THE CONTEXT OF ORGANIC RESIDUES IN ARCHAEOLOGICAL VESSELS OF CERAMIC AND BRONZE

PART 1: TEXT

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ABSTRACT

Since the 1970s, the study of molecular organics preserved in archaeological ceramics, commonly referred to as organic residue analysis, has been used to infer vessel use and study dietary, economic, and ritual activities in the past. The purpose of this project is to analyse organic residues from a variety of ancient vessels and attempt to understand further the relationship between molecular organic preservation and vessel characteristics. It has been previously assumed that the absorption of these organics in the ceramic matrix is predominantly responsible for their preservation. The clarification of this or other preservative mechanisms and the further understanding of the relationships of vessels with their contents has a direct impact on the interpretation of organic residues and vessel use. The first section addresses the preservation of molecular organics in pottery vessels from Tel Kabri, Israel; Tel Megiddo, Israel; and Lefkandi, Greece. The one hundred and thirty-three samples from these three sites represent vessels used in domestic, burial, ritual, and elite contexts from the Early Bronze Age through the Iron Age Eastern Mediterranean.

The focus of the study is the quantification of residue yields and identification of potential links with vessel properties and characteristics of the ceramic samples. Sequential extractions using two methods, conventional chloroform/methanol solvent extraction and direct FAME extraction/derivatisation, were applied to the sherds to test the absorption and adsorption of organics into ceramic materials. The majority of samples were tested non-destructively, enabling the comparison of residue yields to certain vessel properties and characteristics displayed in the same sherds. Where available, data concerning vessel form, sampling location on the vessel profile, thickness measurements were recorded, and XRF measurements were taken, with this in mind.

The second section investigates the question of whether bronze and copper alloy vessels have the capability to preserve molecular organics within their corrosion products. Twenty-two samples of corrosion and associated material from five Early Roman bronze vessels found in cremation burials during the A2 Pepperhill to Cobham project in County Kent, United Kingdom were studied for organic material. These samples provide some of the first evidence that the residues of original content are preserved in copper alloy vessels either through entrapment in or reactions with copper corrosion.

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THE CONTEXT OF ORGANIC RESIDUES IN ARCHAEOLOGICAL VESSELS OF CERAMIC AND BRONZE

1. INTRODUCTION

The study of molecular amorphous organic material, or organic residue analysis, has been used to great effect over the last 40 years to interpret vessel use, cooking practices, feasting, trade, and ritual activities in the past.[1] Since the 1970s, both the visible remains of original contents, linings, or by-products of use,[2] as well as those not visible to the naked-eye and absorbed into the ceramic fabric,[3] have been studied to make 'residue analysis' a fairly routine procedure in archaeology. Included in this class of archaeological evidence are the remnants of fats, oils, resins, pitches, tars, and other animal and plant materials, amongst others. By nature, these substances lack definable morphological features that are common in other biological materials such as bone, seeds, pollen, and wood which survive in the archaeological record.[4] These residual substances have been tied back to sources of illumination, foods, beverages, trade items, cosmetics, perfumes, medical substances, and many other activities of many societies and cultures. While the degradation pathways of the major classes of organic materials represented in these residues are generally well-known, the exact mechanisms behind the existence of these molecular organics is not nearly as well understood or investigated. It has generally been assumed that the organic contents of unglazed pottery seep into or are absorbed by the porous structure of ceramics and are thus protected from degradative forces such as microbial degradation, chemical alteration, and leaching.[5] While this assumption has formed the basis of the selection of ceramic materials for analysis, the assumption precludes the possibility of similar organic materials being

[1] A more in-depth review of the use of organic residue analysis in archaeology is provided in Chapter 4.
[2] Evans and Biek, 1977.
[3] Condamin, *et al.* 1976; Rottländer and Schlichtherle, 1979.
[4] Heron and Evershed, 1993.
[5] e.g. The identification of a ceramic as a "protected niche" (Weiner 2010:Ch 9). See also Evershed, 1993 and 2008a; Stern, *et al.* 2000.

preserved in a wider range of ceramic and non-ceramic vessels (e.g. fine wares and metals). In this project, ceramic materials from three sites in the Eastern Mediterranean (Tel Kabri, Israel; Tel Megiddo, Israel; and Lefkandi, Greece) were evaluated for organic residues and some of the ceramic properties were measured and compared to quantitative residue results. The ceramics were excavated in a variety of contexts (domestic, ritual, palatial, and burial) dating to the Early Bronze Age through the Iron Age and represent a variety of fabrics. It is hypothesized that the quantitative preservation of organics is not solely due to the porosity of a sherd but also to the chemical composition of the ceramic. To investigate further the possibility of organic preservation in other vessel "micro-contexts"[6], several samples of bronze corrosion from Early Roman bronze vessels from Britain were also evaluated for organic content.

In order to interpret molecular organics recovered from archaeological vessels to their fullest extent, an understanding of the immediate "micro-context", i.e. the vessel, is ideally combined with the "macro-context", i.e. the site or culture in which the vessel existed and functioned, is needed. By way of introduction in the following chapter, a theoretical framework for the study of archaeological materials and vessels is laid out and some of the problems in the study of archaeological vessels and their contents are discussed. Following this framework, the aims and objectives of this study regarding residue analysis methods and preservation are laid out. This serves as the foundation for the analysis of invisible amorphous organic residues in ceramic and bronze vessels found in archaeological contexts described in this thesis.

[6] Here *micro-context* is taken to mean the immediate context of a residue encapsulated, absorbed, or adsorbed within the vessel matrix. As discussed later in Chapter 2, a residue can be viewed and interpreted in several contexts of varying scales from micro-, the physical space in which it is preserved, to macro-, the site and culture in which it was formed.

1a. Materiality and Culture

From the tastes of regional foods, the aural markers of language and accent, the aromas characteristic of a particular culture and environment, visual distinctions of architectural styles and manners of dress, and intellectual concepts of social identity, economics, philosophy, and religion, all of the sensory and mental capabilities can be and are used by individuals or groups to distinguish between and identify with one culture or another. In an archaeological context, only portions of these sensory pathways are available in the investigation of societies and cultures from the remote past. While occasionally we are fortunate to have access to ethnographic records, historiographies, or linguistic data to inform our perceptions of the past, frequently archaeologists are left with the remnants of material culture only. Despite much of the original culture being lost (for example those without written documents, recorded histories, or deciphered languages), a phenomenal amount of information can be gathered from the archaeological record and used to interpret the customs, ideologies, economics, social and political structures of past societies. One of the distinguishing markers of humanity is the presence of what is termed *culture*.[7] Curiosity and creativity have been identified as some of the most basic characteristics of humanity. Humans fundamentally need to create and have things. This can be seen in our desire not only to manufacture objects, but even in the pastimes of children and adults alike – the instinct to build a sand castle, model clay, or whittle a shape from wood. Creativity is a common human experience and the results are objects that reflect the culture and society in which an individual resides and functions. C. S. Smith even goes so far as to posit that

[7] The notion of *society* can also be seen in non-human groups and herds, political hierarchy certainly exists in the demarcation of alpha-individuals. The notion of *culture* and *society* being characteristically human is problematic and one can easily find exceptions to the rule. In actuality, the first use of the term *culture* was used in reference to non-primates and the use of tools, especially amongst primates, can be referred to as *material culture*. (see Hulme, 2010.) That noted, much of the discussion concerning common notions of *culture* are human prerogatives, possibly due to the structured nature of what we identify as *culture* and *material culture* in archaeology and anthropology.

technological development is driven by aesthetics, as curiosity is driven by aesthetics and the pleasing nature of order and structure.[8]

Material culture has been defined as *the study of material, raw or processed, transformed by human action as expression of culture*.[9] A large section of material culture consists of artefacts, i.e. objects which are made or modified by people. These objects are intrinsically related to people's needs, capabilities, and aspirations as they use objects to define, punctuate, perpetuate, and manipulate their social personae.[10] If archaeology can be very generally defined as the study of past individuals and their societies via their material culture, artefacts are the objects manufactured, used, and discarded by those individuals, and are thus directly reflective of the individual, the society in which they lived, and those individuals or societies with whom they interacted. The major materials that archaeologists find and use to interpret past societies are the architectural record (e.g. stone walls, floors, installations, and post holes), the artefact record (e.g. lithics, pottery, figurines, and jewellery), human remains (e.g. biological parameters, such as race, sex, age, posture, disease, and ethnicity), other biological remains (e.g. animal remains and botanical remnants, including seeds and phytolith), historical sources, and ethnographies.

Materials science in archaeology seeks to study this artefact record and place material objects in the context of their production and use. A materials science approach to the study of archaeological artefacts is based on a core paradigm of material science and engineering: the selection of particular materials and the processing of these materials lead to specific structures that result in a set of properties in the object which, in turn, define the object's performance.[11] According to this paradigm, production, structure, properties, and

[8] C. S. Smith, 1981:112-126, "Matter versus Materials: A Historical View".
[9] Prown, 1996.
[10] Hurcombe, 2007:3.
[11] Kingery, 1996b.

performance are inextricably linked in a feedback system which drives innovation, supply, and demand (Figure 1-1[12]).

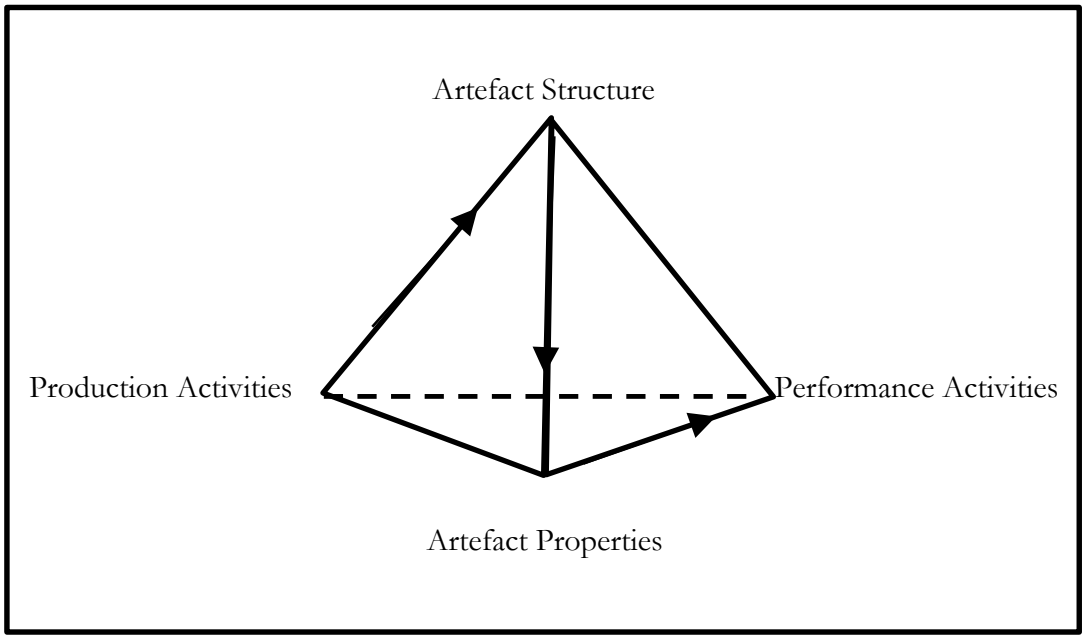

Figure 1-1: A Materials Science Paradigm
The connection between and opportunities for feedback in production, structure, properties and performance.
(After Kingery, 1996b)

The desire for and demand of certain performance traits lead to the creation of new things by the production of new structures and properties, through the selection of materials and/or new manufacturing techniques. The illustration of this system and the relationship between production, structure, properties, and performance, such as the one in Figure 1-1, allows the materials scientist to investigate any aspect of the system and draw conclusions concerning the others for any given material or object. In light of this paradigm, a material culture system can emerge and be discussed, in which object attributes have a role in and inform upon design, creation, distribution, exchange, and use within the culture and society in which it exists and functions. In Figure 1-2,[13] the paradigm of material science studies is

[12] after Kingery, 1996b.
[13] after Kingery, 1996a.

applied to a material culture system, bringing to light not just the technologies and properties of an artefact, but also influencing the cultural perceptions of an object. Such cultural perceptions extend beyond the physicality and mechanics of an artefact to include the context of an object and any cultural function, whether it be as a tool, sign, or symbol. In the context of archaeological inquiry, artefacts become more than a category of "manufactured materials" that would draw the attention of a modern-materials scientist or engineer. For material culture to be meaningful in archaeological and anthropological terms, the materials or objects must be concerned with human activity, organization, and behaviour, causing the artefact to be a signifier for and inform upon the interpretation of past society and culture.[14]

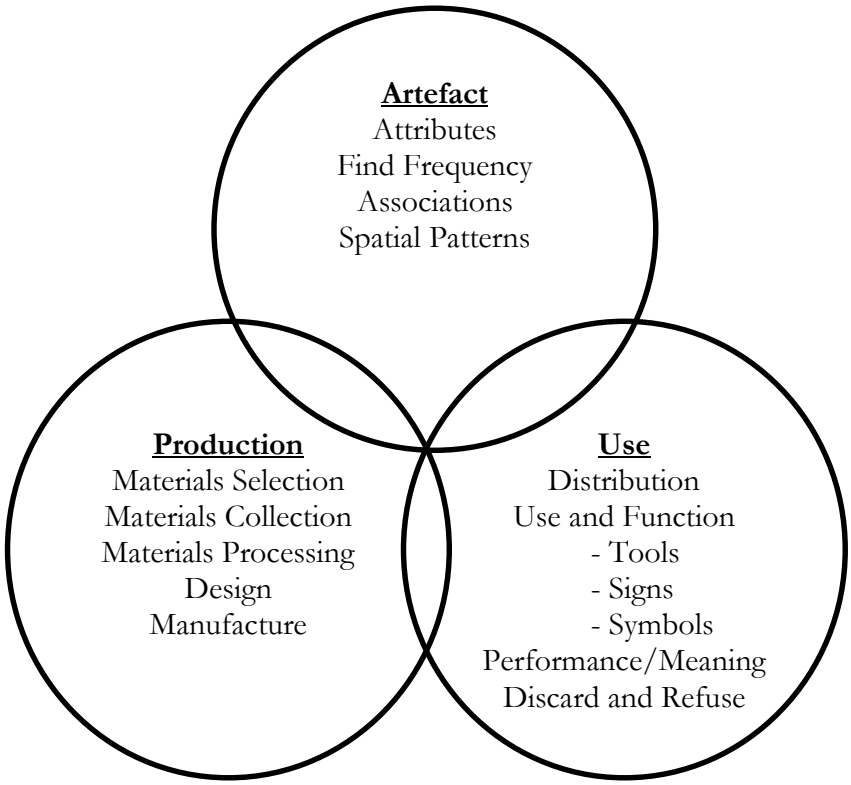

Figure 1-2: A Material Culture System
Artefact structures and properties form part of an interconnected system in which materials science can be applied to cultural contexts. Production, the nature of an artefact, and its use overlap and impact each other.
(After Kingery 1996a)

[14] Kingery, 1996b.

