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In situ XRF investigations to unravel the provenance area of Corinthian ware from excavations in Milazzo *(Mylai)* and Lipari *(Lipára)*

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Abstract

In this contribution a non-destructive approach has been used aiming at investigating the chemical composition of 35 ceramic items belonging to the collections of the Regional Aeolian Museum "Luigi Bernabò Brea" in the Lipari Island (Sicily, Italy). Different vessel types have been selected for analysis, including aryballoi, kotylai, olpai, anforiskoi, oinochoai, and alabastra, belonging to the "Proto-Corinthian and Corinthian" ware classes. The items, dating back to the period comprised between the early eighth and the first half of the sixth century BC, come from two different archaeological sites in the province of Messina (Sicily), specifically the Istmo necropolis of Milazzo, in the northern Sicilian coast, and the acropolis and necropolis of Lipari, in the Aeolian islands. The chemical characterization of ceramics, carried out through portable X-ray fluorescence spectroscopy (pXRF), aimed at gaining information on the production area of examined items whose autoptic analysis pointed to Corinthian imports. The possibility of carrying out experimental investigations on the most ancient materials from the archaic necropolis of Milazzo and on fragments from Lipari, albeit limited to pXRF investigations, allowed to enrich the knowledge on the Corinthian production exported to western areas as well as to discriminate, no longer based solely on autoptic observations and stylistic evaluations, between Corinthian productions and "local" imitations.

Keywords: Pottery, Corinthian ware, Sicily, pXRF spectroscopy, Provenance

Introduction

Between the eighth and sixth centuries BC the Corinthian ware was widespread throughout the Mediterranean and assumed a decisive role in archaeological research as an indicator of the diffusion of the Greeks in the West as well as a dating tool for their settlements and contexts. This thanks to the chronological succession defined by Payne [1] and confirmed by materials from excavations in Corinth and the sanctuary of Perachora [2]. Being the most widespread and abundant fabric of that time, Corinthian pottery is considered to be the major guide-line to ascertaining the chronology of the eighth–sixth centuries BC [3].

In the face of so much emphasis given to this ceramic class in the archeological research, there was no parallel in-depth study based on investigations of the composition that would allow the provenance attribution of materials found in distant areas. Previous studies of Corinthian pottery have been mainly concerned with the composition of Corinthian clay and the determination of possible clay sources, while analysis has mainly concentrated upon coarse or semi-coarse ware, particularly amphoras, and only subordinately on fine ware of the Archaic period [4–7]. Therefore, the pioneering studies by Farnsworth [8, 9], Farnsworth et al. [10], Jones [11],

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and Whitbread [12, 13], although no more recent, still remain the main references in the existing literature on Corinthian ceramics. In particular, Farnsworth was the first to analyze ceramics from Corinth by combining petrographic analysis with neutron activation analysis (NAA) [8–10]. A great deal of clay prospection and study, including petrographic and chemical analysis along with firing experiments, has been carried out by Jones [11] in the attempt to identify the possible Corinthian clayey raw material sources. Then, Whitbread [12] in his petrographic study aimed at ascertaining the provenance of Greek amphoras, also focused on many common Corinthian fine wares. He also sampled and characterized a variety of clays and other raw materials around the ancient city through refiring tests and petrographic study in the attempt to find the raw materials used in the production of the Corinthian amphoras and the other ceramic products [13].

In this contribution a non-destructive analytical approach has been used aiming at investigating the chemical composition of 35 ceramic finds belonging to the collections of the Regional Aeolian Museum "Luigi Bernabò Brea" of the Lipari Island (Sicily, Italy), whose autoptic analysis pointed to Corinthian imports for most of them. Different vessel types have been selected for analysis, including *aryballoi, kotylai, olpai, anforiskoi, oinochoai*, and *alabastra*, all belonging to the "Proto-Corinthian" and "Corinthian" ware classes. The findings, dating back to the chronological range comprised between the early eighth and the first half of the sixth century BC (720–550 BC), come from two different archaeological sites in the province of Messina (Sicily) (Fig. 1). Specifically, seventeen samples have been recovered from the Istmo necropolis of Milazzo, in the northern Sicilian coast, while eighteen findings come from the acropolis, the sanctuary and the necropolis of Lipari, in the Aeolian islands.

The elemental composition of ceramics, in terms of major, minor and trace elements, was carried out through portable X-Ray Fluorescence spectroscopy, a technique increasingly used for in situ analysis of museum collections which cannot be removed and/or sampled. Investigations aimed at assessing if all the selected items are properly Corinthian, as supposed on the basis of archaeological and stylistic considerations, or if they include foreign imitations.

Several authors used non-destructive techniques for the characterization of ceramic artefacts. In particular, X-ray spectroscopic techniques (XRF, PIXE) are among the most widely employed [e.g. 14–21], since they provide multi-elemental analysis together with easy preparation. In some cases, the authors wanted to test the potentiality of non-invasive techniques in the identification of production centers of artefacts and for such a scope they investigated findings previously analyzed through the use of conventional destructive instrumentation. It was found

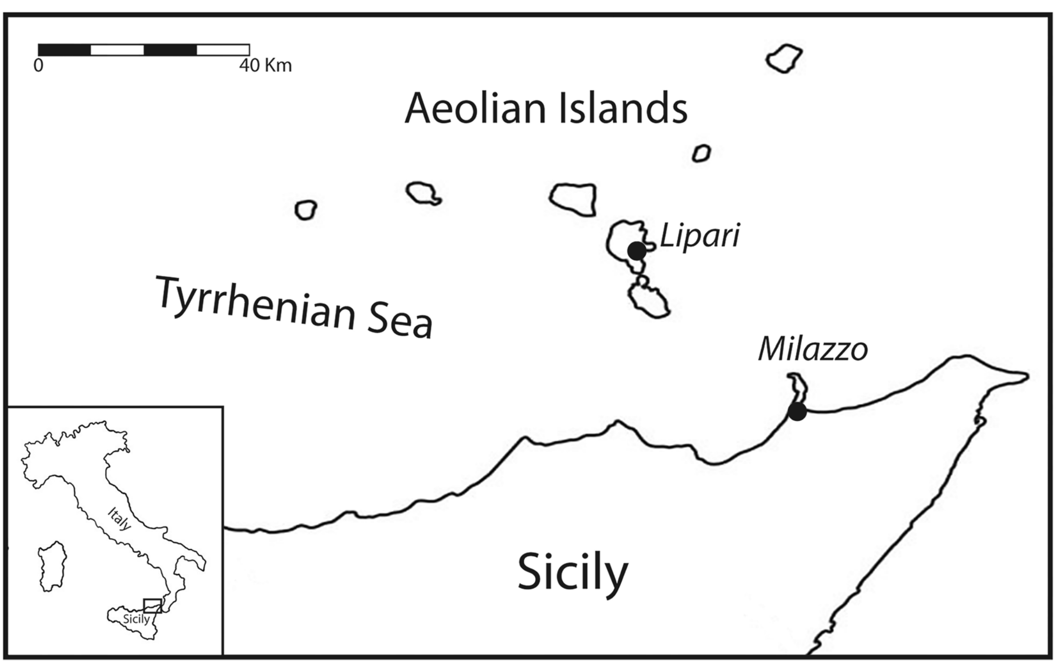

Fig. 1 Map showing the north-eastern coast of Sicily and the Aeolian archipelago, with location of the two investigated sites

that the application of non-invasive analytical methods to the study of archaeological pottery (despite the intrinsic limitations of instrumentation), supported by statistical processing of data, may contribute to the resolution of important archaeometric issues, such as the provenance attribution.

