

# Chemical characterization of organic residues on Late Roman amphorae from shipwrecks off the coast of Marsala (Trapani, Italy)

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## ABSTRACT

Organic residues were extracted from thirty-three different types of Roman and Late Antique amphorae retrieved from underwater contexts in the custody of the Archaeological Museum “*Baglio Anselmi*” of Marsala in Sicily. The samples were analysed using GC-MS and <sup>1</sup>H NMR, finding biomarkers of plant oils (including saturated and unsaturated fatty acids, alcohols and alkanes present in plant waxes) were identified in seven samples. The biomarkers for *Pinaceae* spp., used for making pitch, were identified in one sample. The results obtained shed light on the function of different types of North African amphorae, traditionally interpreted as containers for olive oil, wine and fish sauce, presenting new evidence to reassess the system of trade between Sicily and North Africa in Late Antiquity.

## 1. Introduction

Due to its central position in the Mediterranean, the westernmost port of Sicily, Marsala represents a fundamental viewpoint for the study of the Mediterranean trade in the Roman period and specifically of the circulation of products between Sicily and North Africa (Figs. 1 and 2). The Archaeological Museum “*Baglio Anselmi*” of Marsala, the Roman *Lilybaeum*, houses a remarkable collection of hundreds of Roman and Late Antique amphorae recovered from shipwrecks dated to between the 1st and the early 8th centuries CE that reflect the complex system of trade routes and intense traffic of merchant ships in the Strait of Sicily in this period (Arnaud, 2005). Most of the amphorae in the museum’s collection come from fortuitous finds. However, research conducted in the museum archives to trace the findspot of the amphorae identified their provenance in the stretch of sea between Mazara del Vallo, Marsala, Trapani, and the Egadi islands. The great collection of Marsala compares with the latest research and discoveries carried out in terrestrial and maritime sites of western Sicily (Malfitana and Bonifay, 2016; Oliveri, 2016; Oliveri and Testa, 2016).

In order to fully comprehend the phenomenon of trade routes related

to Sicily, especially the direct routes between Rome, Africa, Spain, and the Eastern Mediterranean and to understand the peculiar role played by the southwestern coast of Sicily and Cape Bon in Tunisia, different interdisciplinary approaches were applied, mostly to define production centres of the amphorae (Malfitana and Bonifay, 2016) (Fig. 2). The emphasis of archaeometric studies has been primarily focused on the characterization of ceramic fabrics to identify and correlate with specific North African production centres (Ben Tahar and Capelli, 2018; Capelli et al., 2006), highlighting the important role of the region as a hub for the production of amphorae and a commercial behemoth for the export of wine, olive oil, and other products (Capelli et al., 2016).

One aspect of the circulation of African amphorae in the Strait of Sicily in the Late Roman and Late Antique periods, that has been neglected so far is organic residues analysis to ascertain the contents of those containers. The transported good, at times olive oil, wine, or fish by-products, is traditionally hypothesized on the basis of ceramic typologies or the presence of a commercial stamp on the amphorae, often indicating origin, destination and type of product transported (*titulus pictus*). In types of amphorae lacking that peculiar commercial inscription, hypotheses could be made based on the container’s morphology

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Fig. 1. Map of Sicily with indication of the site of Marsala, ancient Lilybaeum.

could be made but not proven. Thus, the specific function of several African types of amphorae has remained unknown, although advances in organic residues analysis have initiated a new field of study (Panagou, 2016). The encouraging results obtained with Gas chromatography-mass spectrometry investigations on organic residues from various Dressel types of Roman amphorae allegedly containing oil and wine from contexts in from Italy and Portugal (Manhita et al., 2020; Pecci et al., 2017) has opened new perspectives for the study of African amphorae.

In order to generate novel evidence from archaeometric studies on the content of this important class of Roman containers, a group of amphorae from the Archaeological Museum “Baglio Anselmi” of Marsala

was sampled and submitted to chemical analyses.

The analytical techniques chosen to study our samples are Gas Chromatography-Mass Spectrometry (GC-MS), one of the most powerful techniques for analysis of trace amounts of materials, and Nuclear Magnetic Resonance (NMR) that offers a fingerprint for each particular type of nucleus examined. Both techniques present advantage and disadvantages if used alone, but, when combined to obtain complementary information, the two techniques are accepted for the study of archaeological pottery and residues with previous extraction methods (Beck et al., 1974; Colonese et al., 2017; Copley et al., 2005; Ghisalberti and Godfrey, 1998; Lambert et al., 2000; Oudemans et al., 2007; Pitonzo et al., 2017; Tanasi et al., 2017).

