	79.1	69.9	49.5	42.4	42.9	35.9	39.9	38.4	39.2	37.6	38.1	44.7
U	18.4	20.1	21.6	18.7	18.8	22.0	19.5	14.3	12.9	12.9	12.0	11.5	11.5	12.1	11.8	11.7	12.7

Table 2 — *continued...*

Provenance	Lipari																	
Samples	476	478	479	480	481	483	485	486	487	488	490	492	493	494	495	468	491	503
Sc	2.14	1.87	2.14	1.69	1.91	2.08	1.89	1.71	1.63	1.74	1.75	1.33	1.89	1.59	1.64	3.46	3.18	3.47
Zn	46.5	45.2	48.6	51.8	46.1	51.3	42.7	38.8	38.7	42.3	44.7	50.3	48.5	48.7	46.9	42.3	46.0	49.1
Rb	252	255	246	255	230	253	234	226	228	244	208	237	260	259	245	246	258	269
Sr	13.72	12.59	11.77	12.70	11.65	12.57	12.25	10.60	11.45	12.26	10.37	12.26	13.24	12.46	12.40	11.92	12.12	14.28
Y	34.3	32.6	28.7	32.7	31.9	32.6	31.4	26.6	30.0	32.5	28.3	32.4	33.6	32.6	33.8	34.4	32.5	37.7
Zr	141	135	118	136	128	135	130	112	125	131	116	132	137	130	132	137	128	149
Nb	28.8	29.6	28.1	30.2	28.5	30.5	26.3	25.3	26.8	28.2	25.1	27.5	29.4	27.7	26.3	26.7	28.4	28.3
Cs	14.3	14.0	13.2	12.9	12.5	13.1	12.1	11.2	12.2	13.0	11.9	12.9	13.0	12.6	12.3	12.5	13.2	13.8
Ba	13.1	11.5	11.3	12.0	9.9	13.1	10.8	9.3	10.7	11.5	11.4	11.2	12.7	10.5	11.1	13.1	11.1	13.3
La	48.2	46.0	42.1	45.6	42.7	44.3	41.5	35.8	40.4	44.0	39.2	43.2	44.9	42.2	43.0	44.5	43.9	47.4
Ce	94	90	89	93	84	90	83	76	83	90	77	86	93	87	85	91	90	93
Pr	10.4	9.2	8.9	10.0	9.3	9.6	8.7	8.1	8.5	9.0	8.0	8.8	9.5	9.1	8.8	9.3	9.0	9.5
Nd	33.9	33.8	30.5	33.4	31.6	34.4	30.1	27.7	29.7	34.8	29.0	32.1	33.3	31.6	31.6	33.6	29.2	35.2
Sm	6.9	7.7	6.4	7.1	6.4	7.5	5.8	4.9	6.3	7.0	5.0	6.3	7.0	6.2	6.3	5.7	7.0	6.6
Gd	5.9	5.7	5.3	5.5	4.8	6.4	5.1	4.5	4.7	5.1	4.4	5.1	4.9	5.1	5.4	6.3	6.0	5.8
Tb	0.81	0.94	0.90	0.90	0.79	0.89	0.83	0.69	0.75	0.73	0.668	0.88	0.73	0.78	0.85	0.81	0.99	0.96
Dy	5.63	5.31	5.45	5.67	5.51	5.45	4.31	4.36	5.26	5.57	4.3	5.65	5.66	5.35	5.30	6.00	5.32	6.20
Ho	1.27	1.05	1.01	1.35	1.11	1.11	1.12	1.02	1.03	0.97	1.09	1.12	1.17	1.13	1.09	1.36	0.99	1.28
Er	4.07	3.37	2.91	3.63	3.48	2.97	3.43	2.64	3.31	3.05	3.21	3.29	3.30	2.85	3.08	3.83	4.15	4.66
Tm	0.55	0.60	0.54	0.57	0.55	0.58	0.54	0.43	0.46	0.50	0.381	0.48	0.55	0.52	0.53	0.55	0.52	0.58
Yb	3.89	3.53	3.43	4.06	3.34	3.78	3.58	3.28	3.80	3.98	3.2	4.32	3.97	3.76	3.76	3.49	3.91	3.80
Lu	0.59	0.50	0.56	0.57	0.56	0.53	0.55	0.51	0.61	0.55	0.613	0.53	0.59	0.54	0.59	0.61	0.53	0.49
Hf	5.05	4.19	4.70	5.39	4.99	6.07	4.48	4.26	4.35	4.45	4.84	4.00	5.25	4.81	4.87	5.08	4.81	6.10
Ta	2.23	2.02	2.20	2.27	2.14	2.48	1.96	1.86	2.23	2.10	1.9	2.04	2.21	2.13	2.02	2.13	2.07	2.30
Pb	27.1	26.4	27.2	27.9	24.7	27.8	22.9	21.1	23.1	24.9	22.9	24.3	25.7	24.8	23.8	24.6	26.6	26.4
Th	46.3	43.9	40.3	44.6	43.0	44.5	37.3	34.1	36.7	38.4	38.0	38.7	40.9	38.8	39.4	42.8	41.9	44.8
U	12.5	12.5	12.6	12.8	12.1	12.8	11.2	10.7	10.8	11.8	11.5	11.7	12.9	12.1	11.6	12.2	13.2	13.1

