Absorbed Organic Residue Analysis of Amphorae from the Black Sea Region (3rd to 6th c. AD): Analyses and Methodological Considerations

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ABSTRACT

Amphorae were used during antiquity for the inter-regional transport of different classes of commodities. The study of these vessels has formed a significant aspect in understanding inter-regional trade dynamics. The places of production and the distribution of many classes of amphorae have been extensively studied; however, the content of many classes of amphorae has not been ascertained. The focus of this thesis is to examine six types of Black Sea amphorae that have not been previously studied with respect to content in order to determine the types of commodities they were used to transport. This will shed light on the nature of export production from several key Black Sea sites. In order to achieve this, vessel samples will by analyzed by gas chromatography/mass spectrometry (GC/MS) using both established techniques as well as developing new methods of analyis that may assist in the continuing research in inter-regional trade during antiquity.

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CHAPTER 1

INTRODUCTION

The study of long distance trade in antiquity has formed a significant aspect of the understanding of inter-regional distribution of commodities and economic relationships of production and distribution. During later antiquity, the role of production and distribution of commodities from the Black Sea region has remained poorly understood. Until recently, the Black Sea coastal areas, and the region as a whole, have been largely considered an area remote from the trade networks of the Mediterranean and, as such, thought to have had little involvement in large scale inter-regional trade. An increase in the research of the Black Sea region in recent years, as well as a renewed interest in the study of amphorae with respect to inter-regional commerce and the specific commodities borne in them, has begun to challenge this previous thought.

Amphorae are a useful proxy for investigating inter-regional sea-borne trade during antiquity. Initial work for some Black Sea amphora forms was initiated during the Soviet period, analyzing forms encountered in territories of the USSR (e.g. Myrmekion amphorae). It has only recently been that more concerted and extensive research has been conducted involving the whole of the Black Sea littoral as well as distribution in the Mediterranean, resulting in a better understanding of typologies, provenances and distribution of at least the more ubiquitous forms.[1] Although a greater understanding of the generalities of production and distribution is now better understood, the commodities contained and, as such, distributed in specific forms have yet to be addressed. The application of methods of chemical analysis, such as absorbed residue analysis, offers the potential to provide additional information in the study of inter-regional trade in antiquity.

[1] Concerning typologies and distribution of amphorae manufactured in the Black Sea region, see *inter alia* Abadie-Reynal (1999); Erten et al. (2004); Inaishvili and Vashakidze (2010); Kassab Tezgör (2002a); concerning trade within the Black Sea region, see *inter alia* Inaishvili and Vashakidze 2010; Khalvashi and Inaishvili 2010; Magomedov 2010; Opait 2004a; Sazanov 2007; concerning the distribution of Black Sea amphora in the Mediterrean, see *inter alia Bezeczky 2010; Klenina 2010; Lund and Gabrielsen 2005; Opait 2010a*

In order to understand the ways in which amphora were used and reused, it will be useful to first examine the concept of use and reuse of amphorae. They were used not only to transport goods over long distances but were sometimes, perhaps even frequently, reused for a variety of purposes, either as storage vessels or modified to suit another use. After examining the conceptualization of vessel use and reuse, the primary contents carried in amphorae as transport vessels will be examined. Much of this information derives from classical sources, both literary and epigraphic, as well as archaeological evidence. The association of amphorae with commodity production sites has long been used as indirect evidence of the commodity that would have been contained in the vessels for transport elsewhere. In exceptional circumstances, physical remains have also been recovered from amphorae, providing insight into the vessel's content. These finds, however, are rare. More common is the presence of amorphous organic remains, most commonly encountered as residues absorbed within the ceramic itself.

Excavations in many sites of the Black Sea littoral have either identified or suggested the production of a variety of commodities, some of which may have been produced for export in amphorae. Additionally, literary sources and other evidence such as epigraphy or other textual information provide further potential evidence of the use of specific forms. Empirical evidence, however, has proven elusive to date. Few recovered amphorae retain identifiable macrobotanical remains. In the instance in which macrobotanical remains are observed, they are almost invariably identified in a singular vessel. The determination as to the specific commodity or commodities transported in any given form on the basis of one example is problematic. Research into amphora types manufactured in the Black Sea region is, in some respects, still in an early period of development. Some typologies, such as the vessel forms produced at Sinope, have only recently been developed. Other types, such as the Myrmekion (Zeest 72) amphora, have been studied and production sites identified by archaeologists since the 1950's.[2]

To date there has not been a full synthesis of previous and current Russian research into

[2] e.g. Zeest 1960.

the Black Sea region with that which has and is being conducted by other countries, including that in Turkey and eastern and western Europe. Part of the aim of this thesis is to attempt to bring together the available published archaeological information concerning the studied vessel types as well as what information is known that might assist in determining primary content of these vessels types.

Research on Black Sea amphorae, however, is still very much ongoing. As some typologies have only been recently developed, it is most likely the extent of export and distribution within the Black Sea region has not been fully realized. At the same time, research in the Black Sea region continues to develop. There are undoubtably many as yet unidentified kiln sites for many vessels forms that have not yet been discovered. Further excavations will provide additional insight into the distribution of various forms within the Black Sea region itself. From the perspective of the Mediterreanean, the research into Black Sea amphora forms and the refinement of developed typologies will improve the understanding of the specific forms that were exported as well as the distribution and prevalence.

It is the purpose of this thesis to investigate, by means of absorbed residue analysis of some of the most frequently inter-regionally exported amphora forms produced or believed to have been produced in the Black Sea littoral in order to ascertain the content(s) for which the vessels were exported. In order to approach the research objectives of determining content as well as the degree to which amphorae were reused, established techniques of absorbed residue analysis of lipids will be utilized. Additionally, new methodologies will be tested. Some types of amphorae were internally coated with an organic compound, most commonly derived from the Pine (*Pinaceae*) family, to reduce vessel porosity. The extant levels of such residues can complicate residue analysis as the relative levels of the organics may be either significantly greated in quantity relative to the abosorbed organic compounds that were transported in the vessel or co-elute during analysis.[3] Both conditions hinder identification of vessel content. In order to approach this analytical issue, an attempt to separate fatty acids, potentially indicative of vessel content, from resin acids, the organic constituents of

[3]See Chapter 5.7.

the vessel's lining, will be explored. The potential of the presence of wine will also be examined using various biomarkers and evaluated as to their related presence in the archaeological samples and their potential relative specificity in determining wine content, e.g. the correlation between the presence of tartaric and syringic acids as well as other compounds that are associated with wine including:

- The effect of phthlate contamination on analyses
- The relationship between succinic acid and other compounds associated with wine
- The relationship between syringic acid and other compounds associated with wine

The sample material used for analysis was recovered from the excavations of central Beirut after the Lebanese civil war, primarily that excavated by the Anglo-Lebanese excavations headed by the American University of Beirut in the area of the city center commonly referred to as the Beirut Souqs. The aim of this study is to attempt to determine the primary use, as well as degree of reuse, of well-documented Black Sea amphora forms as recovered from the excavations.

CHAPTER 2

CONTENT, USE AND REUSE

2.1 Introduction

Amphorae are a useful proxy for quantifying inter-regional trade. Considerable work has been conducted on establishing the provenance of many classes of amphorae, as well as their distribution. Taken with the known capacity of the specific amphora type, as there is considerable variation in capacity between types, which varies not only with respect to its point of origin but chronologically as well during the vessel's 'evolution', the volume of trade in the contents can be estimated.[1] The remaining matter is the content of the vessels themselves. This is relevant not only so that the types of commodity can be quantified but also for determining what was being produced for export regionally. For some amphora types this has already been established. For example, the Dressel 20 is known to have been used for the transport of olive oil by both epigraphic evidence (*dipinti*) and chemical analysis.[2] The Dressel 1 was used to transport wine, the Beltrán II for some type of *salsamentum*.[3] The picture, however, is less clear for many types of amphorae. The Haltern 70 is known from *dipinti* to have carried defrutum, olives in defrutum as well as muria.[4] Absorbed residue analysis of a Haltern 70 from an Augustan-period shipwreck off Esposende, Portugal indicated a content consistent with of wine or defrutum, although the presence of organic compounds associated with a vegetable source (e.g. olives/olive oil) was also observed.[5] For many other types, their content(s) are either unknown or not definitively established.

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[1]Concerning chronological changes in volume this is apparent, for example, at Sinope where different forms are introduced with a considerable change in volume. Sinopean amphorae of the 3rd c. AD had a volume of approximately 30 L whereas forms from the 5th c. AD have a capacity of approximately 6 L. This is also apparent in a more gradual manner in Beirut locally manufactured amphorae, where it slowly evolved from its largest form in the early 3rd c. AD (with a capacity in the range of 30 L) to a diminutive form by the 6th c. AD (with a capacity closer to that of 6 L). On the 'evolution' of amphora forms, see Reynolds 2008.

[2]Condamin et al. 1976; Condamin and Formenti 1978.

[3]Wilson 2009, 232.

[4]Carreras Monfort 2003; Wilson 2009, 232.

[5]Oliveira et al. 2015.

In order to establish the content of specific types of amphorae, it is useful to begin with the way with which they were used before examining the types of commodities they were used to transport both most frequently and less commonly as well. Generally, amphorae are considered to be transport vessels as their principal use and storage vessels, i.e. vessels holding a commodity for a period of time but without a significant change in its location, as a secondary use.

2.2 Definitions of Use and Reuse[6]

In Theodore Peña's seminal work *Roman Pottery in the Archaeological Record*, he establishes a paradigm in which the nature of the use and reuse of amphorae can be contextualized. The first category is that of 'prime use'. Peña defines 'prime use' as 'the use of a [previously unused] vessel for the application or applications for which it was manufactured.'[7] After the vessel's episode of prime use, subsequent use would fall within three general categories of reuse. Type A reuse involves the reuse of a vessel for 'an application similar to the vessel's prime-use application without any physical modification to it.'[8] Type B reuse is defined like Type A but for a different application. Type C reuse involves physical modification of the vessel for an application different from its prime use application.[9] Within the context of amphorae, reuse would be considered Type A if the vessel were reused as a packaging container for a commodity without respect to whether the type of commodity (e.g. wine, olive oil, *garum*) was the same or different to that of the vessel's prime use.[10] However, for the vessel's reuse to be considered Type A, Peña requires that the qualification of 'packaging' be maintained in its reuse life cycle. That is, 'packaging' is defined not simply as involving storage or local transfer but for 'distribution over some distance' (i.e. regional or inter-regional

[6]Some aspects of the description of the types of reuse according to Peña have been adapted and updated from Woodworth 2011.

[7]Peña 2007, 8.

[8]Peña 2007, 10.

[9]Peña 2007, 10.

[10]Peña 2007, 63.

trade.[11] In instances in which a vessel was subsequently used for storage or for local trade, this type of use pattern is considered as utilizing a different 'application' from prime use and, as such, is classified as Type B.

The reasoning behind this distinction is the significance from a 'behavioral' perspective. Presumably, Type A reuse with amphorae would involve a relatively large number of vessels, systematically collected, prepared, filled with content and transported some distance at which time transfer of ownership/possessionship of the contents (and, most likely, the vessels as well) would take place.[12] Peña is, in essence, defining Type A reuse as large-scale commerce. In contrast, Type B reuse is argued to more likely have involved a limited number of vessels that may not have undergone a change in ownership/possessionship and, as such, had a greater potential for having been subsequently used in an *ad hoc* or adventitious capacity.[13]

Finally, Type C reuse would involve the physical modification of an amphora for another purpose. An example would be the removal of the shoulder and neck for use as a burial urn. It should be noted, however, that physical modification of an amphora is not exclusively a property of Type C reuse. Apertures were sometime made in an amphora for the purpose of removing prime use content. From Roman period finds in North Africa, Michel Bonifay indicates several different ways in which amphorae were modified for accessing content, including the chipping or drilling of small diameter holes in the body or neck, cutting or chipping to make large apertures in the upper body or removal of a portion of the base to create a hole (Fig. 2.1).[14]

Within the categories of prime use and reuse lies the phenomenon of depositional use, i.e. the vessel's use 'effectively removed it from contact with or manipulation by people.'[15] Peña considers such use as an expression of prime use or reuse rather than a distinct category of use as considered by some other scholars.[16] As such, for example, drainage pipes used for

[11]Peña 2007, 63.

[12]Peña 2007, 63f.

[13]Peña 2007, 64.

[14]Bonifay 2004, 467ff.

[15]Peña 2007, 10.

[16]Concerning this categorization, see Peña 2007, 10.

Figure 2.1: Photographs of amphorae that have been modified for the purpose of removing content. 1: A Hammamet 1 amphora with small holes drilled in the body; 2: an African I amphora with large aperture cut into the upper body, presumably for the removal of *garum*; 3: a Hammamet I amphora base modified with a hole. Source: Bonifay 2004, Fig. 264.

a drainage feature would constitute prime use or a dolium converted to be used as a sewer conduit would be Type C reuse.

Peña defines discard as 'the deliberate and voluntary abandonment of a vessel or vessel part by those using it with the intent of no longer using it.'[17] Some types of Type C reuse of amphorae bridge this category. For example, the use of emptied amphora for ground leveling below construction would be most likely considered Type C reuse. It is somewhat a philosophical matter to consider if 'the Romans' would consider these ceramic fragments to still remain in use after their deposition.

There is a pratical relevance to the theoretical framework of use and reuse with respect to determining vessel content by residue analysis. Residues absorbed by a ceramic vessel diffuse throughout the matrix. As such there is no ability to determine sequentially for what content a vessel was used. If the prime use of an amphora had been for wine and then subsequently reused to contain wine (Type A reuse), the ceramic matrix would contain organic compounds associated with wine from its prime use and organic compounds associated with wine from its reuse. In this senario, the determination of primary content of that ceramic

[17] Peña 2007, 9.

sample would not be effected. If, however, a vessel had been used to store two different types of commodity (e.g. wine and then olive oil) during its uselife, there may be preserved organic compounds that are associated with both wine and vegetable oils in the ceramic matrix. This complicates the determination of prime use content as the order in which the vessel was used (i.e. which content came first) can not be determined. As such, it would be necessary to consider if wine were the primary content and the reuse was Type B (for oil) or if the prime use might have been for an irregular content (oil) and then reused (Type B) for containing wine.

2.3 Nature of content

Having defined prime use and the categories in which vessels may be reused, the matter of the nature of their content, especially concerning amphorae, is of importance. Many different types of commodities are known to have been transported or stored in amphorae. The content of a newly manufactured, previously unused amphora would be considered the vessel's prime use content; the content of a previously used amphora would constitute its reuse.[18] This categorization applies to a vessel as a specific entity without regard to what other vessels of the same type may have contained. Peña contextualizes the content of an amphora with the nature of its content with respect to the content of other vessels of its type as either principal, irregular or non-standard contents.[19] Principal content is defined as the 'one specific food stuff' that the particular amphora type was used to hold.[20] For most types of amphorae this would be a single commodity, although for some types there is evidence that more than one type of commodity was regularly transported in them.[21] Secondly, irregular content is defined as a content other than the principal content of the vessel's type, whether occurring in the instance of the vessel's prime use or secondary use.[22] Finally, non-standard content

[18]Peña 2007, 64.

[19]Peña 2007, 64.

[20]Peña 2007, 64.

[21]For example, the Haltern 70 may be one of these.

[22]Peña 2007, 64.

is defined as a subclass of irregular content, one which does not fall within the categories of commodity typically transported in amphorae.[23] Examples of this would include, for example, grain or chickpeas or non-food goods such as mortar or even clay.[24]

2.4 Principal content of amphorae

Amphorae are known to have contained a wide variety of commodities both comestible and non-comestible. Examples include edibles such as nuts, berries, beans, lentils, honey and even other goods such as unguents, dipilatories, urine and even clay.[25] However, the most common categories of amphora contents are far less numerous, most frequently being wine, olive oil and fish products (‘*salsamenta*’). Additionally, and probably to a rather lesser extent, they were used to transport some types of fruits most probably in some type of liquid. Carbonized dates are known from Beirut carrot amphorae (Camulodunum 189).[26] At least some Haltern 70 amphorae contained olives preserved in defrutum.

2.5 Determination of content

In order to elucidate the content of amphorae, what means are there to determine the content of amphorae? The two categories of the types of evidence can be separated into direct and indirect evidence.

2.5.1 Direct evidence

Physical remains of the vessel’s ‘paleocontent’ is the most obvious evidence of an amphora’s use. This may be in the form of macro-remains, comprised of floral or faunal material that has at least partially survived. With the most frequent amphora contents, this most commonly includes fish bones and scales, olive pits and grape seeds. There are some limitations

[23] Peña 2007, 64.

[24] Peña 2007, 26, 100f, 132; Callender 1965, 41.

[25] Callender 1965.

[26] Callender 1965, 39.

on the utility of macro-remains on a large scale for content identification. Firstly, it is necessary that the content have some compositional elements that have the potential to survive the period of deposition and that the depositional environment be favorable for the preservation of such. Amphorae that contained olive oil or wine would not be expected to have any associated macro-remains. While olive pits and grape seeds are associated with their respective fruits, the seed should have been separated from their liquid fraction during processing. The presence of olive pits or grape seeds instead more probably represents the surviving portion of packaged partial or whole fruits stored in some type of liquid medium (olive oil, brine, wine or grape product ('defrutum')) as appears, for example, to be the case for at least some Haltern 70 amphorae.[27] Grape seeds recovered from amphorae would most likely indicate a vessel content of grapes or raisins, also probably preserved in a liquid medium or possibly defrutum.[28] Macro-remains of grapes (especially pips) have been recovered from sites indicative of grape processing.[29] Macro-remains may also be absent in some types of fish products. Fish products that were produced from small fish species would have significant quantities of bones and scales, especially if it had not been filtered (Fig.2.2).[30] Conversely, if the fish were processed in such a way that the scales and bones were removed, no macro-remains would be transferred to the amphora. Salted fish from large fish species, such as tunas, especially from the ventral part of the fish, may have been readily prepared without scales or bone. This may account for the near absence of tuna in analyzed amphora content despite the fact that tuna was known to have been a significant and valuable product in industrial fish processing.[31]

In addition to macro-remains, micro-remains may also be useful in determining vessel content. Micro-remains may consist of partially degraded floral or faunal material, such as small fish bones, or floral material such as pollen. Microscopic remains may have a

[27] Bernal Casasola 2015, 63.

[28] Concerning examples of the former, see Bernal Casasola 2015, 66.

[29] e.g. Margaritis and Jones 2006.

[30] Bernal Casasola 2015, 65f.

[31] Bernal Casasola 2009, 15-19; Bernal Casasola 2015, 64ff.

Figure 2.2: Contents of a late Punic amphora from the Garum Shop at Pompeii principally composed of fish scales and bones. Source: Bernal Casasola 2015, Fig. 3.

greater potential for preservation. However, some micro-remains, e.g. pollen, are very easily distributed within the environment both during the vessel's use life and post-depositional period, which may present a significant concern about ancient or modern contamination.

Finally, amorphous residues, either adhering to or absorbed within the walls of the vessel may contain organic matter that can identify vessel contents, specifically by aDNA, proteonomics or organic residue analysis.

2.5.1.1 Limitations of direct content remains

The principal limitations of macro-remains for content identification is that it relies on the vessel having not been entirely emptied and favorable depositional conditions for preservation. Amphorae recovered from shipwrecks are the most frequent source of the former. Terrestrial examples are rare and are generally associated with destruction levels were a catastrophic event suddenly terminated habitation (e.g. Pompeii). Preservation of macroscopic remains are generally more favorable in maritime contexts.[32]

Microscopic remains have somewhat different considerations. The systematic removal and scientific examination of the fill material of whole amphorae where macroscopic remains are not apparent is still not universally practised. Additionally, 'well-designed and analytic

[32]Garnier et al. 2011.

protocols' have only recently begun to be applied.[33] Small quantities of floral or faunal material, such as pollen, may be captured within the open pore structure of the ceramic or retained by a resinous coating if present. There is significant potential for contamination of microscopic remains. Pollen may be introduced during any period when the vessel was unsealed in non-sterile conditions including the period between manufacturing and the sealing of the vessel after filling, during any period when the amphora was unsealed during its uselife, as well as potentially after post-deposition, e.g. whilst exposed during excavation or left open in ceramic storerooms. Depositional contamination by soil-dwelling insects and rodents is also a potential vector for contamination.[34]

2.5.2 Dipinti

Dipinti are a potential direct source of information for content. The nature and frequency of *dipinti* on amphorae are highly variable as a whole. They appear with regularity on a few types of amphorae, such as the Dressel 20. The text may contain a variety of different types of information including content, origin, filled capacity, date of filling and personal names associated with ownership and/or distribution.[35] The paint used for *dipinti* requires a favorable depositional environment for preservation. Frequently, deterioration of the paint during deposition renders them as only detectable bits of paint or only partially recognizable to any degree, as is the case of many of the *dipinti* found on amphorae excavated in Beirut. When *dipinti* are extant and legible, there are three complications for their use in identifying vessel content. Firstly, is that a relatively small number of *dipinti* actually refer to the vessel's content. Bernal Casasola notes that the number that indicate content represent only a small proportion of the total number recorded and a significant proportion of those originate from a small geographical area (the region of Mt. Vesuvius).[36]

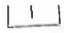
The second complication for those *dipinti* indicating content is that the text is frequently

[33]Bernal Casasola 2015, 63.

[34]Bernal Casasola 2015, 63.

[35]Peña 2007, 26.

[36]Bernal Casasola 2015, 66f.

abbreviated, sometimes cryptically, or employs almost idiosyncratic symbols.[37] Some can be expanded reasonably, such as OLIVA ‖NIGRA‖ EX DEFR[UTO] and MUR[IA] HISP[ANA].[38] Others are more cryptic, e.g. POL[ENTA? or LEN?] meaning ‘barley’ or ‘fine flour’, respectively.[39] Finally are those which defy deciphering, e.g. the symbol  found on a Group D Sinopean amphora from the YK 35 shipwreck at Yenikapı.

For those *dipinti* identifying content, the final consideration is between the *dipinti* and its relation to the vessel’s use life. As mentioned above, for a few types of amphorae it is clear that they can be related to the vessel’s principal content of its prime use. For the *dipinti* on many other types of amphorae, this is less certain. There are occasional instances of amphorae bearing multiple *dipinti* and these are unambiguous examples of the vessel having been used on more than one occasion, serving as label’s indicating the vessel’s prime use or reuse (Fig. 2.3).[40] Amphorae with a single *dipinto* are more complicated to interpret the relationship of the indicated commodity and the vessel’s prime use content. For many amphora types, *dipinti* are an irregular occurrence implying that instances in which *dipinti* are observed may represent either irregular content for prime use or reuse. Approximately 2500 *dipinti* have been cataloged from the region of Mt. Vesuvius. Some of these indicate amphorae that were used to store irregular and nonstandard goods, e.g. chickpeas, flour, honey, beans even unguents such as *lomentum* (possibly a skin cleaner) and *psilothrum* (hair remover).[41] Unfortunately, the types of amphorae on which the *dipinti* appeared were not recorded so the prevalence of *dipinti* in designating reuse for standard contents is more difficult to ascertain. The wide variety of nonstandard contents in amphorae as documented at Vesuvian sites does demonstrate the flexibility with which amphorae could be re-purposed for reuse as storage vessels. Based on extant examples of *dipinti*, Peña argues that *dipinti* appear more frequently to refer to irregular content than that to primary content.[42]

[37]Peña 2007, 26.

[38]Callender 1965, 39.

[39]Callender 1965, 40.

[40]Peña 2007, 99.

[41]Peña 2007, 99f; Callender 1965.

[42]Peña 2007, 95f.

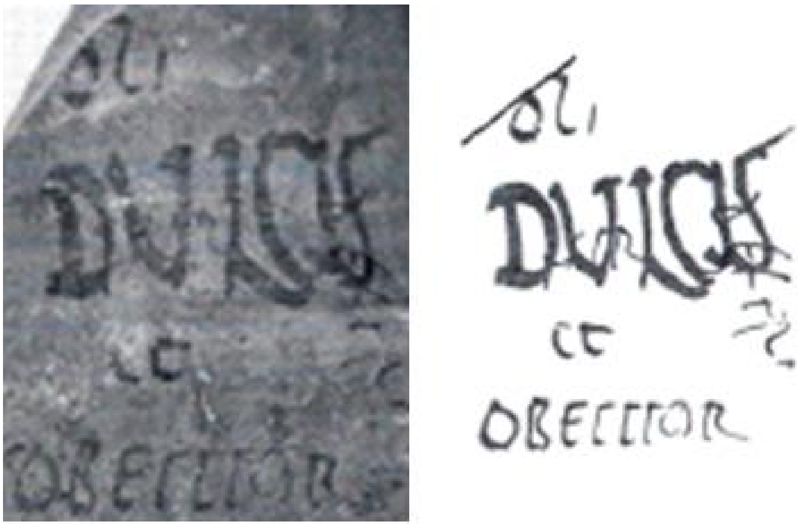


Figure 2.3: A double *dipinti* indicating vessel reuse on a August 21 amphora. Source: Bernal Casasola 2015, Fig. 8.

2.6 Indirect evidence

There are several categories of indirect evidence for the content of amphorae but these provide less certain information.

2.6.1 Pitch Linings

Perhaps the most frequently used indirect evidence for content is the presence of a resinous internal lining. It has long been argued that resinous linings are indicators of amphorae that were used to transport wine, and to a lesser degree *salsamenta*.[43] Pitching wine amphorae was a routine procedure important in preventing loss of the vessel's content such that pitch is known to have been imported in regions where members of the Pine family do not grow.[44] The argument against the use of pitch as an internal sealant in amphorae containing olive oil comes principally from the admonition against it by classical authors. Columella states that vessels used for the purpose of storing olives (and implicitly olive oil as well) should not be treated with pitch as it has a negative effect on the quality of the oil.[45] Cato and Pliny make

[43]Bernal Casasola 2015, 69.

[44]Mayerson 2004.

[45]Columella *Rust.* 12.49.11.

similar arguments.[46] Upon this basis, it has been presumed that evidence of a pitch lining would indicate the vessels had not been used to hold oil.[47]

Recent evidence from absorbed residue analyses has begun to call this into question.[48] Several Dressel 1 amphorae from Pisa San Rossore indicated organic compounds consistent with wine and vegetable oil.[49] The analyses of two Dressel 2 amphorae from Thamusida, Morocco also demonstrated organic compounds consistent with wine and vegetable oil as well as in two 'late Roman amphorae' from Via de Castellani in Florence and LRA 2 examples from Gortina, Crete.[50] Traces of ricinoleic acid (castor oil) was found in conjunction with biomarkers for Pine resin or pitch in a LRA 2 and oil, possibly olive oil, in a LRA 1 from the excavations at Efestia (Lemno, Greece).[51] The analysis of five Spatheia and five North African cylindrical amphorae, dating to the 5th-6th c. AD, indicated resin in conjunction with vegetable oils.[52] A Dressel 20 amphora, long known to have contained olive oil, from the Garum Shop at Pompeii as well as an example excavated at Thamusida, Morocco showed indicators of vegetable oil and resin or pitch derived from the Pine family.[53] Of the Dressel 20 amphorae analyzed by Garnier, 13 of 17 showed biomarkers for a resinous lining.[54] Other studies, however, have shown no indicators of resin in Dressel 20 samples.[55]

The frequency with which resin biomarkers co-occur in vessels that contain organic compounds consistent with vegetable oils has led one researcher to conclude 'si l'hypothèse autrefois admise qu'une amphore à l'huile ne pouvait être poissée, l'expérience le réfute'.[56] For at least some types of amphorae, it is possible that the vessels were pitched before reuse

[46] Cato *Agr.* 69; Pliny *NH* 15.8.

[47] *inter alia* Heron and Pollard 1988; Garnier 2007b; Beck and Borromco 1990.

[48] e.g. Pecci and Cau Ontiveros 2010.

[49] Garnier 2007b, 46.

[50] Salvini et al. 2007; Pecci and Cau Ontiveros 2010, 597, respectively.

[51] Pecci and Cau Ontiveros 2010, 597.

[52] Pecci et al. 2010b.

[53] Pecci and Cau Ontiveros 2010, 598; Salvini et al. 2007, respectively.

[54] Garnier et al. 2011, 407.

[55] Heron 1989, 92ff; Condamin et al. 1976.

[56] Garnier 2007b, 27.

but not before their prime use. This would account for the discrepancy in results with Dressel 20 amphorae. The examples from Pompeii and Thamusida may have been pitched after their prime use in order to hold a different commodity. The absence of organic compounds consistent with wine or other commodities, however, suggests that they were reused to contain oil. At present our understanding of lining practices of amphorae used to transport oil is incomplete. This is in part due to a limited number of samples of specific amphora types that have been analyzed for absorbed organic residues. A fuller picture may be revealed when a greater number of studies including large sample sizes of individual amphora types have been conducted. At this point, it is clearly present that the presence of a resinous lining does not by necessity preclude that the vessel was used to transport oil.

According to classical authors, the vessel's interior still requires conditioning in order that the oil is not lost by absorption through the ceramic matrix. This has been reflected in modern replication studies.[57] Columella advocates that the vessels be treated in the same manner as olive casks, that is, soaked with liquid gum (*liquida gummi*) and dried.[58] Cato recommends a similar practice: first the vessel should be filled with amurca, the watery liquid by-product of olive oil pressing, for seven days before being decanted and the vessel allowed to dry. Gum (*gummi*) should be soaked in water for a day and on the following day diluted; the vessel should be heated and the gum introduced and applied.[59] Pliny accounts a similar process.[60] According to Cato, four Roman pounds of gum (approximately 1.3 kg) were sufficient to treat a 50 amphora-capacity dolium.[61] Unfortunately, the exact nature of *gummi* is not specified. The general description given by the classical authors suggests that it is resinous plant secretion. It is possible that *gummi* may even refer to Pine resins that were extracted without thermal modification (e.g. tapping).

[57]Pecci and Cau Ontiveros 2010, 598.

[58]Columella *Rust.* 12.49.11.

[59]Cato *Agr.* 69.

[60]Pliny *NH* 15.8. The best manuscript renders it as *cummi.*

[61]Cato *Agr.* 69.

2.6.2 Vessel shape

Another type of indirect evidence for the content of amphorae may be due to vessel shape. Some scholars have argued that vessel use has a significant bearing on an amphora's shape and content. It has been argued that wine amphorae have flat bottoms with long, narrow necks, although morphological preferences vary over time.[62] During the Republican and early Imperial periods, they featured large feet. During the middle Imperial period and later, bases tend to have a 'umbilicated' profile.[63] By contrast, olive oil amphorae have a bulbous body with almost vestigial feet.[64] Amphorae for transporting *salsamenta* had wide mouths and necks, a wide neck not being a good form for a liquid content as it could spill.[65] To a degree there is undoubtedly a relationship between form and function, for instance, at the very least, if one were to want to transport large pieces of preserved fish, a mouth and neck wide enough would be necessary for the product to be introduced and, potentially, extracted. Beyond this there is perhaps insufficient evidence to draw any definitive conclusions, or at least preclude the use of form as a reliable predictor of content. There are notable examples of amphora types that violate this paradigm. For example, the LRA 5, for which is there is significant evidence supporting its use as a wine amphora, has the shape profile that would be ascribed to an oil amphora, having a negligible neck and large bulbous body. It may be interesting to note, however, there are observable trends in amphora shape. For example, amphorae at Sinope adopted a wide variety of shapes over a 3-4 century period. Some examples might include 'carrot'-shaped amphora which include Sinopean Group C 'carrots' as well as the Beirut 'carrot' amphora (Camulodunum 189) as well as the later locally produced Beirut amphorae (Beirut 6, 7 and 8) as well as the Egyptian-made LRA 7. All were manufactured in a roughly contemporaneous period before which carrot-shaped amphorae were rarely produced. Similarly, there is a trend toward smaller format amphorae during the later periods

[62] Bernal Casasola 2015, 70.

[63] Bernal Casasola 2015, 70.

[64] Bernal Casasola 2015, 70; Opait 2007, 101.

[65] Bernal Casasola 2015, 70; Opait 2007.

(5th-7th c. AD) such as the LRA 1 and Sinopean D Group amphorae.

2.7 Shipwrecks

Amphorae recovered from shipwrecks offer a special opportunity for the identification of amphora contents. In general maritime deposition provides a more favorable environment for the preservation of organic remains. Shipwrecks also provide a snapshot of the cargo's transport. From material recovered from a shipwreck it is sometimes possible to determine the geographic area from which the ship departed. Amphorae recovered from shipwrecks typically are from their prime use period. Especially during the Roman period, there is very little evidence of reused amphorae on shipwrecks. There is definitive evidence of reuse on only one Roman period shipwreck, the Grado.[66] There is more evidence, however, during later periods. Merchants aboard the Sirce Limani A reused their amphorae indicated by the repairs done to chipped or otherwise damaged rims.[67] The Yasi Ada B contained 'several' LRA 2, which bore *graffiti* indicating they had been used to package either olives or lentils.[68]

[66]Peña 2007, 72.

[67]van Doorninck, Frederick 2002, 903f.

[68]Peña 2007, 74f.

CHAPTER 3

PREVIOUS AMPHORA STUDIES

3.1 Literature Review of Previous Amphora Studies[1]

Amphorae have been the focus of a number of studies utilizing analytical separation techniques. As a pottery class, amphorae were the subject of several studies during the early application of organic characterization techniques with archaeological ceramics, Condamin, Formenti and Rothschild-Boros being amongst the first to analyze specimens in an attempt to identify their contents and the presence of internal organic linings.[2] After this initial period of interest and until recently, organic characterization studies of amphorae received relatively little interest as a proportion of the total organic characterization studies of archaeological ceramics. Recent published work on amphorae as a subject matter in particular and as a subject for the application of new analytical methodologies indicate a resurgence of interest in the use of amphorae.

The first residue analysis studies of amphorae were conducted in the late 1970's.[3] While the primary focus of some early studies was the applicability of chromatographic techniques in archaeometric enquiries (e.g. Condamin et al. (1976)), the majority of investigations during that period and subsequently concerned either vessel content (e.g. Passi et al. (1981), Rothschild-Boros (1981)), the nature of vessel linings (e.g. Heron and Pollard (1988), Beck et al. (1989)) or both. The study of amphorae, in general, has progressed significantly since Peacock and Williams' seminal work *Amphorae and the Roman Economy* was published in 1986.[4] While amphorae were a focus of residue analysis studies in its early years, there was a noticeable decline of studies on the subject afterwards that began to be reversed during the last decade.

[1]Some aspects of the following section were adapted and updated from Woodworth 2011.

[2]Condamin et al. 1976; Condamin and Formenti 1978; Formenti et al. 1978; Rothschild-Boros 1981.

[3]Condamin et al. 1976; Condamin and Formenti 1978; Formenti et al. 1978.

[4]Peacock and Williams 1986; Lund and Gabrielsen 2005, 162.

While a considerable number of studies have involved analysis of organic residues in amphorae, only a few studies have attempted to analyze more than a few samples (see Table 3.1). If the corpus of available published material as a whole is taken into consideration, only a few amphora forms have had more than a few samples analyzed (specifically the Dressel 20, LRA 1 and local Sagalassos forms). The limitations of many previous studies are due to the small sample sizes presumably in part a result of the limited number of archaeological samples available to the researchers for study. The wet sample preparation used in most residue analysis studies (i.e. for GC/MS analyses) is a time consuming process and requires sterile laboratory conditions whereas inorganic characterization studies (i.e. fabric analysis) are more rapid to conduct and do not require such fastidious analytical conditions. Additionally, there is the complexity of the resultant data inherent in residue analysis, most significantly with respect to identifying degradation products with the correct precursor compound and associating it with the correct floral or faunal source. These considerations may account for the greater frequency of fabric studies in the published literature to date.

Table 3.1: Summary of Previous Organic Residue Analysis Studies of Roman and Byzantine Period Amphorae (1st c AD-6th c AD). The terms used in the column "Lining" are the terms used by the respective authors.

Amphora Type	Content Wine	Content Oil	Content Fish Product	Pitch/Resin Lining	Number of Vessels	Studies
"Augenti"	X	X		X	1	Pecci et al. 2010b
Camulodunum 185				X	1	Heron and Pollard 1988
Camulodunum 186				X	3	Stern et al. 2008b
Camulodunum 189				X	1	Heron and Pollard 1988
Dressel 1	X			X	1	Garnier et al. 2003
Dressel 1				X	1	Izzo et al. 2013
Dressel 2-4				X	2	Heron and Pollard 1988
Dressel 20		X		Not Studied	20	Condamin et al. 1976
Dressel 20		X		X	20	Condamin and Formenti 1978
Dressel 20		X		X	2	Salvini et al. 2007
Dressel 20				X	1	Stern et al. 2008b
Dressel 20		X		X	17	Garnier et al. 2011
Dressel 30				X	1	Heron and Pollard 1988
Empoli	X			X	1	Pecci et al. 2010a
"Gauloise flat-based"				X	3	Stern et al. 2008b
Haltern 70				X	3	Dorrego et al. 2004
Haltern 70	X			X	1	Garnier et al. 2003
Haltern 70	X			X	1	Oliveira et al. 2015
Haltern 70 similis (London 555)				X	1	Stern et al. 2008b
Imitation Agora		X		X	2	Romanus et al. 2009
Keay 8		X		X	1	Pecci et al. 2010b
Keay 25				X	13 (?)	Garnier 2007b
Keay 52				X	1	Izzo et al. 2013
Keay 57b	X	X		X	1	Pecci et al. 2010b
Keay 61a		X		X	1	Pecci et al. 2010b
Keay 62a		X		X	2	Garnier 2007b
Keay 62q		X		X	1	Pecci et al. 2010b
Lamboglia 2	X			X	1	Formenti et al. 1978
LRA 1	X	X	X	X	7	Pecci et al. 2010a
LRA 1		X		X	7	Romanus et al. 2009
LRA 3	X	X		X	1	Romanus et al. 2009
LRA 3 var.				X	1	Pecci et al. 2010a
LRA 3 (?)		X		Not Studied	1	Passi et al. 1981
LRA 3 (?)		X		Not Studied	Unknown	Rothschild-Boros 1981
LRA 4		X		Not Studied	2	Passi et al. 1981
LRA 4					1	Romanus et al. 2009
LRA 4 (?)		X		Not Studied	2	Rothschild-Boros 1981
LRA 5/6	X		X	X	2	Pecci et al. 2010a
"Africano Grande"		X		Not Studied	2	Passi et al. 1981
"African white-slipped"		X		X	unknown	Rothschild-Boros 1981
Africana 2A				X	1	Heron and Pollard 1988
Pelichet 47/Gauloise 4				X	1	Heron and Pollard 1988
Rhodian				X	1	Heron and Pollard 1988
Rhodian				X	1	Stern et al. 2008b
Sagalassos (local form)		X		X	16	Romanus et al. 2009
Spatheia 1		X		X	5	Pecci et al. 2010b
Unknown				Not Studied	1	Rothschild-Boros 1981
Unknown				X	1	Shackley 1982
Unknown		X		X	3	Romanus et al. 2009
Unknown (Roman period)				X	1	Ribechini et al. 2008
Unknown ("Roman amphorae")				X	2	Font et al. 2007
Various (Identified by Period)				X	31	Beck et al. 1989
"Kados"				X	2	Izzo et al. 2013

3.2 Review of Previously Applied Techniques[5]

A diverse variety of analytical techniques have been utilized in analyzing amphora content and linings, including chemical spot tests and spectroscopic techniques (e.g. Fourier transform infrared spectroscopy (FTIR)), as well as chromatographic techniques coupled with

[5]Some aspects of the following section were adapted and updated from Woodworth 2011.

spectrometry, including gas chromatography/mass spectrometry (GC/MS) and high performance liquid chromatography/mass spectrometry (HPLC/MS). Chemical spot tests, while benefiting from simple sample preparation, have proven problematic because of false positives.[6] Additionally, the low concentration of organic substances retained with the ceramic matrices of archaeological samples requires that methods with exceptionally low detection limits be employed (e.g. GC/MS and HPLC/MS). FTIR has proven a reliable technique for characterizing visible resinous linings in amphorae but is less well suited for non-resinous absorbed organics than combined separation and characterization techniques (i.e. GC/MS and HPLC/MS) due to lower degree of sensitivity to trace residues as well as less specificity in characterization. Despite these limitations, FTIR has been demonstrated to be a useful preliminary technique for organic analysis. Short sample preparation time and low cost of analysis permit a greater number of samples to receive at least preliminary analysis as compared to GC/MS or HPLC/MS.[7]

With respect to investigations into the identifcation of wine in archaeological ceramics, a variety of techniques have been employed. The first studies took place during the 1970's.[8] The trend in more recent research has focused on the use of GC/MS or HPLC/MS techniques. Guasch-Jané et al. (2004) used HPLC/MS/MS for the identification of tartaric and syringic acids in ancient Egyptian vessels. Syringic acid was produced by alkaline fusion of malvidin in the samples. Pecci et al. (2013) used a similar technique for the release of syringic acid from malvidin and additionally examined other organic compounds associated with wine by GC/MS.

Syringic acid may also exist in a free form in nature. It is known to be present in degraded lignin as well as in small quantities in some plants, e.g. some cereals.[9] Barnard et al. (2011) developed an HPLC/MS technique that first extracted free syringic acid from the sample matrix before employing alkaline fusion. The technique allows the determination

[6]Stern et al. 2008a, 2210; Boulton and Heron 2000.

[7]Concerning the use of FTIR for lining characterization, see Font et al. 2007; concerning the disadvantages of FTIR, see Stern et al. 2008a and Boulton and Heron 2000.

[8]e.g. Condamin and Formenti 1978; Formenti et al. 1978.

[9]Garnier and Valamoti 2016, 196.

of the presence of syringic acid with higher specificity as to origin. However, as malvidin is only present in red grapes, the method is unable to identify if a vessel had been used to contain a white grape product (e.g. white wine). Most recently, Garnier and Valamoti (2016) developed a combined lipid and wine biomarker extraction technique that extracts tartaric and syringic acids as well as other organic compounds associated with wine (similar to that by Pecci et al. (2013)).

3.3 Previous Amphora Studies[10]

Early residue analysis studies were primarily concerned with testing the potential for utilizing developed chemical analytical techniques in archaeological contexts (Table 3.2). Potential pitfalls specific to archaeological samples had to be evaluated and there were substantive concerns that required experimental enquiries concerning low concentration of extant organics within the ceramics; the degree to which absorbed organics migrate out of the ceramic matrix during deposition (e.g. leaching due to water exposure) or, alternatively, the potential for lipid migration into the ceramic from the depositional environment; and the effects of diagenesis on the molecular composition of the absorbed organics. In fact, some of these are still the subject of experimental inquiry today. For these reasons, the nature of the samples (e.g. ceramic form and fabric) was sometimes not reported and, with respect to archaeological contextual information, rarely if ever. For example, in Rothschild-Boros' pilot application (Rothschild-Boros (1981)) of high performance liquid chromatography (HPLC) analysis, one of the vessels is of an unknown type while the other two are identified with a vernacular 'type'.

With a greater understanding today of specific complications in the application of organic analysis in archaeological contexts, as well as a developing body of experimental data and improvements in analytical equipment itself, the quality of organic residue identification studies has considerably improved. However, amphora residue analysis studies remain constrained in two general aspects. Firstly, the occasional tendency to exclude typological

[10] Aspects of this section have been adapted and updated from Woodworth 2011.

form information as well as archaeological contextual data remains present. Sometimes the vessel is identified by region only or by a vernacular form name. Frequently form drawings are not included. The reason for this is primarily two-fold. Many of the analyses are conducted by chemists who are not archaeologists (and as such are not familiar with ceramic typologies and contextual data). Also, most of the subsequent publications are made in scientific journals in which page limits restrain the amount of data that may be expressed, the archaeological data being the less immediately relevant. The second aspect is that chemical analytical amphora studies tend to focus on a very small number of samples. The significant amount of time required for sample preparation for organic analysis as well as the significant expense of external laboratory analysis has traditionally limited analysis to either vessels of particular interest or small assemblages. Recent studies involving relatively high number of samples indicate, however, the beginning of change in this trend, due in part to an increased interest in the application of scientific techniques in archaeology, especially in Europe.[11]

With the exception of special vessels in which their particular content is of interest, the study of amphorae in general (i.e. distribution, provenance analysis, content analysis) serves to reconstruct regional and interregional trade in antiquity and, in doing so, regional and interregional economics. The problem lies in that much of the dynamics of use (i.e. content) of amphorae is still poorly understood. Homogeneity of content within a single form during a single period is still considered to be generally the case, although some recent research indicates exceptions to this rule.[12]

[11] Gregg 2009, Chapter 7. Concerning the difference in the level of development of the archaeological sciences in North America and Europe, see Gregg 2009, Chapter 7.3.

[12] e.g. Pecci and Cau Ontiveros 2010.

Table 3.2 Summary of Techniques Used in Organic Residue Analysis of Amphorae

Study	Primary Identified Biomarkers	Content/Lining Determination	Technique
Condamin et al. (1976)	fatty acids	olive oil	GC/MS
Condamin and Formenti (1978)	tartaric acid, diterpenes	wine, resin (lining)	GC/MS
Formenti et al. (1978)	tartaric acid	wine	GC/MS
Rothschild-Boros (1981)	linoleic acid, arachidic acid	olive oil, sesame oil	TLC/HPLC
Passi et al. (1981)	fatty acids (esp. linoleic acid) also arachidic acid	olive oil, sesame oil (?)	TLC/HPLC
Shackley (1982)	diterpenes	resin	GC/MS
Heron and Pollard (1988)	diterpenoids	pitch, probably pine (*Pinaceae*) (lining)	GC/MS
Beck and Borromco (1990)	diterpenes	resin (lining)	GC/MS
McGovern and Michel (1996)	tartaric acid	wine	FTIR
Stern et al. (2000)	C_{10}-C_{24} fatty acids	oil	GC/MS
Garnier et al. (2003)	polyphenols, diterpenes	wine, defrutum, resin (lining)	Py/GC/MS
Stern et al. (2003)	triterpenes	resin (*Pistacia* sp.)	GC/MS
Petit-Domínguez et al. (2003)	tannins (associated with grape products)	wine	Folin-Denis Reagent
Kimpe et al. (2004)	fatty acids; mono-, di- and tri-acylglycerols	vegetable and/or animal products	GC/MS HPLC/MS
Dorrego et al. (2004)	C16-C18 fatty acids, triterpenoids	linseed or olive oil mixed with resin (*Pistacia* sp.) (lining)	HPTLC GC/MS
Guasch-Jané et al. (2004)	tartaric acid, syringic acid	wine	HPLC/MS/MS

Colombini et al. (2005a)	diterpenoids	pine pitch (*Pinaceae*) (lining)	DE/MS GC/MS
Colombini et al. (2005a)	diterpenes	pine pitch (*Pinaceae*) (lining)	DE/MS GC/MS
Guasch-Jané et al. (2006)	tartaric acid	wine	HPLC/MS/MS
Font et al. (2007)	diterpenes	pitch (lining)	FTIR GC/MS
Salvini et al. (2007)	fatty acids	pitch	GC/MS ESI/MS
Salvini et al. (2007)	diterpenes, fatty acids	oil, resin	GC/MS ESI/MS
Linke et al. (2008)	diterpenes	resin (lining)	GC/MS
Ribechini et al. (2008)	diterpenes	resin (contents)	DE/MS
Stern et al. (2008a)	triterpenoids	resin (*Pistacia* sp.)	HPLC/MS/MS GC/MS FTIR Feigl Spot
Stern et al. (2008b)	diterpenes, triterpenes	heated resin, pitch	GC/MS GC/C/IRMS (provenance by bulk isotopic analysis)
Romanus et al. (2009)	fatty acids, diterpenes, polyphenols	oil, resin, wine	GC/MS
Pecci et al. (2010a)	fatty acids, tartaric, syringic and other diacids	vegetable oil, red wine or fruit, fish products (poss.)	GC/MS
Pecci et al. (2010b)	fatty acids	pitch	GC/MS
Barnard et al. (2011)	syringic acid	wine	HPLC/MS
Izzo et al. (2013)	diterpenes	pitch	FTIR GC/MS
Garnier and Valamoti (2016)	tartaric, syringic and other diacids	wine	GC/MS

CHAPTER 4

ORGANIC COMPOUNDS IN WINE, OLIVE OIL, FISH AND PINE RESIN

A considerable number of different types of commodities are known to have been transported or stored in amphorae. Of these the classes of commodities that were transported as principal contents of amphorae are much fewer, consisting of wine or wine-related products, olive oil and fish products (i.e. *salsamenta*). This chapter seeks to review the organic compounds or 'biomarkers' that are specific to particular classes of commodities. The nature of resinous compounds used to coast the interior of amphorae is also examined.

4.1 Wine and its products

Analytical investigations for evidence of a content of wine has been the focus of perhaps more studies than other contents associated with amphorae.

4.1.1 The nature of wine

Wine, most simply described, is an alcoholic beverage resulting from the fermentation of grapes or other fruits. Berries, such as raspberries, strawberries and elderberries can be used as substrates for wine production as can tree fruits, such as apples and pears.[1] For the purpose of this chapter, wine produced from grapes or grape-products, as known to have been the principal if not exclusive source for large-scale wine production during the Roman period, will be the subject of consideration.

The result of the fermentation of grape juice is a 'complex mixture of several classes of organic compounds, including alcohols, aldehydes, acids, carbohydrates, esters, polyhydroxyphenols such as flavonols and anthocyancins, proteins, lipids and vitamins, as well as inorganic minerals.'[2] This complexity originates from the numerous pathways that convert

[1]Hutkins 2008, 351.

[2]Boulton and Heron 2000, 599f; see also Hutkins 2008, 357.

the juice to wine. Grape juice is primarily composed of water (700-800 g/L), carbohydrates (150-250 g/L), and sugars (glucose and fructose each representing approximately 80-120 g/L).

There are a variety of organic acids present in grapes and its juice (Fig. 4.1). One of the most prevalent is tartaric acid, which may be in concentrations as high as 15 g/L in unripe grapes.[3] There is a correlation between latitude and concentration levels of tartaric acid–concentrations in musts from the northerly regions often exceed 6 g/L whereas southerly regions may be as low as 2-3 g/L.[4] Malic acid is the second most prevalent organic acid. Concentration levels in unripened grapes may be as high as 25 g/L.[5] Concentrations levels decrease significantly once ripening begins due to dilution (as the water content increases as the grapes mature) as well as conversion. Similar to tartaric acid, there is a correlation between latitude and malic acid concentration, ranging from 4-6.5 g/L in mature fruits in northerly regions to 1-2 g/L in southerly regions.[6]

Citric acid is also present in grapes, its presence being on account of its role in the tricarboxylic acid (TCA) cycle. Concentrations in must range between 0.5-1.0 g/L.[7] Ascorbic acid is present in small quantities as a cyclic ester. Ascorbic acid functions as a Redox system, preventing the oxidation of phenols.[8] In modern vinification, it is used as an adjuvant to sulfur dioxide to inhibit oxidation during and after fermentation.[9]

While tartaric, malic and citric acids comprise the majority of acidity in grapes, there are several additional acids present in lesser quantities. Gluconic acid is present only in very small quantities in normal grapes although concentrations pay be as high as several g/L in the juice of grapes affected by noble or gray rot.[10] Mucic, or gelactaric, acid is derived from

[3]Ribereau-Gayon et al. 2000, 4.

[4]Ribereau-Gayon et al. 2000, 4.

[5]Ribereau-Gayon et al. 2000, 4.

[6]Ribereau-Gayon et al. 2000, 5.

[7]Ribereau-Gayon et al. 2000, 5.

[8]Ribereau-Gayon et al. 2000, 5.

[9]Ribereau-Gayon et al. 2000, Vol. 1, 224.

[10]Ribereau-Gayon et al. 2000, 5.

galactose by oxidation and is considered undesirable as it causes turbidity.[11] The presence of mucic acid is associated with wines produced from grapes affected by noble or gray rot. Finally, there are cinnamic series phenolic acids often esterified with an alcohol function of tartaric acid (Fig. 4.1).[12]

4.1.2 Phenolic compounds

The most important compounds in grapes concerning human consumption are a chemically diverse group broadly responsible for the color, flavor and aroma of grapes and their product. Phenols possessing a single phenolic ring and a functional group at carbon 1 or 3 are referred to as nonflavonoids (Fig. 4.2).[13] Compounds possessing two or more phenolic rings that are connected by pyran ring structures are referred to as flavonoids. [14] As a group, flavonoids are composed of several different classes of compounds, including flavonols, catechins and anthocyanins. Anthocyanins, primarily malvidin-3-glucoside), are the pigmentation compounds in grapes and their products.[15] Although both red and white grapes contain phenolic compounds, the concentration of phenolics is at least four times higher in red grapes.[16]

4.1.3 Ethanolic fermentation and its products

While there are two types of fermentation that may occur during wine production, the first or primary fermentation is ethanolic fermentation and common to all wine production regardless of grape color or wine style. Prior to ethanolic fermentation, grapes are crushed and macerated. The crushed grape material contains juice, seed, skins and, in some cases, some degree of stems.[17] The period of time and the temperature at which maceration is con-

[11] Ribereau-Gayon et al. 2000, 5.

[12] Ribereau-Gayon et al. 2000, 5.

[13] Hutkins 2008, 360ff.

[14] Hutkins 2008, 363.

[15] Singleton 1996, 70.

[16] Ribereau-Gayon et al. 2000, 152.

[17] Hutkins 2008, 366.

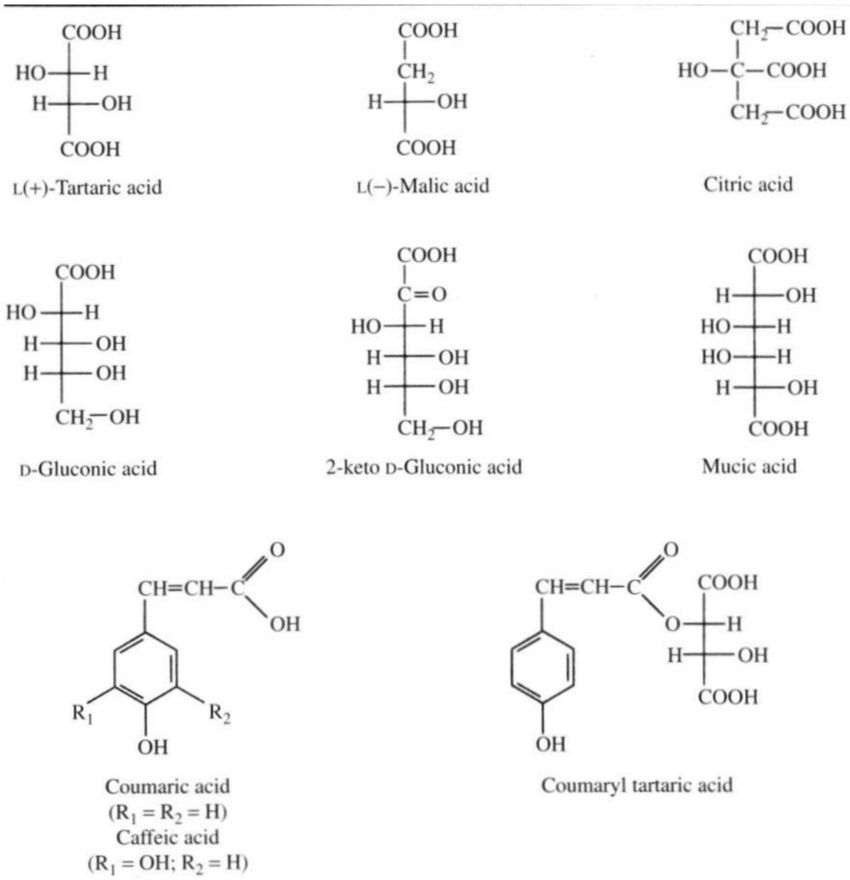


Figure 4.1: Primary organic acids present in grapes. Source: Ribéreau-Gayon et al. 2000, Table 1.2.

ducted varies widely according to wine style in modern viticulture. In general, the length of time and temperature of maceration for white wines is considerably shorter/lower than that of red wines, which is primarily responsible for the lower total phenolic content of white wine.[18]

Primary fermentation begins after or during the maceration process. Spontaneous or natural fermentation may be allowed to proceed in which the naturally occurring micro-flora on the grape skins and in the production environment are responsible for ethanolic fermentation. The second option is controlled fermentation in which the indigenous micro-flora are deactivated, most commonly by the introduction of either SO_2 (as a gas) or potassium bisulfate before a specific yeast culture is introduced by the vintner. The use of controlled fermentation is predominantly practiced in modern viticulture as it produces a more consistent final

[18]Hutkins 2008, 366.

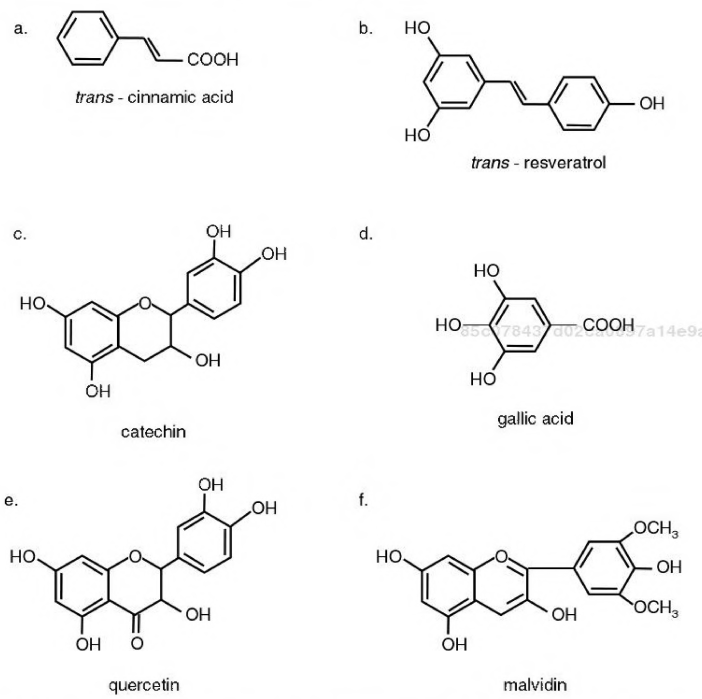


Figure 4.2: Primary flavonoids in grapes. Source: Hutkins 2008, Fig. 10.2.

product. Wine produced by spontaneous fermentation has been argued to produce wine with greater complexity of flavor owing to the wider variety of microfloral species with a greater variety of metabolic pathways and resulting compounds–recent research has supported this traditionally held opinion.[19]

Microflora responsible for ethanolic fermentation, including *S. cerevisiae*, the primary wine yeast, and other species involved in spontaneous fermentation, are capable of metabolizing sugars via the TCA cycle as well as via the Embden-Meyerhoff (EM) glycolytic pathway.[20] The TCA cycle produces a number of intermediary compounds (Fig. 4.1). At the beginning of fermentation, the TCA cycle is strongly favored by aerobic conditions. The metabolism of sugar yields CO_2 and H_2O end products.[21] The consumption of oxygen and production of CO_2 rapidly results in a lowered redox potential such that anaerobic conditions develop.[22] Anaerobic conditions result in sugar metabolism shifting to the EM

[19]Hutkins 2008, 367ff; Boulton 1996, 124f.

[20]Hutkins 2008, 375.

[21]Hutkins 2008, 375.