Archaeological sites

The ceramic finds selected for this study are exposed at the Regional Aeolian Museum "Luigi Bernabò Brea" of Lipari, though they were recovered from two distinct archaeological sites in the province of Messina, namely the Istmo necropolis of Milazzo (*Mylai*), in the northern Sicilian coast, and the acropolis and necropolis of Lipari (*Lipára*), in the Aeolian Archipelago (Fig. 1). The two Greek *poleis* were "founded" [cfr. 22] in areas inhabited since prehistory and which, in historical times, belonged to the to the world of Western Greeks, *Mylai* as a sub-colony of *Zankle* (Messina) and *Lipára* as a refuge for a group of Knidian people which fused with the few local inhabitants [cfr. 23, 24]. If the foundation of *Mylai* dates back to the end of the eighth century BC according to the information provided by Eusebius and Jerome (716–715 BC) [25] and confirmed by excavations, two hypotheses have been made for *Lipára*: the first one, consistently with the tradition accepted for Milazzo**,** based on Eusebius and Jerome, locates the arrival of the Greek contingents in the last quarter of the seventh century [26]; the second hypothesis, founded on the text of Diodorus Siculus and shared by the excavators, points to the 50th Olympiad (580–576 BC) as the moment of "foundation" [25].

The chronology of Eusebius and Jerome (627–626 or 630–629 BC) seems to be confirmed by fragments of Middle Corinthian vases, which represent the oldest imports, a quarter of a century later than the date of arrival of the Greeks [3, p. 490 and 27, p. 77].

In both cases, the settlements of archaic and classical periods were almost erased by their transformation into fortresses in medieval and modern times. Conversely, the necropolises, investigated during several excavation campaigns, appeared to be partly preserved.

The Istmo necropolis of *Mylai* [28] was excavated in 1950–1951 and its materials were preserved at the museum of Lipari. The burials excavated systematically are about 172, the most ancient of which are concentrated in the part of the Istmo corresponding to the current Via XX Settembre, the nearest to the settlement. Funerary goods offer many interesting elements thanks to the various ware production including imported pottery (Corinthian) and colonial products (Corinthian-type and Euboic-type pottery, banded ware and dipping ware, aniconic Chalcidian type and black glaze pottery).

As regards *Lipára*, the first excavations (1950–1956) have brought to light some areas of the settlement on the cliff as well as parts of the necropolis on the plain. The *bothros* was discovered on the acropolis only in 1964 while the oldest tombs after almost twenty years from the beginning of excavations [29, 30]. Among the discovered materials, many of these, considered to be sporadic due to the excavation method that did not allow to recognize the small earthly tombs [31], have not been identified during the excavation. The Corinthian ware (consisting of about 300 pieces, of which 59 from the bothros, 179 from the polis and 61 sporadic from the necropolis) has been studied by François Villard. In the two cases under examination, according to Neeft [3], "the earliest datable vases" were the Corinthian ones, being only these latter, along with the Attic ware, ascribable to a consolidated systematic seriation with universally accepted chronologies. Conversely, as in most western *poleis*, many materials of local production or imported from other sites than Corinth, also referable to the initial decades of the settlements but without seriations, have not been dated.

Studied materials

The 35 artifacts selected for analysis from both sites consist of several vessel types belonging to the "Proto-Corinthian" and "Corinthian" ware classes. Tables 1 and 2 report a list of examined findings including type, chronology and finding spot/burials. In particular, seventeen samples (Table 1, Fig. 2), whose chronology ranges from Early Proto-Corinthian to Early Corinthian (720–595 BC), come from the Istmo necropolis of Milazzo, while eighteen finds (Table 2), Fig. 3), which can be dated to the period comprised between Middle Corinthian and Late Corinthian II (595-post 550 BC), according to Neeft and Amyx chronologies, come from the acropolis and necropolis of Lipari.

In detail, the items selected from Milazzo include two alabastra, six aryballoi, one achrome miniaturistic aryballos, one globular vessel, four kotylai, one olpe, and one bottle/olpe, while those from Lipari include seven aryballoi, one anforiskos, five kotylai, one cup, two pyxes, one oinochoe, and one olpe or trilobated oinochoe. The state of conservation of the finds is quite different, being in a better state those from Milazzo coming from well identified tombs, while highly fragmented those from Lipari, coming from uncertain stratigraphic units within the acropolis and the necropolis.

Methods

The chemical characterization of selected pottery was carried out through portable Energy Dispersion X-ray Fluorescence Spectroscopy (pXRF) by using a Bruker Tracer IV-SD system, endowed with an X-ray tube with

Table 1 List of examined pottery items from the Istmo necropolis of Milazzo

Type	N. Inv	Chronology	Burials	Bibliography
Globular aryballos	6842a	720–675 BC	T. No. 5	[28] p. 39; [32] IX, p. 41, n. 9
Globular aryballos	6842b	720–675 BC	T. No. 5	[28] p. 39; [32] XIII, p. 45, n. 12
Globular aryballos	7061c	720–675 BC	T. No. 65	[28] p. 58; [32] VIII a, p. 40
Globular aryballos	7022a	720–675 BC	T. No. 37	[28] p. 52; [32] XVI, p. 47, a*
Kotyle	6843	720–675 BC	T. No. 5	[28] p. 39
Kotyle	7022b	720–675 BC	T. No. 37	[28] p. 52
Olpe or bottle	6898	700–650 BC	T. No. 21	[28] p. 48
Olpe	7145	630–615 BC	T. No. 116	[28] p. 71
Alabastron	7010	615–595 B.C	T. No. 25	[28] p. 49
Globular aryballos	7140a	615–595 BC	T. No. 118	[28] p. 72
Globular aryballos	2154	625–600 BC	T. No. 123	[28] p. 73
Achromatic aryballos	7029	620–595 BC	T. No. 77	[28] p.60–61 and 106
Kotyle	7003	640–615/ 615–595 BC	T. No. 23	[28] p.49
Alabastron	7139	615–595 BC	T. No. 118	[28] p. 72; [32] p. 356–357
Kotyle	7002	615–595 BC	T. No. 22bis	[28] p. 48
Globular aryballos	6882	615- 595 BC	T. No. 14	[28] p. 46
Globular vessel (oinochoe?) Milazzo Painter	7018	630–615 BC	T. No. 32	[28] p. 51; [33] 1, p. 77