## 2. Materials and methods

Samples were collected from thirty-three different types of Roman and Late Antique amphorae from underwater archaeological contexts in the custody of the Archaeological Museum “Baglio Anselmi” of Marsala in Sicily. The artefacts came from different seizures of private collectors in different decades, but they share the general origin of shipwrecks off the coast of Marsala. Due to the peculiar environmental conditions to which the amphorae were exposed for centuries, sitting on the seabed, only 7 of the sampled containers yielded successful results, whereas the others did not keep any detectable trace of lipids (Table 1). The production and use of those seven sampled amphorae cover a chronological arch spanning a millennium, from the 2nd century BCE to the early 8th century CE. The group includes some important typologies, some of which were produced in North Africa and related with the trade system between that province and Sicily, such as Africana Antica, produced in North Africa (Bonifay, 2016; Contino and Capelli, 2013), Africana I and II (Bonifay, 2007) and Keay 8A (Mukaï et al., 2014), the latest in chronology (Bonifay, 2004, pp. 141–143); the sampled materials counted

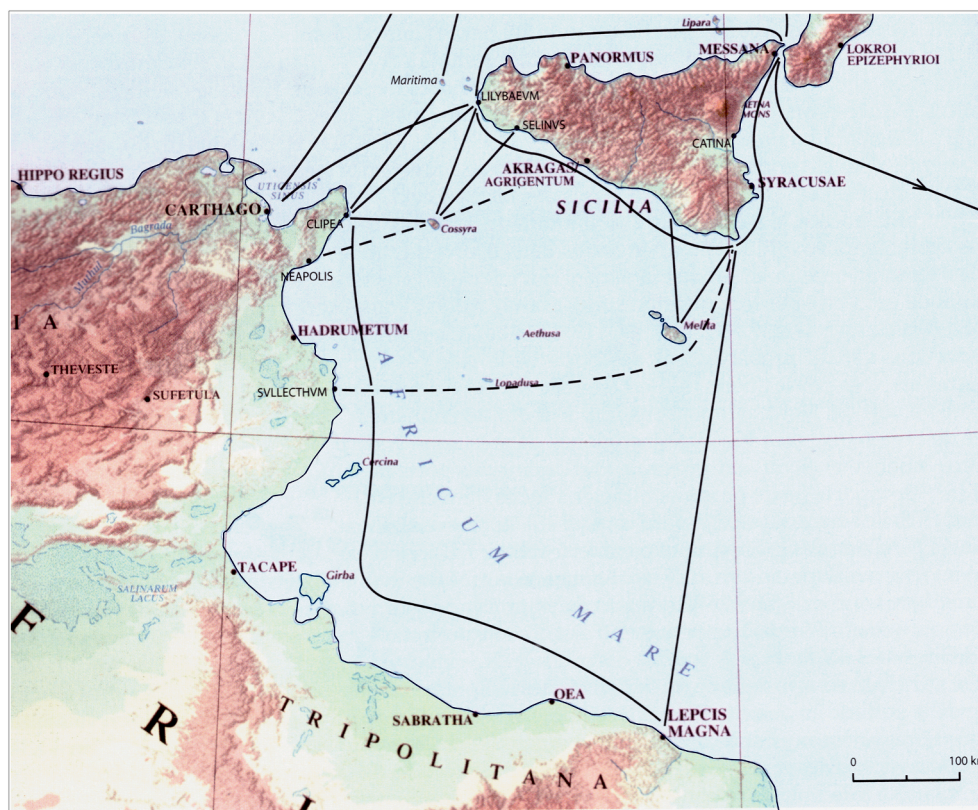


Fig. 2. The commercial routes between North Africa and Sicily in the Late Roman period (after Malfitana and Bonifay, 2016).

also type Keay 27 amphorae and a rare variant of Keay 35A/B. With respect to the possible contents of those amphora types, olive oil was suggested, though not always on a secure basis, whereas it had not yet been possible to determine with any certainty what the amphora types African IIA and Keay 8A contained.

The object of this study is then to validate the traditional hypotheses about the contents of these types of amphorae, and in particular to shed light on the function of the containers of type African IIA and Keay 8A. To do so, it was decided to submit collect samples for Gas Chromatography-Mass Spectrometry (GC-MS) and Nuclear Magnetic Resonance (NMR).

With respect to the sampling process, each amphora was sampled using a diamond cutter (2 cm diameter). The most internal surface layer (about 3 cm<sup>2</sup>) was removed by using a solvent-cleaned scalpel and then ground into a powder using a solvent-cleaned agate mortar and pestle. The collected powder was then stored in glass vials to avoid any additional contamination.

All solvents and reagents used in this research were ultrapure or GC-MS grade. Chloroform (CHCl<sub>3</sub>), deuterated chloroform (CDCl<sub>3</sub>), methanol (MeOH), hexane, sodium hydroxide (NaOH), hydrochloric acid (HCl), and boron trifluoride-methanol solution 14% (w/v) in methanol, were obtained from Sigma-Aldrich. All the water used was ultra-purified by the Milli-Q Integral Water Purification System (Merck).

From a methodological point of view, about 0.5 g of each sample was placed in a 10 ml VOA vial. A solution of CHCl<sub>3</sub>:MeOH:H<sub>2</sub>O in a 1:1:0.9 ratio was added to suspend the powder and then split into two 5 ml VOA vials and sonicated for 30 min in a water bath. The solutions were centrifuged at 2000xg for 10 mins, and the bottom organic layer (CHCl<sub>3</sub>) was removed with a syringe. This method allowed us to obtain the TLE (Total Lipid Extraction) of 'free' lipids. The solid part was separated from the solvent and the extraction was initially dried under N<sub>2</sub> and then in a vacuum desiccator overnight.