[22]Hutkins 2008, 375.

glycolytic pathway yielding ethanol and CO_2. The glycolytic pathway begins with glucose and fructose, synthesizing ethanol and CO_2 through a number of intermediary steps (Fig. 4.3).[23] Both metabolic pathways are exothermic. If temperature conditions exceed 30 °C, fermentation may cease in what is referred to as a 'stuck fermentation'.[24] The result is a low Thalia solution with significant residual sugars, which is susceptible to spoilage because of the availability of sugar to potentially undesirable microflora.[25]

The theoretical conversion rate of sugars to ethanol is 180 g sugars resulting in 88 g CO_2 and 92 g ethanol (51.1% by mass).[26] Empirical evidence indicates a lower conversion efficiency rate. Pasteur's original experiments indicated a conversion yield of 48.5% by weight with 46.7% as CO_2 and the remaining 4.8% being composed of glycerol, succinate and other TCA and EM intermediary products as well as yeast cell mass.[27]

4.1.4 Malolactic fermentation

The second type of fermentation that may occur during vinification is malolactic or secondary fermentation. A degree of acidity is a desirable quality in wine. Modern red wines have a typical pH of 3.3-3.6, while white wines generally have a slightly lower pH.[28] If the grapes from which a wine was made have too high a level of organic acids, the wine will suffer from excess acidity, which is considered a flavor defect in both modern wines and those of antiquity.[29] Of the organic acids present in grapes and wine, malic acid has the most potential to affect pH. Not only is malic acid the most prevalent organic acid in grapes, malic acid is a dicarboxylic acid, meaning that it can donate two protons.[30] In wines that are too acidic, malolactic fermentation provides a means of 'deacidifying' the wine by con-

[23] Boulton 1996, 135ff.
[24] Hutkins 2008, 377ff.
[25] Hutkins 2008, 377ff.
[26] Boulton 1996, 137.
[27] Boulton 1996, 137.
[28] Hutkins 2008, 382.
[29] Hutkins 2008, 382.
[30] Hutkins 2008, 382.

verting malic acid to lactic acid, a monocarboxylic acid. Lactic acid bacteria may be present naturally in the wine and initiate, like that of ‘spontaneous fermentation’, without external intervention. As controlled fermentation is preferred in modern viniculture for primary fermentation, it is now common to introduce malolactic strains directly to the must.[31] Malolactic fermentation is commonly but not universally practiced in modern viticulture. Grapes from more northerly regions tend to contain higher levels of malic acid and thus potentially benefit from a reduction in acidity; however, grapes from southerly regions may suffer the opposite problem–too little acidity. Generally in modern viticulture malolactic fermentation is more commonly employed in red wine production than in white. There are some white wines where malolactic fermentation is frequently employed, such as chardonnay, where the presence of greater acidity is considered to be a desirable trait in the style.

Malolactic fermentation occurs by the catalyst of a malolactic enzyme whereby malic acid is directly decarboxylated to lactic acid without an intermediate product.[32]

4.1.5 Organic extracts in wines

In dry wines, glycerol ranges between 5-8 g/L and is dependent upon a variety of parameter including initial sugar content, fermentation temperature and microfloral stains.[33] Tartaric acid concentration in wine are lower than that of grapes owing to the formation of potassium bitarrate during and after fermentation which is insoluble. Malic acid levels are also variable, primarily dependent on the malic acid content of the grapes and conversion by malolactic fermentation, if employed. Succinic acid levels range between 0.8 and 1.5 g/L, whereas lactic acid levels are more modest in the range of 0.3-0.5 g/L.[34] Finally, small quantities of acetic acid (~0.5 g/L) may be present.[35]

[31]Hutkins 2008, 382.

[32]Hutkins 2008, 382.

[33]Boulton 1996, 138.

[34]Boulton 1996, 138.

[35]Hutkins 2008, 138.

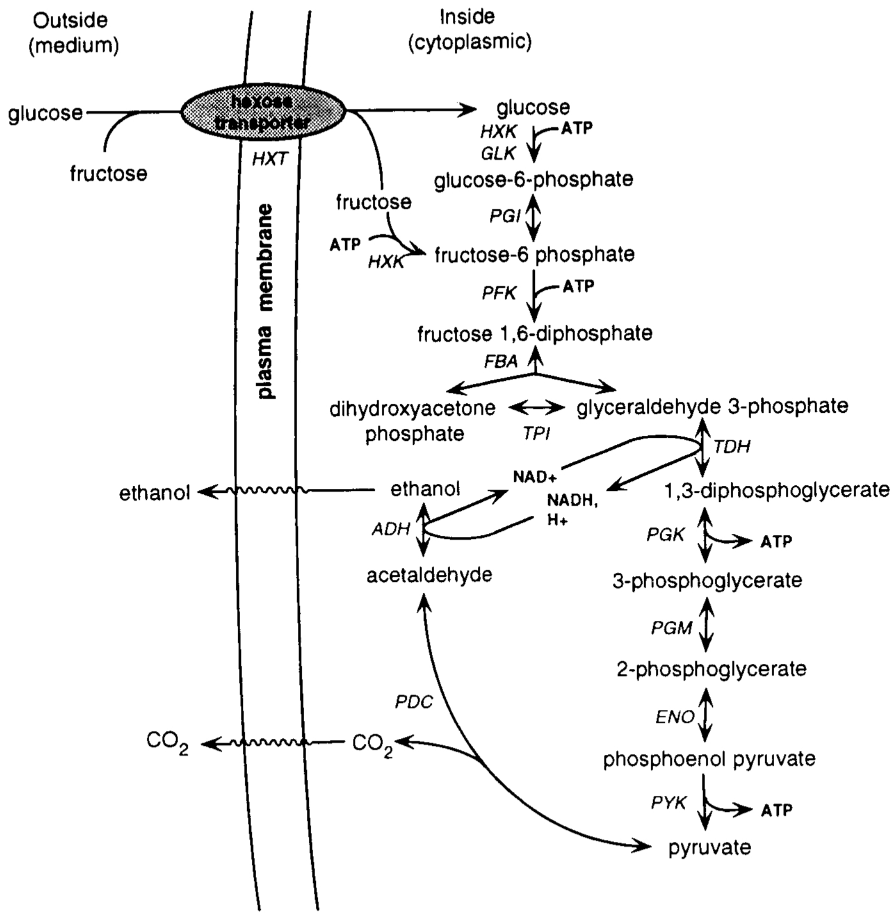


Figure 4.3: Pathways of glycolytic fermentation. Source: Boulton 1996, Fig.4-12.

4.1.6 Phenolics in Wine

Despite constituting only 2-3 g/L of wine, phenolic compounds are a significant component of grapes and contribute significantly to wine, being responsible for many favor aspects as well as the color of red wine. Phenolics may undergo chemical changes during vinification and aging. For example, the complexities of polymerization are an area of ongoing research, complicated by the matter that modern liquid chromatography are only able to characterize only marginally polymerized samples.[36]

[36]Ribéreau-Gayon et al. 2000, 129.

4.2 Olive Oil

Olives and olive oil have long been an important component of diet in the Mediterranean region. The earliest finds of olive pits date to the Neolithic with prevalence significantly increasing during the Chalcolithic period.[37] Today olive oil is not only a major component of diet in the Mediterranean area but also a significant source of revenue for several countries (especially Spain and Italy).

Traditionally, stone mills were used to crush the olives to produce a slurry. Once crushed, the slurry is slowly stirred (the malaxation stage) for a period of time (approximately 30 minutes in modern practice).[38] After malaxation, the paste is principally composed of olive oil, water and pieces of olive pit and other solid organic matter. The paste is then separated by pressure, filtration or centrifugation (the most frequently used method in modern oleoculture).[39] The resulting oil may or may not be considered of sufficient quality for consumption if the oil's acidity is too high or there are taste or smell defects. Such oil is typically filtered to improve quality and is termed 'refined olive oil'. The residual solid material left after pressing ('pomace') may be solvent-extracted (typically with hexane).[40]

4.2.1 Olive oil composition

Like animal fats and other vegetable oils, olive oil is primarily composed of triacylglycerols with a small proportion of free fatty acids, mono- and di-acylglycerols. Non-glyceridic components comprise 0.5-1.5% by weight of the liquid.[41]

[37] Serpico and White 2000, 399.

[38] Boskou 1991, 244.

[39] Boskou 1991, 244ff.

[40] Boskou 1991, 246f.

[41] Boskou 1991, 247.

4.2.1.1 Triacylglycerols and fatty acids

The principal triacylglycerol (TAG) in olive oil is triolein (OOO) representing 40-59% by weight of total TAGs in modern samples.[42] The remainder of the TAGs are comprised of palmitoyl-dioleoyl-glycerol (POO) (12-20%), dioleoyl-linoleoyl-glycerol (OOL) (12.5-20%), palmitoyl-dioleoyl-glycerol (POL) (5.5-7%) and stearoyl-dioleoyl-glycerol (SOO) (3-7%).[43] In fresh olive oil, the presence of mono- and di-acylglycerols are due either to incomplete biosynthesis or hydrolytic reactions.[44] In archaeological samples, free fatty acids comprise the majority of lipids due to the susceptibility of triacylglycerols to degradation during deposition.

Fatty acid composition demonstrates considerable variability. Zone of production, latitude, climate, olive variety and stage of fruit maturity have all been associated with variation in relative fatty acid ratios.[45] Greek, Italian and Spanish olives have relatively low $C_{16:0}$ and $C_{18:2}$ acid levels and a relatively high level of $C_{18:1}$; conversely, Tunisian olives contain higher levels of $C_{16:0}$ and $C_{18:2}$ with lower $C_{18:1}$ (oleic acid) levels.[46] Recent research in palmitoleic acid ($C_{16:1}$) levels has indicated cultivar cross-breeding may have a significant effect on FA composition.[47] $C_{18:1}$ (oleic acid) comprises 55-83% of total fatty acids with palmitic ($C_{16:0}$), palmitoleic ($C_{16:1}$), stearic ($C_{18:0}$) and linoleic ($C_{18:2}$) acids representing the primary fatty acids (Fig. 4.4). Small quantities of myristic ($C_{14:0}$), heptadecanoic ($C_{17:0}$), heptadecenoic, arachidic ($C_{20:0}$), behenic ($C_{22:0}$), and lignoceric ($C_{24:0}$) acids are also observed.

[42] Garnier 2007b; Boskou 1991, 247.

[43] 'O', 'P', 'L', 'S' represent oleic, palmitic, linoleic and stearic acids, respectively. Boskou 1991, 247.

[44] Boskou 2006, 43.

[45] Boskou 2006, 41.

[46] Boskou 2006, 41.

[47] Medina et al. 2014

Lauric acid	(C 12:0)	Not present in discernible amounts
Myristic acid	(C 14:0)	< 0.1
Palmitic acid	(C 16:0)	7.5 – 20.0
Palmitoleic acid	(C 16:1)	0.3 - 3.5
Heptadecanoic acid	(C 17:0)	< 0.5
Heptadecenoic acid	(C 17:1)	< 0.6
Stearic acid	(C 18:0)	0.5 - 5.0
0leic acid	(C 18:1)	55.0 – 83.0
Linoleic acid	(C 18:2)	3.5 – 21.0
Linolenic acid	(C 18:3)	< 1.5
Arachidic acid	(C 20:0)	< 0.8
Behenic acid	(C 22:0)	< 0.3
Erucic acid	(C 22:1)	Not present in discernible amounts
Lignoceric acid	(C 24:0)	< 1.0

Figure 4.4: Principal fatty acids in olive oil. Source: Codex Alimentarius 2001, 25f.

4.2.1.2 Hydrocarbons

Two hydrocarbon species are present in significant quantities in olive oil: squalene and β-carotene. Squalene is an intermediary metabolite in sterol ring formation and is present in concentrations of between 200 and 7500 mg/kg in olive oil, representing approximately 90% of the hydrocarbon fraction.[48] The presence of squalene is unusual in vegetable oils and is used for olive oil authentication. Apart from squalene and β-carotene, there are small quantities of di- and tri-terpenes, isoprenoidal polyolefins and long chain n-alkanes.[49]

4.2.1.3 Tocopherols

Of the eight known E-vitamin isomers, the α homologue represents approximately 90% of total tocopherolic content.[50] Tocopherol content varies widely, being affected by cultivar

[48]Boskou 2006, 44.

[49]Boskou 2006, 44.

[50]Boskou 2006, 44.

type and oil extraction factors as well as by environmental and geographic factors.[51] Levels range from 55-370 mg/kg in reported data sets.[52]

4.2.1.4 Pigments

Chlorophylls responsible for the green hew of olives are pheophytins, predominated by pheophytin α.[53] The principal carotenoids present in olive oil are lutein and β-carotene.

4.2.1.5 Alcohols

The main fatty alcohols present in olive oil are docosanol, tetracosanol, hexacosanol and octacosanol, predominated by tetracosoanol and hexacosanol.[54] Fatty alcohol levels in virgin olive oils do not typically exceed 250 mg/kg.[55] Esters of fatty acids (waxes) are also present in olive oils. Principal waxes are even numbered and range between 36 and 46 carbon atoms.[56] The level of waxes is principally dependent on oil extraction technique. Levels in virgin olive oils are generally lower than 150 mg/kg in contrast to solvent extracted oils in which wax levels may exceed 2000 mg/kg.[57]

4.2.1.6 Sterols

Principal sterols in olive oils are β-sitosterol, Δ^5-avenasterol and campesterol.[58] A number of additional sterols have also been reported in trace amounts including, stigmasterol, brassicaserol, ergosterol and campestanol.[59] Like waxes, total sterol content is significantly affected by extraction technique. Virgin olive oils typically have a total sterol content of

[51] Boskou 2006, 44.
[52] Boskou 2006, 44.
[53] Boskou 2006, 45.
[54] Reiter and Lorbeer 2001; Boskou 2006, 46.
[55] Boskou 2006, 46.
[56] Reiter and Lorbeer 2001.
[57] Boskou 2006, 46.
[58] Boskou 2006, 47.
[59] Boskou 2006, 47.

1000-2000 mg/kg (the lower limit being set by European Union Commission regulation).[60] Refined olive oils have a lower sterol content relative to virgin oils; solvent extracted oils may contain up to three times the sterols of virgin oils.[61] β-sitosterol is the principal sterol, comprising 75-90% of total sterols, Δ^5-avenasterol 5-7% and campesterol 2-4%.[62]

4.3 Fish and Fish Products

Fish products and their derived commodities are very difficult to identify by biomarker analysis in archaeological ceramics. The lipid composition of marine fauna varies significantly from terrestrial organisms due to the different environmental demands and evolutionary pathways on the organisms.[63] The most characteristic compounds for marine animals are polyunsaturated fats, specifically $C_{20:5}$, $C_{22:5}$ and $C_{22:6}$, as well as saturated fatty acids with a carbon chain length between 12 and 24 and unsaturated fats between 14 and 22.[64] Unsaturated fatty acids, especially polyunsaturated fatty acids, are especially prone to diagenetic degradation over archaeological time scales and, therefore, rarely detected except in exceptional depositional circumstances.[65] It has been proposed that $C_{16:1}$, $C_{20:1}$ and $C_{22:1}$ fatty acids may be useful biomarkers for fish oils.[66] The fatty acids $C_{16:1}$ and $C_{20:1}$, however, are also present in other sources in small quantities in ruminant and some vegetable oils.[67]

Several fatty acids with a significant specificity to marine organisms and their commodities have been identified. Specifically, they are phytanic acid (3,7,11,15-tetramethylhexadecanoic acid), pristanic acid (2,6,10,14-tetramethylpentadecanoic acid) and 4,8,12-TMTD (4,8,12-trimethyltridecanoic acid).[68] These isoprenoid fatty acids have long been

[60] Boskou 2006, 48.

[61] Boskou 2006, 48.

[62] Boskou 2006, 48ff.

[63] Brown and Heron 2005, 68; Cramp and Evershed 2014, 321.

[64] Brown and Heron 2005, 68. See Table 5.4. Another study on fish oil composition can be found in Enser 1991.

[65] Brown and Heron 2005, 68; Evershed et al. 2008, 102.

[66] Brown and Heron 2005, 70.

[67] Brown and Heron 2005, 70.

[68] Evershed et al. 2008, 102; Cramp and Evershed 2014, 323.

known to be characteristic of marine oils, whereas they are absent or present only in very small quantities in plants.[69] Additionally, ω-(o-alkylphenyl)alkanoic acids with a chain length of 16-20 carbons have been indicated to be produced during high temperature processing of marine organisms.[70] The formation of ω-(o-alkylphenyl)alkanoic acids require a processing temperature of at least 200 °C and would not be present in low temperature processing of marine commodities, such as the production of *salsamenta*.[71]

4.4 Pitch and Resin

Amphorae were frequently lined with pitch, primarily derived from members of the *Pinaceae* family (Fig. 4.5). Pitches derived from *Pinaceae* resins are characterized by a predominance of dehydroabietic acid with lesser constituents typically comprised of abietic, pimaric and isopimaric acids and their oxidation products.[72] Methyl dehydroabietate, also frequently observed in pitch samples and pitched ceramics, is a biomarker of the method of production.[73] The compound is produced by 'destructive distillation' by which pieces of wood are combusted to produce pitch, as opposed to high temperature treatment of resin exuded by the plant by means of techniques such as tapping. Additionally, minor constituents include polycyclic aromatic hydrocarbons (PAH's), such as retene as well as anthracene and phenanthrene species.[74]

4.4.1 Historical background on pitch and resin[75]

The words used to describe the products of resin (e.g. pitch, tar, etc.) and even the term 'resin' itself have been used in various and, at times, seemingly interchangeable capacities.[76]

[69] Ackman and Hooper 1968; Evershed et al. 2008, 102.

[70] Hansel et al. 2004; Evershed et al. 2008, 102f; Cramp and Evershed 2014, 323.

[71] Cramp and Evershed 2014, 324.

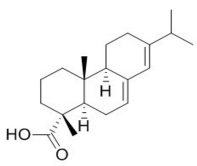
[72] Evershed et al. 2001, 343ff.

[73] Mills and White 1994.

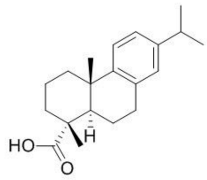
[74] See also Chapter 5.1 concerning experimental analysis of pitch extractions.

[75] Aspects of this subsection were adapted from Woodworth 2011.

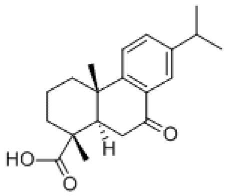
[76] Serpico 2000, 450.



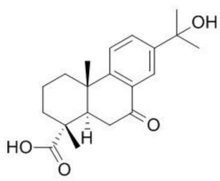
abietic acid



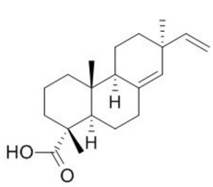
dehydroabietic acid



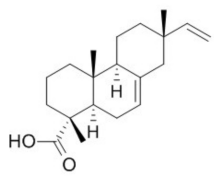
7-oxodehydroabietic acid



15-hydroxy-7-oxodehydroabietic acid



pimaric acid



isopimaric acid

Figure 4.5: Principal resin acids identified in amphora analyses.

The problem of terminology is not new; the Latin word *pix* was used to describe both the liquid exudate from resiniferous plants and the resultant product after its exposure to heat. To prevent terminological confusion, 'resin' is used herein to describe the raw liquid exudate produced by and harvested from resiniferous plants. With respect to types of resin identified in Roman-period amphorae, resin was primarily extracted from members of the pine family (Pinaceae) and, to a considerably lesser extent, members of the Pistachio genus (*Pistacia* sp.).

'Pitch' is produced by thermal treatment by which either extracted resin or the resiniferous source material (i.e. pine wood) is heated to high temperature in an open-air environment.[77] Pitch is dark in color and highly viscous at room temperature. Pitch was used

[77] Serpico 2000, 450; Heron and Pollard 1988, 433; Beck et al. 1989, 370.

for a number of purposes, including as a sealant in amphorae and as a flavorant in wine.[78] The visible presence of pitch in excavated amphorae has traditionally been interpreted as an indication that the vessel was used to transport wine due to the admonishment of Roman authors that amphorae for wine must be pitched and that amphorae for olive oil must not be pitched.[79]

The material used to line amphorae has been investigated in several studies.[80] Visible residue of lining has been frequently observed in amphorae, especially in those recovered from maritime contexts. Of the organic compounds associated with amphorae that have been the focus of various analyses (e.g. oils and fats, wine products, etc.), resin products have proven to be relatively straightforward. Resins and their products are insoluble in water, are readily extractable with organic solvents, and have distinctive biomarker and degradation products.[81]

[78]While most of the commentary by Roman authors on the production of wine appear to indicate that pitch was used as a wine flavorant, both Cato and Pliny do specify that resin (*resina*) may be added as a flavorant. Cato *Agr.* 23.2; Pliny *NH* 14.24.

[79]e.g. Pliny *NH* 14.24; Columella *Rust.* 12.49.

[80]*inter alia* Mills and White 1977; Heron and Pollard 1988; Beck et al. 1989, 2002; Stern et al. 2008b; Izzo et al. 2013.

[81]Mills and White 1977.

CHAPTER 5

ANALYTICAL TECHNIQUES

Several techniques were used for analysis (Fig. 5.1). All samples were subject to separate extractions for the lipid component (e.g. fatty acids, resin acids) as well as other organic compounds associated with grapes and their products. Samples were randomly selected for analysis and coded for blind extraction and analysis. Before extraction, samples were surface cleaned to a depth of approximately 1 mm using a clean diamond-coated rotary drill bit. After surface cleaning, approximately 750 mg of sample was drilled from the cleaned area with a cleaned drill bit to a depth no greater than approximately 6 mm. The ceramic powder was collected on clean, baked (500 °C) aluminium foil before being transferred to a clean vial for weighing and extraction.

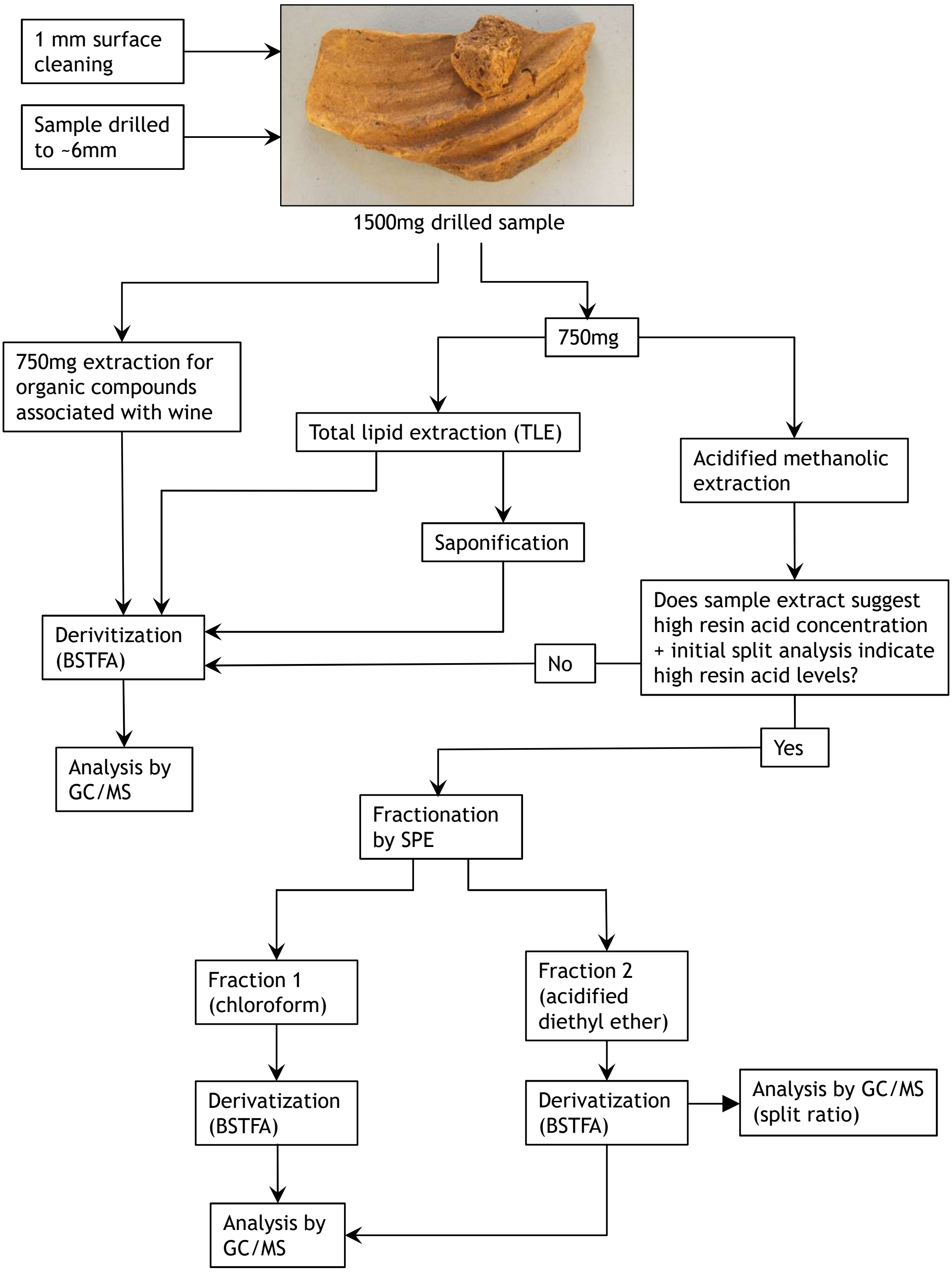


Figure 5.1: Flowchart of applied analytical techniques.

5.1 Total Lipid Extraction

Total lipid extraction (TLE) method was based upon the procedure of Mottram et al. (1999). The sample was extracted twice with 3 ml of chloroform/methanol (2:1 v/v), sonicated for 45 minutes at 50 °C and centrifuged (2500 rpm for 10 minutes) to separate ceramic particles from the solvent. The supernatant was removed and the solvent evaporated by nitrogen blow down, resulting in a total lipid extract (TLE). Samples were then derivatized with 50 µl of *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) for 60 minutes at 70 °C. 10 µl of 0.500 mg/ml of tetratriacontane was used as an internal standard. Samples were derivatized immediately prior to analysis.

5.2 Extraction of Bound Lipids

5.2.1 Sodium hydroxide saponification

The ceramic residue after total lipid extraction (TLE) was dried and then saponified with 2 ml of sodium hydroxide (2 M) in methanol, agitated and heated at 70 °C for 60 minutes (after Mottram et al. (1999), Giorgi et al. (2010)). After heating, vials were centrifuged (2500 rpm for 10 minutes) and the supernatant removed. The supernatant was acidified with hydrochloric acid (16 M) and liquid-liquid extracted three times with hexane (3 ml). The solvent was evaporated under nitrogen blowdown. Samples were then derivatized with 50 µl of *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) for 60 minutes at 70 °C. 10 µl of 0.500 mg/ml of tetratriacontane was used as an internal standard. Samples were derivatized immediately prior to analysis.

5.3 Acidified methanolic saponification

The ceramic residue after TLE extraction was dried and then saponified with 3 ml of sulfuric acid (2% v/v) in methanol and heated at 70 °C for 60 minutes (after Correa-Ascencio and Evershed (2014)). After heating, the solution pH was checked. If the pH were >3, additional extraction solvent was added and the sample reheated. Samples were then centrifuged (2500 rpm for 10 minutes) and the supernatant removed to a clean vial. The extraction solvent was then liquid-liquid extracted three times with hexane (3 ml). The solvent was evaporated under nitrogen blowdown. Samples were then derivatized with 50 µl of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) for 60 minutes at 70 °C. 10 µl of 0.500 mg/ml of tetratriacontane was used as an internal standard. Samples were derivatized immediately prior to analysis.

5.4 Single step extraction and derivatization

Correa-Ascencio and Evershed (2014) developed a high throughput extraction technique for single step extraction and methylation of fatty acids in archaeological pottery, which is described in Section 5.3. The primary advantage of the technique is that it extracts in a single step what would otherwise be extracted in the total lipid extract and bound lipid extraction, thus saving a considerable amount of time in the analysis of a large number of samples. The technique does have limitations. Some structural information is lost, i.e. acylglycerols and wax esters are rendered to their constituent fatty acids although n-alkanols, n-alkanes and ketones are not altered.[1] Small quantities of methyl dehydroabietate, a biomarker for 'pyrolitic distillation' of pine resin, are produced from dehydroabietic acid and thus, without other thermal modification biomarkers, e.g. retene, can not be used as evidence of the means of pitch production. Derivatization with BSTFA is still required in order to render resin acids as their trimethylsilyl esters as they do not readily methylate. This technique was used after data analysis of the initial samples (after deblinding). It was principally used for sample rerun and additional sample analysis in vessel types that did not contain generally contain diagnostic lipids.

[1] Correa-Ascencio and Evershed 2014, 1334.

5.5 Analysis of Organic Compounds Associated with Wine

The extraction technique used for the analysis of organic compounds associated with wine was that developed by Pecci et al. (2013). Each powdered ceramic sample was extracted with 3 ml of an aqueous solution of potassium hydroxide (1 M) in an ultrasonic bath (for 90 minutes at 70 °C). The samples were then removed from the bath and allowed to cool to room temperature before being centrifuged (2500 rpm for 10 minutes). The supernatant was removed to a clean vial and then acidified to a pH of approximately 2 with hydrochloric acid (16 M). After acidification, the extraction solvent was twice liquid-liquid extracted with 3 ml of ethyl acetate. The ethyl acetate was removed to another vial and evaporated to dryness under a stream of nitrogen gas. Samples were then derivatized with 50 µl of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) for 60 minutes at 70 °C. 10 µl of 0.500 mg/ml of tetratriacontane was used as an internal standard. Samples were derivatized immediately prior to analysis. Identification of tartaric and syringic acids was achieved by comparison of retention times and mass spectra against authentic standards as well as comparison against the NIST11 mass spectral database.

5.6 Analytical Conditions

Samples were analyzed by GC/MS using an Agilent 7820A gas chromatograph equipped with a Restek Rxi-5ms column (30 m length, 0.25 mm ID, 0.25 µm film thickness) and an Agilent 5975 quadrupole mass spectrometer. The temperature program for the GC oven was a 50 °C hold for 2 minutes, 50-300 °C at 10 °C/min with a 10 minute isothermal hold at 300 °C. Helium was used as the carrier gas; flow rate was 1.2 ml/min. Injection volume was 1 µl. Injector temperature was 300 °C, transfer line temperature was 280 °C. Electronic ionization was 70 eV and the mass scan range was *m/z* 40-650. Compound identification was achieved by comparison of mass spectra against the NIST11 mass spectral database.

5.7 Lipid and resin acid fractionation

5.7.1 Introduction

As discussed previously, amphorae were used to transport a variety of products, most commonly wine, olive oil and *garum*, and were frequently internally coated with pitch, most commonly derived from members of the Pine family (*Pinaceae*).[2] A complication of the analysis of samples from vessels that were lined with pitch is that a significant quantity of extractable resin acids (relative to extant fatty acids) may be present. Pitches derived from *Pinaceae* resins are characterized by a predominance of dehydroabietic acid with lesser constituents typically comprised of abietic, pimaric and isopimaric acids and their oxidation products (Figure 5.2). Methyl dehydroabietate, also frequently observed in pitch samples and pitched ceramics, is a biomarker of the method of production (Mills and White 1994). The compound is produced by 'destructive distillation' by which pieces of wood are combusted to produce pitch, as opposed to high temperature treatment of resin exuded by the plant by means of techniques such as tapping. Additionally, minor constituents include PAH's, such as retene as well as anthracene and phenanthrene species. PAH's typically typically represent a small proportion of pitch samples and generally present little potential for co-elution with diagnostic fatty acid methyl esters (FAME's). The prevalence of resin acids, especially the dominant dehydroabietic acid, may necessitate that samples be analyzed in a more dilute state (resulting in a decrease signal from fatty acids (if present in any significant quantity) or co-elution with potential analytes of interest. A means of resolving the issue of high-relative resin acid concentrations is to separate the sample extract, allowing separate analytical analyses. Previous work in fractionation of solvent extractions of archaeological material has had various degrees of success despite the increased molecular complexity of samples due to diagenetic effects. Gregg and Slater (2010) used solid phase extraction (SPE) cartridges to separate alkanes, PAH's and fatty acids from calcolithic Middle Eastern pottery. Modugno et al. (2006) utilized liquid-liquid extraction to separate acidic and neutral fractions of

[2] Heron and Pollard 1988; Beck et al. 1989.

amalgamated cinnamic and benzoic resin acids. However, fractionation of samples containing resin acids and fatty acids has had less success. Facchetti et al. (2012) fractioned lipid extracts of an Egyptian beaker into acidic and neutral fractions, using a similar technique to that of Modugno et al. (2006). However, both the fatty acids and resin acids were extracted in the acidic fraction. Gutiérrez et al. (1998) used aminopropyl stationary phase SPE to fraction lipophilic wood and pitch extracts. The resulting four fraction samples separated many classes of analytes (including n-alkanes, triglycerides and sterols); however, free fatty acids (FFAs) and resin acids both eluted in the final (acidified diethyl ether) fraction. The technique developed by Gutiérrez et al. (1998) has two limitations. Firstly, the separation of the sample into four fractions results in a considerable increase in sample preparation and run time which is not desirable when a large number of archaeological samples require analysis. Secondly, and more importantly, the technique was unable to separate fatty acids (as FFA's) from resin acids. The technique described below was developed by the author to allow a two fraction separation of fatty acids from resin acids in order to allow more rapid sample preparation and analysis (and reduced material expense) with the ability to separate fatty acids from resin acids.

5.7.2 Materials and method

All reagents were GC grade (with the exception of sulfuric acid which was ultra-trace grade) and were obtained from Sigma-Aldrich (Gillingham, UK). Sep-Pak Aminopropyl (NH2) solid phase extraction cartridges (500 mg stationary phase) were obtained from Waters UK (Elstree, UK). Water was obtained from an in-house Milli-Q water system. Modern tissue samples of European sprat (*Sprattus sprattus*) and lamb's liver were obtained from Sainsbury's Ltd. (London, UK). Archaeological pitch sample, provided by Michel Bonifay, was recovered from the interior lining of a Keay 25.1 amphora from the Pampelonne wreck (Saint-Tropez, France) that had been previously determined to be pitch derived from

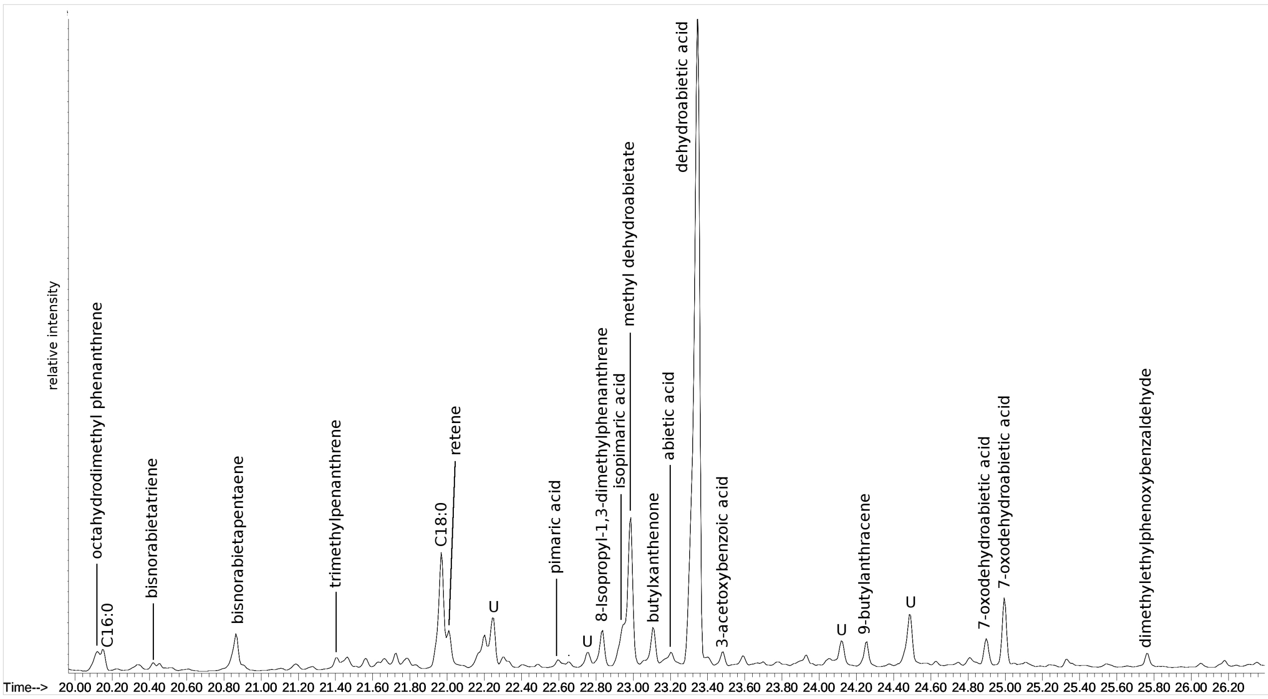


Figure 5.2: Partial total ion chromatogram (TIC) of the trimethylsilyated total lipid extract (TLE) of a sample from a Keay 25.1 amphora (AIX/42). 'U' denotes an unknown compound.

Pinaceae resin.[3] The modern replication sample was composed of a combination of the archaeological pitch, lamb's liver and European sprat sample materials to create a sample material with a wide variety of both fatty and resin acids. Archaeological samples were selected from Late Roman amphorae and unguentaria recovered from the excavations of central Beirut, Lebanon by the Anglo-Lebanese Beirut Souks excavation.

5.7.2.1 Extraction Method

The extraction protocol was that developed by Correa-Ascencio and Evershed (2014). Samples were placed in screw-top 10 ml centrifuge tubes with PTFE-lined caps and extracted with 4 ml of 2% sulfuric acid in methanol (v/v) for 60 minutes at 70 °C in a sonicated bath. After sonication, samples were centrifuged at 2500 RPM for 10 minutes to separate the extraction solvent from insoluble matter. Solvent was checked to verify the pH was below 2 and then removed to a clean vessel and diluted with 2 ml of water. The solvent was twice

[3] Woodworth et al. 2015.

liquid-liquid extracted with 3 ml of hexane and evaporated to dryness under a stream of nitrogen and then reconstituted in a known amount of hexane/chloroform (5:1 v/v).

5.7.2.2 SPE Fractionation

The 4-fraction separation method was adapted from that used by Gutiérrez et al. (1998). The SPE was pretreated with 8 ml hexane. Samples were prepared at a volume of 60 µl in hexane/chloroform (5:1 v/v). After loading, the sample was fractioned and individually collected with 4 ml each of hexane, 4 ml hexane-chloroform (5:1 v/v), chloroform and, finally, diethyl ether with 2% acetic acid (v/v). A simplified extraction protocol was also used. Samples were separated into two fractions: first with 4 ml chloroform and, secondly, with 4 ml diethyl ether with 2% acetic acid.

5.7.2.3 Post-Fractionation Sample Preparation

Each sample fraction was evaporated under a stream of nitrogen until dry and derivatized with 50 µl of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) by heating at 70 °C for 60 minutes. 10 µl of tetratriacontane (0.500 mg/ml) was added as an internal standard.

5.7.2.4 Analytical Conditions

Samples were analyzed by GC/MS using an Agilent 7820A gas chromatograph equipped with a Restek Rxi-5ms column (30 m length, 0.25 mm ID, 0.25 µm film thickness) and an Agilent 5975 quadrupole mass spectrometer. The temperature program for the GC oven was a 50 °C hold for 2 minutes, 50-300 °C at 10 °C/min with a 10 minute isothermal hold at 300 °C. Helium was used as the carrier gas; flow rate was 1.2 ml/min. Injection volume was 1 µl. Samples were initially assayed at a split ratio of 25:1 and subsequent injections at either 10:1 or splitless depending upon the concentration of analytes in the sample. Injector temperature was 300 °C, transfer line temperature was 280 °C. Electronic ionization was 70 eV and the mass scan range was *m/z* 40-650. Compound identification was achieved by comparison of mass spectra against the NIST11 mass spectral database.

5.7.3 *Results and Discussion*

The fractionation method was first tested on the modern replication sample in order conserve archaeological material during method development. The four fraction separation method produced good separation of analyte classes in the modern sample (Figure 5.3-5.6). The first fraction contained n-alkanes. The second fraction (hexane/chloroform) contained FAME's, methyl dehydroabietate and trace quantities of two benzene species. The third fraction (chloroform) contained sterols (specifically cholesterol) as well as several varieties of plasticizers. Predominant plasticizers observed in the fraction included isobutyl trans-hex-3-enyl ester phthalic acid, dibutyl phthalate, butyl citrate and bis(2-ethylhexyl) phthalate. The fourth fraction (acidified diethyl ether) contained dehydroabietic acid as well as the saturated fatty acids $C_{16:0}$ and $C_{18:0}$ and the monounstaturated fatty acid $C_{18:1}$, all of which were present as their trimethylsilyl esters. The general results were similar to that of produced by lipophilic wood extracts by Gutiérrez et al. 1998. However, the fractionation of fatty acids from predominantly resin acids was possible by introducing them as FAME's as derived by the extraction method. The only resin acid co-elution occurred with the elution of methyl dehydroabietate in the fraction containing FAME's (Fraction 2). This was considered to have negligible effect on the utility of the separation protocol as methyl dehydroabietate is (1) generally present in relatively low concentration relative to fatty acids and (2) methyl dehydroabietate does not co-elute with any of the FAME species. It should be noted, however, that the extraction procedure result in the production of small amounts of methyl dehydroabietate by methylation of dehydroabietic acid (data not shown). If this analyte is of particular interest, conventional lipid extraction and preparation by silylation (e.g. Charters et al. 1993) is preferable.

Some fatty acids, as their trimethylsilyl esters, were present in some of the samples fractions– $C_{16:0}$ in Fraction 2; $C_{16:0}$ and $C_{18:0}$ in Fraction 3 and relatively significant quantities of $C_{14:0}$, $C_{16:0}$. $C_{18:0}$ and $C_{18:1}$ in Fraction 4. Comparison against laboratory blanks indicate that the source of the FFAs was the SPE cartridge, probably from the cartridge walls, as opposed to, for example, incomplete methylation of the sample's FFAs. The in-

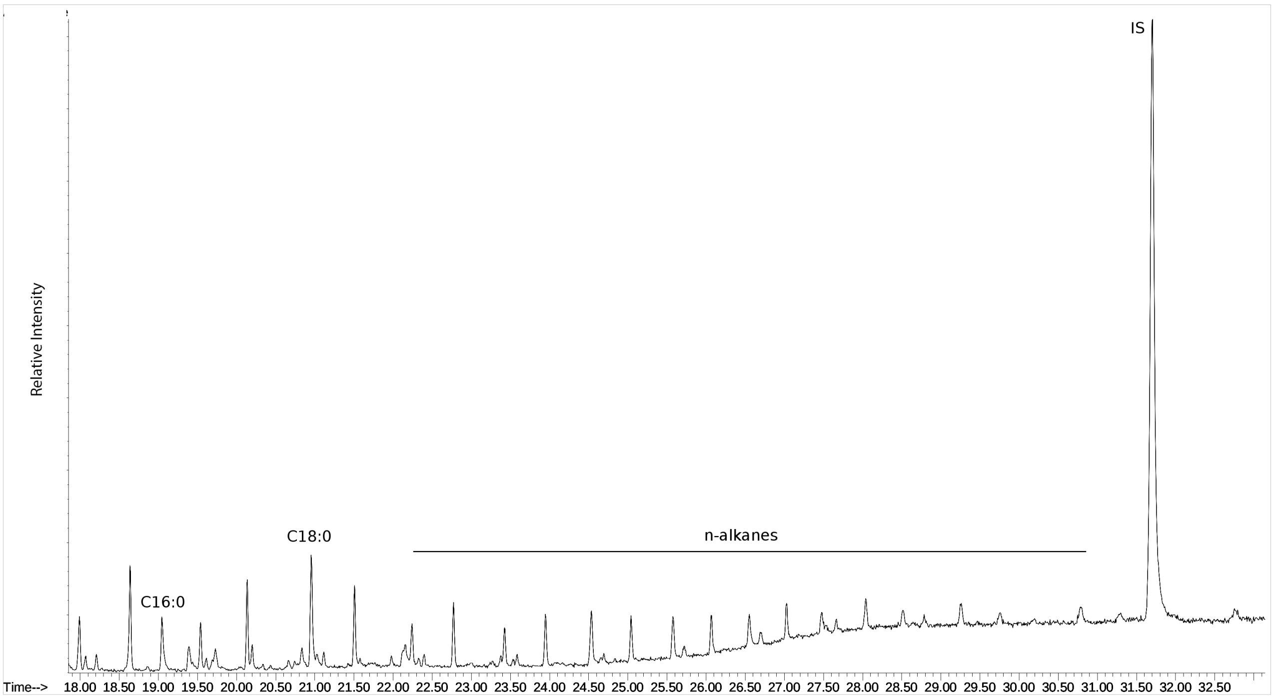


Figure 5.3: Fraction 1 (hexane) of the modern replication sample. 'IS' is the internal standard.

crease in FFA elution with increasing solvent polarity is also consistent with leaching from the cartridge's plastic body. Contamination levels were negligible in Fractions 2 and 3 and did not co-elute with any other analytes. While relative quantities were significant in Fraction 4, again no co-elution occurred. The use of glass syringes with bulk stationary phase media should minimize or eliminate FFA presence as well as plasticizers, especially those present in Fraction 3. While the adapted 4 fraction method resolved the issue of separating predominant resin acids from fatty acids, the method results in 16 ml of solvent split between 4 fractions that must be evaporated and 4 fractions that must be analyzed. As such, the fractionation method is not entirely consistent with the extraction method, the purpose of which is to permit high-throughput sample analysis. A simplified two fraction (chloroform and acidified diethyl ether) separation was evaluated first using the modern replication sample (Figure 5.7). The simplified separation method eluted n-alkanes, FAMEs and sterols (cholesterol) in the first fraction (chloroform). Primary resin acids were eluted in the second fraction (acidified diethyl ether). Methyl dehydroabietate and retene were observed to have been eluted in the first fraction. However, like that of the four fraction separation, they were

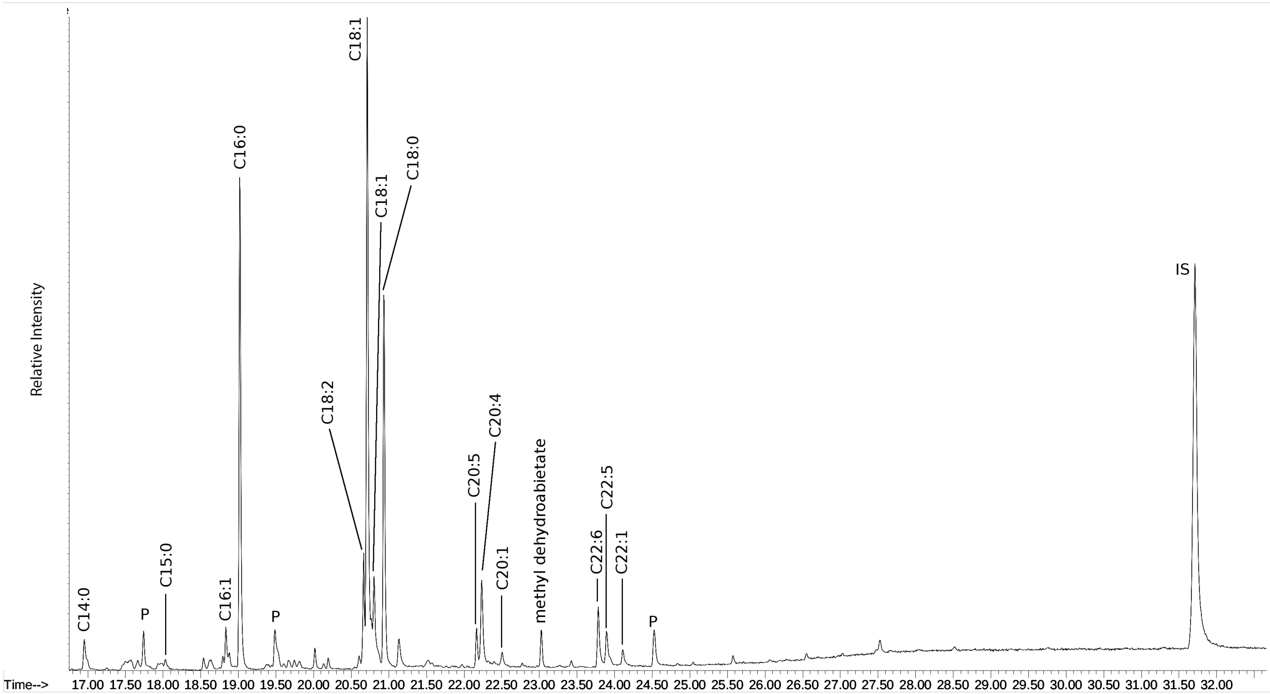


Figure 5.4: Fraction 2 (hexane/chloroform) of the modern replication sample.

of relatively low concentration (with respect to FAMEs) and did not co-elute with any other analytes. Analysis of archaeological material was also evaluated using the two fraction separation method. The material included late Roman amphorae and unguentaria. Some samples had been previously analyzed after extraction (prior to fractionation) and were observed to have significant quantities of resin acids that necessitated analyses be conducted with a high split ratio (generally 50:1 or 25:1).

Figures 5.8 and 5.9 illustrate a representative example of the fractioned archaeological samples in which fatty acid constituents were overwhelmed by significant quantities of resin acids, primarily dehydroabietic acid. The sample is from a late Roman amphora that had been previously extracted and analyzed (at a split ratio of 25:1). While the significant amounts of FAMEs were observed, high concentrations of resin acids (predominated by dehydroabietic acid) with several partial co-elutions and required analyses with a high-split ratio, preventing analysis of trace analytes, such as sterols and minor fatty acids constituents which are present in low concentrations. The first fraction eluted FAMEs and demonstrated a wide variety of FAMEs, ranging in chain-length up to 26 carbons, predominated by $C_{24:0}$.

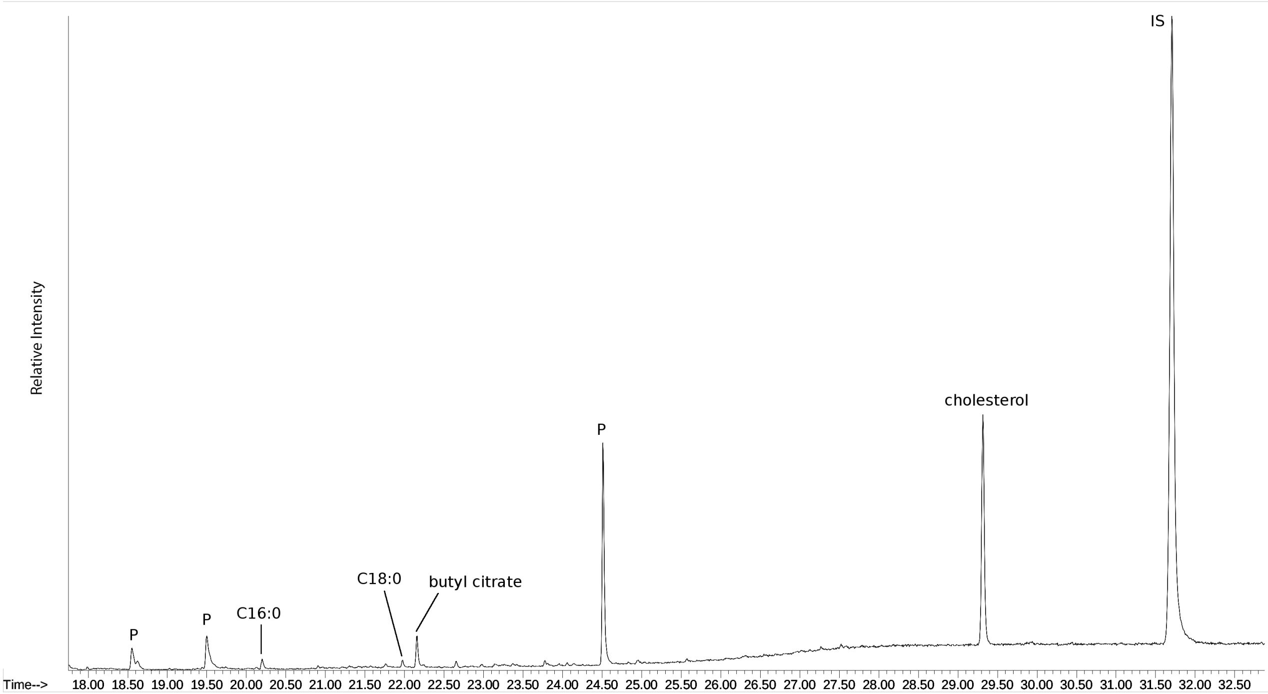


Figure 5.5: Fraction 3 (chloroform) of the modern replication sample.

The plant sterol, β-sitosterol, was also observed. The fraction also contained very long chain fatty alcohols (docosanol and tetracosanol). Like the modern replication sample, archaeological samples eluted retene and methyl dehydroabietate in the first fraction with FAMEs and sterols; however, levels were low enough to permit splitless injection and did not co-elute with any other compounds. Some phenanthrene species were observed in the chloroform fractions of archaeological samples, understood to be partial combustion by-products constituents of pitch. As per retene and methyl dehydroabietate, levels were low (relative to FAMEs) and no co-elution with analytes of interest was observed. The second fraction, containing resin acids, were analyzed with a split ratio. Archaeological samples presented similar separation profiles to that of the replication sample. Typical resin acids included pimaric, isopimaric, dehydroabietic (the predominant resin acid) as well as other resin acid oxidation by-products (e.g. 7-oxodehydroabietic acid). Polyaromatic hydrocarbon (PAH) combustion by-products were also detected. The fractionation of samples using aminopropyl SPE cartridges has demonstrated the ability to separate analyte classes of archaeological samples in order to allow detailed analysis of complex sample matrices. Specifically, the separation of

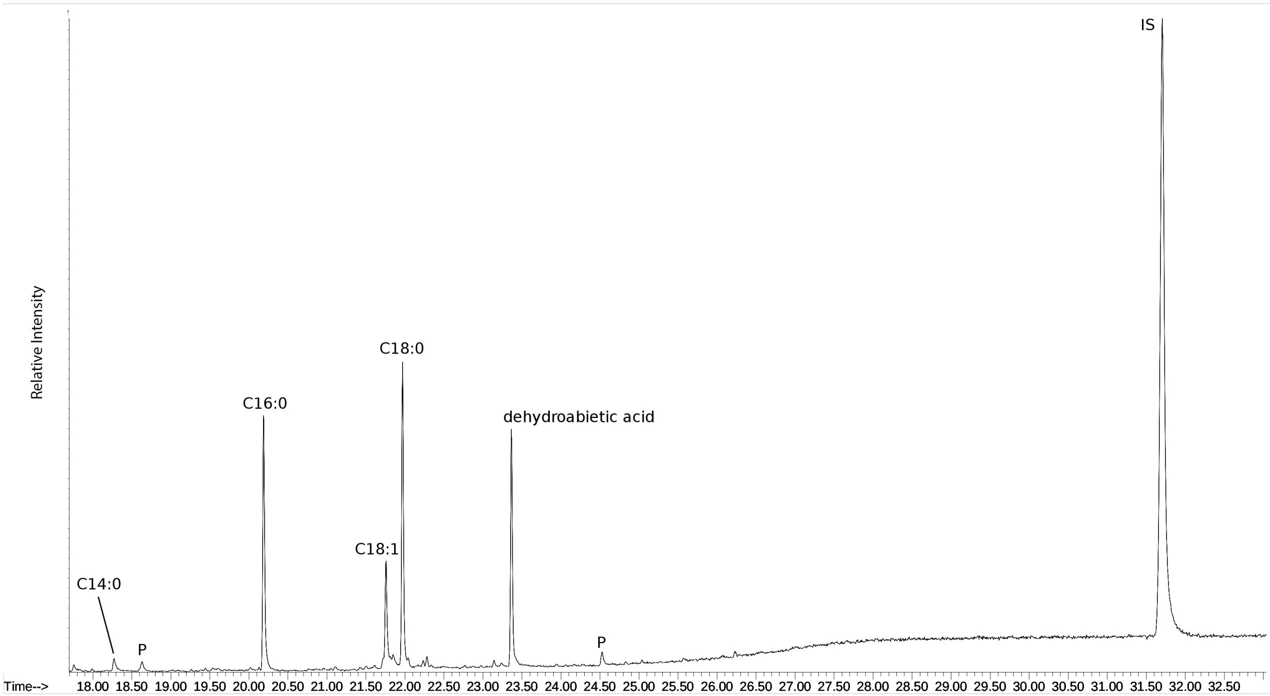


Figure 5.6: Fraction 4 (acidified diethyl ether) of the modern replication sample, compounds represented as their trimethylsilyl esters.

resin acids from other analytes of interest permits trace analysis of FAMEs and sterols when significant quantities of pitch constituents are present. By simplifying the fractionation to a two-part separation, large numbers of samples may still be processed, consistent with the aims of the extraction protocol.

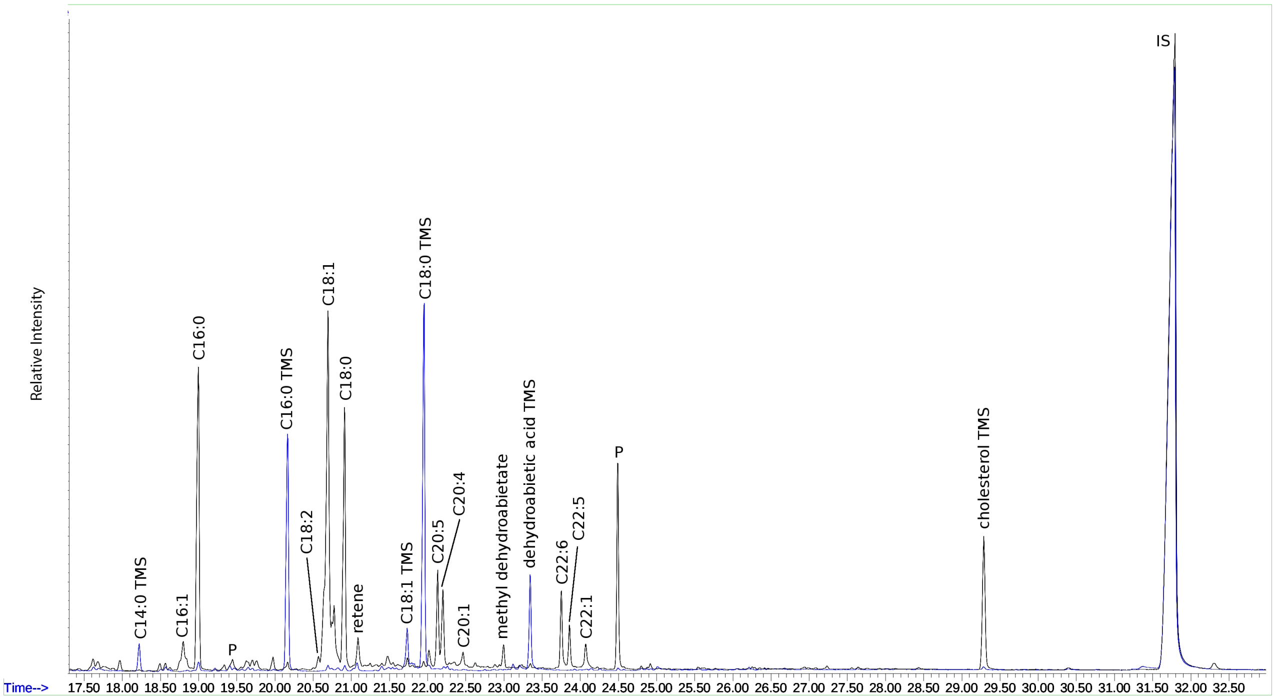


Figure 5.7: Overlay of the partial total ion chromatograms of the fractions of the modern replication sample using 2 fraction separation. Fraction 1 (chloroform) in black; Fraction 2 (acidified diethyl ether) in blue.

