

Investigations on provenance and content of archaic transport amphorae from Castello di Alceste (S.Vito dei Normanni-Br) by chemical analyses through XRF/FP and GC-MS

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Abstract – The aim of this work was to determine the provenance and the content of a group of archaic transport amphorae of different typologies retrieved during the archaeological excavations in the archaic settlement of Castello di Alceste (S.Vito dei Normanni-Br). We analysed a group of 16 samples belonging mainly to “Corinthian B” amphorae, which are widely diffused in the western Mediterranean basin and in Greece, but whose geographical provenance is still under discussion.

XRF/FP analyses revealed that the amphorae were manufactured in three different areas of the Mediterranean: southern Italy, Ionian Islands and Corinth.

GC-MS analyses revealed that most of the amphorae contained wine markers, together with pine resin, probably used as a sealant for the vessel or an additive to preserve wine. The contemporary presence of oil or animal fats in some containers suggests a possible reuse of the amphorae to store and preserve other foodstuffs.

INTRODUCTION

The excavations carried out by the University of Salento in the archaic settlement of Castello di Alceste (S.Vito dei Normanni-Br) have brought to light an indigenous settlement with a continuous occupation from the Iron Age until the end of the archaic period, when the site was abandoned [1]. The importance of the settlement, in particular during the VIth century B.C., is clear from the archaeological evidence: a big habitation area, several luxury goods, Greek pottery and numerous handmade local ceramics were retrieved during the stratigraphic

investigations. Greek imported ceramics - mainly Ionic, Corinthian and Attic products - are drink cups and craters associated to wine consumption, together with a high number of sherds belonging to transport amphorae [2].

All these artefacts reflect the intensity of maritime trade throughout the Mediterranean during the VIth century BC and the wide diffusion of imported goods among the indigenous societies of southern Italy.

The chemical investigations were aimed at defining the provenance and the content of some transport amphorae (fig. 1) referable to the most common typologies attested in western Mediterranean and in the indigenous settlements of the Salento Peninsula during the archaic period [3].

Among the selected vessels, Corinthian Type B, identifiable by fabric and morphological features, is the most represented transport container. The present state of research proposes different hypotheses about the manufacture centres: Corinth, Corcyra and some settlements in Magna Graecia.

Certainly, this typology was produced from the middle of the sixth century BC in ancient Corcyra, on the island of Corfu, where kilns were discovered, thus bringing into question their manufacture also in Corinth [4]. The latest research suggests a possible Magno-Greek origin of this typology, probably in the ionic area near Sibari [5; 6; 7].

“Corinthian B” amphorae are generally described as wine jars in the archaeological literature, as suggested by the presence of a resinous coating on the interior surface [8], confirmed also by previous lipid analyses [9; 10; 11].

On the other hand, the provenance of “Corinthian A” amphorae has been securely attributed to Corinth by petrological analysis [4], but the commodities that might have been carried in the jars are still unknown. The

absence of a visible coating on these amphorae suggested that this container could be associated with oil transport [12].

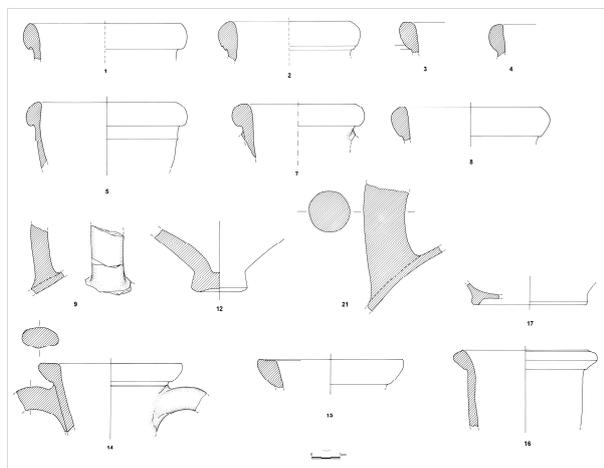


Fig. 1. Archaic transport amphorae sampled for XRF/FP and GC-MS analyses.

1. MATERIALS AND METHODS

Corinthian Type B transport amphorae represent the largest group of samples from Castello di Alceste (fig. 1 and tab.1, nn. 2-4, 7-9, 12). Other samples belong to Corinthian Type A (fig. 1 and tab.1, nn. 20-21), "Ionic" transport amphorae (fig. 1 and tab.1, nn. 1, 5) and one toe fragment classified as an East Greek production (fig. 1 and tab.1, n. 17). The containers are datable in the second half of the sixth century BC.