The obtained aliquot was then treated with 0.5 M NaOH/MeOH (methanolic NaOH) and heated to 70 °C for 1 h. The neutral fraction was removed using 3x3 mL of hexane. The remaining solution was treated with 3 M HCl to bring them to a pH of 3. Samples were washed with 3x3 mL CHCl<sub>3</sub> to extract the Fatty Acids (FA). The FA solution was then treated with 100 µL of 14% BF<sub>3</sub>/MeOH (w/v) and incubated at 70 °C for 1 h on a heat block. The samples were then cooled to room temperature. The Fatty Acid Methyl Esters (FAMES) were extracted with 3x2 mL CHCl<sub>3</sub>, the solvent was removed using N<sub>2</sub>, and the samples were resuspended in hexane, ready for the analysis using GC-MS using the conditions as follow.

An Agilent 6890 N Gas Chromatographer (GC) coupled with an Agilent 5975 Mass Selective Detector was used in order to separate each marker molecule from the complex mixture and safely identify it by its mass spectrum. In order to improve the collection of useful information, a method was adapted for the extraction of lipids and fatty acids (Tanasi et al., 2018).

The Gas Chromatographer was equipped with a Zebron ZB-1 dimethylpolysiloxane column 15 m length, 0.25 mm I.D., 0.10 mm film thickness. 1 µL of each sample was injected in splitless mode for a sampling time of 1 min with the injector temperature set at 250 °C and a helium column flow of 1.5 mL·min<sup>-1</sup>. The mass spectrometer operated in pulsed splitless mode (25 psi pulse). The ion source temperature was set at 240 °C and the interface temperature was maintained at 280 °C. The GC oven temperature program was set at 50 °C for 2 min, then ramped to 300 °C at 5 °C·min<sup>-1</sup> to 270 °C and 35 °C·min<sup>-1</sup> to 310 °C, followed by a 1 min isothermal period. The temperature was then increased again to 400 °C at 10 °C·min<sup>-1</sup> and held for 5 min. The mass spectra were scanned from 40 to 1090 m/z. National Institute of Standards and Technology (NIST) and Wiley mass spectra libraries were used for the assignment of the peaks.






The lipid extraction for the NMR analysis was performed using about 0.5 g of each powdered sample suspended in 20 ml of CDCl<sub>3</sub>, vortexed for 5 min and sonicated in a water bath for 30 min. The samples were

then transferred into Eppendorf tubes and centrifugated a high speed for 20 min to separate the powders from the extraction solutions.

All the (1D) <sup>1</sup>H NMR spectra were acquired at 300 K with a Bruker AVL HD 500 MHz operating a proton frequency of 500.13 MHz, 16 scans, in Single Pulse Experiment (SPE) with a 90° pulse length of 12 µs and D1 of 1 s, and a spectral width of 10 kHz.

**Table 1**



Sampled materials that yielded successful results with indication of typology, chronology and hypothesized content.

Sampled material	Type	Chronology	Hypothesized content
	Africana Antica	2nd –1st century BCE	Olive oil (supposed)
	Africana IIA	2nd –3rd cent. CE	unknown
	Africana IA	2nd – 4th cent. CE	Olive oil
	Africana IC	2nd – 4th cent. CE	Olive oil
	Keay 27	4th – 6th cent. CE	Olive oil

(continued on next page)



Table 1 (continued)

Sampled material	Type	Chronology	Hypothesized content
	Keay 35A/B	5th – 6th cent. CE	Olive oil (supposed)
C28			
	Keay 8A	7th – 8th cent. CE	unknown
C6			

### 3. Results and discussion

It is difficult to find definite identifiers of olive oil in archaeological samples because there is no specific biomarker in olive oil that survives in ancient ceramics, and the Marsala samples were especially degraded after centuries underwater. Currently, olive oil certification and identification of possible adulterations with other oils relies often on the identification of the fatty acid and steroid profiles of the oil and their comparison with fresh samples (Aparicio et al., 2013). Sterols are particularly useful in this regard, as fresh oils contain high levels of  $\beta$ -sitosterol and  $\Delta^5$ -avenasterol, and low levels of campesterol and stigmaterol (Aparicio et al., 2013). In the case of fatty acids, which are primarily contained within triglycerides, previous research has established a profile containing the following: myristic acid (C14:0) < 0.5%, palmitic acid (C16:0) 7.5–20%, palmitoleic acid (C16:1, cis- $\Delta$ 9) 0.3–3.5%, stearic acid (C18:0) 0.5–5%, oleic acid (18:1 cis- $\Delta$ 9) 55–83%, linoleic acid (C18:2 cis- $\Delta$ 9,12) 3.5–21%, linolenic acid (18:3 cis- $\Delta$ 9,12,15) < 1.0%, arachidic acid (C20:0) < 0.6%, behenic acid (C22:0) < 0.2%, and lignoceric acid (C24:0) < 0.2%) (Aparicio et al., 2013; Steele et al., 2010).

However, taphonomic processes take their toll, and archaeological olive oil samples are unlikely to present a fatty acid profile resembling that of fresh oil, unless they were unusually well preserved. Rather, detectable fatty acids are most likely to be found in free form as olive oil's high content of unsaturated fatty acids are prone to oxidation processes that result in the formation of hydroxy-acids, oxo-acids, and di-acids (Copley et al., 2005; Hansel et al., 2011). In addition, selective leaching of fatty acids occurs over time in archaeological samples which further complicates the interpretation of the fatty acid profile. For example, selective leaching causes palmitic acids to become twice as soluble as stearic acid in water at 20 °C (Steele et al., 2010).