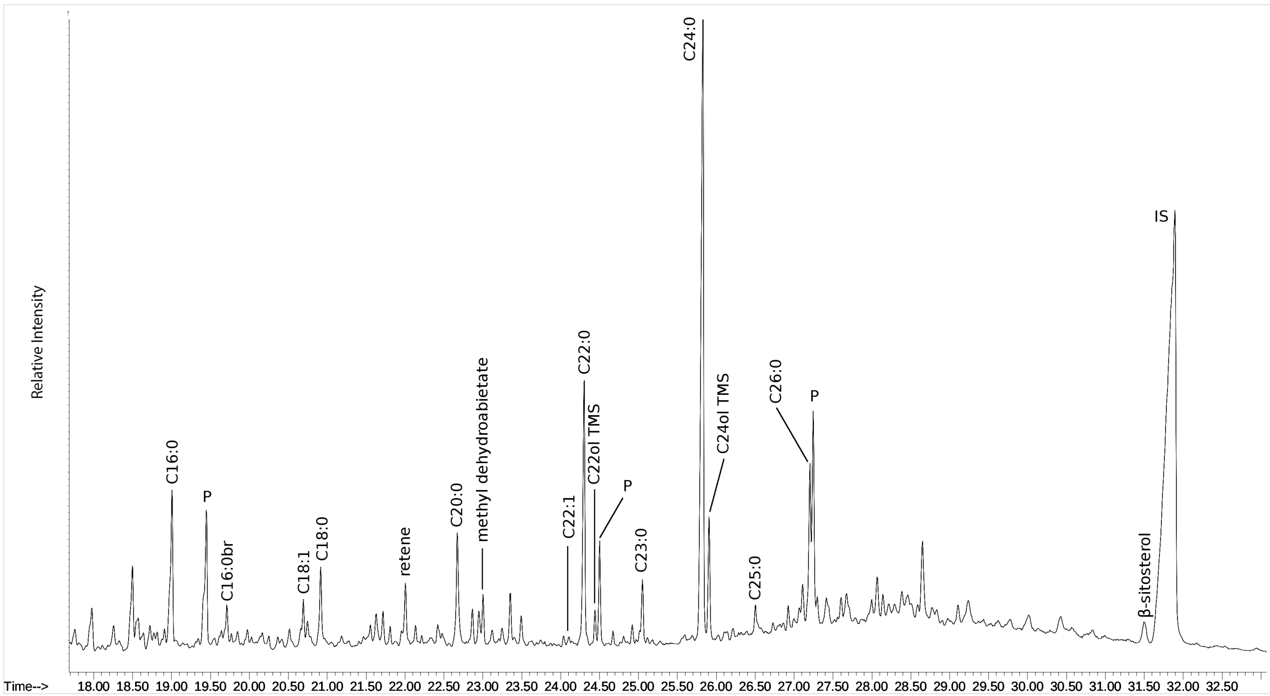


Figure 5.8: Fraction 1 (chloroform) of a late Roman amphora believed to originate from the region of Sinope (Reynolds fabric group FAM62B).

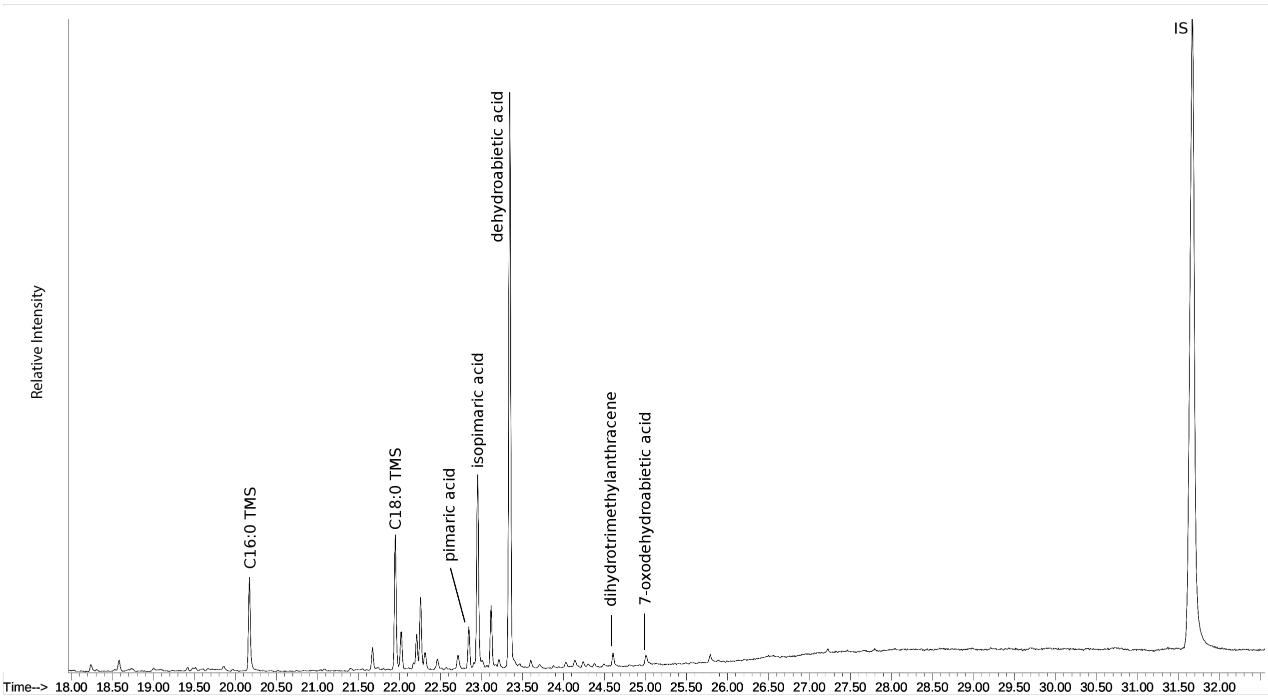


Figure 5.9: Fraction 2 (acidified diethyl ether) of a late Roman amphora from the region of Sinope, compounds represented as their trimethylsilyl esters. Analysis conducted with a split ratio of 10:1.

5.8 Analysis of $C_{18:1}$ positional isomers

5.8.1 Introduction

5.8.2 Materials

All reagents were GC grade (with the exception of sulfuric acid which was ultra-trace grade) and were obtained from Sigma-Aldrich (Gillingham, UK). Water was obtained from an in-house MilliQ water system. Five modern plant oils were selected for analysis. Olive and grapeseed oils were obtained from Tesco Stores Ltd. (Cheshunt, UK), mustard oil from KTC (edibles) Ltd (Wednesbury, UK), and sesame oil and sunflower oil from Sainsbury's Ltd. (London, UK). Nine fish species were chosen for analysis (Table 5.1). In addition, two terrestrial ruminant samples were also analyzed: lamb tissue was obtained from Lewis's Butchers (Bicester, UK) and the NIST 1577b Bovine Liver Standard (NIST Standard Reference Material). Archaeological samples were selected from Late Roman amphorae recovered from the excavations of central Beirut, Lebanon by the Anglo-Lebanese Beirut Souks excavation. Sample selection was based on previous analyses that indicated possible biomarkers or lipid profiles consistent with marine products.

5.8.3 Method Extraction, Saponification and Methylation

Approximately 10 g of each frozen tissue sample was macerated and homogenized, from which 1 g was removed for extraction. Approximately 150 mg of the vegetable oils and 200 mg of the bovine liver standard were used for extraction. The extraction protocol, adapted from Correa-Ascencio and Evershed (2014), permits single step extraction, saponification and methylation of fatty acids. Samples were placed in screw-top 10 ml centrifuge tubes with PTFE-lined caps and extracted with 4 ml of 2% sulfuric acid in methanol (v/v) for 60 minutes at 70 °C in a sonicated bath. After sonication, samples were centrifuged at 2500 RPM for 10 minutes to separate the extraction solvent from insoluble matter. Solvent was removed to a clean vessel and diluted with 2 ml of water. The solvent was twice liquid-liquid extracted with 3 ml of hexane and evaporated to dryness under a stream of nitrogen and then reconstituted in a known amount of hexane. Samples were stored at -20 °C until analysis. A blank was prepared with each sample batch to control for intra-laboratory contamination. Immediately prior to GC/MS analysis, an aliquot of the prepared sample was transferred to a 2 ml auto-sampler vial and diluted with 990 ml hexane to which 10 µl of tetratriacontane (0.500 mg/ml in hexane) was added as a standard.

5.8.4 Preparation of DMDS Adducts

DMDS adducts were prepared after the method used by Nichols et al. (1986). In short, an aliquot of the methylated sample was transferred to a clean 2ml vial. Carrier solvent was evaporated under a gentle stream of nitrogen. 100 µl of dimethyl disulfide and 2 drops of iodine in diethyl ether (6% w/v) were added. The vials were sealed with a PTFE-lined cap, briefly vortexed and stored at room temperature. After 24 hours, the reaction was stopped by the addition of 500 µl of aqueous sodium thiosulfate (5% w/v) and then 3 times extracted with 1 ml hexane. The hexane was evaporated under a stream of nitrogen and then reconstituted with 990 µl hexane to which 10 µl of tetratriacontane (0.500 mg/ml in hexane) was added as a standard.

5.8.5 Analytical Conditions

Samples were analyzed by GC/MS using an Agilent 7820A gas chromatograph equipped with a Restek Rxi-5ms column (30 m length, 0.25 mm ID, 0.25 µm film thickness) and an Agilent 5975 quadrupole mass spectrometer. The temperature program for the GC oven was a 50 °C hold for 2 minutes, 50-300 °C at 10 °C/min with a 10 minute isothermal hold at 300 °C. Helium was used as the carrier gas; flow rate was 1.2 ml/min. Injection volume was 1 µl. Samples were initially assayed at a split ratio of 25:1 and subsequently injected at either 25:1, 10:1 or splitless dependent upon the concentration of analytes in the sample. Injector temperature was 300 °C, transfer line temperature was 280 °C. Electronic ionization was 70 eV and the mass scan range was *m/z* 40-650. Compound identification was achieved by comparison of mass spectra against the NIST11 mass spectral database.

5.8.6 FAME Analysis

For FAME analyses, the temperature program for the GC oven was a 50 °C hold for 2 minutes, 50-300 °C at 10 °C/min with a 10 minute isothermal hold at 300 °C. Flow rate was 1.2 ml/min (constant flow). Injector temperature was 300 °C, transfer line temperature was 280 °C. Helium was used as the carrier gas. Electronic ionization was 70 eV and the mass scan range was *m/z* 40-650. Compound identification was achieved by comparison of mass spectra against the NIST11 mass spectral database.

5.8.7 DMDS Adduct Analysis

For DMDS adduct analyses, the temperature program for the GC oven was a 50 °C hold for 2 minutes, 10 °C/min to 270 °C, and then 4 °C/min from 270 °C to 300 °C with a 10 minute isothermal hold. Flow rate was 1.0 ml/min (constant flow). Injector temperature was 300 °C, transfer line temperature was 280 °C. Helium was used as the carrier gas. Electronic ionization was 70 eV. DMDS adduct samples were analyzed with two mass scan ranges: 40-650 m/z and 70-395 m/z. Compound identification was achieved by comparison of mass spectra against the NIST11 mass spectral database and published literature.

5.8.8 Results

FAME Analyses Samples were first analyzed to determine FAME composition prior to DMDS adduct analysis. Vegetable oils were typically predominated by $C_{18:1}$ and $C_{18:2}$ fatty acids with lesser quantities of saturated $C_{16:0}$ and $C_{18:0}$ fatty acids. Mustard oil presented a different profile—$C_{22:1}$ as well as $C_{20:1}$ were also observed, consistent with the published literature in modern and archaeological samples.[4] In olive oil samples, $C_{18:1}$ was the predominant fatty acid with lesser amounts of $C_{16:0}$, $C_{18:0}$ and $C_{18:2}$ (Figure 5.10). A significant presence of squalene was detected as well as trace amounts of $C_{16:1}$, also consistent with the published literature.[5] All vegetable oil samples contained significant levels of $C_{18:1}$ as a percentage of total fatty acids with olive oil having the highest. Fish samples were characterized by the prominence of polyunsaturated fatty acids (PUFAs) such as $C_{20:4}$, $C_{20:5}$, $C_{22:5}$ and $C_{22:6}$ (see Figure 5.11 for the chromatogram of the FAME analysis of the mackerel sample). Primary monounsaturated fatty acids (MUFAs) were $C_{18:1}$ and $C_{20:1}$. Small quantities of $C_{17:1}$ and the isoprenoid fatty acid 4,8,12 trimethyltridecanoic acid were also consistently observed in the fish samples. A sample of recently butchered lamb tissue was analyzed as a reference sample for $C_{18:1}$ isomeric distribution in ruminants. Fatty acid composition was

[4] Alim et al. 2012; Colombini et al. 2005b.

[5] Owen et al. 2000; Dubois et al. 2007, respectively.

predominated by $C_{18:1}$ and secondarily by $C_{16:0}$ and $C_{18:0}$ fatty acids. PUFAs were represented by $C_{20:4}$, $C_{20:5}$, $C_{22:5}$, $C_{22:6}$ as well as $C_{18:2}$ and small quantities of $C_{18:3}$. The MUFAs $C_{16:1}$ and $C_{17:1}$ were observed as well as low quantities of branched $C_{15:0}$ and $C_{17:0}$ fatty acids. The bovine liver standard, manufactured in 1991 and stored at room temperature, was included as an 'aged' modern ruminant reference sample. The fatty acid profile was depleted in unsaturated fatty acids. The only PUFA detectable was a low quantity of $C_{18:1}$. The absence of any significant quantities of PUFAs and the reduction in $C_{18:1}$ (relative to $C_{16:0}$ and $C_{18:0}$) compared to the the fresh liver sample is consistent with the susceptibility of double bounds to hydrolysis and oxidation.[6]

5.8.8.1 DMDS Derivative Analyses

$C_{18:1}$ positional isomer samples were first analyzed with a mass scan range of *m/z* 40-650 and then reanalyzed with a limited mass scan range of *m/z* 70-395. The broader scan range permitted a full assay of eluted compounds and an evaluation of peak purity for the target analytes (i.e. $C_{18:1}$ isomers). The limited scan range was selected as diagnostic fragment ions of DMDS derivatives of $C_{18:1}$ positional isomers fall within the range of *m/z* 75-315 with the M^+ ion at *m/z* 390 (Table 5.2) under electron ionization. Ruminant tissue samples are known to demonstrate a wide variety of positional $C_{18:1}$ isomers due to 'biohydrogenation of unsaturated fats in the rumen'.[7] The ruminant samples were used as reference samples for complex positional $C_{18:1}$ isomer mixtures. The reference samples were used to establish the retention time of the different isomers for which commercial reference standards are not available and were used for optimization of isomer separation during method development. The ruminant reference samples produced chromatograms in which $C_{18:1}$ positional isomers were predominated by ${C_{18:1}}^{\Delta 9}$ and ${C_{18:1}}^{\Delta 11}$ with lesser quantities of other $C_{18:1}$ positional isomers Analyses of the vegetable oils produced consistent results. A single $C_{18:1}$ positional isomer, ${C_{18:1}}^{\Delta 9}$ was identified by the diagnostic fragmentation ions at *m/z* 173 and 217, and

[6]Evershed et al. 1995.

[7]Mottram et al. 1999, 217.

M+ ion at *m/z* 390. Trace amounts of ions with a *m/z* of 145 and 245 eluting after the $C_{18:1}{}^{\Delta 9}$ peak indicating trace quantities of $C_{18:1}{}^{\Delta 11}$ in three vegetable oil samples: olive oil, mustard oil and sunflower oil. The quantity of $C_{18:1}{}^{\Delta 11}$ as percentage total of $C_{18:1}$ positional isomers was determined to be approximately 0.5% and 0.65% in the olive oil and mustard oil samples, respectively. Extracted ion analysis was necessary to identify the $C_{18:1}{}^{\Delta 11}$ constituent of the sunflower oil sample. Due to low concentration it could not be quantified but was estimated to be under 0.1% of total $C_{18:1}$ isomers. $C_{18:1}{}^{\Delta 11}$ was not identified in the other vegetable oil samples. Analysis of the fish samples indicated a common trend among all the samples analyzed. $C_{18:1}$ positional isomers were characterized by a predominance of $C_{18:1}{}^{\Delta 9}$ with $C_{18:1}{}^{\Delta 11}$ as a significant secondary isomer (Table 5.3). No other positional isomers were observed in the samples. The relative amount of $C_{18:1}{}^{\Delta 11}$ relative to $C_{18:1}{}^{\Delta 9}$ varied significantly between different fish species. With one outlier, that of basa fish (*Pangasius bocourti*), $C_{18:1}{}^{\Delta 11}$ represented between 14.1% to 46.7% of total $C_{18:1}$ isomers. The average proportion of $C_{18:1}{}^{\Delta 11}$ was 24.3% (26.4% if the basa fish sample is excluded). Atlantic cod (*Gadus morhua*) and Alaskan pollock (*Theragra chalcogramma*) demonstrated the largest proportion of $C_{18:1}{}^{\Delta 11}$ with 46.1% and 46.7%, respectively. Basa fish contained the least with only 7.2%, significantly lower than the second lowest proportion sample, Rainbow trout (*Oncorhynchus mykiss*), at 14%. While a limited number of species were studied, 4 of 9 species fell within the range of 20-23%. In addition to basa fish and rainbow trout, the farmed Atlantic salmon (*Salmo salar*) sample contained a lower than average percentage of $C_{18:1}{}^{\Delta 11}$ (18%). While the consistency of the composition of $C_{18:1}$ isomers is significant, the underlying cause for the wide distribution in the percentage of $C_{18:1}{}^{\Delta 11}$ is not immediately apparent, which is, at least in part, due to sample size. For example, Alaskan pollock and Atlantic herring (*Clupea harengus*) demonstrated widely different $C_{18:1}{}^{\Delta 11}$ ratios, pollock having the highest proportion of $C_{18:1}{}^{\Delta 11}$ (46.7%) in the analyzed samples while herring had an 'average' amount at 21.9%. Both species are small fish that feed on zooplankton, including copepods; however, in addition to being from geographically distinct regions (the Bering Sea and the north Atlantic, respectively), herring are semi-plagic foragers while pollock are demersal. The ratio may be affected by food source, for example, where the $\Delta 11$ isomer is present, not from *de novo* synthesis by fish but obtained from its food source. The $C_{18:1}$ positional isomers of copepods have been previously researched and demonstrated to possess a $C_{18:1}$ isomeric profile in which $\Delta 9$ is the predominant isomer with significant quantities of $\Delta 11$.[8] Considerable variation was observed between species and different latitudes, although the authors were not able to model variation in lipid composition of copepods in general due to limited data, the multiplicity of factors that may affect lipid composition (such as seasonality, latitude, etc.) as well as a limited understanding of biosynthetic pathways and metabolism that may also affect lipid composition. If the $\Delta 11$ isomer were a result of the absorption of lipids from zooplankton rather than *de novo* synthesis by the fish itself, one would expect to observe a trophic effect where fish species positioned higher on the food chain were depleted in the $\Delta 11$ isomer relative to those species lower on the food chain. Yellow-fin tuna subsist on smaller fish species, pelagic crustacea and squid. Atlantic cod is an apex predator. Smaller cods primarily feed upon crustacea, whereas larger cod feed on fish such as mackerel, haddock and herring.[9] While both of these species are positioned high on the food chain, the relative proportion of $\Delta 11$ was significantly different. Cod had 46.1% $\Delta 11$, the second highest percentage, while tuna had 19.7%. The diet of smaller cod, however, more closely resembles that of smaller fish species (such as herring) and this diet may be, at least in part, responsible for the observed isomeric distribution. The size of the fillets used in analysis indicate that the cod would have been a smaller cod (>50 cm in total length). Cod overfishing, as well as resulting trophic cascades due to the depletion of larger cods in the population, has been well documented.[10] Geographical location also appears to have a significant role in diet. The analysis of stomach content of cods in Daan (1973) indicated that small cods (<50 cm in length) derived approximately one-third of their diet from commercial fish species (e.g. Atlantic mackerel, whiting, haddock, other cods) in the northern North Sea, while similarly sized specimens from the southern North Sea received

[8]Kattner and Hagen 2009.

[9]Daan 1973.

[10]Frank et al. 2005.

less than 6% of their diet from these sources. As such, if $\Delta 11$ is obtained, at least in part, from diet, one would expect an isomeric differential between similarly sized cod specimens from different regions of the North Sea. As indicated in Table 5.3, basa fish presented itself as an outlier, having a very low relative quantity of ${C_{18:1}}^{\Delta 11}$ compared to other fish species samples. In addition to having an outlying $C_{18:1}$ isomeric profile, basa fish also presented a different fatty acid profile. Basa fish was especially enriched in $C_{20:4}$ (6.57%) compared to other analyzed species samples ($\leq$1%). Conversely, $C_{22:6}$ was depleted in comparison (2.24%) compared to an average of 18.4% for other species. Unlike other fish samples, several PUFA species, $C_{20:5}$, $C_{20:4}$ and $C_{22:6}$, were noticeably absent in basa fish. The very-long chain MUFA, $C_{22:1}$, was also absent. Two PUFA species, $C_{20:3}$ and $C_{20:2}$, were observed only in the basa fish and rainbow trout samples. Although rainbow trout was not as depleted as basa fish in its relative ${C_{18:1}}^{\Delta 11}$ percentage (14.1% of total $C_{18:1}$ isomers), it did present some similarities to basa fish in its fatty acid composition. While the PUFA species absent in Basa were present in rainbow trout, they were the only species to lack $C_{22:1}$ and contain $C_{20:2}$ and $C_{20:3}$. It is notable that these represent the two freshwater species included in the study and two of the three farmed species. Previous study has indicated that fatty acid ratios, especially of some PUFA species, of freshwater fish do vary from that of saltwater fish; however, the mechanism for such is uncertain, in part due to the large number of possible contributing factors (e.g. diet, size, age, geographic location, etc.).[11] Unfortunately, the paucity of commercial freshwater fish species available at the time of study, and none of them non-farmed, in conjunction with the lack of any previous research on $C_{18:1}$ isomers in fish, prevent any conclusions as to the reason for the high isomeric ratio in basa, trout and, to a lesser degree, salmon.

[11] Diraman and Dibeklioglu 2009.

Table 5.1: List of fish species analyzed.

Common Name	Scientific Name	Source
European sprat	*Sprattus sprattus*	Sainsbury's Ltd.
Rainbow trout (farmed, UK)	*Oncorhynchus mykiss*	Sainsbury's Ltd.
Atlantic mackerel	*Scomber scombrus*	Sainsbury's Ltd.
Atlantic herring	*Clupea harengus*	Sainsbury's Ltd.
Alaskan pollock	*Theragra chalcogramma*	Sainsbury's Ltd.
Atlantic salmon (farmed, UK)	*Salmo salar*	Sainsbury's Ltd.
Basa fish (farmed, Vietnam)	*Pangasius bocourti*	Sainsbury's Ltd.
Yellow-fin tuna	*Thunnus albacares*	Sainsbury's Ltd.
Atlantic cod	*Gadus morhua*	Sainsbury's Ltd.

Table 5.2: Diagnostic fragment ions of DMDS derivatives of $C_{18:1}$ positional isomers by electron ionization, after Evershed (2000); Baeten et al. (2013).

Positional Isomer	Diagnostic Fragment Ions (*m/z*)
Δ^{7}	189, 201
Δ^{8}	187, 201
Δ^{9}	173, 217
Δ^{10}	159, 231
Δ^{11}	145, 245
Δ^{12}	131, 259
Δ^{13}	117, 273
Δ^{14}	103, 287
Δ^{15}	89, 301
Δ^{16}	75, 315

Table 5.3: Approximate percentages of $C_{18:1}\Delta^{11}$ as a total of $C_{18:1}$ positional isomers of the 9 fish species studied. Average of three analyses per sample.

Common Name	Percentage $C_{18:1}\Delta^{11}$
European sprat	22.7
Rainbow trout (farmed, UK)	14.1
Atlantic mackerel	22.3
Atlantic herring	21.9
Alaskan pollock	46.7
Atlantic salmon (farmed, UK)	18.0
Basa fish (farmed, somewhere in Asia)	7.2
Yellowfin tuna	19.7
Atlantic cod	46.1

Table 5.4: Fatty acid percentages of reference fish samples as determined by FAME analyses.

Sample	C14:0	Tridecanoic acid, 4,8,12-trimethyl	C15:0	C15:0br	C16:1	C16:0	C17:0	C16:0br	C17:1	C17:0br	C18:3	C18:2	C18:1	C18:0	C19:1
RT	**16.946**	**17.503**	**18.039**	**18.664**	**18.84**	**19.03**	**20.027**	**20.028**	**19.804**	**20.551**	**20.612**	**20.673**	**20.721**	**20.945**	**21.63**
pollock	1.52	tr	0.15	nd	2.24	21.20	0.13	tr	0.14	nd	0.42	0.71	13.05	3.21	nd
catfish	1.06	nd	nd	nd	1.36	19.29	nd	nd	tr	nd	nd	7.62	25.72	7.88	nd
cod	0.88	tr	0.28	tr	1.97	17.97	0.10	0.30	0.29	tr	nd	0.95	11.05	3.93	tr
herring	9.61	0.20	0.19	tr	4.31	19.27	nd	0.22	tr	nd	nd	2.17	9.53	1.40	nd
mackerel	4.21	tr	0.36	nd	4.35	15.23	nd	0.44	tr	nd	nd	1.52	20.72	3.55	nd
trout	1.01	nd	tr	nd	1.47	21.64	nd	0.18	tr	nd	nd	8.52	28.67	5.01	nd
salmon	2.49	nd	0.23	nd	3.59	18.17	0.18	nd	0.22	nd	0.57	8.62	27.84	3.41	nd
sprat	4.28	0.28	0.12	nd	4.67	22.00	0.21	nd	tr	nd	1.49	0.79	13.50	3.13	nd
tuna		tr	tr	nd	1.05	27.80	tr	nd	0.51	nd	nd	0.39	11.06	13.38	0.25
grapeseed oil	tr	nd	nd	nd	tr	7.37	tr	nd	nd	nd	nd	59.74	23.88	3.51	nd
mustard oil	tr	nd	nd	nd	nd	7.48	nd	nd	nd	nd	nd	36.68	34.67	2.76	nd
olive oil	tr	nd	nd	nd	0.41	9.21	nd	nd	nd	nd	nd	3.17	73.61	2.43	nd
sesame oil	nd	nd	nd	nd	nd	8.94	nd	nd	nd	nd	nd	33.98	44.04	4.77	nd
sunflower oil	tr	nd	nd	nd	tr	7.36	nd	nd	nd	nd	nd	57.58	26.59	4.65	nd
bovine	1.07	nd	0.52	tr	1.00	24.32	1.80	nd	nd	tr	nd	0.90	19.09	43.91	nd
lamb	1.60	nd	0.59	nd	2.67	17.71	0.78	0.47	0.59	tr	nd	5.76	30.72	16.18	0.11

Sample	C19:0	C20:5	C20:4	C20:3	C20:2	C20:1	C20:0	C22:6	C22:5	C22:4	C22:1	C22:0	C24:1	C24:0
RT	**21.841**	**22.234**	**22.391**	**22.316**	**22.465**	**22.472**	**22.710**	**23.789**	**23.891**	**23.823**	**24.108**	**24.325**	**25.663**	**25.825**
pollock	nd	18.95	0.79	nd	nd	3.12	nd	21.91	1.90	nd	0.82	nd	nd	nd
catfish	nd	nd	6.57	3.78	0.38	0.95	nd	2.24	nd	1.44	nd	nd	nd	nd
cod	tr	13.83	0.38	nd	nd	1.98	nd	28.68	2.54	nd	0.82	nd	nd	nd
herring	nd	5.60	0.59	nd	nd	8.82	nd	9.78	0.71	nd	9.99	nd	nd	nd
mackerel	nd	8.92	1.01	nd	nd	3.84	nd	12.81	nd	nd	2.68	nd	nd	nd
trout	nd	3.33	0.57	0.48	0.60a	1.56	nd	16.88	1.43	nd	nd	nd	nd	nd
salmon	nd	6.71	0.76	nd	nd	2.59	nd	17.61	2.46	nd	1.47	nd	nd	nd
sprat	nd	10.22	0.61	nd	nd	3.90	nd	17.25	1.28	nd	6.24	nd	nd	nd
tuna	nd	3.00	1.57	nd	nd	tr	nd	16.42	0.59	nd	nd	nd	nd	nd
grapeseed oil	nd	nd	nd	nd	nd	nd	0.35	nd	nd	nd	nd	0.33	nd	nd
mustard oil	nd	nd	nd	nd	nd	2.36	0.37	nd	nd	nd	6.79	0.46	0.35	0.15
olive oil	nd	nd	nd	nd	nd	nd	0.20	nd	nd	nd	nd	nd	nd	nd
sesame oil	nd	nd	nd	nd	nd	nd	0.55	nd	nd	nd	nd	0.18	nd	nd
sunflower oil	nd	nd	nd	nd	nd	0.30	0.41	nd	nd	nd	nd	0.89	nd	0.23
bovine	0.21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
lamb	tr	3.62	2.52	0.25	nd	nd	tr	3.88	3.74	nd	nd	nd	nd	nd

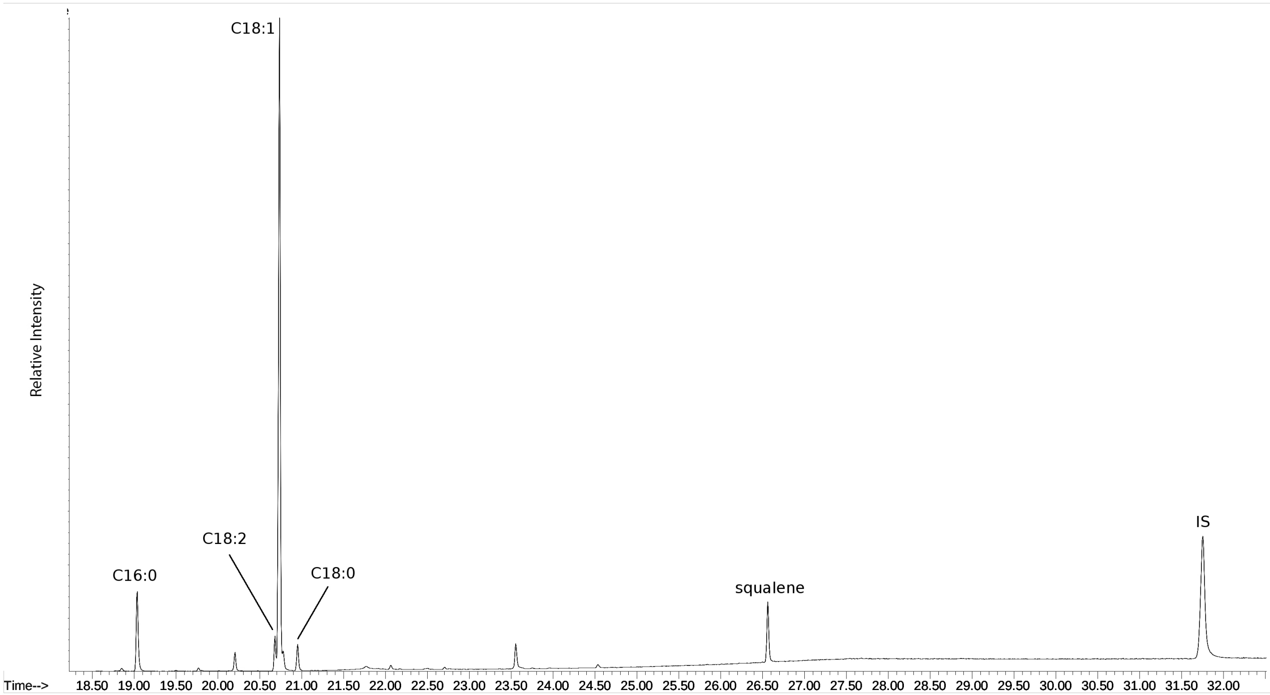


Figure 5.10: Partial total ion chromatogram of the FAME analysis of the olive oil sample.

5.8.9 Archaeological Sample Comparison

The $C_{18:1}$ positional isomer method was developed in anticipation that some of the Black Sea amphora types analyzed in this thesis may have been used to transport fish-based products. The case, however, is that examples of amphora samples in which biomarkers of marine commodities or biomarkers consistent with such were rarely observed. Only two examples within the primary research material were observed to contain organic compounds consistent with a marine-based commodity.[12] As a result, in order to test the validity of the method against archaeological samples samples were chosen from other amphorae not part of this study and other vessel types that contained biomarkers indicative of marine commodities as well as samples that either indicated a vegetable oil content or cooking pots that indicated a mixture of ruminant and marine lipids. The saponified extraction of an amphora believed to originate from the region of Sinope contained biomarkers indicative of a marine commodity (Fig. 5.12). The sample was characterized by a significant quantity of a large number of

[12]The samples consist of one amphora from the region of Sinope and one Colchean amphora. See Chapter 12 for the data analysis of Colchean samples, respectively.

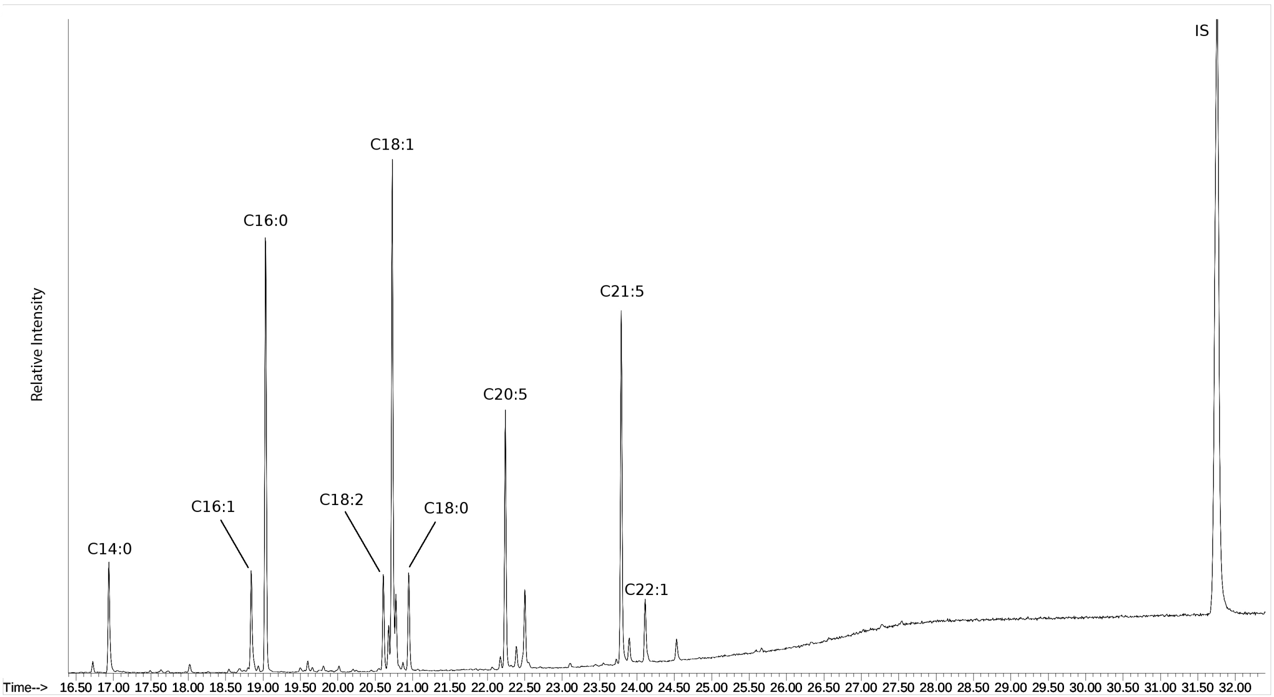


Figure 5.11: Partial total ion chromatogram of the methylated lipid extract of the mackerel sample with primary fatty acids identified (as their respective FAME's).

fatty acids and resin acids. Fatty acids were predominated by $C_{16:0}$ and $C_{18:0}$ with a significant quantity of $C_{18:1}$ (relative to $C_{16:0}$ and $C_{18:0}$). The very long-chain fatty acids $C_{22:1}$, $C_{22:0}$, $C_{24:1}$ and $C_{24:0}$ were also observed. A significant quantity of cholesterol was detected as well as the isoprenoid fatty acid 4,8,12 trimethyltridecanoic acid, which is considered a reliable indicator of marine commodities.[13] The sample was re-extracted using the single step extraction and derivatization method and converted to DMDS adducts. The resulting chromatogram indicated two positional isomers (${C_{18:1}}^{\Delta 9}$ and ${C^{18:1}}^{\Delta 11}$) consistent with the isomeric profile of modern fish samples.

[13]Hansel et al. 2004.

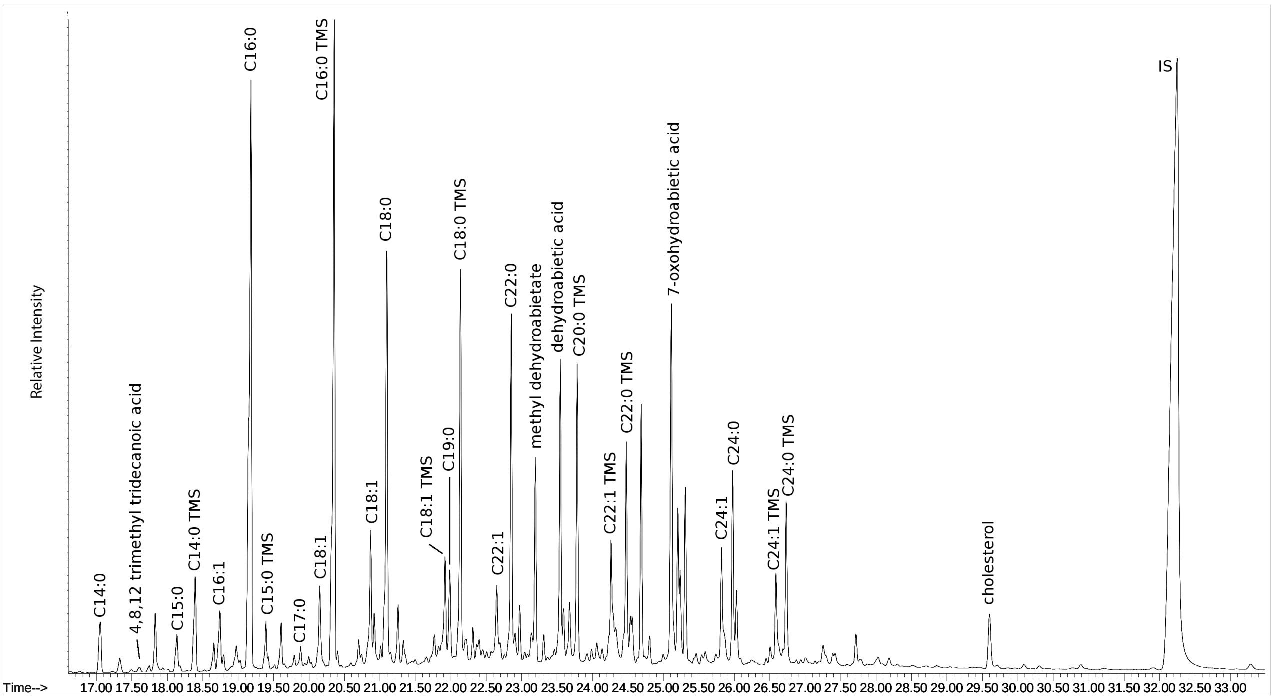


Figure 5.12: Partial total ion chromatogram of the saponified extract of an amphora believed to originate from the region of Sinope (Reynolds fabric group FAM 62B).

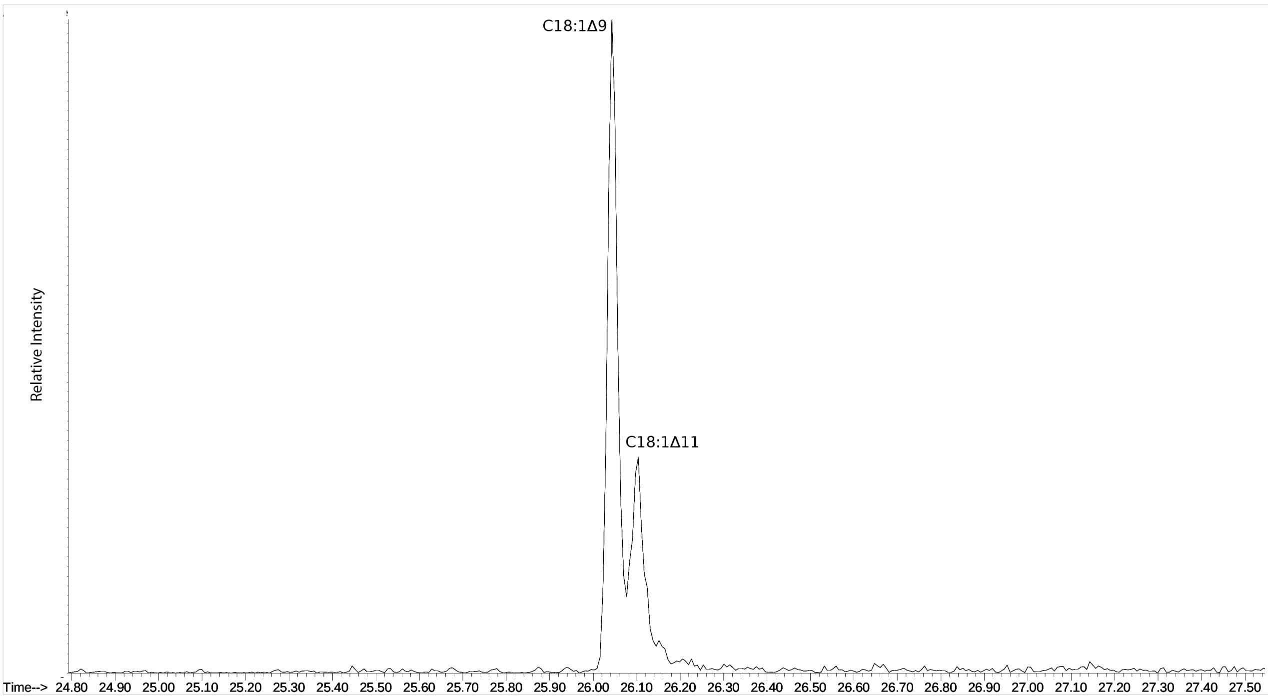


Figure 5.13: Partial extracted ion chromatogram (*m/z* 390) of DMDS adducts, indicating $C_{18:1}{}^{\Delta 9}$ and $C_{18:1}{}^{\Delta 11}$.

CHAPTER 6

BLACK SEA AMPHORA TYPES IN BEIRUT

6.1 Introduction

Ceramic assemblages from the Beirut excavations have been previously analyzed in order to determine trends in ceramic imports.[1] Inter-regional trade with the Black Sea region has been consistently observed in the excavated ceramics.[2] Ceramic assemblages dated to the early 3rd c. AD indicate eastern connections, including that of Black Sea amphorae.[3] The BEY 045 piscina fill, dated between 200 and 230 AD, 3rd century. Sinopean amphorae are well represented amongst imports, representing nearly 5% of total amphorae (approximately 16% of foreign imports).[4]

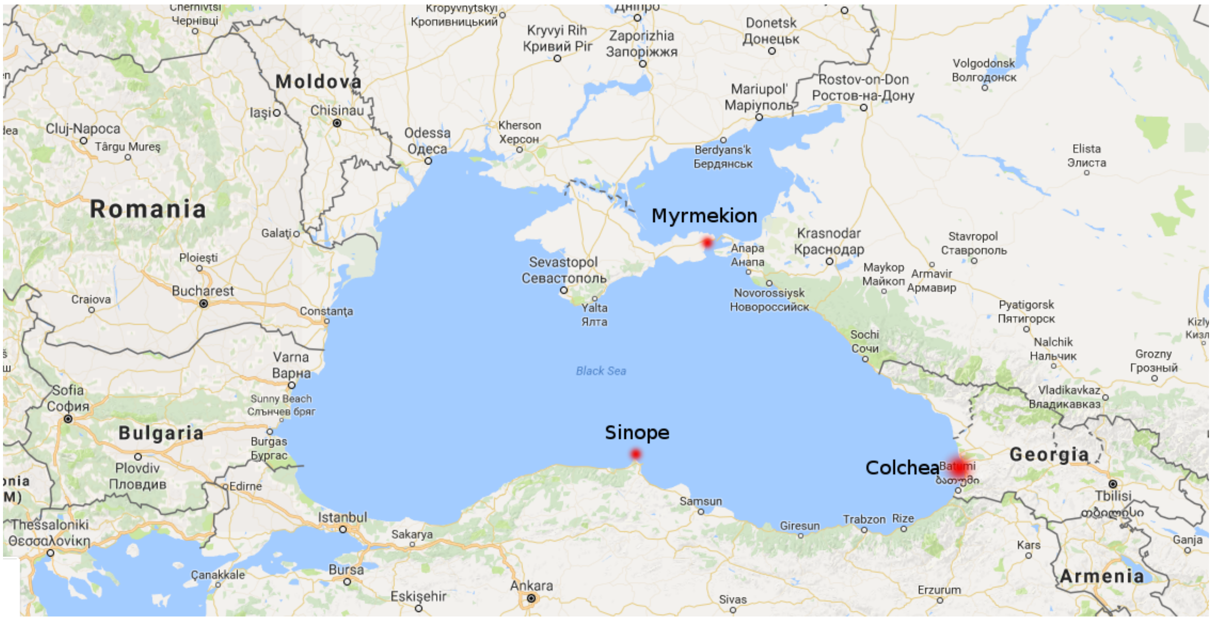


Figure 6.1: Principal known production sites of Black Sea amphorae examined in this study.

[1] *inter alia* Reynolds 2000, 1998, 2005; Reynolds and Waksman 2007; Reynolds 2010b.

[2] See Figure 6.1 and , illustrating primary Black Sea amphora production sites in this study.

[3] Reynolds 2010b, 89.

[4] Reynolds 2010b, Table 1.

Figure 6.3: Drawing of a mid 3rd c. AD Sinopean amphora. Adapted from Reynolds 2010b, Fig. 2e.

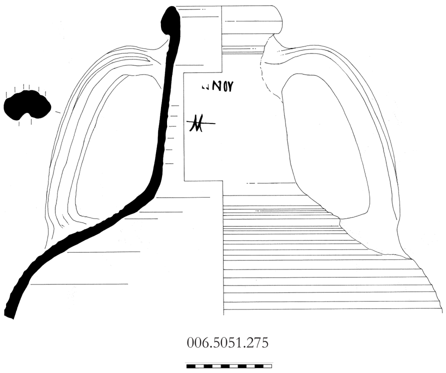


Figure 6.4: Drawing of a mid 3rd c. AD Zeest 72 amphora. Adapted from Reynolds 2010b, Fig. 2d.

The form is a large amphora with an orange-colored fabric (Fig. 6.3), similar to that of Kassab Tezgör's Snp I/III.[5] The other well-established Black Sea amphora type evidenced in

[5]Kassab Tezgör 2003.

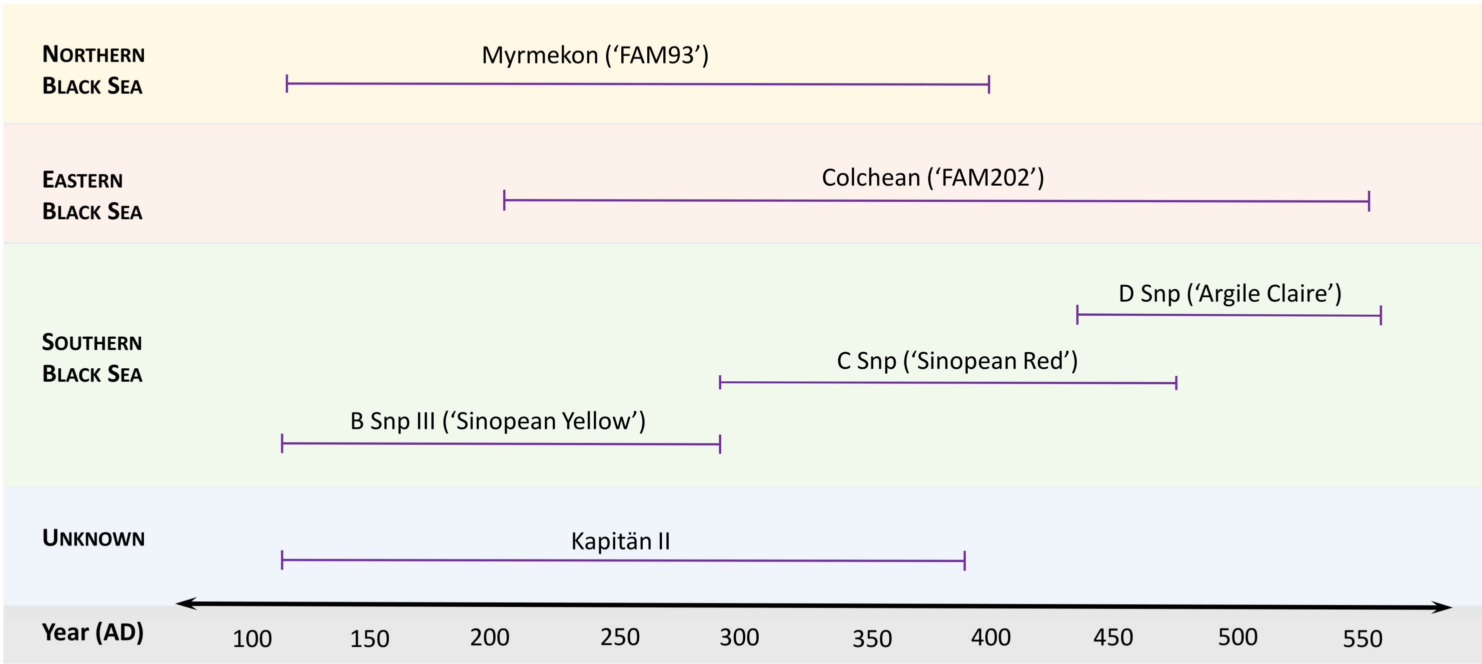


Figure 6.2: Chronology of analyzed Black Sea amphora types

this assemblage are Zeest 72/73 amphorae, representing a considerably smaller proportion of imports at 0.4% of total amphora (1.48% of imports) (Fig. 6.4).[6]

Kapitan 2 amphorae also share a relatively modest representation at 0.9% (nearly 3% of total imports).[7] Mid-3rd century deposits indicate a continuation of Black Sea imports but at a lower relative presence. Sinopean amphorae decline considerably (to 5% of total imported amphorae) while Zeest 72/73 and Kapitan 2 amphorae remain relatively constant (at 2% and 2.4%, respectively).[8]

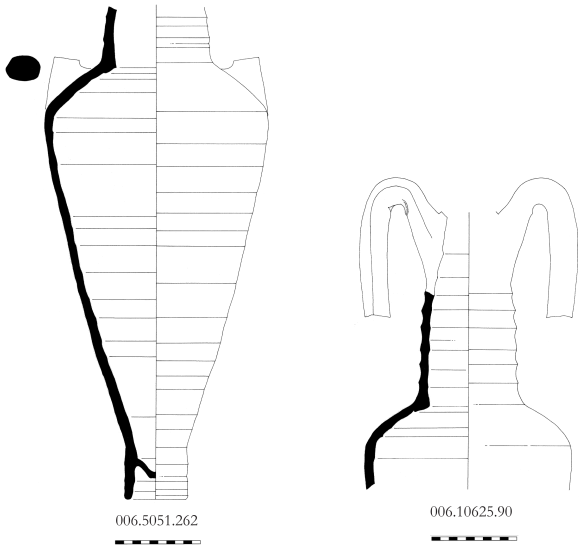


Figure 6.5: Drawing of a Kapitan 2 amphora. Adapted from Reynolds 2010b, Figs. 2a-b.

The 4th century deposits suggest a significant reduction in Black Sea trade with Sinopean and Crimean amphorae representing less than 1% of total imports.[9] Kapitan 2 amphorae, however, continue to be attested at relatively similar proportions to that of mid-3rd century deposits (approximately 1.25-2% of total imports).[10] It is notable that the form and fabric color of the Sinopean amphorae has changed. The Sinopean amphora possesses a 'tall

[6]Reynolds 2010b, Table 1.

[7]Reynolds 2010b, Table 1. For the purposes of this section, Kapitan 2 amphorae are included with Black Sea imports; however, the provenance of the amphorae themselves is still in debate.

[8]Reynolds 2010b.

[9]Reynolds 2010b, Table 2b.

[10]Reynolds 2010b.

necked, 'carrot-bodied' type' and the fabric is now a pale red (Fig. 6.6).[11] It is similar in form to Kassab Tezgör's form Snp III.[12] The form of the Crimean amphora have changed as well and are smaller with 'short, plain handles' than their 3rd century counterparts.[13]

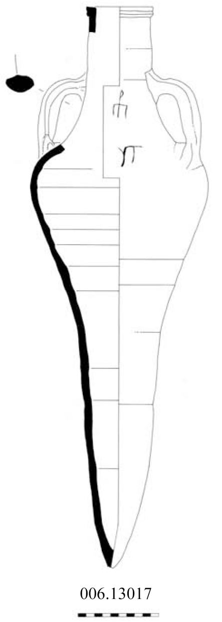


Figure 6.6: Drawing of a Sinopean "carrot" amphora, c. 410 AD. Adapted from Reynolds 2010b, Fig. 4a.

The early 5th century material indicates an increase in Sinopean amphorae to approximately 9% of total imports.[14] Crimean amphorae, however, are nearly absent.[15] Colchean amphorae first appear during this period but at low relative proportions (>1% of total amphora imports), becoming more frequent during the later half of the century.[16] The relatively small pale green/yellow fabric Sinopean/Heraclean 'argile claire' (Fig. 6.7) amphora replaces the 'carrot-bodied' red fabric Sinopean amphorae towards the end of the century.[17]

[11]Reynolds 2010b, 93.

[12]Kassab Tezgör 2003.

[13]Reynolds 2010b, 93.

[14]Reynolds 2010b, Table 3.

[15]Reynolds 2010b, 94.

[16]Reynolds 2010b, Table 3.

[17]Reynolds 2010b, 96.

Figure 6.7: Drawing of a an 'argile claire' amphora from c. 551 AD. Adapted from Reynolds 2010b, Fig. 7e.

Ceramic evidence from the first half of the 6th century indicates that amphora were still imported on a large scale but a decreasing number of sources, indicated by the reduced number of forms of both Black Sea and others.[18] The only Black Sea amphora type attested during this period, apart from a solitary Opaiţ B amphora (Fig. 6.8), is the 'argile claire' at a low level of frequency relatively low at approximately 2% of total imports.[19] The ceramic evidence for the period after the devastating earthquake of 551 AD to the end of the 6th century does not indicate a resurgence in Black Sea trade; 'argile claire' amphorae become scarce.[20]

[18]Reynolds 2010b, 96.

[19]Reynolds 2010b, Table 6.

[20]Reynolds 2010b, 98.

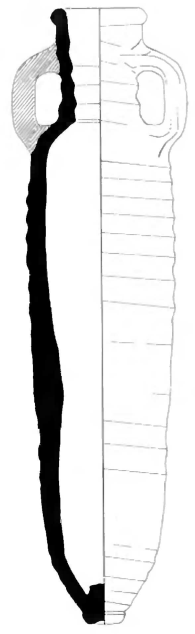


Figure 6.8: Drawing of a an Opaiţ B amphora, scale 1:10. Source: Swan, Fig. 26.

6.2 Beirut sample material

Beirut was considered a suitable candidate for the analysis of Black Sea amphorae for two reasons. Firstly, the Beirut Souqs excavations produced a large quantity (approximately 20 tons) of ceramic material which included large quantities of amphorae including a significant amount of Black Sea forms. This material had also been previously studied by Paul Reynolds (University of Barcelona) for vessel fabric and form (including statistical analyses) that greatly facilitated selection, identification and locating potential samples from such a large body of collections. Secondly, Beirut itself has previously been indicated as a good location for the recovery of Black Sea exports. Previous research by Paul Reynolds has indicated that Beirut consistently received trade from the Black Sea region during late antiquity.[21] While Black Sea amphorae are attested at many sites in the Mediterranean, the consistent presence throughout late antiquity is rather rare as trade patterns, especially in the west and North Africa, changed.

Two areas of central Beirut were excavated by the Anglo-Lebanese teams, Area BEY006

[21] *inter alia* Reynolds 2003, 2010a,b, 2013

was termed the ‘Beirut Souqs’ on account that the modern souq in central Beirut was located over the area of excavation. The second area, BEY045, comprised the Roman baths area. The baths were constructed during the 1st c. AD before being dismantled during the 3rd c. AD. Most of the sample material in this study were recovered from fill or levelling contexts. The known details of the date and nature of the contexts are given in the relevant sections.

Beirut is unusual in comparison to other Near Eastern or North African sites in that trade from the Black Sea region, as observed from amphora imports, continued uninterupted throughout the late Roman and early Byzantine periods. This provides an uncommon opportunity to examine both the significance of Black Sea imports into Beirut as a proxy for trade levels (as has been previously been examined by Paul Reynolds) as well as the potential to identify what commodities were being exported from the Black Sea region during the period under study.

CHAPTER 7

KAPITÄN 2 AMPHORAE

7.1 Background

7.1.1 General Description

The Kapitän 2 is a distinctive amphora characterized by two thick, broad handles that extend above the rim and a large, thick-walled hollow base, with a total length of approximately 75 cm (Fig. 7.2).[1] The amphora has a relatively small capacity of approximately 15 L.[2] The unusually prominent handles and the hollow base have been suggested to be features to aid ship-side loading and unloading as these aspects would have facilitated handholds for workmen (Fig. 7.1). The hollow base allows for four fingers to grasp it from the interior, while the large handles allow for an easy grasp from above. Several aspects of the Kapitän 2 have invited significant scholarly debate.

Figure 7.1: Demonstration of the potential utility of the characteristic handles and base of the Kapitän 2 amphora. Source: McCormick 2012, 63.

[1]McCormick 2012, 62.

[2]Dyczek 2010, 993.

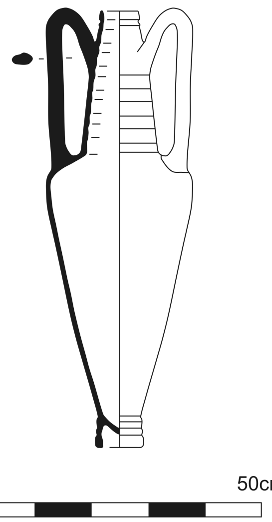


Figure 7.2: Drawing of Kapitän 2 amphora after Panella 1973.

7.1.2 Date Range and Distribution

The Kapitän 2 is first attested at Ostia in deposits dating to the late 2nd c. AD.[3] At a similar time, the form also appears in Rome via Brindisi as well as eastern Sicily.[4] The Terrauzza wreck, south of Syracuse, contained both Kapitän 1 and 2 forms and was dated to c. 200 AD.[5] The form appears more or less concurrently in Dacia.[6] The forms are most prevalent in strata dated to the 3rd c. AD before its decline and subsequent disappearance between the early to mid-late 4th c. AD.[7]

7.1.2.1 General Distribution and Periodicity in the West and East

The Kapitän 2 was very widely distributed, attested as far west as Britain to Iraq in the east, in north Africa as well as Nubia and, to the north, in the Black Sea region and as far as southern Russia with frequency being higher in the east relative to the west. In Britain, the form is present at multiple sites but rare (Fig. 7.3). Only 15 examples are known, appearing

[3] Panella 1973.

[4] Reynolds 2010a, 67.

[5] Parker 1992.

[6] Negru et al. 2003.

[7] See Peña 1999, 84 for an early 4th c. AD terminus, alternatively Reynolds 2010b dates its terminus to the end of the century.

primarily at coastal sites with the greatest concentration in the region of Londinium and dating to the late 3rd and 4th c. AD.[8] It is present in Germany, almost exclusively in the Rhine valley.[9] Sporadic finds have also been made in modern Belgium (Patrick Monsieur *pers. comm.*). The form is scantly present in Iberia, almost exclusively at coastal sites with distribution concentrated in the region of Tarraconesis.[10]

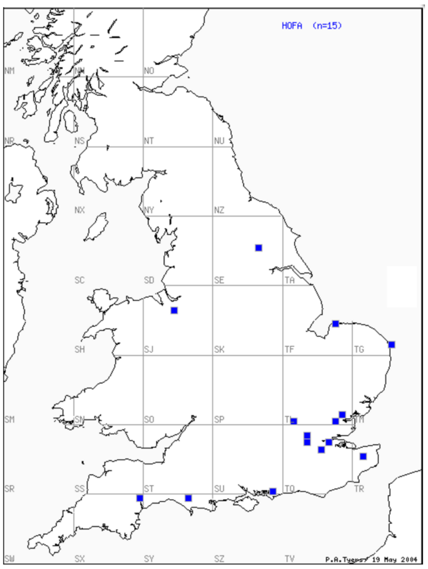


Figure 7.3
Map of Kapitän 2 ('HOFA') distribution in Britain. Source: Tyers 2014.