Table 2 List of examined pottery items from Lipari

Type	N. Inv	Chronology	Finding spot	Bibliography
Kotyle	9597c	595–570 BC	Necropolis (Tr. XXXI, T. 966)	[30] XI, 1, p. 344
Kotyle	*19**	595–570 BC	Necropolis (Tr. XXX?)	Inedited
Kotyle	20402	595–570 BC	Acropolis (Tr. CE 3–4)	Inedited
Globular aryballos	21110b	595–570 BC	Necropolis (Tr. XXXVI sag. 1/II)	[34] p. 247, no photo
Aryballos	20400a	595–570 BC	Acropolis (Tr. B, tg 11)	[34] p. 247,114, 10
Globular aryballos	*23**	595–570 BC	Necropolis (Tr. XXXVI sag. 1/II)	[35] p. 799
Kotyle	19578	595–570 BC	Necropolis (Tr. XXXII)	[35] p. 799, 308, 1f
Aryballos	20399a	595–570 BC	Acropolis (Tr. BA, tg 9)	Inedited
Pyx	20401	580–570/570–550 BC	Acropolis (Tr. BB, tg 6–7)	[34] p. 247, 115, 31
Spherical aryballos	21204	580–570 BC	Acropolis (Tr. BA, tg 4)	[34] p. 247, tav. 65, 5
Anforiskos	19442	570–550 BC	Necropolis (Tr. XXXI, Spo)	[35] p. 799, tav. 308, 1c
Aryballos	20399b	570–550 BC	Acropolis (Tr. BA)	[34] p. 247, tav. 114, 13
Aryballos	20399d	570–550 BC	Acropolis (Tr. B, tg. 11)	[34] p. 247, tav. 114, 11
Cup	21196	570–550 BC	Acropolis (Tr. Z, tg 1–5)	[34] p. 247, tav. 115, 25
Pyx	19579	570–550 BC	Necropolis (Tr. XXXII, Spo/68–69)	[35] p. 799, 308, 1 g
Oinochoe	18688	post 550 BC	Bothros	[34] p. 247, tav. 65, 4
Broad-bottomed oinochoe?	19892	not defined	Sanctuary (Tr. XXIII)	Inedited
Olpe or trilobed oinochoe	18686	end VI–V cent BC	Acropolis *Bothros*	[34] p. 224, tav. 67, 12

19* and 23* are labels assigned to identify these two items which do not have inventory number

Fig. 2 The examined artifacts recovered from the Istmo necropolis of Milazzo (photos are to scale)

Fig. 2 continued

Fig. 3 The investigated artifacts recovered from the acropolis and necropolis of Lipari (photos are to scale)

Rh target (and Pd slits) source and a 10 mm^2 Silicon Drift Detectors (SDD). Two different instrumental setups were used for light and heavy elements and specifically: (a) 15 kV, 35 mA, no filter and vacuum condition for elements from Mg to Ca; and (b) 40 kV, 17 mA, 304.8 µm aluminum + 25.4 µm titanium filter for the heavier elements. In most of artifacts, measurements have been carried out at the base of the vessels or, in any case, in pigment-free portions of the surface. Two consecutive measurements per spot were carried out with an accumulation time of 60 s and then the average composition was calculated for each spot. In cases where the visual examination of the finds has highlighted chromatic inhomogeneity, multiple analyses were performed on specific points.

Identification of the elements' peaks was gained directly on the laptop connected to the instrumentation by means of the software S1PXRF, while quantitative data were obtained by using PyMCA software based on fundamental parameter calculations [36].

The major elements determined as oxides included SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, K_2O, and P_2O_5 (sodium and magnesium were also determined, nevertheless data were not used since they were considered to be affected by large measurement errors), while the minor/trace elements included Cr, Ni, Rb, Sr, Y, Zr, and Nb.

The calibration was performed by using the best fit method calculated on 39 international mineral and rock standards (AL1, ANG, BCR1, BEN, BIR1, BR, BXN, DNC1, DRN, DTN, DTS1, FE-MICA, FKN, G2, GA, GH, GSN, GSP1, KK, MAG1, MAN, MG-MICA, MGR1, NIMD, NIMG, NIML, NIMN, NIMP, NIMS, PCC1, SCO1, SDC1, SGR1, STM1, SY2, SY3, UBN, W2). All best fits displayed R^2 values higher than 0.9, as observable in the diagrams given in Additional file 1 (see blue circles). Additionally, the standardization procedure was also applied to ceramic matrices by using a set of 11 archaeological pottery as internal standards, whose sherds were analyzed through portable XRF and then the data were compared with those deriving from the analysis of powder pellets of the same samples by using a laboratory WD-XRF spectrometer. Even in this case, all best fits exhibited R^2 values higher than 0.9 for both major and minor elements (see orange circles in the diagrams of Additional file 1). The only exception is represented by P_2O_5 data which display low R^2 value and for this reason have been excluded by the statistical analysis. The additional use of pottery samples as internal standards had a dual purpose: (i) support the assumption that standardization is consistent with the ceramic materials under study; (ii) verify that analyses carried out on the fragments do not create any sensitive errors related to the morphology of a single sherd. In any case, it's worth to note that all the ceramics investigated, both the internal standards and those under study, are fine-grained so as to overcome any problems due to the heterogeneity of the paste.

In order to identify possible chemical groupings among the examined set, the analytical data obtained by pXRF analysis underwent statistical treatment by means of hierarchical cluster analysis and principal component analysis (PCA). The data were firstly transformed according to Aitchison approach to central log-ratio with the aim to avoid the constant sum problem:

$$x \in S^D \rightarrow y = \ln\left(\frac{x_D}{g_D(x)}\right) \in R^D$$

where x = composition, $x_D = (x_1, x_2, \ldots x_D)$, y = log transformed composition and $g_D(x) = \sqrt[D]{(x_1, x_2, \ldots x_D)}$. This transformation transposes the data from its constrained sample space, the simplex S^D, into the real space R^D [37]. The statistical analysis was made by using CoDaPack and Origin softwares.

Results and discussion

Results obtained from in situ pXRF analysis of the selected ceramic items are reported in Tables 3, 4, 5, 6 and graphically represented in the variation diagrams of Fig. 4. As observable, major elements do not allow to identify any specific chemical grouping among the investigated samples. Indeed, their amounts show a wide variability in both groups, Milazzo (blue circles) and Lipari (red circles), whose compositional ranges are almost totally overlapped (Fig. 4a–c). Specifically, SiO_2 ranges from 42.68 to 58.79% in Milazzo group and from 41.94 to 54% in Lipari one. CaO is higher than 8% in all examined items, except for two olpai (6898 from Milazzo and 18686 from Lipari) whose CaO concentrations are around 5%. Al_2O_3 and TiO_2 vary from 11.31 to 20.79% and from 0.75 to 1.58%, respectively, in samples from Milazzo, while from 8.64 to 19.67% and from 0.57 to 1.46% in samples from Lipari. Even Fe_2O_3 and K_2O show wide variability, ranging the first from 7.25 to 13.67% in Milazzo items and from 6.39 to 14.86% in Lipari ones, while the second from 1.1 to 4.19% in Milazzo group and from 0.97 to 5.34% in Lipari group (see Tables 3 and 4).

Conversely, as for the minor and trace elements, mainly nickel and chromium but also rubidium and strontium allow to make some distinctions. Specifically, almost all of samples from Lipari are characterized by high nickel (126–233 ppm), chromium (up to 364 ppm) and rubidium (79–162 ppm) concentrations (Table 6 and Fig. 4d, e), except for one olpe sample (18686) whose Ni amount is much lower (57 ppm). Conversely, the finds from Milazzo can be distinguished into two different groups,

Table 3 Concentrations (wt.%) of major elements obtained by pXRF analysis of the investigated pottery from Milazzo