The ways in which an artefact can relate to and be interpreted within the culture(s) which created and consumed it as a whole can be approached in two main ways. In a behavioural framework, as primarily described by Schiffer, an artefact's importance lies in the modes in which it participated in, relates to, and can inform researchers about human behaviour.[15] In other words, an artefact is important solely within its ultimate context and particular function(s) in a given society. A more holistic way in which to approach the study of artefacts is from a materials point of view, as lined out above, to view an artefact as the product of a number of social constructs indicative of a lager system. In this framework, an artefact's importance lies in its own biography and the interactions of the community that created, exchanged, and used it. The biography, or *chaîne opératoire,*[16] and societies are integral parts of a system in which the social structures, economics, aesthetics, learned behaviours, and ideologies associated with an object are equally or more important than the structure and properties of that object. If this latter view is taken, then a narrative surrounding an object and including all aspects of its biography can be constructed and interpretations concerning its place and function within a society can be made on the widest and most informative scale.

This narrative begins with the selection of materials, design, and manufacture, and moves through distribution, use, and discard, through to its present analysis and study. The beginning stages of this biography are what are normally included in a definition and concept of *technology*. The technology of an object includes its material make-up, production, and innovation or discovery. This aspect can be interpreted both physically and socially. For example, the firing of clay into ceramic can be seen as a chemical change in the removal of water and sintering of silicate minerals (chemical and physical interpretation) or as a form of mystic change from the universe or deity or magic (socio-cultural and religious

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[15] Schiffer, 1976.
[16] Leroi-Gourhan, 1964. A term taken to mean the operational chain or stages through which something exists, develops, and functions.

interpretation). These constructs can be that of the craftsmen or lookers-on in attempt to make sense of things that are not always understood.

Manufacturing techniques, discovery, innovation, alteration, and repair are all included in the physical manifestations of an object that fall under the concept of *technology*. This linear progression of the technology of an object along with time, from past to present, can then serve as a basis upon which to layer a utilitarian, spiritual, emotional, creative, and aesthetic narrative which flows contrary to the first. This second layer is that is the material culture of an object. This cultural narrative is one that includes the use of an object by an individual or individuals, whether it be as a tool for utilitarian purpose (i.e. a jug to carry water), a sign (i.e. a form of a vessel that implies wealth or status), or a symbol (i.e. an heirloom or memory of a loved one). In light of this premise, the purposes of objects can be seen not only as utilitarian tools, but also as sociological and ideological signs and symbols.

In the interpretation of archaeological artefacts, the line of deduction by a researcher flows opposite to the physical and cultural processes that constitute the object's biography. Each step can only be fully interpreted in light of the subsequent step and any changes those steps has brought about in the object. The fullest understanding of an object comes with the description of as many of the object's biographical phases as possible and the understanding of the processes which have altered it since its creation. For residues, this involves understanding not only the degradation processes that have affected the residue and its biography, but also the characteristics and biography of its matrix, the vessel.

1b. Vessels

In archaeology throughout the world, pottery analysis is one of the most ubiquitous tools used to study past cultures and their practices. Pottery[17] analysis in its many forms has risen to prominence in archaeology for a number of reasons. First, as fired clay is practically indestructible,[18] pottery sherds are the most common find in archaeological excavations across the globe.[19] The earliest clay use has been documented in the Upper Palaeolithic in the Moravia, Czech Republic, where some 10,000 ceramic pieces, a few of which are associated with clay figurines, have been dated to ca. 26,000 BCE.[20] The first fired pottery vessels worldwide, are first seen in Japan around 17,000 BCE during the Jōmon period, used in a hunter-gather context.[21] This emergence of pottery in Japan is approximately contemporary with that in China and eastern Siberia, while in the Near East, it has been documented in Anatolia to date to 8,500-8,000 BCE.[22] Even if the original clay object (vessel, figure, tablet, etc.) has been broken, damaged, or discarded, there is a high probability that pieces of it will remain in the archaeological record. Second, and equally as important, the study of vessels (a significant proportion of which are ceramic but also include bronze, iron, other metals, woven baskets, etc.) and their life cycles can be used to reconstruct a number of cultural traits and phenomena with varying degrees of success. Many of the theoretical constructs surrounding pottery analysis and the study of ceramic vessels also can

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[17] It is acknowledged that a differentiation can be drawn between the terms *pottery* and *ceramic*, with *pottery* referring to low-fired silicate-based clay materials, and *ceramic* referring to partially or majorly vitrified high-fired silicate clay material. In the context of this study, the terms will be used interchangeably. The fired-clay materials in this study originate in the Eastern Mediterranean and date to the Bronze through Iron Ages, where the corpus of fired-clay materials are low-fired and such a distinction in terms between high or low fired is not necessary as it would be elsewhere, such as the designation of porcelain and earthenware vessels in the Far East. In general, the term *pottery* will be used in reference to vessels and *ceramic* to the material itself.

[18] Ceramics do undergo degradation in the burial environment, but it rarely results in complete disappearance from the archaeological record. In most archaeological contexts, pottery sherds are one of the most abundant types of macroscopic remains, regardless of burial environment (See Weiner, 2010:198; Freestone, 2001; Golitko, *et al.* 2012; Mata, *et al.* 2002; Schwedt, *et al.* 2004.; Zacharias, *et al.* 2007.).

[19] It is noted that some cultures do not use pottery, but pottery use is nevertheless distributed widely and common archaeologically.

[20] Zimmerman and Huxtable, 1972; Vandiver, *et al.* 1989; Yasuda, 2002.

[21] Nakamura, *et al.* 2001 provides an earliest date of 16,850-15,240 cal BP based on charred residues; Kuzmin, 2006 suggests a widening of this date to a probable 17,200 cal BP.

[22] Rice 1989:7.

be applied to vessels made of other materials. In the following discussion, an effort is made to speak broadly of the class of artefacts constituting the term *vessels*. When relevant, the theories and methods of interpretation pertaining only to pottery or metal vessels is indicated.

Tite defines the three stages of the pottery life cycle as production (including the selection, procurement, and processing of raw materials, forming, surface treatment, and firing), distribution (which also marks the transition between production and consumption), and consumption (including use, maintenance, repair, reuse, and discard).[23] In a more complete approach, one more stage should be added to this scheme: preservation. This stage, usually approached through burial, includes the alteration of artefacts by the burial environment, excavation, conservation, analysis, and storage/display (Figure 1-3). While this scheme was originally designed to describe specifically pottery vessels, this progression equally applies to vessels of any material. Each of these stages has an impact on the object and its future. In the context of vessels, to which this dissertation is dedicated, each stage in the life of the vessel also has an impact on its contents and any resulting residue. Vessel analysis seeks to reconstruct these stages, particularly production and consumption, by studying the remnants of the vessel (for ceramics: sherds or whole vessels; for metals: corrosion products and/or the remaining vessel), context, stylistic markers, and residual contents.

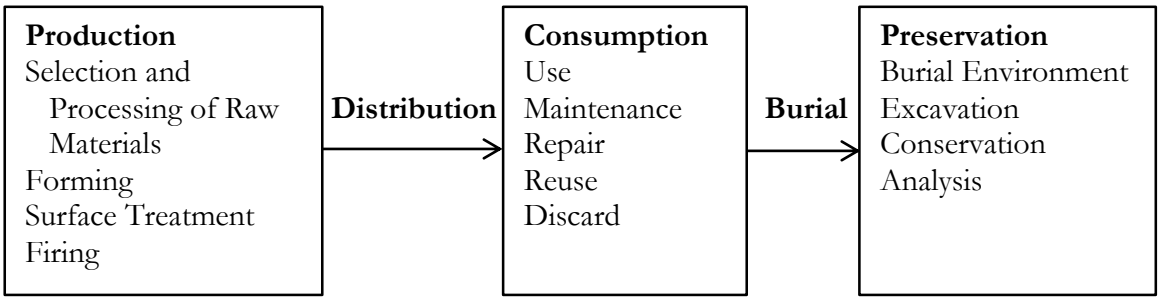

Figure 1-3: The Life Cycle of a Vessel
(after Tite 1999, with added preservation scheme)

[23] Tite, 1999.

The primary aim of all vessel studies is to gain a better understanding of the cultural context in which the item was created, existed, and functioned.[24] The understanding of a vessel type or assemblage can also in turn be used to define specific cultures and time periods archaeologically through the creation of typo-chronologies. Each stage in the life cycle can provide a window into aspects of culture such as technological development (production), economics (distribution), cooking and feasting (consumption), ritual (consumption), discard (burial), etc. There is a danger, however, in focusing only on a single portion of the life cycle without considering the effects of the others. Shape, composition, and style have an impact on the distribution, use, and preservation of a vessel, but the preservation and degradation of a vessel and its contents have a significant influence on the way that its production, distribution, and consumption are understood. The line of deduction and interpretation of an artefact flows in the opposite direction to the artefact's biography as each stage of the biography can only be interpreted through the lens of the stages that followed it. As an object is studied, one also must consider the current setting of the artefact (in excavation, analysis, or conservation) and the effects of these processes on the artefact and its interpretation.

Shanks and Tilley lay out a fourfold hermeneutic which helps to clarify the multiple viewpoints from which deductions can be drawn for an object in its current context. These are the following:[25]

1. The discipline of archaeology and its schools of thought (i.e. the theoretical framework).
2. The contemporary society of the archaeologist.
3. The society or societies in which the artefact was manufactured and used.
4. The distance in time between the objects manufacture/use and the present, which limits the degree of knowledge.

This is not a perfect theory for the interpretation of archaeological and archaeometrical data, but the general acknowledgement that the data are a result of varying viewpoints is valid. In

[24] Matson, 1965.
[25] Shanks and Tilley, 1992:107-8.

particular, the extent to which point four is a relevant or significant issue is dependent on the material and can be debated. Especially as archaeological scientists learn how time and environmental conditions affect any given class of object, distance and time become irrelevant in the hindering of knowledge. In actuality, the amount of information increases along the timeline as changes in structure allow for the reconstruction of the object biography rather than removing information from the system (the driving force of point four). It must be stated that the data set exists within a system with its own limits and complexity which can capture the attention of and be relevant to a wide array of disciplines and sub-disciplines. It has been argued that to address adequately the complexities of such systems, the "science of archaeology", and their relevance within social, historical, and scientific communities one must apply rigorously the Heisenberg Uncertainty Principle and acknowledge that time does not necessarily limit knowledge to be gained. The complexity of the system can pose new challenges of interpretation which add to the limitations the field and its related disciplines impose upon themselves.[26]

In addressing the hermeneutic, while recognizing the qualifications and issues that arise, aspect four has been already mentioned in the difficulties arising from the lines of deduction flowing opposite to the timeline of an object biography and will later be expanded in the discussion of how a residue comes to be. In this project, point one is addressed by using a materials science approach and the theoretical framework laid out in this introduction. Point three will be discussed in the laying out of archaeological and historical context of the sample set. In regard to the second point, the issue arises of what Hurcombe describes as the "tripartite divide".[27] This takes into account not just the current state of the archaeological discipline, but also the fact that archaeology is a widening field which incorporates a variety of specialities and is far beyond the research and expertise of a single

[26] Pollard, 1995.
[27] Hurcombe 2007:12.

individual. Hurcombe divides the vast number of people into three categories: the Archaeologist, the Hard Scientist, and the Social Scientist. Whether one accepts this simplified and narrow division of fields within archaeology,[28] the single fact is that the field is a cooperative and collaborative one and must be so to remain successful and meaningful. Archaeological artefacts are excavated and recorded to the best of the team's current corporate knowledge, all of whom may not be period or material specialists (the brunt of field work often falls to volunteers and students). Then the objects are passed onto specialists for analysis whether technical and scientific (dating, compositional analysis, technological, characterization, genetic sequencing, wear analysis, residue analysis, and many others) or social (psychology, cognition, semiotics, perception, agency, etc.). These specialists may or may not have in depth knowledge of the archaeological or historical context.

Finally, all of these individuals take part in and influence the interpretation and publication of the field, technical, and social analyses. The variety of information able to be gleaned from the past and archaeological record is vast and creates a richness of understanding. However, it is important to note that everyone is limited to their own understanding and experience, as well as limited by the information passed on from one researcher to another and the comparable and relevant evidence presented in the scholarly literature. In this project, an attempt has been made to mitigate some of this by being a participant in the excavation of two of the four sites (Kabri and Megiddo), and combining archaeological, historical, and chemical techniques.

Most vessel and pottery analysis is based on the assumption that vessel form, style, and function are so entrenched in culture that changes in the ceramic tradition are indicators

[28] For example, this project like many others incorporates multiple of these subdivisions and often specialists possess expertise in aspects not confined to a single category. An argument can be made that in the progression of archaeological thought, theory, and practice, such categories are increasingly meaningless, idealized, and not representative of reality.

of larger cultural processes. An example of how physical aspects of vessels are linked to cultural phenomena is given in Figure 1-4.[29]

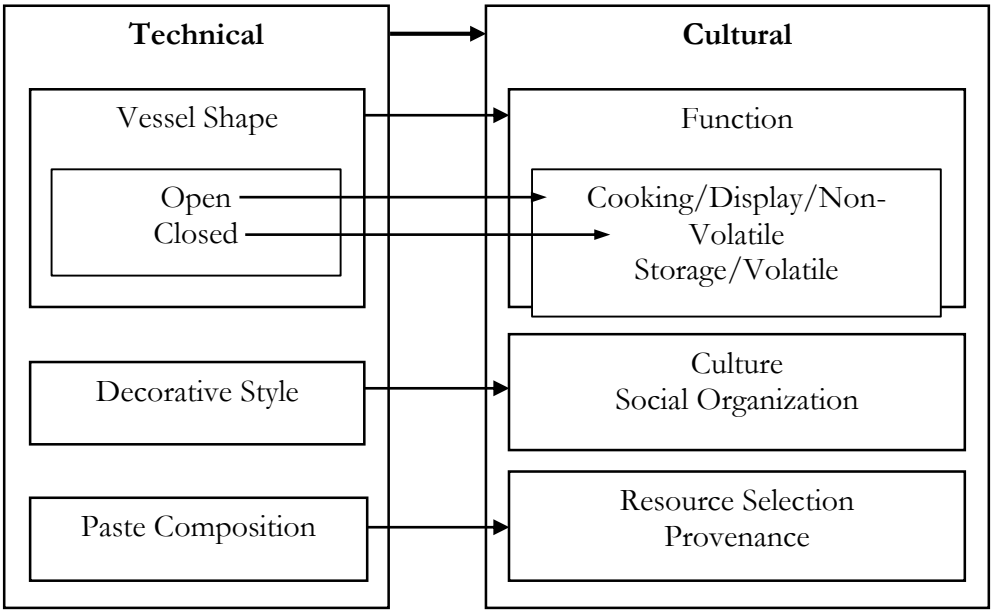

Figure 1-4: Technical Aspects of Vessels and Their Cultural Correlates

Similar typological attributes are often viewed to be the result of cultural contact, trade, and diffusion.[30] To this end, stylistic analyses are regularly used to construct cultural sequences and chronologies,[31] as well as to demonstrate cultural relationships. Material analyses demonstrate technological development and economic growth both within and between societies, while functional analyses are used to explain cultural practices such as cooking practices,[32] feasting,[33] and ritual[34]. With the progression towards a more rigorously scientific archaeology in the 1970s, the ability to study pottery on a chemical level made pottery analysis an even more significant tool. Analyses such as petrography, mineral composition and structure, and chemical analyses are able to help track technological

[29] This diagram simply shows some of the technical characteristics of a vessel that can be and are used to form cultural conclusions. It is simplistic in its one-directionality but illustrates how one point in a structural system can be used to inform another, problematic though it may be to ignore the feedback mechanisms.
[30] Arnold, 1985.
[31] e.g. Amiran, 1969; Mazar, 1992.
[32] e.g. Charters, *et al.* 1995.
[33] e.g. Tzedakis, Martlew, and Jones, 2008.
[34] Hall, *et al.* 1990.

development and the movement of vessels by determining original clay sources[35]. A particularly important addition to the study of pottery consumption has been in the field of organic residue studies. Prior to this point and even to a great extent today, contents have been assumed based on reconstructed vessel forms, performance characteristics, or ethnographic data. The identification of residual organic compounds allows for further discussion of precise cultural practices and day-to-day life in the past.