In the environs of Rome and points east, the Kapitän 2 is represented in more locales and in more significant quantities. On the Italian peninsula, the form is most prominent at Ostia and in strata from the Palantine Hill during the period between 325 and 350 AD before declining in frequency during the second half of the century.[11] It is generally rare in the Maghreb with the notable exception of finds in modern Tunisia and Libya, including at Carthage.[12] At Benghazi, frequency peaks during the early 3rd c. AD before declining during the later half of the century, following a distribution pattern similar to that of Rome.[13]

[8]Tyers 2014.

[9]Peacock and Williams 1986, 193ff.

[10]Keay 1984; Tyers 2014; Reynolds 2010a, 72, footnote 217.

[11]Reynolds 2010a, 104.

[12]Peacock and Williams 1986, 193ff; Riley 1979 1979, 189ff.

[13]Reynolds 2010a, 67.

In the Balkans, the Kapitän 2 appears at Butrint during the mid 3rd c. AD.[14] There is also one example known from the city wall excavations at Durrës dating to the early to mid 3rd c. AD.[15]

The Kapitän 2 is present in Athens, Corinth and Crete.[16] In the Aegean, the form is attested on the islands of Kos, Lesbos, Samos and Rhodes, all of which have been suggested as possible production sites.[17] The form is especially prevalent on Rhodes.[18] A high concentration of the vessels is also found at Ephesus and its environs.[19]

The form is very frequent in the lower Danube, primarily in the 3rd and 4th c. AD, including a 4th c. AD tomb at Constanta.[20] It was one of the most common imports at Novae and, in particular, demonstrates an association with military sites.[21] In the region of the lower Danube on the basis of distribution, the form may have been transported first by sea then up the Danube until the beginning of Roman roads (see Fig. 7.4).[22] Due to its strong association with military establishments, at least in the lower Danube, the Kapitän 2 may have served a role in the military *annona* (Paul Reynolds *pers. comm.*).

The Kapitän 2 is also very frequent in the western Black Sea littoral. It is attested at Olbia Pontica (modern Ukraine), present during the 3rdto early 4th c. AD. [23] Additionally, it is present at a number of cities including Apollonia, Odessos, Histria, Tyrcis, Tiritaka, Iluraton.[24] The form is also prevalent in the Bosporan Kingdom.[25] Specifically, significant quantities are attested in 3rd and 4th c. AD strata at Chersonesus.[26] Further afield to the

[14] Reynolds 2010a, 67.

[15] Reynolds 2010a, Table 3a.

[16] Reynolds 2010a, 67; Peña 2007, 98. For a complete example from the levels associated with the 267 AD destruction of Athens, see Grace 1979, Fig. 37.

[17] See Section 7.1.3.1 for a treatment of these possible production sites.

[18] Riley 1979.

[19] Bezeczky 2010.

[20] Dyczek 2001, 141; Concerning the example recovered from a tomb, seeScorpan 1975, 268.

[21] Dyczek 2010; Swan 2004, 378ff.

[22] Negru et al. 2003, 212.

[23] Krapivina 2010a, 71.

[24] Dyczek 2001, 141.

[25] Zeest 1960, 114.

[26] Klenina 2010.

east, sporadic examples of the Kapitän 2 known in the Middle East. It has been attested at Homs.[27] Kapitän 2 finds are also known from Dura Europos dating to 215/216 AD.[28] At Zeugma it is present in the destruction layers of 257 AD and is one of the more common amphora imports.[29] In modern Iraq, an example is known from a 3rd c. AD fort at Ain Sinu.[30]

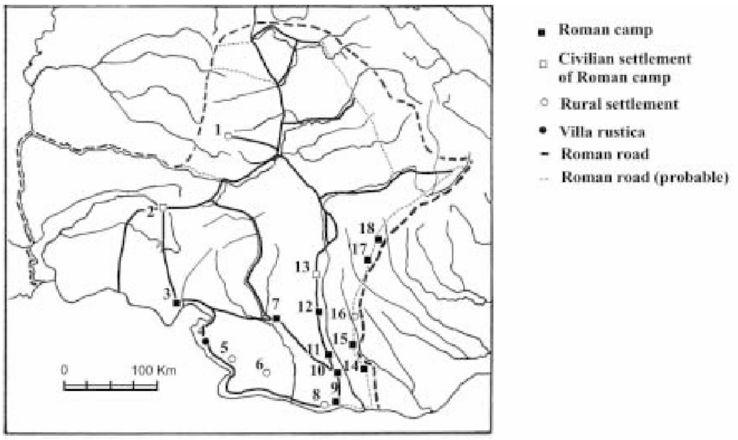


Fig. 3: Map of discoveries.
1 Ampelum. — **2** Tibiscum. — **3** Dierna. — **4** Gârla Mare. — **5** Izîmºa. — **6** Cioroiul Nou. — **7** Rãcari. — **8** Orlea. — **9** Sucidava. — **10** Slãveni. — **11** Romula. — **12** Acidava-Enoºeºti. — **13** Buridava. — **14** Gresia. — **15** Crâmpoia. — **16** Coloneºti-Mãrunþei. — **17** Jidava. — **18** Râºnov.

Figure 7.4: Map of the distribution of Kapitän 2 in the area of the lower Danube with a reconstruction of Roman roads. Source: Negru et al. 2003, 213.

7.1.2.2 Mapping Distribution by Shipwreck

Kapitän 2 amphorae are fairly well represented in the number of shipwrecks on which they appear.[31] At present, 11 wrecks are known to have Kapitän 2 amphorae (see Fig. (7.5)). The greatest concentration of wrecks are in the waters off Sicily. Of the 4 wrecks, the Terrauzza is the earliest to attest the Kapitän 2, dating to c. 200 AD. Located approximately 10 km

[27]Reynolds 2010b, 90.

[28]Dyczek 2001, 143.

[29]Reynolds 2010a, 91; Reynolds 2013, 99.

[30]Reynolds 2010a, 91.

[31]The information contained within this section is a compilation from several, largely overlapping works. Parker 1992 presented the first comprehensive catalog of ancient shipwrecks and their contents. McCormick et al. 2013 and Strauss 2013 have independently created digital databases of Parker's original work with updated records for finds subsequent finds. Except where noted below, the identities of shipwrecks and related information were obtained from these sources.

south of Syracuse, the wreck is composed of a concretion of Kapitän 1 and 2 amphorae. Additional cargo included a colorless glass bottle and unidentified table pottery. Approximately 60 km north of Syracuse near modern Catania, the Ognina A shipwreck dates to the early 3rd c. AD. Again Kapitän 1 and 2 amphorae co-occur as well as two Spanish forms (Dressel 20 and Beltrán 2B). Additional cargo included approximately 13 kg of blue frit and various luxury items including glass vessels and bronze statuettes. The wreck was dated by coins (minted between 210 and 215 AD) and were issues of Perinthos, Smyrna and Byzantium. Approximately 30 km to the south of Syracuse, the Marzamemi A shipwreck is a *navis lapidaria* dating to the first half of the 3rd c. AD. The primary cargo of the ship was Attic marble, some of which was partially shaped. In addition to the marble, an unspecified number of Kapitän 2 amphorae were observed as well as some fragmentary amphorae tentatively identified as 'Africano'. The fourth shipwreck from the waters off Sicily is located toward the western end of the island, approximately 10 km southeast of Mazara del Vallo. The Capo Granitola is another *navis lapidaria* dating to the mid to late 3rd c. AD. The principal cargo was marble from Proconnesus as well as fragmentary marble from Parian and Asiatic marble that was probably residual from previous cargoes. Only the upper portion of one Kapitän 2 was observed.

To the south of Sicily, there is the Lampedusa 1 shipwreck, which contains an unspecified number of Kapitän 2 and Africana 2 amphorae and dates to the first half of the 4th c. AD. Further west in the Mediterranean there are two additional shipwrecks bearing Kapitän 2 amphorae. One is the Porticcio wreck off the western coast of Corsica south of Ajaccio. Dating to the 3rd c. AD, the cargo was primarily amphorae with a diverse number of types. In addition to Kapitän 1 and 2's, Dressel 20, Gauloise (type unspecified), Almagro 50 and 51c, Béltran 72 and unspecified Egyptian amphorae were documented. In addition to the widely varied amphora cargo, north African coarsewares and mill stones were present as well as two fragmentary marble statues (Emperor Philip 1 of Arabia and his wife Marcia Otacilia) and at least 230 kg of glass, composed of both sheets and objects. The second wreck is off the west coast of Île de Bagaud. The Bagaud A, dated to the 3rd c. AD, Kapitän

Figure 7.5: Map of Kapitän 2 finds from maritime contexts. Based primarily upon Parker 1992; McCormick et al. 2013; Strauss 2013.

2 and spatheion amphorae as well as at least two mortaria.

Moving eastward, there is one shipwreck off the western coast of Greece near Pilos. The Methone, dating to the first half of the 3rd c. AD, principally contained salvaged Aswan marble as well as 10 Kapitän 2 amphorae. In modern Libya, the Cyrene Archaeological Museum has a small collection of Kapitän 2 amphorae recovered from a shipwreck discovered in the area. There is a poorly documented shipwreck off the northeast coast of Kos containing Kapitän 1 and 2 amphorae, ascribed generally to the 3rd c. AD. During late summer 2015, 22 shipwrecks were identified off the north coast of the isle of Fournoi (directly west of Samos). These discoveries have increased the total number of shipwrecks found in Hellenic waters by 12% and span the Archaic through the late Medieval period. One shipwreck which was surveyed contained principally Zeest 72 amphorae with a small number of Kapitän 2's as well. One of the Zeest 72 amphorae was recovered and found to have been tightly packed with a type of crustacean (George Koutsouflakis *pers. comm.*). The final examples of Kapitän 2's recovered from maritime contexts occur at the Yenikapı Marmaray and metro excavations. Thirty-five shipwrecks have been excavated with some 27,000 small finds.[32] These include two Kapitän 2 amphorae (see Figure 7.6). Study and publishing of the shipwrecks is currently ongoing, at present only a catalog of some of the amphora finds is available. It is unclear from the catalog whether these vessels were recovered from a shipwreck or were isolated finds.

Figure 7.6: Kapitän 2 amphorae recovered from the Yenikapı excavations, catalog numbers YKM’09 9555 and MRY’07 4615, respectively. Source: Asal 2010, 29ff.

The examination of shipwrecks can provide additional insight into trade that may not or may not as easily be determined by the examination of terrestrial finds and their distribution patterns. Most intuitively, shipwrecks are essential for reconstructing maritime pathways. Distribution maps of terrestrial finds can establish to where goods were transported. Provenance studies of amphora, including identification of kiln sites, can establish where the vessels were manufactured. However, to establish the routes used shipwrecks are essential.[33] Conversely, the analysis of the distribution of shipwrecks and the types of amphorae carried as cargo can provide insight into possible regional origin of amphora types the origin of which has yet to be determined. Analysis of hulls can determine technological levels and development. In conjunction with data from terrestrial excavations, shipwrecks can contribute valuably to the quantification and frequency of trade as well as to the nature of the production

[32]Asal 2010, 1.

[33]Parker 2008, 187.

of goods and their distribution, such as underlying social structures.[34]

The general distribution of shipwrecks containing Kapitän 2 amphorae is significantly biased toward the western Mediterranean compared to the east. In fact, until recently their distribution or lack thereof had been described in the eastern Mediterranean as 'absent' despite the prevalence of the form in several eastern regions such as Samos and Beirut.[35] Furthermore, while there are two general competing theories for the origin of the form, schools of thought place the Kapitän 2's manufacture in the east. Recent finds have started to populate the eastern Mediterranean but the considerable bias remains. Part of this may be due to the distribution of discovered shipwrecks itself to be biased toward the west (Fig. 7.7). However, at least for some amphora types, west vs. east regional distribution trends are borne out with shipwreck data despite the majority of discoveries being in the west (e.g. distribution trends of Dressel 1 and 6 amphorae).[36] For some regions there are apparent reasons for the absence of Kapitän 2 shipwreck finds. Despite its frequency in the Black Sea region, no Kapitän 2 amphorae have been found on shipwrecks. Very few shipwrecks, however, have been found in the Black Sea. The author is aware of only one maritime survey in the Black Sea for shipwrecks.[37] Similarly, bureaucracy and security concerns (as well as funding difficulties) complicate conducting maritime survey work on much of the Levantine coast.

Some general trends can be observed from the Kapitän 2 wrecks. Kapitän 1 and 2 amphorae do show a correlation in cargoes, both being found on the Terrauzza, Ognina A, Porticcio and the unnamed shipwreck off Kos. Attempting to gain insight into regional origin of the Kapitän 2 by way of the regional origin of other amphora types, however, is less than clear. The Porticcio wreck, in addition to the Kapitän 1 and 2's, contained amphorae originating from (most probably) Gaul, Iberia and Egypt as well as north African coarsewares. The Ognina A, found off Sicily, contains eastern forms (the Kapitän 1 and 2's) but also Spanish forms (Dressel 20 and Béltran 2B). It is interesting that the coin evidence points

[34]Kingsley 2009, 31.

[35]Lewit 2015.

[36]Parker 2008.

[37]Ballard et al. 2001.

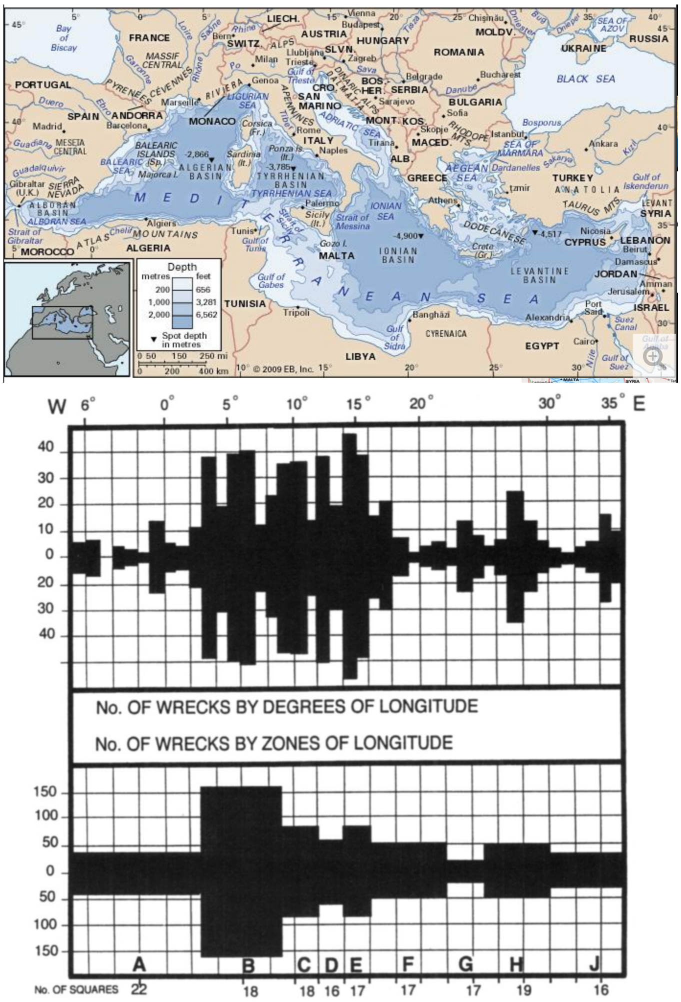


Figure 7.7: Map of the Mediterranean (top) compared against a longitudinal distribution map of ancient shipwrecks (bottom). Sources: Encyclopaedia Brittanica Online 2015; Parker 2008, 190, respectively.

to the ship having put to port, perhaps most recently, at Byzantium or its environs. The cargo of the Marzamemi A indicates the ship travelled from at least as far east as Attica via north Africa. The final caveat is that the simple presence of a particular amphora type aboard a shipwreck does not necessitate that it was part of the ship's cargo. A single find or a very limited number may simply be vessels kept aboard ship from a previous voyage as a container for its particular commodity or may have been reused in another capacity. Both the Proconnesus and the newly discovered wreck off Fournoi fall into this category. This applies as well when available data on the shipwreck simply indicates the form was present but not how many (e.g. the unspecified number of Kapitän 2's on the Lampedusa 1). The utility of the Fournoi shipwreck has yet to be determined and will have to wait until excavation.

7.1.2.3 The View from Beirut

Kapitän 2 amphorae are first attested in late 2nd c. AD contexts (BEY006.11629/11603).[38] During the early 3rd c. AD, the form is attested in several large contexts (including the BEY045 piscina fill and BEY006.5051), representing ~1-1.5% of total amphorae (based upon RBH) or ~2.5-3% of imported amphorae.[39] By the mid 3rd c. AD, it becomes common, for example 'abundant samples' are present in BEY006.10625 dating to c. 250 AD, where it represents ~13% of total amphorae (~18% of imported amphorae).[40] Frequency during the end of the 3rd c. AD remains largely stable before declining in mid to late 4th c. AD contexts to a 'regular though rare import'.[41]

7.1.3 Production

The source or sources for the production of the Kapitän 2 two amphora have yet to be definitively ascertained. No tituli picti, *graffiti* or stamps are known on any Kapitän 2 vessels which might have been useful in determining the amphora's origin.[42] Additionally, no identifiable contents have been observed. Several samples, however, have demonstrated traces of pitch on their interiors from examples found at Topraichioi, Murighiol/Halmyris and Caesarea.[43] Generally, arguments for the area of production are based upon fabric, morphology and/or distribution. There are two principal theories on the origin of the Kapitän 2: the first is production in the Aegean region including Asia Minor; the second is an origin in the Black Sea region, possibly from the Crimea or alternatively in the Pontic or possibly in the area of Dacia.

[38] Reynolds 1998, 54.
[39] Reynolds 2010b, Table 1.
[40] Reynolds 2005, 569; Reynolds 2010b, Table 1.
[41] Reynolds 2010b, 93.
[42] Dyczek 2010, 993.
[43] Opait 2004b, 299.

7.1.3.1 Possible Eastern Mediterranean Provenances

An Aegean provenance for the Kapitän 2 has been the earliest argument and that made by the most scholars. The characteristic shape of the form has frequently formed the basis of an Aegean origin.[44] Keay (1984) argued for an origin at Kos. Peña (1999) noted that the Kapitän 1 and 2 amphorae share an 'indistinguishable fabric' and are frequently found together on shipwrecks. On several terrestrial sites, the Kapitän 1 and 2 also occur, including at Brindisi-S. Foca and Ostia.[45] The Kapitän 1 shares a similar typology with some 4th c. BC amphorae from Lesbos and, as such, the possibility of the Kapitän 2 having been manufactured on Lesbos was suggested.[46] Based upon distribution, the significant presence of the amphora on Samos has led the island to also be suggested as a point of manufacture.[47]

Many of the arguments for an Aegean origin of the Kapitän 2 are based upon fabric. The Kapitän 2 fabric is noted to contain relatively high amounts of chromium and nickel, indicating that the clay is from an ophiolitic zone. [48] Additionally, mica is present in abundance in some samples.[49] This would be consistent with manufacture in the eastern Mediterranean. Central Greece, Euboea, Rhodes, Lesbos, Cyprus, the littoral region of north Syria and the area surrounding Antalya have been identified to contain significant ophiolite deposits.[50] Prior to the discovery and excavation of LRA 1 kiln sites, some had postulated that the LRA 1 form was of Egyptian origin due to the significant finds of this vessel type in Egypt. In fact, it was the petrographic analysis of LRA 1 by Williams that indicated the clay originated from an ophiolite-bearing area, thus excluding Egypt as a clay source.[51] Subsequent research has established that the amphora form was produced at a number of sites including Cyprus and

[44] Dyczek 2010, 593.

[45] Reynolds 2010b, 91.

[46] Peña 1999, 86.

[47] Riley 1979, 192; Grace 1971, 72.

[48] Empereur and Picon 1989, 233.

[49] Empereur and Picon 1989, 233.

[50] Demesticha and Michaelides 2001, 291.

[51] Demesticha and Michaelides 2001, 291.

Cilicia.[52] Similarly, an Aegean or Asia Minor origin for the Kapitän 2 is based upon fabric type. Rhodes has been suggested as a possible manufacturing site.[53] Chemical analyses of samples from the lower Danube have been analyzed and indicated residual chromium and nickel, supporting earlier analyses by Empereur and Picon (1989).[54] Dyxzek argued that this supports the conclusion that the amphorae could have been produced in many areas of the Aegean, including Rhodes.[55] Despite the arguments for Rhodes as a production center for the Kapitän 2, there has been to date no archaeological evidence to support the theory. As of 1989, approximately 20 amphora workshops had been excavated in Rhodes, none identified Kapitän 2 examples.[56] Subsequent surveys and excavations have not identified any production sites for the amphora in Rhodes. Finally, in addition to Aegean islands, the possibility of manufacture in Syria or Asia Minor has been suggested as well as more specifically the region surrounding Ephesus.[57]

7.1.3.2 Possible Black Sea Provenances

More recently some scholars have argued for possible production sites for the Kapitän 2 in the Black Sea region. With respect to the availability of clay sources consistent with the composition of the Kapitän 2 fabric, there are a number of possible locales. Beyond the eastern Mediterranean discussed above, ophiolite-bearing rock is also found in the Pontidies (Black Sea coast of Turkey).[58] Armenia also has significant ophiolite deposits.[59] Additionally, Crimea contains ophiolitic outcrops although they are not as well documented as those of the eastern Pontidies or Armenia.[60]

It has been observed that the fabric of the Kapitän 2 bears a strong resemblance to the

[52] *inter alia* Empereur and Picon 1989; Demesticha 2003; Demesticha and Michaelides 2001.

[53] Empereur and Picon 1989.

[54] Dyczek 2001.

[55] Dyczek 2001, 141.

[56] Empereur and Picon 1989, 233.

[57] Scorpan 1977; Bezeczky 2010, respectively.

[58] Okay and Sahinturk 1997.

[59] Dercourt et al. 1986.

[60] Yudin et al. 2009.

Zeest 72.[61] The Kapitän 2 and the Zeest 72 share some similarities in distribution; for example in the region of Homs, the forms co-occur at the same sites.[62] The Zeest 72 has been established to have been produced in the area surrounding Myrmekion in the Crimea.[63] Taken together this may suggest a manufacturing origin on the Crimea. Parallels between the Kapitän 2 and the Zeest 80 have also been drawn. Under optical magnification the Kapitän 2 fabric has been suggested to bear a strong resemblance to a coarse-textured version of the Zeest 80.[64] There are also typological similarities to these contemporaneous forms. Both feature unusually massive, rounded handles with grooving down the exterior.[65]

7.2 Kapitän 2 Samples and Analysis

Fifteen ceramic samples from distinct Kapitän 2 vessels were sampled from the storerooms of the American University of Beirut. The ceramic samples were prepared and analyzed at the Research Laboratory for Archaeology and the History of Art, University Oxford using gas chromatography/mass spectrometry. The samples were characterized for both lipid constituents and organic compounds associated with wine using the protocols described in Chapter 5. The material had previously been studied by Paul Reynolds (University of Barcelona) who compiled a database of the ceramic and contextual data. Samples were selected from a variety of contexts dating to the 3rd c. AD (see Table 7.1). Emphasis was given to samples from contexts with deposition dates close to the known period of manufacture of the Kapitän 2 and which compositionally had uniform dating. Emphasis was also given to select samples that did not demonstrate concretions or other evidence of significant depositional exposure to water. Photographs of the samples are found in Appendix A.

[61] Reynolds 2010b.
[62] Reynolds 2010b, 90.
[63] Sazanov 2012; Zeest 1960.
[64] Swan 2004, 380; Slane 2000, 303.
[65] Swan 2004, 380.

Table 7.1: Context and sample data for Kapitän 2 analyses, data retrieved from the ceramic database developed by Paul Reynolds.

Area	*Context*	*Sherd Number*	*Date of Context (AD)*	*Nature of Context*	*Position of Sample*	*Visible Residue*
006	*10622*	*106*	5th c., some 3rd c.	?	*base*	*no*
006	*10625*	*90*	c. 250	dump	shoulder	no
006	*10625*	*92*	c. 250	dump	neck	no
006	*10625*	*105*	c. 250	dump	base	no
006	*10625*	*x3*	c. 250	dump	wall	no
006	*10629*	*104*	3rd.c ?	fill?	base	no
006	*10632*	*103*	3rd.c ?	fill?	base	no
006	*10632*	*88*	3rd.c ?	fill?	neck	no
006	*10632*	*89*	3rd.c ?	fill?	neck	no
006	*5051*	*262*	225-250	fill?	base	no
006	*5051*	*263*	225-250	fill?	base	no
006	*5051*	*264*	225-250	fill?	base	no
006	*5051*	*267*	225-250	fill?	shoulder	no
045	*1242*	*97*	early 3rd c.	fill	shoulder	no
045	*1510*	*24*	early 3rd c.	fill	base	no

7.2.1 Results of Analyses

7.2.1.1 Sample from BEY006.10622.106

Context 10622 is a mixed context primarily containing material dating to the 5^{th} c. AD with some 3^{rd} c. AD material present. The sample was removed from a base fragment. Lipid analyses indicated pine resin biomarkers–dehydroabietic acid, 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid. The fatty acids $C_{16:0}$ and $C_{18:0}$ as well as trace amounts of $C_{14:0}$ were also detected (Fig. 7.8). Analysis of organic compounds associated with wine identified malonic, fumaric, succinic, malic, vanillic, citric and tartaric acids (Fig. 7.9). Tartaric acid was identified by comparison against an authentic standard as well as comparison against the NIST mass spectral database (Fig. 7.10)

7.2.1.2 Sample from BEY006.10625.90

Context 10625 is a fill context ('dump') composed of material dating to c. 250 AD. The recovered portion of the vessel was the shoulder and neck; the sample was removed from lowest extant part of the shoulder. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well

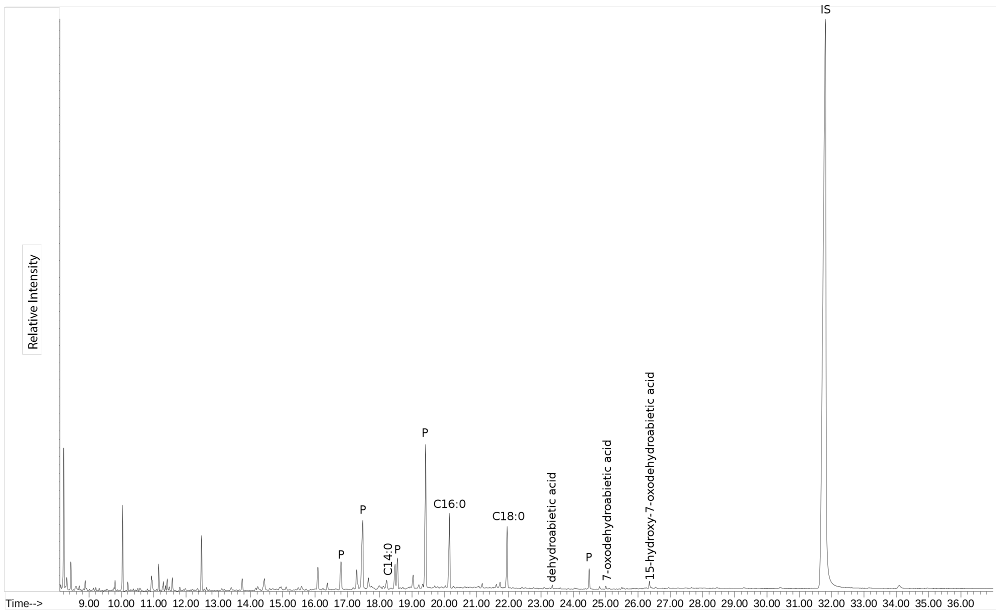


Figure 7.8: Total ion chromatogram of the total lipid extract (TLE) from Sample BEY006.10622.106. Plasticizers are denoted by 'P', the internal standard is identified as 'IS'.

as dehydroabietic acid. A large number of specifies and significant quantities of plasticizers were observed in the chromatograms relative to other analyzed samples. The analysis of organic compounds associated with wine indicated only fumaric and succinic acids.

7.2.1.3 Sample from BEY006.10625.92

This vessel is represented as an upper handle, the sample was removed from the interior of the handle attachment (upper portion of the neck) (see Fig. 7.2). Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids and dehydroabietic acid. The analysis of organic compounds associated with wine indicated only fumaric and succinic acids.

7.2.1.4 Sample from BEY006.10625.105

This vessel is represented as a base, the sample was removed from the lower interior portion of the base. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ as well as a small quantity of $C_{14:0}$ fatty acids (Fig. 7.11). The pine resin biomarkers dehydroabietic acid, 7-oxodehydroabietic acid, 15-hydroxydehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid were identi-

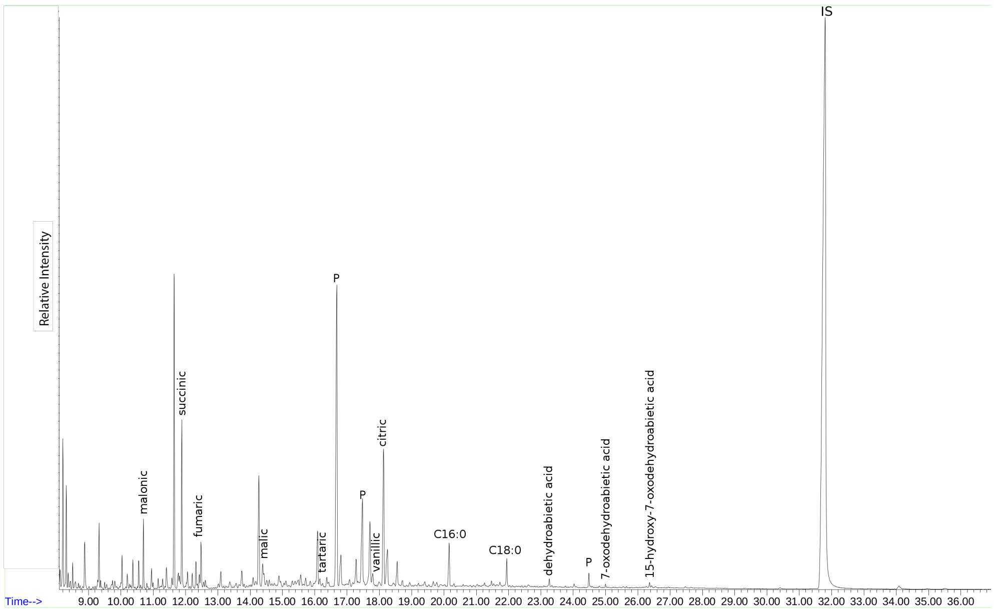


Figure 7.9: Total ion chromatogram of the analysis of organic compounds associated with wine extract from Sample BEY006.10622.106.

fied. Additionally, this was the only Kapitän 2 sample in which the resin acid, pimaric acid, was identified. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic, malic, vanillic, citric and tartaric acids (Fig. 7.12).

7.2.1.5 Sample from BEY006.10625.x3

This vessel is represented by mid to lower wall sections. Due to the lower body of the vessel having been fragmented into a number of sherds and not reconstructed (i.e. glued back together), a photo of the entirety was not feasible. Lipid analyses identified $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ fatty acids and dehydroabietic acid as well as an unidentified peak that is probably a plasticizer contaminant. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic, and malic acids.

7.2.1.6 Sample from BEY006.10629.104

Context 10629 represents a probably fill context. The context appears to be fill dating to the 3rd c. AD. The vessel is represented by a base, the sample was taken from the side wall. Lipid analyses identified $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ fatty acids and dehydroabietic acid. Additionally,

Figure 7.10: Mass spectrum of the peak identified as tartaric acid in Sample BEY006.10622.106 (top) compared against the mass spectrum of tartaric acid (as its trimethylsilyl ester) from the NIST11 database (bottom).

trace quantities of the monounsaturated fatty acids $C_{16:1}$ and $C_{18:1}$ were identified and are possibly a result of bacterial contribution. No anthropogenic or potentially anthropogenic contaminants, such as cholesterol or octocrylene, were identified. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic and vanillic acids.

7.2.1.7 Sample from BEY006.10632.103

Context 10632 represents a probably fill context. The context appears to be fill dating to the 3^{rd} c. AD. The vessel is represented by a base, the sample was taken from the side wall. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids, dehydroabietic acid and 7-oxodehydroabietic acid. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic, malic and tartaric acids.

7.2.1.8 Sample from BEY006.10632.105

Sample BEY006.10632.104 represents another sample from Context 10632. The vessel was represented by its base and a portion of the lower body. The sample was taken from the side

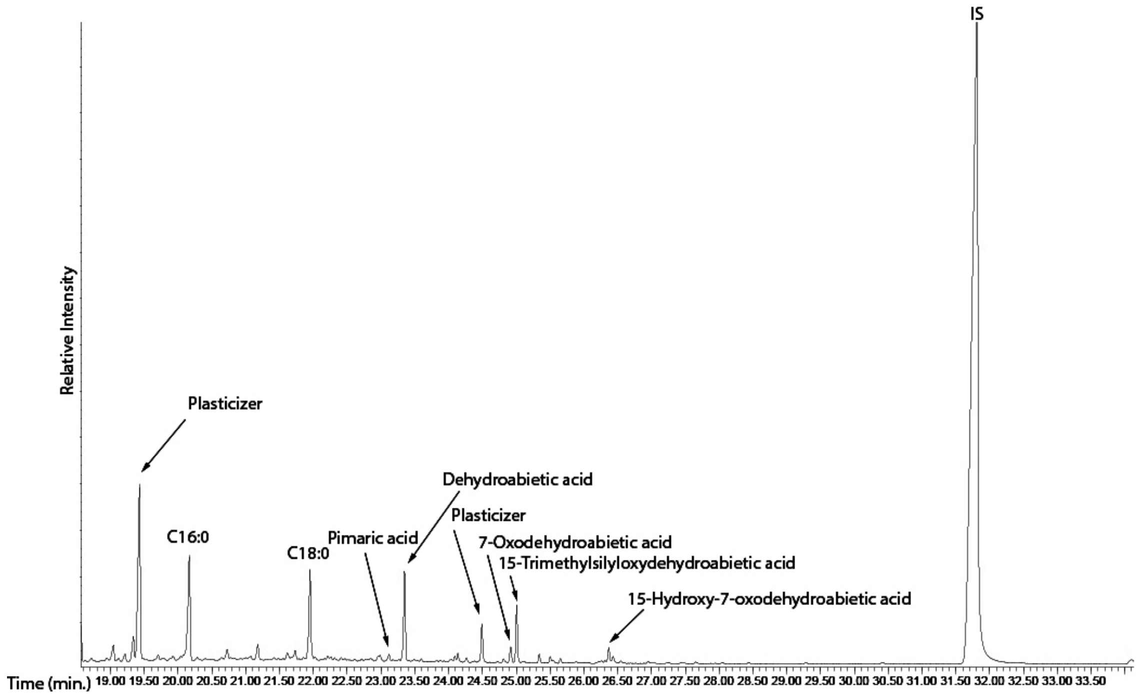


Figure 7.11: Total ion chromatogram of total lipid extract (TLE) of Sample BEY006.10625.105.

wall of the base. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids. The principal ion of dehydroabietic acid (as its trimethylsilyl ester), *m/z* 239, was observed at the retention time for dehydroabietic acid; however, the extremely low signal to noise ratio prevented positive identification. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic and malic acids.

7.2.1.9 Sample from BEY006.10632.88

Sample BEY006.10632.88 represents another sample from Context 10632. This vessel is represented by the portion of the vessel from the rim to lower neck. The sample was taken from the lowest extant portion of the neck. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin acids dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic and malic acids.

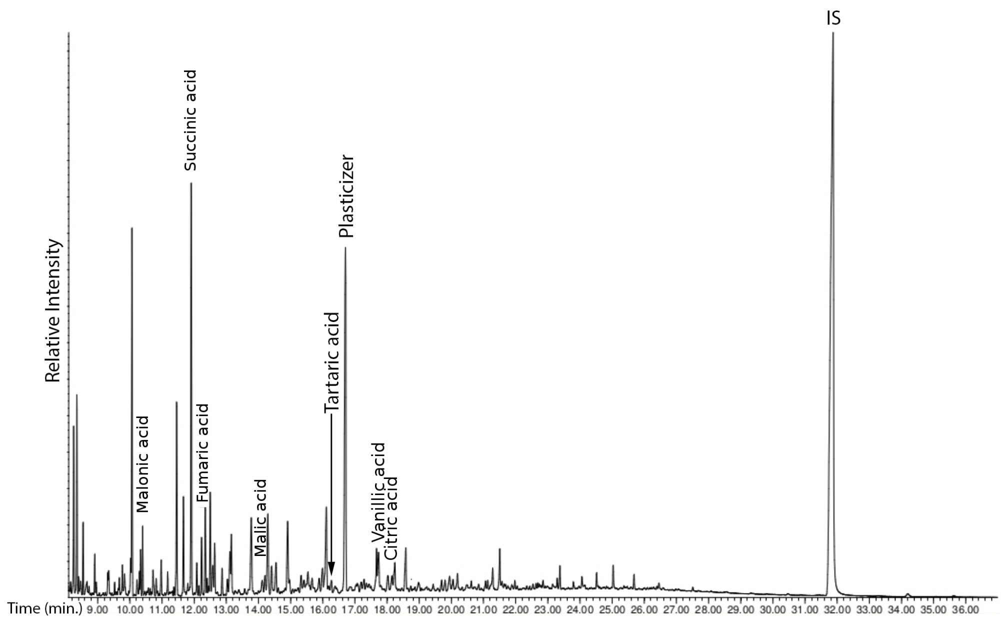


Figure 7.12: Total ion chromatogram of the analysis of organic compounds associated with wine of Sample BEY006.10625.105.

7.2.1.10 Sample from BEY006.10632.89

Sample BEY006.10632.89 represents another sample from Context 10632. This vessel is represented by the portion of the vessel from the rim to upper neck. The sample was taken from the lowest extant portion of the neck. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin acids dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic and malic acids.

7.2.1.11 Sample from BEY006.5051.262

Context 5051 is a large fill context dating to 225-250 AD. The vessel is represented by a base, the sample was taken from the side wall. The lipid extract indicated significant amounts (relative to $C_{18:0}$) of the fatty acids $C_{18:1}$ and $C_{18:2}$, as well as the plants sterols stigmasterol and β-sitosterol (Fig. 7.13). The presence of C_{18} unsaturated fatty acids and plant sterols are consistent with a vegetable oil. The sample was also characterized by a series of long-chain even and odd n-alkanes, ranging between C_{23} and C_{33}, maximizing at C_{27}. The presence of even-numbered n-alkanes (as well as the absence of long-chain alcohols and wax esters) are inconsistent with beeswax.[66] Instead the range and distribution of the n-alkanes is consistent with a relatively heavy petroleum product (possibly diesel). The analysis of organic compounds associated with wine identified malonic, fumaric, succinic, malic, and vanillic and tartaric acids. The presence of tartaric acid as well as other fruit/fermentation associated compounds provide evidence that the vessel contained wine at some point during its use life. The combination of the lipid and the organic compounds associated with wine analyses show evidence for a vegetable oil and wine content, as well as hydrocarbon contamination that may have occurred during deposition or post-deposition.

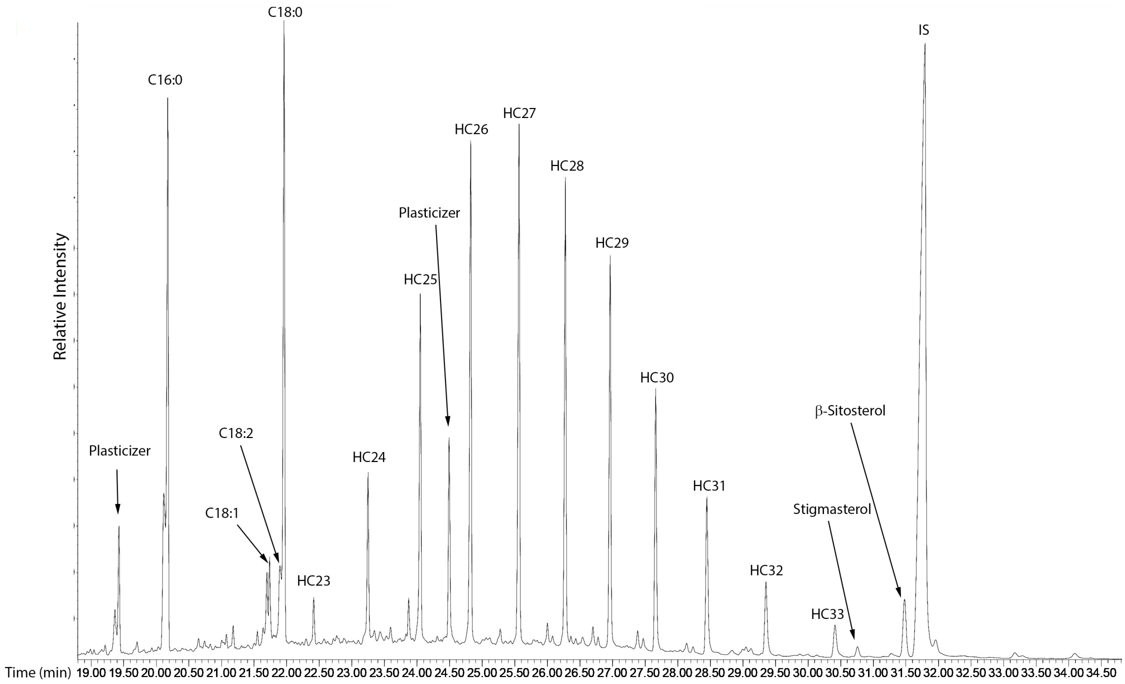


Figure 7.13: Partial total ion chromatograph of the total lipid extract (TLE) of Sample BEY006.5051.262. 'HCxx' indicates n-alkanes with a chain length of 'xx'.

7.2.1.12 Sample from BEY006.5051.263

The vessel is represented by a base and lower wall, the sample was taken from the side wall of the base. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well as dehydroabietic

[66] Evershed and Dudd 2003.

acid. The analysis of organic compounds associated with wine identified malonic, fumaric and succinic acids.

7.2.1.13 Sample from BEY006.5051.264

The vessel is represented by a base and lower wall, the sample was taken from the side wall of the base. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids, dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic, malic, citric and tartaric acids. Additionally, a small peak corresponding to the retention time for vanillic acid was identified (Fig. 7.14)

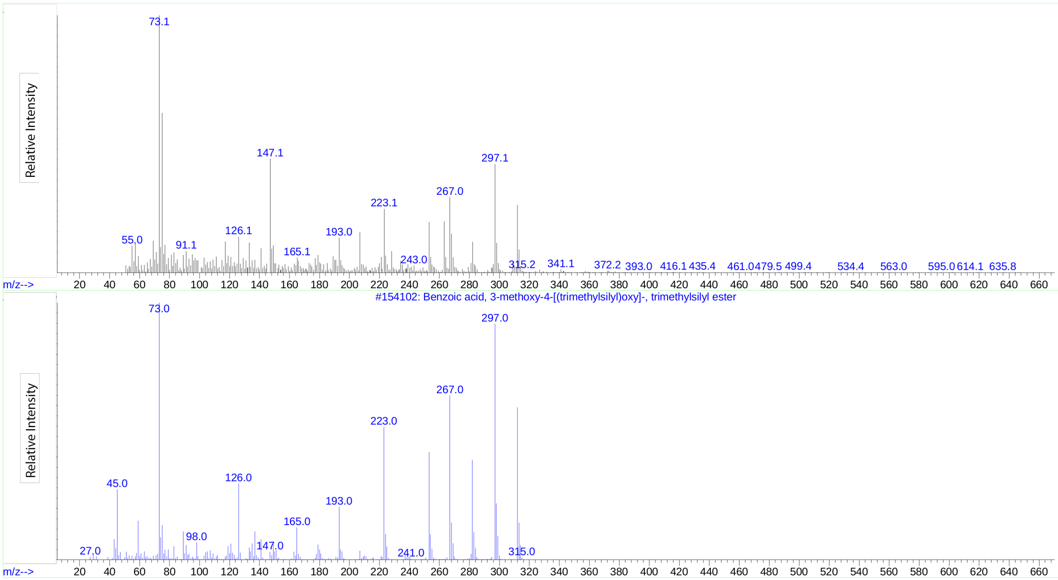


Figure 7.14: Mass spectrum of the peak identified as vanillic acid in Sample BEY006.5051.264 (top) compared against the mass spectrum of vanillic acid (as its trimethylsilyl ester) from the NIST11 database (bottom).

7.2.1.14 Sample from BEY006.5051.267

The vessel is represented by a shoulder and upper wall. The sample was taken from the lowest portion of the wall section. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well as dehydroabietic acid. The analysis of organic compounds associated with wine identified malonic, fumaric, succinic and malic acids.

7.2.1.15 Sample from BEY045.1242.97

Context 1242 is a large early 3rd c. AD deposit that forms a fill of the *natatio* of the Roman Baths. The vessel is represented by a complete handle. The sample was taken from the interior of the lower attachment (the vessel's shoulder). Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids, dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified fumaric, succinic, malic and vanillic acids.

7.2.1.16 Sample from BEY045.1510.24

Context 1510 is another fill context from *natatio* of the Roman baths dating to the early 3rd c. AD. The vessel is represented by a whole base. The sample was taken from the interior wall of the base. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids, dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine demonstrated the sample was notably depleted in organic compounds and only succinic acid was identified.

7.2.2 Analysis of results

The results of the lipid analyses, with a singular exception, are very consistent and show no indications that the Kapitän 2 was used to transport a lipid-rich commodity such as olive oil or *garum*. On the whole, only $C_{16:0}$ and $C_{18:0}$ fatty acids were identified. These themselves are ubiquitous, occurring in both animal and plant sources and probably derive from pine resin in these samples. The analyses do show that the vessels were lined with pitch derived from the pine family (with BEY006.10632.103 being the exception probably owing to the lack of preservation of the relevant biomarkers) (Table 7.2). This is consistent with examples recovered from Topraichioi, Murighiol/Halmyris and Caesarea that macroscopically maintained visible pitch. The significant outlier in the group is BEY006.5051.262. It is the only sample to demonstrate unsaturated fatty acids ($C_{18:1}$ and $C_{18:2}$) as well as plant sterols (stigmasterol and β-sitosterol) which are consistent with a vegetable oil. It is again an outlier in having a significant hydrocarbon profile. This is the only sample analyzed from the Beirut excavations that has demonstrated such a profile. Examination of the laboratory samples did not indicate intralaboratory contamination and, as such, it is reasonable to conclude that this contribution occurred at some time in the past, either during deposition or after excavation. It is possible that this contamination occurred during deposition. The areas of the Beirut excavations lay within the 'green line' during the Lebanese civil war and the buildings of the area suffered significant damage. Resulting ground soil contamination could potentially account for this. However, the lack of contamination in other samples from the same context suggest that either the contamination was very localized and did not reach other analyzed samples or that the contamination occurred after excavation to this particular sample.

The sum of the data shows strong evidence for the Kapitän 2 having contained wine. Tartaric acid was detected in 5 of the 16 vessels which is, for this period and region, specific to grapes and their products (Table 7.3). The frequency of the detection of tartaric acid in the samples is consistent with the 'success rate' of such analyses in vessels that are believed to have contained wine from the author's previous research.[67] In general, even for samples in which tartaric acid was not detected, other organic compounds consistent with wine were present. Three samples did demonstrate low preservation of organics in general: BEY006.10625.90, BEY006.10625.92 and BEY045.1510.24. The first two of these samples were from the shoulder and neck of the vessels, respectively. While it is possible that the position of the sample was from an area with poor exposure to the vessels' contents, other samples from such positions (e.g. BEY006.5051.267 and BEY006.10632.88) did contain a significant amount of wine associated compounds. BEY045.1510.24 was a base sample, which would have had significant exposure to the vessel's content. It is then possible that the nature of the depositional environment had an impact on the preservation of absorbed organic compounds. Many vessels from the piscina fills, which includes contexts such as BEY045.1510, had visible surface residues that suggested significant depositional water exposure.

[67] Woodworth 2011.

The absence of the detection of syringic acid in the samples may either be on account of the type of grapes used for the wine (i.e. white rather than red) or due to insufficient extant residue for detection. Syringic acid is often absent in samples containing tartaric acid and other organic compounds associated with wine, possibly due to poor penetration into the ceramic matrix (Alessandra Pecci *pers. comm.*). As such, a determination as to the color of the wine would be premature.

Table 7.2: Resin/pitch biomarkers detected in Kapitän 2 samples

Sherd Number	pimaric acid	DHA	abietic acid	7-oxoDHA	15 hydroxy 7oxoDHA
006.10625.90		X			
006.10625.92		X			
006.10632.88		X		X	
006.5051.262		X		X	
006.10632.103		X		X	
006.5051.267		X			
045.1242.97		X		X	
006.5051.262		X			
006.5051.263		X			
006.5051.264		X		X	
006.10625.105	X	X		X	X
006.10629.104		X			
006.10632.89		X		X	X
006.10632.103					
045.1510.24		X		X	
006.10622.106		X	X	X	X
006.10625.x3		X			

Table 7.3: Results of the analyses of organic compounds associated with wine

Sherd Number	Lab Sample #	POSITION	malonic acid	fumaric acid	succinic acid	malic acid	vanillic acid	vanillin	citric acid	tartaric acid	syringic acid
006.10625.90	277ETO	shoulder		X	X						
006.10625.92	382ETO	neck		X	X						
006.10632.88	355ETO	neck	X	X	X	X					
006.5051.262	352ETO	base	X	X	X	X	X			X	
006.5051.267	283ETO	shoulder		X	X	X	X				
045.1242.97	354ETO	shoulder		X	X	X	X				
006.10632.103	087ETO	base	X	X	X	X				X	
006.5051.263	089ETO	base	X	X	X						
006.5051.264	094ETO	base	X	X	X	X			X	X	
006.10625.105	096ETO	base	X	X	X	X	X		X	X	
006.10629.104	095ETO	base	X	X	X		X				
006.10632.89	090ETO	neck	X	X	X	X					
006.10632.103	093ETO	base	X	X	X	X					
045.1510.24	088ETO	base			X						
006.10622.106	092ETO	base	X	X	X	X	X		X	X	
006.10625.x3	400XETO	wall	X	X	X	X					

CHAPTER 8

SINOPE FORMS

8.1 Early History

The earliest known inhabitation of the area of Sinope was during the Hittite period known from Hittite sources to have been called 'Sinuwa'. The port was subsequently refounded during the 7th c. BC as a colony from the city of Miletus. The city fell under Persian domination during the 4th c. BC. During the Hellenistic period, Sinope enjoyed strong relations with Greece. Indicators of this connection are Sinopean coinage struck in Attic weight standards and bearing the head of Athena.[1] During the attack on Sinope by Mithridates II in 220 B.C., Rhodes supplied Sinope with arms and money as well as 10,000 amphorae of wine.[2] In 183 B.C. Sinope was conquered by Pharnaces I and became the capital of the Kingdom of Pontus. The city was conquered by the Romans under Miletus in 70 BC. In 47 BC Julius Caesar established the colony Colonia Julia Felix Sinope.[3] Strabo commented the walled city was 'splendidly' equipped with a gymnasium, forum and colonnades during his visit to the city during the late 1st c. BC.[4]

The development of Sinope during the Roman empire and early Byzantine periods is less conspicuous than in the city's earlier periods, at least with respect to the quantity of commentary by classical authors. Production and distribution of its commodities are well documented–the quantity and distribution of the city's amphorae interregionally increased significantly over the post-Hellenistic period during which the city was a possession within the Kingdom of Pontus. Field surveys have indicated that settlements around Sinope expanded significantly during the Roman period. In the Hellenistic period, occupation outside

[1]Robinson 1906b, 249.

[2]Robinson 1906b, 250.

[3]Doonan 2004, 93.

[4]Doonan 2004, 93ff; Strabo XII.iii.11.

the city was almost exclusively restricted to a 1-1.5 km distance from the shore.[5] Roman period settlements extended considerably further inland.[6] Additionally, in the late Roman period there is evidence of significant industrial activity. In the Demirci valley nearly a dozen kiln sites have been identified; although, to date only a few have been excavated.[7]

8.2 Production at Sinope

8.2.1 Timber

Sinope was known to produce a wide variety of products, much of this information is received from the accounts of classical authors. Sinope was well known for its timber production during the Greek and Roman periods.[8] Xenophon provides one of the earliest accounts on the quantity of high quality timber that grows in the Pontus when he described Kalpe Limen, a promontory halfway between Byzantion and Heracleia, as having a 'great deal of timber of various sorts' and an especially significant amount of 'fine ship timber' running along the coast.[9] Three centuries later Strabo commented similarly, 'both Sinopitis and all the mountainous country extending as far as Bithynia and lying above the seaboard have ship building timber that is excellent and easy to transport.'[10] Oak and conifers were preferred for shipbuilding; the later was considered an especially good material for construction as it is both light and resistant to decay.[11] Theophrastus noted that fir and larch grow in the Pontus and ranked the Pontus as second only to Macedonia for the quality of its shipbuilding timber.[12] In addition to timber for shipbuilding, Sinope also produced maple and walnut used for the construction of luxury products such as tables and couches.[13]

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[5]Doonan 2002, 193.

[6]Doonan 2002, 193.

[7]Doonan 2002, 193.

[8]Hannestad 2007, 86.

[9]*An* 6.4.4; Hannestad 2007, 86.

[10]Strabo 13.3.12 from Hannestad 2007, 92.

[11]Robinson 1906a, 141; Hannestad 2007, 92.

[12]Hannestad 2007, 92.

[13]Robinson 1906a, 141; Hannestad 2007, 96.

8.2.2 Mineral Production

Sinope was also known for mineral production, although the extent to which mineral resources were exploited is less evident. Sinopean steel was reported to have been of high quality and significant deposits of copper, silver, lead and jasper were known to have been exploited, at least during the Greek period, from the city's colonies of Giresun and Trabzon.[14] The most famous mineral export was that of a red ochre, known as μίλτος and *minium*.[15] The red ochre was also known as *sinopis* after the city. Mined in central Anatolia, the namesake according to Pliny is because Sinope was the first known exporter of the material.[16] By the Roman period, however, the material may no longer have been exported by Sinope. Pliny is silent as to whether the material was still an export but Strabo states, 'it [*sinopis*] had the name Sinopic, because the merchants used to bring it down from Sinope, before the traffic of the Ephesians extended as far as Cappadocia.'[17] The clear implication is that by the 1st c. BC trade patterns had shifted and the Sinopean monopoly, or even entire trade, in *sinopis* had ceased.[18]

8.2.3 Fishing

If judged by the frequency of mention by classical authors, fishing was an important industry at Sinope and appears to have been an industry diverse both in methods and of products.[19] The fish most frequently referenced were pylamydes–small tunnies, probably under one year of age although some sources treat pylamydes and tunnies as separate species.[20] Pliny, however, does examine the nomenclature, specifying that young fish at their first autumn are called *cordyla*, in the following spring they are referred to as *pelamides* and after they are a

[14] Doonan 2002, 195.
[15] Robinson 1906a, 141.
[16] *NH* XXXV.11 from Doonan 2002, 194.
[17] Hamilton 1903 from Doonan 2002, 194.
[18] Doonan 2002, 195.
[19] Doonan 2002, 187.
[20] Tekin 1996.

year old, *thynni* (i.e. tunnies).[21] Said to spawn in the Azou (east of the Crimea), the shoals followed the eastern cycladic current of the Black Sea in a clockwise fashion, easterly and southerly; by the time they reached Sinope, they were of considerable size and immense in number.[22] Polybius in his account of the Rhodian and Byzantian war (220-219 BC) recalls that the Pontus, although Sinope is not specifically named, supplied Greece with luxuries including salt fish (τάριχος) in abundance while taking excess Greek production–olive oil and wine.[23] Strabo and Pliny both commented on the bounty of pelamydes and that they were a commercial product that was exported to Rome.[24] Athenaeus in the 3rd c. AD recalled Dorion who praised the quality of mullet from Sinope.[25] Aelian, also writing during the 3rd c. AD, described teams of ten men working together to catch pelamydes, and larger crews of 30 for small tunnies.[26]

8.2.4 Olive Oil

Olives and its oil may have played a significant role in Sinopean agricultural and export. Prior to the Roman period, little is known about the cultivation of the olive at Sinope. As mentioned in Section 8.2.3, Polybius stated that Sinope traded salt fish for the Greek excess production of olive oil and wine during the Hellenistic period. This implies that neither of these commodities were produced at Sinope or at least not in sufficient quantities to satisfy local demand. By the Roman period, however, a more clear picture emerges. Strabo vividly describes the territory of Sinope, 'the whole country is planted with olive and cultivation begins a little above the sea coast.'[27] It has been suggested that Strabo's comments on olive cultivation reveal a shift in Sinope's production model where olive oil may have become the

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[21] *NH* 9.18

[22] Robinson 1906a, 140.

[23] Polybius IV.38. Concerning the use of τάριχος as a type of preserved fish product, see Curtis 1991, 66ff.

[24] Doonan 2002, 187; Doonan 2004, 95.

[25] *Ath.* III.87

[26] Animals XV.10 and XV.4-5 from Doonan 2004, 95.

[27] Strabo XII.iii.12 from Doonan 2004, 95.

city's primary export.[28] Survey work has indicated a shift in land use between the Hellenistic and Roman periods. Whereas the Hellenistic period settlements were primarily located on the peninsula of Sinope and a thin stretch of coast, the Roman period is characterized by a significant advance into the interior.[29] This may have been a result of the intensification of the production of olives and olive oil.

8.2.5 Wine

The evidence for the production of wine at Sinope is sparse. It has been traditionally argued that the amphorae of the Hellenistic period were used to contain wine by several elements of indirect evidence. Firstly, some of the handle stamps from Hellenistic period amphorae include grape leaves and grape clusters (Fig. 8.1).[30] While a small subset of all Hellenistic stamps (after which the practice of handle stamps ceases), it is a reoccurring motif. The shape of the amphora has also been considered by some scholars as indicative of the vessel's content. Opait argues that the earlier Sinopean forms imitated Aegean amphora forms that were associated with wine.[31] Classical accounts are silent concerning the topic of wine and viticulture at Sinope. As discussed in Section 8.2.4, Strabo mentions olive groves at Sinope but makes no comment about the growing of grapes. Moving eastward in his account of the coast of the Pontus, Strabo does comment that the area of Phanaroea, approximately 180 km east of Sinope, is planted with olives and grapes.[32] During the Hellenistic period there is not textual evidence for Sinopean production of wine. Theophrastus is silent about Sinope but does note that the wine of Heracleia Pontica was familiar in Hellenistic Athens.[33] In other accounts during the Hellenistic period when wine is mentioned in reference to Sinope, it is being exported to the city. Polybius recounts a shipment of 10,000 Rhodian amphorae of

[28] Doonan 2004, 95.

[29] Doonan 2002, 196.

[30] Garlan and Kara 2004, 36.

[31] Opait 2010b, 398ff.

[32] Strabo XII.3.31. Similarly, Pliny makes the same observation but erroneously names the place as 'Phanagoria', *NH* 6.4; Smith 1854.

[33] de Boer 2013, 111.

wine during the Rhodian-Byzantian war.[34] As mentioned in Section 8.2.3, at another point Polybius' account of trade dynamics implies Sinope did not produce wine or at least was dependent on import to satisfy local demand. Xenophon does mention a shipment of 1500 amphorae of wine and 3000 *medimnoi* of barley to the Greek army, although it is uncertain if the wine was a product of Sinope or an import.[35] Again during the Byzantine period, there is no available commentary on the status of Sinope's wine production.