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	K_2O	P_2O_5
6842a	47.37	1.22	15.49	11.81	0.13	13.43	1.20	1.28
6842a_bis	46.33	1.58	14.93	13.67	0.43	15.51	1.33	1.85
6842b	48.11	0.75	15.09	7.40	0.10	12.42	1.20	0.57
6842b_bis	49.93	1.02	16.46	10.79	0.50	13.90	2.02	1.29
6843	54.76	1.06	16.58	8.23	0.20	11.40	1.63	1.06
7022a	45.96	1.06	16.81	9.46	0.17	14.32	2.25	0.81
7022b	48.51	1.05	17.39	9.81	0.39	11.00	3.09	1.56
7022b_bis	43.71	0.86	13.85	7.25	0.31	15.44	2.65	5.00
7029	54.51	1.08	17.00	9.25	0.21	8.55	3.85	1.45
7029_bis	46.44	1.19	14.71	12.02	0.48	13.77	4.12	5.12
7061c	58.79	1.00	15.98	7.51	0.20	8.57	1.98	1.13
7061c_bis	56.93	0.98	16.10	7.52	0.18	8.19	2.00	1.08
7010	52.74	0.86	16.09	7.76	0.13	12.60	1.07	3.40
7018	50.79	0.91	15.05	9.40	0.21	13.50	1.45	0.61
7139	42.68	0.83	16.18	10.07	0.21	13.65	2.03	1.05
7139_bis	46.55	0.86	14.03	10.45	0.20	17.82	1.10	0.55
7140a	47.51	0.92	16.42	11.58	0.15	13.49	2.10	0.65
6882	46.43	0.99	15.62	10.50	0.13	12.00	1.25	1.76
6882_bis	44.29	1.06	12.86	13.29	0.24	16.20	1.12	3.11
7002	43.18	1.10	12.40	13.41	0.22	18.88	1.26	0.70
2154	42.95	1.17	11.31	13.15	0.18	17.02	1.74	0.99
7145	47.65	0.94	14.02	10.93	0.17	15.15	2.21	0.99
6898	48.25	1.09	20.79	11.89	0.17	5.12	4.19	0.83
7003	47.92	1.00	13.82	11.14	0.19	15.06	2.77	1.29

Table 4 Concentrations (wt.%) of major elements obtained by pXRF analysis of the investigated pottery from Lipari

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	K_2O	P_2O_5
21110b	53.95	0.71	15.57	7.19	0.17	10.67	2.35	0.42
21110b_bis	49.82	1.03	13.84	12.07	0.22	12.78	3.14	0.47
23*	52.72	0.79	15.21	8.94	0.19	12.12	2.19	0.38
203999a	50.70	0.67	16.39	6.92	0.12	13.37	3.08	0.51
20399b	49.97	1.01	12.88	13.28	0.13	13.07	2.73	1.19
20399d	43.84	1.40	11.67	16.88	0.32	15.59	2.82	0.89
20400a	49.13	0.62	15.80	6.39	0.13	12.97	2.54	0.69
20401	40.64	1.46	9.03	14.76	0.37	12.13	4.93	0.48
20402	47.15	0.83	15.15	11.56	0.12	15.33	1.64	0.22
19442	44.89	0.57	19.29	11.72	0.13	8.23	5.34	0.18
19578	49.59	0.79	14.57	10.56	0.19	9.75	2.53	0.63
19579	41.94	0.91	19.67	14.75	0.09	8.72	7.22	0.17
19892	50.88	0.81	14.77	9.01	0.13	12.04	3.40	0.37
18686	49.25	1.00	19.17	11.18	0.09	5.63	4.56	0.24
18688	45.19	0.72	14.11	8.15	0.11	13.91	3.54	0.29
18688_bis	46.45	0.84	14.16	10.15	0.12	13.02	4.67	0.27
21196	45.66	0.75	8.64	14.86	0.12	11.20	4.42	4.31
19*	50.07	0.84	14.36	8.63	0.14	17.50	1.63	1.35
19*_bis	49.09	0.71	14.38	6.81	0.10	15.25	1.49	0.55
9597c	47.11	0.79	13.07	9.20	0.12	18.81	0.97	0.25
21204	49.81	0.88	16.46	10.32	0.28	13.13	1.95	0.66

Table 5 Concentrations (ppm) of minor/trace elements obtained pXRF analysis of the investigated pottery from Milazzo

Sample	Cr	Ni	Rb	Sr	Y	Zr	Nb
6842a	283	226	36	885	41	219	21
6842a_bis	319	201	21	818	31	183	20
6842b	174	185	35	1091	31	189	21
6842b_bis	159	171	41	1012	25	162	26
6843	185	159	33	905	23	134	19
7022a	151	56	90	578	21	164	21
7022b	70	29	107	971	27	208	25
7022b_bis	94	45	134	775	29	242	29
7029	43	46	173	700	45	351	29
7029_bis	81	37	148	641	40	292	25
7061c	114	57	114	949	32	236	29
7061c_bis	140	68	109	803	36	246	28
7010	206	195	45	1200	27	152	21
7018	287	277	56	644	31	182	21
7139	287	224	45	523	27	169	20
7139_bis	288	230	43	609	31	173	17
7140a	276	190	90	887	35	174	26
6882	229	185	46	1148	32	174	23
6882_bis	205	171	44	803	31	151	20
7002	183	151	53	340	25	156	16
2154	268	201	52	828	34	222	28
7145	234	156	64	556	27	184	18
6898	107	70	181	353	39	317	32
7003	220	181	96	1350	31	170	22

Table 6 Concentrations (ppm) of minor/trace elements obtained by pXRF analysis of the investigated pottery from Lipari

Sample	Cr	Ni	Rb	Sr	Y	Zr	Nb
21110b	196	192	148	425	26	197	23
21110b_bis	170	169	134	381	24	182	19
23*	221	187	147	462	28	171	23
203999a	246	213	122	1583	23	120	17
20399b	163	164	103	376	26	147	21
20399d	288	166	160	646	28	189	28
20400a	211	210	134	905	30	155	20
20401	120	148	104	293	20	117	20
20402	202	195	160	371	32	156	23
19442	364	158	150	346	25	147	20
19578	102	158	117	383	22	132	19
19579	279	213	162	493	28	159	20
19892	251	162	145	449	25	151	23
18686	207	57	127	340	33	278	30
18688	132	126	79	215	14	80	12
18688_bis	293	184	145	531	22	152	23
21196	198	233	131	461	25	160	19
19*	241	196	113	539	30	168	26
19*_bis	242	175	106	494	22	153	20
9597c	207	210	145	344	26	168	20
21204	182	194	162	507	21	163	19