"Corinthian B" amphorae have a clay mixture with a colour ranging from light brown to pale yellow. Fragments of rims with rounded profile were sampled, together with single sherds of toe, wall and handle.

"Ionic" amphorae have an almond-shaped rim, a clay mixture with many inclusions and a light reddish brown colour. This shape is considered a transition to Corinthian Type B [13].

"Corinthian A" amphorae are characterised by a roughly spherical body, a horizontal rim, and heavy vertical handles. The fabric of Corinthian Type A can be easily recognised by its reddish colour and large red and grey inclusions.

The amphora classified as an East Greek production is a toe fragment with a micaceous and reddish yellow clay mixture, similar to some amphorae from the site of Incononata at Metaponto [14].

All the pottery sherds were water washed and stored in aluminium sheets or paper bags and put in sealable plastic bags, at room temperature, until required for analysis.

Table 1. Description of the samples analysed by XRF/FP and GC-MS

Sample nr.	Provenance	Description	XRF/FP	GC-MS
1	SV 96 9/1	Rim of "Ionic" amphora	●	●
2	SV 96 R/4	Rim of Corinthian Type B amphora	●	●
3	SV 97 104/1	Rim of Corinthian Type B amphora	●	●
4	SV 96 43/1	Rim and neck of Corinthian Type B amphora	●	●
5	SV 99 379/1	Rim of "Ionic" amphora	●	●
7	SV 99 368/1	Rim and neck of Corinthian Type B amphora	●	●
8	SV 99 335/8	Rim of Corinthian Type B amphora	●	●
9	SV 97 69/6	Handle of Corinthian Type B amphora	●	●
12	SV 99 378/1	Toe of Corinthian Type B amphora	●	●
13	SV 96 46/8	Wall fragment of Corinthian Type B amphora	-	●
14	KERKYRA 248	Rim and neck with handles of Corinthian Type B amphora from Corcyra	●	-
15	KERKYRA 249	Rim of Corinthian Type B amphora from Corcyra	●	-
16	KERKYRA 250	Rim and neck of Corinthian Type B amphora from Corcyra	●	-
17	SV 99 356/2	Toe of "East Greek" amphora	●	●
20	SV 96 52	Wall fragment of Corinthian Type A amphora	-	●
21	SV 99 356/1	Handle of Corinthian Type A amphora	●	●

X-Ray Fluorescence/Fundamental Parameters (XRF/FP) chemical analyses were carried out on the amphorae samples with the main aim of determining the production area, which had been hypothesized in the past on the basis of technical and typological features.

As a comparison term for XRF analyses on the amphorae from Castello di Alceste, three fragments of Corinthian Type B amphorae manufactured in Corcyra were analyzed (fig. 1 and tab.1, nn. 14-16), together with two pottery sherds manufactured in Corinth and three archaic tiles of local production from Castello di Alceste.

The XRF equipment consists of the MINI X (Amptek) and the X-123 spectrometer. The active silicon wafer area of the detector is 25mm², 500 µm thickness, and it has a 12.5 µm Be window. The detector has an energy resolution of 126-140 eV at 5.9 KeV FWHM (⁵⁵Fe). The silver target of the MINI X has 0.75 µm thickness with an end-window of 127 µm thickness. The detector and the x-ray tube are very close together at an angle of 45°, in order to minimize the source-sample and sample-detector distance and maximize the efficiency of the

measurement.

The measurements were carried out under the following conditions: 40 kV tube potential difference with a current of 15 μ A; acquisition time of 600 seconds. The X-ray spectrum was processed with the XRF-FP software (Amptek Inc., USA) using the basic parameters of the calibration method (FP).

Gas chromatography-mass spectrometry (GC-MS) was applied to the chemical characterization of the organic residues absorbed into the ceramic matrix, with the aim of identifying the original content of the vessels.