The extraction method adopted for this study is universally accepted for the analysis of ancient organic materials in archaeological ceramics (Colonese et al., 2017; Copley et al., 2005; Hansel et al., 2011; Pitonzo et al., 2017; Pollard and Heron, 2015; Tanasi et al., 2018); however, it does not allow for the extraction of non-esterifiable molecules or other precipitated molecules bound to the clay. It is nevertheless efficient in removing lipids and other non-polar compounds such as terpenes, long chain alcohols, and alkanes from the pores of the ceramics fabric.

Each of the samples taken turned out to be highly polluted, mainly by plastics residues (alkanes, phthalates, plasticizers, antioxidants), making the analysis very complicated during the data treatment phase. However, chromatography is easily able to isolate and distinguish markers related to contamination from those related to the original contents. Furthermore, most of the pollution markers are eliminated during extraction, greatly increasing the readability of the results.

The samples C2, C4, C6, C12, C15, C27, and C28 show the presence of short chain (5:0–12:0) fatty acids and the presence of hexadecanoic and octadecanoic acid, known as palmitic and stearic acids (Fig. 3). The samples from the amphorae n. C2, C12, and C27 also show the presence of 9,12-Octadecadienoic acid (Z,Z) (linoleic acid) and the complete chromatograms in absolute intensity vs. retention time are reported in Fig. 3.

The presence of palmitic and stearic acids in all the samples represents a good marker for the presence of vegetable oil. This presence can be further confirmed by the occurrence of plant sterols in the samples. In sample C15 it was also possible to identify a very low amount of stigmasta-3,5-dien-7-one, a product of the oxidation of stigmaterol which is a good indicator of olive oil (Guardiola, 2004). All the other 26 samples tested and not discussed in this paper showed no presence of lipids after the extraction. A small presence of dehydroabiatic acid and 7-oxodehydroabiatic acid, was detected in two samples from an amphora types the contents of which were unknown: C23, an amphora of transitional type between Africana type 2D and 3A, dated to between the 3rd and the 4th centuries CE, and C24, an Africana type 3A dated to the same period.

The same biomarkers (dehydroabiatic acid – DA – and 7-oxodehydroabiatic acid – 7ODA) were also identified on sample C15, and are indicative of diterpenic resins originating from plants of the *Pinaceae* family (Cabaret et al., 2019; Colombini et al., 2005; Izzo et al., 2013; Peacock and Williams, 1986; Pollard and Heron, 2015). These resins were subjected to hard-heating treatments in order to obtain denser and stickier resin that served to waterproof the amphorae. Pliny and Columella called these modified substances *tars* or *pitches* and were the result of modifications of the original material including aromatization, demethylation and decarboxylation reactions, that led to the formation of new compounds with lower chemical mass (Izzo et al., 2013). One of the many applications of resinous waterproofing material was to treat the internal surface of amphorae in order to reduce the porosity of the ceramic fabric and therefore minimise fluid diffusion through it (Manhita et al., 2020; Pecci et al., 2017).

In Fig. 4, the  $^1\text{H}$  NMR spectra of the samples C2, C4, C6, C12, C15, C27, and C28 all show typical patterns of samples that contain lipids. The intense multiplet signals that arise in the aliphatic region at 1.28 ppm, correspond to  $-(\text{CH}_2)_n$  protons. The multiplet signals in the region of 0.89 ppm correspond, rather, to  $\text{CH}=\text{CHCH}_2\text{-CH}_3$ , as well as several other signals that can be attributed to free fatty acids and lipid fragments (Sacchi et al., 1997). Two additional signals, one at 5.25 ppm, and one at 2.03, can be assigned to  $-\text{CH}=\text{CH}-$ , and  $\text{CH}_2\text{CH}=\text{CH}$  protons of unsaturated fatty acids. Another double set of signals at 1.60 ppm and 2.33 ppm can be assigned to  $\text{CH}_2\text{CH}_2\text{COOH}$  and  $\text{CH}_2\text{COOH}$  protons of acyl chains. The small multiplet in the region around 2.78 ppm might be assigned to  $\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}$  protons of linoleyl-linolenyl acids, which is a good indicator for the presence of unsaturated carbon chains. However, based on the relative intensity of the signals, it is clear that the abundance of unsaturated chain fragments is less significant compared to that of saturated chain fragments.

To further test the hypothesis that the samples from the amphorae contained vegetable or olive oil, we compared the  $^1\text{H}$  1D spectra of the seven samples to the  $^1\text{H}$  1D spectrum of a modern olive oil standard sample prepared with a method indicated in previous work (Tanasi et al., 2018). Overall, the lipid composition of olive oil is similar to the composition of other vegetable oils, and we would expect this comparison to yield an indication of origin (Codony et al., 2002). There is an excellent correspondence between the spectra of our archaeological