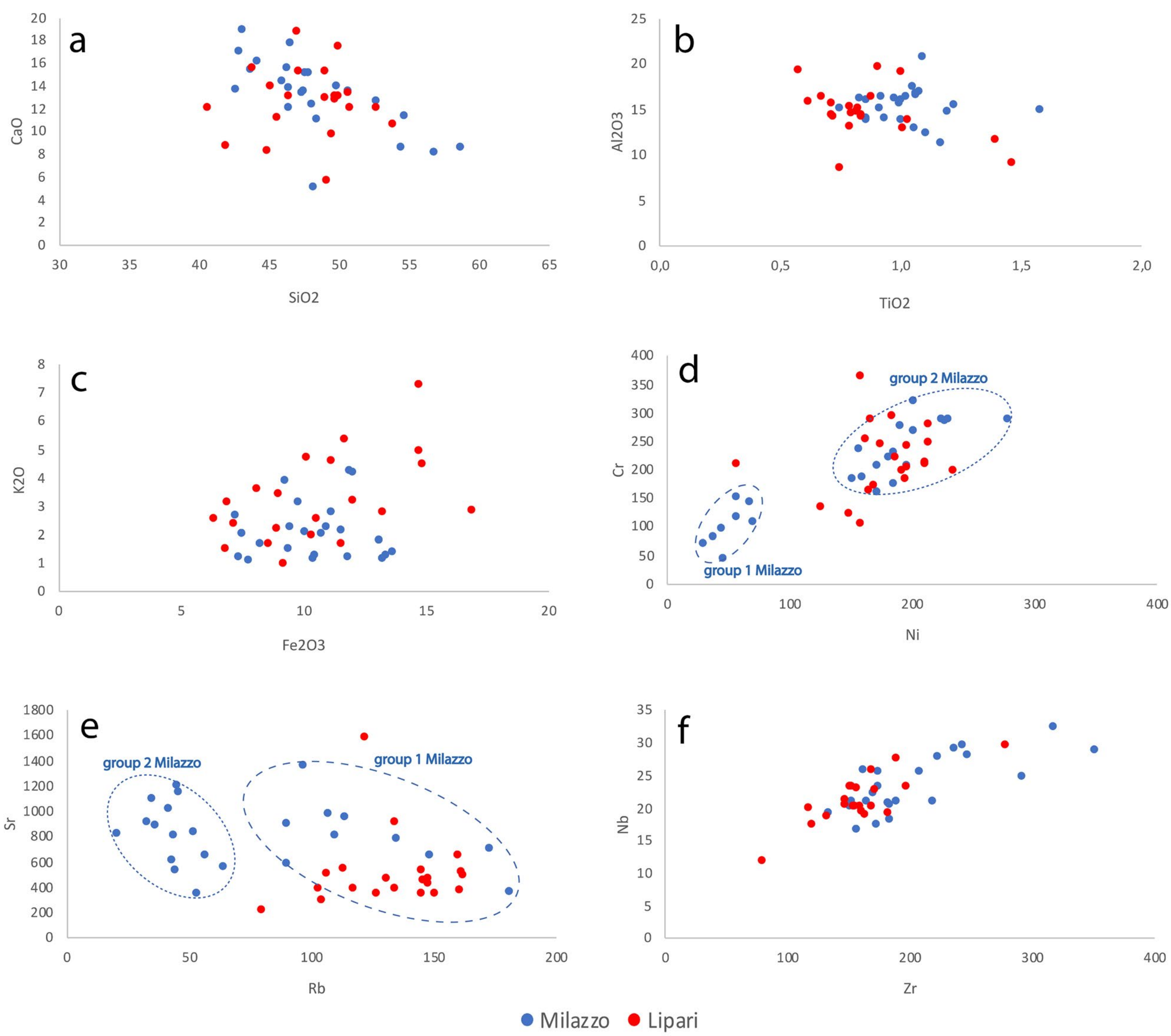

Fig. 4 Variation diagrams of the most significant major and minor/trace elements determined through pXRF analysis of items from Milazzo (blue circles) and Lipari (red circles)

one of which has low amounts of nickel (29–68 ppm) and chromium (43–151 ppm) and high rubidium (90–173 ppm) (*group 1* in Fig. 4d, e; Table 5), while the other one with high nickel (152–277 ppm) and chromium (up to 319 ppm) similarly to samples from Lipari but with averagely lower rubidium contents (21–96 ppm) (*group 2* in Fig. 4d, e; Table 5). As concerns strontium, it shows a very high variability among examined ceramics, ranging from 340 to 1350 ppm in the artefacts from Milazzo and from 215 to 1583 ppm in those from Lipari. On the whole, it can be observed that Sr concentrations are averagely higher in the Milazzo group, where they generally exceed 500 ppm, compared to the Lipari group, where most of samples display Sr contents lower than 550 ppm (Tables 5, 6 and Fig. 4e). Similarly, zirconium amounts, also showing a noteworthy variability within the analyzed set, are averagely higher in samples from Milazzo, where they vary from 134 to 351 ppm, than those from Lipari, whose values from a minimum of 80 ppm go up to 190 ppm, with the only exception of sample 18686 (Zr = 278 ppm) (Tables 5, 6 and Fig. 4f).

Cluster analysis was performed using trace elements (being the most discriminant) with the aim to evidence groups formed by ceramics with similar chemical composition. The dendrogram (Fig. 5), made using the Euclidean distance and the ward clustering method, evidenced

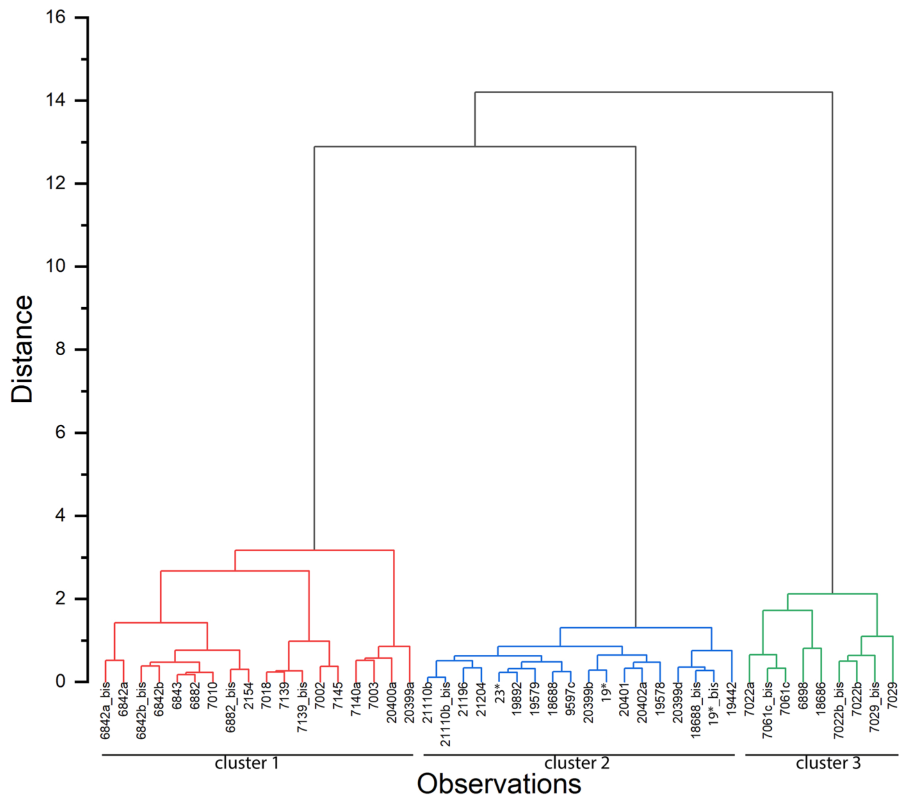

Fig. 5 Dendrogram deriving from the hierarchical cluster analysis of examined items from Milazzo and Lipari

the presence of three well defined clusters. In detail, *cluster 1* (Fig. 5) is almost totally constituted by items coming from the Istmo necropolis of Milazzo which, from a chronological viewpoint, date back to Proto-Corinthian–Early Corinthian period. Among the most ancient materials (Proto-Corinthian), this group includes the two aryballoi 6842a and 6842b and the kotyle 6843. Instead, the olpe 7145, the alabastron 7010, and the aryballos 7140 belong to the Late Proto-Corinthian, the globular vessel 7018 to the transitional period, while the aryballoi 2154 and 6882, the kotylai 7002 and 7003, and the alabastron 7139 can be ascribed to the Early Corinthian. This group also includes two Middle Corinthian aryballoi from Lipari, namely 20399a and 20400a.

Cluster 2 (Fig. 5) is formed exclusively by items coming from Lipari, which date back to the period Early Corinthian–Late Corinthian II. The most ancient artefacts of this group (Early Corinthian–Middle Corinthian) include three kotylai samples (9597c, 20402, and the one without inventory number). To the Middle Corinthian can be ascribed the figured aryballos 21110b and the kotyle 19578. The aryballos,204 (recomposed from several fragments) and the pyxis 20401 belong to the period Middle Corinthian–Late Corinthian I, while the fragment of aryballos without inventory number, along with the anforiskos 19442 (cfr. [38], Gela, II, tav. 22, 5G 113), the fragment of cup 21196, and the two fragments of aryballoi 20399b and 20399d, can be ascribed to the Late Corinthian I. Lastly, to the Late Corinthian II can be referred the fragment of pyxis 19579 and the fragment of oinochoe 18688 (cfr. [1], n. 1547 A), this latter coming from the *bothros*. Not chronologically definable is the fragment of kotyle 19892 coming from excavations in the sanctuary.