If vessels can perform a number of functions and the technological choices affect these functions, it is important to take into account when discussing a residue the other functions that its host container might have. These functions will not only have an effect on the nature of the residue, but certain aspects of its lifeway that may be inherent to the vessel and not necessarily the residue. This arises in the idea that pots can be tools or signs or symbols, but in the context of a residue a pot is a container.[36] All of its potential functions lie in the fact that it is a contained space, whether that be for a residue, a depiction, or a sentimental memory. To understand the residue, one must understand its context. In some ways the structures of both the residue and the vessel can be known, but as C.S. Smith so eloquently said: *the future offers great opportunities for the exploration of the principles of interaction between levels.*[37]

[35] e.g. Goren, *et al.* 2004.
[36] Knappett, *et al.* 2010.
[37] Smith, 1981: Apologia.

1c. Form, Structure, Function, and Use

Here it is helpful to define four important aspects of the study of vessels: form, function, structure, and use. *Form* can be defined as the structure or the materials, shape, and decoration of a vessel. For the purposes of this discussion and project, a more limited definition of *form*, as referring solely to the shape and decoration of a vessel, i.e. its aesthetic qualities, is more useful. *Structure*[38] has previously been defined in this chapter to encompass the material composition and its processing in the creation of an object. While structure can easily be encompassed in the broader definition of *form*, drawing a distinction between the two terms allows for a separation of ethnographic, cultural, and stylistic typologies from chemical, petrographic, and other physical analyses. The form and structure of a vessel together give rise to a set of properties that define how an artefact can function or be used within a culture (see Figure 1-1).

Shanks wrote *an artefact is always active – tying together heterogeneous things, material and human*.[39] While all objects serve a purpose or purposes in a society, these purposes are not necessarily all or solely utilitarian; they can also perform social functions as signs or symbols. That is a marker for a culture, social class, social role, or specific group of people (sign) or representative of an ideology or belief (symbol). Herein lies the distinction between function and use. *Function* entails all utilitarian and social identities of an artefact across time and may change throughout the course of said time. *Use* is a distinctly human utilitarian action which implies cognition and intent. An object can also have multiple uses throughout time, but use is inherently a single event which can be repeated or changed. Thus, function can entail a broad spectrum of uses. For example, a jar can be used to serve water or used as a vase in its function as a container, handed down to an individual to function as an heirloom, or function as a reminder of a journey or event. The residual contents of the canopic jars of

[38] See also: Smith, 1981.
[39] Shanks, 1998:27.

Ramses II serve as a good example of the distinction between function and multiple uses. These four faience jars from the Louvre have long been described as the canopic jars of Ramses II, based on the presence of his cartouche on their exterior. Upon characterization of some of the residual material and their dating via single compound radiocarbon dating methods, it was discovered that the jars contained unguents composed of animal fat and coniferous oil used not in a funerary context, but one of worship during the Third Intermediate Period. Later during the Ptolemaic period, the jars were reused as canopic jars for viscera embalmed with pistacia resin.[40] All of these uses, as containers for unguents presumably stored in a nearby temple and subsequently as canopic jars for embalmed organs combined with the correlations in mortuary ritual and ritual ideology constitute the function of these vessels.

Function can take into account context, use, wear, and other aspects of an artefact's place in society, however references to function do not always include the entirety of an object's biography. In this way, function has been defined as the place of a vessel, its typology, and its related assemblage have and the roles which they take in the social and economic context of a given cultural system.[41] For example, there are many *uses* for clay (waterproofing, containers, construction, tools, figurines, bricks, etc.) or vessels (storage, transport, cooking, eating, etc.), or metals (tools, monuments, coins, vessels, etc.). However, the colour, shape, decoration, or size of an object can also encode social information such as social and economic status, religion, ethnicity, and history, i.e. non-utilitarian *functions*. Taking this into account, a transformative technology emerges which can have its own socio-political, economic, and ideological ramifications.

Material culture, in essence, is a social construct based on the properties of various materials, the procurement of those materials, and the formation of them into artefacts. In

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[40] Charrié-Dahut, *et al.* 2007.
[41] Henrickson, 1990.

categorizing, analysing, and describing materials and their materiality, one must take into account their form, structure, use, and function. To categorize solely on structure is to take artefacts out of their cultural context. Identifications only on form (and assumptions of use) or function implies that function is static over time, when in reality, function can be and is usually fluid, linked with style, design, social status, relationships, pragmatism, economics, and conceptual plan.[42]

Prown draws a distinction between "hard" material culture studies and "soft" material culture studies. She describes the "hard" material culture pursuit as one that is concerned predominantly with the objects themselves, including technological characteristics, configuration, and use, that is events and actions. This approach uses deduction, scientific facts, statistics, and data that are conscious and intentional. On the other hand, "soft" material culture is that which is focused on the culture itself. How an object functions in its context, belief systems, and the principles that constitute a society are the most important questions in this line of predominantly inductive inquiry/reasoning. The distinction between "hard" and "soft" material culture is not used here to state that one is more useful than the other in any way but to make the point that reality must be somewhere in between these two extremes. The technological choices, evident in form and structure, must be seen in light of the culture and context in which it was created; the interpretations of function and use must be evaluated with the macroscopic and microscopic properties of the object.[43] In this project, the focus will be mostly on the structure of vessels and their use. The impact that one has on the other in terms of preservation and interpretation will be highlighted.

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[42] Hurcombe, 2007: 111-112.
[43] Prown, 1996.

1d. Purpose, Goals, and Hypotheses

Analysis of organic residues preserved in a great range of archaeological materials has the potential to provide information on the specific uses of objects in antiquity and give meaningful insight into a culture's diet, technology, ritual life, and economy. Because living things are organic in nature, organic materials and substances are abundant in the archaeological record. However, while organics are the most frequent category of material culture in life, they are generally grossly under-represented in the macroscopic archaeological record because of their susceptibility to chemical and biological attack.[44] Macroscopic organic materials with mineral fractions are the majority of what is readily visible, such as mineralized bone and plant remains such as carbonised seeds and phytoliths. Molecular organics, such as those preserved in amorphous residues including lipids, carbohydrates, proteins and nucleotides, are specific to their roles in living organisms and frequently can be connected with at least a class of organism if not a specific species. Lipids in particular play a number of vital roles in all living things and are unique to each organism as an integral part of biological pathways. These lipids and other molecular organic species are found in a number of archaeological materials, the most important being absorbed residues in pottery (Figure 1-5).

[44] Hurcombe, 2007:119.

Pottery
- Vessel Fills *
- Surface or Visible Residues ****
- Absorbed Residues *****

Human and Animal Remains
- Skeletal Remains ****
- Soft Tissues ***
- Mummies ****

Plant Remains
- Waterlogged Remains ***
- Desiccated Remains **
- Carbonized seeds *

Dyes and Pigments
- Textiles ****
- Art ****

Soils and Sediments
- Midden and Other Organic Wastes ***
- Agricultural Soils ***
- Habitation Deposits **
- Ritual Deposits **

Resins and Bitumen
- Natural Resins *****
- Plant Gums **
- Fossil Resins ***
- Petroleum Bitumens ***

Miscellaneous
- Glass Containers **
- Metal Containers **
- Stone Objects **
- Hoards; e.g., Bog Butter **

Figure 1-5: Common Archaeological Sources of Molecular Organic Material
Asterisks relate to the importance of the source dependent on the frequency and preservation of molecular organics, ***** equalling high importance and * corresponding to lower importance. (Evershed, 2008b)

Organic residue analysis of archaeological materials has the potential to provide information on day-to-day life, economic pathways, social structures, ritual practices, and the development of technology in the past. It is estimated that up to ninety percent of assemblages have the capacity to produce useful absorbed residues[45]. This statistic is encouraging for the usefulness of residue analysis in archaeological inquiry worldwide, despite other estimates that state a success rate for individual sherds at approximately ten percent. This dichotomy indicates that while the number of individual samples that could produce an organic signal is small, the majority of overall assemblages might produce useful residue data that can be tied back to social and material culture. While organic residues have been used to great success in the identification of past vessel contents,[46] the mechanisms that lead to the preservation of these organic molecules are still poorly understood and the

[45] Evershed, 2008b.
[46] e.g. Charrié-Duhaut, *et al.* 2007; Mills and White, 1989; Stern, *et al.* 2003; Stern, Heron, *et al.* 2008; Tzedakis, Martlew, and Jones, 2008.

relationships between these residues and their matrices have not been addressed. As a result, it can be difficult to form secure cultural conclusions on the basis of residues alone.

There are several potential mechanisms that contribute to the preservation of molecular organics (lipids, proteins, etc.) in vessels. First, organics may seep into the ceramic matrix and be trapped within the natural pores through absorption. These pores then protect the molecules from microbial attack, oxidation, and leaching. It is also possible that there is a reaction that binds the organic molecule to the inorganic ceramic matrix at cation exchange sites or other chemical processes through adsorption. The burial environment also plays a role in the preservation and degradation by controlling the species that come into contact with the ceramic and residue. In all likelihood, all of these factors influence the degradation and preservation of organics within the ceramic matrix. The extent to which they have an effect has the potential to influence the interpretation of analysed residues.

The primary goal of this project is to elucidate the relationship of organic residues with their vessel matrices, whether ceramic or bronze/copper alloy corrosion. As most data on archaeological residues come from those absorbed into the ceramic, this is a particularly important factor to be considered in the interpretation of the results of organic residue analysis. The problem focuses on one part of the last stage in the life of a vessel, preservation. In the past, studies have been predominantly focused on the degradation pathways of organics but little has been said about how what survives is preserved. Understanding the mechanism behind the preservation of organic materials in archaeological ceramics is an important factor underlying the study of these organics and the interpretation of the results.

The clarification of the relationship between molecular organic preservation and the properties of the matrix not only affects the interpretation but could also have implications on the identification of other materials which may provide matrices for preservation. By relating residual yields to vessel characteristics we can gain an understanding of whether

there are any interactions or forces that specifically keep molecular organics in the archaeological record as residues. These interactions and forces may act directly to prevent removal of organics from the system by binding them to the vessel or by limiting the degradative forces in the system through the provision of protective niches or alteration of the environment. If preservation of absorbed lipid residues in ceramics is not solely a function of the porosity of the ceramic, it would suggest that organic material may survive in other micro-contexts and open the application of residue studies to other artefacts and vessel types. The investigation of other potential sources of residue data, specifically non-ceramic vessels, allows for further discussion of the exploitation of organic commodities in antiquity.

Within the aim of further understanding the preservation of residues and its impact on interpretation of vessel use, the objectives of this project are fourfold: to identify organic residues in archaeological vessels; to evaluate a new methodology for the recovery and analysis of such residues; to investigate the capability of bronze corrosion products to preserve molecular organics related to vessel use; and to elucidate potential mechanisms responsible for the preservation of organic residues. Each of these objectives is related to one another as illustrated in Figure 1-6.

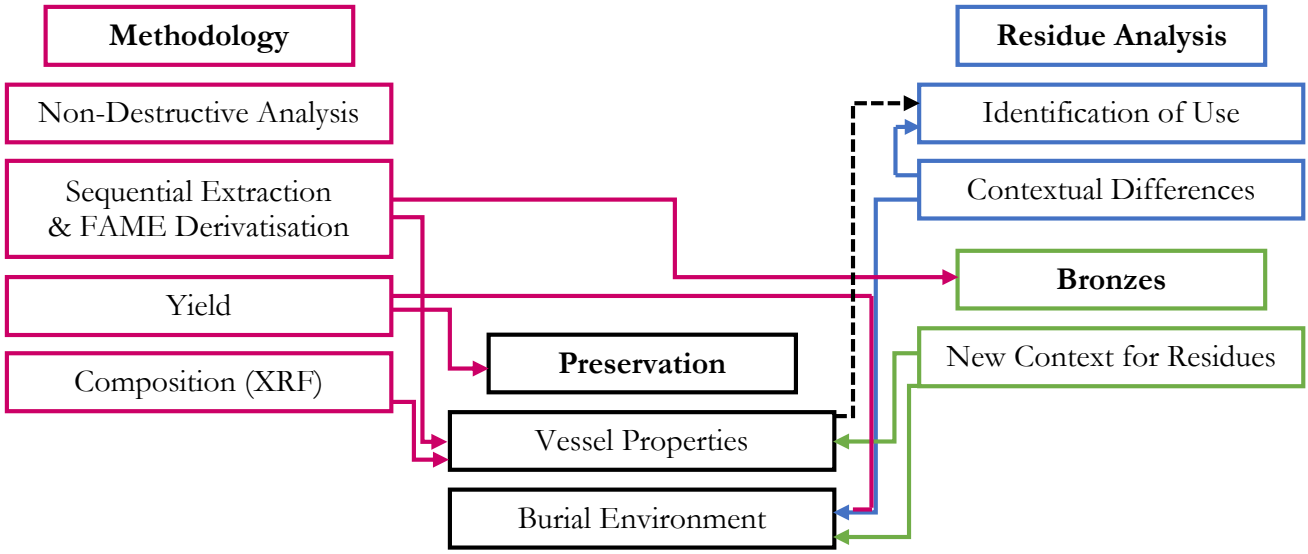

Figure 1-6: Project Objectives

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One hundred and thirty-three ceramic samples from Tel Kabri (Israel: Middle Bronze Age), Tel Megiddo (Israel: Early Bronze Age to Iron Age), and Lefkandi (Greece: Protogeometric) along with twenty-two bronze corrosion samples from the A2 Project (UK: Roman) were evaluated for residual organic content in order to achieve these objectives. These samples represent different cultural (domestic, mortuary, ritual, and palatial), regional (Levant, Aegean, and Britain), and temporal (Bronze Age, Iron Age, and Roman) contexts. By choosing samples with an array of vessel types and contexts, points of comparison can be identified upon which to form conclusions on the relationship between residue preservation and the burial environment. Possible differentiation of function and use of vessels across different areas and contexts within the same sites and differentiation between sites can be identified and discussed. Of some particular interest is the hypothesis that vessels found in burials may have different uses and residual contents than similar vessels employed in domestic contexts. The question here relates to the distinction between function and use. Vessels in mortuary and ritual contexts most surely have different functions from vessels used in domestic contexts, even if these functions are related. The question, however, is if the use remains the same in each context. For example, are vessels filled with the same food items of substances with which corresponding domestic vessels are filled? The answer to this question could affect the interpretation of burial rituals, a practice that can be argued depending on the culture[47] and ideology is predominantly for the living. Vessels used for their symbolism or as an utilitarian offering for the enjoyment of the dead, deities, or spirits could be construed as a significant departure in ideology or inform upon our perception of cultural identity and ideology.