Potsherds (1-2 g) were crushed into a fine powder using a mortar and pestle. After the addition of 1 ml of a standard solution of nonadecane, the powdered ceramics were solvent extracted and derivatized using two different extraction procedures:

1. A chloroform/methanol mixture (4 ml, 2:1 v/v, 2x20 min ultrasonication) was used for the extraction of lipids [15; 16; 17]. Aliquots of the total lipid extract were gently dried under a stream of nitrogen. A portion of the dried extract was saponified by adding 4ml of 0.5M NaOH in MeOH/H₂O (9:1 v/v, 10 ml) and heating at 70°C for 1 hour in ultrasonic bath. The liquid fraction was acidified with HCl (1 M) and extracted with chloroform (2x5 ml). The solvent was then evaporated under a gentle stream of nitrogen.

2. For the identification of wine markers, portions of the powdered samples were extracted with KOH (1 M, 3 ml) in a sonicated bath at 70°C for 90 min [18]. The liquid fraction was acidified and ethyl acetate (2x3 ml) was added. The extract was separated and dried using a gentle stream of nitrogen.

All the extracts were derivatized with few drops of bis(trimethylsilyl)trifluoroacetamide (BSTFA)+1% trimethylchlorosilane (TMCS) at 80°C for 1 hour to produce trimethylsilyl derivatives. The excess solvent was removed under a slow stream of nitrogen and analysed by GC-MS, after the addition of hexane.

Samples were analysed using an Agilent Technologies 6850 II series gas chromatograph (5% phenyl-polymethylsiloxane capillary column, 30 m, internal diameter 0.25 mm, 0.25 μ m film thickness), with a split/splitless injection system used in the splitless mode and maintained at 300°C, coupled to an Agilent 5973 Network mass spectrometer operated in the EI mode (70 eV). The mass spectrometer was set to scan in the range of m/z 50 to 600 in a total cycle time of 1 s. The GC oven temperature was programmed from 100°C to 280 °C at 10°C/min, and held at 280°C for 15 min. Helium was used as the carrier gas at a constant flow rate of 1 ml/min. Compounds were identified partially by their retention time within the GC, based on comparisons with analysed reference compounds, but mainly by their mass spectra. Mass spectral data were interpreted manually with the aid of the NIST Mass Spectral Library and comparison with

published mass spectra and chromatograms.

2. RESULTS AND DISCUSSION

A. XRF/FP analyses

From the quantitative tables obtained by XRF/FP analysis, the concentrations of Ni and Cr elements (tab. 2) were in particular considered, in order to cluster Greek and southern Italy productions and to distinguish Corinthian from Corcyrean productions [19]. Corcyrean pottery has, in fact, higher concentrations of Cr, Ni and Al than Corinthian products.

Table 2. Chromium and nickel concentrations (ppm)

Sample nr.	Chromium	Nickel
1	410	200
2	310	110
3	90	10
4	410	200
5	447	209
7	400	230
8	320	190
9	190	30
12	76	353
13	620	290
14	560	200
15	70	30
16	160	60
17	130	30

As evidenced by the data in the diagram (fig. 2), the amphorae can be divided into three main groups that can be assigned to different production areas based on the concentration of Cr and Ni and the associations with the analysed pottery fragments from Corcyra, Corinth and Castello di Alceste.

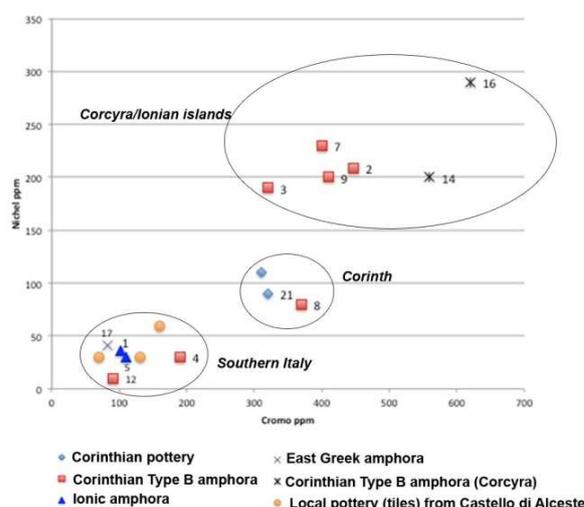


Fig. 2. Scatter plot of Cr and Ni concentrations of the

analysed samples

The group above indicates a possible provenance from the Ionian Islands, also confirmed by the association with the Corinthian Type B amphorae from Corcyra (nn. 14-16). The wide dispersion area of the group reflects a trend already observed on pottery samples produced in Corcyra [19]. Only the Corinthian Type B samples (fig. 2, nn. 2, 3, 7, 9) belong to this group.