Cluster 3 (Fig. 5) is constituted almost exclusively by items from the Istmo necropolis of Milazzo, which include: four Proto-Corinthian items (the kotyle 7022a, the two aryballoi 7022b and 7061c, and the olpe 6898), and one Early Corinthian miniaturistic aryballos (7029). In addition, this cluster also includes one olpe (18686) of the end VI–V cent from the *bothros* of Lipari.

The chemical data were also treated by principal component analysis (PCA) in order to further explore the compositional differences among the examined sample set. The biplot reported in Fig. 6 was made by using the minor/trace elements as variables and considering the first two principal components which account for 86% of the total variability. The biplot confirms the three main

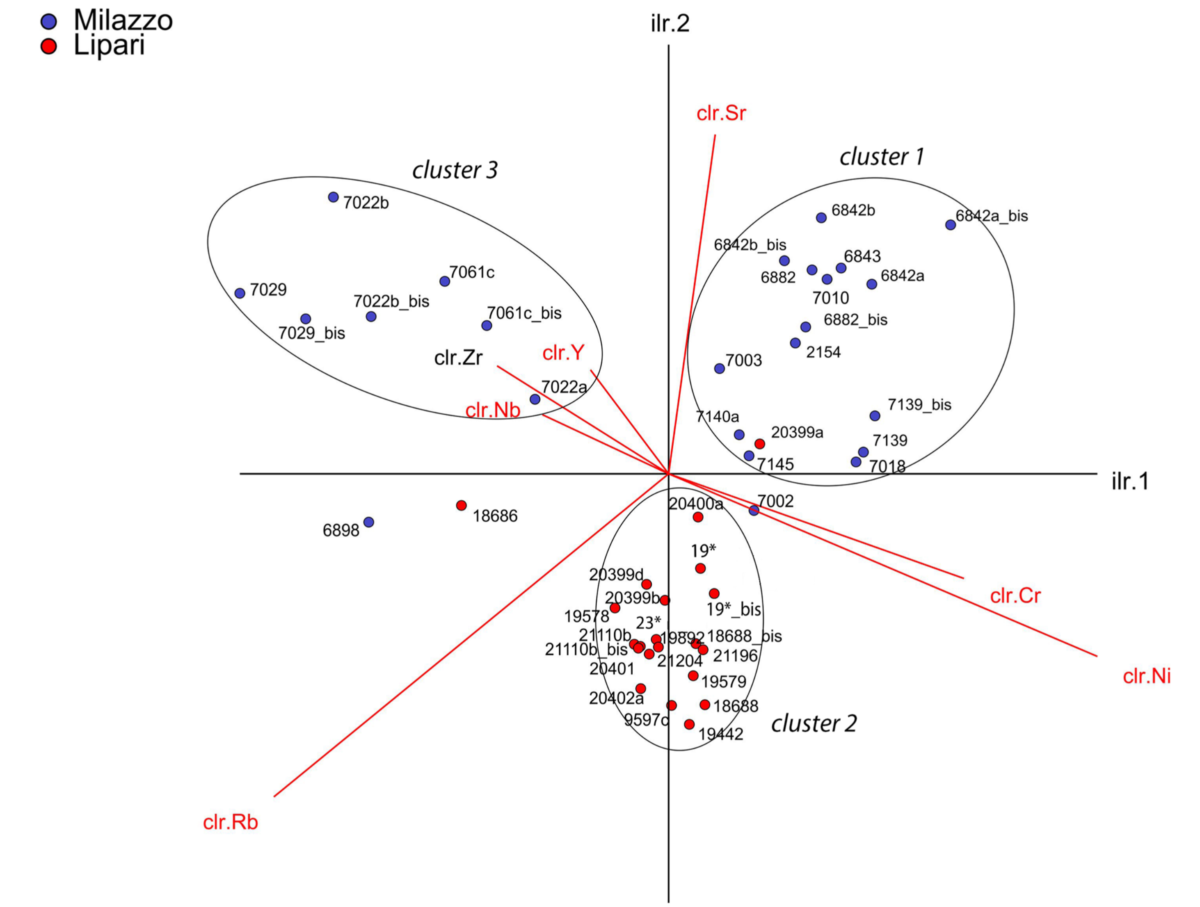

Fig. 6 Biplot of the PC analysis of examined items from Milazzo (blue circles) and Lipari (red circles)

groups highlighted by cluster analysis. Specifically, *cluster 1*, in the right upper part of the diagram, comprises those samples from Milazzo which exhibit high Ni and Cr, low Rb and variable Sr concentrations. *Cluster 2*, in the lower central part of the diagram, includes exclusively samples from Lipari characterized by high Ni, Cr and Rb and low Sr amounts. *Cluster 3*, in the left upper quadrant of the biplot, is formed by items from Milazzo with low Ni and Cr and high Rb contents. The two samples 6898 from Milazzo and 18686 from Lipari, which in the dendrogram of Fig. 5 clearly belong to cluster 3, here are ouliers in the lower left quadrant, being characterized by low Ni and Cr contents, similarly to samples of cluster 3 but with lower Ca and Sr and higher Nb amounts. The two aryballoi 20399a and 20400a from Lipari, which in the dendrogram of Fig. 5 belong to cluster 1, even in this case stand out from the rest of the Lipari group due to their higher Sr concentrations which cause them to shift towards the upper right quadrant of the biplot.

As concerns the artifacts belonging to *clusters 1 and 2* (Figs. 5 and 6), some of the major experts of Corinthian ware, namely Villard (for the materials found in Lipari), Neeft and Amyx (for those coming from Milazzo), definitely recognized them as properly Corinthian imports (see references in Tables 1 and 2) on the basis of autoptic examination (color of the clay of the ceramic body, decorative motifs, stylistic characters, etc.). In the case of Corinthian ceramics, such macroscopic characteristics are well known thanks to the studies of Payne, Dunbabin and the same Amyx, Neeft, and Villard. Results of pXRF analysis seem to support the archaeological hypothesis, since, due to their high concentrations of Ni (126–233 ppm in artifacts from Lipari and 152–277 ppm in samples from Milazzo) and Cr (up to 364 ppm in samples from Lipari and up to 319 ppm in samples from Milazzo), they cannot be certainly ascribed to a “local” (southern Italy) manufacture but rather to a Greek one, as demonstrated by a wide existing literature on ancient pottery [e.g. 5, 7, 10, 11, 14–16, 19, 39–43]. In this respect, in fact, several authors ascertained that the major role in discriminating Greek from southern Italian products is played by nickel and chromium, two provenance-sensitive elements [11], whose contents are much higher in the former than in the latter as a consequence of the different geological constitution of the two territories. In particular, the chemical composition of raw materials in Greece seems to be influenced by the outcropping of ophiolite nappe which justifies the high Ni and Cr abundances [5, 15]. By assuming that all of the items from both *cluster 1* (samples from Lipari) and *cluster 2* (samples from Milazzo) are produced in the Corinthian area, the compositional variability observed which accounts for the discrimination into two different groups (Figs. 5 and 6) should be explained by a likewise variability in the raw materials sources which, in turn, could reflect: (a) a change over time in the raw materials supply by the same workshop; or (b) the choices of different potters (workshops) working at different times with the same range of resources. In this respect, Farnsworth in 1970 [9] undertook the first major study of clays in the Corinthian area. In particular, she characterized three broad classes of clays from the region: Acrocorinth red clay, Acrocorinth white clay, and white clay of the Corinthian plain, and for the first time she assessed the wide diversity in the nature of Corinthian clay deposits, attributing different types of clays to different localities. She also suggested that the clay from Acrocorinth was in use during the Proto-Corinthian period, whereas that from the plain was used in the "Classical" (by this she evidently meant to include the Corinthian Archaic) period. So, this wide variability in the clay sources available in the Corinthian area could explain the compositional differences registered between the findings from Lipari and those from Milazzo, also considering that the latter exhibit a more pinkish color than the former ones pointing to the use of different clayey materials. Certainly, the alternative hypothesis that one the two groups of artifacts is not of Corinthian manufacture but rather produced in a workshop outside Corinth, cannot be completely ruled out, although it is in contradiction with what asserted by the major experts of Corinthian ware. In this respect, Amyx [33] stated that "in most cases the distinction between Corinthian-made pottery and its foreign imitations can be made on the basis of the shape, style of decoration and character (color and texture) of the clay, but there are some pieces for which doubts cannot easily be resolved on these features only, even under expert examination". Additionally, several attempts have been made overtime to find some discriminating features between the "original" Corinthian pottery and its Greek imitations by using the elemental composition, but with no success.