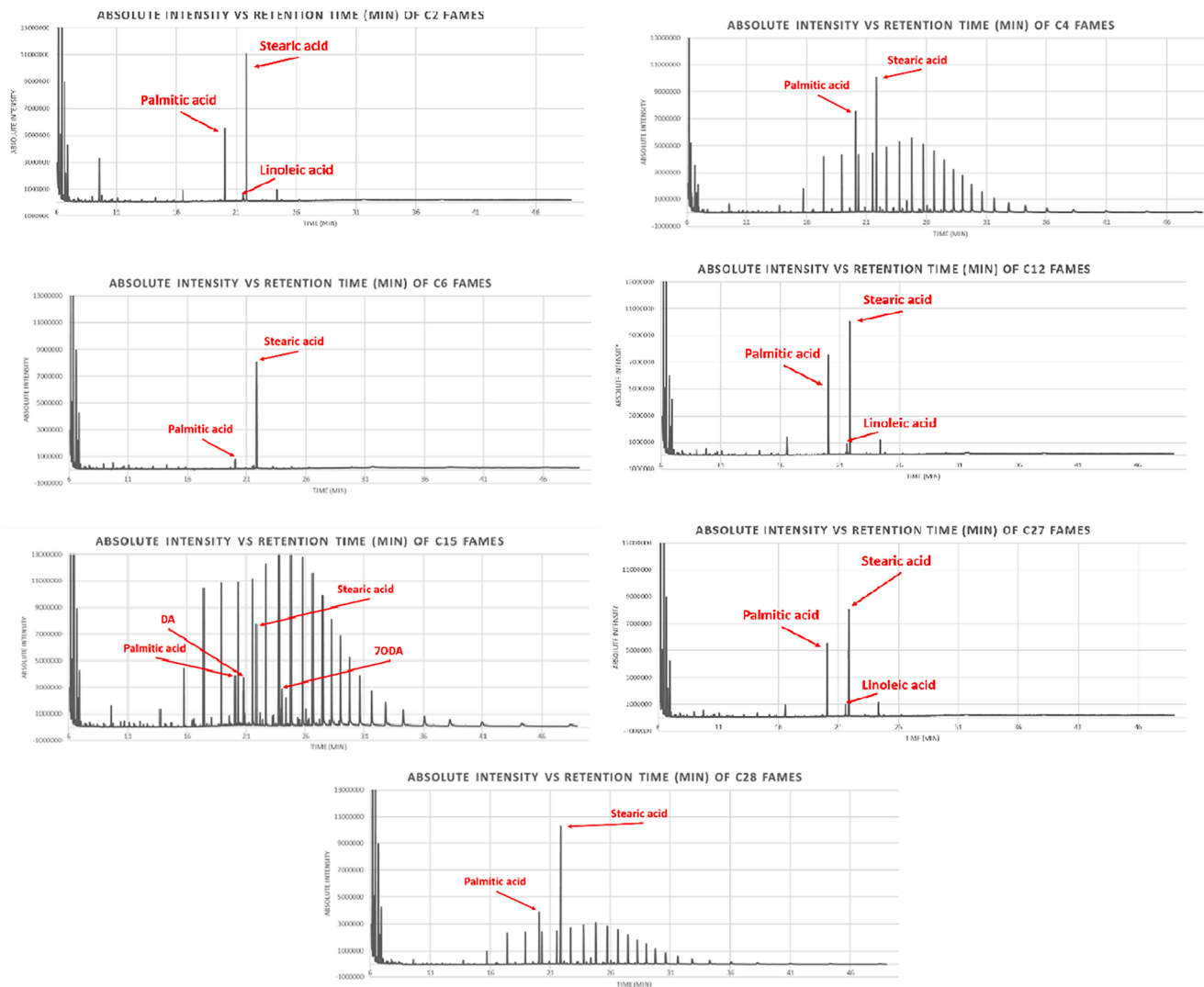


Fig. 3. Absolute intensity vs. retention time of samples C2, C4, C6, C12, C15, C27, C28.

samples and the standard sample both in terms of chemical shift (position of each signal in the spectrum), and in terms of multiplicity (the splitting of each signal). Thus, as all the archaeological samples contained organic residues with the same spectroscopic signature as vegetable oils, it is highly likely that they can be designated as having contained olive oil.

#### 4. Conclusions

The study of one of the largest and most varied collections of amphorae will clarify important points about the economy, history, and trade that took place in the Mediterranean as a whole and Sicily in particular ranging from the Roman to the Late Antique periods in Sicily. Certainly, with the tools and methods of the 21st century, a combination of archaeometric study to identify the origin of the amphorae and chemical analyses to analyse their contents, together with archaeological and historical research, seems today to be the best way to examine many of the questions inherent in the study of ancient economies and trade. The presence of the palmitic, stearic, and linoleic acids together in the samples C2, C4, C6, C12, C15, C27, and C28, suggests that vegetable fat residues are present in these amphorae. Though the high level of stearic acid may suggest the presence of animal fats, the absence of cholesterol and other animal sterols reinforces the interpretation of a vegetable origin. Furthermore, the identification of vegetable oil

biomarkers, on the amphorae Africana IIA (C15), interpreted as hypothetically containing wine (Bonifay, 2007) and Keay 8A (C6), whose function was still unknown, has shown for the first time that these vessels were, at a certain point of their use life, circulated to transport olive oil. In particular, the identification of the biomarkers of *Pinaceae* spp. pitch in sample C15, informs us about the practice, well attested in the written sources, to impermeabilize the inner surface amphorae destined to contain liquids or semi-liquid substances, especially wine. Although the impermeabilization of oil amphorae is not referred by the classical authors, the recent findings from archaeometric studies (Manhita et al., 2020) have demonstrated that pitch lining could also be present in amphorae containing oil, although common sense would tell that oil could have dissolved the pitch coating (Peña, 2007). It could be possible that the olive oil residue came from the pitch itself, which could consist of a resin-oil mixture as has been found in Haltern 70 amphorae (Dorrego et al., 2004). In that case the ratio between molecular markers of olive oil and resin was very much in favor of the latter, with only traces of oil; however, in our case, the exact opposite occurs. Thus, we hypothesize that the resin dissolved in a much larger amount of oil. It is very likely that example C15 was initially used to package contents requiring a pitch lining, such as wine and fish sauce, and the emptied, cleaned and reuse to transport oil (Garnier et al., 2011) according to the model of Type A reuse of Roman amphorae spelled out by Peña (Peña, 2007). In this perspective, the use of the amphora Africana IIA (C15) to