Related in the wider context of ritual, the identification of use and the differences between this use and domestic use can provide information into the nature of ritual and daily

[47] Egyptian grave offerings are known to be for the use of the individual in the afterlife, but in other circumstances burial offerings could be for the enjoyment of deities/spirits, a symbolic offering, or a token of affection.

life. Such a distinction would have a large impact on the understanding of ritual feasting and rites of preparation and how they correlate or diverge from those within the home. In the determination of function/use, properties of vessel shape and aesthetic play a significant role in the perception and interpretation of a vessel. This relationship, indicated by the black dotted arrow in Figure 1-6, is relevant in pottery analysis overall but is not a major factor in this study as the primary aim to the study of contents themselves and not the aesthetics of morphology of a vessel. The effects of vessel technology on the suitability of a vessel to perform a certain function are discussed briefly in Chapter 2.

The bronze corrosion samples studied in this project represent an avenue of organic residue analysis that has not been previously explored. It is hypothesized that bronze corrosion products have the capability to preserve molecular organics by encapsulation of the organics within the corrosion, through the inhibition of microbial action, and/or through the formation of organo-metallic complexes. This study presents some of the first evidence for such preservation in vessels which are not ceramic or stone. The contribution of such preservation in metal, non-porous vessels to the study of vessel function and use is discussed and the implications on the understanding of the relationship of molecular organic residues with their matrices evaluated. The specific samples used here also have the potential to inform upon burial practice and the introduction of Roman culture in Britain. The vessels from the A2 project were part of high-status Roman graves dating soon after the conquest. Also, these types of vessels are known from other contexts in the Roman Empire, so the question concerning burial and domestic use is also relevant to these samples.

Thirdly, a new methodology was evaluated for the recovery and identification of organic residues in archaeological vessels of both ceramic and bronze. The components of this methodology were chosen for their potential to answer several key questions and for their relationship to other project goals as shown in Figure 1-6. First, a non-destructive protocol for extraction of organic materials from ceramics was tested. If as effective as other

conventional extraction methods,[48] non-destructive analysis is not only attractive to the analysis of materials unavailable for destructive analysis and for those desired for vessel restoration, but also for the further correlation of vessel properties to residue preservation and yield. The ability to directly measure residual content, yield, and characteristics of the same matrix within which the residue is found allows for direct comparison of data and, in the long-run, reduces sampling size requirements. The evaluation of this method would in the future allow researchers to pinpoint ideal sampling locations and assemblages while distinguishing vessel related reasons for preservation and information from other practices such as cooking[49] which have been seen to alter the absorption and preservation of organics. Secondly, a fatty acid methyl ester (FAME) derivatisation protocol, taken from modern food science, was applied to the samples. While derivatisation via trimethylsilylation or other methylation methods has been used to great success in the past,[50] there is always the desire to develop new techniques that have the potential to be more effective, reduce experimental expense and time, and answer new questions. This particular protocol employs reagents that are common to most laboratories, easy to prepare, and stable. The use of this method directly relates to the elucidation of the potential connection between vessel properties and the preservation of residues.

It is hypothesized that the preservation of organic residues in ceramic vessels is not solely the product of absorption into the pores of a vessel, but also of chemical interactions with the ceramic matrix. If this is true, conventional solvent extraction would not be sufficient to remove all preserved organic materials from a vessel matrix. By employing sequential solvent extraction and base assisted extraction/direct FAME derivatisation, the extent of hypothesized chemical interactions and the efficiency of extraction can be tested. The extent to which direct FAME extraction and derivatisation is effective on sherds of

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[48] Primarily the drilling or crushing of sherd material prior to extraction. See Evershed, 2008a.
[49] Charters, *et al.* 1993.
[50] For review see: Evershed, 2008a; Stern, *et al.* 2000; Heron, *et al.* 1991.

various types can then be used to evaluate the role of the interaction between the ceramic and its contents based on the properties of the ceramic. Following the hypothesis that the composition of a ceramic matrix may have a direct effect on preservation of vessel contents, x-ray fluorescence (XRF) data was taken with the aim to correlate potential ionic bonding sites within the ceramic to residual extraction yield.

The determination of residual yield is of utmost importance in this study as it is the primary basis for the interpretation of preservation rates and any connection to vessel properties and context. In a systematic review of residue analysis in archaeology, the success of such studies is illustrated as it is represented in the academic literature. Careful attention is paid to any differences indicated between coarse and fine wares, changes in success rates resulting from different burial environments, and the results of different extraction protocols to published materials. The quantification of residue yield, and not solely qualitative identification, is necessary to form conclusions and interpretations concerning preservation. Relating yield to burial environments and vessel characteristics has the potential to provide data concerning how significant these factors are and their impact on the qualitative information in a residue. This in turn can have a vast impact on how residues are understood and interpreted in their physical and cultural contexts as well as having implications for the sampling of vessel for analysis and the execution of said analysis.

Understanding the mechanisms behind organic preservation in ceramics has the potential to affect how resides are interpreted in that it could provide information on the reasons why certain organic species are observed while others are not (i.e. distinguishing between what was never there and what has been removed or altered over time). It also informs as to how they may or may not interact with the ceramic itself, not just the burial environment. This in turn can affect the way in which cultural conclusions are formed on the basis of residue data. Through a discussion of the identification and quantification of organic substances preserved in vessels of ceramic and bronze, the overall purpose of this

project is to clarify the exact nature of the micro-context's (ceramic or bonze) role in preservation of content. The vessel plays a significant physical and chemical role in the creation and preservation or residues and this role is defined by the nature of the vessel itself. By understanding the micro-context of the studied organics, it is hoped that the relationship between vessel and organic can be clarified, having the capacity to alter interpretive approaches to residue analysis and vessel analysis within the macro-context (the context of the vessel). Such an analysis aims to lead to a better understanding of cultural processes that affect vessel use and the way in which they are perceived by the archaeologist and scientist.

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2. VESSEL PRODUCTION AND THE LIFE OF RESIDUES

In this chapter, the object biography of vessels and the processes which influence the production of residues are discussed in detail. As mentioned in Chapter One, the identification, interpretation, and significance of a residue and its matrix, in this case the vessel, relies on an understanding of how it has come to be in its present state. This process begins by constructing general object biographies for vessels and vessel contents. These biographies extend beyond the lifetime of the individual or individuals that created and used the vessel, to include production, use, discard, excavation, and analysis. Vessels fall in the sphere of "containerism";[51] that is they are designed to hold things. Containers or vessels offer a relatively hygienic and stable surface which to shelter their contents from the environment (animals, children, contamination, dirt, and others). By serving this function, they solve challenges of transport, storage, cooking, and serving. Inherently vessels are protective both pragmatically and ideologically. The pragmatism of containers is self-evident and ubiquitous. The commonality of vessels has led to the incorporation of such items into ideologies and linguistics. Frequently, the concept of symbolic or idealized "vessels" is connected with ideas of protection and safe haven. Linguistically, *vessel* has been applied to everything from true containers to pregnant women, graves, and ships. The implication of the ideological vessel is inherent protection for any type of item that is carried or held, and in the context of archaeological residues, it is not any less true. Ceramic vessels, and potentially those of other materials, protect their contents through their use and potentially continue to carry and protect remnants of these contents within the fabric long into the archaeological record.

This chapter addresses the production of vessels which results in certain structures appropriate for intended and unintended functions. Then it turns to focus on the biography

[51] Hurcombe, 2007:171.

of residues and its connection to that of vessels. As absorbed or adsorbed residues in ceramics particularly, but also in other vessels, exist only in the micro-context of the vessel either within the fabric or encrustations adhering to it, each of the biographies are inextricably linked and dependent on one another.

2a. Ceramics and Technology

Broadly speaking, the term *ceramic* refers to fired silicate-clay material. Modern materials science provides a more technical but broader definition of *ceramics* as a class of chemical compounds that combine metallic (electron-donating) and non-metallic (electron-accepting or electron-sharing) elements.[52] In an archaeological context, the first definition is the most workable, chemically defined by rock-forming clay minerals and predominantly consisting of silicates and aluminosilicates. Mineralogically, clays can be quite diverse in composition and can be altered as needed to produce desired characteristics in a piece of pottery. The diversity in crystalline composition between clay sources is such that ceramic vessels can be correlated with original clay sources and provenance to general geographic areas.[53] Colloquially, the terms *pottery* and *ceramic* are easily to conflate. In an archaeological context, it is possible to use the term *pottery* in reference to low-fired clays, such as earthenware, and use the term *ceramic* in reference to high-fired porcelains (a trend especially observed in the Chinese ceramic culture).[54] The pottery studied in this project is confined to samples of low-fired (<1100°C), earthenware vessels, from the Bronze to Iron Age Eastern Mediterranean, so such a distinction between *pottery* and *ceramic* is not necessary at this time. Essentially the two terms will be used interchangeably with *pottery* generally referring to vessels and objects and with *ceramic* generally referring to the material itself.

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[52] Rice, 1987:3; Kingery, *et al.* 1976: 3-9, 16-17.
[53] e.g. Goren, *et al.* 2004.
[54] Rice 1987: 4.

The production of pottery is influenced by a multitude of factors including situation, desired performance characteristics, and intended function. As mentioned above, the ultimate aim of pottery studies is the reconstruction of function and use within the cultural context of the vessel. Much of the way that this goal is accomplished is through the study of the performance characteristics of a vessel or its remnant sherd material. The way in which situational factors and desired characteristics interconnect with physical properties and technological choices in the creation of a vessel is demonstrated in Figure 2-1.

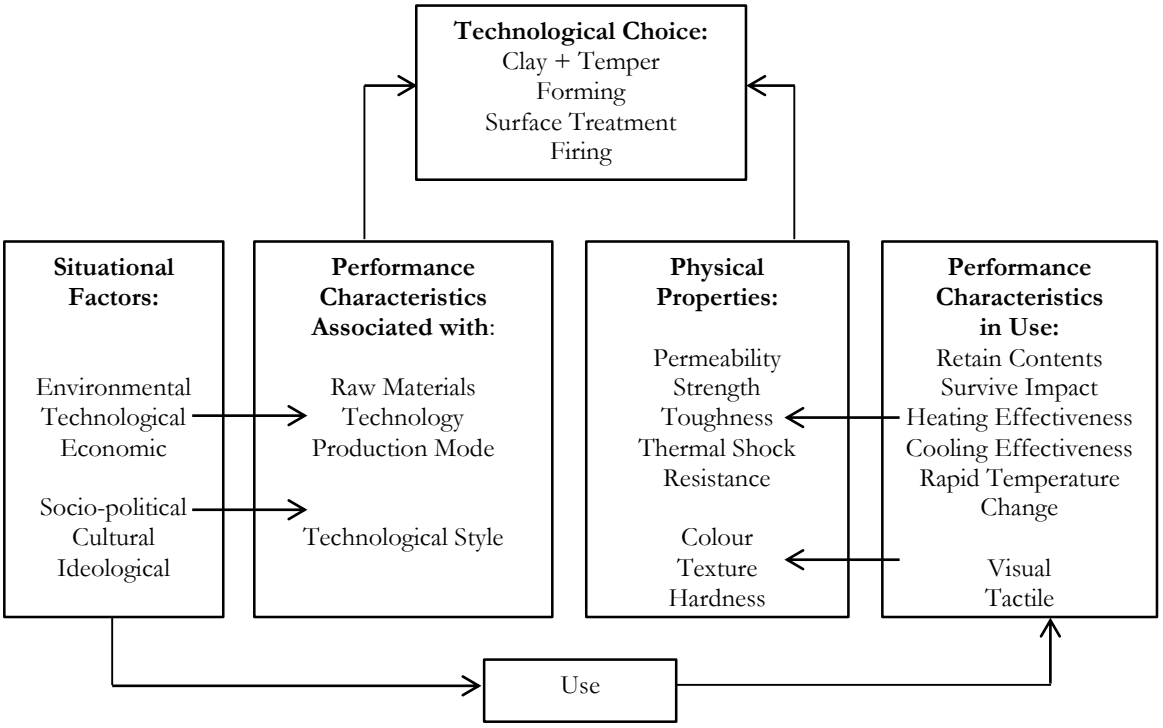


Figure 2-1: Factors Influencing Pottery Production (after Tite, 1999)

The technological choices of the potter (material, shape, surface treatment, etc.) are defined by the intended use of the object within a given set of situational factors (society, culture, environment, technological knowledge, economy, ideology). These choices are then reflected in the vessel and in some ways act back on the culture by defining the realized primary and subsequent uses of the vessel. Each of these factors also affects how the vessel interacts with its contents and, in an archaeological system, its eventual burial environment.

While some of this may not have been consciously considered by the potter (especially once the vessel moves beyond the primary use phase), the physical characteristics are the basis for the interpretation of the potter's and consumer(s)' cultural situation and habits. Such technological choices identified by specific properties are not always easily related back to situational factors as it is always important to note the influence of cultural ideologies that affect technology (cosmological and ecological belief, political motivations, etc.).[55] Regardless of motivation, the technological choices of a potter lead to a set of unique vessel properties. The levels of structure on which a vessel can be interpreted are shown in Figure 2-2.

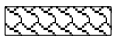
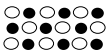
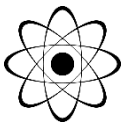
Level 1		**Assemblage**	**Provenience**	**Cultural Context**	**Macroscopic**	
Level 2		**Groupings**	**Spatial Patterns**	**Functional Context**		
Level 3		**Vessel**	**Object**			
Level 4		**Form**	**Macrostructure**	**Typology**		**10mm**
Level 5		**Porosity**	**Microstructure**		**Microscopic**	**100µm**
Level 6		**Silicate/Alloy**	**Crystal Structure**	**Provenance**	**Sub-microscopic**	**10A°**
Level 7		**Atoms**	**Chemical Composition**			

Figure 2-2: Levels of Structure Associated with a Vessel (after Kingery 1996b)

[55] As previously mentioned in Chapter One, the culture, knowledge, and situation of the investigator can also influence these interpretations. The multiple identities, contexts, and functions of a vessel both past and present must be taken into account.

This figure illustrates the many levels upon which associations and contextual conclusions can be formed from the overall context through macroscopic levels down to microscopic and sub-microscopic levels. The information in the first two levels of structure, assemblage and groupings, is encoded within the excavation of a given object and its recording. These levels include find location, the associated materials and structures found in close proximity, and the overall archaeological, cultural, and historical context. The next two macroscopic levels of structure are the object itself and its form, which are studied in the restoration of sherd materials and typological studies. These levels of structure immediately define how the vessel is used in its suitability for a task based on shape, size, and decoration. Even if the first two levels of structural information are lost, for example an object with unknown provenance or a looted artefact, much still can be learned from the shape, decoration, size, and other typological information in level three. Associations with similar objects give a sense of date or use or origin. The breadth of vessel analysis has been constructed on this premise to great effect.