As concerns *cluster 3* of the biplot (Fig. 6), which includes four items from the Istmo necropolis of Milazzo, their low nickel (29–68 ppm) and chromium (43–151 ppm) contents allow to exclude a Corinthian manufacture and rather suggest a western imitation. Even in this case, results of investigations seem to support the starting archaeological hypothesis. Indeed, Neeft [32] already ascribed two of these artifacts (7022a and 7061c) to a western production and, in particular, he suggested an importation from *Pithecusa* (the ancient Ischia island). However, their compositional similarity with the miniaturistic aryballos 7029 points towards a production in a different area of southern Italy. The latter sample, in fact, turned out to be stylistically similar to some items from the votive deposit of the S.mo Salvatore in Messina, whose petrographic and chemical analyses revealed a manufacture with clays from the Strait of Messina area and for which therefore a production in Zancle was supposed [14]. That Zancle was an important center of ceramic production has been ascertained by numerous authors (cfr. VV.AA. in "da Zancle a Messina" 2001, 2002).

A last consideration is concerned with the two outliers in the lower left quadrant of the biplot (Fig. 6), the Proto-Corinthian olpe 6898 from Milazzo and the fragment of olpe 18686 of the end VI–V cent BC from Lipari. The item 6898 belongs to the class of pottery of Ionian [28, p. 48] or Chalcidian tradition, widespread and produced in several "Chalcidian" settlements in the Strait of Messina area (*Zankle* and *Rheghion* with *Matauros* and *Mylai).* The item 18686, coming from the *bothros* of Lipari, is considered to be a production of eastern Greece that Iris Love, Director of the American excavations at *Knidos*, acknowledged as "of knidian tradition" [29, p. 77]. For these two findings, which seem to exhibit similar chemical composition, results of analyses allow to hypothesize a western production, since they have low nickel and chromium concentrations, similarly to samples of *cluster 3* but with lower calcium and strontium contents. It cannot be excluded that the two artifacts belong to the same production area as the finds of *cluster 3* but produced by using Ca-poor clays (CaO ~ 5–6%). In this respect, Barone et al. [44], in a previous provenance study of archaeological pottery through comparison with clay sediments belonging to different geological Fms outcropping in eastern and southern Sicily, found that clays from the Messina Strait area exhibit rather variable CaO contents ranging from ~ 6 to ~ 20%. Therefore, the hypothesis of a local production of Corinthian-style pottery with low calcium-clays is certainly plausible. However, we do not have enough elements to put forward a more precise hypothesis of provenance for these two artifacts.

Archaeological considerations

The examined items from the Istmo necropolis of Milazzo are of crucial relevance since Amyx used them to provide an exceedingly valuable cross-check on the chronology of the Early Proto-Corinthian phase and defined the general chronology of EPC as "the last quarter, or even the last fifth of the eighth century" [33, p. 414].

Their centrality in the scientific debate on Corinthian ceramics can be renewed thanks to the analytical data collected and discussed here, which indicate a future line of research that should define whether the compositional variations found point to: (i) different workshops in the Corinthian area; (ii) chemical variability of the clayey sediments exploited by the same workshop; (iii) similar productions manufactured in different centers. The research could be carried out following the wake of other researches, such as that dedicated to the so-called "Thapsos ware", which has been shown to be produced in many sites [45].

Referring to what has already been highlighted in the previous section as well as in Table 1 (for items from Milazzo) and Table 2 (for items from Lipari), we focus here on some significant points.

Results of analysis confirmed the use of "local" clays for a group (*cluster 3*) which includes the following Proto-Corinthian items, already recognized by Neeft [32] as locally produced: one globular aryballos (inv. 7022a; [32, XVI, p. 47, a*]), one kotyle from the same tomb 37 (inv. 7022b) and one globular aryballos from tomb 65(inv. 7061c; [32, VIII a, p. 40]). Included in the same group is a miniaturistic aryballos from tomb 77 (inv. 7029; [28, p. 60, 61, 106], belonging to a type very common in the area and already attested in the votive deposit of the S.mo Salvatore in Messina [14, 46], which therefore can no longer be considered of Pithecusan production. A local provenance (*Zankle-Mylai*) is also assumed for the olpe inv. 6898 from tomb 21, with spared shoulder, neck and rim, and with black painted tapered tub, bordered by red bands. It is an example of Chalcidian type pottery, attributed to several settlements in the Strait of Messina area, in Milazzo often discovered within archaic tombs and in Lipari repurposed, at the end of 6th and in fifth century, by a group of 24 olpai of similar size from the *bothros* [47]. The use of this local clay also in the following centuries is suggested by the fragment of olpe or trilobed oinochoe inv. 18686 from Lipari, with pink paste and red brush decoration on the surface prepared with light engobe. It can be assigned to a production center in Messina, which since the seventh century imitates Greek-oriental materials (B1 and B2 cups).

Belonging to the first group of "Corinthian" production (*cluster 1*) is the olpe inv. 7145 from tomb 116, Late Proto-Corinthian and transitional (many thanks to Prof. Neeft for confirming the dating), with ovoid body, everted lip, trumpet neck distinguished by a collar, disc-shaped foot, tripartite ribbon handle, decoration on the neck with fine lines. On the shoulder, a serpent-like monster is depicted with a dolphin tail and a three-dimensional body, with two purple and brown bands and overpainting in purple and beige, with seven and eight-petal white rosettes, and purple bands between incisions. Lacking decoration in the two lower registers, with reddish black paint. The item finds comparison in the olpai of the Corinthian Black Polychrome group, as well as in the olpe from Quaranta Rubbie necropolis of Veio, (Rome, Villa Giulia Museum, inv. 55400, Hound Painter, [33, p.27, pl. 7,1]), although the decorative motif of the olpe inv. 7145 seems to be of a collateral production.