Table 2 — *continued...*

| Provenance								Lipari									
Samples	504	505	506	507	509	511	512	513	514	515	516	517	518	519	520	521	522	523
Sc	3.59	2.60	3.24	2.99	2.42	2.38	1.57	1.68	2.05	1.94	1.84	1.68	1.50	1.53	1.38	1.30	1.02	1.27
Zn	52.7	39.4	56.6	48.6	47.8	45.8	52.8	52.0	49.9	48.0	52.1	42.3	41.1	48.5	45.0	46.8	47.7	43.5
Rb	301	226	281	261	249	246	274	261	274	262	258	234	229	235	252	236	260	260
Sr	14.26	11.55	13.66	13.27	13.21	12.34	13.10	13.00	14.36	13.29	13.70	11.71	11.57	12.54	12.63	12.71	13.47	13.56
Y	40.0	25.6	40.7	33.1	33.9	31.1	35.1	34.7	36.9	32.7	36.3	31.4	30.9	32.0	33.9	31.1	34.4	35.0
Zr	163	115	158	137	139	131	146	144	156	136	145	129	128	134	139	127	146	145
Nb	34.6	25.7	31.8	30.4	29.3	28.7	32.6	31.5	33.1	31.5	32.5	28.4	25.9	28.3	30.2	29.0	31.1	30.2
Cs	15.8	11.3	14.8	14.1	14.0	13.9	14.0	13.6	14.3	13.7	13.7	12.1	12.1	12.3	12.6	12.9	13.5	14.0
Ba	14.6	12.0	12.7	12.0	12.8	12.0	12.3	12.3	14.7	12.5	11.1	9.3	11.0	10.8	11.7	11.0	10.5	10.3
La	53.4	38.6	52.7	44.9	46.6	43.9	46.5	45.6	50.1	43.4	47.8	41.4	41.9	44.3	44.4	42.5	48.0	46.9
Ce	113	80	103	93	92	87	96	91	98	91	94	83	82	85	87	86	94	93
Pr	11.1	8.0	10.8	9.9	9.8	9.3	10.1	9.7	10.8	9.7	10.3	8.6	9.3	9.3	9.5	9.4	10.5	10.7
Nd	40.2	29.1	37.1	32.7	34.9	33.1	33.4	31.9	35.9	32.5	34.9	30.7	31.2	30.5	32.1	30.0	34.7	35.8
Sm	9.1	6.4	7.9	7.7	5.8	6.9	7.0	6.1	6.3	5.3	6.4	5.3	6.2	6.8	6.6	6.3	8.0	7.1
Gd	8.5	5.7	7.3	6.0	5.6	5.2	6.0	5.1	6.5	5.4	6.2	4.8	4.7	4.9	5.5	5.0	6.3	4.9
Tb	1.07	0.75	0.96	0.93	0.90	0.87	0.81	0.88	1.10	0.99	0.95	0.85	0.82	0.75	0.95	0.76	1.17	0.81