Figure 8.1: Handle stamp on a Hellenistic period Sinopean amphora, demonstrating a grape cluster. Source: Garlan and Kara 2004, Plate 54.

8.3 Excavated Kiln Sites in the Region of Sinope

Two kiln sites have been found and excavated in the environs of Sinope responsible for producing significant quantities of amphorae. The first is located at Zeytinlik (meaning 'olive grove'), located on the southern portion of the peninsula (see Fig. 8.2). The site was first discovered by David Robinson who mistook it for an amphora dumping ground and wrote an article on the amphora handle stamps recovered from here and other locations in the vicinity of Sinope.[36] Expansion of the coastal road further exposed the site and two small scale

[34]Poly. 4.6.3 from Robinson 1906b, 250.

[35]Xenophon VI.1.15; de Boer 2013, 111.

[36]Robinson 1905; Garlan and Tatlican 1997, 307.

excavations were conducted between 1994 and 1997.[37] The excavations revealed that c. 300 BC one or two ceramic workshops were constructed as well as several kilns. Approximately 30 years later, another kiln was constructed. The site remained active in producing amphorae until the end of the Sinopean stamped amphora tradition, associated with the conquest of the city by Pharnacles I in 183 BC.[38]

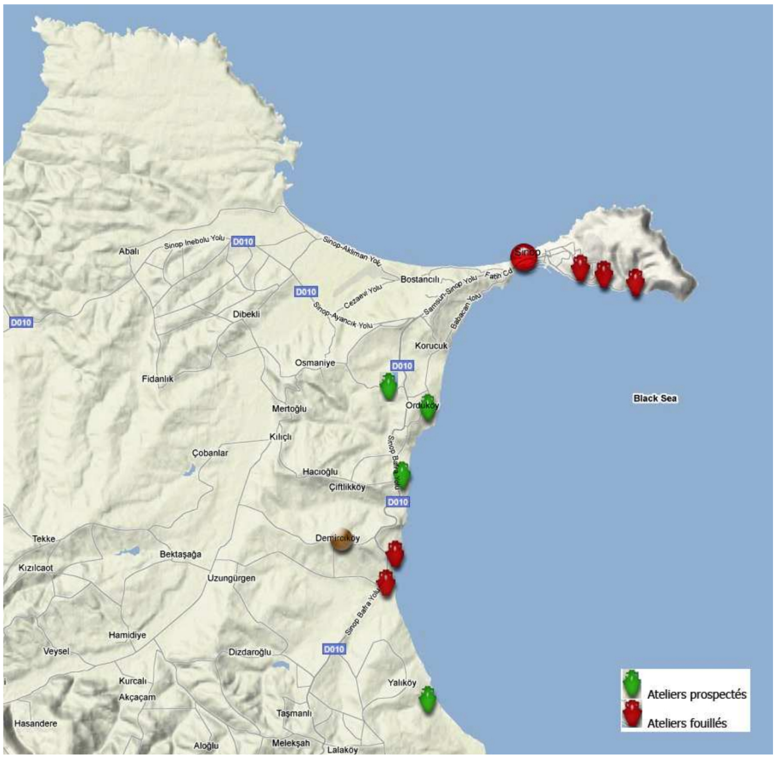

Figure 8.2: Map of kiln sites in the environs of Sinope. Source: Kassab Tezgör 2012, Fig. 1.

In the environs of Sinope to the south, approximately 12 inland kiln sites have been identified by survey dating to the Roman and early Byzantine periods (see Fig. 8.2).[39] A group of kilns were identified at Demirci located approximately 15 km south of Sinope. Four kilns and the surrounding area were excavated between 1994 and 2012 and are composed of two areas of excavation (Zone A and Zone B).[40] The excavations at Demirci were initiated in 1994 after it was observed that the intrusion of the sea was threatening what appeared to be a Roman period kiln site.

[37]Garlan and Tatlican 1997, 1998, 1999; Garlan 2007

[38]Garlan and Tatlican 1997, 316.

[39]Doonan 2002, 193.

[40]For an overview of the excavations, see Kassab Tezgör 2012.

8.3.1 Kilns from Demirci Zone A

In Zone A, Kiln A-UVW-1 is chronologically the oldest kiln and is represented by only part of the firing chamber floor.[41] The upper portion of a bead rimmed amphora was recovered, conforming to Kassab Tezgör's typology as a B Snp I.[42] This form is known to have produced during the 2nd and 3rd c. AD.[43] Ceramic remains also included fragments of 'cols d'amphores renflés', belonging to the group A Snp 1, dating to the late Hellenistic or early Roman periods.[44] Kiln A-UVW-1 is partially overlaid by a second kiln (Kiln A-UVW-2) orientated toward the southwest.[45] The firing chamber wall is preserved at a maximum height of 50 cm, composed of tiles and clay. The floor of the firebox is also preserved, separated from the oven by the remains of a stone arch. Between Kiln 2 and the subsequent construction phase (Kiln A-UVW-3) were large fragments of amphorae in a red fabric (C Snp I-1).[46]

Kiln A-UVW-3 (overlying Kiln A-UVW-2) is only partially preserved. The firing chamber is nearly circular (2.77m by 2.23 m) and the walls are only represented by a single row of tiles. The bases of two central pillars, formed by whitish clay, were observed. Within the oven and around its perimeter were fragments of amphorae classified as C Snp III. The form corresponds to late 4th to early 5th c. AD production and several fragments were observed to have post-firing inscription with a partially extant word ('ΕΥΔω') as well as one example with a cross.[47]

Kiln A-SRT-1 is identified by an extant firing chamber (approximately 1.5 m in diameter), the walls of which are preserved to a maximum height of 48 cm.[48] Fragments of red

[41] Kassab Tezgör and Tatlican 1998, 424. The author has employed a different naming convention from the original publication for the kilns excavated in Zone A. The kiln name is composed of [zone of excavation]-[excavation squares in which the kiln was observed]-[kiln number for the excavation squares]. This is due to the reason that the original excavation reports did not use unique identifiers for the various kilns, which creates confusion when attempting to analyze them as a group.

[42] For a complete example from the Sinop Museum, see Kassab Tezgör 2010a, , Plate 15, 2a.

[43] Kassab Tezgör and Tatlican 1998, 424. See Chapter 7.4 for discussion on Sinopean amphora forms.

[44] Kassab Tezgör 1996, 336;Kassab Tezgör 2010d, 124.

[45] Kassab Tezgör and Tatlican 1998, 424.

[46] Kassab Tezgör and Tatlican 1998, 424.

[47] Kassab Tezgör and Tatlican 1998, 425ff.

[48] Kassab Tezgör and Tatlican 1998, 429.

fabric amphorae matching C Snp III were recovered from the firing chamber. Kiln A-SRT-2 partially overlays A-SRT-1. It has a pear-shaped firing chamber (measuring 2.92 m by 1.77 m) with walls composed of tile, which are preserved to 1.4 m in height.[49] The firebox is composed of clay blocks. The passage between the firebox and firing chamber is composed of volcanic stone (locally known as 'ada taşi') that were lined with clay. This type of volcanic stone does not naturally occur at Demirci; the closest source is Kabali Bucağı, located approximately 10 km south of Demirci.[50] The use of this volcanic stone is similar to that used in the last kiln stage excavated in Zone B (see Section 8.3.2).[51] The floor of the firing chamber contained fragments of white fabric amphorae (group D Snp, type not specified), primarily necks and shoulders. Coins dating to the rule of Justinian (527-565 AD) were recovered and are consistent with the dating of the latest kiln stage in Zone B, slightly bringing forward the terminus post quem.[52]

The final kiln excavated in Zone A was Kiln A-QR-1 and is the largest of the kilns from Zone A. The firing chamber is pear-shaped, measuring 3.65 by 2.76 m.[53] The walls are extant to 77 cm and are composed of tiles and clay blocks. The two central rectangular pillars are composed of whitish clay. The west side of the oven contains a threshold 95 cm in length that was blocked by a deposit of red clay. This is the only kiln at Demirci that has a secondary access passage. The excavators believe that it may have been used to facilitate loading and unloading the firing chamber.[54] The composition of the deposit within the kiln is also distinctive from the other kilns. There was a considerable amount of ash in the firebox and its immediate area. The floor of the firing chamber itself was covered with approximately 10 cm of greenish-white clay with frequent small inclusions. The presence of this material led the excavators to speculate that the kiln may have been converted to a storage area for

[49] Kassab Tezgör and Tatlican 1998, 429.

[50] Kassab Tezgör and Tatlican 1998, 433.

[51] Kassab Tezgör and Tatlican 1998, 433.

[52] Kassab Tezgör and Tatlican 1998, 433.

[53] Kassab Tezgör and Tatlican 1998, 434.

[54] Kassab Tezgör and Tatlican 1998, 434.

levigated clay.[55] The depositional material filling the chamber included tubuli, fragments of red fabric amphorae (presumably C Snp types), bone fragments and other storage vessel fragments including the neck of a Colchean amphora dating to the 3rd or 4th c. AD.[56]

8.3.2 Kilns from Demirci Zone B

Two kilns were excavated in Zone B. Kiln B-1 is a small pear-shaped kiln (measuring 1.98 by 1.41 m) without any evidence of supporting pillars. Only the firing chamber is extant with a maximal extant wall height of 52 cm. The walls consist of tiles packed in clay.[57] Amphora fragments were recovered from the firing chamber as well as a large cache of fragments to the south-east of the kiln. The fragments were identified as 'carrots', most probably C Snp III vessels.[58] Coins were found in associated contexts dating to between the late 4th and first half of the 5th c. AD.[59]

The second kiln, Kiln B-2, partially overlays Kiln B-1. It is a larger structure–the firing chamber, the only extant part of the kiln, measures 2.47 by 2.39 m.[60] The walls are composed of brick and stones overlaid with a greenish-white clay. Two brick pillars are present in the center of the oven. A large volcanic stone was used to close the entrance of the firing chamber.[61] The excavation report does not mention if any amphora fragments were recovered from the kiln itself; however, a large black earth embankment directly to the west of the kiln was found to contain several types of amphorae, including D Snp fragments but more commonly 'carrot' fragments, most probably C Snp III amphorae.[62]

[55]Kassab Tezgör and Tatlican 1998, 438.
[56]Kassab Tezgör and Tatlican 1998, 438.
[57]Kassab Tezgör 1996, 353.
[58]Kassab Tezgör 1996, 353.
[59]Kassab Tezgör 1996, 353.
[60]Kassab Tezgör 1996, 353.
[61]Kassab Tezgör 1996, 353.
[62]Kassab Tezgör 1996, 354.

8.3.3 *Press counterweights recovered from the Demirci excavations*

In addition to the kiln installations excavated in Zone A, three press counterweights were recovered. The first, found in square V20, is a rectangular stone measuring 1.32 m in length.[63] According to the excavation report, it appears to have been refashioned for use as a counterweight.[64] The counterweight is located to the west of the excavated kilns. The position of the stone in the backfill over Kiln A-QR-1 establishes a 5th c. AD terminus post quem.[65] The ceramic composition of the depositional material covering the counterweight was composed of red fabric amphora sherds (C Snp), indicating that the stone was most probably not deposited after the conversion to production of the D Snp fabric group (i.e. some time during the 5th c. AD).

The other two counterweights are cubic in shape. One, measuring 74 x 60 x 51 cm, was recovered from a carbonaceous layer in Square Q26 covering Kiln A-QR-1 (Fig. 8.3).[66] The third counterweight was recovered during the survey of Square P26.[67] It appears that the stone may have been relocated from its use area before deposition as the strata under the stone showed no habitation identifiers.[68] The covering depositional material was a thick layer of D Snp I fragments. The nature of the deposition was characteristic of a waster dump and indicates a terminus post quem for the depositional date during the 6th c. AD.[69]

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[63] Kassab Tezgör and Tatlican 1998, 438.

[64] Kassab Tezgör and Tatlican 1998, 438.

[65] Kassab Tezgör 2010c, 100.

[66] Kassab Tezgör and Tatlican 1998, 438.

[67] Kassab Tezgör and Tatlican 1998, 438.

[68] Kassab Tezgör 2010c, 100.

[69] Kassab Tezgör and Tatlican 1998, 440.

Figure 8.3: Drawing of Kiln A-QR-1 in relation to the recovered counterweight from Square Q26. Source: Kassab Tezgör and Tatlican 1998, Fig. 22.

There are two complications with the press counterweights and their relation to agricultural production in the Demirci area. Firstly, the relationship between the presses and the amphora-producing kilns is unclear. The counterweights are not directly contextually associated with any of the kilns during their use life. Kassab Tezgör argues that the counterweights (and the presses they represent by proxy) are indicative of change from industrial manufacture of amphorae to agricultural production.[70] The evidence from the small area of excavation in Zone A at Demirci could support some elements of this theory. For example, the counterweight recovered from the area of Kiln A-QR-1 appears to have been deposited after the closure of the kiln. The counterweight was recovered from a carbonaceous context (most probably ash waste from kiln use) with C Snp fragments. In Zone A, the latest kiln stages are associated with C Snp production, indicating a termination of use at the end of the 4th to the first half of the 5th c. AD. It is unclear as to the stratigraphic relationship between the rectangular counterweight recovered from the area to the west of the kilns and the kilns themselves. The context overlaying the counterweight recovered from Square P26 indicates,

[70]Kassab Tezgör and Tatlican 1998.

however, that amphora production had not ceased in the vicinity because the counterweight was deposited below a layer of D Snp amphora fragments, the manufacture of which is not attested in the excavated areas of Zone A. This places the counterweight's deposit later than that of the one from Square Q26, although since only the fabric type and not form of the amphora fragments are described, the period of time between the deposition of these two counterweights can not be ascertained.

Secondly, the role of the counterweights in commodity production, specifically the type of commodity produced, remains unclear. The role of the counterweights is also complicated by the fact that they are not associated with any architectural features or remains that might indicate what agricultural product was being produced at Demirci and, more generally, in an attempt by a case study approach to ascertain what Sinope was producing for amphora-borne export. The rectangular shape of the counterweights is seemingly a phenomenon of Pontic presses during this period as opposed to the circular or oval types observed in other regions.[71] They would have been utilized in a screw-press type installation which appeared throughout the Mediterranean world during the 1st c. AD.[72] No architectural remains of the rest of the press or associated architecture (e.g. buildings, pithoi for retention of the extracted liquids) are extant in the direct proximity of the counterweights. This brings into question whether the counterweights were used in this area or were brought to this area after their use life. The general positioning of the counterweights from Squares P26 and Q26 do not immediately suggest discard. Both are orientated vertically (with respect to their use orientation) and were level within the depositional context (the rectangular counterweight from Square V20 is vertically orientated but residing in a reclined position within the depositional context). It is useful to note, however, that the counterweights from Squares P26 and Q26 were recovered from contexts within apparent discard levels. The counterweight from Square Q26 was subsumed within a context of ash and C Snp amphora fragments that were most probably a waste dump from kiln production. The counterweight from Square P26 was buried beneath

[71] Kassab Tezgör and Tatlican 1998, 438.
[72] Brun 1993.

approximately 40 cm of amphora sherd deposits of the D Snp group. Both of these depositional contexts suggest that the counterweights themselves may have been items of discard, despite their seemingly 'careful' positioning with deposition.

The final matter of interest concerning the counterweights is the type of commodity that they were used for processing. Screw-presses to which these counterweights would have belonged were utilized for pressing of both grape and olive.[73] The utilization of such presses in Demirci or indeed the environs of Sinope in general has not been established by archaeological or archaeobotanical remains, probably due to the limited excavations conducted to date in the city's environs. The excavators of Demirci and the principal investigator in Sinopean amphorae, Dr Kassab Tezgör, are inclined to argue that the production in this region and thus the content of the amphorae manufactured here was that of olive oil.[74] This attribution is primarily based upon textual evidence, especially that of Strabo that described Sinope as a renowned producer of oil. There is, however, sparse evidence from the excavated areas as to what was grown or processed in the area of Demirci. For the content of the amphorae the only physical evidence for use come from some vessels recovered from shipwrecks.

8.4 The Amphorae of Sinope, Roman and Byzantine Periods

Dr Kassab Tezgör has developed a typology of amphorae manufactured at Sinope between the 2nd and 6th c. AD. The basis of the typology is separation of the amphorae into four groups (A-D) according to fabric color then by type and variant (e.g. A Snp III-1 represents fabric color group 'A', vessel type 'III', variant '1').[75] An interesting aspect of Sinopean amphorae is the wide range of fabric colors produced during the Roman and Byzantine periods. Fabric colors range from yellowish, pinkish, reddish to whitish and these fabric colors 'succeed each other in time' and are directly associated with specific forms (Fig. 8.4).[76] The clay differs only in color; by visual inspection the same tempers appear to be constant, including

[73]Brun 1993.

[74]Kassab Tezgör and Tatlican 1998; Kassab Tezgör 2012.

[75]It should be noted that this typology is not to be confused with that developed by Sergey Vnukov.

[76]Erten et al. 2004, 103.

black sand (identified as pyroxene) and inclusions of calcite, quartz and feldspar.[77] Additionally, there are some red inclusions that are either hard like a mineral or crumbly/powdery.[78] The material upon which the typology was developed is principally from museum collections as material excavated from kiln sites at Demirci were generally incomplete although the kilns do provide some chronological information, especially with respect to the periodicity of the different fabric color groups.

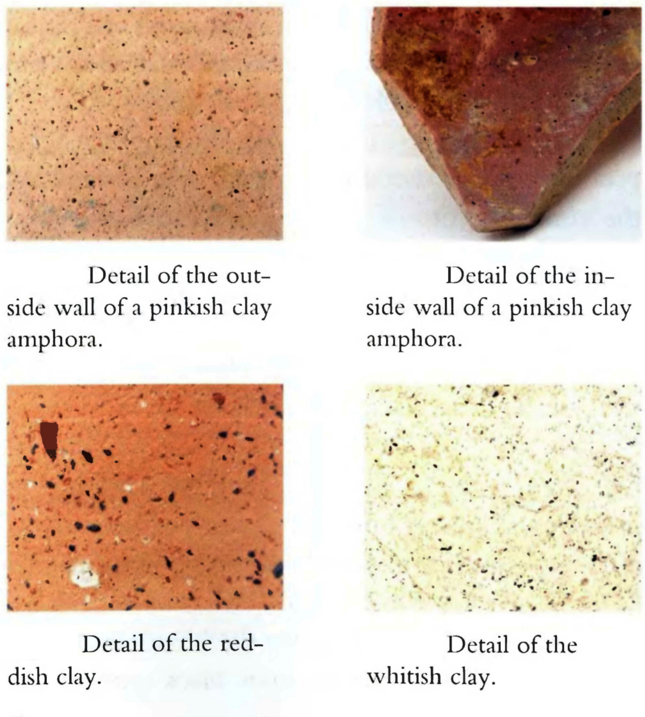

Figure 8.4: Close up images of the four primary fabric colors exhibited in Sinopean amphorae. Source: Erten et al. 2004, Fig. 1d-g.

8.4.1 Group A

Chronologically, Group A is the earliest and is also referred to as 'swollen (renflé) neck' amphorae. This group is poorly represented at the Demirci kilns with only seven necks attested, as well as some other fragments recovered from dumps.[79] No complete examples

[77]Erten et al. 2004, 103;Kassab Tezgör et al. 2007, 199ff.

[78]Erten et al. 2004, 103.

[79]Kassab Tezgör 2010d, 124.

are known. Members of this group were previously classified by Scorpan as a rare northern Black Sea form.[80] The fabric color is an orange to light orange. The rim is oval and projects outward. The body is elongated with curving and tapered walls (Fig. 8.5).[81] It is difficult to establish a date of production for this form. Chronologically, it is the earliest at Demirci such that a terminus ante quem would be expected before or during the 2nd c. AD. Two examples are known from other sites. One example was found at Kharaks (in the Crimea) dated to the first half of the 4th c. AD; the second is a neck from Pityus (in modern Georgia) also dated to the 4th c. AD.[82] No examples are known from Beirut. There is evidently an issue with the production date for this group which is undoubtedly complicated by the scarcity of recovered examples.

Figure 8.5: Photograph of the neck of a Group A amphora. Source: Kassab Tezgör 2010d, Pl. 21.3.

80 Kassab Tezgör 2010d, 124. See Scorpan 1975, 284, Fig. 27.

81 Kassab Tezgör 2010d, 125.

82 Kassab Tezgör 2010d, 125.

8.4.2 Group B

The second color group, Group B, is characterized by a light pink to yellow-orange fabric, although the interior walls sometimes have a purple hue.[83] Necks and neck fragments were recovered from the Demirci excavations; however, they are somewhat rare, leading to speculation that primary production may have been elsewhere at Demirci.[84] With respect to form, the vessels have a rim with a well distinguished convex band.[85] The body is high and wide with rounded walls. The handles are attached below the rim and are massive and slightly oval in cross-section.[86] Some handles demonstrate a wide rib in low relief and grooves are present at the junctions of the handles with the body.[87]

8.4.2.1 Typology

The Group B amphorae are divided into three types. The first, B Snp I, is characterized by a high and wide cylindrical neck and has well-defined, almost angular, shoulders (Fig. **??**.5, Fig. 8.6).[88] The second type, B Snp II, also has a cylindrical neck although, compared to B Snp I, less high and wide and lacks defined shoulders (Fig. 8.7).[89] The widest part of the amphora is in the top third of the body. The third type, B Snp III, features a tapered neck; the shoulders are not clearly defined and the widest part of the amphora is found in the top third of the body.[90] B Snp I and III are clearly differentiated forms whereas B Snp II appears to be an intermediate form possessing a neck similar to B Snp I but shorter and with shoulders and body more closely resembling B Snp III.[91]

[83]Kassab Tezgör 2010d, 125.
[84]Kassab Tezgör 2010d, 125; Kassab Tezgör et al. 2007, 200f.
[85]Kassab Tezgör 2010d, 125.
[86]Kassab Tezgör 2010d, 125.
[87]Kassab Tezgör 2010d, 125.
[88]Kassab Tezgör 2010d, 126.
[89]Kassab Tezgör 2010d, 126.
[90]Kassab Tezgör 2010d, 126.
[91]Kassab Tezgör 2010d, 126.

Figure 8.6: Photograph of a B Snp I amphora. Source: Kassab Tezgör 2010d, Pl. 15.1.

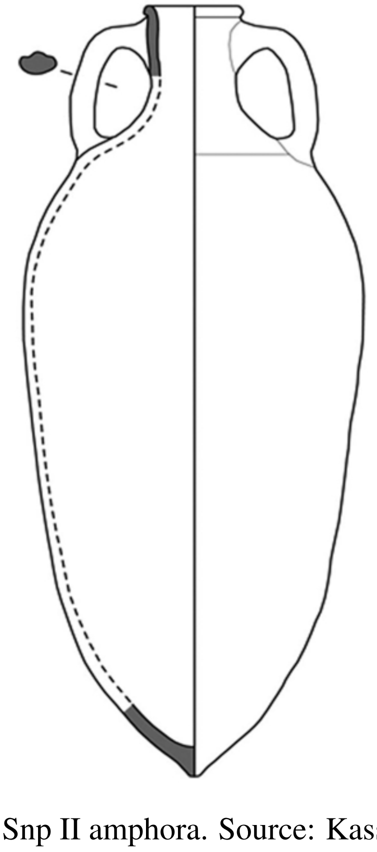

Figure 8.7: Drawing of a B Snp II amphora. Source: Kassab Tezgör 2010d, Pl. 15.2b.

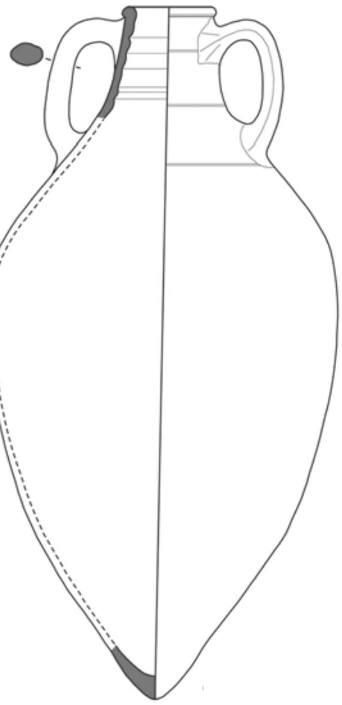

Figure 8.8: Drawing of a B Snp III amphora. Source: Kassab Tezgör 2010d, Pl. 15.4.

8.4.2.2 Chronology

Examples of the B Snp group are attested at several well dated sites, being present at Gorgippia (modern Anapa, Russia) in houses dated to the 2nd and first half of the 3rd c. AD, at Pityus in contexts dating to the first half of the 3rd c. AD and at Tanais in the 3rd c. AD.[92] Most recovered examples belong to types I and II, more rarely III.[93] At Demirci, they are associated with the oldest furnace layers; however, no deposits at Demirci are sufficiently complete to determine a relative chronology within this amphora group.[94] This group demonstrates the end of a tradition of craftsmanship (i.e. techniques and morphological elements) that began during the 4th c. BC–B Snp I and II possess a collar similar to 2nd c. BC forms, while the almost angular shoulder of B Snp I recall Hellenistic forms.[95]

[92] Kassab Tezgör 2010d, 126.

[93] Kassab Tezgör 2010d, 126.

[94] Kassab Tezgör 2010d, 126.

[95] Kassab Tezgör 2010d, 126f.

8.4.3 *Group C*

Group C amphorae (also referred to as 'colored') are characterized by a bright orange/red to light red fabric.[96] There is a greater variability of fabric color compared to Groups A and B but this variability is not associated with specific types.[97] Notable in this group is that the amount of pyroxene in the necks and handles is significantly greater than that observed in the shoulders and bodies.[98] Group C materials is the most prevalent group at Demirci.

8.4.3.1 Typology

The typology for Group C is the most complex because some types or variants do not appear to have been standardized in their dimensions.[99] Classification was made by Kassab Tezgör examining the ratios of height and width of the neck and the height of the neck above the handles as dimensions varied proportionally.[100]

The first type is C Snp I also known as the Zeest 100. The vessel has a conical neck and a wide mouth with a neck height above the handles of at least 7 cm.[101] The body is trapezoidal in shape, featuring slight narrowing in the final third of the body and having a triangular foot (Fig. 8.9.1). The body has slightly visible undulations on the surface which are more prominent on the neck. Handles have a central rib or two parallel ribs.[102]

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[96] Kassab Tezgör 2010d, 127.

[97] Kassab Tezgör 2010d, 127.

[98] Kassab Tezgör 2010d, 127.

[99] Kassab Tezgör 2010d, 127.

[100] Kassab Tezgör 2010d, 128. The typological classification described below is that of Kassab Tezgör 2010d. Several other typologies have been previously developed, including Opait 2004a, Opait Type E-1a,b,d and f; Sazanov 2007, fn. 43; Vnukov 2010b.

[101] Kassab Tezgör, 2010d, 128.

[102] Kassab Tezgör 2010d, 128.

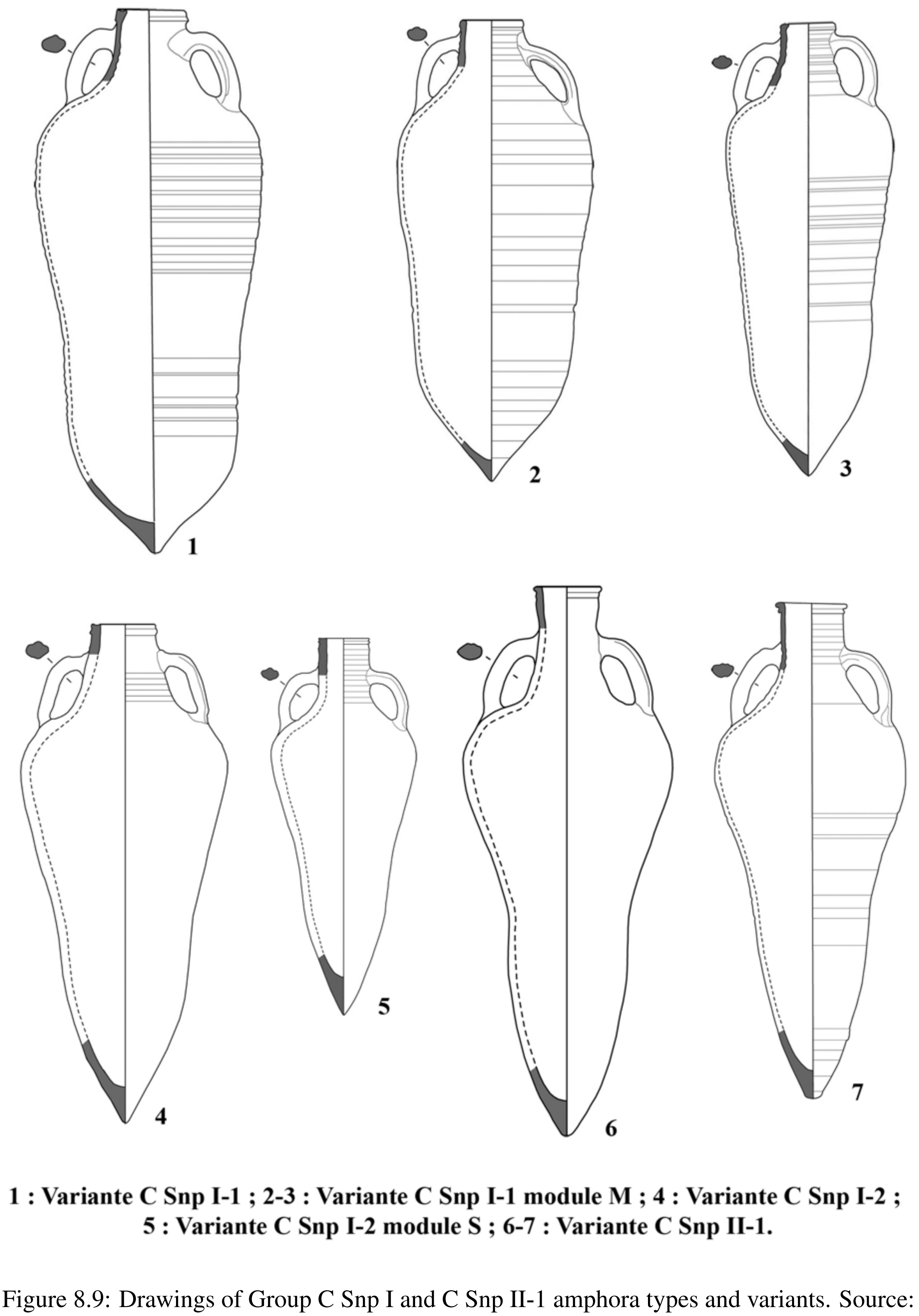


Figure 8.9: Drawings of Group C Snp I and C Snp II-1 amphora types and variants. Source: Kassab Tezgör 2010d, Pl. 18.

C Snp I has two variants. C Snp I-1 has a rim that is concave on the top, which in some examples widens sufficiently to form a double bead, and the lower edge often features a groove separating it from the wall. The foot is pointed, forming at the conjunction of slight convex walls (Fig. 8.9.2-3).[103] The C Snp I-2variant maintains most morphological similarities to C Snp I-1 with the distinction that the rim forms a double bead and the lower third of the body is more narrowed with a more pointed foot. C SnpI-1 is observed to have large, medium and small modules; large and small modules of the C Snp I-2 are also known.[104]

C Snp II continues the evolution of the vessel's form with a narrower body and more pointed base. Kassab Tezgör describes the body as 'triangular' with a tall and cylindrical neck.[105] The neck extends more than 8 cm above the handles, which feature one or two central ribs. This group is further subdivided into three variants and subvariants. C Snp II-1 has a cylindrical and wide neck with a double-beaded lip. C Snp II-2 has a wider and taller neck than C Snp II-1. C Snp II-3 varies from the previous two by having a higher and more narrow neck. Subvariants are identified by the suffix 'a' or 'b', which refers to whether the vessel has a flat rim or a double-beaded rim, respectively.[106]

The final type for Group C is the C Snp III which is the final stage of evolution into a 'carrot' amphora (Fig. 8.10). The vessels are distinguished by their small body size (and thus volume) and long and narrow shape, measuring between 67 and 80 cm in total vessel height with an approximate volume of 6-7 L.[107] The first type, C Snp III-1, has a total vessel height of between 67 and 75 cm. The neck extends above the under handle joint by 8-10 cm and has a shoulder diameter of between 22 and 25 cm.[108] Approximately 200 C Snp III vessels are held in the collections of the Turkish Museum at Sinop. The second type, C Snp III-2, has a similar body profile to C Snp III-1 but has both a longer neck (between 10 and 14.5 cm above

[103] Kassab Tezgör 2010d, 129.
[104] Kassab Tezgör 2010d, 129.
[105] Kassab Tezgör 2010d, 129.
[106] Kassab Tezgör 2010d, 129.
[107] Kassab Tezgör 2010d, 130.
[108] Kassab Tezgör 2010d, 130.

handles) as well as being more slender of body with a shoulder diameter measuring between 19.5 and 21 cm.[109] Both types have ‘a’ and ‘b’ subtypes as per C Snp II. A notable aspect is that while there are considerable dimensional variability in C Snp III vessels, proportionality of the dimensions (i.e. body length to shoulder diameter) remains fairly constant.[110] Additionally, fragmentary evidence at Demirci indicates the amphorae were made in at least four parts: neck, shoulder and top of body, lower body and foot.[111] This would potentially account for observed variations in temper (i.e. pyroxene) previously observed.[112] It has been speculated that the change in morphology found in Group C, and perhaps its later stages of development, may have been to increase the vessels’ space efficiency for shipping.[113]

8.4.3.2 Chronology

The excavated kilns at Demirci indicate manufacture during the 4th and 5th c. AD continuing possibly as late as the early 6th c. AD.[114] Fragments of C Snp I have been recovered from the Kingdom of the Bosporus in houses that were inhabited prior to the invasion of the Goths in 240 AD.[115] In the Chenyakhov culture as well as at Tanais C Snp I are present in relatively significant quantities in contexts dating to the 4th and 5th c. AD.[116] Similarly, at Beirut Group C amphora are associated with 4th and 5th c. AD contexts.

8.4.4 Group D

Group D represents the final stage of amphora production known from Sinope. The form of the vessels demonstrate a sudden and significant departure from the morphology of Group C vessels. Gone are the long and slender ‘carrot’ type amphorae which are instead replaced

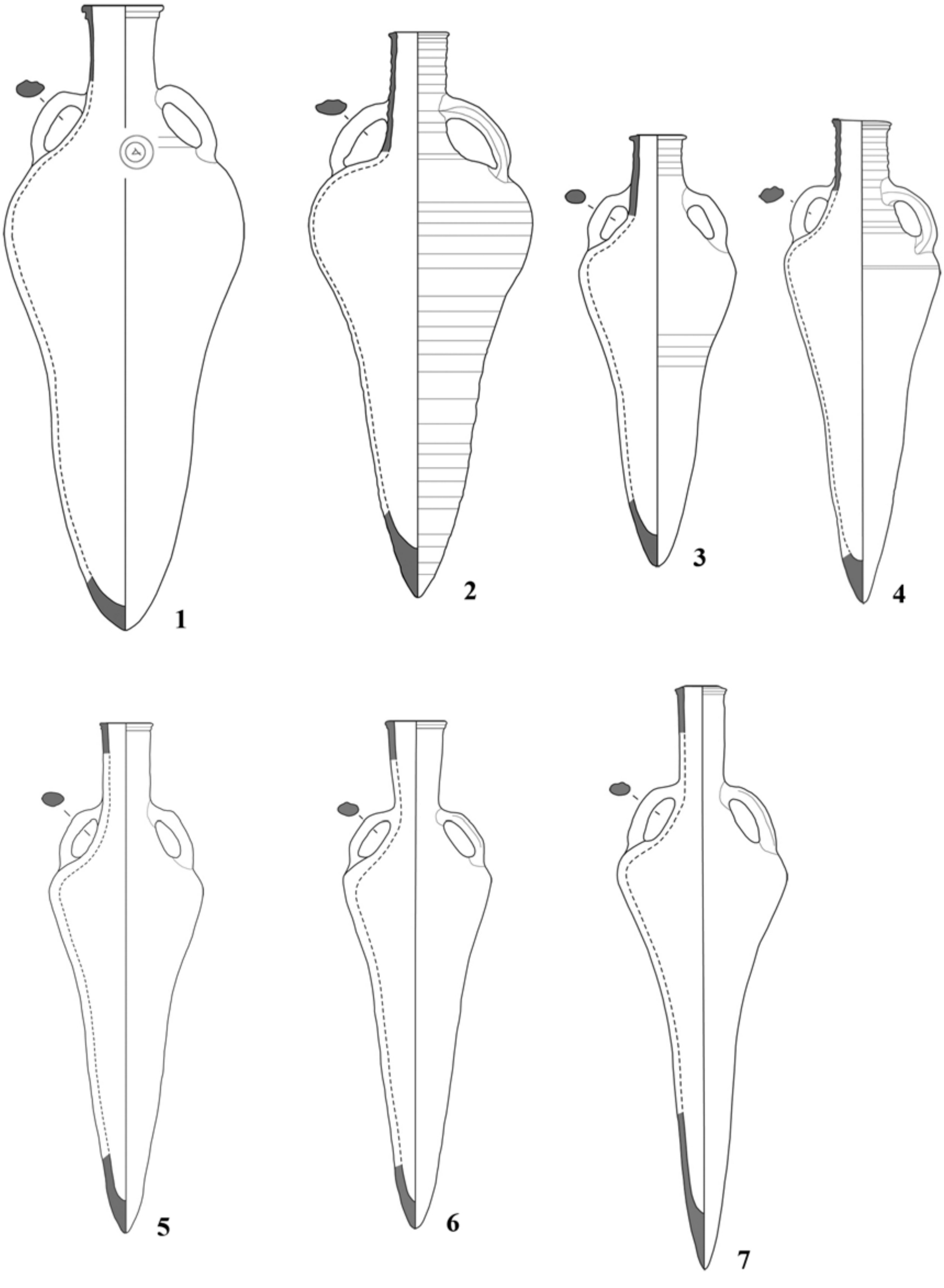
[109] Kassab Tezgör 2010d, 130.
[110] Kassab Tezgör 2010d, 131.
[111] Kassab Tezgör 2010d, 131.
[112] See Section 8.4.3.
[113] Kassab Tezgör 2010d, 134.
[114] Kassab Tezgör 2010d, 132.
[115] Kassab Tezgör 2010d, 132.
[116] Kassab Tezgör 2010d, 132f.

by short, round-bodied vessels that, at least in some types, bear a strong resemblance to the LRA 1. The fabric of this group varies in color between whitish, yellowish, greenish, light tan and even pink.[117] In contrast to Group C, the only variance in the quantity of pyroxene in the vessels is observed in the handles, which are enriched relative to the rest of the vessel.[118] The vessels have a similar capacity to C Snp III vessels, i.e. 6-7 L.[119]

[117] Erten et al. 2004.

[118] Kassab Tezgör 2010d, 134.

[119] Kassab Tezgör 2010d, 137.



1 : Varianate C Snp II-2 ; 2 : Variante C Snp II-3 ; 3-4 : Variante C Snp III-1 a et b ; 5-6 : Variante C Snp III-2b ; 7 : Variante C Snp III-2 a.

Figure 8.10: Drawings of C Snp II-2, C Snp II-3 and C Snp III amphorae. Source: Kassab Tezgör 2010d, Pl. 19.

8.4.4.1 Typology

The general quality of manufacture of Group D vessels appears to be noticeably poorer than those of earlier groups. The lip of the rim is generally irregular, thin and poorly defined.[120] In general, the neck is conical or cylindrical and the upper portion of the handles attach to the bottom of the rim. The handles themselves are either square or oval in section. A series of narrow ribs or undulations cover the shoulder and top of body.[121] The first type, D Snp I, has also been previously referred to as the 'Demirci-type' in earlier publications.[122] The body is conical with slightly curved walls with the foot composed of a rounded cap with a narrow, often flattened, base (Fig. 8.11).[123] This type was previously considered a sub-group of LRA 1 in some publications.[124] A variant of this type, D Snp I col, shares the same morphology but has the orangish-red fabric color of C Group amphorae.[125] The second type, D Snp II, demonstrates a body reduced in width in the lower half and bearing a foot shaped as a rounded cap. Ribbing is apparent on the shoulders and is mostly flat. The final group, D Snp III, features a more elongated body although still conical. Its shoulders, however, are wider and the foot is a tubular and narrow extension of the body.[126] Ribbing or undulations are present as per D Snp II.

Like C Snp III, Group D vessels are composed of four parts: neck, shoulders and top of body, central body and foot.[127] The presence of a conical or cylindrical neck does not coincide with other morphological elements of the amphorae. The same holds concerning where on the vessel ribbing or undulations begin, end or the spacing between them. These differences instead may be simply the result of minor stylistic differences of different pot-

[120] Kassab Tezgör 2010d, 134.

[121] Kassab Tezgör 2010d, 134.

[122] *inter alia* Kassab Tezgör 1996, 2002b.

[123] Kassab Tezgör 2010d, 134f.

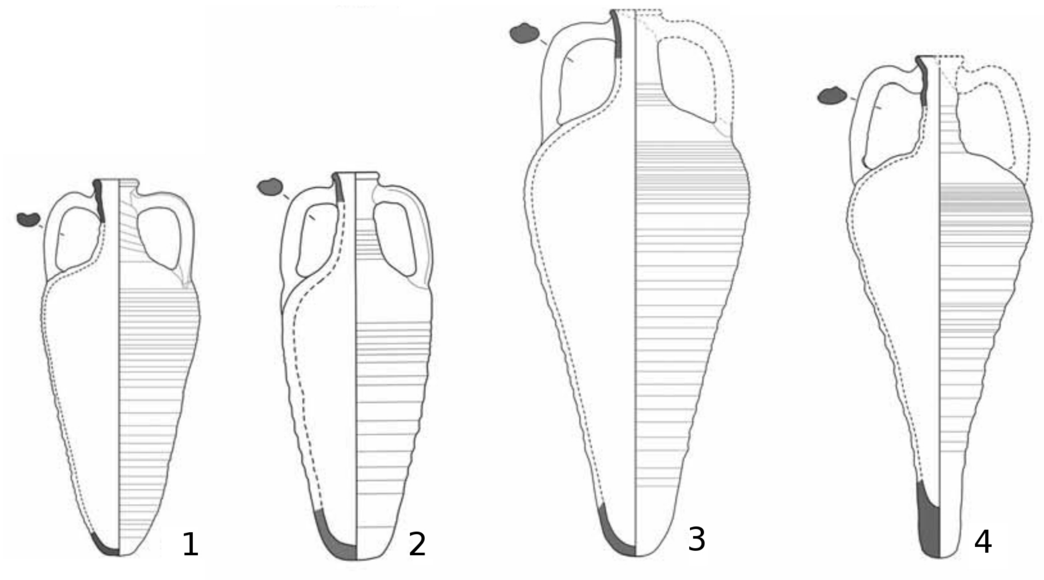
[124] e.g. Pieri 2005, 76f.

[125] Kassab Tezgör 2010d, 135.

[126] Kassab Tezgör 2010d, 136.

[127] Kassab Tezgör 2010d, 136.

ters.[128]



Kassab Tezgör 2010d, 138.

Figure 8.11: Drawings of D Snp amphorae, (1 and 2) D Snp I, (2) D Snp II, (3) D Snp III. Source: Kassab Tezgör 2010d, Pl. 20.

8.4.4.2 Chronology

Excavated contexts at Demirci do not allow us to determine whether D Snp directly replaced C Snp vessels or if there was some degree of chronological overlap.[129] With respect to the morphological evolution of D Snp forms, it may be reasonable to suspect that the forms evolved in the order of Kassab Tezgör's numeration of the typology although the lack of direct evidence from Demirci prevents a definitive conclusion. Small quantities of D Snp III were recovered from kilns at Demirci which contained coins dating to Justinian I (527-565 AD) as well as Justinian II and Sophia (565-578 AD) indicating production probably began, at least with respect to this kiln, during the second half of the 6th c. AD.[130] If the theory that D Snp I precede that of D Snp III is valid, D Snp I production would have begun earlier, perhaps at the beginning of the 6th c. AD judging from the excavated material from

[128]Kassab Tezgör 2010d, 136.

[129]Kassab Tezgör 2010d, 136.

[130]Kassab Tezgör 2010d, 137.

Demirci.[131] The ceramic evidence from sites that attest D Snp imports indicate an earlier date of inception than that of Demirci. At Beirut they appear by the third quarter of the 5th c. AD.[132]

8.4.5 Trends in Group B, C and D forms

Group B types have some similarities to C Snp I. Firstly, they demonstrated some similarities in morphological traits. Secondly, with respect to manufacturing technique, the composition of the fabric remains homogeneous through the vessel.[133] General morphology, however, changes significantly with the introduction of C Snp I. Whilst Group B types demonstrated a continuation of the general morphology of Sinopean amphorae begun in the Hellenistic period, C Snp I marks a distinct shift from the previous paradigm. The shape of the body, handles and foot continue in the form of their Hellenistic predecessors.[134] Group C and D amphorae share similarity in manufacturing methodology in being composed for four parts, the pyroxene content of which varies. C Snp III appears to mark a new phase of production in which smaller volume vessels (in the 6-7 L range) predominate. The quality of manufacturing observed in C Snp III and D Snp vessels declines. This is apparent in the irregularity of the rim (especially in Group D vessels) as well as in significant variations of the point of attachment of handles and visible joins of different vessel parts.

8.5 Distribution

Distribution of Roman and Byzantine period Sinopean amphorae show two main axes: one in the Black Sea region and another in the Mediterranean, especially in the east.[135]

[131] Kassab Tezgör 2010d, 137.
[132] Reynolds 2010b, 96.
[133] Kassab Tezgör 2010d, 138.
[134] Vnukov 2010b, 368.
[135] Erten et al. 2004, 103.

8.5.1 *Group B vessels*

The distribution of Group B amphorae is the least well documented of the Sinopean fabric groups which, at least in part, is reflected in the difficulty establishing a full and relative chronology. According to Vnukov, they are known in the eastern Pontic region and in the Crimea.[136] Kassab Tezgör concurs that the group is well attested in the Pontic region during the 2nd and 3rd c. AD.[137] Examples are known from the northern coast of the Black Sea at Tanais dating to the 2nd or 3rd c. AD as well as at other Crimean sites and at Gorgippia inhabited after the city's sacking by the Goths in 240 AD as well as one example from a 3rd c. AD grave.[138] In the eastern Black Sea region, vessels of this fabric are attested at Pityus, Gudava, Ilore and Gonio-Apsarsus.[139] At Apsarsus, amphorae corresponding to B Snp II are attested in contexts dating to the early 2nd and first half of the 3rd c. AD.[140] In the western Black Sea region, they are present at Murihiol and Topraichioi dated, according to Opait, between the second half of the 4th and the first half of the 5th c. AD and only in the second quarter of the 5th c. AD, respectively.[141] In the Mediterranean, the most westerly known attestation is represented by a single find at Concordia (modern Venice).[142]

8.5.2 *Group C vessels*

The trade of Group C vessels appears to increase as it is present at more sites and in greater numbers compared to Group B finds. In the northern Black Sea region, Group C vessels are especially prominent in the area of the Chernyakhov culture.[143] The Chernyakhov culture inhabited the area that roughly corresponds to modern Ukraine between the 3rd and 5th c.

[136] Vnukov 2010b, 366.
[137] Kassab Tezgör 2010b, 168.
[138] Kassab Tezgör 2010b, 168; Opait 2010b.
[139] Kassab Tezgör 2010b, 168; Kassab Tezgör et al. 2007, 200ff; Khalvashi and Inaishvili 2010, 499.
[140] Khalvashi and Inaishvili 2010, 499.
[141] Opait 2004a, 31.
[142] Kassab Tezgör 2010b, 168.
[143] Magomedov and Didenko 2010.

AD and, population wise, was mostly composed of Goths (Fig. 8.12). From the second half of the 4th through the beginning of the 5th c. AD, Group C amphorae are the dominant amphorae at coastal northern Black Sea sites.[144] Group C amphorae, however, are rare in the interior of eastern Europe during this period, replaced instead by Shelov type F amphorae from Heracleia Pontica.[145] The principal form is C Snp I. C Snp II and C Snp III are rare here although frequent elsewhere in the Black Sea littoral during this period.[146] The general trend in the Chernyakhov culture indicates bulk supply began in the 4th c. AD, becoming more intensive by the end of the century.[147] Olbia Pontica (in modern Ukraine) had a long history of trade with Sinope dating to the 5th c. BC. A hiatus in trade began in 269/270 AD due to the sacking of the city by the Goths and was restored in the early 4th c. AD when C Snp I amphorae are first attested.[148] Group C amphorae (primarily C Snp I) are also known from the Crimea as well as Tanais.[149]

In the east Black Sea region, Group C amphorae are known from Gorgippia, Ravskoe, Ponticapeo and Tyritake.[150] On the southern coast, examples are known the kilns at Demirci as well as at Byzantium.[151]In the west, Group C vessels are known from Thrace, including Mesembria.[152] A C Snp I vessel has been found at Mihai Braun (Dobruja) dating to the beginning of the 4th c. AD.[153] C Snp I vessels are attested at Libida.[154] Both C Snp I and II types are attested at Dunarii de Jos.[155]

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[144]Magomedov and Didenko 2010

[145]Magomedov and Didenko 2010, 479ff.

[146]Kassab Tezgör 2010b, 169.

[147]Magomedov 2010, 78.

[148]Krapivina 2010a; Krapivina 2010b, 474.

[149]Vnukov 2010b, 366; Magomedov 2010, 76, respectively.

[150]Kassab Tezgör et al. 2007; Kassab Tezgör 2010b.

[151]Kassab Tezgör 2010b, 170.

[152]Kassab Tezgör 2010b, 170; Opait 2010b, 375.

[153]Opait 2010b, 375.

[154]Opait and Paraschiv 2012, 117f.

[155]Paraschiv 2002, 174-177.

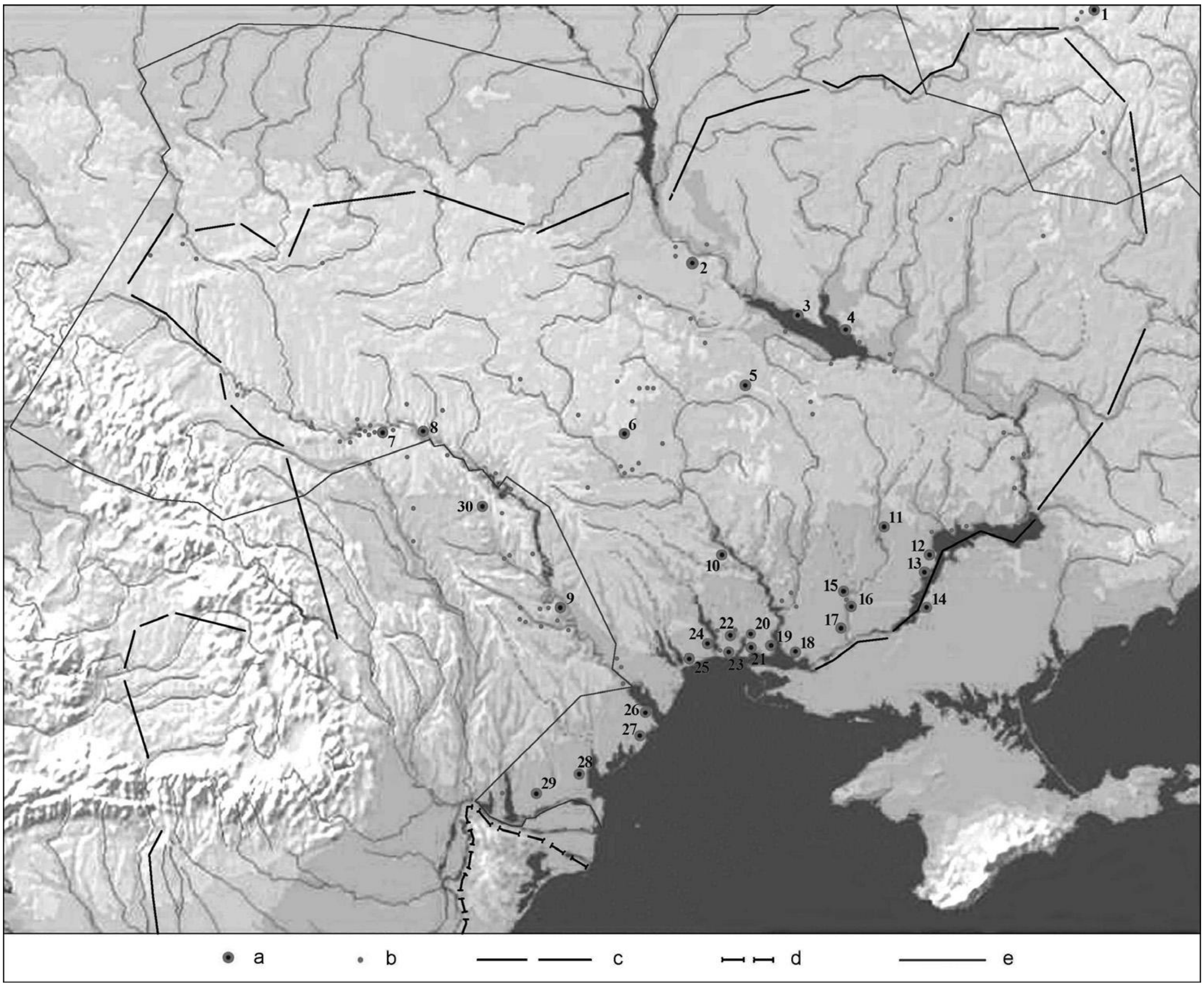

Figure 8.12: Finds of C Snp I amphorae in the region of the Chernyakhov culture. 'a': reliable finds; ''b: probable finds; 'c': borders of the Chernyakhov culture in the middle of the 4th century AD; 'd': Roman limes; 'e': border of modern-day Ukraine. Source: Magomedov and Didenko 2010, Fig. 1.

8.5.3 Group D vessels

The distribution pattern for Group D vessels suggests a change in trade routes and frequency in some regions. The frequency of Group D amphorae appears to decrease in the eastern and western regions of the Black Sea littoral, although they are still attested at many sites, whereas the distribution in the eastern Mediterranean expands.[156] On the whole, however, Group D types are less well documented than that of Group C, which may account for some of the decline in observed frequency. Additionally, D Snp I and II types bear a strong re-

[156]Kassab Tezgör, 2010b, 172.

semblance to the LRA 1.[157] It is possible that examples of Group D vessels may have been misclassified at some sites reducing their apparent frequency.

Group D amphorae are absent in the area that was formerly occupied by the Chernyakhov culture. This may be due to disruption of commerce caused by the arrival of the Huns as the Chernyakhov vulture declined during the 5th c. AD and the presence of Group D types begins after this date. The vessels, however, are common in Tanais and at Gorgippia.[158] They are also attested at Chersonesos and the Kingdom of Bosporus dating to the 6th and early 7th c. AD[159] Further to the east, D Snp I are found in 6th c. AD contexts at Apsarsus and Tsikhisdziri (in modern Georgia). Group D vessels are represented in small numbers compared to other amphora imports.[160]

In the Mediterranean, Group D vessels are found at a large number of sites. They have been recovered from a merchantman shipwreck during the excavations at Yenikapı harbor.[161] The Museum of Antakya has approximately 70 examples from Seleucia Pieira.[162] Some fragments have been recovered at Ras al Bassit and a number of vessels from a cistern at Ras Ibn Hani.[163] The vessels from Ras Ibn Hani have been inorganically characterized and found to match sample from Demirci.[164] At Beirut, they are attested during the 5th and 6th c. AD. Inland in the Levant, Group D amphorae are known at Zuegma.[165] Additionally, they are present at Sergilla and Qal'at Sem'an (modern Syria).[166] Further south, they are attested at Pella (modern Jordan) and the bank of the river Jordan.[167] The southernmost attestation of Group D amphorae are at Alexandria and at Kom el Dikka.[168]

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157 Reynolds 2010b, 96.

158 Erten et al. 2004, 104.

159 Kassab Tezgör et al. 2003.

160 Inaishvili and Khalvashi 2011, 269; Khalvashi and Inaishvili 2010, 501ff.

161 See Section 8.6.

162 Kassab Tezgör et al. 2001, 111.

163 Kassab Tezgör et al. 2001, 111; Kassab Tezgör 2010b, 172ff.

164 Erten et al. 2004.

165 Abadie-Reynal 1999.

166 Pieri 2005, Fig. 8.

167 Kassab Tezgör 2010b, 172.

168 Kassab Tezgör 2010b, 172.

8.6 Shipwrecks

Shipwrecks offer a potentially significant opportunity in garnering not only additional information concerning trade dynamics, such as the ability to attempt to extrapolate the origin of a cargo from an otherwise uncertain manufacturing point, e.g. as is the case of the Kapitän 2 amphora, but also to potentially gain insight into vessel contents by virtue of the preservation of some organic materials in submerged contexts. The number of shipwrecks or recovered stray maritime finds of Sinopean amphorae, however, is considerably less than that of some other forms during the same period. This may be affected by several factors, including the relatively short period of time for which at least some types of Sinopean amphorae have been positively identified by typology.[169]

Three shipwrecks were discovered in 1993 by a research campaign led by Ondokuz Mayıs University (Samsun, Turkey). The shipwrecks are located off the southeast coast of the peninsula of Sinope (Fig. 8.13). Two of the shipwrecks contained amphorae. Shipwreck 2 was found at a depth of 9 m and was represented by a mound of tiles as well as at least one Group D amphora.[170] Shipwreck 3, lying at a depth of 10 m, is composed of a group of amphorae as well as ballast stones and fragments of the hull.[171] Only 12 amphorae were visible in the mound and correspond to Group D vessels. Two complete vessels and a third partial vessel were retrieved.[172] According to the excavation report, the recovered vessels contained blackish water that was decanted and filtered; one of the vessels was found to contain three olive pits.[173] Residue of a pitch lining was visible on the exterior rim and neck of one of the vessels (catalog number SSM 97.2) (Fig. 8.14). No comment was made in the excavation report concerning the presence of a pitch lining in any of the vessels.

The Black Sea has excellent potential for shipwreck preservation due to anoxic condi-

[169]For example, while C Snp I was classified by Zeest in 1960, C Snp III has only recently been established in a coherent typology and other forms, e.g. D Snp I and II, may have been previously confused with other amphora types.

[170]Kassab Tezgör 1998, 444.

[171]Kassab Tezgör 1998, 443.

[172]Kassab Tezgör 1998, 443.

[173]Kassab Tezgör 1998, 445.