Corinthian productions are in the middle of the graph (fig. 2, nn. 8, 21), where there is also one Corinthian Type B amphora. The data is interesting and requires further investigations, since the manufacture of Corinthian B amphorae in Corinth was first hypothesized and subsequently denied [4].

The clay group referring to southern Italy productions is at the bottom of the diagram, due to the low content of Cr and Ni (fig. 2, nn. 4, 12). These data seem to reinforce the evidence emerged in recent years regarding the presence of active ateliers in southern Italy that imitate the shape of Corinthian Type B.

Moreover, the "Ionic" amphorae (fig. 2, nn. 1, 5) probably are archaic Italic productions. Further investigation on the provenance are required in order to confirm these results.

Finally, the presence of sample n. 17 in the group of southern Italy productions is to point out. Due to the very micaceous clay mixture, this fragment was classified as an East Greek production. Despite repeated analyses to test concentrations, the sample always presented very low reference values. Nevertheless, a single sample has little statistical value and needs further confirmation by new analyses on more samples.

B. GC-MS analyses

The results of GC-MS analyses on the lipid extracts showed the presence of vegetable oil in three samples (tab. 3, nn. 1-2, 17), indicated by relatively abundant proportions of oleic and azelaic acids, together with the presence of β -sitosterol (fig. 3). Azelaic acid is produced from the oxidation of $\Delta 9$ fatty acids, such as oleic acid, which are typically found in high amount in vegetable oils [20]. The higher proportion of palmitic acid in comparison with stearic acid also confirms the vegetable origin of the content.

The lipid extraction of all the other samples provided very small amounts of fatty acids, except for the presence of plant sterols (β -sitosterol) and dehydroabietic acid, indicating that the amphorae were coated with pine resin [21]. In one sample (n. 5), also methyl-dehydroabietic acid was detected, considered the marker of the pitch obtained by the distillation of wood from plants of the *Pinaceae* family [21].

Pine resin was probably used for sealing and lining the amphorae, but it could be also be an additive to flavour and preserve the content, in particular wine.

The ceramic samples were also treated with the extraction protocol for wine biomarkers [18]. Tartaric acid was positively identified in 4 samples (tab. 3, nn. 5, 7, 9, 21). In addition to tartaric acid, other fermentation compounds were also detected: succinic, fumaric, malic acids (fig. 4). These acids are present also in 6 samples in which tartaric acid was not identified. For these jars, it is not possible to confirm that they contained wine; therefore, it would be preferable to repeat the analyses in the future through the application of other extraction methods [22].

Animal fats were identified by the presence of cholesterol in four samples (tab. 3, nn. 2, 5, 13, 17), suggesting a possible reuse of the amphorae to store other foodstuffs. It is also possible that animal fat was added to the resin used to line the vessels [22].

The samples containing wine or fermentation markers belong to Corinthian Type B amphorae, except for samples nn. 20-21, which were collected from two Corinthian Type A amphorae. The analyses seem to contradict the generally accepted assumption that Corinthian Type A transported oil and that they were uncoated, since pine resin is present in one sample (n. 21). These results certainly require further verification through analyses on a large number of jars, in order to establish their original content and surface treatment.

Table 3. GC-MS results on amphorae content. S=succinic acid; F=fumaric acid; M=malic acid; T=tartaric acid; β -sit.= β -sitosterol; Chol.=cholesterol.

Sample nr.	Oil	Fermentation markers				Pine resin	β -sit.	Chol.
		S	F	M	T			
1	•					•	•	
2	•						•	•
3		•		•		•	•	
4		•		•		•	•	
5		•	•	•	•	•	•	•
7		•	•	•	•	•	•	
8		•		•		•	•	
9		•	•	•	•	•	•	
12		•	•	•		•		
13		•		•		•		•
17	•							•
20		•		•				
21		•	•	•	•	•		

The presence of a vegetable oil only in three samples could suggest a possible reuse of the amphorae, considering that they come from a secondary context and one of them showed the contemporary presence of pine resin. Pine resin or pitch are generally associated to wine transport [23], although recent experiments have demonstrated that oil and resin are not incompatible and that a resinous coating could be used also to seal amphorae for oil storage [24].