The remaining three levels of vessel structure are the microstructure, crystal structure, and chemical composition, which fall under the category of laboratory studies. Associations and contextual conclusions can also be formed from on the bases of these microscopic and sub-microscopic structures, especially concerning provenience (clay source) and manufacturing methods. However, these levels are also extremely important in defining the relationship between the contents of the vessel and their preservation as residues. It is these levels which directly affect the manners in which the ceramic matrix interacts with its surroundings, externally with the environment and internally with its contents. Some of the technical choices that produce these levels and their effects on the fabric are discussed in the following paragraphs.

Of the technological influences listed in Figure 2-1, firing temperature, in combination with the clay and temper selection, make the largest contribution to the

microstructure and crystalline structure of the finished product. Upon firing, a number of compositional changes occur in the original clay. At low temperatures, organics and carbonates burn off and at temperatures over 800°C, mineralogical changes begin to occur thus changing the overall microstructure. The fabric composition along with surface treatment and firing temperature will define the microstructure of the ceramic including its porosity, hardness, thermal shock resistance, and its ability to retain contents. Each characteristic determines not only how a vessel can be used but also how it will interact with its environment and contents. The resulting physical properties such as permeability, strength, and thermal shock resistance are important in respect to the intended use of the vessel, combine to produce specific performance characteristics. The porosity will impact the degree to which liquids permeate a vessel, a phenomenon which is desirable for evaporation used to cool contents but must be minimized for liquid retention. The porosity and temper contribute to thermal shock capacity, which is especially important for cooking vessels.

In addition to providing specific performance characteristics, the materials used to make a vessel can also perform symbolic functions. Different forms of temper, such as bone fragments and ash or sherd material from old pots, can be used to symbolize cultural and familial relationships as well as to provide thermal shock capacity. It has been documented, that during the Neolithic period in Sweden, potters used both bone and old ceramic to temper vessels. The use of either of these two tempers varied amongst communities throughout the Neolithic, signifying some differences in opinion towards the incorporation of the past into the present and of living beings in clay objects.[56] The incorporation of old materials into new vessels represents a symbolic inclusion of the history of the old vessel and its links to the potter and the individual who used it into the history of the new vessel.

[56] Larsson, 2009:345-355.

Similar sentiments are attributed to several African cultures, amongst them the Songhai of Niger, the Fulani/Gurma of Burkina Faso, and the Nama/Somono of Mali, who use ancient sherds to tie their current vessel-making endeavours to their ancestors who *knew how to make strong pots*.[57]

The mineralogical composition arising from the selection of certain clay(s), mixing, and addition of temper will define the chemical composition and thus any reactivity with the environment or its contents. Clays naturally contain alkaline earth metals which provide electron donating cations. The cation exchange capacity is defined by the quantity of these cations that can be substituted with others from the environment per mass of material. The cation exchange capacity will contribute to the extent to which electrostatic bonds can be formed between substances in the environment or contents and the ceramic at these exchange sites. The crystalline structure in this way constitutes structure levels six and seven from Figure 2-2. In the smallest level, the atomic structure defines the availability and potential channels for ionic exchanges and determines the extent of atomic or ionic mobility throughout the ceramic solid. This level is the base level for chemical interaction with the environment and the removal or addition of ionic and molecular species. The crystalline structure of level six mostly defines the strength and thermal shock resistance. This structure through the firing process gives rise to the porosity which results in some level of permeability for environmental constituents to infiltrate and react with the crystalline structure of level six and seven. *Porosity* can be defined as the volume of space within a solid-state substance, i.e. the holes which may or may not be filled with anything. The *permeability* is directly related to porosity in that it is the measure of how much of a substance can infiltrate the empty spaces that together make up porosity.

[57] Gosselain and Livingston Smith, 2005:41.

These levels of structure not only define the suitability of a vessel for a given function or use, but also the preservation of residues of said use and its reconstruction. The precise nature of the interaction of particular organic substances with ceramic fabrics is hereto undefined. Certainly many organic substances are absorbed[58] or adsorbed into the pores of a ceramic and remain there for long periods of time. This mechanical protection has been assumed to be the primary cause of molecular organic preservation. However it is possible that electrostatic bonds could form between the organics and clay minerals or other species within the fabric in an adsorption mechanism.[59]

Now that the levels of structure set in the technology of a vessel's creation on which a vessel's characteristics can be discussed have been set forth, the discussion moves around from the realm of technology into the realm of culture. In the following section, a generalized object biography for vessels and their contents is constructed and discussed in order to give a framework for the understanding of residues and their preservation.

2b. Factors Influencing the Composition of a Residue/ How a Residue Comes to Be

The majority of organic residues in an archaeological context are dependent on either a surface on which or a space in which they can be preserved. Whether a visible surface deposit on a vessel,[60] a bit of hafting material or residue on a stone tool,[61] lipids contained in or absorbed into mineralized bone,[62] substance absorbed into the porous ceramic material, or material encapsulated within metal corrosion, residues of organic substances, especially fats, oils, and resins, are not generally preserved of their own accord. Because non-mineralized organics are highly susceptible to degradation, they are dependent on particular

[58] *Absorption* being defined as the physical entrapment or containment of one substance within another. *Adsorption* being defined as a chemical adhesion between one substance and another.
[59] The types of these bonds and the evidence for their existence or lack thereof is discussed further below, and in Table 2-1.
[60] e.g. Evans and Biek, 1977.
[61] e.g. Langejans, 2010; Wadley, 2005.
[62] e.g. Evershed, Turner-Walker, *et al.* 1995.

environmental conditions (such as a desiccating or frozen environment), reactions with other items, adhesion to objects, or absorption/encapsulation by something else to survive the burial environment. As a result, the biography of a residue is inextricably linked with that of its matrix, that is the surface upon which or materials within which it exists.

As it has been seen in Chapter 1 and in Figure 1-3, a general vessel biography begins with the vessel as the direct product of technical choices with its resulting characteristics. From this point, it is usually distributed in some way. It could either be passed as it is on to the consumer, or indirectly through another tradesperson, who can also be considered an intermediate consumer, who then fills the vessel with a given commodity such as wine, oil, or perfume, and then distributes it to the next consumer. So here we see that this first distribution can be, but does not necessarily have to be, for the vessel itself and subsequent distributions could be for the vessel itself, for content, or both. The vessel, if not intended for single use, a phenomenon seen more frequently today than in antiquity, proceeds through a cycle of potential distributions, uses, repairs, and modifications until it is broken or no longer needed as a vessel. At this point, sherd material can be reused in another context, or discarded, eventually buried, excavated, analysed and conserved, stored, or displayed as the cycle repeats in that the archaeologist, scientist, conservator, curator, scholar, and museum patron can be viewed as a new generation of consumers.

Depending on the type of vessel, the nature of its use(s) and function(s), the identity of the original contents and any subsequent contents, the maintenance of the vessel, and the properties of the burial environment, the residue extract from a vessel of part of a vessel is the result of a multitude of factors. Figure 2-3 delineates a general object biography for vessels and archaeological residues along with some of the influences that contribute to and alter the residue and its matrix. The residue is not only a reflection of the original contents but also a reflection of the forming, use, repair, burial, and excavation of the vessel. As a vessel progresses in a generally linear fashion, it goes through a number of processes that add

and remove compounds from the vessel in addition to altering the vessel structure itself. The resulting archaeological residue is the sum of sealants and technological choices, primary and subsequent uses, any repair materials, additions and subtractions by the burial environment, natural degradation, and any other cultural manipulation (mixing, processing, and cooking). There is evidence that absorbed residues are not only reflective of last use, as sometimes thought,[63] but retain signals from all uses regardless of proportion[64]. The discussion of these uses and their cultural influences must come from careful analysis of the remaining residue. As the product of a multitude of processes, this can be difficult to achieve and is often based on highly degraded and altered forms of the original commodity.

[63] Craig, *et al.* 2004.
[64] Charters, *et al.* 1995; Evershed, 2008a.

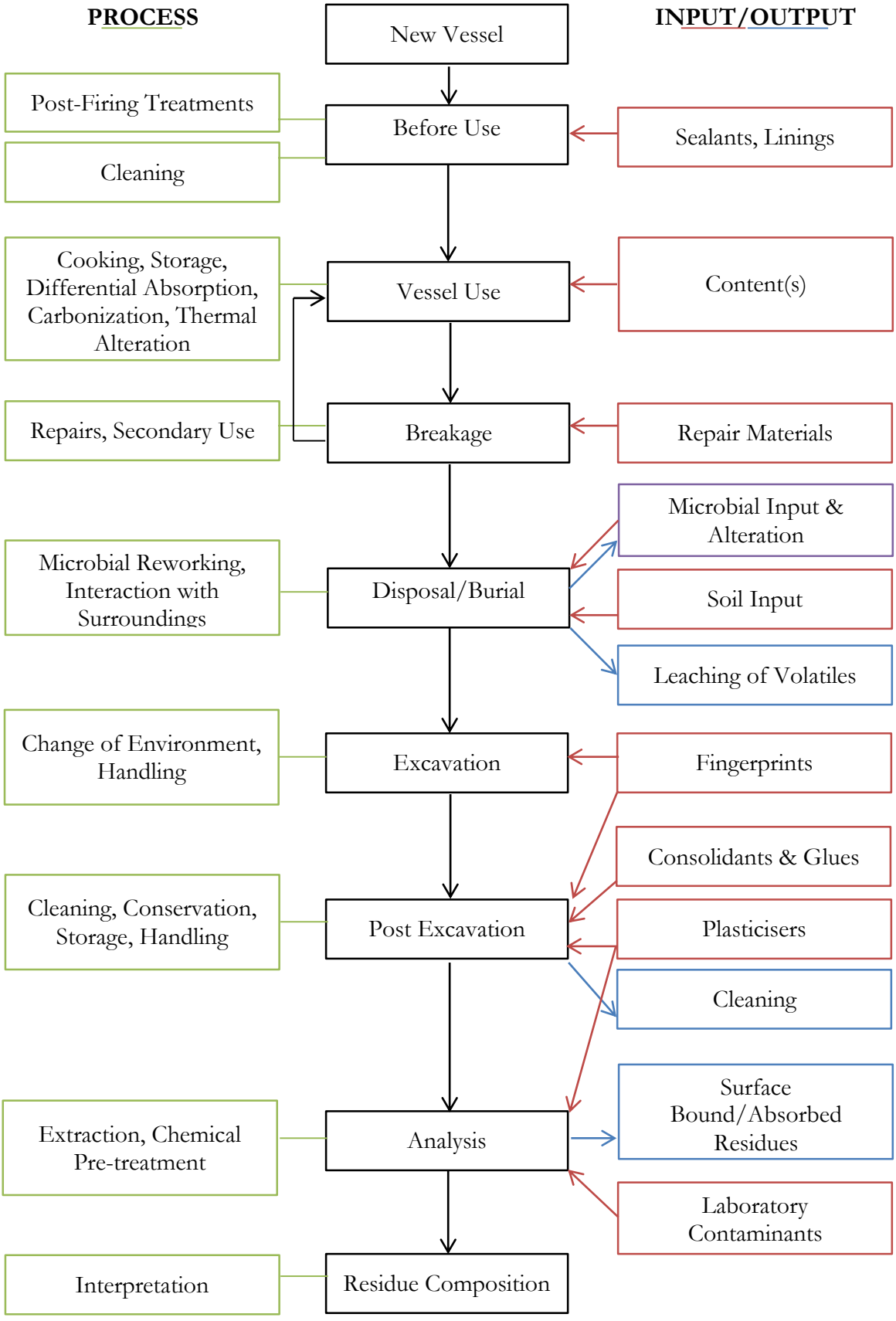


Figure 2-3: The Life Span of a Vessel and Its Contents.
(after Bonfield, 1997 in Pollard, *et al.* 2007)

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While much has been written on the extraction and degradation of organic residues and the structure and technology of ceramics, very little has been done to relate the two fields or to consider the chemistry of organics and other vessel surfaces[65] such as metal corrosion. Although most useful residue data arise from absorbed molecules, how these substances interact with the ceramic matrix in which they are absorbed is not well understood. This fact has led to some misunderstanding in the interpretation of the data, especially in relation to proteins. For some time, it was assumed that proteins were not preserved in archaeological ceramics due to paucity of successful extractions. It is now known that the poor success rate is not due to the absence of preserved proteins but the fact that they are exceedingly difficult to extract.[66] Other studies have shown that the ceramic matrix is a mediator in organic degradation processes. Ketones were once taken as a major indicator of the use of leafy vegetables containing higher epicuticular waxes.[67] Although these ketones remain a marker of the processing of these plants, they are also a degradation product of acyl lipids. In the presence of ceramic, acyl lipids (containing 12-16 carbon atoms) go through a condensation reaction to form long chain ketones.[68] Even though the basic chemistry of lipid degradation is understood outside of archaeological contexts, more needs to be done to understand the role of the ceramic within this system. Also, the ways in which organic molecules are preserved in spite of or in accordance with these degradation mechanisms need to be clarified.

There are a number of mechanisms that have the potential to contribute to organic preservation in archaeological ceramics. These can generally be divided into two categories, forces of degradation and forces of protection. Forces of degradation are mainly caused by the burial environment and include oxidation, hydrolysis, microbial attack, and leaching. On

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[65] The notable exceptions to this are studies of starches on stone tools (e.g. Langejans, 2010.) and the intial work done on stone vessels (Namdar, *et al.* 2009).
[66] Craig & Collins, 2002.
[67] Evershed, *et al.* 1991.
[68] Evershed, Stott, *et al.* 1995; Raven, *et al.* 1997.

the other hand, organics can be protected from degradation either by burial environment (the lack of oxygen, water, and microbes) or by physical and chemical means through porosity or chemical binding to the ceramic surface. Physically, organic molecules have the potential to become trapped in the pores of the ceramic matrix, making it more difficult for microbes, water, and oxygen to affect them. In many ways, organic residue analysis is based on this trait. Visible residues, especially those of resins, heavy sealants, glues, and chars do exist in the archaeological record, but their frequency is much lower than absorbed residues. Much of what we know of vessel contents and the persistence of residues arises from absorbed species. While it is known that these factors play a role in the preservation of not only organic residues, but also archaeological artefacts in general, the precise extent to which these forces play a role in the preservation of organics within ceramic fabrics is unknown. The undefined role of the ceramic in this process is of importance whether through the reduction of general degenerative reactions or an active/intermediate player.

In the fields of soil and clay chemistry, organo-clay complexes are known to form through a variety of interactions. Table 2-1 details some of the bonding forces that could exist between organic molecules and ceramic matrices.