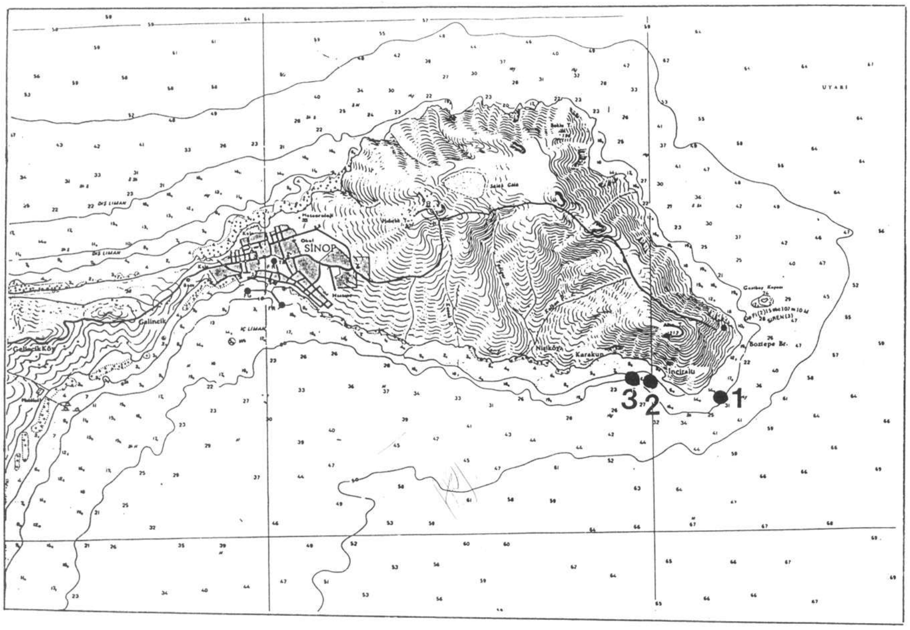


Figure 8.13: Map of the shipwrecks discovered off the southern coast of the peninsula of Sinope in 1993. Source: Kassab Tezgör 1998, Fig. 1.

tions below approximately 200 m.[174] In 2000 and 2003 a survey of the sea in the area of Sinope was conducted by the Institute for Exploration (IFE) that resulted in the discovery of four shipwrecks. Three of the shipwrecks (A, B and C) were found west of Sinope within a relatively small area (Fig. 8.15). Shipwreck A was found at a depth of 101 m and consisted of a mound approximately 20 m long by 10 m wide.[175] The mound was composed of C Snp III amphorae.[176] Shipwreck B was found at a depth of 85 m and consisted of a mound approximately 12 m wide and between 14 and 24 m long.[177] The amphorae were primarily vessels corresponding to C Snp III. The eastern half of the site contained LRA 1 with at least 5 'unambiguous' examples.[178] Shipwreck C consists of two separate mounds of mostly buried C Snp III amphorae at a depth of 85 m.[179]

The fourth shipwreck, Shipwreck D, lies approximately 25 km west of Sinope at a depth

[174] Ward and Ballard 2004, 2.
[175] Ward and Ballard 2004, 4.
[176] Ward 2010, 191.
[177] Ward and Ballard 2004, 5; Ward 2010, 191f.
[178] Ward 2010, 192.
[179] Ward and Ballard 2004, 5.

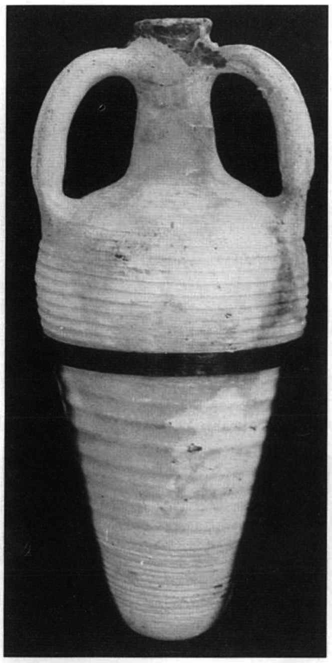


Figure 8.14: A Group D amphora (SSM 97.2) recovered from Shipwreck 3 at Sinope demonstrating pitch on the neck and rim. Source: Kassab Tezgör 1998, Fig. 8.

of 320 m.[180] Unlike Shipwrecks A-c, Shipwreck D is excellently preserved by virtue of lying within the anoxic layer. The mast with extant cordage stands approximately 11 m above the sea-bed.[181] Two samples of wood, one from the rudder support and identified as fir (*Abies sp.*) and a second from an unknown location and identified as belonging to the white oak group (*Quercus sp.*) were subjected to radiocarbon dating. A radiocarbon date calibrated to 410-520 AD was determined. D Snp I amphorae were observed in the shipwreck.[182]

One C Snp III-2 and two LRA 1 were retrieved from Shipwreck B; three C Snp III-2 amphorae were retrieved from Shipwreck C and three 'pate claire' D Snp amphorae were retrieved from Shipwreck D.[183] All vessels were observed to have a pine pitch lining which 'still gleamed', however macrobotanical analysis of sediments within the vessels provided

[180]Ward and Ballard 2004, 6.

[181]Ward and Ballard 2004, 6.

[182]Ward 2010, 192ff.

[183]Ward 2010, 194f.

Figure 8.15: Map of the shipwrecks discovered in the region of Sinope during the surveys by the Institute for Exploration. Source: Ward and Ballard 2004, Fig. 1.

no insight into content.[184]

Several shipwrecks have been located off the cape of Plaka in the Crimea, including one shipwreck containing LRA 1 and 'carrot' amphorae. The shipwreck has been dated to the late 6th to early 7th c. AD due to the presence of LRA 1 category 2 amphorae (after Pieri's 2005 typology) which are attributed to this period.[185] The 'carrot' amphorae rather closely match C Snp III-1, although size and shape of the necks vary from Kassab Tezgör's typology and known examples. Specifically, the necks are considerably smaller in diameter and height relative to Kassab Tezgör's C Snp II and III typologies. The vessels have a rim diameter of 3-5 cm, considerably smaller than that of C Snp II and III amphorae. The height of the neck above the handles is also significantly reduced, measuring approximately 5-7.5 cm compared to 8-14.5 cm for C Snp III types in the established typology.[186] Close parallels to the Plaka vessels have been found at Chersonesos and southern Russian sites dated to the late 6th to early 7th c. AD.[187] Petrographic analyses of the amphorae do not preclude a Sinopean origin for the vessels; however, insufficient reference samples from verified Sinopean amphorae prevents a conclusive determination.[188] In addition to the morphological differences

[184]Ward 2010, 195.

[185]Waksman et al., 920.

[186]Kassab Tezgör 2010d.

[187]Waksman et al. 2014, 920.

[188]Waksman et al. 2014, 922.

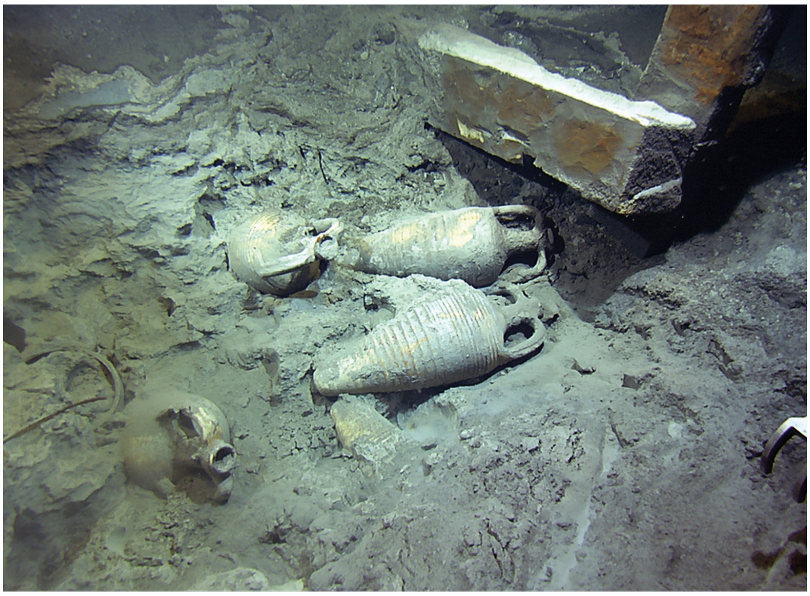


Figure 8.16: Photograph of Shipwreck D featuring D Snp I amphorae. Source: Ward 2010, Fig. 5.

between the Plaka samples and Group C Sinopean amphorae, there is also a chronological discrepancy. Group C Amphorae were manufactured during the 4th and 5th c. AD, whereas the date of the Plaka samples and terrestrial parallels are considerably later suggesting that these samples may not belong to a Sinopean production.

Salvage excavations were conducted in the Yenikapı district of Istanbul between 2004 and 2013 as part of the Marmaray Metro Project. During the course of the excavations 37 shipwrecks dating to the early and middle Byzantine periods were discovered, including a 6th c. AD merchantman (YK 35) (Fig. 8.18).[189] While analysis and publication of the finds is ongoing, a catalog of the amphorae and some of the other finds has been published. YK 35 contained a cargo of at least 35 Dacian amphorae, apparently in which traces of fish bones were found (Fig. 8.19).[190] Additionally, at least 20 Group D Sinopean amphorae were also recovered (Fig. 8.20). *Dipinti* were observed on several of the vessels.[191] Unfortunately, at present no further information concerning the Group D amphorae is available.

[189]Kocabas 2015, 6.

[190]Polat 2013.

[191]See Chapter 8.7 concerning the *dipinti*.

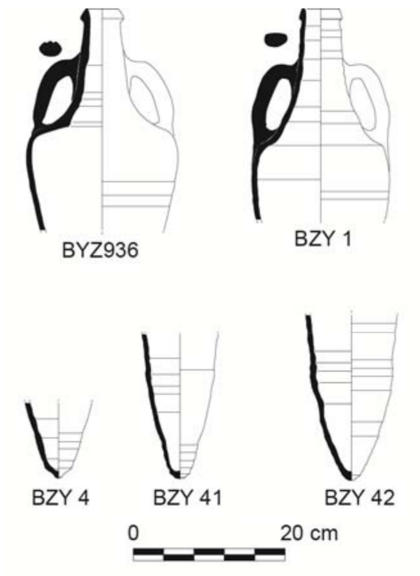


Figure 8.17: Drawings of some of the 'carrot' amphorae recovered from the Plaka shipwreck. Source: Waksman et al. 2014, Fig. 3.

8.7 *Dipinti* and *graffiti*

With respect to Group B and C amphorae, *dipinti* are extremely rare. The author is only aware of two published examples. Both are on C Snp I vessels recovered from Olbia Pontic dating to the 4th c. AD (Fig. 8.21). The first is composed of what appears to be Greek letters that are no longer legible (Fig. 8.21.1). The *dipinto* on the second vessel is composed of two parts (Fig.8.21.2). On the shoulder near the handle is what appears to be a vertical line with three pairs of lines diverging from the central line in an upward orientation. Also on the shoulder are the letters 'ελρ'. From the Beirut excavations, one Group C vessel (BEY006.13557.10) has a *dipinto* of an 'x' on the center of the shoulder (Fig. 8.22).

Dipinti are apparently somewhat common on Group D vessels. Many of the approximately 70 amphorae in the collections of the Hatay Archaeology Museum in Antakya feature *dipinti*, unfortunately none have been published.[192] From the Beirut excavations, *dipinti* are found on a few Group D vessels but are preserved in a very poor condition. One vessel fragment, BEY006.2004.27, consisting of the rim to lower neck has a *dipinto* consisting of three vertical parallel lines (Fig. 8.23). Another Group D vessel, BEY006.14007.5, has a *dipinto*

[192] Kassab Tezgör et al. 2001, 111.

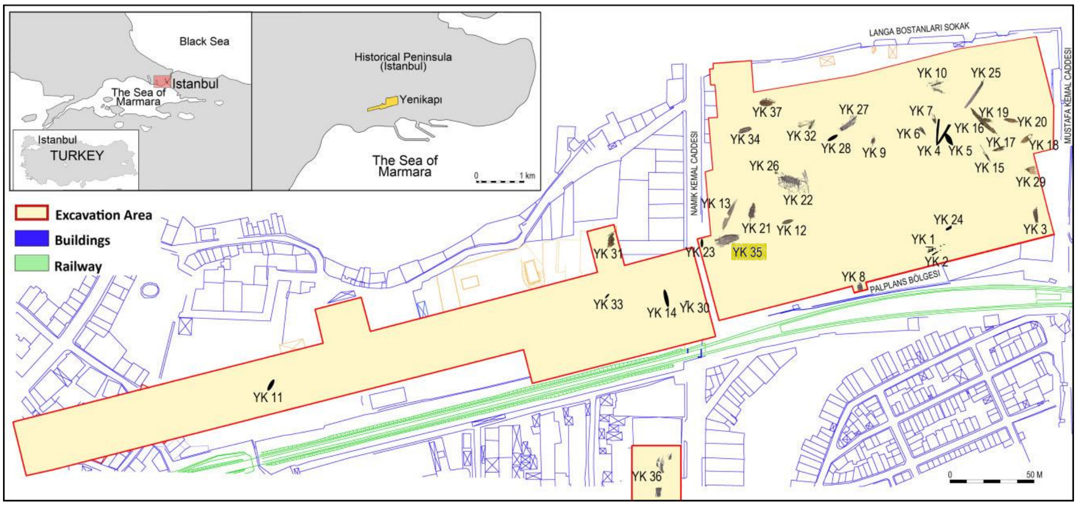
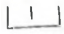


Figure 8.18: Map of the distribution of the Yenikapı shipwrecks, YK 35 highlighted in yellow. Source: Kocabas 2015, Fig. 15.

but the condition is poor rendering it illegible. One Group D amphora from Tsikhisdziri features a *dipinto* on the vessel's shoulder (Fig 8.24). Two Group D vessels from the YK 35 shipwreck at Yenikapı possess *dipinti*. The first vessel, YKM'13.16545, has a *dipinto* on its shoulder that resembles a delta .[193] The second vessel, YKM'13.16538, has two *dipinti*, one on the shoulder , the other on the neck .[194]

Dipinti appear on some Sinopean vessels although the observed trend is that the practice was considerably more common on Group D vessels relative to earlier groups. Unfortunately, this is the extent of the information that can be derived from these *dipinti*. Published examples appear to be letters or symbols, the meaning of which are unknown.

8.8 Content

The content of Sinopean amphorae has been the subject of considerable debate. Traditionally, wine has been considered the primary content. Seemingly this begins during the Hellenistic period where elements of some of the handle stamp motifs demonstrating grape and grapevine iconography. The shape of the Hellenistic vessels bear a resemblance to Koan

[193]Drawing source: Polat 2013.

[194]Drawing source: Polat 2013.

Figure 8.19: A Dacian amphora (YKM'13.16516) from the YK 35 shipwreck at Yenikapı harbor. Source: Polat 2013, 160.

types has also been used as an argument for a content of wine.[195] This trend continues into the Roman period and again without any direct evidence. Maritime finds of recovered Sinopean amphorae from the Ondokuz Mayıs University and Institute for Exploration campaigns consistently showed Group C and D amphorae to have been internally coated with pitch. Additionally, finds from Ismael Karakan also demonstrate a pitch lining.[196] This has reinforced to some scholars the premise that the vessels were used to transport wine.[197] However, classification of content based solely on the presence of a resinous lining is problematic. *Garum* amphorae, for example, were frequently lined with pitch.[198] This is an important consideration as classical sources have frequently commented upon the fishing industry and its exports. It should also be taken into consideration that the use of an internal coating of pitch may not be incompatible with a content of oil as new scholarship appears to be bringing

[195] Opait 2010a.

[196] Kassab Tezgör 2003.

[197] *inter alia* Opait 2010b; Garlan and Kassab Tezgor 1996; Kassab Tezgör 2010d. See Chapter 2.6.1 concerning the relationship between vessel pitching and content.

[198] e.g. Curtis 1991, 12.

Figure 8.20: A Sinopean D Snp I amphora (YKM'13.16545) recovered from the YK 35 shipwreck at Yenikapı harbor. Source: Polat 2013, 164.

Figure 8.21: Two C Snp I amphorae excavated at Olbia Pontica with extant *dipinti*. Source: Krapivina 2010b, Fig. 5.

into light.[199] The sum of the data at present seems to indicate that '[t]here is little proof of wine production at Sinope or in the surrounding territories' at least before the early Roman period.[200]

So what was being produced in Sinope apart from the indications from classical authors that fishing was an important industry? The growing of olives and the production of olive oil is indicated by several means. Strabo commented unambiguously that at least in the early Roman period oleoculture was a significant industry. The field surveys of the regions of

[199]e.g. Pecci and Cau Ontiveros 2010.

[200]de Boer 2013, 111.

Figure 8.22: A Group C amphora (BEY006.13557.10) with *dipinto* from the Beirut excavations.

Sinope has also indicated a significant increase in habitation/exploitation of the land in the interior than would be consistent with increased agricultural production.[201] The recovery of press counterweights at Demirci indicate that pressing was being engaged in during this period. However, whilst the excavator believes that the presses would have been producing olive oil, alternatively, such presses were also used for the production of wine.[202] So whilst the classical sources consider that oleoculture was a significant enterprise at Sinope, at least during the period between the 1st c. BC and 1st c. AD (after which the accounts are silent), other commercial agricultural industries or that involving marine exploitation can not be dismissed.

The consideration of the content by scholars during the late Roman and early Byzantine periods begin to diverge somewhat. Whilst Vnukov has argued that Hellenistic period vessels were probably universal containers for both wine and olive oil, he argues that by the Roman

[201] Doonan 2002.

[202] Kassab Tezgör 1996.

Figure 8.23: A Group D amphora (BEY006.2004.27) with *dipinto* from the Beirut excavations.

period the picture is less clear and that by this point at least one amphora type, B Snp III, may have been used for the transport of oil, although he does not specify the reasons for such a conclusion.[203] Magomedov argues that wine was the content on supply grounds on account that wine consumption by the Goths had become popular.[204] In 331/332 AD the Visigoths sued for peace having been defeated both by Constantine I in battle and by cold and famine, 'thus nearly 100,000 were annihilated by famine and cold through Caesar Constantinus.'[205] Part of the terms of the treaty was the supply of the Goths with foodstuffs. Unfortunately, historical accounts of the Goths in this region and time are very sparse. Whilst wine may have been of interest to the Goths, high caloric foodstuffs such as grain or, with respect to amphora-borne commodities, olive oil or (probably to a considerably lesser degree) *garum*, should also be considered likely candidates.[206]Hitherto, beyond classical reference to the production of Sinope and the agricultural products established there and the interpretation of distribution vis-a-vis content, there is no solid evidence indicating what the content(s) of Sinopean amphorae may have been. There is, however, a Group D vessel, recovered from

[203]Vnukov 2010b, 362ff.

[204]Magomedov 2010, 78; Magomedov and Didenko 2010, 483ff.

[205]Anonymi Valesian 6.31.

[206]*Garum* might be the least likely possibility at least as a majority of the amphora trade considering the prevalence of a single amphora type in the region during this period (C Snp I vessels) as well as the fact that *garum* can not be consumed in significant quantities by an individual notwithstanding the matter if *garum* would have been something with which the Goths were familiar and accustomed.

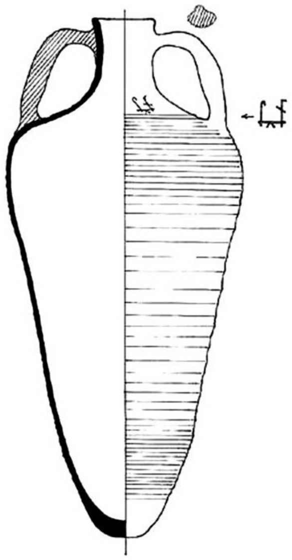


Figure 8.24: Drawing of a Group D amphora from Tsikhisdziri featuring a *dipinto*. Source: Khalvashi and Inaishvili 2010, Fig. 8.3.

Shipwreck 3 at Sinope, that was filled with a dark liquid that contained three olive pits. This suggests that the content of the vessel might have been olive oil. It is difficult to extrapolate from a singular specimen the content for an entire class of amphorae let alone the earlier types produced at Sinope. This example does, however, offer the most compelling indication of content so far discovered.

CHAPTER 9

ANALYSES OF B SNP III ('SINOPE YELLOW') AMPHORAE

9.1 Samples

Fifteen ceramic samples from distinct B Snp III ('Sinopean Yellow') amphorae were sampled from the storerooms of the American University of Beirut. The ceramic samples were prepared and analyzed at the Research Laboratory for Archaeology and the History of Art, University Oxford using gas chromatography/mass spectrometry. The samples were characterized for both lipid constituents and organic compounds associated with wine using the protocols described in Chapter 5. The material had previously been studied by Paul Reynolds (University of Barcelona) who compiled a database of the ceramic and contextual data. Samples were selected from a variety of contexts dating to between the 4th to 6th c. AD (Table 9.1). Photographs of the samples are found in Appendix A.

Table 9.1: Context and sample data for Sinope C Snp III ('Sinope Yellow') analyses, data retrieved from the ceramic database developed by Paul Reynolds.

Area	*Context*	*Sherd Number*	*Date of Context (AD)*	*Nature of Context*	*Position of Sample*	*Visible Residue*
006	4104	x1	4th c.	fill	mid wall	no
006	5051	915	4th c. (?)	fill	rim	no
006	5051	916	4th c. (?)	fill	shoulder	no
006	5051	917	4th c. (?)	fill	mid wall	no
006	5051	x1	4th c. (?)	fill	rim	no
006	5503	310	late 6th c. ?	pit fill	shoulder	no
006	7313	7	mixed	cleaning	base	no
006	8615	1	late 2nd-early 3rd c.	single find context (amphora)	mid wall	no
045	1242	11	early 3rd c.	fill	lower wall	no
045	1242	560	early 3rd c.	fill	mid wall	no
045	1242	562	early 3rd c.	fill	mid wall	no
045	1503	3	early 3rd c.	cleaning	shoulder	no
045	1609	1	early 3rd c.	fill?	lower wall	no
045	1660	3	early 3rd c.	fill?	shoulder	no
045	2074	21	mid 2nd c. ?	fill?	shoulder	no

9.1.1 Results of Analyses

9.1.1.1 Sample from BEY006.4104.x1

Context 4104 represents a fill context, dated to the 4th c. AD. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified the presence of succinic and vanillic acids.

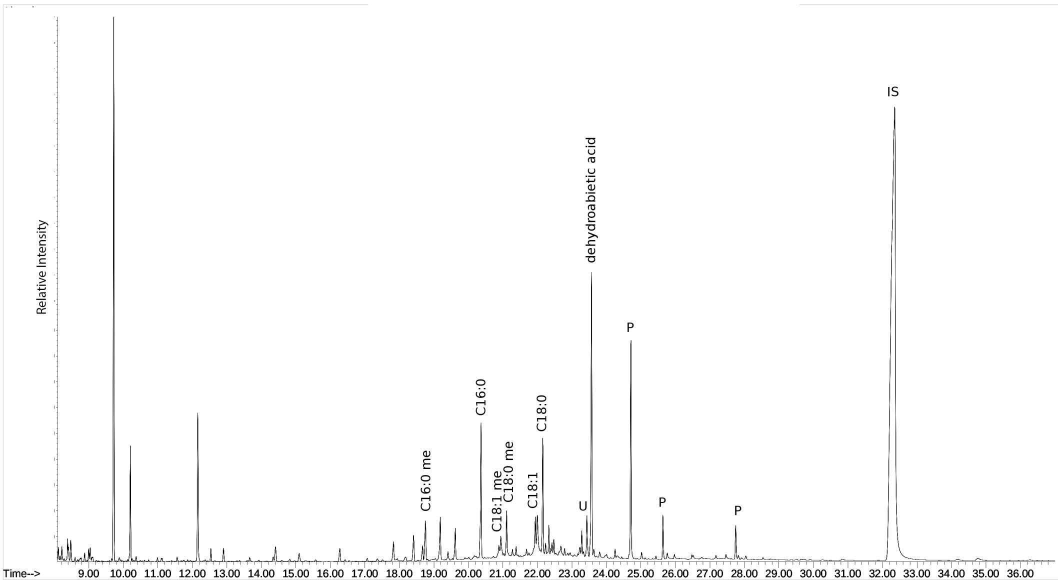


Figure 9.1: Total ion chromatogram of the saponified extraction of Sample BEY006.4104.x1.

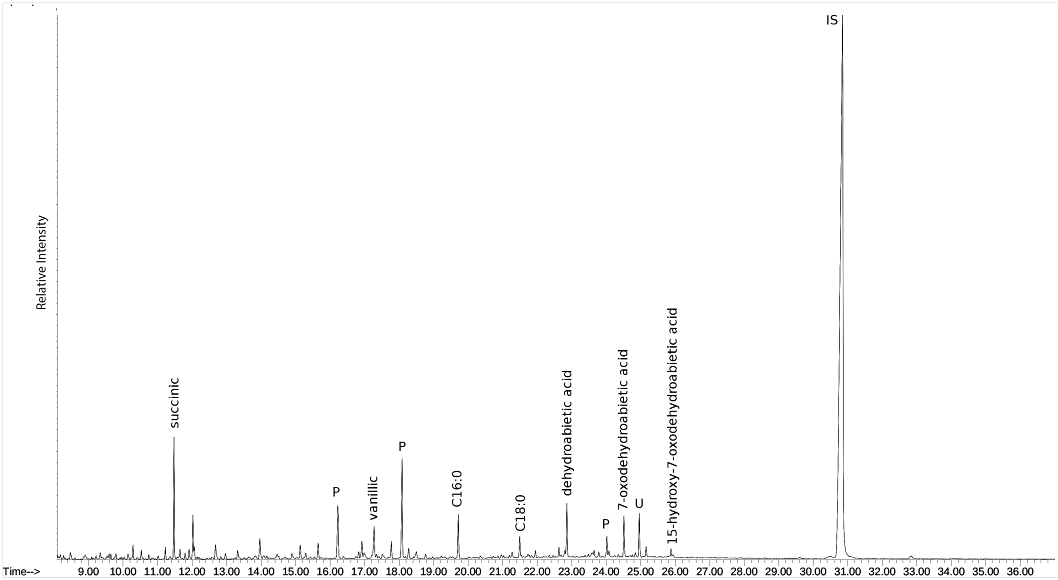


Figure 9.2: Total ion chromatogram of the analysis of organic compounds associated with wine in Sample BEY006.4104.x1.

9.1.1.2 Sample from BEY006.5051.915

Context 5051 represents a fill context, dated approximately to the 4th c. AD. The vessel is represented by its rim. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The fatty alcohol 1-octadecanal was also detected in the TLE. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid (Fig. 9.3).

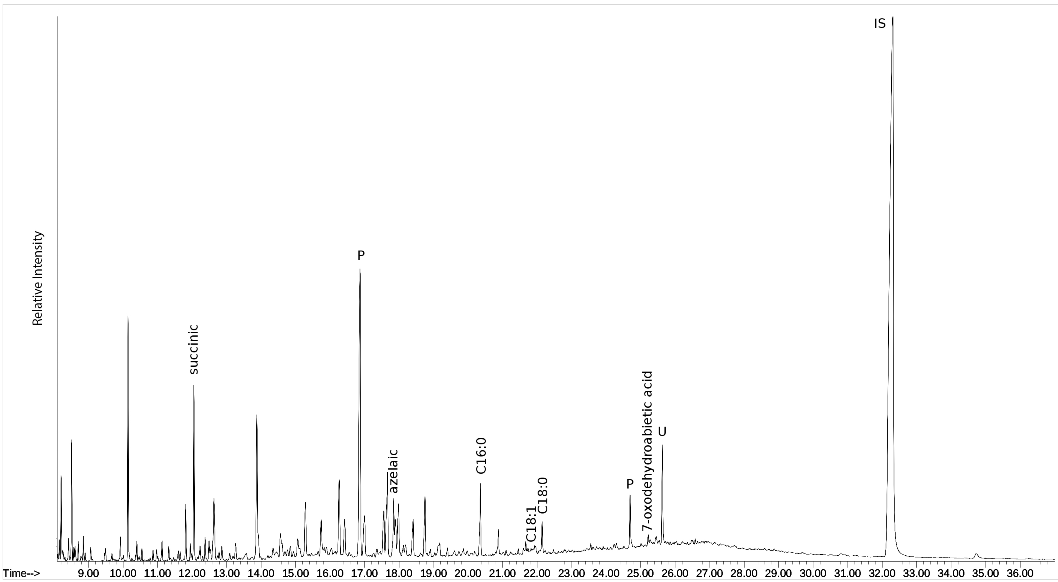


Figure 9.3: Total ion chromatogram of the analysis of organic compounds associated with wine in Sample BEY006.5051.915.

9.1.1.3 Sample from BEY006.5051.916

Sample BEY006.5051.916 represents another sample from Context 5051. The vessel is represented by its shoulder. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.4 Sample from BEY006.5051.917

Sample BEY006.5051.917 represents another sample from Context 5051. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The fatty alcohol 1-tetracosanol and cyclo-octasulfur were also detected in the TLE extract (Fig. 9.4). The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were detected as well as retene. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

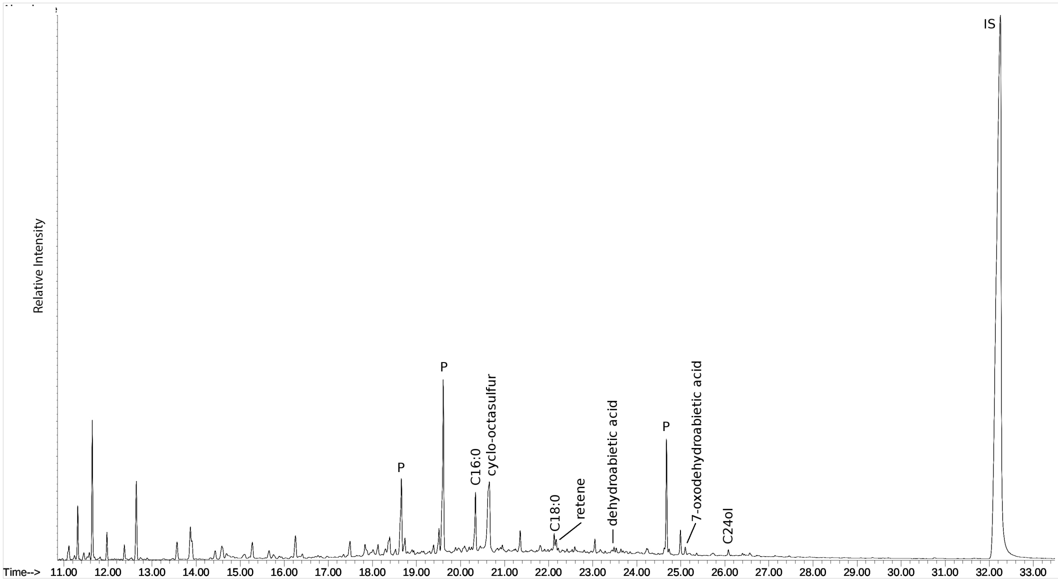


Figure 9.4: Total ion chromatogram of the total lipid extract (TLE) of Sample BEY006.5051.917.

9.1.1.5 Sample from BEY006.5051.x1

Sample BEY006.5051.917 represents another sample from Context 5051. The vessel is represented by its rim. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified the presence of fumaric and succinic acids.

9.1.1.6 Sample from BEY006.5503.310

Context 5051 represents a pit fill context. The context is mixed, although primarily 6^{th} c. AD in date from ceramic evidence. The vessel is represented by its shoulder. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. Monopalmitin was also detected in the TLE in trace quantities. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.7 Sample from BEY006.7313.7

Context 5051 represents a cleaning context, dated approximately to the 3rd-4th c. AD. The vessel is represented by its base. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.8 Sample from BEY006.8651.1

Context 5051 represents a single find context of a Sinopean amphora, dated to the late 2nd to early 3rd c. AD. The sample was taken from the mid wall section. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The fatty alcohol 1-tetracosanol was detected. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids as well as retene were detected. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.9 Sample from BEY045.1242.11

Context 5051 represents a fill context, dated to the early 3rd c. AD. The vessel is represented by its lower wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.10 Sample from BEY045.1242.560

Sample BEY006.1242.560 represents another sample from Context 1242. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarker dehydroabietic acid was detected. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.11 Sample from BEY045.1242.562

Sample BEY006.1242.560 represents another sample from Context 1242. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarker dehydroabietic acid was detected. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.12 Sample from BEY045.1503.3

Context 1503 represents a cleaning context, dated to the early 3^{rd} c. AD. The vessel is represented by its shoulder. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as the sterol β-sitosterol. The resin biomarker dehydroabietic acid was detected. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

9.1.1.13 Sample from BEY045.1609.1

Context 1609 represents a fill context, dated to the early 3^{rd} c. AD. The vessel is represented by its lower wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids (Fig. 9.5). The resin biomarker dehydroabietic acid was detected. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

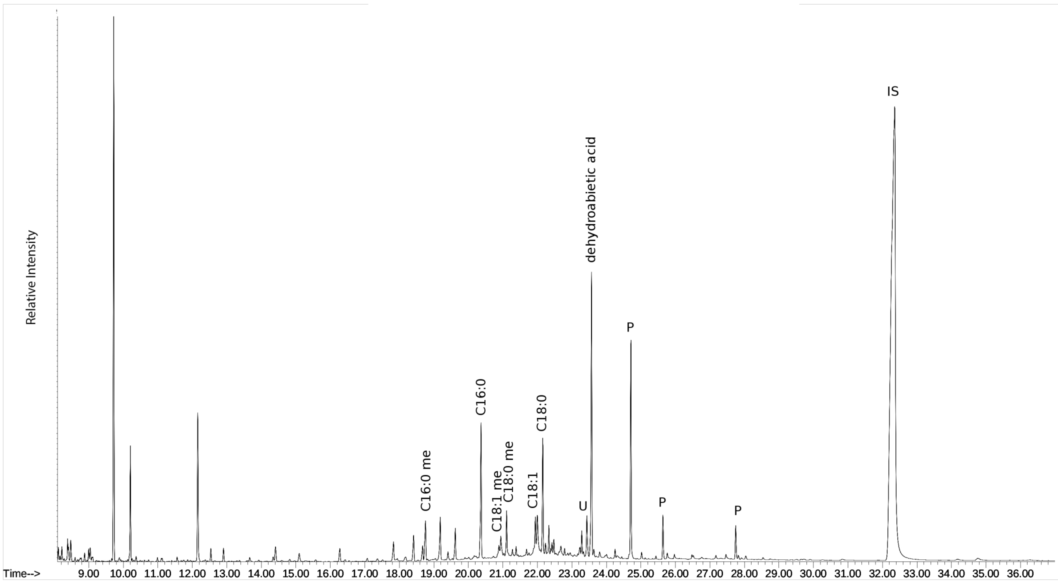


Figure 9.5: Total ion chromatogram of the saponified (SAP) extraction of Sample BEY045.1609.1.

9.1.1.14 Sample from BEY045.1660.3

Context 1660 represents a fill context, dated to the early 3rd c. AD. The vessel is represented by its shoulder. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarker dehydroabietic acid was detected. The analysis of organic compounds associated with wine identified no relevant biomarkers.

9.1.1.15 Sample from BEY045.2074.21

Context 2074 represents a fill context, dated to approximately the 2nd c. AD. The vessel is represented by its shoulder. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were detected. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

Table 9.2: Resin/pitch biomarkers detected in B Snp III samples.

Sherd Number	pimaric acid	isopimaric acid	retene	methyl DHA	DHA	7-oxoDHA	15 hydroxy 7oxoDHA
006.4104.x1					x	x	x
006.5051.915					x	x	
006.5051.916					x	x	x
006.5051.917			x		x		
006.5051.x1					x	x	x
006.5503.310					x	x	x
006.7313.7					x	x	x
006.8651.1			x		x	x	x
045.1242.11					x	x	
045.1242.560					x		
045.1242.562					x		
045.1503.3					x		
045.1609.1					x		
045.1660.3					x		
045.2074.21					x	x	

9.1.2 Analysis of Results

The fifteen analyzed samples of B Snp III ('Sinopean Yellow') amphorae produced generally homogeneous data. No compounds associated with grape products were observed (with the exception of fumaric acid in Sample BEY006.5051.x1).[1] With respect to resin/pitch biomarkers, dehydroabietic acid was detected in all samples, although the level of dehydroabietic acid was very low in several samples. Comparison of laboratory and inter-sample blanks indicated that the dehydroabietic acid detected in these samples was not the result of intra-laboratory contamination during sample preparation or carry-over between GC/MS analyses. Other resin/pitch biomarkers, specifically 7-oxodehydroabietic and/or 15-hydroxy-7-oxodehydroabietic acid, were identified in a majority of samples (Table 9.2). Additionally, retene, indicative of 'pyrolitic distillation', was identified in two samples (BEY006.5051.917 and BEY006.8651.1).

The fatty acid $C_{18:1}$ was detected in a majority of samples in addition to the non-diagnostic $C_{16:0}$ and $C_{18:0}$ fatty acids. The fatty alcohol tetracosanol was detected in two samples (BEY 006.5051.917 and BEY006.8651.1) and plant sterol, β-sitosterol, in Sample BEY045.1503.3.

[1]See Chapter 14.4 for a discussion of the genesis of succinic and fumaric acids in analyzed samples.

Table 9.3: Results of the analyses of organic compounds associated with wine.

Sherd Number	position	malonic acid	fumaric acid	succinic acid	maleic	malic acid	vanillin	tartaric acid	vanillic acid	hyrdocinnamic acid	syringic acid
006.4104.x1				x					x		
006.5051.915				x							
006.5051.916				x							
006.5051.917				x							
006.5051.x1			x	x							
006.5503.310				x							
006.7313.7				x							
006.8651.1				x							
045.1242.11				x							
045.1242.560				x							
045.1242.562				x							
045.1503.3				x							
045.1609.1				x							
045.1660.3				x							
045.2074.21				x							

On the whole, residual lipids were low in B Snp III samples, with several samples falling below the 5 μg/g threshold generally considered to be the lower limit for the analysis of use-derived lipid constituents.[2] New analytical techniques currently under development might serve useful in increasing extractable lipids and assisting in a more definitive determination of the use of this vessel form.[3] At present, the bulk of the evidence is not inconsistent with a vegetable oil, such as olive oil, having been transported in this vessel type. The low level of lipid preservation; however, prohibits any conclusive determination. While absence of presence does not indicate presence of absence, the lack of any diagnostic compounds associated with wine in the samples does seem to indicate that wine was not transported in this vessel type.

[2]See Table 9.4. Evershed 2008, 28.

[3]See Chapter 14.5 concerning new analytical techniques under development.

Table 9.4: Total lipid extract (TLE) quantifications of fatty acids for B Snp III amphora samples.

Sample number	Extraction type	µg/g total lipid extraction per sample analysis
BEY006.4041.x1	SAP	30
BEY006.5051.920	LIP	12
BEY006.5051.915	LIP	3.3
BEY006.5051.915	SAP	11
BEY006.5051.916	LIP	4
BEY006.5051.916	SAP	~6
BEY006.5051.917	LIP	9
BEY006.5051.917	SUL	17
BEY006.5251.X1	LIP	4
BEY006.5251.X1	SAP	11
BEY006.5503.310	LIP	3
BEY006.5503.310	SUL	6
BEY006.7313.7	LIP	6
BEY006.7313.7	SAP	15
BEY006.8651.1	LIP	2
BEY006.8651.1	SUL	8
BEY006.8652.1	LIP	8
BEY006.8652.1	SAP	12
BEY045.1242.11	LIP	10
BEY045.1242.11	SAP	15
BEY045.1242.560	LIP	8
BEY045.1242.560	SAP	10
BEY045.1242.562	LIP	9
BEY045.1242.562	SAP	16
BEY045.1503.3	LIP	11
BEY045.1503.3	SAP	20
BEY045.1609.1	LIP	9
BEY045.1609.1	SAP	33
BEY045.1660.3	LIP	60
BEY045.1660.3	SAP	10
BEY045.1660.3	LIP	5
BEY045.1660.3	SAP	20
BEY045.2074.21	LIP	17
BEY045.2074.21	SAP	50

CHAPTER 10

ANALYSES OF C SNP (‘SINOPE RED’) AMPHORAE

10.1 Samples

Thirteen ceramic samples from distinct Sinopean ’red’ amphorae (C Snp) vessels were sampled from the storerooms of the American University of Beirut. The ceramic samples were prepared and analyzed at the Research Laboratory for Archaeology and the History of Art, University Oxford using gas chromatography/mass spectrometry. The samples were characterized for both lipid constituents and organic compounds associated with wine using the protocols described in Chapter 5. The material had previously been studied by Paul Reynolds (University of Barcelona) who compiled a database of the ceramic and contextual data. Samples were selected from a variety of contexts dating to between the 4th to 6th c. AD (Table 10.1). Photographs of the samples are found in Appendix A.

Table 10.1: Context and Sample Data for Sinope C Snp ‘Sinope Red’ Analyses, data retrieved from the ceramic database developed by Paul Reynolds.

Area	*Context*	*Sherd Number*	*Date of Context (AD)*	*Nature of Context*	*Position of Sample*	*Visible Residue*
006	10625	x1	3rd c. +?	dump	upper wall	no
006	10632	x5	4th c.?	?	upper wall	no
006	11357	8	late 4th c.	floor - make-up/levelling	shoulder	no
006	13017	597	late 4th c.	floor - make-up/levelling	rim	no
006	13017	7	late 4th c.	floor - make-up/levelling	mid wall	no
006	13357	10	late 4th c.	floor - make-up/levelling	base	no
006	13017	8	late 4th c.	bedding	base	no
006	11357	9	late 4th c.	bedding	mid wall	no
006	13017	15	late 4th c.	floor - make-up/levelling	base	no
006	13017	16	late 4th c.	floor - make-up/levelling	base	no
006	5212	2	late 5th c	cistern fill	upper shoulder	no
006	5503	303	late 6th c.	pit fill	base	no
006	5503	320	late 6th c.	pit fill	upper wall	no

10.1.1 Results of Analyses

10.1.1.1 Sample from BEY006.5212.2

Context 5212 represents a cistern fill, dated to the 4^{th} c. AD. The vessel is represented by its shoulder. Lipid analyses identified resin biomarker dehydroabietic acid. Fatty acids identified were $C_{16:0}$, $C_{18:0}$ and trace amounts of $C_{18:1}$ and $C_{24:0}$. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic and malic acids. Lipid analysis (primarily TLE) also indicated significant amounts of phthalate contamination.

10.1.1.2 Sample from BEY006.5503.303

Context 5503 represents a pit fill dating most probably to the late 6^{th} c. AD. The vessel is represented by its base. Lipid analyses identified resin biomarkers dehydroabietic acid and 7-oxodehydroabietic acid. Fatty acids identified were $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ (Fig. 10.1). The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and syringic acids.

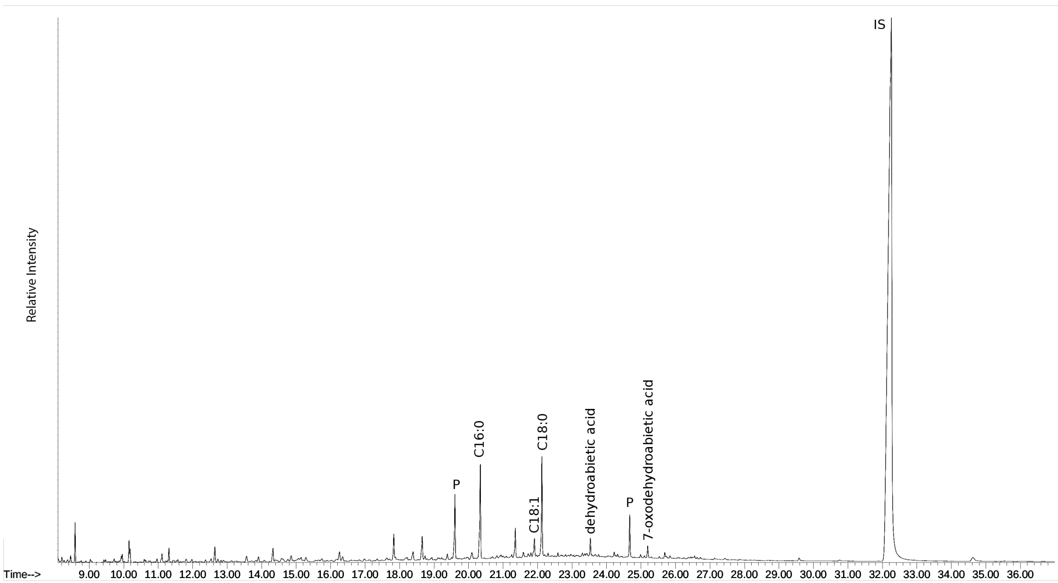


Figure 10.1: Total ion chromatogram of the total lipid extract (TLE) of Sample BEY006.5503.303.

10.1.1.3 Sample from BEY006.5503.320

Sample BEY006.5503.320 is represents another vessel from Context 5503. The vessel is represented by its upper shoulder. Lipid analyses identified resin biomarkers dehydroabietic acid and 7-oxodehydroabietic acid. Fatty acids identified were $C_{16:0}$ and $C_{18:0}$. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic, vanillic and syringic acids as well as vanillin.

10.1.1.4 Sample from BEY006.10625.x1

Context 10625 is a large dump context, dated to the 3rd c. AD or later (mixed context). The vessel is represented by its upper wall. Lipid analyses identified resin biomarkers dehydroabietic and 7-oxodehydroabietic acids. Fatty acids identified were $C_{16:0}$ and $C_{18:0}$. The analysis of organic compounds associated with wine identified the presence of malonic and fumaric acids.

10.1.1.5 Sample from BEY006.10632.x5

Context 10632 is a probable fill context, dated to the 4th c. AD. The vessel is represented by its upper wall. Fatty acids identified were $C_{16:0}$ and $C_{18:0}$. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric and succinic acids.

10.1.1.6 Sample from BEY006.11357.7

Context 11357 represents a floor - make-up/levelling context, dated to the late 4th c. AD. The vessel is represented by its mid wall. Initial TLE and saponification extractions indicated very high levels of phthalate contamination. The sample was redrilled and re-extracted and again demonstrated high levels of contamination (but lower than the initial extractions) (Fig. 10.2). Lipid analysis indicated $C_{16:0}$, $C_{18:0}$, $C_{18:1}$ and $C_{18:2}$ fatty acids as well as dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

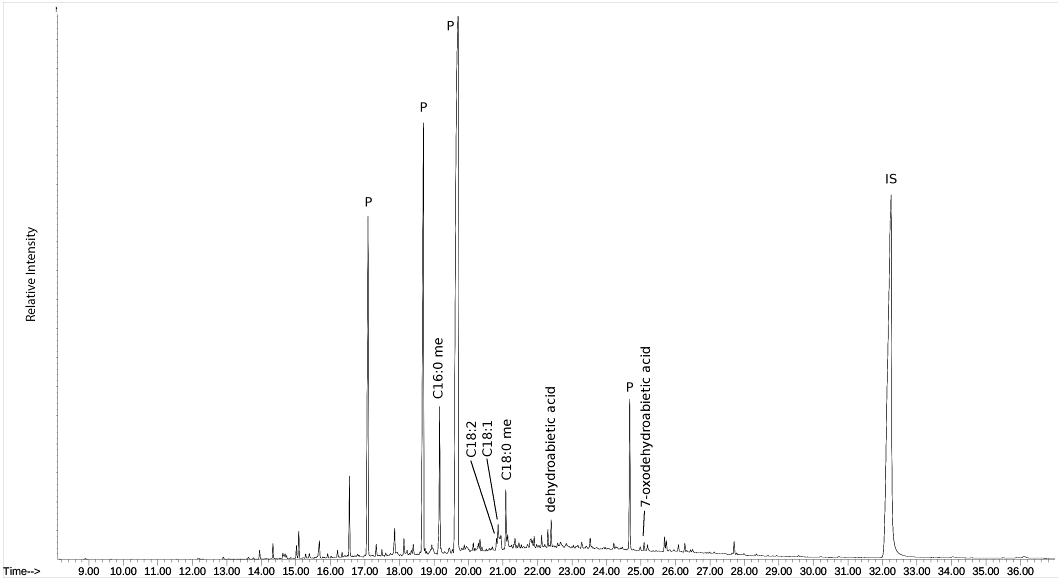


Figure 10.2: Total ion chromatogram of the acidified methanolic extraction of Sample BEY:006.13357.7.

10.1.1.7 Sample from BEY006.11357.8

Sample BEY006.11357.8 represents another sample from Context 11357. The vessel is represented by its shoulder. Lipid analyses identified resin biomarker dehydroabietic acid. Fatty acids identified were $C_{16:0}$, $C_{18:0}$ and trace amounts of $C_{18:1}$. Lipid analyses identified resin biomarkers dehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of succinic acid.

10.1.1.8 Sample from BEY006.13017.7

Context 13017 represents a bedding context, dated to the late 4th c. AD. The vessel is represented by its mid wall. Lipid analysis indicated $C_{16:0}$, $C_{18:0}$ and trace amounts of $C_{18:1}$ (in the saponified extraction) as well as dehydroabietic and 7-oxodehydroabietic acids. Lipid analyses indicated high levels of phthalate contamination. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

10.1.1.9 Sample from BEY006.13017.8

Sample BEY006.13017.8 represents another vessel from Context 13017. The vessel is represented by its base. Lipid analyses identified resin biomarkers dehydroabietic and 7-oxodehydroabietic acids. Fatty acids identified were $C_{16:0}$ and $C_{18:0}$. The analysis of organic compounds associated with wine identified the presence of fumaric, succinic and maleic acids.

10.1.1.10 Sample from BEY006.13017.9

Sample BEY006.13017.9 represents another vessel from Context 13017. The vessel is represented by its mid wall. Lipid analysis indicated $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids, as well the C_{22} and C_{24} fatty alcohols (Fig. 10.3). The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

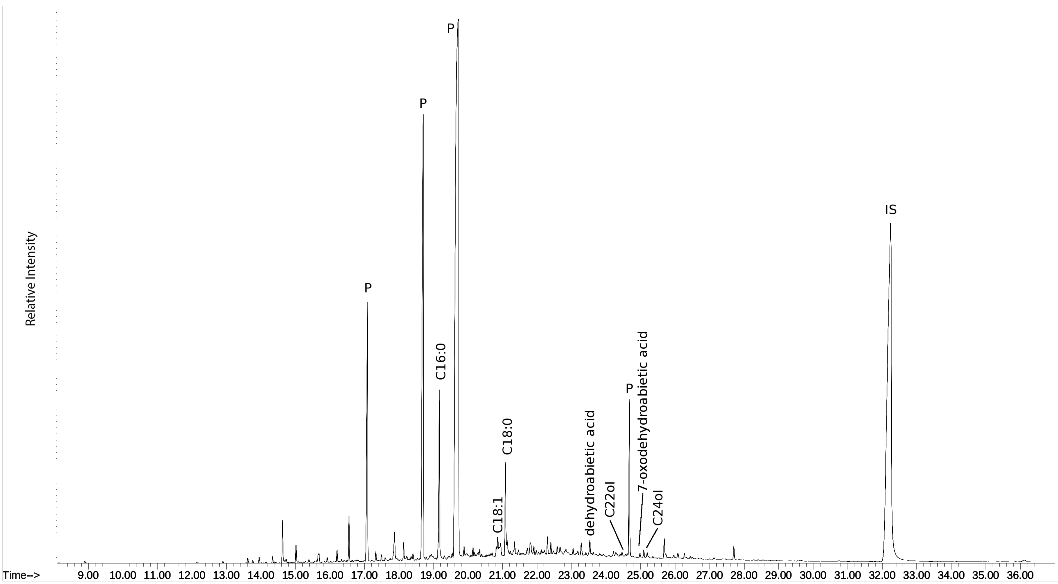


Figure 10.3: Total ion chromatogram of the acidified methanolic extraction of Sample BEY.006.13017.9. ‘C22ol’ and ‘C24ol’ identify the fatty alcohols of chain length C22 and C24, respectively.

10.1.1.11 Sample from BEY006.13017.15

Sample BEY006.13017.15 represents another vessel from Context 13017. The vessel is represented by its base. TLE analysis indicated $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic acids (Fig. 10.4). The saponified lipid extract further indicated $C_{18:1}$, $C_{20:0}$, $C_{22:0}$ and $C_{24:0}$ fatty acids (Fig. 10.5). The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids (Fig. 10.6). Significant phthalate contaminants were identified in all extractions.

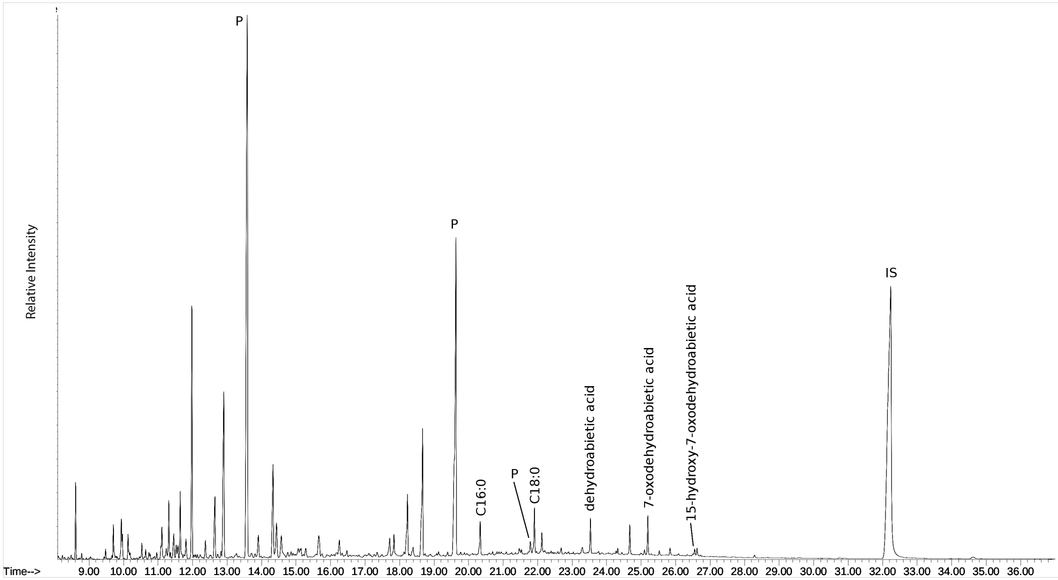


Figure 10.4: Total ion chromatogram of the total lipid extract (TLE) of Sample BEY006.13017.15.

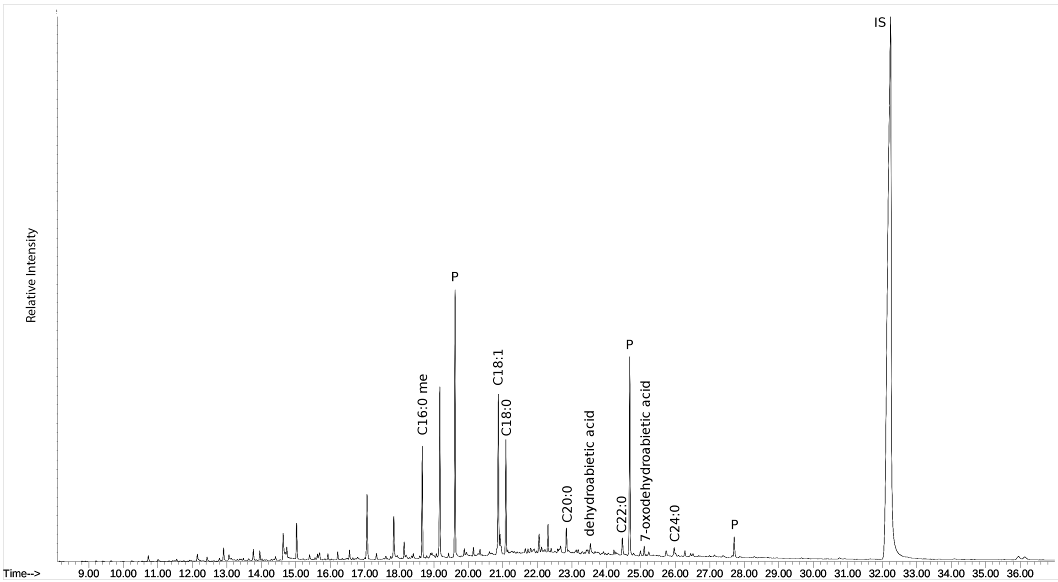


Figure 10.5: Total ion chromatogram of the acidified methanolic extraction of Sample BEY.006.13017.15.

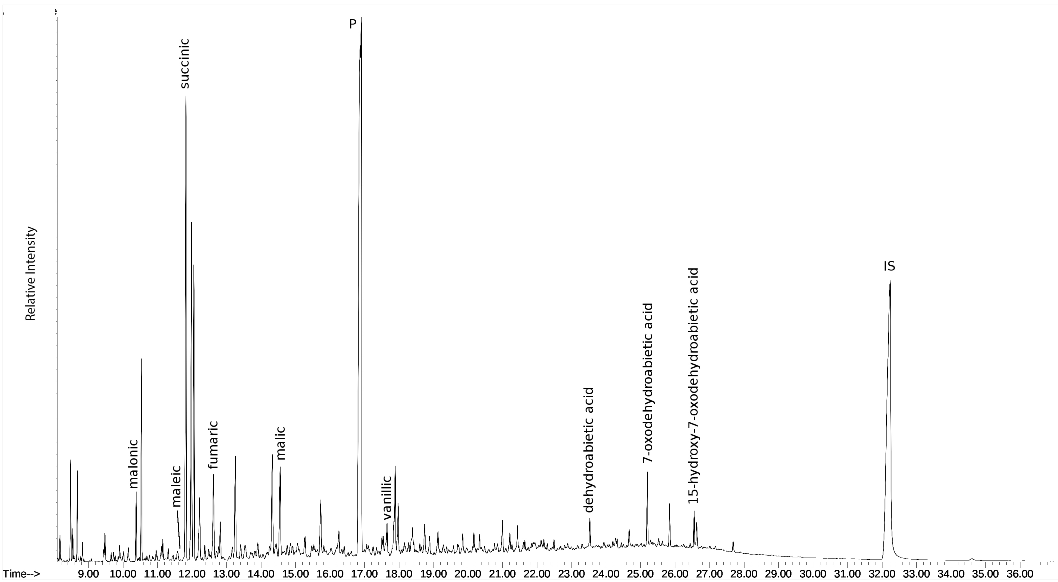


Figure 10.6: Total ion chromatogram analysis of organic compounds associated with wine in Sample BEY.006.13017.15.

10.1.1.12 Sample from BEY006.13017.16

Sample BEY006.13017.16 represents another vessel from Context 13017. The vessel is represented by its base. Lipid analyses indicated $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin biomarker dehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of fumaric, succinic, maleic, malic and vanillic acids.

10.1.1.13 Sample from BEY006.13017.597

Sample BEY006.13017.597 represents another vessel from Context 13017. The vessel is represented by its rim. Lipid analyses indicated $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin biomarkers dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

10.1.2 Analysis of Results

C Snp ('Sinope Red') amphora samples proved to be the most analytically complex samples in the study with respect to analysis. On the whole, the analyzed samples demonstrated low levels of preservation similar to that of the B Snp III ('Sinope Yellow') samples. Resin/pitch biomarkers were consistently observed in most samples–dehydroabietic acid was detected in all but three samples (BEY006.10632.x5, BEY006.13357.10 and BEY006.13357.8). Additionally, 7-oxodehydroabietic was detected in most of the dehydroabietic positive samples.[1]

With respect to organic compounds associated with wine, tartaric acid was not detected in any of the samples. Generally, however, other compounds associated with wine were well represented.[2] Similar to analyzed samples of Colchean amphorae, vanillic acid was frequently present as well as syringic acid in one sample (BEY006.5503.303). On account of the lack of tartaric acid identification in the samples, a definitive conclusion for the use of this vessel form for the transport of wine can not be made. However, the prevalence of other compounds associated with wine does suggest a content of wine.

Fatty acids, excluding non-diagnostic $C_{16:0}$ and $C_{18:0}$, were observed in six of the samples, three of which contained only trace amounts of $C_{18:1}$, three of which contained high

[1]See Table 10.2.

[2]See Table 10.3.

levels of contaminant phthlates.[3] The other samples, however, contained either contained a polyunsaturated fatty acid ($C_{18:2}$ in Sample BEY006.11357.7) or fatty alcohols (tetracosanol in Sample BEY006.5212.2; docosanol and tetracosanol in Sample BEY006.13017.9). These compounds could be associated with a vegetable oil that has, in the case of the latter, fatty alcohols (e.g. olive oil). The synthesis of the data suggests that these vessels may have been reused to contain a vegetable oil although the data from the chemical analyses is not definitive. These samples might benefit from re-analysis using a more efficient extraction protocol as described in Chapter 14.5.

Table 10.2: Resin/pitch biomarkers detected in C Snp samples.

Sherd Number	pimaric acid	isopimaric acid	methyl DHA	DHA	7-oxoDHA	15 hydroxy 7oxoDHA
006.10625.x1				x	x	
006.10632.x5						
006.11357.8				x	x	
006.13017.597				x	x	
006.13357.10						
006.13357.15				x	x	x
006.13357.16				x		
006.13357.7				x	x	
006.13357.8						
006.13357.9				x	x	
006.5212.2				x		
006.5503.303				x	x	
006.5503.320				x	x	

[3] See also Chapter 12 concerning this in Colchean samples.

