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LRCW3
Late Roman Coarse Wares, Cooking Wares and Amphorae in the Mediterranean
Archaeology and archaeometry
Comparison between western and eastern Mediterranean

Edited by
Simonetta Menchelli, Sara Santoro, Marinella Pasquinucci and Gabriella Guiducci

Volume II
BAR International Series 2185 (II)
2010
CASTOR OIL AT CLASSE (RAVENNA – ITALY): RESIDUE ANALYSIS OF SOME LATE ROMAN AMPHORAE COMING FROM THE PORT

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During a fire at the end of the 5th century (about 490-500), among other buildings, a warehouse of the port of Classe was completely burnt. Inside there were different ceramic materials, such as lamps, amphorae, bowls and dishes, all coming from Africa, that remained in situ, thanks to the sudden event that destroyed the warehouse (building 17). The excavations were carried out during the years 2002 - 2005 by the University of Bologna and the Soprintendenza Archeologica of Emilia-Romagna. Among the amphorae recovered there were 200 spatheia type 1 (Bonifay 2004, type 31) and about 180 wide cylindrical amphorae dated between the end of the 5th and the first quarter of the 6th century. In order to understand what these amphorae contained, chemical analysis of residues were carried out. Ten amphorae were selected to be analyzed (five spatheia and five cylindrical amphorae). All were sampled with a small drill and analyzed in collaboration between the Archaeometric Laboratory and the Centro di Analisi e Determinazioni Strutturali of the University of Siena with spot tests and gas chromatography - mass spectrometry. The results of the analyses were surprising: regardless the form of the amphorae, some of the spatheia and of the cylindrical amphorae contained castor oil, and only two amphorae showed the markers of a possible different vegetable oil. No fish traces were present in either type of amphora, suggesting that these spatheia were not used to transport it. Furthermore, all the amphorae showed resin or pitch traces, although almost all of them contained oil. These data point out several problems on the attribution of a specific content to amphorae types, and on the presence of an organic coating in oil containers. Furthermore, the presence of castor oil is quite interesting, as it is one of the first times that it was identified in ancient materials.

KEYWORDS: LATE ROMAN AMPHORAE, ORGANIC RESIDUES, GC-MS, CASTOR OIL, CLASSE.

INTRODUCTION

During a fire at the end of the 5th century (approx. 490-500), among other buildings, a warehouse of the port’s area of Classe was completely burnt (Fig. 1 - building 17: Augenti e Cirelli in the proceedings of this Workshop). Inside there were different ceramic materials, such as lamps, amphorae, bowls and dishes, all coming from Northern Africa. All of them remained in situ, thanks to the sudden event that destroyed the warehouse (Fig. 2).

The excavations were carried out during the years 2002 - 2005 by the Archaeological Department of the University of Bologna, Ravenna’s see, and the Soprintendenza per i Beni Archeologici dell’Emilia-Romagna, directed by prof. Andrea Augenti and dr. Maria Grazia Maioli.

The context has been dated to the end of the 5th century, thanks to the pottery assemblage and others findings connected to the warehouse’s floor, such as coins, dated to the decade 490-500 AD. In this period, northern African imports are the best represented materials in almost all the contexts excavated, and among them, especially ARS ware, that travelled with wheat and other primary goods (Cirelli 2006, 152; Augenti et al. 2007, 266).

Among the amphorae recovered there were 200 spatheia (Spatheion type 1 - Bonifay 2004, type 31) and different types of wide cylindrical amphorae. Inside the warehouse were contemporary contained Keay VIII, Keay XXXVb, Keay LVlb, Keay LXla, Keay LXIIa, e, f, j, Keay LXVIlg. But the most important quantity of amphorae were two different types of cylindrical vessels (Augenti and Cirelli, fig. 10 in the proceedings of this Workshop).

In order to understand what the amphorae contained, chemical analysis of residues were carried out on ten amphorae samples (five spatheia type 1 - Bonifay 2004, type 31 and five cylindrical amphorae – Table 1).

METHODOLOGY

The sherds of the amphorae were sampled drilling small holes in the ceramic body, after having cleaned smoothly the surface. About 2 g of powder were recovered from each sample.

The samples were analyzed using gas chromatography - mass spectrometry (GC-MS) performed at the Archaeometric Laboratory and the Centro di Analisi e Determinazioni Strutturali of the University of Siena.

The lipids were extracted following the procedure described in Mottram et al. 1999.

500 mg of the pulverized sample were treated as reported by Salvini et al. 2008, in order to verify the presence of tartaric acid, marker of wine.

The GC-MS analyses were performed using a gas chromatograph CP3800 (Varian, Walnut Crick, CA, USA) equipped with a 30 m x 0.25 mm (i.d.) x 0.25 μm film thickness fused silica capillary column (Rtx-5MS, Restek corporation, Bellefonte, PA, USA), and a mass spectrometer Saturn 2000 (Varian, Walnut Crick, CA, USA) operated in the electron ionization mode (70 eV). The mass range was scanned in the range of m/z 40-650. The GC oven temperature was held...
RESULTS

Spatheia Bonifay type 1

Spatheia are considered to be wine or fish sauce containers (Reynolds 1995, 50; Bonifay 2004, 129; Bonifay and Garnier 2007, 24), even if the content has always been considered uncertain (Panella 1993, 674), but the chemical analyses of the samples do not show any fish product. On the other hand neither tartaric acid, considered to be wine marker (McGovern 2004; Guash Jané et al. 2004), nor fermentation processes markers, are present in the samples.