Also belonging to the same *cluster 1* is the globular vase inv. 7018, body sherd of Corinthian black-figured pottery closed vessel, possibly an oinochoe, considered eponymous vase of the "Milazzo Painter", "Rough Late-Transitional painter of olpai and oinochoai" [33, p. 77, pl. 31 and p. 374]. Decorated on the ball with trichrome tabs and, below, from a frieze with a theory of animals, panther, swan or water-bird, goat and lion; half-moon in circle as filling ornament (Fig. 7).

Even the two small Early Corinthian alabastra examined, attributable to contemporary workshops, belong to

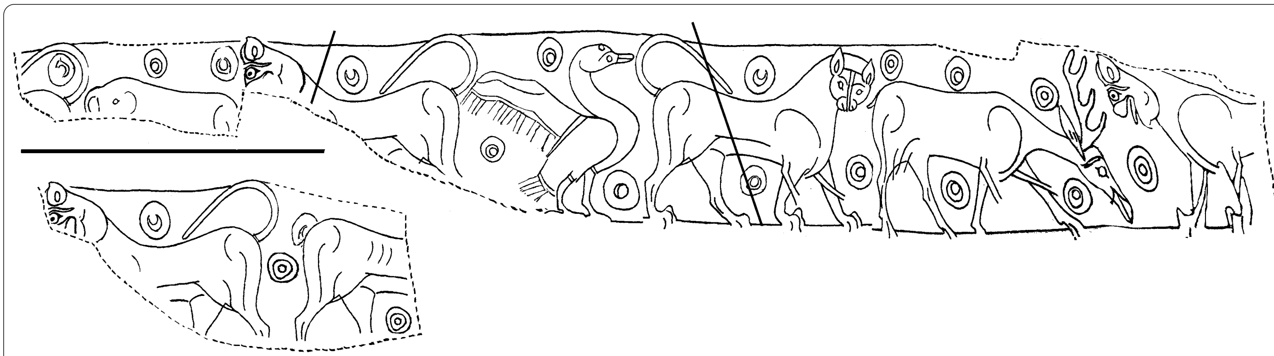

Fig. 7 Graphic elaboration of the decorative motif in the globular vase inv. 7018—tomb 32 (from Bernabò Brea & Cavalier [28], p.51 Fig. 8, modified)

the first group of Corinthian production (*cluster 1*). The alabastron inv. 7010, from tomb 25, is decorated with a swan facing right and a rooster facing left, separated by a line of rosettes. It can be assigned to the *panther-bird group*, sharing with it both size and morphology of the figures and the way to engrave the plumage in the swan and rooster. The swan has a neck decorated with white dots, which perhaps were originally red or purple. The rooster has the neck feathers made in parallel incisions, the wing with a circular shoulder, divided into two parts by thin double lines, from which the flight feathers and long feathers in the tail branch off (cfr. Taranto 20683, [33, p. 93 pl. 43,2]). The second alabastron (inv. 7139), from tomb 118, is now almost totally illegible,except for the head of lion-headed bird with spread wings and some incisions of the plumage with traces of red (cfr. British Museum from Gela 1863, 0728.60). Dated to the Early Corinthian by Neeft [32, p. 285 group CXIV, subgroup E, pp. 356–357 Fig. 189], it can be approached to the productions of the *panther-bird group.*

As for the seventeen artifacts from Lipari, the results of analyses suggest a constant supply for over half a century from the same restricted production area, if not from the same workshop. Their compositional diversity with respect to the items from Milazzo, which we suppose as arrived in *Mylai* through the Zanclean supplying, put into question their arrival in Lipari through the same market, despite the role of redistributor of Corinthian ceramics already hypothesized for Zankle [48], on an autoptic basis.

Noteworthy is the fragment inv. 21196 from the Trench Z (tg 1–5), the latter substantially unpublished (Area insula IV, Excavations 1950 and 1954; the trench is marked in Bernabò Brea & Cavalier [49, p. 25, Fig. 2 and Atlas, plan no. 3]. The fragment is attributable to a distinct-lipped cup, with fillets on the edge and below the lip, with decoration depicting a retrospective bird (of which part of the body, the neck, and the head remain) and a griffin-bird, with areas defined by deep incisions and colored in black and purple; of the lower dark band remains only a small part. It is very similar to two exemplars, one from Taranto [50, p. 162, Fig. 140a; 33, p. 253, 17] and the other from Lentini [51, es. 803, KC3465 of pp. 121 and p. 123, n. 803]. The comparison with this last piece allows us to assign the cup fragment from Lipari to the painter Wellcome R 367/1936, identified by Neeft as the creator of the Lentini cup [51] and whose activity is part of the wide cup production of the group of Vogelfriesmaler.

Two of the examined items from Lipari exhibit slightly different composition with respect to the others. They both come from the acropolis trench B (excavated in 1950 before the arrival of M. Cavalier), which yielded the oldest materials and remained unpublished. Villard [34, p. 247] reports from this trench five fragments datable to the Middle Corinthian and four to the Late Corinthian I, none to a later age. Among them, a fragment of globular aryballos (inv. 20399a from tg 9), of which only the cylindrical neck and the shoulder decorated with tabs within parallel lines are preserved, was here examined along with the tub fragment of a globular aryballos with floral decoration (inv. 20400a from tg. 11).

Lastly, not chronologically definable is the fragment of a closed shape (inv. 19892) of Corinthian production, slightly concave and perhaps attributable to the basin of a flat-bottomed oinochoe, found in the excavations of the sanctuary (Tr. XXIII). This, with a few other pieces, attests the frequentation of the site already in an epoch preceding that of the altar of the end of the V–IV century BC.

Conclusions

A set of 35 pottery items, currently preserved at the Regional Aeolian Museum of Lipari, was studied by means of pXRF spectroscopy in order to gain information on their provenance.

Investigations concerned, in the case of Milazzo, artifacts of great archaeological value and in a good state of conservation. On such items, dating back to the end of the VIII–VI century BC, Amyx and Neeft based the reconstruction of some phases of Proto-Corinthian and Corinthian productions. Therefore, the research permitted to get back the study of such exceptional artifacts after more than fifty years, updating their framing and providing graphic and photographic documentation so rekindling attention on them. The results of analyses also provided indications for an unparalleled piece, such as the olpe inv. 7145, whose attribution to a Corinthian manufacture might otherwise have been questioned. Furthermore, the study permitted to describe with a major detail the item 7018 which allows a greater knowledge of the work of the Milazzo painter, as well as to attribute the exemplary 21196 to the painter Wellcome R 367/1936 who works in the group of Vogelfriesmaler.

The identification of two distinct chemical groups (clusters 1 and 2) of Greek production suggested two different supply channels from the Corinthian area and, probably, two different manufacturing workshops for the two poleis (*Mylai* and *Lipára*). However, it should be noted that the two groups are in chronological succession, since the items from Milazzo reach up to the Early Corinthian while those from Lipari start at the Middle Corinthian. And this could explain the use of different clay deposits over time.

Instead, the identification of a non-Corinthian group (cluster 3) has provided further information on a local production referred to a large chronological period (late VIII-V century BC). Such production, probably ascribable to *Zankle* and his subcolony *Mylai*, imitated products of different origin (Proto-Corinthian, Corinthian, Chalcidian and Greek-oriental) by using clay sources from the Messina Strait area. The identification of such a local Corinthian production opens a new perspective in the framing of the production of imitation, a crucial topic in the current international scientific debate.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-022-00667-9.

Additional file 1. Standardization of major (A) and minor/trace elements (B) by using 39 international mineral and rock standards (blue circles) and 11 internal ceramic standards (orange circles).

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Availability of data and materials
All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Competing interests
The authors declare that they have no competing interests.

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