Table 10.3: Results of analyses for compounds associated with wine

Sherd Number	position	malonic acid	fumaric acid	succinic acid	maleic	malic acid	vanillin	tartaric acid	vanillic acid	hyrdocinnamic acid	syringic acid
006.10625.x1	upper wall		x	x							
006.10632.x5	upper wall	x	x	x	x						
006.11357.8	shoulder			x							
006.13017.597	rim	x	x	x	x	x			x		
006.13357.10	shoulder		x	x	x	x					
006.13357.15	base	x	x	x	x	x			x		
006.13357.16	base		x	x	x	x			x		
006.13357.7	mid wall	x	x	x	x	x			x		
006.13357.8	base		x	x	x						
006.13357.9	mid wall	x	x	x	x	x			x		
006.5212.2	upper shoulder	x	x	x	x	x					
006.5503.303	base	x	x	x	x	x	x		x		x
006.5503.320	upper wall	x	x	x	x	x					
006.9999.x3											

CHAPTER 11

ANALYSES OF D SNP ('ARGILE CLAIRE') AMPHORAE

11.1 Samples

Twenty-one ceramic samples from distinct D Snp ('Argile Claire') vessels were sampled from the storerooms of the American University of Beirut. The ceramic samples were prepared and analyzed at the Research Laboratory for Archaeology and the History of Art, University Oxford using gas chromatography/mass spectrometry. The samples were characterized for both lipid constituents and organic compounds associated with wine using the protocols described in Chapter 5. The material had previously been studied by Paul Reynolds (University of Barcelona) who compiled a database of the ceramic and contextual data. Samples were selected from a variety of contexts dating to the 5th and 6th c. AD (Table 11.1). Photographs of the samples are found in Appendix A.

11.1.1 Results of Analyses

11.1.1.1 Sample from BEY006.11081.203

Context 11081 is a large context that forms a levelling above a drain. The context is characterized by large numbers of LRA 1, LRA 5 and Sinopean D Snp vessels as well as significant amounts of local Beirut amphorae. The vessel is represented by a complete base. Lipid analyses identified resin biomarkers dehydroabietic acid, 7-oxodehydroabietic acid, 15-trimethoxy dehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid. Methyldehydroabietate was observed in the saponified extract. Additionally, several species of fatty acids were observed. In addition to $C_{16:0}$ and $C_{18:0}$, a considerable quantity of $C_{18:1}$ (relative to $C_{16:0}$ and $C_{18:0}$ fatty acids) was observed as well as $C_{24:0}$ and the plant sterol, β-sitosterol (Fig. 11.1). The analysis of organic compounds associated with wine identified the presence

Table 11.1: Context and sample data for Sinope D Snp 'Argile Claire' analyses, data retrieved from the ceramic database developed by Paul Reynolds.

Area	*Context*	*Sherd Number*	*Date of Context (AD)*	*Nature of Context*	*Position of Sample*	*Visible Residue*
006	11081	203	525-550	Levelling above drain	base	No
006	11081	204	525-550	Levelling above drain	base	No
006	11081	205	525-550	Levelling above drain	base	No
006	11081	206	525-550	Levelling above drain	base	No
006	11081	208	525-550	Levelling above drain	shoulder	No
006	11081	209	525-550	Levelling above drain	shoulder	No
006	11081	210	525-550	Levelling above drain	shoulder	No
006	11081	295	525-550	Levelling above drain	shoulder	No
006	11081	x1	525-550	Levelling above drain	shoulder	No
006	11081	x5	525-550	Levelling above drain	shoulder	No
006	13017	34	c. 410	Levelling under floor	shoulder	No
006	13017	122	c. 410	Levelling under floor	mid wall	No
006	13017	181	c. 410	Levelling under floor	base	No
006	13559	4	c. 551	Cistern fill - lower level	base	No
006	13559	5	c. 551	Cistern fill - lower level	base	No
006	2004	27	550-575	Robber fill	base	No
006	2013	11	c. 5th c.	Cleaning	shoulder	No
006	3077	169	late 4th to early 6thc.	Fill	shoulder	No
006	5503	x2	late 6th c.	Pit fill	base	No
006	8754	2	551	Destruction layer	upper wall	No
045	1967	8	mid to late 6th c.	Fill	upper wall	No

of malonic, fumaric, succinic, malic, vanillic and tartaric acids as well as azelaic acid (Fig. 11.2 and 11.3).

11.1.1.2 Sample from BEY006.11081.204

Sample BEY006.11081.204 is from another vessel from Context 11081 and the vessel is represented as a base. Lipid analyses indicated $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. Dehydroabietic acid was also observed. The analysis of organic compounds associated with wine identified the presence of fumaric, succinic, malic, vanillic acids as well as azelaic acid.

11.1.1.3 Sample from BEY006.11081.205

Sample BEY006.11081.203 is from another vessel from Context 11081 and the vessel is represented as a base. Lipid analyses identified a wide array of resin biomarkers, specifically,

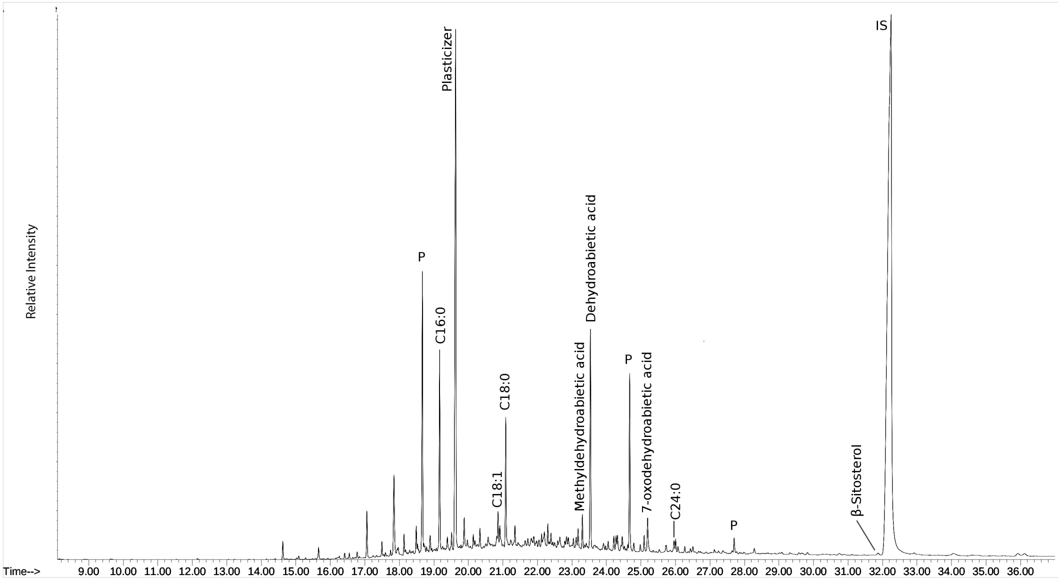


Figure 11.1: Total ion chromatogram of the acidified methanolic extraction of Sample BEY006.11081.203.

isopimaric acid, pimaric acid, dehydroabietic acid, 7-oxodehydroabietic acid and methyl dehydroabietate (in the saponified extract). The fatty acids $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, $C_{22:0}$ and $C_{24:0}$ were also observed. Additionally, the plant sterol β-sitosterol was identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and tartaric acids.

11.1.1.4 Sample from BEY006.11081.206

Sample BEY006.11081.206 is from another vessel from Context 11081 and is represented as the lower wall just above the base. Lipid analyses indicated the resin biomarkers dehydroabietic and 7-oxodehydroabietic acids; $C_{16:0}$ and $C_{18:0}$ fatty acids were identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic and vanillic acids.

11.1.1.5 Sample from BEY006.11081.208

Sample BEY006.11081.206 is from another vessel from Context 11081 and is represented as the vessel's shoulder. Lipid analyses indicated the dehydroabietic acid and the fatty acids

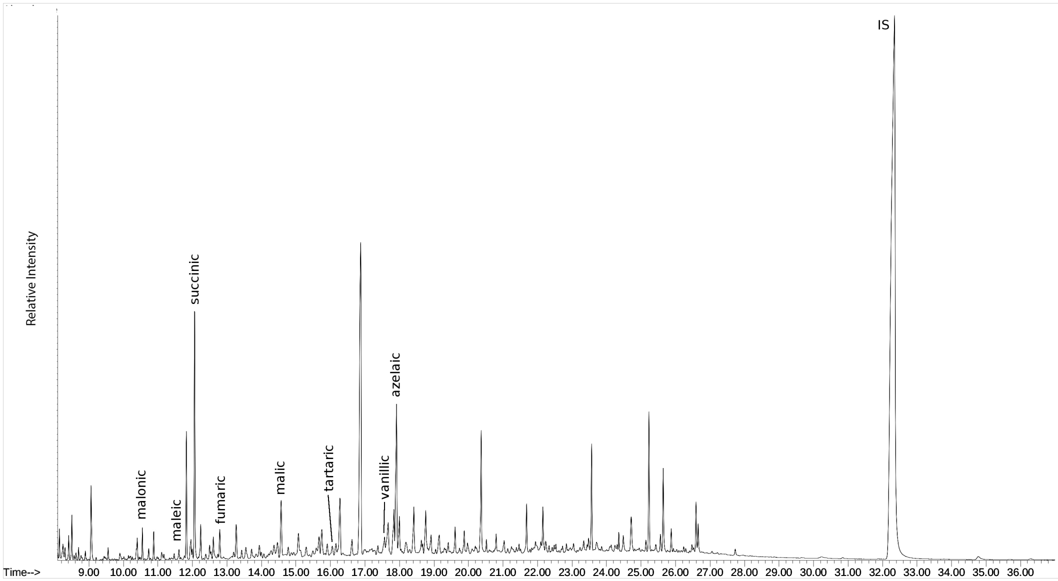


Figure 11.2: Total ion chromatogram of the analysis of compounds associated with wine in Sample BEY006.11081.203.

$C_{16:0}$ and $C_{18:0}$. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic acids.

11.1.1.6 Sample from BEY006.11081.209

Sample BEY006.11081.209 is from another vessel from Context 11081 and is represented as the vessel's shoulder. Lipid analyses indicated the resin biomarkers dehydroabietic and 7-oxodehydroabietic acids; $C_{16:0}$ and $C_{18:0}$ fatty acids were identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic and vanillic acids.

11.1.1.7 Sample from BEY006.11081.210

Sample BEY006.11081.209 is from another vessel from Context 11081 and is represented as the vessel's shoulder. Lipid analyses indicated the resin biomarkers dehydroabietic and 7-oxodehydroabietic acids; $C_{16:0}$ and $C_{18:0}$ fatty acids were identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and syringic acids.

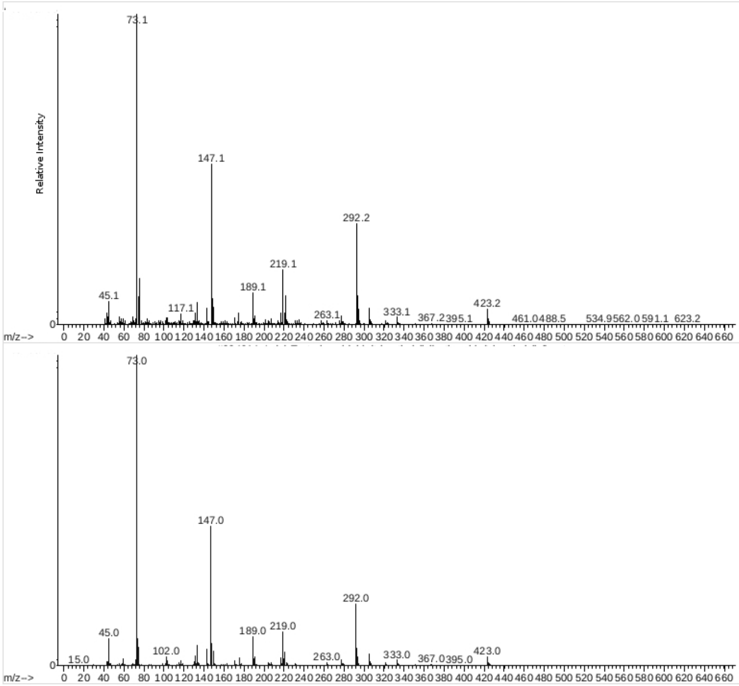


Figure 11.3: Mass spectrum of the peak identified as tartaric acid in Sample BEY006.11081.203 (top) compared against the mass spectrum of tartaric acid (as its trimethylsilyl ester) from the NIST11 database (bottom).

11.1.1.8 Sample from BEY006.11081.x1

Sample BEY006.11081.209 is from another vessel from Context 11081 and is represented as the vessel's shoulder. Lipid analyses indicated dehydroabietic acid; $C_{16:0}$ and $C_{18:0}$ fatty acids were also identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic and malic acids.

11.1.1.9 Sample from BEY006.11081.x5

Sample BEY006.11081.x5 is from another vessel from Context 11081 and is represented by the vessel's midwall section. Lipid analyses identified resin biomarkers dehydroabietic acid, 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid; $C_{16:0}$ and $C_{18:0}$ fatty acids were also identified. The analysis of organic compounds associated with wine identified the presence of fumaric, succinic, malic and vanillic acids.

11.1.1.10 Sample from BEY006.13017.34

Sample BEY006.13017.34 is from Context 13017 which forms levelling below a floor and is represented by the vessel's shoulder. Lipid analyses identified the resin biomarker dehydroabietic acid; $C_{16:0}$ and $C_{18:0}$ fatty acids were also identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic acids.

11.1.1.11 Sample from BEY006.13017.122

Sample BEY006.13017.122 is another sample from Context 13017 and is represented by the vessel's mid wall. TLE analysis identified the resin biomarker dehydroabietic acid; $C_{16:0}$ and $C_{18:0}$ fatty acids were also identified as well as trace amounts of $C_{18:1}$. The saponified lipid extract, however, additionally identified greater amounts of $C_{18:1}$ (relative to the TLE extract) and small amounts of $C_{20:0}$, $C_{22:0}$ and $C_{24:0}$ as well as the sterol β-sitosterol (Fig. 11.4). The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic acids.

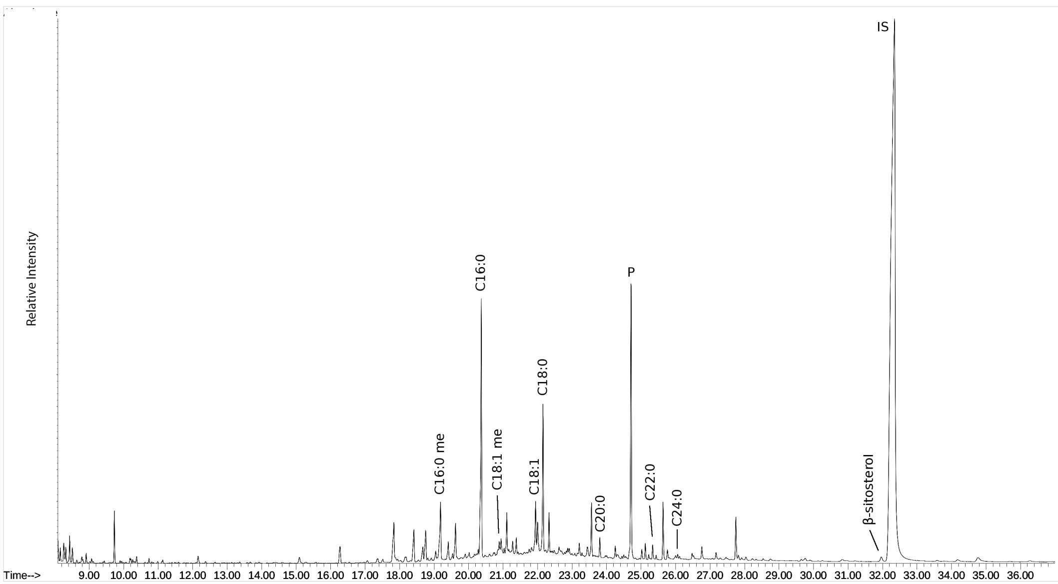


Figure 11.4: Total ion chromatogram of the saponified (SAP) extraction of Sample BEY006.13017.122.

11.1.1.12 Sample from BEY006.13017.181

Sample BEY006.13017.181is another sample from Context 13017 and is represented by the vessel's base. TLE analysis identified the resin biomarkers dehydroabietic acid and methyldehydroabietic acid; $C_{16:0}$ and $C_{18:0}$ fatty acids were also identified as well as trace amounts of $C_{18:1}$. The saponified lipid extract additionally identified 7-oxohydroabietic acid as both TMS and methyl esters. The analysis of organic compounds associated with wine identified the presence of fumaric, succinic, malic and vanillic acids.

11.1.1.13 Sample from BEY006.13559.4

Context 13559 represents a large cistern filled, dated to c. 551 AD. Sample BEY006.13559.4 is represented by the vessel's base. TLE analysis indentified dehydroabietic acid, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as the sterol β-sitosterol. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

11.1.1.14 Sample from BEY006.13559.5

Sample BEY006.13559.5 is another sample from Context 13559 and is represented by the vessel's base. TLE analysis identified $C_{16:0}$ and $C_{18:0}$ fatty acids. Lipid analyses identified resin biomarkers dehydroabietic acid, 7-oxodehydroabietic acid, 15-trimethoxy dehydroabietic acid and 15-hydroxy-7-oxodehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic and vanillic acids.

11.1.1.15 Sample from BEY006.2004.27

Context 2004 represents the fill of a robber trench, dated to c. 550-575 AD. Sample BEY006.2004.27 is represented by the vessel's shoulder. TLE analysis indicated $C_{16:0}$, $C_{18:0}$ and $C_{24:0}$ fatty acids. The saponified lipid extract indicated a significantly greater quantity and number of species of fatty acids: $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, $C_{20:0}$ and $C_{22:0}$. Dehydroabietic acid was also identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and tartaric acids as well as azelaic acid.

11.1.1.16 Sample from BEY006.2013.11

Context 2013 represents a mixed context, dated to approximately the 5th c. AD. Sample BEY006.2013.11 is represented by the vessel's shoulder. The TLE indentified $C_{16:0}$, $C_{18:0}$, $C_{18:1}$ and $C_{20:0}$ fatty acids. Additionally, octadecanol and trace n-alkanes were also detected (Fig. 11.5). The saponified lipid extract indicated $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, $C_{20:0}$, $C_{22:0}$, $C_{24:0}$ and $C_{26:0}$ fatty acids as well as 9,10-dihydroxyoctadecanoic acid (Fig. 11.6). The analysis of organic compounds associated with wine identified the presence of fumaric, succinic, malic, vanillic acids.

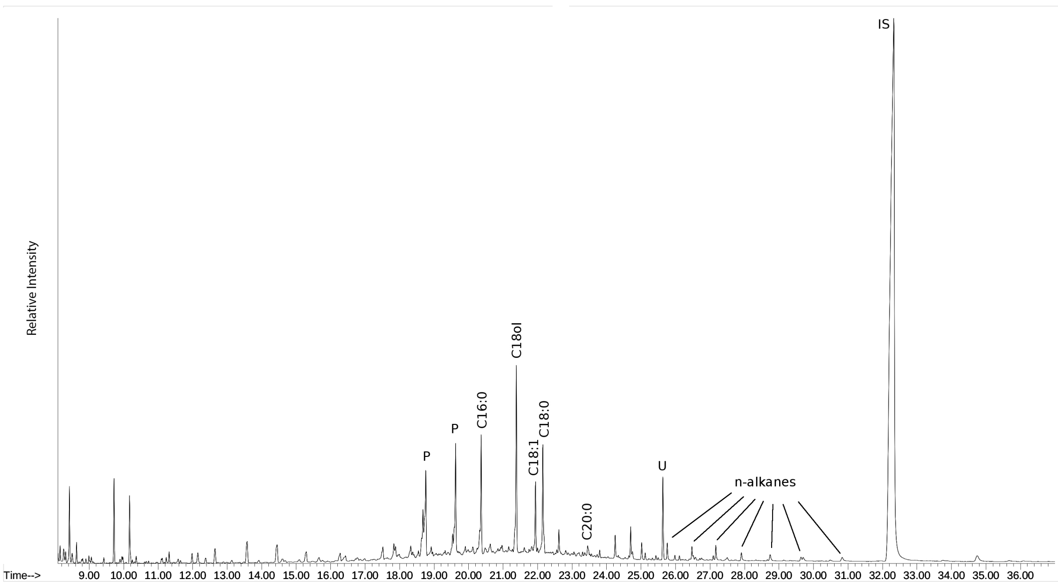


Figure 11.5: Total ion chromatogram of the total lipid extract (TLE) of Sample BEY006.2013.11.

11.1.1.17 Sample from BEY006.3077.169

Context 3077 represents a fill context, dated to between late 4^{th} and early 6^{th}c. AD. Sample BEY006.2013.11 is represented by the vessel's base. TLE analysis indicated $C_{16:0}$ and $C_{18:0}$ fatty acids. Dehydroabietic acid and 7-oxodehydroabietic acid were also identified.

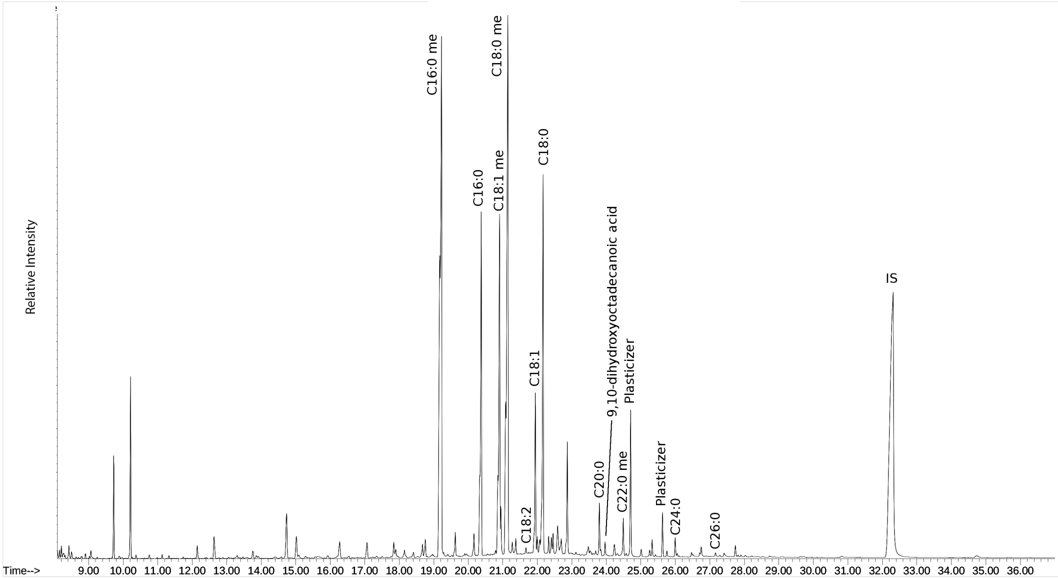


Figure 11.6: Total ion chromatogram of the saponified (SAP) extraction of Sample BEY006.2013.11. Octadecanol is identified as 'C18ol'.

The analysis of organic compounds associated with wine identified the presence of fumaric, succinic and malic acids.

11.1.1.18 Sample from BEY006.5503.x2

Context 5503 represents a pit fill context, dated to the late 6th c. AD. Sample BEY006.5503.x2 is represented by the vessel's base. Lipid analyses identified the resin biomarker dehydroabietic acid; $C_{16:0}$ and $C_{18:0}$ fatty acids were also identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and syringic acids.

11.1.1.19 Sample BEY006.8754.2

Context 8754 represents a destruction layer, dated to the 551 AD earthquake that devestated Beirut. Sample BEY006.8754.2 is represented by the vessel's upper wall. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin biomarkers dehydroabietic acid and 7-oxodehydroabietic acid. Trace amounts of $C_{18:1}$ were present in the TLE but were absent from the saponified lipid extract. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic and vanillic acids.

11.1.1.20 Sample BEY045.1967.8

Context 1967 represents a fill layer in the Roman bath area (BEY045), dated to the mid-late 6th c. AD. Sample BEY045.1967.8 is represented by the vessel's upper wall. Lipid analyses identified $C_{16:0}$ and $C_{18:0}$ fatty acids as well as the resin biomarkers dehydroabietic acid and 7-oxodehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic and vanillic acids.

11.1.2 Analysis of Results

On the whole, the results of the analyses of the D Snp samples produced consistent data concerning organic compound associated with wine. With the exception of two samples (BEY006.11081.295 and BEY006.13559.4), a wide range of organic compounds associated with wine were observed. Additionally, tartaric acid was identified in three samples (BEY006.11081.203, BEY006.11081.204 and BEY006.2004.27). The rate of detection of tartaric acid in samples demonstrating other organic compounds associated with wine was lower in D Snp vessels (~14%) compared to results from Kapitän 2 vessels (~29%) or previous analysis of local Beirut amphorae (~25%).[1] It is uncertain what mechanisms are responsible for the apparent lower retention potential of tartaric acid in this form/fabric class, although the nature of the particular ceramic matrix may be at least possibly responsible.

Resin/pitch biomarkers were well represented in the analyzed samples. Deyhydroabietic acid was detected in all samples, with 7-oxodehydroabietic and/or 15-hydroxy-7-oxodehydroabietic acid identified in a majority of samples.[2] One sample (BEY006.11081.203) also demonstrated the undegraded resin acids (pimaric and isopimaric acids). This presents evidence that the D Snp vessels were lined with resin/pitch to reduce porosity. The presence of methyl dehydroabietic acid in the TLE extracts of several samples (BEY006.11081.203,

[1] Woodworth 2011.

[2] See Table 11.2.

BEY006.13017.181 and BEY006.3077.169) is indicative of 'pyrolitic distillation' of pine resin in order to form pitch.

Seven samples (BEY006.11081.203, BEY006.11081.204, 006.11081.205, BEY006.13017.122, BEY006.13559.4, BEY006.2004.27 and BEY006.2013.11) did indicate fatty acids that might be associated with vegetable oils, specifically $C_{18:1}$ and very long chain species including $C_{20:0}$, $C_{22:0}$, $C_{24:0}$ and $C_{26:0}$. Additionally, the plant sterol β-sitosterol was detected in four samples. The analyses, on the whole, appear to indicate that these compounds may be present due to vessel use/reuse for a content consistent with a vegetable oil such as olive oil.

Table 11.2: Resin/pitch biomarkers detected in D Snp samples.

Sherd Number	pimaric acid	isopimaric acid	methyl DHA	DHA	7-oxoDHA	15 hydroxy 7oxoDHA
006.11081.203	x	x	x	x	x	x
006.11081.204				x	x	x
006.11081.205				x	x	x
006.11081.206				x	x	x
006.11081.208				x		
006.11081.209				x	x	
006.11081.210				x	x	
006.11081.295				x		
006.11081.x1				x		
006.11081.x5				x	x	x
006.13017.34				x		
006.13017.122				x	x	
006.13017.181			x	x	x	x
006.13559.4				x	x	
006.13559.5				x		
006.2004.27				x		
006.2013.11				x	x	x
006.3077.169			x	x	x	x
006.5503.x2				x		
006.8754.2				x	x	x
045.1967.8				x	x	x

Table 11.3: Results of analyses for organic compounds associated with wine

Sherd Number	POSITION	malonic acid	fumaric acid	succinic acid	malic acid	vanillic acid	vanillin	citric acid	tartaric acid	syringic acid
006.11081.203	base	x	x	x	x	x			x	
006.11081.204	base	x	x	x	x	x			x	
006.11081.205	base	x	x	x	x	x				
006.11081.206	lower wall	x	x	x	x	x				
006.11081.208	shoulder	x	x	x	x					
006.11081.209	shoulder	x	x	x	x					
006.11081.210	shoulder	x	x	x	x	x				x
006.11081.295	shoulder			x						
006.11081.x1	shoulder	x	x	x	x					
006.11081.x5	mid wall		x	x	x	x				
006.13017.122	base	x	x	x	x	x				
006.13017.34	base	x	x	x	x	x				
006.13559.4	base			x						
006.13559.5	base		x	x	x	x				
006.2004.27	shoulder	x	x	x	x	x			x	
006.2013.11	shoulder		x	x	x	x				
006.3077.169	base		x	x	x					
006.5503.x2	upper wall		x	x	x	x				x
006.8754.2	upper wall	x	x	x	x	x				
006.13017.181	base		x	x	x	x				

CHAPTER 12

ANALYSES OF MYRMEKION AMPHORAE (‘FAM 93’) AMPHORAE

12.1 Background

12.1.1 General Description

The Myrmekion amphora, also known as the fabric class ‘FAM 93’ in the ceramic analyses of Paul Reynolds of amphorae excavated from Beirut, was one of the earliest forms of Black Sea amphorae identified. I. B. Zeest identified the form in his 1960 work on Black Sea amphorae, designating it as Zeest 72.[1] Despite having been one of the earliest forms identified, the Zeest 72 has remained largely excluded from typological research until very recently.[2] Vessel dimensions are a rim of 14-15cm and a body maximizing at a diameter of 38-40 cm with a total vessel height of approximately 100 cm.[3] Vessel capacity is approximately 40 L.[4] The vessel’s fabric is reddish yellow and light red with lime, fine sand, grog and iron oxide inclusions with an outer surface often demonstrating a white coating.[5]

12.1.2 Date Range and Distribution

The Myrmekion amphora is known to have been produced from the 2nd c. AD until the first half of the 4th c. AD, most commonly observed in 3rd c. AD contexts.[6] In Beirut, Myrmekion vessels are primarily observed in late 2nd to late 3rd c. AD contexts.[7]

[1] Zeest 1960.

[2] Dyczek 2001, 228.

[3] Dyczek 2001, 228.

[4] Dyczek 2001, 230.

[5] Klenina 2015, 85.

[6] Dyczek 2001, 232f; Klenina 2015, 85; Opait and Paraschiv 2012, 319.

[7] Data retrieved from the ceramic database developed by Paul Reynolds.

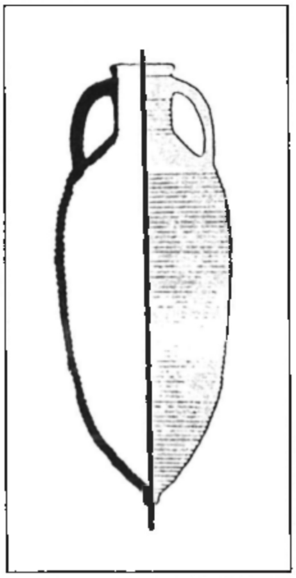


Figure 12.1: Drawing of the Myrmekion amphora form from Dyczek 2001, 228.

With respect to distribution, Myrmekion amphorae are most frequently encountered in the Bosporus and north Black Sea littoral, including Tanais, Myrmeki and Pantikapaion, Iluraton, Cherosenosos, the Scythian Neapolis and Olbia.[8]

12.1.3 Shipwrecks

Myrmekion vessels have not been attested in any known excavated shipwrecks. In 2016 a shipwreck was identified near the Greek island of Fourni that preliminary observation indicated a significant number of Myrmekion amphorae. One amphora was raised and found to be packed with crustaneans.[9] The shipwreck is planned to be be later excavated.

12.1.4 Production

The Myrmekion amphora has been determined to have been produced at Pantikapaion Myrmeki from the identification of wasters at several kiln sites.[10]

[8]Zeest 1960, 112; Dyczek 2001, 231; Klenina 2015, 85; Krapivina 2010a; Opait and Paraschiv 2012, 319.

[9]George Koutsouflakis *pers. comm.*

[10]Zeest 1960, 111.

12.1.5 Content

The content of Myrmekion amphorae has been the subject of debate. The region of Myrmeki was well known during the Roman period for the production of both wine and fish products (*salsamenta*). No epigraphic evidence by means of stamps or tituli picti are known apart from some vessels recovered from Beirut.[11] Unfortunately, vessels demonstrating tituli picti from Beirut samples are too poorly preserved to obtain any information apart from the tituli picti were applied on the shoulder below the vessel's neck and were written in Greek characters. Content of the Myrmekion amphora has been variously hypothesized as containing wine, olive oil, grain by comparison to commodities known to have been produced at Cherosenosos.[12] Opait and Paraschiv (2012) proposed a content of wine.[13] The most common hypothesis, however, is that the vessel was used to transport a form of *salsamentum*.[14]

The production of *salsamenta* is most known from western provinces, e.g. Spain, Gaul, North Africa and Sicily although the Strait of Kerch at Tyritat and Myrmekion as well as at Cheronesos in the Crimea are well known exceptions.[15] The region of Myrmekion itself was well known for fish processing.[16] It has been estimated that had an annual production capacity of at least 3000-3500 metric tons of *salsamenta*, requiring at least 800 tons of salt per annum.[17] Circumstantial evidence for the use of Myrmekion amphorae for transporting *salsamenta* has been suggested by their presence in back-filled vats used for *salsamenta* production as well as their presence in the direct vicinity of such production sites (Figs. 12.2 and 12.3).[18] It addition to *salsamenta*, Myrmeki is known to have also been a major supplier of wine during the Roman period (Fig. 12.4).[19]

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[11] Dyczek 2001, 231.

[12] Lund and Gabrielsen 2005, 163.

[13] See also Savvonidi 1993 concerning production of wine on the north coast of the Black Sea during the late Roman period.

[14] e.g. Dyczek 2001, 231; Klenina 2015, 84; Paul Reynolds *pers. comm.*

[15] Curtis 2001, 411.

[16] Dyczek 2001, 231; Højte 2005, 133.

[17] Højte 2005, 152.

[18] Højte 2005, 151; Dyczek 2001, 231.

[19] Klenina 2015, 84.

Figure 12.2: Fish salting vats at Myrmekion with a capacity of at least 116 m^3. Source: Højte 2005, Fig. 11.

12.2 Samples

Fifteen ceramic samples from distinct Myrmekion Amphorae ('FAM 93') vessels were sampled from the storerooms of the American University of Beirut. The ceramic samples were prepared and analyzed at the Research Laboratory for Archaeology and the History of Art,

Figure 12.3: Tiles and Myrmekion amphorae recovered from the vicinity of fish salting vats in Myrmekion. Source: Højte 2005, Fig. 12.

University Oxford using gas chromatography/mass spectrometry. The samples were characterized for both lipid constituents and organic compounds associated with wine using the protocols described in Chapter 5. The material had previously been studied by Paul Reynolds (University of Barcelona) who compiled a database of the ceramic and contextual data. Samples were selected from a variety of contexts dating primarily to the 4th and 5th c. AD (Table 12.1). Photographs of the samples are found in Appendix A.

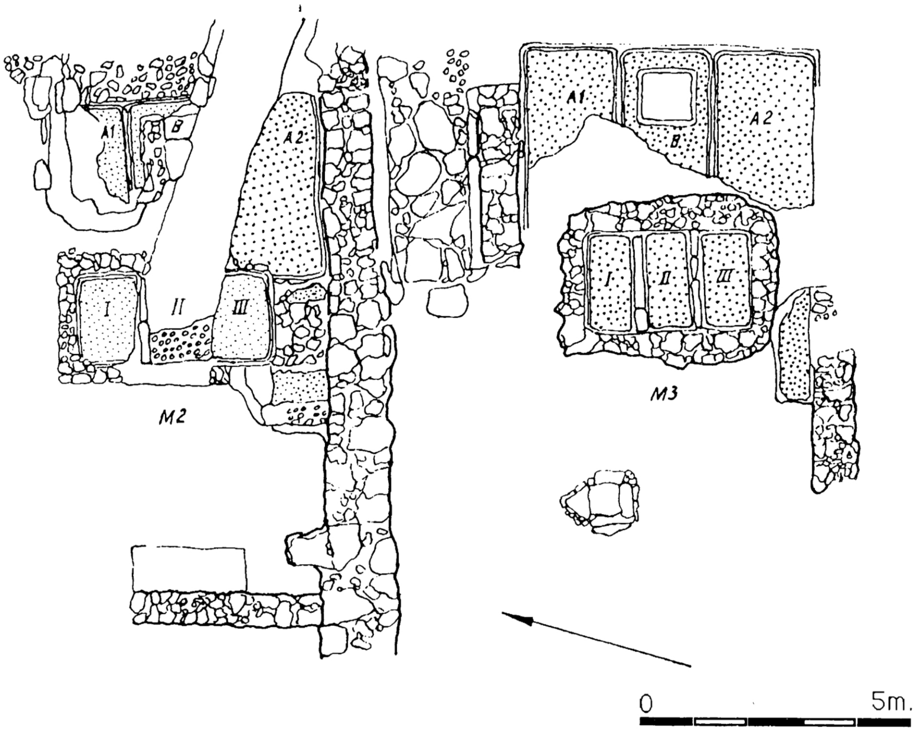

Figure 12.4: Plan of wineries from Myrmeki. Source: Savvonidi 1993, Fig. 1.

12.2.1 Results of Analyses

12.2.1.1 Sample from BEY006.4601.3

Context 4601 represents a cleaning context with a mixed date range of ceramic finds. The vessel is represented by its shoulder. Due to the significant levels of resin acids, the sample was reanalyzed using the lipid fractionation technique. The fatty acids $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, $C_{22:0}$, $C_{23:0}$, $C_{24:0}$, $C_{26:0}$ were observed as well as the fatty alcohols docosanol and tetracosanol. The sterols cholest-5-en-24-one and β-sitosterol were also observed (Figs. 12.5 and 12.6). Detected resin acids included pimaric, isopimaric, dehydroabietic acid and 7-oxodehydroabietic acid. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

Table 12.1: Context and sample data for Myrmekion analyses, data retrieved from the ceramic database developed by Paul Reynolds.

Area	*Context*	*Sherd Number*	*Date of Context (AD)*	*Nature of Context*	*Position of Sample*	*Visible Residue*
006	4601	3	mixed	cleaning	shoulder	no
006	5051	554	4^{th} c. (?)	fill	base	no
006	5051	275	4^{th} c. (?)	fill	mid wall	no
006	5051	555	4^{th} c. (?)	fill	lower wall	no
006	5051	557	4^{th} c. (?)	fill	lower wall	no
006	5051	559??	4^{th} c. (?)	fill	lower wall	no
006	5251	x2	late 5^{th} c.	fill?	mid wall	no
006	5251	x3	late 5^{th} c.	fill?	mid wall	no
006	5251	x4	late 5^{th} c.	fill?	mid wall	no
006	5251	x5	late 5^{th} c.	fill?	mid wall	no
006	7313	6	mixed	cleaning	neck	no
006	10543	1	4^{th} c.?	levelling	mid wall	no
006	13039	x2	?	levelling	upper shoulder	no
178	204.218	282	4^{th}-5^{th} c.?	fill?	neck	no
045	940	16	4^{th}-5^{th} c.	drain	base	no

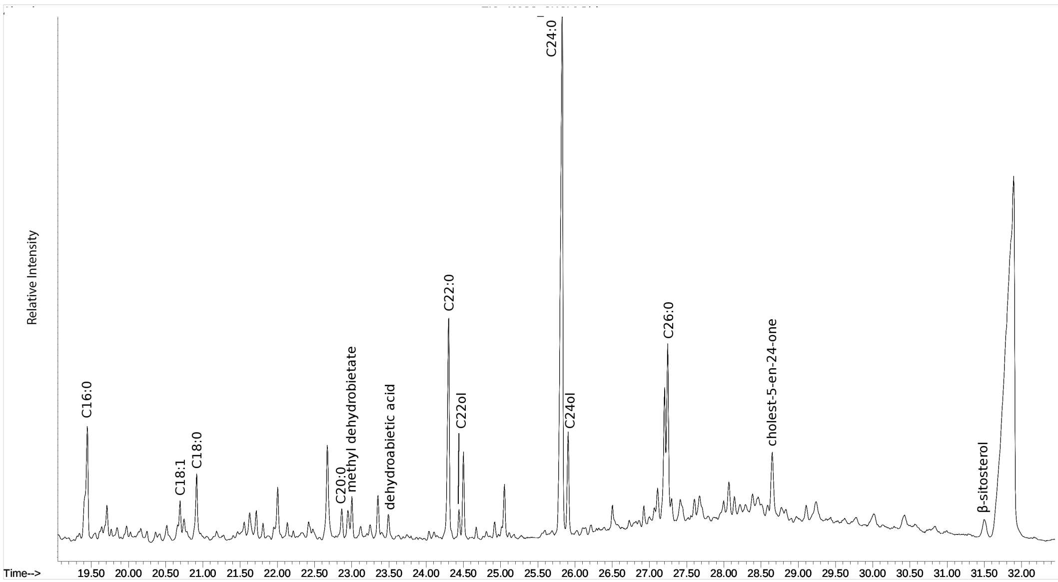

Figure 12.5: Partial total ion chromatogram of Fraction 1 (chloroform) by lipid and resin fractionation of Sample BEY006.4601.3. 'C22ol' and 'c24ol' indicate docosanol and tetracosanol, respectively.

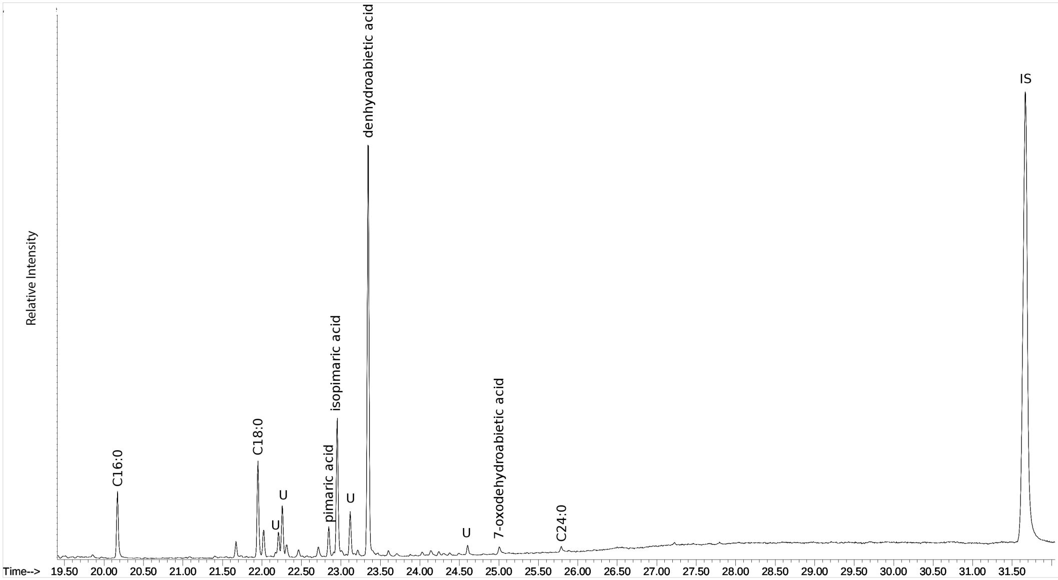

Figure 12.6: Partial total ion chromatogram of Fraction 2 (acidified diether ether) by lipid and resin fractionation of Sample BEY006.4601.3.

12.2.1.2 Sample from BEY006.5051.554

Context 5051 represents a fill context, dated approximately to the 4rd c. AD. The vessel is represented by its base. Lipid analyses indicated the presence of $C_{15:0}$, $C_{16:0}$, $C_{16:1}$, $C_{17:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol (Fig. 12.7). The resin biomarker dehydroabietic acid was also observed. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and tartaric acids.

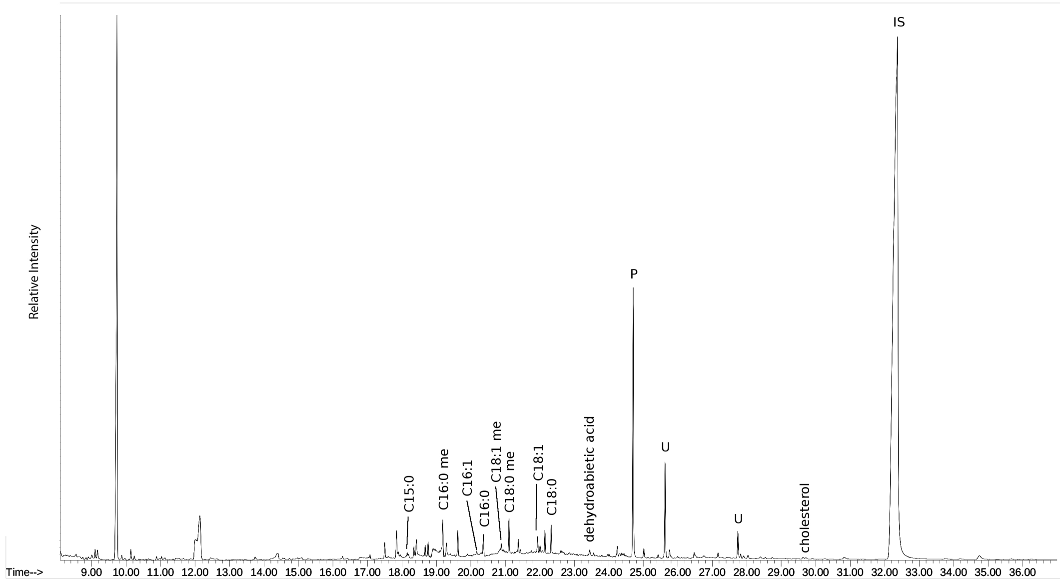

Figure 12.7: Total ion chromatogram of the saponified (SAP) extraction of Sample BEY006.5051.554.

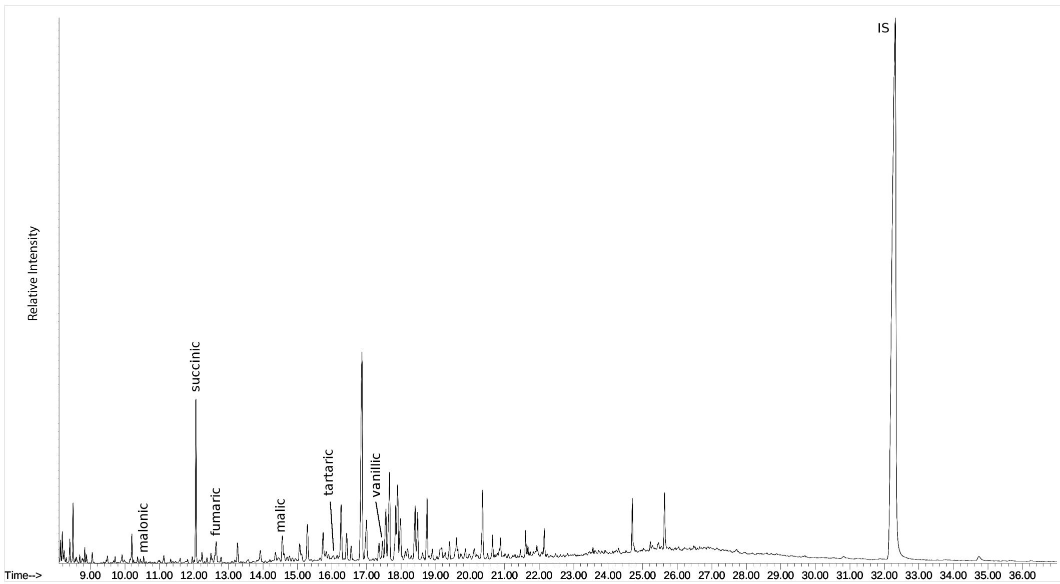

Figure 12.8: Total ion chromatogram of the organic compounds associated with wine in extract of Sample BEY006.5051.554.

12.2.1.3 Sample from BEY006.5051.275

Sample BEY006.5051.275 is another vessel from Context 5051. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{15:0}$, $C_{16:0}$, $C_{17:0}$, $C_{18:0}$ and $C_{18:1}$, $C_{22:0}$ and $C_{24:0}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic and 7-

oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.4 Sample from BEY006.5051.555

Sample BEY006.5051.275 is another vessel from Context 5051. The vessel is represented by its lower wall. Lipid analyses indicated the presence of $C_{15:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.5 Sample from BEY006.5051.557

Sample BEY006.5051.275 is another vessel from Context 5051. The vessel is represented by its lower wall. Lipid analyses indicated the presence of $C_{15:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ and $C_{18:1}$ and $C_{24:0}$ fatty acids as well as cholesterol (Fig. 12.9). The resin biomarker dehydroabietic acid was also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

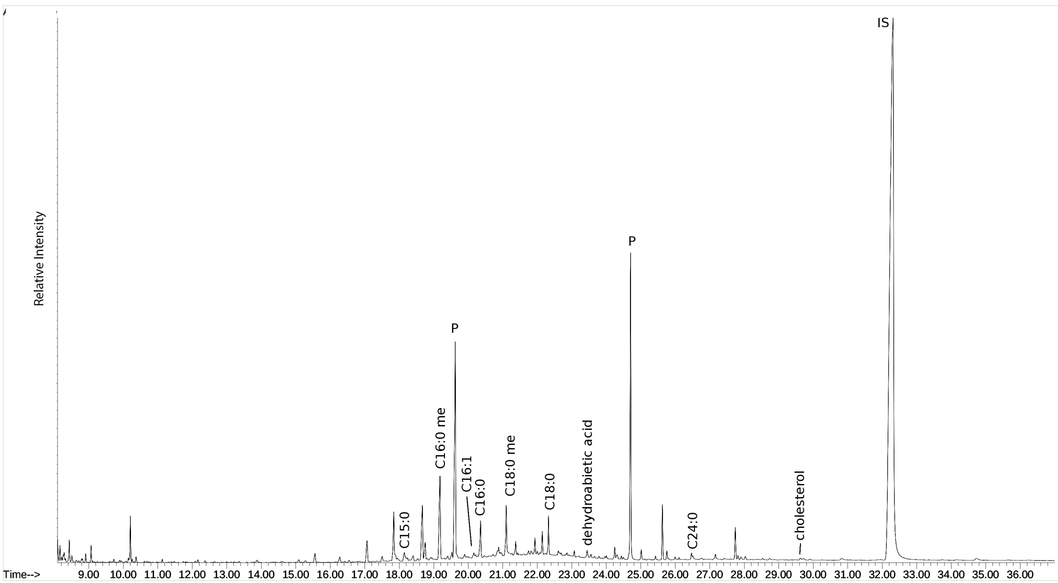

Figure 12.9: Total ion chromatogram of the saponified (SAP) extraction of Sample BEY006.5051.557.

12.2.1.6 Sample from BEY006.5051.559

Sample BEY006.5051.275 is another vessel from Context 5051. The vessel is represented by its lower wall. Lipid analyses indicated the presence of $C_{15:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of fumaric and succinic acids.

12.2.1.7 Sample from BEY006.5251.x2

Context 5251 represents a probable fill context, dated approximately to the late 5th c. AD using ceramic evidence. The vessel is represented by its mid wall. The fatty acids $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, $C_{22:0}$ and $C_{24:0}$ were observed. Cholesterol was also observed. Detected resin acids included pimaric, isopimaric, dehydroabietic acid, 7-oxodehydroabietic acid and 15-hydroxy-7-oxodehydroabietic as well as retene (Fig. 12.10). The analysis of organic compounds associated with wine identified the presence of malonic and succinic acids.

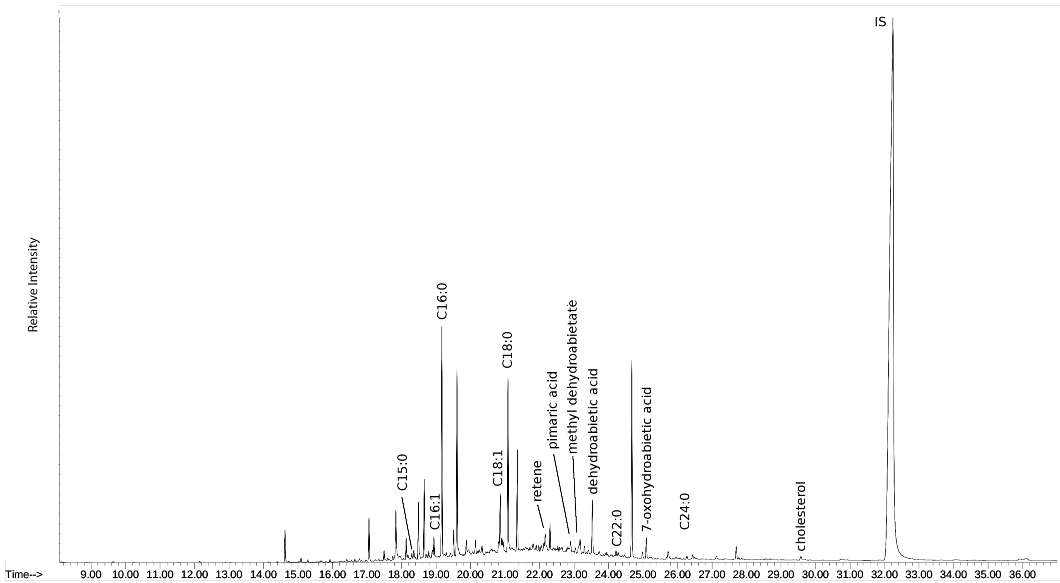

Figure 12.10: Total ion chromatogram of the acidified methanolic extraction of Sample BEY006.5251.x2.

12.2.1.8 Sample from BEY006.5251.x3

Sample BEY006.5251.x3 is another vessel from Context 5251. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{15:0}$, $C_{16:0}$, $C_{16:1}$, $C_{17:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.9 Sample from BEY006.5251.x4

Sample BEY006.5251.x4 is another vessel from Context 5251. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic were also observed. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, malic, vanillic and syringic acids.

12.2.1.10 Sample from BEY006.5251.x5

Sample BEY006.5251.x5 is another vessel from Context 5251. The vessel is represented by its mid wall. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic were also observed. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic and malic acids.

12.2.1.11 Sample from BEY006.10543.1

Context 10543 represents a levelling context, dated approximately to the 4^{rd} c. AD. The vessel is represented by its mid wall. The fatty acids $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, and $C_{24:0}$ were observed as well as cholesterol. Detected resin acids included pimaric, isopimaric, dehydroabietic acid and 7-oxodehydroabietic acid as well as retene. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.12 Sample from BEY006.7313.6

Context 5051 represents a cleaning context with a mixed date range of ceramic finds. The vessel is represented by its neck. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic, 7-oxodehydroabietic and 15-hydroxy-7-oxodehydroabietic were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.13 Sample from BEY006.13039.x2

Context 10543 represents a levelling context, the date of which has not be ascertained. The vessel is represented by its upper shoulder. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.14 Sample from BEY006.178.204.218.282

Context 174.204.218 represents a drain context dated to the 4^{th} or 5^{th} c. AD. The vessel is represented by its neck. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.1.15 Sample from BEY045.940.16

Context 940 represents a fill context dated to the 4^{th} or 5^{th} c. AD. The vessel is represented by its base. Lipid analyses indicated the presence of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids as well as cholesterol. The resin biomarkers dehydroabietic and 7-oxodehydroabietic acids were also observed. The analysis of organic compounds associated with wine identified only the presence of succinic acid.

12.2.2 Analysis of Results

The fifteen analyzed samples of Myrmekion ('FAM 93') amphorae produced generally homogeneous data. Resin/pitch biomarkers were well represented in the analyzed samples. Deyhydroabietic acid was detected in all samples, with 7-oxodehydroabietic and/or 15-hydroxy-7-oxodehydroabietic acid identified in 13 of the samples.[20] Three samples (BEY006.4601.3, BEY006.5251.x2 and BEY006.10543.1) also demonstrated the undegraded resin acids (pimaric and isopimaric acids). Additionally, two of the previous samples were determined to contain retene (BEY006.5251.x2 and BEY006.10543.1). This presents evidence that the analyzed Myrmekion vessels were lined with resin/pitch, most probably to reduce porosity as is consistent with previous archaeological information and classical sources concerning amphora lining practices. The presence of methyl dehydroabietic acid in the TLE extracts of several samples (BEY006.11081.203, BEY006.13017.181 and BEY006.3077.169) is indicative of 'pyrolitic distillation' of pine resin in order to form pitch.

Analysis of extracted lipids proved more complicated. The lipid profiles from the extracted samples generally produced profiles that included $C_{18:1}$ and cholesterol (or oxidation products of cholesterol). However, the general level of preservation, presuming a lipid-rich content was low. This general trend is similar to that of B Snp III ('Sinopean Yellow') samples with respect to the total extractable lipid content but the level of residue in the samples did not fall below 'background noise' levels. The general trend of samples to have significant levels of $C_{18:1}$ to $C_{16:0}$ and $C_{18:0}$ fatty acids suggests a lipid-rich content. The presence of cholesterol (determined by comparison of laboratory and inter-sample blanks indicating that cholesterol was not the result of intra-laboratory contamination) suggests a lipid content of animal origin (i.e. terrestrial or marine). No definitive marine biomarkers were observed in the samples (i.e. isoprenoid fatty acids); however, due to the low level of extractable lipids it is not unexpected that lipid constituents that are at or near trace levels in modern samples might be absent. Like B Snp III ('Sinopean Yellow') amphora samples, the Myrmekion

[20]See Table 12.3.

sample material might benefit from enhanced extraction techniques under development.

Organic compounds associated with wine were conspicuously absent from samples (with the exception of succinic acid) except for Samples BEY 006.5051.275, BEY006.5251.x4 and BEY006.5251.x5.[21] The prevalence of organic compounds associate with wine, including the presence of tartaric acid in Sample BEY006.5051.554, suggests, in conjunction with the lipid data, a secondary use for containing wine.

[21] See Table 12.2. See Chapter 14.4 for a discussion of the genesis of succinic acid in analyzed samples.

Table 12.2: Results of analyses for organic compounds associated with wine

Sherd Number	POSITION	malonic acid	fumaric acid	succinic acid	maleic	malic acid	vanillic acid	vanillin	tartaric acid	syringic acid
006.4601.3	shoulder			x						
006.5051.554	base			x	x	x	x		x	x
006.5051.275	mid wall			x						
006.5051.555	lower wall			x						
006.5051.557	lower wall			x						
006.5051.559	lower wall		x	x						
006.5251.x2	mid wall	x		x						
006.5251.x3	mid wall			x						
006.5251.x4	mid wall	x	x	x	x	x	x			x
006.5251.x5	mid wall	x	x	x	x	x				
006.7313.6	neck			x						
006.10543.1	mid wall			x						
006.13039.x2	upper shoulder			x						
178.204.218.282	neck			x						
045.940.16	base			x						

Table 12.3: Resin/pitch biomarkers detected in Myrmekion samples.

Sherd Number	pimaric acid	isopimaric acid	retene	methyl DHA	DHA	7-oxoDHA	15 hydroxy 7oxoDHA
006.4601.3	x	x			x	x	
006.5051.554					x		
006.13039.x2					x		
006.5051.275					x	x	
006.5051.555					x		
006.5051.557					x		
006.5051.559					x	x	
006.5251.x2	x	x	x		x	x	x
006.5251.x3					x	x	
006.5251.x4					x	x	x
006.5251.x5					x	x	x
006.7313.6					x	x	x
006.10543.1	x	x	x		x	x	
006.13039.x2					x	x	
178.204.218.282					x	x	
045.940.16					x	x	

CHAPTER 13

COLCHEAN AMPHORAE

13.1 Introduction

The region of Colchis is located on the eastern shore of the Black Sea, principally in what is modern Georgia. Colchis was an independent polity until the 6th c. BC when it fell under the suzerainty of Achaemenidian Persia.[1] The region was conquered by Mithridates I of Pontus c. 101 BC and assimilated into the 'Kingdom of Pontus'. The campaigns of Pompey and Lucullus in 65 BC defeated the Kingdom of Pontus and the region was incorporated into the Roman Empire as a province. There is some disagreement as to the western extent of the province: Strabo states Trapezus (modern Trabzon in northeast Turkey) as the western extent, whereas Ptolemy limits the southern extent to the Rioni river in modern Georgia.[2] Similarly, Xenophon recognizes Trapezus as part of the region of Colchis.[3]

13.2 Typology

Amphora production in the region of Colchis is documented to have begun during the 4th c. BC and continued at least until the mid 7th c. AD.[4] The typology is divided into four chronological variants. All forms from the Hellenistic through the late Roman period form are comprised of 'one big variable morphological type', Ch1 according to Vnukov's typology.[5] Hellenistic forms bear a similarity to Sinopean forms of the same period featuring a rounded, ovoid body with a tall neck and beaded rim (Fig. 13.1).[6] The vessels subsequently develop to a more tapering body style before adapting a 'wasp-like' waist in later forms (in-

[1] Encyclopaedia Britannica, Colchis

[2] **?**, 138.