In the presence of the markers of beeswax (even long chain alcohols C_{24} - C_{32}, and fatty acids C_{19} - C_{28} Regert et al. 2001) one spathéon (CC94) suggests that it was probably used as coating, mixed to the resin. As beeswax and honey markers are considered to be the same (Evershed et al. 2005), it is also possible that honey was once contained in the amphora.

The charred encrustations of CC94 were also analyzed to verify the presence of a possible content of the amphora. No organic residues were identified, so that it was probably charred material produced by the burning of the warehouse.

Cylindrical amphorae

The content of the big cylindrical amphorae is uncertain, but most of the scholars consider them oil or fish sauce transport vessels (Keay 1984, 299; Bruno 2005, 389).

The results of the analyses show that actually all of them contained oil. But, surprisingly it was not olive oil, but castor oil (ricinoleic acid is in fact present together with azelaic acid, Copley et al. 2005). This suggests, as often supposed, that the oil contained in the amphora was not used for food consumption, but for different purposes, such as body care or illumination.

In CC140, besides castor oil, also products usually due to fermentation processes (malic, maleic, oxalic, vanillic and hydroxybenzoic acids) are present and could be related with the presence of fruits or wine (Cappelli and Vannucchi 1994, 582). Nevertheless, as tartaric acid, considered to be wine marker, is not present, it is difficult to say whether wine was contained. In this case we are probably facing the traces of the re-use of the amphora. The same residues were identified in CC33. In this sample, also a vegetable oil, characterized by a relatively abundant C_{18:1} azelaic acid and 9,10-dihydroxyoctadecanoic acid, was detected together with castor oil.

In CC7 the high abundance of C_{18:1} and C_{18:2} suggests the presence of another vegetable oil, such as linseed oil or another similar kind of oil. These data suggest a re-use of the amphora or that different oils could be mixed, as suggested by the analyses of lamps carried out in different sites (Kimpe et al. 2004; Copley et al. 2005).

All the amphorae were coated with Pinaceaee resin. This is an unexpected datum for oil transport containers. In amphorae CC140 and CC9 the resin markers are so abundant that it could also be suggested that they were not only the coating, but also part of the content (Fig. 4). In this case they could have been mixed to the oils or could have been contained in different moments. Unfortunately the analyses do not allow to solve this kind of problems.

DISCUSSION ON THE CONTENTS OF THE AMPHORAE

No contamination traces were identified through the analysis of the blank sample and the internal encrustations.

All the amphorae (spathéia and cylindrical amphorae) contained castor oil. This is quite interesting, as it is one of the first times that this oil was identified in ancient materials.

Some of the amphorae analysed showed also the markers of different vegetable oils, that could be explained by the reuse of the amphora or the fact that the oils were mixed together.

An indication of the reuse of two cylindrical amphorae could also be the presence of fermentation traces, possibly due to the presence of fruit.

Although it does not exist an established agreement on the markers of fish, usually it is possible to consider that the presence of cetyl alcohol, together with C_{20:0}, C_{20:1}, C_{21:0}, C_{21:1}, C_{22:0}, C_{22:1}, isoprenoid fatty acids and phytanic acid suggest its presence (Rottlander 1990; Malainey et al. 1999a, 1999b; Hansel et al. 2004; Craig et al. 2007; Evershed et al. 2008). In none of the amphorae analysed these compounds are present, indicating that no fish traces were present in either type of amphora, and that spathéia, in particular, were not used to transport it. No wine traces were found in them, either.

The data obtained for the samples recovered from Classe, therefore, point out some problems on the attribution of a specific content to amphorae types, at least for the materials analyzed.

The identification of castor oil at Classe is particularly important as it opens a window not only on the use of castor oil, but also on its transport, as it was identified for the first time in some amphorae.

Castor oil plant (Ricinus communis) is a plant that is easy to grow and has a tendency to self sow. It is wide diffuse in
Northern Africa nowadays and it is very likely to have been in ancient times as well. This could justify its presence in the amphorae analysed in this study, that come from that region. More difficult it is explaining the presence of castor oil also in a LR2 amphora recovered in Efestia (Lemno), that was identified together with wine markers, that suggests a possible reuse of the ceramic (Camporeale et al. 2009, 226).

Castor oil has been recently used especially for medicinal purposes such as illumination or body care.