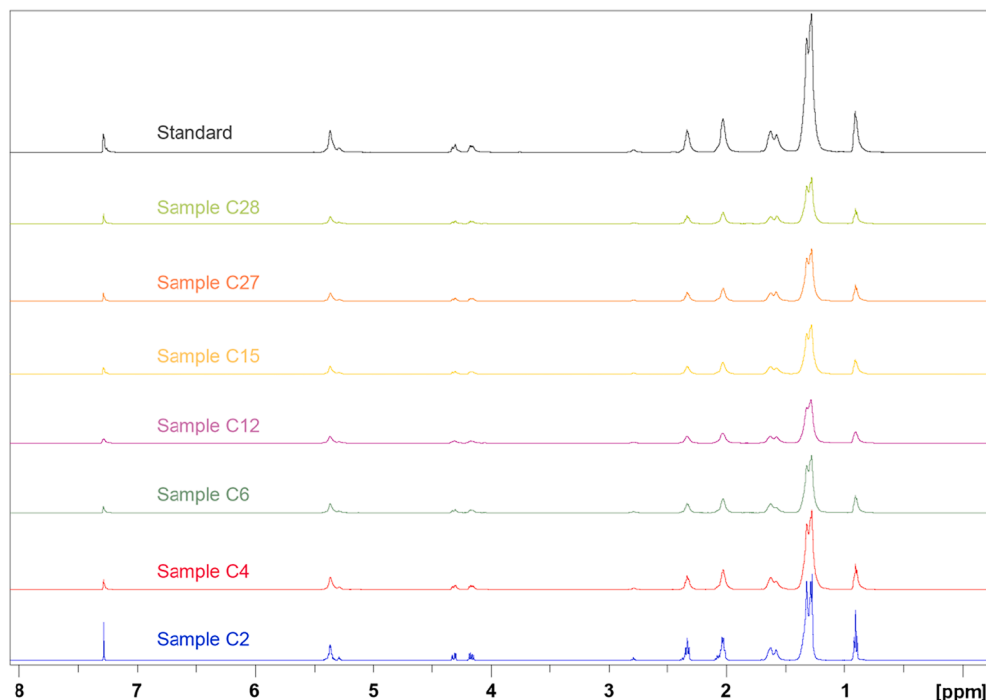


Fig. 4.  $^1\text{H}$  NMR of the samples C2, C4, C6, C12, C15, C27, C28, after the extraction process.

package wine, before it was repurposed to circulate oil, as our research has highlighted, cannot be fully excluded.

#### CRediT authorship contribution statement

**Davide Tanasi:** Conceptualization, Funding acquisition, Writing – original draft, Writing – review & editing. **Enrico Greco:** Project administration, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Filippo Pisciotta:** Resources. **Stephan Hassam:** Resources, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Notes and references

- Aparicio, R., Morales, M.T., Aparicio-Ruiz, R., Tena, N., García-González, D.L., 2013. Authenticity of olive oil: Mapping and comparing official methods and promising alternatives. *Food Res. Int.* 54 (2), 2025–2038. <https://doi.org/10.1016/j.foodres.2013.07.039>.
- Arnaud, P., 2005. *Les Routes de la Navigation Antique. Itinéraires en Méditerranée*, Errance.
- Beck, C.W., Fellows, C.A., Mackennan, E., 1974. Nuclear Magnetic Resonance Spectrometry in Archaeology, in: *Archaeological Chemistry, Advances in Chemistry*. American Chemical Society, pp. 226–235.
- Ben Tahar, S., Capelli, C., 2018. L'atelier céramique d'Henchir Chougaf (Ouedhref, Tunisie). <http://journals.openedition.org/antaf/157>–166. <https://doi.org/10.4000/ANTAFR.995>.