Table 2-1: Geochemical Processes Involved Organic-Mineral Interactions (after Craig and Collins, 2002)					
Name	**Cation Exchange**	**Anion Exchange**	**Water Bridge and Ion-dipole**	**Van der Waal Bonds**	**Hydrophobic Interactions**
Type of Interaction	Electrostatic	Electrostatic	Short Range	Short Range	Short Range
Description	Cationic regions of protein replace metal ions bound to the negatively charged mineral surface.	Negatively charged regions of protein bind to the positively charged regions of the mineral surface.	Exchangeable cations on the surface of the clay minerals interact via ion-dipole and water bridges with organic molecules.	In close proximity, weak van der Waals interactions between mineral and protein occur. Especially relevant for large polymers as overall sorption will be favoured as each segment bonds.	Proteins form hydrophobic interactions with surface bound organics. Participating surfaces: any organic rich mineral surface.
Participating Surfaces	All clay minerals	Crystal edges of clay minerals: particularly significant for kaolinite	All clay minerals	Any mineral surface	Any organic rich mineral surface
Participating Proteins/Structures	Positively charged amino groups	Negatively charged carboxyl groups	A diverse range of functional groups (e.g. –OH, C-H groups)	A diverse range of functional groups (e.g. –OH, C-H groups) but particularly relevant to large molecules	Hydrophobic regions
References	Theng, 1974; Mortland, 1970; Hedges & Hare, 1987	Haung, 1990; Hedges & Hare, 1987	Greenland, Laby & Quirk, 1964	Lyklema, 1986	Boyd & Mortland, 1990

As an organic molecule comes into contact with a clay mineral surface, long-range electrostatic interactions will initially dominate as mineral surfaces have a high surface charge (in comparison to other materials such as stone). Other forces then have the opportunity to overcome repulsive electrostatic interactions to form more covalent bonds. The extent to which electrostatic connections will occur and their strength will depend on the cation exchange potential of the ceramic and the nature of the organic molecule's functional groups. In the case of proteins, these interactions are also highly dependent on the pH of the system and the isoelectric point of the molecule. The ability of certain solvents to disrupt bonding and remove organics does provide some indication of what forces are at work. The disruption of electrostatic interactions with proteins and lipids can occur through extraction with ionic solvents with higher affinity for cation exchange with the mineral surface. Urea and other chaotropic are cationic and act by cation exchange, which would be expected to disrupt hydrogen bonds, ion-dipole interactions, and water bridges to a greater extent than ammonia. Anionic detergents disrupt non-covalent bonds, disrupting any mineral-organic and organic-organic electrostatic and short-range bonds as well as binding strongly to hydrophobic regions imparting a net negative charge.

It is quite possible that similar interactions occur between lipids and other molecular organics and the clay minerals in a ceramic vessel. There are two pieces of evidence that support this theory. First work, on proteins from ceramic vessels indicate that they are not simply solvent removable and must be chemically removed. This factor has been proposed for the general lack of proteins being identified in archaeological residues.[69] It has also been suggested that some oxidation products are bound to the ceramic surface via ester linkages as they are solvent insoluble, but can be extracted with alkaline solutions.[70] The second piece of evidence that could support the suggestion that some lipid material binds to the surface of

[69] Craig and Collins, 2000 and 2002.
[70] Regert, *et al.* 1998; Stern, *et al.* 2000.

ceramics as adsorbed residues is the results of the sequential extractions presented here. It is seen that in modern test sherds as well as some archaeological pottery, the treatment of a sample with a strong base releases further materials than would be removed by conventional solvent extraction. This seems to particularly occur if an oil has been heated in the presence of the clay mineral surfaces of a ceramic. Recently, data have emerged that indicate acid-assisted extraction is even more effective than base treatments or solvent extractions, releasing lipid material in greater quantities even in vessels that had not previously been found to contain residue.[71] The researchers indicate that it appears that acid treatment opens up the mineral surfaces to liberate small amounts of absorbed lipid material.

While this is the case, the attribution of residue preservation and yields are not yet directly correlated with a clay mineral constituent, such as calcium or iron. Even if this is true, it would not necessarily discount preservation through absorption into the empty pores of a ceramic or encapsulation within another substance as Correa-Ascencio and Evershed concluded that the increased recovery with acid is not only releasing bound material but providing further access to mineral surfaces. Clay minerals and ceramics have been used in both capacities, for their porous nature as well as their binding properties, in order to filter out contaminants from water. In its unfired form, clay minerals are known to form complexes with organic materials, effectively removing them from aqueous solutions. For example, this property was used in Ancient Greece and Cyprus to bleach clothes and remove grease and stains.[72] The cation exchange points are able to interact with substances such as urea and remove them from a system.[73] In fired form, clay minerals have also been used as ceramic micro-filters in environmental remediation.

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[71] Correa-Ascencio and Evershed, 2014.
[72] Rytwo, 2008.
[73] Bissada, *et al.* 1967; De Paiva, *et al.* 2008.

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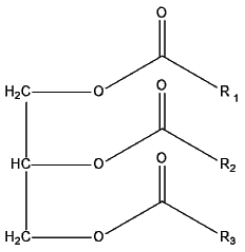
3. Lipids and Lipid Chemistry

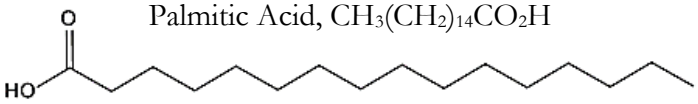
The majority of organic residue analysis in archaeology deals with the identification of lipids, a class of biogenic materials, which are insoluble in water and soluble in organic solvents. Lipids have a number of important functions in both plants and animals and can be frequently correlated with their origins based on their specific functions. The class of organic molecules that constitute the category of lipid, includes triacylglycerols which are found in the fats and oils of plants and animals and primarily function in energy storage, phospholipids which are a primary component of cell membranes, sterols which serve structural functions in cell walls as well as being the precursors to some hormones, long-chain alkyl moieties which are found in most plant and animal waxes, and terpenoids which serve protective roles in plants as natural resins. The basic structures of these materials are shown in Figure 3-1. In this chapter, the importance and exploitation of plant and animal extracts, namely fats and oils which are a major focal point for residue analysis, are discussed in terms of their history of use, basic chemistry, and issues concerning their preservation.

Triacylglycerols

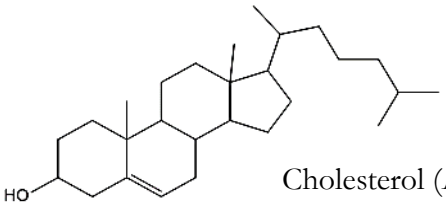


Fatty Acids

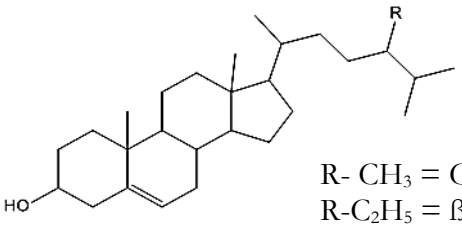
Palmitic Acid, $CH_3(CH_2)_{14}CO_2H$



Sterols

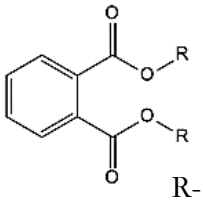


Cholesterol (Animal)



R- CH_3 = Campesterol
R-C_2H_5 = ß-Sitosterol
(Plant Sterols)

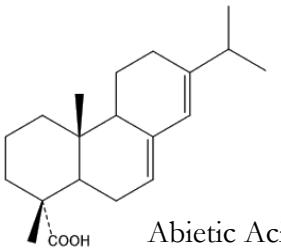
Contaminants



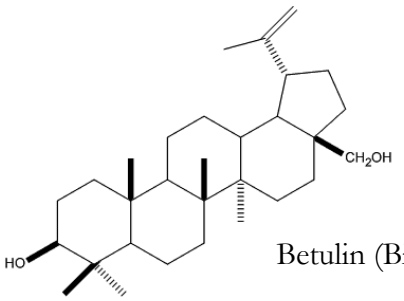
Phthalate Plasticizer

R- alkyl group

Terpenoids



Abietic Acid (Pine)



Betulin (Birch Bark)

Figure 3-1: Lipid Structures

3a. Fats, Oils, and Other Organic Extracts: Historical Context and Present Use

Fats and oils, the predominantly triacylglycerol-containing extracts from animal tissues and plant matter, have been important commodities since antiquity in a variety of contexts including as foodstuffs, fuel, lubricants, and unguents. In modernity, the production and consumption of vegetable oils, including soybean, rapeseed, palm, sunflower, and olive, has continued and over at least the last twenty years steadily increased. Nearly seventy-five percent of all fats and oils produced today are plant based and together soy, palm, sunflower, and rapeseed oils account for over seventy percent of those oils[74]. It is estimated that 183 tonnes of vegetable oils were produced worldwide in 2012. The current oil production and figures according to the United States Food and Drug Administration is 175.84 million metric tonnes for 2014/15 worldwide, up from 148.97 million metric tonnes in 2010.[75] Since 1987, the production and consumption of these oils have averaged a growth of 3.86 million metric tonnes per year.[76] Many of the modern uses of fats and oils, such as in cooking, perfumes and unguents, cosmetics, fuel, and lubricants are similar to the function of these substances in antiquity.

Some of the early terminology and references to oils in antiquity have given rise to many of the terms used presently to refer to the biogenic compounds and distinguish between fat or oil types. A look into the number of different words that were used in reference to fats and oils also gives an indication of their importance in ancient societies (Table 3-1).

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[74] The REA Group, http://www.rea.co.uk/rea/en/markets/oilsandfats/worldproduction. Accessed last on 30 August, 2014.
[75] USDA Foreign Agriculture Service: www.fas.usda.gov/pdsonline, accessed last on 29 August 2014. Includes worldwide production of coconut, cottonseed, olive, palm kernel, peanut, rapeseed, soybean, and sunflower oils.
[76] Rosillo-Calle, *et al.* 2009.

Table 3-1: Ancient Terminology Relating to Oils and Fats[77]			
L.B	𐀏	Linear B - Oil	
GREEK	ἄλειφαρ (aleiphar)	Unguent, Anointing Oil	
	ἄλειμμα (aleimma)	Anything uses as unguent	
	ἔλαιον (elaion)	Olive oil	
	(thermolukhnon)	Lamp Oil	
	πισσέλαιον (pisselaion)	Oil with pitch	
	δημός (demos)	Fat	
	λίπος (lipos)	Animal fat, lard, tallow	Engish: lipid
	πῖαρ (piar)	Fat	
	πιμελή (pimeleh)	Soft fat, lard	
	στέαρ (stear)	Hard fat, suet	
	παχύς (paxus)	Thick, curdled, fat	
LATIN	Oleum	Oil, olive oil	From ἔλαιον (elaion) English: oil
	Adeps	Soft fat, grease, lard	English: Adipose
	Sebum	Hard fat, tallow, suet	English: Serum
	Pinquis	Fatty	From παχύς (paxus) πῖον (fat rich milk)

The Greeks did not only distinguish between plant and animal fats and oils, but also between oils according to their use, such as an unguent oil or an illuminant oil. They also linguistically distinguished between a number of plant oils providing substantial evidence of the number of plant oils readily available and known in the classical Greek world. The corpus of these plant oils includes olive oil, radish oils, bay oils, fragrant oils, mustard oils, chamomile oil, cedar oil, castor oil, almond oil, dill oil and others. In total, the Liddell-Scott-Jones Greek-English Lexicon records 139 entries of Greek terms relating to oils, items having to do with oils, and people who worked with or used oils. Fats are referred to at least 60 times. By the time of the Roman Empire, there are fewer terms in use which mostly

[77] Greek definitions from Liddell-Scott-Jones *Greek-English Lexicon.* Latin definitions from Lewis & Short, *A Latin Dictionary* (1879)

correspond to the physical nature of the oil or fat and less with its origin or potential uses. *Oleum* was used for oils, *adeps* for soft fats, greases, or lard, and *sebum* for hard fats, tallow, and suet. The modern term *fat* came into use about 1539 CE with the following definition: *oily concrete substance of which the fat parts of the animal bodies are chiefly composed*. This comes from the Anglo-Saxon *faett* (to fatten) from Latin *pinguis*, from Greek *paxus*, from the Sanskrit, *payate* meaning swells, grows, leems, fattens.[78]

In *Naturalis Historia (The Natural History)*, Pliny the Elder describes at length the *natural world, that is life,*[79] known to the Roman world circa 77-79 CE. In this encyclopaedic work, Pliny wrote upon the topics of astronomy, meteorology, geography, mineralogy, zoology, and botany, along with addendums concerning human invention and institutions such as agriculture, medicine, art history, and metallurgy. Books 20-27 are mostly concerned with trees, plants and flowers and especially their use in medicine. He writes the following in regards to the use and extracts of the plants known to him in the classical Roman world: f*or of the plants mentioned, already the greater number (owing to their excellence as food, perfume or ornament) have led to repeated experiments; of the rest it is their efficacy that proves nothing is created by Nature without some more hidden reason than those mentioned.*[80] From stomach ailments, to infections, to improving the complexion, Pliny describes in great detail the medicinal and non-medicinal uses for plant and their extracts. He includes supposedly tried and tested medicines, some of which are still used today (such as castor oil for loosening bowl movements and joint health[81], or almond oil for cosmetic use to clear and moisturize the face[82]) and some of which Pliny admits were suspect and based on hearsay (such as the positive and negative effects of wine[83]).

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[78] Gidez, 1984.
[79] *Rerum natura, hoc est vita.* Pliny the Elder, *Natural History*, 1:13.
[80] Pliny the Elder, *Natural History*, 22.1
[81] Pliny the Elder, *Natural History,* 23.83.
[82] Pliny the Elder, *Natural History*, 23.85.
[83] Pliny the Elder, *Natural History,* 23.33-54

Whether or not he had first-hand knowledge of the preparation of such medicines and substances, Pliny provides not only information of some of the benefits and disadvantages of using these plants and their extracts, but also occasional information concerning the preparation and differing qualities of the substances. He speaks of the preparation of beeswax and honey to greater or lesser qualities,[84] certain plants used in the dying of textiles[85], and an array of wines some of which are better or worse for regular consumption or for specific ailments along with warnings of overindulgence. Specifically he mentions several different types of olive oil classified based on purity, comparable to modern olive oil grading scales. He notes that the oil is useful for medicinal purposes but primarily the type *omphacium* is best, followed by green oil. The distinction between medicinal olive oil and that for general consumption as a foodstuff is specific: the oil should be *as fresh as possible, unless there is a special need for the oldest oil, thin, with a pleasant odour, and no pungent taste – in fact the reverse of what we look for when it is used in food.*[86] Many of these recipes are also referred to in the earlier writings of Theophrastus[87] and the roughly contemporary writings of Dioscorides[88] who refers to Pliny's work several times. In total, the discussion includes at least eleven different varieties of oil which must have been regularly used in the Roman world: almond oil, laurel oil, myrtle oil, cypress oil, balsam oil, narcissus oil, radish oil, sesame oil, oil of lily (also known as Syrian oil), palm oil, and olive oil. Pliny's *Naturalis Historia*, along with Theophrastus' *Historia Planatarum* and Dioscorides' *De Materia Medica*, provide unique insights into the knowledge of oils in antiquity and form the basis of comparison for residues in vessels dating to the surrounding periods.