The use of castor oil in ancient times as an illuminant is suggested by Herodotus, who states that “The Egyptians who live around the marches use an oil that drawn from the castor-berry, which they call kiki. They sow this plant, which grows wild in Hellas, on the banks of the rivers and lakes. It was abundantly sown in Egypt and produces abundant fruit, though malodorous; when they gather this, some bruise and press it, others boil after roasting it, and collect the liquid that comes from it. This is thick and useful oil for lamps, and gives off a strong smell” (Herodotus, The Histories, II, 94). Diodorus Siculus also mentions castor oil among the different agriculture and collection products coming from Egypt, saying that “Into their lamps they pour for lighting purposes, not the oil of the olive, but a kind which is extracted from a plant called kiki” (Diodorus Siculus, Bibliotheca historica, I, 34). The use of castor oil as an illuminant has been demonstrated by its identification in a lamp found at Qasr Ibrim, Egyptian Nubia (Cogley et al. 2005).

Another possible use of this oil could be for the body care, as suggested by Strabo (The Geography XVII, 2, 5) who reports “...kiki is a kind of fruit sown in the fields, from which oil is pressed, which is used not only in lamps by almost all the people in the country, but also for anointing the body by the poorer classes and those who do the heavier labour, both men and women...”.

At the moment, we still do not know which was the production area of the two new types of amphora identified inside the warehouse, even if a comparison could be find in a context identified in Marsiglia at rue Malaval basilica (Moliner, B. and Bonifay 2007: fig. 6, n.6). Nevertheless it is certain the provenance from northern African area. The identification of the production area of this type of amphora could be really helpful for the understanding of the products traded in them. A new project oriented in this direction has recently started and we are waiting for new data.

In any case, even if we still do not know the real diffusion of castor oil in the northern African territories, the evidence of this product as content of the amphorae could give hints on the understanding of the regional economy.

**DISCUSSION ON THE PRESENCE OF AN ORGANIC COATING IN THE AMPHORAE**

All the amphorae showed resin traces, although all of them contained a vegetable oil. This is not in accordance with the idea that the resin was not used to coat oil amphorae, as it could alter oil quality, or that oils dissolve resins (Heron and Pollard 1988; Beck et al. 1989), and with the literature on the theme (Bernal Casasola, D. and Petit Dominguez 1999). For instance Bonifay, regarding the spatheia, says “ce qui est certain, c’est qu’il faut exclure l’huile car ces conteneurs sont toujours poissés”(2004, 129).

Nevertheless, these results are not unique. Some analyses carried out by Bonifay and Garnier showed traces of resin in an amphora that contained olive oil (Keay 62A) and led the authors to suggest that “si l’hypothèse autrefois admise qu’une amphore à l’huile ne pouvait être poissée, l’expérience le réfute” (Bonifay and Garnier 2007, 27). Furthermore a study carried out at the Siena University allowed to identify traces of resin in a possible LR2 amphora found at Gortina (Creta) during the excavations carried out by E. Zanini, in which there are also the markers of wine and vegetable oil. Similar results were obtained from the analyses of the amphorae of Via Castellani in Florence (see Pecci et al. in the proceeding of this workshop), and the analyses of some amphorae coming from Lemno (Camporeale et al. 2009, 226). Two Dr20 amphorae recovered at Thamusida, Morocco, during the excavations carried out by E. Papi show abundant traces of pitch together with olive oil (Salvini et al. 2007). These amphorae come from a secondary context, but it is possible to think that the lining of the amphora was related to the original use and not to the re-use.

This is an important issue, as it points out some problems in the classification of amphorae that is often carried out on the basis of the presence/absence of an organic coating. It is of course not the first time that the problem of the presence of a coating shows up. For instance, Sodini in 2000 wrote “Mais le verdict de la poix sont parfois déroutants” (Sodini 2000, 185).

It will anyway be necessary to go on with this kind of studies in order to evaluate the results of a greater number of samples.

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Table 1. Samples analysed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amphora</th>
<th>Castor oil</th>
<th>Other vegetable oil</th>
<th>Fermentation products</th>
<th>Resin/pitch</th>
<th>Beeswax/honey</th>
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<tr>
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<td>Spathion type 1</td>
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<td>X</td>
<td>X</td>
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<tr>
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<td></td>
<td>X</td>
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<tr>
<td>CC195</td>
<td>Spathion type 1</td>
<td>X</td>
<td></td>
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<tr>
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<tr>
<td>CC94</td>
<td>Spathion type 1</td>
<td>X</td>
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</tr>
<tr>
<td>CC9</td>
<td>Keay VIII</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>CC 33</td>
<td>Augenti, Cirelli, LRCW3 fig. 10.1</td>
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<tr>
<td>CC7</td>
<td>Keay LXII var. q</td>
<td>X</td>
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<tr>
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<td>Keay LXI, var. a</td>
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<tr>
<td>CC94 encr</td>
<td>Augenti, Cirelli, LRCW3 fig. 10.2</td>
<td>X</td>
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<td></td>
</tr>
</tbody>
</table>

Table 2. Synthesis of the results of the GC-MS analyses of the samples.

Fig. 1. Warehouse n.17, plan (E. Salvadori, B. Tulli).
Fig. 2. Warehouse n. 17. African Amphorae *in situ*. Excavation 2005.

Fig. 3. Chromatogram resulting from the analysis of the total lipid extract of sample CC122.

Fig. 4. Chromatograms resulting from the analyses of the total lipid extract of samples CC140 (above) and CC9 (bottom).