- Bonifay, M., 2016. Eléments de typologie des céramiques de l'Afrique romaine, in: Malfitana, D., Bonifay, M. (Eds.), *La Ceramica Africana Nella Sicilia Romana - La Céramique Africaine Dans La Sicile Romaine*, Monografie Dell'Istituto per i Beni Archeologici e Monumentali, C.N.R. Istituto per i Beni Archeologici e Monumentali, pp. 507–574.
- Bonifay, M., 2007. Que transportaient donc les amphores africaines ?, in: Papi, E. (Ed.), *Supplying Rome and the Empire*. Journal of Roman Archaeology, pp. 8–32.
- Bonifay, M., 2004. *Etudes sur la céramique romaine tardive d'Afrique*. BAR Publishing, Oxford, BAR International Series.
- Cabaret, T., Harfouche, N., Leroyer, L., Ledeuil, J.-B., Martinez, H., Charrier, B., 2019. A study of the physico-chemical properties of dried maritime pine resin to better understand the exudation process. *Holzforchung* 73, 1093–1102.
- Capelli, C., Bonifay, M., Franco, C., Hugiet, C., Leitch, V., Mukai, T., 2016. Etude archéologique et archéométrique intégrée, in: Malfitana, D., Bonifay, Michel (Eds.), *La Ceramica Africana Nella Sicilia Romana / La Ceramique Africaine Dans La Sicile Romaine*, Monografie Dell'Istituto per i Beni Archeologici e Monumentali, C.N.R. Istituto per i Beni Archeologici e Monumentali, Catania, pp. 273–352.
- Capelli, C., Bonifay, M., Lazreg, N., 2006. Nuove prospettive nelle ricerche archeometriche sulle ceramiche nordafricane: l'esempio dell'atelier di Sullecthum-Salakta, Tunisia centrale (I-VI secolo).
- Codony, R., Savage, G., Dutta, P., Cuadriola, F., Savage b, G., Dutta a, P., 2002. Formation and Content of Phytosterol Oxidation Products in Foods, in: *Cholesterol and Phytosterol Oxidation Products*. <https://doi.org/10.1201/9781439822210.ch15>.
- Colombini, M.P., Modugno, F., Ribechini, E., 2005. Direct exposure electron ionization mass spectrometry and gas chromatography/mass spectrometry techniques to study organic coatings on archaeological amphorae. *J. Mass Spectrom.* 40 (5), 675–687. [https://doi.org/10.1002/\(ISSN\)1096-988810.1002/jms.v40:510.1002/jms.841](https://doi.org/10.1002/(ISSN)1096-988810.1002/jms.v40:510.1002/jms.841).
- Colonese, A.C., Lucquin, A., Guedes, E.P., Thomas, R., Best, J., Fothergill, B.T., Sykes, N., Foster, A., Miller, H., Poole, K., Maltby, M., Von Tersch, M., Craig, O.E., 2017. The identification of poultry processing in archaeological ceramic vessels using in-situ isotope references for organic residue analysis. *J. Archaeol. Sci.* 78, 179–192. <https://doi.org/10.1016/j.jas.2016.12.006>.
- Contino, A., Capelli, C., 2013. Amphores tripolitaines anciennes ou amphores africaines anciennes ? *Antiq. africaines* 49 (1), 199–208. <https://doi.org/10.3406/antaf.2013.1550>.
- Copley, M.S., Bland, H.A., Rose, P., Horton, M., Evershed, R.P., 2005. Gas chromatographic, mass spectrometric and stable carbon isotopic investigations of organic residues of plant oils and animal fats employed as illuminants in archaeological lamps from Egypt. *Analyst* 130, 860–871. <https://doi.org/10.1039/B500403A>.
- Dorrego, F., Carrera, F., Luxán, M.P., 2004. Investigations on Roman amphorae sealing systems. *Mater. Struct.* 37 (5), 369–374. <https://doi.org/10.1007/BF02481686>.
- Garnier, N., Silvino, T., Casasola, D., 2011. L'identification du contenu des amphores: huile, conserves de poissons et poisson. In: *SFECAG. Actes Du Congrès d'Arles*. SFECAG, Marseille, pp. 397–416.
- Ghisalberti, E.L., Godfrey, I.M., 1998. Application of nuclear magnetic resonance spectroscopy to the analysis of organic archaeological materials. *Stud. Conserv.* 43 (4), 215–230. <https://doi.org/10.1179/sic.1998.43.4.215>.