Furthermore, we cannot exclude that these containers transported a wide range of goods (wine, oil, spices), as

emerged also by recent DNA investigations on some 5th-3rd century B.C. Corinthian B amphorae from Corcyra and Mende [25].

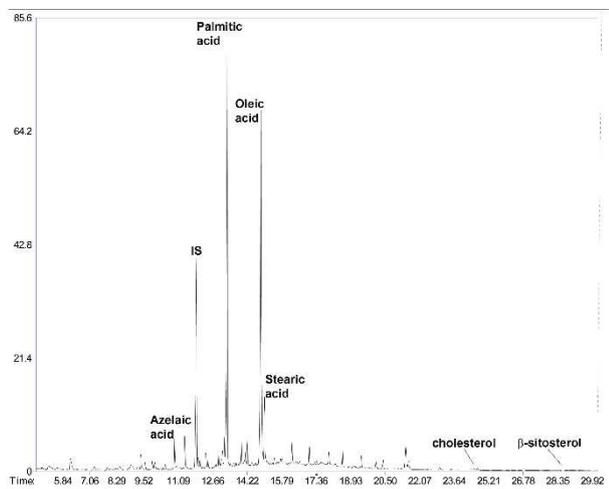


Fig. 3. Chromatogram of the analysis of the total lipid extract of sample 2, showing the presence of vegetable oil. IS=Internal Standard.

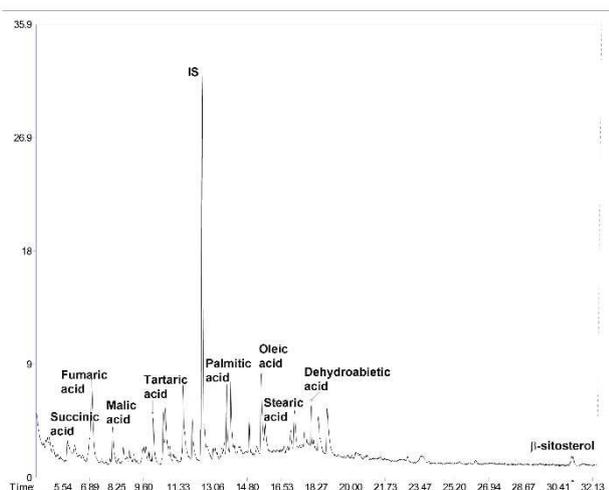


Fig. 4. Chromatogram of the analysis of the KOH extract of sample 9, showing the presence of wine biomarkers and pine resin. IS=Internal Standard.

CONCLUSIONS

The XRF chemical analysis carried out on the amphorae from Castello di Alceste provided interesting data compared to the initial hypothesis about their provenance. The analyses showed that the amphorae were manufactured in three different areas of the Mediterranean (Corinth, Corcyra, southern Italy), highlighting the complexity of commercial routes during the archaic period and the development of local economies through regular trade relations with the Greek

world.

GC-MS analyses revealed that the amphorae were used prevalently for wine transport but some of them contained vegetable oils. These data suggest several possibilities relating to amphora use in the archaic settlement of Castello di Alceste. Probably the original content of the amphorae was a resinated wine, but later the amphorae were re-used to store and preserve different goods, such as olive oil. Another possibility is that the amphorae transported a wide range of goods, not only oil or wine, but also grapes, vinegar or other agricultural products that probably were carried during multiple trading voyages along the Mediterranean coasts.

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XRF/FP analyses were carried out at CEDAD (Centre for Dating and Diagnostics), Department of Mathematics and Physics “Ennio de Giorgi”, University of Salento, under the scientific direction of L. Calcagnile, F. D’Andria and G. Semeraro. G. Quarta coordinated the work with the collaboration of M. Macchia, who oversaw the technical part of the analyses.

GC-MS analyses were carried out at the Organic Chemistry Laboratory of Di.S.Te.B.A. (Department of Biological and Environmental Sciences and Technologies), University of Salento, under the scientific direction of G. Semeraro and L. Troisi.

F. Notarstefano conceived the archaeological study of the amphorae from Castello di Alceste, performed GC-MS analyses and interpreted the related data, as part of the activities of the project “FutureInResearch” co-financed by Fondo di Sviluppo e Coesione 2007-2013 – APQ Ricerca Regione Puglia.

R. Caldarola conceived the petrological study on pottery production, performed XRF/FP analyses and interpreted the results.

All the authors read and approved the final manuscript.

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