The medicinal uses mentioned here are simply one of the many functions and uses of fats, oils, and other plant extracts in antiquity and today. The use of fats and oils as a

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[84] Pliny the Elder, *Natural History*, 21.83-85
[85] Pliny the Elder, *Natural History*, 22.1
[86] Pliny the Elder, *Natural History*, 23.79
[87] *Historia Planatarum*, Greek text, 3rd century BC.
[88] *De Materia Medica*, Greek text, 1st century AD.

foodstuff cannot be underestimated in its commonality, however there is interest in the many other potential uses and functions. Oils, fats, and waxes can serve as illuminants and fuels in the form of candles, oil lamps, torches, etc. Oils and resins have been used throughout antiquity to the present as the base for perfumes, embalming materials, and incense. Beyond these the utilitarian functions and the many others that these substances have in society, it is worth noting that like other materials, oils and organic extracts can also have societal meanings and serve functions as symbols. In the Near East and elsewhere, oils have been used in ritual peace offerings. Incense frequently has religious or spiritual implications, representing prayers, cleansing, or centring of the mind. In many cultures, especially in the Christian, Jewish, and Muslim traditions, oils are used in anointing and consecration. The Old Testament details uses of oils in consecrations such as that of Aaron and Moses (Exodus 30:22-25) and also gives a prohibition of consumption of the fats of oxen, sheep, or goats (Leviticus 7:23-25) for religious purposes. In the Christian era, these oils of consecration and offering are echoed in anointing during baptismal rites, prayers for the sick, and funerals. Oils of blessing, anointing, and consecration can also be seen in the coronation rites of many European monarchs.

3b. Lipid Chemistry

Oils and fats are both chemically defined as predominantly containing triacylglycerols, the only differentiation between the two being their physical state at room temperature (i.e. fats taking the form of a solid, and oils the form of a liquid). Main non-triacylglycerol components of fats and oils are phospholipids (2-3%), carotenoids (minor amounts; the reason for yellowness in oils), and steroids (including the sterols, stigmasterol and cholesterol, sterol esters, and hopanoids). Most freshly extracted oils will also contain a

certain concentration of free fatty acids, the degradation products of triacylglycerols.[89] Together these compounds make up the class of compounds referred to as lipids. Lipids are defined as a chemically heterogeneous group of substances which are insoluble in water and soluble in organic solvents such as chloroform, hydrocarbons, or alcohols.[90]

In addition to their widespread functions in the natural world, lipids are one of the most well preserved organic molecular species according to the following degradation order:

Lignin and plant polymers < lipids < carbohydrates < proteins < nucleotides.

This order is based on the susceptibility of each of these molecules to chemical and microbial attack on key functional linkages.[91] The preservation of lipids in archaeological contexts, while better than other biomolecules such as proteins[92] and DNA[93], is still far from perfect. In any environmental situation, but especially in a burial environment, specimens are subjected to intense chemical and microbial attack. Depending on the physical and chemical properties of the material and the conditions of the burial environment, certain materials will be preferentially preserved or destroyed. In general, organics exhibit the best preservation in dry and arid (desiccating),[94] waterlogged,[95] or frozen[96] environments, where chemical and microbial attack is minimized. Lipids, however, have properties that allow for their survival over other biomolecules in most environments. The partially polar and hydrophobic nature of lipids prevents their leaching into the soil with ground water. Likewise, the protection of

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[89] Ratledge, 1994.
[90] Gurr and Harwood, 1991.
[91] Evershed, 1993.
[92] Barker, *et al* 2012; Craig and Collins, 2000 and 2002; Craig, *et al.* 2001. Note difficulties in detecting the preservation of proteins have been affected by their identification via immunological assays. As a result of the employment of this technique, degraded proteins which have lost their conformational structure are not normally detected as they lose reactivity with the loss of conformational attributes. Work has been done by Craig, Collins, and others to investigate new methods of detecting proteins to abate this bias in the archaeological record.
[93] Gilbert, *et al.* 2005; Pääbo, *et al.* 2004. DNA studies have significant difficulties due to the poor preservation of nucleotides and their preservation generally confined to waterlogged, frozen, or desiccated environments. The high levels of potential contamination also pose significant challenges.
[94] E.g. Mummies and Extremely Arid Environments: Buckley, *et al.* 1983.; Kuksis, *et al.* 1978.; Gülaçar, *et al.* 1990.
[95] E.g. Bog bodies and Waterlogged Environments: Evershed, 1990 and 1992; Evershed and Connolly, 1988 and 1994.
[96] E.g. Icemen and Frozen environments: Mayer, *et al.* 1997.

lipids by inorganic matrices (such as lipids absorbed into ceramics) results in a high frequency of lipids in archaeological contexts.[97] While lipid preservation is higher than other biomolecules in most contexts, it is still essential to note that lipid mixtures and especially larger biomolecules can be highly fragmented and the complex and fragmented mixtures that result can make analysis and identification extremely difficult.[98] In the following paragraphs, some major sub-classes of lipids which are commonly found in archaeological residues are outlined.

Triacylglycerols and Fatty Acids

As mentioned above, triacylglycerols are the major constituent of fats and oils. The structure of triacylglycerols consists of three acyl lipid moieties attached to a glycerol backbone. The degradation of these triacylglycerols leads to the breaking off of theses acyl groups into free fatty acids, also sometimes referred to as non-esterified fatty acids (Figure 3-2). The degradation of triacylglycerols into free fatty acids and the degradation reactions which affect free fatty acids is discussed in further detail in Section 3c. These free fatty acids are hydrocarbons with carboxyl functional groups. These compounds are hydrophobic in nature and are micelle forming, a phenomenon that can be easily seen in the separation and beading of oils within water.

[97] Evershed, 1993 and 2008a.
[98] Evershed, *et al.* 2001.

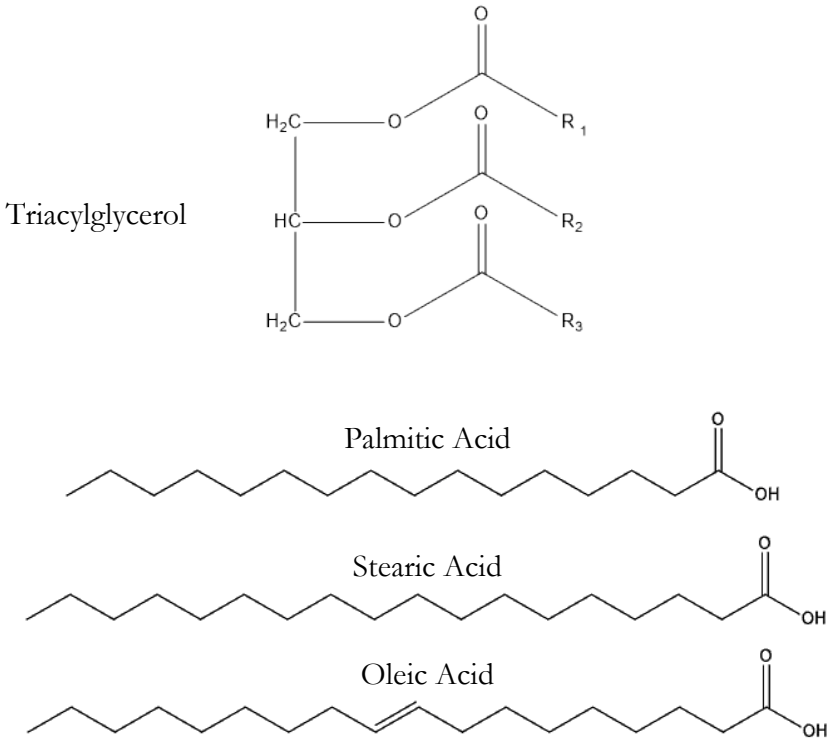

Figure 3-2: Triacylglycerols and Fatty Acids

Most fatty acids do not typically exist as free fatty acids within biorganisms and those that do are generally even carbon chain molecules which have carbon chains ranging in length between C12 and C22. Fatty acids can either be saturated straight chain molecules or have unsaturation sites with double bonds. Unsaturated fatty acids are slightly less common in nature, beyond oleic ($C_{18:1}$) and linoleic acids ($C_{18:2}$), and their conformations and double bonds cause them to be more susceptible to chemical attack and degradation. The most abundant fatty acids in triacylglycerols are palmitic ($C_{16:0}$), stearic ($C_{18:0}$), oleic ($C_{18:1}$), and linoleic acids ($C_{18:2}$). Plants usually have higher proportions of unsaturated fatty acids, with the exception of coconut and palm oils.[99] Milks have higher proportions of short chain fatty acids (2-10 carbon lengths) than their host animal fats.[100]

[99] Gurr and Harwood, 1991.
[100] Gurr and Harwood, 1991.

Triacylglycerols primarily function as energy storage in plants and animals. In the human body, consumed fats and oils can either be immediately used in energy production or stored for later use. The free fatty acids that result from the metabolism of triacylglycerols in storage fats, are converted to thiol esters and enter the metabolic cycles of the human body directly through the ß-oxidation cycle within mitochondria. The dietary lipids that humans consume in fats and oils are broken down by bile acids and are transported through the blood stream as complexes with proteins (lipoproteins) and are either resynthesized as storage fats or enter the metabolic cycle. These reactions involving the component fatty acids are both anabolic (synthetic) and catabolic (degradative) mechanisms. Fatty acids can be converted into thiol esters with either ACP or coenzyme A. Coenzyme A fatty acid esters then enter the ß-oxidation metabolic cycle in mitochondria to provide energy, breaking down by 2 carbon lengths with each revolution of the cycle. Once the compound reaches its base carbohydrate (CH3CO-S-CoA), it can then enter the TCA cycle and the electron transport chain, resulting in energy, CO_2, and water. In predominantly oxygen-rich environments, these same lipids are involved in peroxidation reactions which are increasingly being regarded as important players in non-enzymatic reactions which have uses both in industry and medicine. In biological tissues, uncontrolled lipid production causes membrane destruction and this process is thought to be a factor in the early development of certain diseases and their eventual diagnosis and treatment.[101]

Terpenoids

Terpenoids are the main constituents of resins and gums, a group of plant exudates which can be heated to form tars and pitches.[102] These materials are water insoluble, having

[101] Gurr and Harwood, 1991.
[102] Gurr and Harwood, 1991.

protective functions within plants and can be used for adhesives,[103] sealants,[104] preservatives,[105] incense,[106] paint binders,[107] flavourings,[108] and medicinal treatments.[109] Terpenes or terpenoids are chemically defined as hydrocarbons of biological origin derived from isoprene units (CH_2═ $CH(CH_2)_nCH$═CH_2). This class of compounds can be further classified into groups according to the number of isoprene units, namely monoterpenoids (C10 compounds), sesquiterpenoids (C15), diterpenoids (C20), and triterpenoids (C30). Each of these sub-classifications can be broadly attributed to and serve as biomarkers for specific classes or species of plants and the oils and resins that they exude.

Monoterpenoids and sesquiterpenoids (Table 3-2) broadly make up the major compounds found in essential oils and are the predominantly aromatic constituents of these oils. Generally these molecules are volatile and do not survive the archaeological record well. The exception to this trend is fossilized resins where camphor and fenchone have been detected[110] and in resins found upon shipwrecks[111], where they are found within solidified resinous material which protects them from oxidation and removal.[112]

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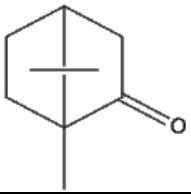
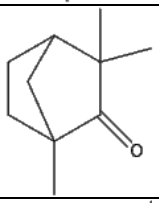
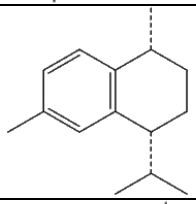
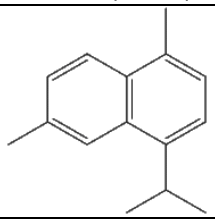
[103] Charters, *et al.* 1993a.; Fraser, *et al.* 2013.
[104] Sealing of pottery: Beck, *et al* 1989.; Lampert, *et al.* 2002.; Romanus, *et al.* 2009.
Waterproofing as seen in the construction of the Mary Rose: Evershed, *et al.* 1985 and Robinson, *et al.* 1987.
[105] Embalming agent: Buckley, *et al.* 1999; Nicholson, *et al.* 2011. Preservative for wine: McGovern, 1997.
[106] Evershed, van Bergen, *et al.* 1997.
[107] Colombini, *et al*, 2003.
[108] McGovern, *et al.* 1996; Tzedakis, *et al.* 2008.
[109] Edwards, *et al.* 2004.
[110] Mills, *et al.* 1984.
[111] Robinson, *et al.* 1987.
[112] Pollard and Heron, 2008:238.

Table 3-2: Monoterpenoids and Sesquiterpenoids			
Compound	Origin	Structure	Other Information and Uses
Camphor	Camphor Laurel, other laurel trees		Modern medicinal uses.
Fenchone	Oil of fennel		
Calamenene	Softwood tar		
Cadalene	Softwood tar		

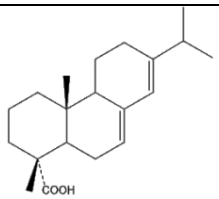
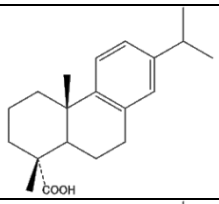
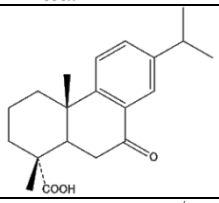
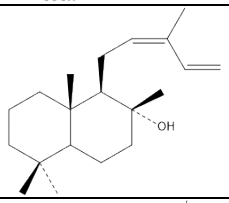
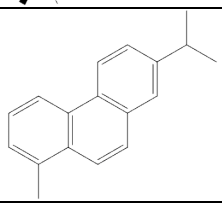
The diterpenoids, containing 20 carbon centres, are the main constituents of coniferous resins, namely *Pinaceae* (pine), *Cupressaceae* (cypress), and *Araucariaceae* (Table 3-3). The major diterpenoid compound is abietic acid, and its oxidation products dehydroabietic acid and oxodehydroabietic acid, both of which make up only trace amounts of fresh coniferous resins but increase in concentration with heating and aging. These two compounds have formed the basis of the identification of pine resins in the waterproofing of the Mary Rose[113] and linings of Roman transport amphorae[114]. Triterpenoids are among the most common terpenoids in nature and rarely occur in the same substances which diterpenoids exist (Table 3-4). Important archaeological resins which are primarily

[113] Evershed, *et al.* 1985; Robinson, *et al.* 1987.
[114] Heron and Pollard, 1988.