[3] Vnukov 1995, 188.

[4] Kassab Tezgör et al. 2001, 112.

[5] Vnukov 2010a, 29. Vnukov's typology is the only well developed chronological typology to date.

[6] Vnukov 2010a, 29f.

sert fig here). The capacity of the Roman period form, ChID, is approximately 15-20 L (Fig. 13.2).[7] The form observed during the Roman period continues largely unchanged into the Byzantine period although the typology of the later period is less well studied.[8]

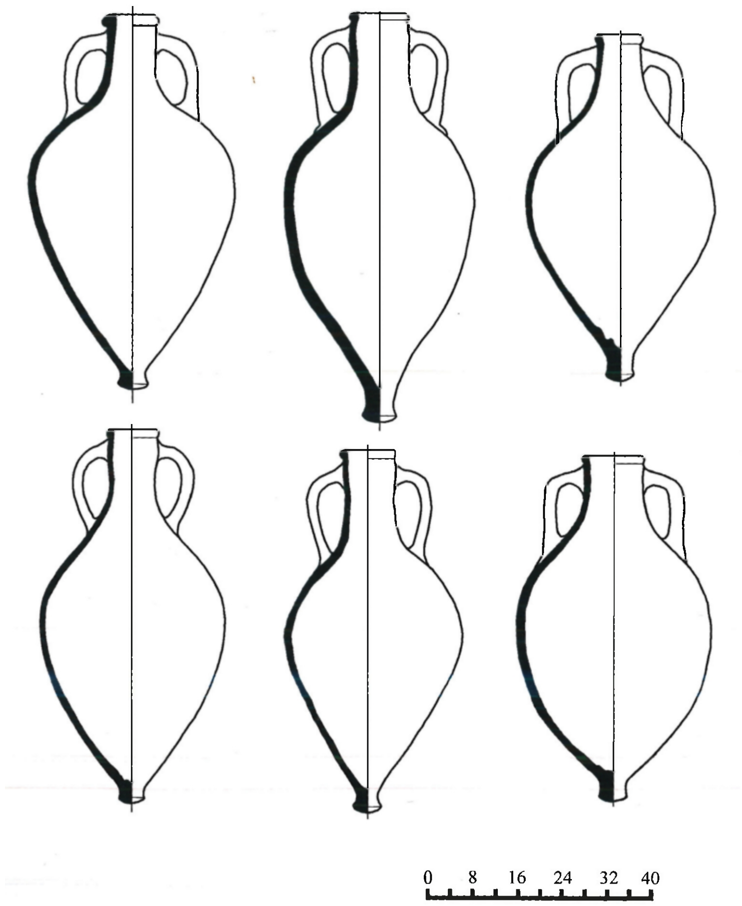

Figure 13.1: Hellenistic Colchean amphora forms. Source: Vnukov 2010a, Plate 14.

13.3 Fabric

13.3.1 Fabric Groups

The general appearance of Colchean amphorae is brown in color. Two fabric groups are observed in Colchean amphorae. The first fabric group includes inclusions of pyroxene and

[7] Klenina 2015, 84.

[8] Vnukov 2010a, 30; Kassab Tezgör et al. 2007, 205.

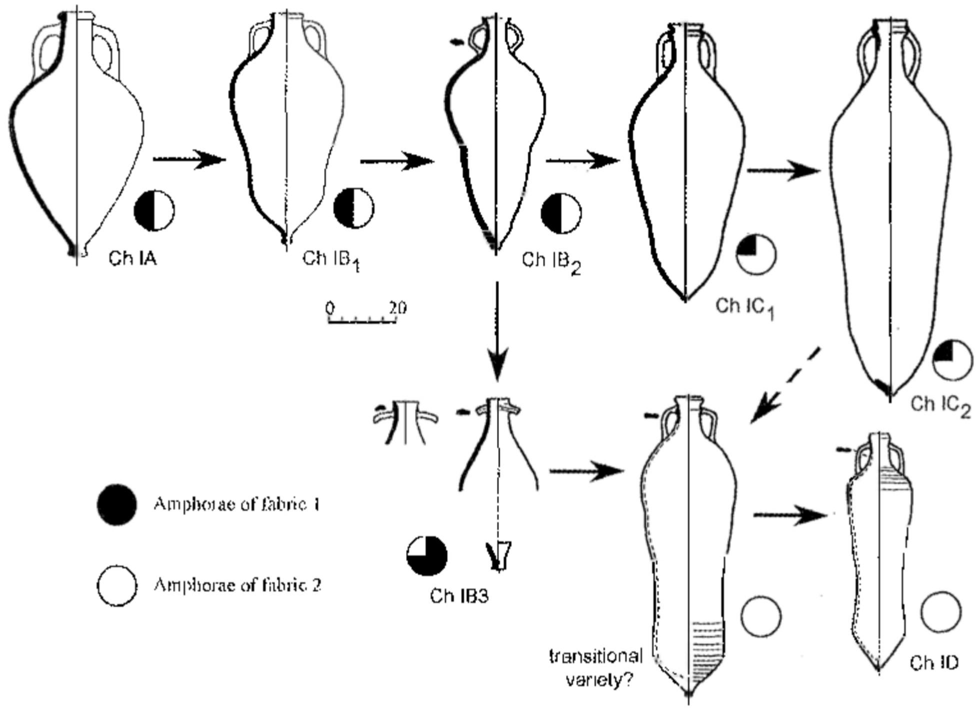

Figure 13.2: Typology of Colchean amphorae. Source: Vnukov 2011, Fig. 8.

basaltic sand that are 'identical to the mineral additions in Sinopean ceramics' of the same period.[9] Basaltic sand occurs in several regions in the southern and east Black Sea region, including the southern littoral encompassing Sinope, Amisos (modern Samsun) and Trapesus (modern Trabzon) and, to the east, the region of Ajaria.[10] Unlike fabric group 1, the second fabric group is not homogenous. Group 2 is characterized by grains of rocks of differing origin including volcanic (basalt, liparite), plutonic (granite, diorite) and sedimentary (sandstone, shale) as well as some minerals rare in the southern Black Sea littoral, e.g. olivine (Fig. 13.3).[11]

[9] Vnukov 2010a, 30.

[10] Vnukov 2011, 271.

[11] Vnukov 2010a, 30.

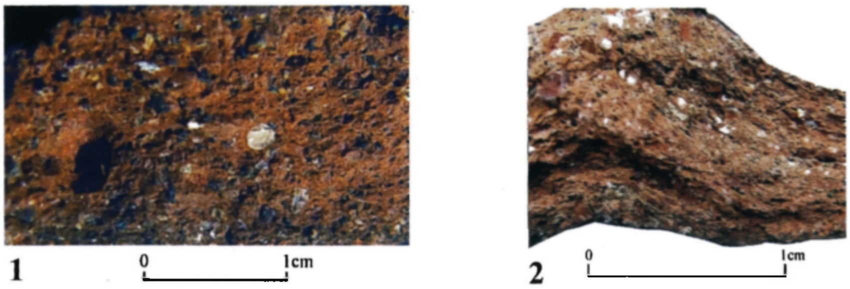

Figure 13.3: Photographs of the cross section of Colchean Group 1 (1) and Group 2 (2). Source: Vnukov 2010a, Pl. 6.1-2.

13.3.2 Origin, Prevalence of Colchean Fabric Groups and Distribution

13.3.3 Origin

The differing nature of the two Colchean fabric groups indicates that there are at least two geographically distinct provenances for the vessels. Vnukov has suggested that Group 1 may have been manufactured in the Pontic region of the Black Sea on account of the basaltic sand inclusions and more specifically in the region near Sinope on account of the similarity of the temper of the two fabrics.[12] More specifically, Vnukov suggests production at or near Trapezus as the city is recounted by Strabo as being a 'Sinopean colony in the region of Colchis' and this may account for similarity in form to Sinopean vessels of the same period and a fabric that he describes as being more Colchean in nature.[13]

Group 2, as noted above, is also notable for the lack of homogeneity of fabric, suggesting multiple spatially separated production sites. The nature of some of the inclusions is inconsistent with a provenance in the Pontic region. Instead, it is argued that origin in the region of Colchis in modern Georgia is the probable provenance.[14] Abkhazia may be one manufacturing location due to the similarity of local raw material and the fabric of locally produced wares.[15]

[12] Vnukov 1995, 198; Vnukov 2010a, 31.

[13] Vnukov 2010a, 31.

[14] Vnukov 2010a, 31.

[15] Tsetskhladze and Vnukov 1992, 382; Vnukov 2011.

13.3.4 Chronological Prevalence of Fabric Groups

The Group 1 fabric predominates during the Hellenistic period until approximately the 2nd c. AD after which vessels of the fabric become increasingly less frequent.[16] The general trend of the prevalence of the two fabric groups with the 'evolution' of vessel typology from the Hellenistic to late Roman period can be observed in Figure 13.2. Vnukov theorizes that after production began in the region of Trapezus during the 4th c. BC, it then spread to the 'barbarian' regions to the east where production began to outstrip that of Trapezus. Economic development in Colchis after the region was consolidated by the Roman army resulted in an increase of goods production (and possibly increased trade networks) which resulted in the later prevalence of Group 2 vessels.[17] It is interesting to note that a fabric group is observed in Beirut, dating primarily to 3rd and 4th c. AD contexts bears similarity to the Group 1 fabric type. The fabric is brown in color and contains basaltic inclusions. Paul Reynolds attributed it to the region of Sinope on account of the nature of the fabric.[18] It is very rare with only approximately 10 sherds observed, none of which are diagnostic. It is possible that these may belong to Group 1 vessels.

13.3.5 Distribution

Generally, distribution, with respect to quantity, of Colchean vessels increases significantly in the Black Sea region after the 2nd c. AD.[19] There is, however, differences in the distribution patterns of Group 1 and 2 vessels. Group 1 vessels are found mostly in the north Black Sea region between the 4th c. BC and 1st c. AD.[20] Conversely, Group 2 vessels are relative rare in this region during the same period but become frequent thereafter.[21] Most published finds of Colchean amphorae do not distinguish as to which fabric group they belonged, how-

[16] Vnukov 2010a, 31; Vnukov 2011.

[17] Vnukov 2010a, 31f.

[18] Paul Reynolds pers. comm.

[19] Vnukov 2010a, 31.

[20] Vnukov 2010a, 31.

[21] Vnukov 2010a, 31.

ever considering that the finds detailed below are from the late Roman and early Byzantine periods it is reasonable to expect most, if not all, belong to Group 2. In the north Black Sea region, between the 3rd and 6th c. AD 'significant quantities' were observed in the region, especially the Crimea, representing approximately 1.8-2.0% of total ceramic finds.[22] In the Crimea, they are especially abundant at the sites of Chesonesos and Tiritake.[23]

In the west, Colchean amphorae have been recovered at Tomi, Murighiol, Topraichioi, Capidava, Sacidava and Tropaeum Traianii.[24] On the Bulgarian coast, they have been recovered at Messambria, Apollonia and Odessos.[25]

On the southern Black Sea littoral, one neck in Group 1 fabric was recovered from the excavations of the kilns at Demirci.[26] A full example is housed at the Archaeological and Atatürk Museum at Samsun. 'Numerous' examples have been recovered at Samsun; the dates of the vessels is not given but they are identified as belonging to Group 1.[27] More generally, they have been ascribed as being 'well distributed' in the Kingdom of Bosporus.[28]

In the east, Colchean amphorae are known from several excavated sites. The best documented with respect to Colchean amphorae is that of Abkhazia. Early Colchean vessels are dated between the 4th-2nd c. BC and belong to variants Ch IA and $ChIB_1$.[29] The fabric of these vessels is very similar to local wares suggesting the amphorae are locally manufactured, although some Group 1 vessels were also observed during this period.[30] Colchean amphorae are also known from the excavations at Gudava and Ilori. Both sites were excavated by the National Museum of Georgia in the early 1970's. 'Significant' quantities of Colchean, as well as Sinopean, amphorae were recovered at Gudava, although no informa-

[22] Klenina 2015, 84.

[23] Opait and Paraschiv 2012, 116.

[24] Scorpan 1975; Opait and Paraschiv 2012, 116.

[25] Opait and Paraschiv 2012, 116.

[26] Kassab Tezgör 2002b, 200. The fabric type is described as 'pseudo-Colchean'.

[27] Opait and Paraschiv 2012, 116.

[28] Kassab Tezgör et al. 2001, 111f.

[29] Vnukov 2011, 272.

[30] Vnukov 2011, 272f.

tion concerning the typology, fabric or period of the amphorae is available to the author.[31] A kiln was also found during the course of excavations at Gudava but no waster material was recovered.[32] As for the site of Ilori, unfortunately the only available information concerning Colchean amphorae is that vessels were recovered. Kassab Tezgör et al. 2007 did analyze the recovered Sinopean amphorae, determining the vessels recovered at Ilori corresponded to types C Snp I and II. If the periodization of recovered Colchean vessels corresponds to that of Sinopean amphorae, this would place their date of manufacture somewhere during the 4th or 5th c. AD.

In the eastern Mediterranean, Colchean amphorae are very rarely recorded with the exception of Beirut.[33] Fragments of Colchean amphorae are known from Ras Ibn Hani.[34] The rarity of the Colchean amphorae in the eastern Mediterranean is quite possibly a result of two factors. First, although Colchean amphorae have been identified since the time of Zeest's work during the 1950's and 1960's, these vessels have remained a rather obscure and rarely studied group until recently.[35] This may have the result of underreporting, especially in older excavations. Second, if the trend in Beirut is consist with that of other coastal eastern Mediterranean sites, Colchean amphorae may not have been imported in significant quantities. At Beirut, Colchean amphorae are relatively scarce compared to other Black Sea vessel types (e.g. Sinopean amphorae) and are often represented by non-diagnostic body sherds. This fact, in conjunction with the only recent recognition of two distinct fabric types, may complicate identification of such vessels during the analysis of excavated material.

13.3.6 Epigraphic information

The lack of epigraphic information on Colchean vessels offers no insight as to possible content. No *dipinti* or *graffiti* have been observed on Colchean vessels. Stamps are known

[31] Kassab Tezgör et al. 2007, 198.
[32] Kassab Tezgör et al. 2007, 199.
[33] Kassab Tezgör et al. 2001, 114.
[34] Kassab Tezgör et al. 2001, 112.
[35] e.g. Vnukov 2010a, 2011.

from Hellenistic examples, most probably indicating ownership, but, like the trend observed in Sinopean amphorae, terminate after the Hellenistic period.[36] Finally, no examples of Colchean amphorae are known from any of the published documentation on shipwrecks either in the Black Sea or the eastern Mediterranean.

13.3.7 Content

As described in Section 13.3.6, no epigraphic evidence is known for the content of Colchean amphorae. Some examples of Colchean amphorae have been observed to have a pitch lining both during the Hellinistic and Roman periods. This has formed the basis of the argument that Colchean amphorae were used to transport wine. It has also been argued that the vessels were used to transport wine as the region is too cold to support oleoculture.[37]

13.4 Analysis of Samples

13.5 Samples

Twelve ceramic samples from distinct Colchean amphorae were sampled from the storerooms of the American University of Beirut. The ceramic samples were prepared and analyzed at the Research Laboratory for Archaeology and the History of Art, University Oxford using gas chromatography/mass spectrometry. The samples were characterized for both lipid constituents and organic compounds associated with wine using the protocols described in Chapter 5. The material had previously been studied by Paul Reynolds (University of Barcelona) who compiled a database of the ceramic and contextual data. Samples were selected from a variety of contexts dating to the 5th and 6th c. AD (Table 13.1). Photographs of the samples are found in Appendix A.

[36] Tsetskhladze and Vnukov 1992, 372f.

[37] Klenina 2015, 84.

Table 13.1: Context and sample data for Colchean analyses, data retrieved from the ceramic database developed by Paul Reynolds.

Area	*Context*	*Sherd Number*	*Date of Context (AD)*	*Nature of Context*	*Position of Sample*	*Visible Residue*
006	10013	2	late 5th c.?	floor construction	neck	no
006	11139	31	mid 6th c.?	levelling	mid wall	no
006	11139	x1	mid 6th c.?	levelling	mid wall	no
006	13059	x1	5th c.?	levelling	shoulder	no
006	3606	3	late 4th c. and later	levelling?	shoulder	no
006	5119	x1	mid 4th c.+?	fill?	neck	no
006	5503	302	late 6th c.	pit fill	base	no
006	9023	19	mid 5th c.	pit fill	base	yes
006	9023	x1	mid 5th c.	pit fill	lower wall	no
006	9029	4	mid 5th c.+	fill?	neck	no
006	9999	x3	5th c.?	fill?	shoulder	no
006	9999	x5	5th c.?	fill?	shoulder	no

13.5.1 Results of Analyses

13.5.1.1 Sample from BEY006.10013.2

Context 10013 represents a floor construction level, dated approximately to the late 5th c. AD. The vessel is represented by its neck. Lipid analysis identified a wide variety of fatty acids as well as resin acids and sterols (Fig. 13.4). $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, $C_{20:1}$, $C_{22:0}$, $C_{22:1}$, $C_{24:0}$ and $C_{26:0}$ fatty acids were identified. The sterols cholesterol, cholesta-3,5-dien-7-one and ergosta-4,6,22-trien-3β-ol were identified. Additionally, the resin acids, pimaric acid, dehydroabietic acid and methyl dehydroabietate (in the acidified methonalic extract) were also identified. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

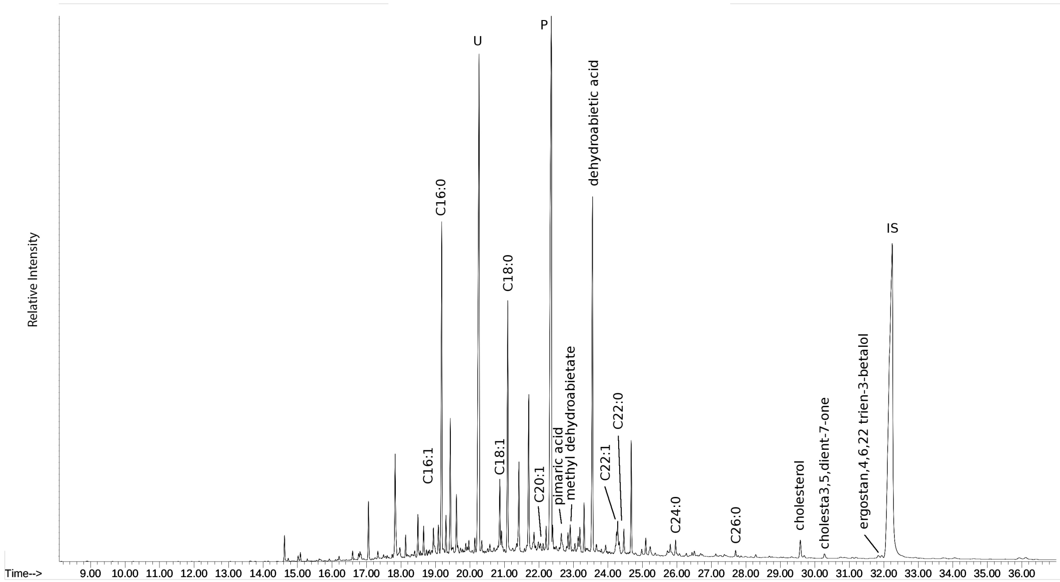

Figure 13.4: Total ion chromatogram of the acidified methanolic extraction of Sample BEY.006.10013.2.

13.5.1.2 Sample from BEY006.11139.31

Context 11139 represents a levelling context, dated to approximately the mid 6th c. AD. The vessel is represented by its mid wall. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as significant quantities of dehydroabietic and 7-oxodehydroabietic acid as well as pimaric and isopimaric acids. Due to the significant levels of resin acids, the sample was reanalyzed using the lipid fractionation technique. No additional fatty acids were identified from the analysis. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

13.5.1.3 Sample from BEY006.11139.x1

Sample BEY006.11139.x1 represents another vessel sample from Context 11139. The vessel is represented by its mid wall. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acids 7-oxodydroabietic and 15-hydroxy-7-oxodehydroabietic acids; retene and significant quantities of dehydroabietic acid were also detected. Due to the significant levels of resin acids, the sample was reanalyzed using the lipid fractionation technique. No additional fatty acids were identified from the analysis. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

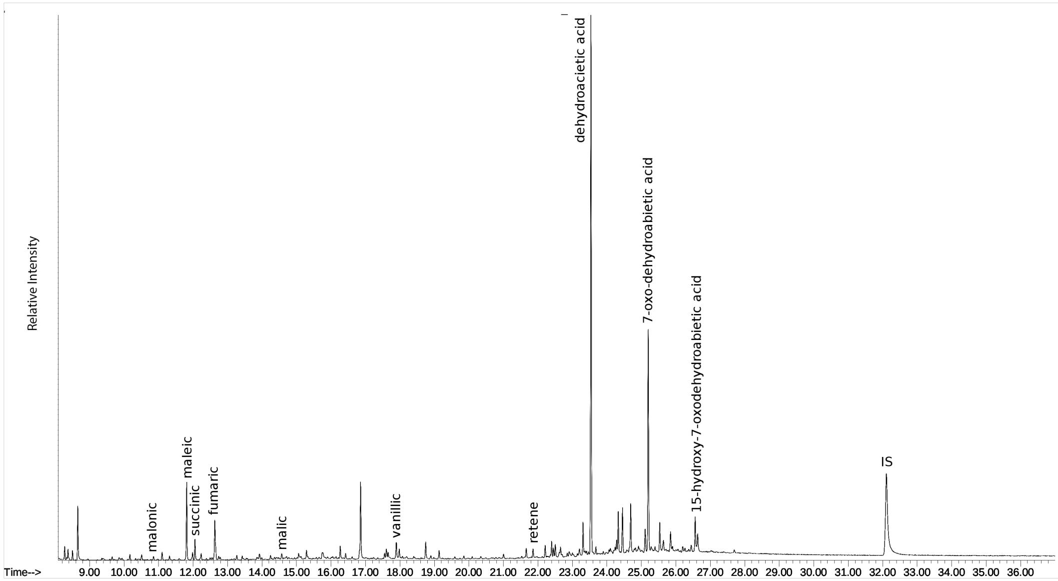

Figure 13.5: Total ion chromatogram of the analysis of organic compounds associated with wine in Sample BEY006.11139.x1, analyzed at a split ratio of 25:1.

13.5.1.4 Sample from BEY006.13059.x1

Context 13059 represents a levelling context, dated to approximately the 5^{th} c. AD. The vessel is represented by its shoulder. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acid 7-oxodydroabietic acid and retene and significant quantities of dehydroabietic acid (methyl dehydroabietate was also detected in the acidified methanolic extraction). The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

13.5.1.5 Sample from BEY006.3606.3

Context 13059 represents a possible levelling context late 4^{th} c. AD and later. The vessel is represented by its shoulder. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acid dehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic and malic acids.

13.5.1.6 Sample from BEY006.5119.x1

Context 5119 represents a context mid 4th c. AD and later, the nature of the context is a probable fill context. Lipid analysis identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acid dehydroabietic acid (Fig. 13.6). The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic and malic acids.

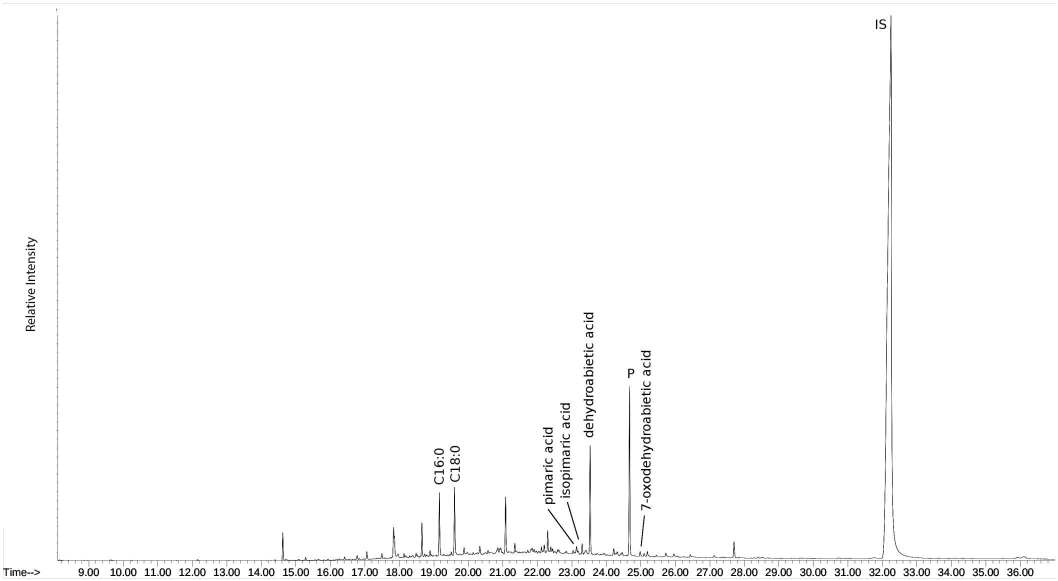

Figure 13.6: Total ion chromatogram of the acidified methanolic extraction of Sample BEY.006.5119.x1.

13.5.1.7 Sample from BEY006.5503.302

Context 5503 represents a large pit fill context, dated to approximately the late 6th c. AD. The vessel is represented by its base. Lipid analysis identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acids dehydroabietic acid, methyl dehydroabietate, pimaric and 7-oxodehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

13.5.1.8 Sample from BEY006.9023.19

Context 5503 represents a pit fill context, dated to approximately the mid 5th c. AD. The vessel is represented by its base. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acids dehydroabietic and 7-oxodehydroabietic acids. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic and malic acids.

13.5.1.9 Sample from BEY006.9023.x1

Sample BEY006.9023.x1 represents another vessel sample from Context 9023. The vessel is represented by its lower wall section. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as significant quantities of dehydroabietic acid; retene and 7-oxodehydroabietic acid were also detected (as well as methyl dehydroabietate mostly probably a result of partial methylation of dehydroabietic acid by the acidified methanolic extraction technique) (Figs. 13.7 and 13.8). Due to the significant levels of resin acids, the sample was reanalyzed using the lipid fractionation technique. No additional fatty acids were identified from the analysis, with the exception of trace amounts of $C_{18:1}$ and significant levels of phthalate contaminates. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic and malic acids (maleic acid could not be positively detected probably due to co-elution with another compound).

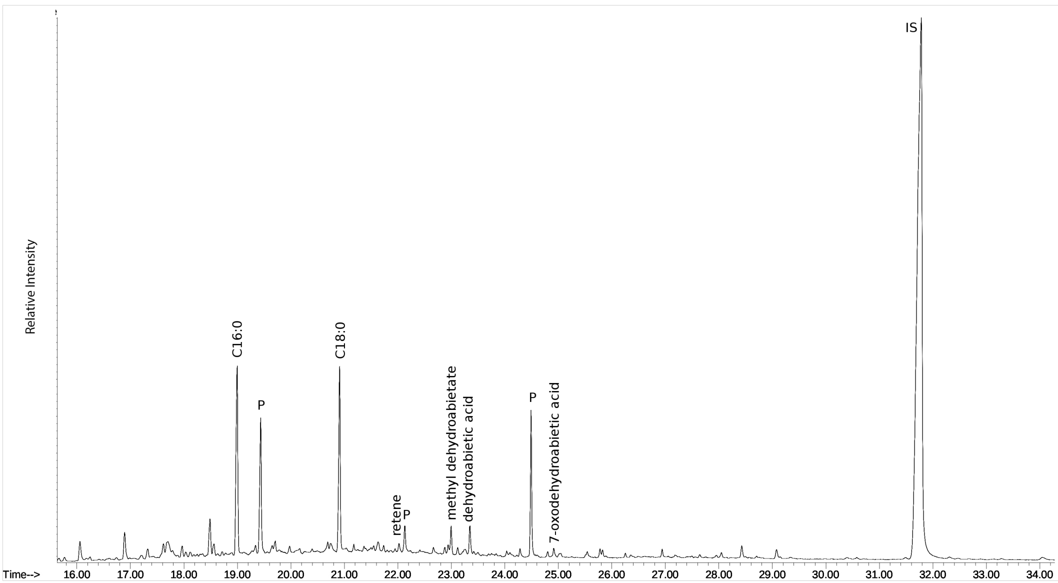

Figure 13.7: Total ion chromatogram of Fraction 1 (chloroform) by lipid and resin fractionation of Sample BEY006.9023.x1.

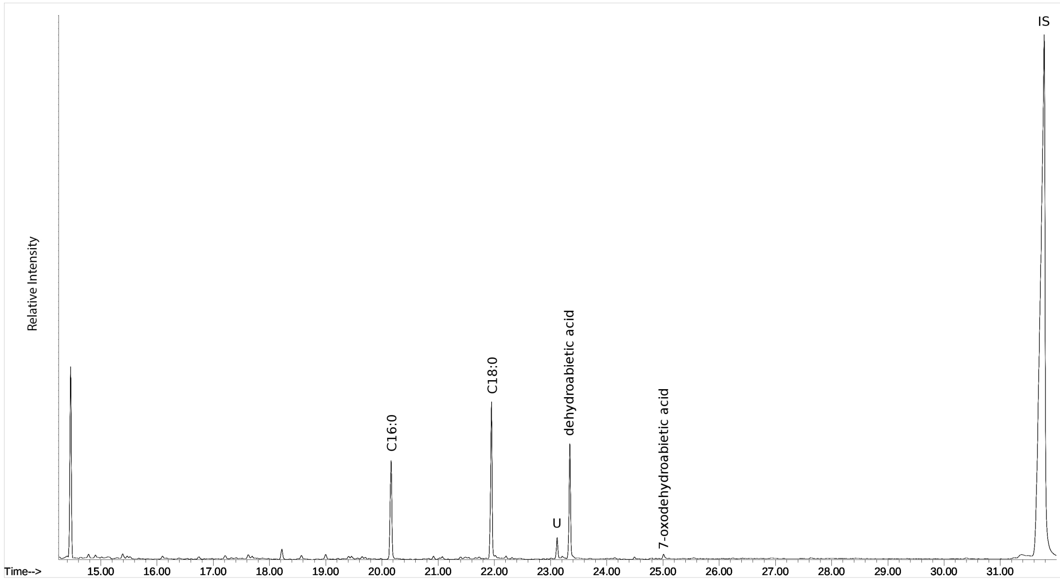

Figure 13.8: Total ion chromatogram of Fraction 2 (acidified diether ether) by lipid and resin fractionation of Sample BEY006.9023.x1.

13.5.1.10 Sample from BEY006.9029.x4

Context 9029 represents a pit fill context, dated to approximately the mid 5th c. AD or possibly later. The vessel is represented by its neck. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as the resin acid 7-oxodydroabietic acid and retene and significant quantities of dehydroabietic acid (methyl dehydroabietate was also detected in the acidified methanolic extraction). The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

13.5.1.11 Sample from BEY006.9999.x4

Context 9999 represents a probable fill context, dated to approximately the mid 5th c. AD or possibly later. The vessel is represented by its shoulder. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as significant quantities of dehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic and malic acids

13.5.1.12 Sample from BEY006.9999.x5

Context 9999 represents a probable fill context, dated to approximately the mid 5th c. AD or possibly later. The vessel is represented by its shoulder. Lipid analyses identified the fatty acids $C_{16:0}$ and $C_{18:0}$ as well as significant quantities of dehydroabietic acid. The analysis of organic compounds associated with wine identified the presence of malonic, fumaric, succinic, maleic, malic and vanillic acids.

Table 13.2: Resin/pitch biomarkers detected in Colchean amphora samples.

Sherd Number	pimaric acid	isopimaric acid	retene	methyl DHA	DHA	7-oxoDHA	15 hydroxy 7oxoDHA
006.10013.2	x				x		
006.11139.31	x	x			x	x	
006.11139.x1			x		x	x	
006.13059.x1			x		x	x	
006.3606.3					x		
006.5119.x1					x		
006.5503.302	x				x	x	
006.9023.19					x	x	
006.9023.x1					x		
006.9029.4	x	x			x		
006.9999.x3					x		
006.9999.x5					x		

13.5.2 Analysis of Results

One of the distinguishing characteristics of the sample analyses of Colchean amphorae is the significant amount of resin/pitch observed in many of the samples. While the reason is not immediately apparent for such large amounts of pitch in some samples, it may be due to the macroscopically porous nature of the ceramic fabric. Resin/pitch biomarkers were uniformly observed in the vessels–in all vessels dehydroabietic acid was detected. Additionally, 7-oxodehydroabietic acid was detected in six of the 12 samples.[38] Four samples (BEY006.10013.2, BEY006.11139.31, BEY006.5503.302 and BEY006.9029.4) also demonstrated undegraded resin acids (pimaric acid as well as isopimaric acid in two samples). Additionally, two of the previous samples were determined to contain retene (BEY006.5251.x2 and BEY006.10543.1). This presents evidence that the analyzed Colchean vessels were lined with resin/pitch, most probably to reduce porosity as is consistent with previous archaeological information and classical sources concerning amphora lining practices.

Lipid analyses indicated only one sample that contained potentially diagnostic fatty acids (BEY006.10632.2) with one demonstrating trace levels of $C_{18:1}$ (BEY006.9023.x1). In Sample BEY006.10632.2, the fatty acids $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, $C_{20:1}$, $C_{22:0}$, $C_{22:1}$, $C_{24:0}$ and $C_{26:0}$ fatty acids were identified. While most of the fatty acids identified could be attributed to multiple sources, and some of which are not entirely diagnostic as to origin (i.e. $C_{16:1}$ and $C_{20:1}$), $C_{22:1}$ was identified which has been considered to be a relevant biomarker for marine organisms. The sterols cholesterol and ergosta-4,6,22-trien-3β-ol were identified as well as the cholesterol degradation product, cholesta3,5-dien-7-one. Cholesterol is directly associated with faunal organisms both terrestrial and marine. While ergostanol is typically recognized as a plant sterol, it is also present in at least some marine faunal species. The combination of evidence appears to indicate that this particular vessel was used to contain a marine product.

[38] See Table 13.2.

Table 13.3: Results of analyses for organic compounds associated with wine

Sherd Number	position	malonic acid	fumaric acid	succinic acid	maleic	malic acid	vanillin	tartaric acid	vanillic acid	hydrocinnamic acid	syringic acid
006.10013.2	neck	x	x	x	x	x			x		
006.11139.31	mid wall	x	x	x	x	x			x		
006.11139.x1	mid wall	x	x	x	x	x			x		
006.13059.x1	shoulder	x	x	x	x	x			x		
006.3606.3	shoulder	x	x	x	x	x					
006.5119.x1	neck	x	x	x	x	x					
006.5503.302	base	x	x	x	x	x			x		
006.9023.19	base	x	x	x	x	x			x		x
006.9023.x1	lower wall	x	x	x		x			x		
006.9029.4	neck	x	x	x	x	x			x		
006.9999.x3	shoulder	x	x	x		x			x		
006.9999.x4	shoulder	x	x	x	x	x			x		

Trace levels of $C_{18:1}$ were detected in BEY006.9023.x1. The sample also demonstrated significant levels of phthalate contamination. The sample was re-drilled and analysed to ascertain if the compounds were a result of intra-laboratory contamination; however, re-analysis confirmed the origin results. It is possible that the trace levels of $C_{18:1}$ may be the result of plastic contaminate as has been previously observed by Nicolas Garnier (*pers. comm.*).

Multiple organic compounds associated with wine were identified in all samples (Table 13.3). Tartaric acid, however, was not detected in any of the samples. On account of the lack of tartaric acid identification in the samples, a definitive conclusion for the use of this vessel form for the transport of wine can not be made. However, the prevalence of organic compounds associated with wine suggests that wine may have been the prime use content. Interestingly, the identification of vanillic acid was strongly associated with the analysed samples (being present in all but two–BEY006.3606.3 and BEY006.5119.x1). Vanillic acid, in addition to having been associated with grape products has also been identified as a constituent of pine tar as well as other wood products.[39] As noted above, it is possible that the trace levels of $C_{18:1}$ may be the result of plastic contamination as has been previously observed by Nicolas Garnier (*pers. comm.*).

[39]Pecci et al. 2013; Simoneit et al. 2000, respectively.

CHAPTER 14

CONCLUSION

The analysis of six types of amphorae from the Black Sea region (or believed to have originated there in the case of Kapitän 2 vessels–the provenance research of which is currently ongoing[1]) has presented insight into the use and re-use of amphorae during late antiquity with respect to Beirut.

Previously developed techniques (i.e. total lipid extract (TLE)), saponified extraction using sodium hydroxide, extraction by acidified methanol and the extraction of diacids using the technique developed by Pecci et al. (2013) for the analysis of compounds associated with wine have proved, consistent with previously published literature, to be efficient methods for the extraction of lipids and diacids, allowing insight into the use of these vessel types. Two additional techniques have also been developed during the course of this study. One serves to assist in the disambiguation of resin and fatty acids; the second assists in the discrimination of vessel use by examination of $C_{18:1}$ positional isomers. Unfortunately, the level of preservation of $C_{18:1}$ fatty acids in samples of interest for the second technique proved too low to provide definitive data.

The analysis of the amphora types in this study did, however, result in useful information. Several of the amphora types did result in consistent data with respect to vessel use. Kapitän 2 samples produced consistent results indicating the primary use as a wine transport vessel. Similarly, in the latest stage of Sinopean amphorae, the D Snp ('Argile Claire'), most samples demonstrated organic compounds consistent with wine. Myrmekion amphorae were also generally consistent in lipid analyses. Although significantly degraded, the relevant fatty acid and sterol biomarkers are indicative of, and consistent with previous archaeological information, of having been used to transport a faunal commodity, possibly that of a *salsamentum*.

[1]Paul Reynolds *pers. comm.*

Although some classes of vessels provided definitive results, some other types produced less conclusive data. Low preservation, especially of lipids, has been previously documented from the Mediterranean and Middle Eastern regions.[2] The earliest Sinopean vessel type analyzed, the B Snp III ('Sinopean Yellow') amphora, provided consistent evidence of a lipidic content although the level of preservation was very low compared to other ceramics analyzed from Beirut or to analyzed material from a similar period in Europe.

One of the most noticeable aspects of the amphorae analyzed in this study is the relatively low levels of extant lipids in the samples. Despite the depletion of lipid content and significant degradation of lipids, especially mono- and polyunsaturated fatty acids, analysis of content has largely been possible.

14.1 Review of analyses

A complication in the analysis of Black Sea amphorae recovered from Beirut is partly due to low preservation of lipids and the extent of degradation of extant lipids. Some amphora types (i.e. B Snp III ('Sinopean Yellow') and Myrmekion ('FAM93') amphorae) and, to a lesser degree C Snp ('Sinopean Red') amphorae, demonstrated generally low levels of extractable lipids. Despite the relatively low level of extractable lipids and complications in analysis of some samples due to high level of phthalate contamination that required re-analysis, information determining the primary use of the studied vessel forms was possible. The results of some vessel forms confirmed what had long been proposed to have been their primary content: the Kapitän 2 was used to transport wine, the Colchean most probably for wine and the Myrmekion an animal-derived commodity (possibly a *salsamentum*). The most interesting results were obtained from the three Sinopean forms. Amphora-borne export commodities from Sinope have long been subject to debate. The three forms, produced subsequently over several centuries, indicate that the primary export commodity changed during the period. While the middle form, the C Snp ('Sinopean Red') amphora, proved the most difficult to analyze, the earlier form is consistent with a content such as a vegetable

[2] Gregg 2009; R. P. Evershed *pers. comm.*

oil, such as olive oil, and the latest with wine. This suggests that agricultural production in Sinope and its environs changed during the period of study. The use of the latest form, the D Snp ('Argile Claire') to transport wine has been previously hypothesized due to its similarity to the LRA 1.[3]

14.2 Reuse

The reuse of amphorae has long been a concern especially in organic residue analysis. Reuse for the same content can not be determined by residue analysis as content is not retained linearly but diffuses throughout the ceramic matrix. While reuse for the same content can not determined, reuse for a different content can often be ascertained. The inability to determine the former is not a significant issue as the primary interest of residue analysis with respect to amphorae is to determine primary content of the various vessel classes as a proxy for determining types and quantities of exported commodities. As such, for example, an amphora that was used to transport wine and then subsequently reused to store wine would not affect relevant results. On the whole, indications of reuse may occur with some degree of frequency in at least some vessel forms while others demonstrated no indication of having been reused for a different content. Neither Kapitän 2 nor B Snp III samples showed any indication of having been reused for a different content.[4]

Other vessel forms did indicate some degree of reuse. Four of the 15 Myrmekion samples contained organic compounds consistent with wine (BEY006.5051.275, BEY006.5251.x4 and BEY006.5251.x5), in which tartaric acid was identified in one (BEY006.5051.554). Two of the 13 C Snp ('Sinopean Red') amphorae contained fatty acids or fatty alcohols that might be associated with a vegetable oil: $C_{18:2}$ in Sample BEY006.11357.7, the fatty alcohol tetracosanol in Sample BEY006.5212.2, and the fatty alcohols docosanol and tetracosanol in Sample BEY006.13017.9. Three additional samples contained trace quantities of

[3] Paul Reynolds *pers. comm.*

[4] One Kapitän 2 sample, BEY006.5051.262 did provide an anomalous lipid profile; however, due to the nature of the n-alkane distribution this is most likely a result of modern contamination.

$C_{18:1}$. Of the 12 Colchean amphorae analyzed, only one demonstrated a lipid profile consistent with another commodity: in Sample BEY006.10632.2, the fatty acids $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$, $C_{20:0}$, $C_{20:1}$, $C_{22:0}$, $C_{22:1}$, $C_{24:0}$ and $C_{26:0}$ fatty acids were identified. D Snp ('Argile Claire') samples, however, indicated a significantly greater incident of possible reuse. Of 21 analyzed samples, seven (BEY006.11081.203, BEY006.11081.204, BEY006.11081.205, BEY006.13017.122, BEY006.13559.4, BEY006.2004.27 and BEY006.2013.11) indicated fatty acids that could be associated with vegetable oils in which the plant sterol β-sitosterol was additionally detected in four.

It is uncertain what factors may be responsible for the significant variation in the frequency of reuse between different forms. None of the samples analyzed was found *in situ*; contexts were generally fills of some type (levelling, cistern fill, etc.). As such, any evidence of the nature of their use (or reuse) prior to final deposition is unknown. In general, from the available data, reuse does not appear to be frequent with the exception of D Snp ('Argile Claire') vessels. The reason for such a significant potential reuse or irregular use of this particular form (33% of the 21 analyzed samples) is unclear. This vessel form is the latest analyzed in this study. It is possible that economic decline in the eastern Roman empire, especially during the 6^{th} c. AD, may have promoted reuse as a container rather than a building material. It is also possible that the relatively small size of the vessel made it more amenable to reuse compared to large capacity vessels (e.g. B Snp III ('Sinopean Yellow')) amphorae or forms that were perhaps less convenient due to their unusual shape (e.g. the Kapitän 2 amphora).

14.3 Vessel shape and content

It has been hypothesized that vessel shape may be used to determine the content of an amphora form.[5] There is certainly a practical aspect to part of this hypothesis. For example, in amphorae used to transport a *salsamentum* that contained large pieces of fish it would be pragmatic to have a vessel with a large diameter neck to aid in removal of content. The

[5]especially Andrei Opait.

degree to which this hypothesis can be extended to amphora forms used to transport other commodities has remained uncertain, in part due to the fact that large scale analysis of different amphora forms remains rare. In the current study, several different general vessel forms were analyzed. Large volume vessels with a rounded body and relatively small diameter neck/rim (i.e. the B Snp II ('Sinope Yellow') and Myrmekion forms), vessels with an elongated body of relatively small capacity (Kapitän 2, C Snp ('Sinope Red') and Colchean forms), as well as a small capacity round form (the D Snp ('Argile Claire') form). The preliminary observations of association between vessel content and shape is not clearly defined. The two large format amphora forms transported different commodities–possibly a vegetable oil and a marine product. The other vessel forms, smaller in capacity but varying in shape from generally conical to a rounded body were used to transport wine. The sample size of the number of different forms analyzed in this study is too small to provide any definitive results. It is also possible that vessel form was also affected by general trends in amphora manufacturing ('amphora style') during a given period. The vessels analyzed in this study span three centuries, during which common trends in vessel shape may have changed. For example, the Beirut local amphora was manufactured continuously from the 2nd c. BC until the 6th c. AD. During this period, the form continuously evolved, starting from a large, round-bodied vessel of approximately 30 L to a small flat-bottomed conical amphora in the mid-6th c. AD.[6] Starting in the 4th c. AD in the eastern Mediterranean and continuing for several centuries, conical 'carrot' amphora forms became commonplace (e.g. Beirut 8, LRA 3, LRA 7, C Snp 'Sinopean Red'). It is possible that the shape of any given amphora form may be influenced as much by the 'style' of the period during which it was manufactured as that of its content.

[6] Reynolds 2008.

14.4 Additional observations

14.4.1 Phthlates

Several trends were observed in the analyzed samples, which primarily concerned contamination by phthalates. The ceramic samples studied had been stored in plastic bags for approximately 20 years. Additionally, they were stored in unairconditioned buildings in Beirut that are subject to hot weather during the summer months. Hot storage conditions may have assisted in leaching of phthalates from the bags themselves. Regardless, phthalate contamination is to be expected in ceramics stored in plastics. The level of contamination varied significantly in the samples. Most samples did not demonstrate levels of contamination that complicated residue analysis. The level of phthalate contamination in some samples, however, was very significant. The reason for this variation is not known although it could be due to a factor as simple as the proximity of the ceramics to the plastic bags.

14.4.2 Succinic acid

Correlation between some analytes and levels of phthalate contamination were observed. Succinic acid was ubiquitous in nearly all samples. While succinic acid has been identified as a constituent of grape products, it is also known to be associated with plasticizers.[7] The direct correlation between high levels of succinic acid in samples that also demonstrated high levels of phthalate contamination supports the hypothesis that the genesis of succinic acid may be not exclusively from vessel use but post-depositional contamination. Similarly, trace levels of $C_{18:1}$ was also observed in some samples that did not otherwise contain lipids indicative of a lipidic content (apart from diterpenoids). It has been suggested to the author that this sometimes occurs as a contaminant from plastics.[8] The general correlation of the presence of trace quantities of $C_{18:1}$in samples that also contained high levels of phthalates appears to corroborate this.

[7]Middleditch 1989.

[8]Nicolas Garnier *pers. comm.*

14.4.3 *Syringic acid*

Syringic acid has been considered to be another biomarker for wine, specifically red wine being derived from of a pigment anthyocyanin. Some previous studies have demonstrated a strong correlation between the presence of tartaric and syringic acids, supporting the premise that it is a useful biomarker for grape products.[9] However, evidence from this study as well as previous research into North African amphorae has indicated that there is often a lack of such correlation.[10] The presence of syringic acid in samples otherwise not demonstrating organic compounds associated with wine indicates another possible source for the analyte. Interestingly, vanillic acid is strongly associated with specific amphora forms analyzed in this study. Both syringic and vanillic acids are known to occur in small quantities in wood. It is therefore possible that the source of these acids comes not from the content of the vessel itself but possibly that of the stopper used to close the vessel (i.e. a cork stopper).[11] This would account for the strong association of vanillic acid with specific forms as well as the discrepancy between the presence of syringic acid with other strongly associated grape product compounds (i.e. tartaric acid). This evidence indicates that the use of singular organic compounds (such as syringic acid for the detection of wine) can provide false positives, instead a consensus of several biomarkers is crucial in proper determination of content.

14.5 New Methods of Analysis

14.5.1 *$C_{18:1}$ positional isomers*

Despite limitations in the analysis of some samples due to low extant lipids, other aspects of the study have indicated new directions for amphora analysis. The study of $C_{18:1}$ positional isomers in fish has revealed a novel positional isomer distribution that indicates a new biomarker for the determination of the origin of lipids in ceramics.

[9] e.g. Pecci et al. 2013; Woodworth 2011.

[10] Woodworth et al. 2015.

[11] Alessandra Pecci and Nicolas Garnier *pers. comm.*

14.5.2 *Resin and fatty acid fractionation*

Additionally, a new technique was developed to separate fatty acids from resin acids in samples with high resin acid content. This approach marries the high-throughput single-step extraction and methylation developed by Correa-Ascencio and Evershed (2014) with sample fractionation. This combined technique allows more rapid assay of potential lipids in samples. In samples that have significant quantities of resin acids that interfere with fatty acid analysis, the same extracted sample can then be fractioned and analyzed with re-drilling and extracting another sample.

14.6 Future work

Future work with respect to some aspects of absorbed residue analysis of amphorae has been approached before.[12] Systematic investigations of 'significant' quantities are necessary in order to give a reasonable identification of primary vessel content. The utilization of readily available (at least within the analytical chemistry range) instrumentation using comparable protocols would assist in that the resulting data may be compared meaningfully between different examining bodies. The review of the relationship between a vessel's content and the application or not of a resin/pitch lining in future absorbed residue studies may also prove insightful.

More specifically, the present work, the author believes, does reveal some definitive areas for improvement. The first issue of archaeological and post-excavation contamination is most often by plasticizers. It is frequently unavoidable in the practical aspect of excavation in the field and unavoidable with respect to previously excavated material.

The degree of preservation of organics in ceramics from different geographical areas is one area of examination. There has begun to appear a trend in the quantity of extractable organics from ceramic vessels of similar types and uses from different periods but also from difference geographical regions. Previously, it has been understood that the use of a vessel

[12]e.g. Pecci and Cau Ontiveros 2010; Garnier 2007a.

has an impact on the potential for the quantity of extractable lipids–vessels that have been used to heat lipid rich liquids are more likely than those that held unheated low lipid liquids to have significant levels of extant extractable lipids. Other potential biomarkers in aqueous solutions less and then finally volatile compounds.

The period of deposition may also play a role, especially in those ceramics deposited for a very significant period of time.[13] The geographical region in which similar types of ceramics presumably containing similar compounds has also become a more recent area of interest. Gregg (2009) has suggested that the retention of undegraded lipids is significantly lower in the Middle East, irrespective of period, than that of other regions. This presents two complications: the extraction of highly degraded lipids, sometimes represented primarily by diacids (e.g. azelaic acid in the case of $C_{18:1}{}^{\Delta 9}$) or simply low recoverable levels of all lipids (including those non-diagnostic for GC/MS analysis with respect to vessel use (e.g. $C_{16:0}$ and $C_{18:0}$)).

Recent advances are being made to increase the amount of extractable lipids from ceramic sherds. The use of a microwave accelerated reaction system (MARS) has been employed previously to improve extraction yields from neolithic Middle Eastern ceramic samples from which conventional extraction techniques provided negligible results.[14] Most recently, the use of supercritical fluid extraction (SFE) has been recently tested at the Research Laboratory for Archaeology and the History of Art (RLAHA) for the extraction of absorbed lipids in ceramics as well as other organic compounds. SFE has been utilized in the commercial field, principally in the food industry for a variety of purposes, including decaffeination of coffee, the extraction of essential oils, lipids, waxes as well as a wide variety of plant extracts.[15] While SFE has been widely utilized in the food industry, it has yet to be employed in archaeological science for the purpose of organic residue extraction and analysis. To date, the only application of SFE to archaeological materials has been for the cleanup of lipids

[13] Gregg 2009.

[14] Gregg et al. 2009.

[15] Dean et al. 2000; Sedlaková et al. 2003; Sahena et al. 2009; Athukorala and Mazza 2010, respectively. For a review, see de Melo et al. 2014.

from ^{14}C samples.[16] Preliminary research at RLAHA has indicated the SFE has the potential to increase lipid extraction yields from archaeological ceramic samples by 6-9 times.[17] Further extraction methodology development and application of this technique to samples demonstrating low lipid yields from conventional extraction techniques, such as some samples from this current study, might provide a better lipid profile and thus more conclusive data for the determination of content for these vessel forms.

Other spectrometric techniques for the analysis of vessel content may also provide additional methods of analysis. Pyrolysis-gas chromatography-mass spectrometry (Py/GC/MS) has been previously applied to archaeological macro-remains.[18] There is potential for this analytical technique to be applied to the analysis of absorbed residues.[19] The potential for the application of off-line thermochemlysis, allowing a significantly greater sample quantity for analysis over traditional Py/GC/MS is another possibility in accessing compounds that are poorly solvent extractable.[20] Finally, the application of compound specific isotope analysis by gas chromatography-combustion-mass spectrometry (GC/C/IRMS) has not been examined for its applicability in determining amphora content. It would be potentially worthwhile to examine the effect of the resin/pitch lining, observed in many amphora forms, with the isotopic ratio analysis of vessel content.

In addition to refinements in applied methodologies with respect to GC/MS and HPLC/MS in the extraction and analysis of abosrbed residues, the development of new techniques of analysis of organic compounds observed in archaeological ceramics offer potential new insights into amphora content analysis. The analysis of aDNA has begun to be applied with respect to amphorae.[21] Proteonomics are also being examined for the applicability to the analysis of amphora content.[22] The application of these techniques in the analysis of am-

[16] King et al. 2012.

[17] van Ham-Meert 2016.

[18] Garnier et al. 2003.

[19] e.g. Regert et al. 2001; Kaal et al. 2014.

[20] McKinney et al. 1995.

[21] Milanesi et al. 2011; Foley et al. 2012.

[22] Dallongeville et al. 2011.

phorae may offer further insight into the content of amphorae and, furthermore, to a more nuanced understanding of the nature of inter-regional trade during antiquity.

APPENDIX A

PHOTOGRAPHS OF SAMPLES ANALYZED

Photographs were taken before sample selection in most cases. In some instances, the vessel was fragmentary and the area of the sample was photographed instead. For a few samples, there was an error in the memory disc of the camera. For these samples, ‘no image available’ is displayed.

A.1 Kapitän 2 samples

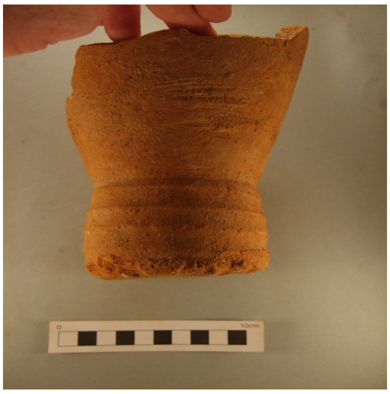

Figure A.1: BEY006.11603.171

Figure A.2: BEY006.10625.90

No image available

Figure A.3: BEY006.10625.92

Figure A.4: BEY006.10625.105

Figure A.5: BEY006.10625.x3 (post sample photo)

Figure A.7: BEY006.10632.103

Figure A.6: BEY006.10629.104

Figure A.8: BEY006.10632.88

Figure A.9: BEY006.10632.89

Figure A.11: BEY006.5051.265

Figure A.10: BEY006.5051.262

Figure A.12: BEY006.5051.264

Figure A.13: BEY006.006.5051.267

Figure A.15: BEY045.1510.24

Figure A.14: BEY045.1242.97

Figure A.16: BEY006.5051.264

A.2 B Snp III ('Sinope Yellow') samples

Figure A.17: BEY0064104.x1

Figure A.19: BEY006.5051.916

Figure A.18: BEY006.5051.915

Figure A.20: BEY006.5051.917

Figure A.21: BEY006.006.5051.267

Figure A.22: BEY006.5051.X1

Figure A.23: BEY006.7313.7

Figure A.24: BEY006.8651.1

Figure A.25: BEY045.1242.11

Figure A.27: BEY045.1242.562

Figure A.26: BEY045.1242.560

Figure A.28: BEY045.1503.3

Figure A.29: BEY045.1609.1

Figure A.31: BEY045.2074.21 (post sample photo)

Figure A.30: BEY045.1660.3

A.3 C Snp ('Sinope Red') samples

Figure A.32: BEY006.10625.x1 (post sample photo)

No image available

Figure A.33: BEY10632.x5

No image available

Figure A.34: BEY006.11357.8

No image available

Figure A.35: BEY006.13017.597

No image available

Figure A.36: BEY006.13017.7

No image available

Figure A.37: BEY006.11357.10

No image available

Figure A.38: BEY006.13017.8

No image available

Figure A.39: BEY006.13357.9

No image available

Figure A.40: BEY006.13017.15

Figure A.41: BEY006.11357.16

Figure A.42: BEY006.5212.2

Figure A.43: BEY006.5503.303

Figure A.44: BEY006.5503.320 (post sample photo)

A.4 Sinope D Snp ('Argile Claire') samples

Figure A.45: BEY006.11081.203

Figure A.47: BEY006.13017.8

Figure A.46: BEY006.11081.204 (post sample photo)

Figure A.48: BEY006.13357.9

Figure A.49: BEY006.11081.208

Figure A.51: BEY006.11081.x5

Figure A.50: BEY006.11081.X1

Figure A.52: BEY006.13017.34

Figure A.53: BEY006.13017.122

Figure A.54: BEY006.13017.181

Figure A.55: BEY006.13559.4

No image available

Figure A.56: BEY006.13559.5

Figure A.57: BEY006.2004.27

Figure A.59: BEY006.3077.169

Figure A.58: BEY006.2013.11

Figure A.60: BEY006.5503.x2 (post sample photo)

Figure A.61: BEY8754.2

Figure A.62: BEY045.1967.8

A.5 Myrmekion samples

Figure A.63: BEY006.4601.3

Figure A.64: BEY006.5051.554 (post sample photo)

Figure A.65: BEY006.5051.275

Figure A.66: BEY006.5051.555

Figure A.67: BEY006.5051.559

Figure A.69: BEY006.5251.x3 (post sample photo)

Figure A.68: BEY006.5251.x2 (post sample photo)

Figure A.70: BEY006.5251.x5 (post sample photo)

Figure A.71: BEY006.5251.x5

Figure A.73: BEY006.10543.1

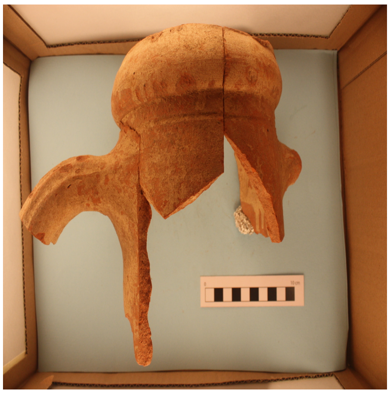

Figure A.72: BEY006.7313.6 (post sample photo)

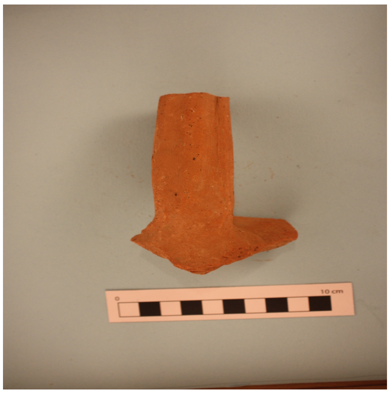

Figure A.74: BEY006.13039.x2

Figure A.75: BEY178.204.218.282 (post sample photo)

Figure A.76: BEY045.940.16

A.6 Colchean samples

Figure A.77: BEY006.10013.2

Figure A.79: BEY006.11139.x1

Figure A.78: BEY11139.31

Figure A.80: BEY006.13059.x1

Figure A.81: BEY006.3606.3

Figure A.82: BEY5119.x1 (post sample photo)

Figure A.83: BEY006.5503.302

Figure A.84: BEY006.9023.19

Figure A.85: BEY006.9023.x1

Figure A.87: BEY006.9999.x3 (post sample photo)

Figure A.86: BEY006.9029.4 (post sample photo)

Figure A.88: BEY006.9999.x4

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