Dy	7.09	5.35	6.32	5.68	5.93	5.37	6.29	6.37	6.71	6.04	6.45	5.30	5.20	5.03	5.47	5.45	6.08	6.18
Ho	1.38	0.96	1.46	1.21	1.08	1.17	1.26	1.17	1.27	0.89	1.30	0.99	1.09	1.19	1.06	1.13	1.25	1.19
Er	4.29	3.19	4.34	3.72	3.37	3.39	3.63	3.53	4.11	3.59	4.12	3.19	3.01	3.10	3.19	3.30	3.61	4.26
Tm	0.85	0.45	0.63	0.50	0.54	0.59	0.61	0.59	0.48	0.72	0.60	0.58	0.53	0.52	0.56	0.52	0.48	0.56
Yb	5.09	3.43	4.43	3.64	3.76	3.81	3.97	4.36	5.50	4.70	4.51	4.14	3.68	3.69	4.19	3.92	5.09	4.67
Lu	0.78	0.42	0.55	0.62	0.63	0.55	0.73	0.56	0.64	0.66	0.53	0.57	0.55	0.48	0.58	0.49	0.59	0.60
Hf	6.17	4.99	6.43	5.62	5.41	4.28	5.20	4.37	5.90	4.97	6.48	4.52	5.22	5.45	5.08	4.75	5.03	5.30
Ta	2.63	2.01	2.27	2.46	2.10	2.22	2.41	2.46	3.00	2.43	2.50	2.37	2.34	2.44	2.04	2.04	2.49	2.11
Pb	30.9	23.9	29.2	28.1	27.3	26.4	27.3	25.2	28.4	26.0	26.7	24.8	23.9	23.1	24.5	23.8	28.4	26.8
Th	51.4	38.5	49.7	41.1	43.8	42.0	43.2	44.4	47.4	42.3	44.6	39.7	37.6	39.3	40.6	39.6	46.0	46.3
U	15.8	11.8	14.8	13.7	13.4	13.1	12.5	13.0	13.9	12.6	12.2	12.0	11.1	11.6	12.8	11.5	13.9	13.2
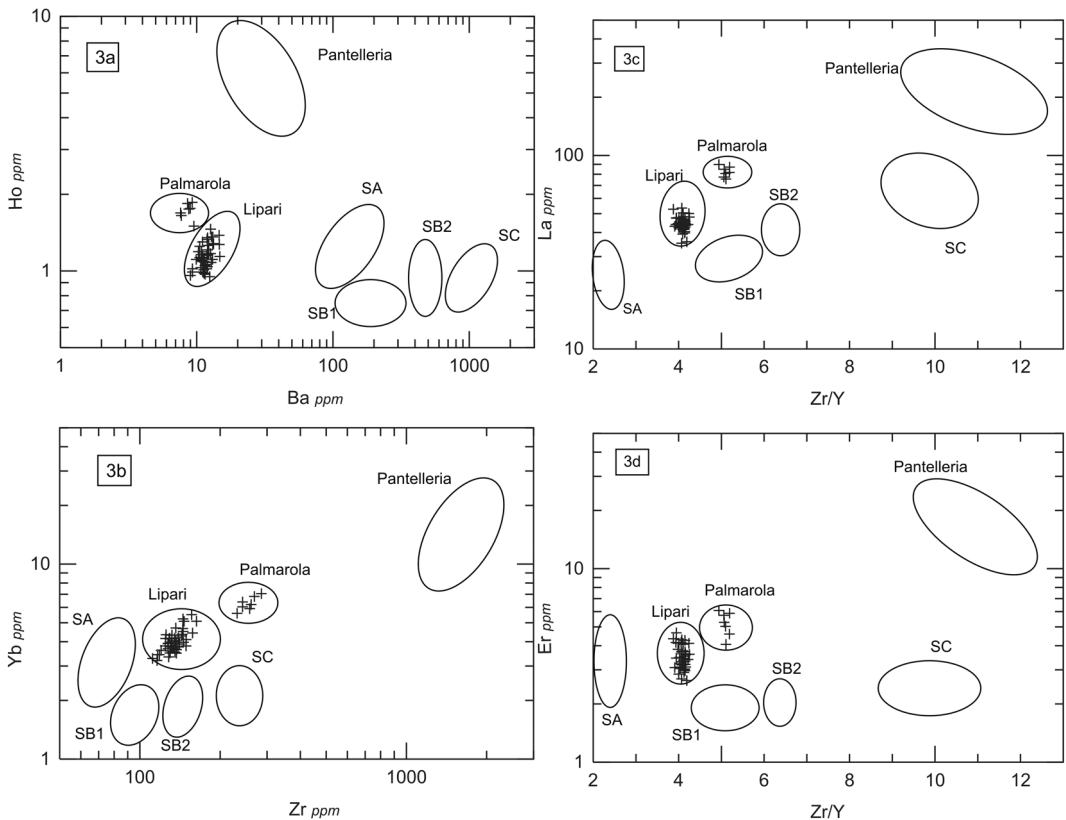
Fig. 3 – a) Ba-Ho; b) Zr-Yb; c) Zr/Y-La; d) Zr/Y-Er diagrams for all studied archaeological artefacts. Ellipses enclose compositional groups of source areas distinguished by using LA-ICP-MS data from Barca *et al.* (2007). The indication of Lipari, Palmarola and Pantelleria groups are clearly reported; The acronyms SA, SB1, SB2 and SC are referred to the four obsidian subgroups of the M.te Arci (Sardinia).

Lipari and Palmarola provenances similar to that of Catignano.

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