- Guardiola, F., 2004. Phytosterol oxidation products: state of the art. *Reprod. Nutr. Dev.* 44 (6), 597–598. <https://doi.org/10.1051/rnd:2004056>.
- Hansel, F.A., Bull, I.D., Evershed, R.P., 2011. Gas chromatographic mass spectrometric detection of dihydroxy fatty acids preserved in the 'bound' phase of organic residues of archaeological pottery vessels. *Rapid Commun. Mass Spectrom.* 25, 1893–1898. <https://doi.org/https://doi.org/10.1002/rcm.5038>.
- Izzo, F.C., Zendri, E., Bernardi, A., Balliana, E., Sgobbi, M., 2013. The study of pitch via gas chromatography-mass spectrometry and Fourier-transformed infrared spectroscopy: The case of the Roman amphoras from Monte Poro, Calabria (Italy). *J. Archaeol. Sci.* 40 (1), 595–600. <https://doi.org/10.1016/j.jas.2012.06.017>.
- Lambert, J.B., Shawl, C.E., Stearns, J.A., 2000. Nuclear magnetic resonance in archaeology. *Chem. Soc. Rev.* 29 (3), 175–182.
- Malfitana, D., Bonifay, M., 2016. La ceramica africana nella Sicilia romana / La ceramique africaine dans la Sicilie romaine, Monografie dell'Istituto per i beni archeologici e monumentali. C.N.R. Istituto per i Beni Archeologici e Monumentali, Catania.
- Manhita, A., Martins, S., Gomes da Silva, M., Lopes, M. da C., Barrocas Dias, C., 2020. Transporting Olive Oil in Roman Times: Chromatographic Analysis of Dressel 20 Amphorae from Pax Julia Civitas, Lusitania. *Chromatographia* 83, 1055–1064. <https://doi.org/10.1007/s10337-020-03927-7>.
- Mukai, T., Tréglià, J.-C., Dantec, E., Heijmans, M., 2014. Arles, enclos Saint-Césaire. La céramique d'un dépôt urbain du Haut Moyen Âge Milieu du VIIe-début du VIIIe siècle apr. J.-C., in: LRCW 5: Late Roman Coarse Wares, Cooking Wares and Amphorae in the Mediterranean: Archaeology and Archaeometry (Alexandria, April 6-10 2014). Vol. 1. pp. 171–200.
- Oliveri, F., 2016. Canale di Sicilia [Sito 113], in: Malfitana, D., Bonifay, M. (Eds.), *La Ceramica Africana Nella Sicilia Romana / La Ceramique Africaine Dans La Sicilie Romaine*, Monografie Dell'Istituto per i Beni Archeologici e Monumentali, C.N.R. Istituto per i Beni Archeologici e Monumentali, Catania, pp. 262–267.
- Oliveri, F., Testa, A., 2016. Relitto di Marausa (Trapani) [Sito 107], in: Malfitana, D., Bonifay, M. (Eds.), *La Ceramica Africana Nella Sicilia Romana / La Ceramique Africaine Dans La Sicilie Romaine*, Monografie Dell'Istituto per i Beni Archeologici e Monumentali, C.N.R. Istituto per i Beni Archeologici e Monumentali, Catania, pp. 248–257.
- Oudemans, T.F.M., Boon, J.J., Botto, R.E., 2007. Ftir and Solid-State  $^{13}\text{C}$  Cp/Mas Nmr Spectroscopy of Charred and Non-Charred Solid Organic Residues Preserved in Roman Iron Age Vessels from the Netherlands\*. *Archaeometry* 49, 571–294. <https://doi.org/https://doi.org/10.1111/j.1475-4754.2007.00321.x>.
- Panagou, T., 2016. Transport Amphorae and Their Contents.
- Peacock, D.P., Williams, D.F., 1986. *Amphorae and the Roman Economy*. Longman, London, An Introductory Guide, Longman archaeology series.
- Pecci, A., Clarke, J., Thomas, M., Muslin, J., van der Graaff, I., Toniolo, L., Miriello, D., Crisci, G.M., Buonincontri, M., Di Pasquale, G., 2017. Use and reuse of amphorae. Wine residues in Dressel 2–4 amphorae from Oplontis Villa B (Torre Annunziata, Italy). *J. Archaeol. Sci. Reports* 12, 515–521. <https://doi.org/10.1016/j.jasrep.2017.02.025>.
- Peña, J.T., 2007. Roman Pottery in the Archaeological Record, Roman Pottery in the Archaeological Record. Cambridge University Press. <https://doi.org/10.1017/CBO9780511499685>.
- Pitonzo, R., Armetta, F., Saladino, M.L., Caponetti, E., Oliveri, F., Tusa, S., 2017. Application of Gas Chromatography coupled with Mass Spectroscopy (GC/MS) to the analysis of archaeological ceramic amphorae belonging to the Carthaginian fleet that was defeated in the Egadi battle (241 B.C.). *Acta IMEKO* 6, 67–70. [https://doi.org/10.21014/acta\\_imeko.v6i3.457](https://doi.org/10.21014/acta_imeko.v6i3.457).
- Pollard, A.M., Heron, C., 2015. Archaeological chemistry. Royal Society of Chemistry Publishing.
- Sacchi, R., Addeo, F., Paolillo, L., 1997.  $^1\text{H}$  and  $^{13}\text{C}$  NMR of virgin olive oil. An overview. *Magn. Reson. Chem.* 35, S133–S145. [https://doi.org/https://doi.org/10.1002/\(SICI\)1097-458X\(199712\)35:13<S133::AID-OMR213>3.0.CO;2-K](https://doi.org/https://doi.org/10.1002/(SICI)1097-458X(199712)35:13<S133::AID-OMR213>3.0.CO;2-K).
- Steele, Valerie J., Stern, Ben, Stott, Andy W., 2010. Olive oil or lard?: Distinguishing plant oils from animal fats in the archeological record of the eastern Mediterranean using gas chromatography/combustion/isotope ratio mass spectrometry. *Rapid Commun. Mass Spectrom.* 24 (23), 3478–3484. <https://doi.org/10.1002/rcm.4790>.
- Tanasi, D., Greco, E., Di Tullio, V., Capitani, D., Gulli, D., Ciliberto, E., 2017.  $^1\text{H}$ - $^1\text{H}$  NMR 2D-TOCSY, ATR FT-IR and SEM-EDX for the identification of organic residues on Sicilian prehistoric pottery. *Microchem. J.* 135, 140–147. <https://doi.org/https://doi.org/10.1016/j.microc.2017.08.010>.
- Tanasi, Davide, Greco, Enrico, Noor, Radwan Ebna, Feola, Stephanie, Kumar, Vasantha, Crispino, Anita, Gelis, Ioannis, 2018.  $^1\text{H}$  NMR,  $^1\text{H}$ - $^1\text{H}$  2D TOCSY and GC-MS analyses for the identification of olive oil in Early Bronze Age pottery from Castelluccio (Noto, Italy). *Anal. Methods* 10 (23), 2756–2763. <https://doi.org/10.1039/C8AY00420J>.