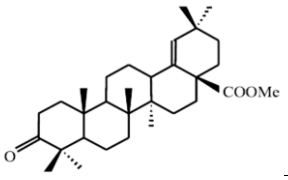
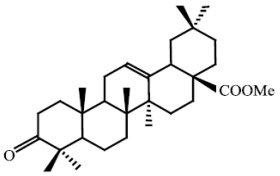
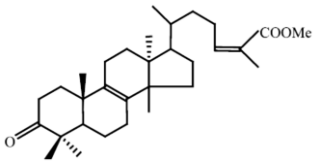
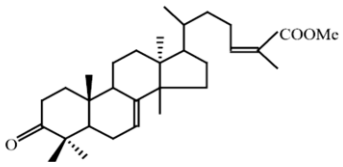
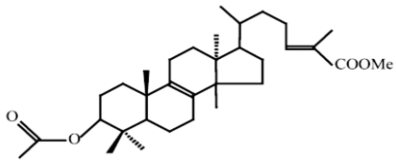
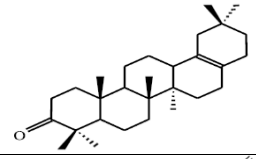
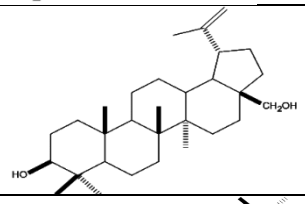
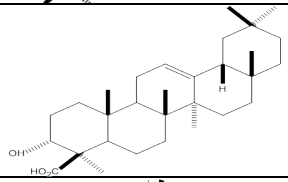
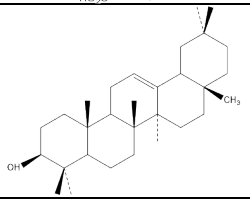
composed of triterpenoid compounds are frankincense,[115] dammar resins,[116] and pistacia resins.[117]

Terpenoids become defunctionalized through heating to become aromatic, alkyl-substituted, dehydrogenated, and decarboxylated compounds. The breakdown of original terpenoid compounds follows predictable pathways. For example, diterpenoids usually end in the compound retene with dehydroabietane, dehydroabietin, simonellite, and nor-abietatriene intermediates. These defunctionalized constituents can be biomarkers in their own right as the distillation of certain resins into pitches or tars is desirable for any number of similar functions. Pine pitch is the diterpenoid containing pitch which results from the distillation of pine resin has been used on the Mary Rose[118] and other shipwrecks[119]. Similarly, the triterpenoid tar made from birch bark is also a common archaeological find[120].

[115] Evershed, *et al.* 1997; Evershed, van Bergen, *et al.* 1999.
[116] Pollard and Heron, 2008: 241.
[117] Mills and White, 1989; Nicholson, *et al.* 2011; Stern, *et al.* 2003.
[118] Evershed, *et al.* 1985; Robinson, *et al* 1987
[119] Reunanen, *et al.* 1989.
[120] Charters, *et al.* 1993a; Reunanen, *et al.* 1993.; Aveling and Heron, 1998 and 1999.

Table 3-3: Diterpenoids			
Compound	Origin	Structure	Other Notes
Abietic Acid	*Pinaceae*[121] and most of the Coniferae family.		diterpenoid
Dehydroabietic Acid	*Pinus* and other coniferous[122]		Most abundant in aged *Pinus*.
7-oxodehdyroabietic acid	*Pinus* and other coniferous		
cis-abienol	Fir		
Retene	Tars made from diterpenoid resins, particularly those of Coniferae family		Defunctionalized diterpenoid

[121] Beck, *et al.* 1989; Evershed, *et al.* 1985
[122] Heron and Pollard, 1988; Robinson, *et al.* 1987.

Table 3-4: Triterpenoids			
Compound	**Origin**	**Structure**	**Other Notes**
Methyl Moronate	Pistacia Resin		Most abundant triterpenoid in Ancient Resin
Methyl Oleanonate	Chios Turpentine[123], Pistacia Resin		
Methyl Isomasticadienonate	Pistacia resin		One of first triterpenoids to degrade at 300C
Methyl Masticadienonate	Pistacia Resin, Terebinth		One of first triterpenoids to degrade
3α-acetoxy-isomasticadienolate	Pistacia Resin		Only present in modern resins
28-norolean-17-en-3-one	Heated/degraded pistacia resin[124]		Archaeological resins – heating of oleanonoic acid
Lup-20(29)-ene-3ß, 28-diol (Betulin)	Birch Bark[125]		
Boswellic Acid	Frankincense[126]		
ß-Amyrin	Chios Turpentine[127], Pistacia Resin		

[123] Mills and White, 1989.
[124] Stern, *et al.* 2003.
[125] Ruthenberg, *et al.* 2001.; Charters, *et al.* 1993a.; Urem-Kotsou, *et al.* 2002.
[126] Evershed, *et al.* 1997; Evershed, van Bergen, *et al.* 1999.
[127] Mills and White, 1989.

3c. Issues in Preservation: Alteration, Removal, and Contamination

In the following section, some of the main issues in the preservation of lipid materials in archaeological contexts are discussed. The bias of the archaeological record is twofold. First, there are cultural, social, and economic factors that can result in the presence or absence of molecular organic materials in the record. Factors such as cleaning, recycling, breakage, intentional discard, or unintentional discard dictate whether the artefact and any associated materials may be preserved (i.e. the encapsulation of a residue within a charred deposit, adhesion to a tool, or absorption within pores). Secondly, lipids and other biomolecules are subject to a number of degradation reactions (oxidation, hydrolysis, pyrolysis) that have been studied extensively and are known to chemists and archaeological scientists. Intact lipid profiles of original contents are rarely, if ever, found in archaeological contexts due to these reactions. In the reconstruction of past vessel use, the extrapolation of original contents must be made on the basis of these degradation products rather than the original lipid profile. The nature of the burial environment, including soil moisture and pH levels, ground water flux, microbial content, and natural lipid content, contributes greatly to the extent of degradation. In general, the preservation of biomolecules and artefacts is the highest in extreme environments where the influences of the burial environment are minimized (i.e. desiccating, frozen, and waterlogged environments). Oxidation, hydrolysis, and pyrolysis reactions are some of the most common degradation reactions that plague biomolecules once they have left the living system. Such reactions can then be intensified and changed with the attack of microbes in the system. Each of these processes are discussed below.

Oxidation and Hydrolysis

As mentioned above, triacylglycerols are one of the most common lipid moieties in animal fats and plant oils. These molecules contain three acyl lipid chains connected via a glyceride backbone. These chains are highly susceptible to hydrolysis reactions that result in di- and mono-acylglycerols and free fatty acids. The mechanism by which this occurs is shown in Figure 3-3.

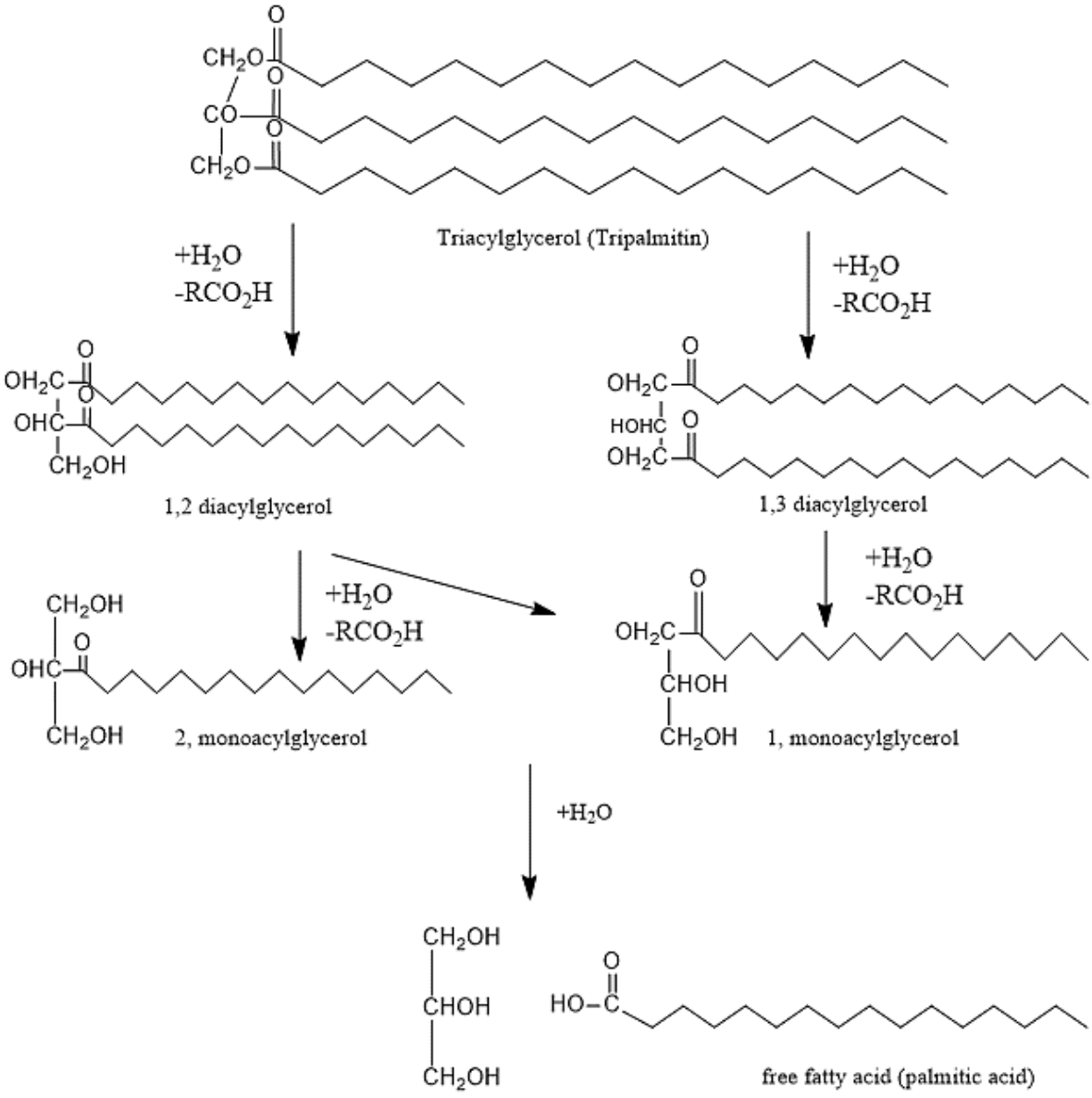
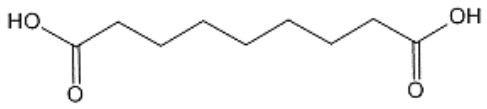


Figure 3-3: Hydrolysis of Triacylglycerols (Evershed, *et al.* 2001)
Tripalmitin to palmitic acid and glycerol.

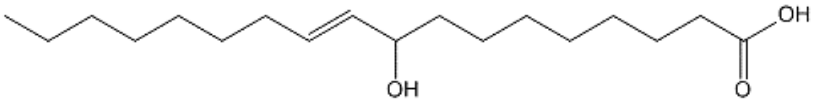
The free fatty acids that are produced from the above hydrolysis reaction are much more stable in their conformation and size than their parent triacylglycerols. The hydrolysis of triacylglycerols results in a lipid profile for animal fats consisting of small amounts of tri-, di-, and mono- acylglycerols with large quantities of the saturated fatty acids $C_{14:0}$, $C_{16:0}$, and $C_{18:0}$. The triacylglycerol profiles for plant oils such as olive oils will have different proportions of the constituent fatty acids as well as the addition of unsaturated fatty acids. The creation of unsaturated fatty acids, either through the hydrolysis of acylglycerols or by their natural presence, opens the residue up to oxidation reactions.

Oxidation usually proceeds where there is an unstable double bond in the hydrocarbon chain, resulting in the formation of unsaturated and substituted species (Figure 3-4).

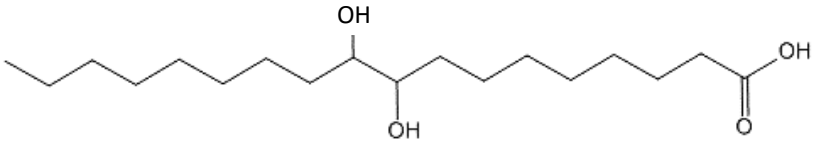
C_9:α,ω-dicarboxylic acid/nonanedioic acid (azaleic acid)



9-hydroxyoctadecenoic acid



9,10-dihydroxyoctadecanoic acid



ω-hydroxydodecanoic acid

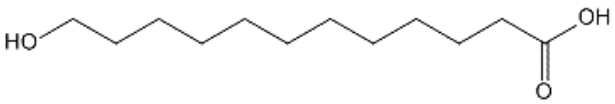


Figure 3-4: Examples of Fatty Acid Oxidation (Regert, *et al.* 1998)

The oxidative mechanisms that create these dicarboxylic acids, ω-hydroxy acids, hydroxyl, and dihydroxy acids can be quite complex. Four main oxidation mechanisms are typically reflected in the product profile: 1) cleavage of the double bond, 2) hydration/hydroxylation followed by cleavage of the double bond, 3) ω-oxidation followed by cleavage of the double bond, and 4) ω-oxidation, hydration/hydroxylation, and then cleavage of the double bond. An example of one of these mechanisms is demonstrated in Figure 3-5, which shows the oxidation of oleic acid by dihydroxylation and dehydrative cleavage.[128]

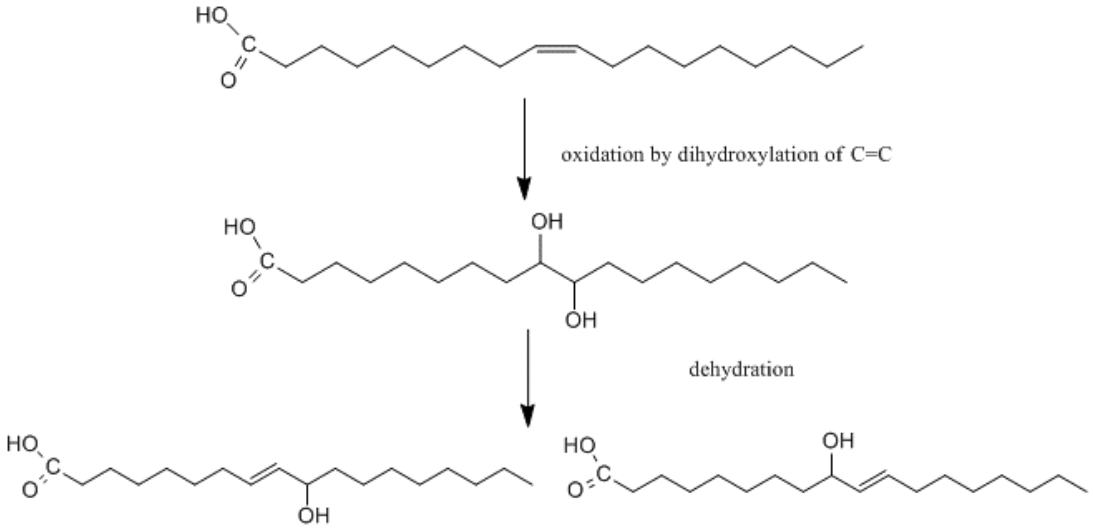


Figure 3-5: The Oxidation of Oleic Acid (Regert, *et al.* 1998)

The products of the hydrolysis of triacylglycerols are well attested in archaeological residue samples,[129] but interestingly enough, while it is known that oxidation products should be present in such samples, they are not often observed. Because these products are much smaller than their acylglycerol and longer free fatty acid counterparts, it has been assumed that these oxidation products are leached out of archaeological samples during burial. It is now known that the opposite is true. These diacids are not leached out of ceramic samples

[128] Regert, *et al.* 1998.
[129] Evershed 2008a.

but also cannot be extracted with conventional solvents leading to their apparent absence in archaeological residues. By using an alkaline extraction, these molecules can be removed from the ceramic matrix. This suggests that they are bound to the ceramic itself, possibly through ester linkages.[130] In this way, α,ω-dicarboxylic acids from C_7 to C_{12}, α-hydroxy carboxylic acids, and unsaturated hydroxyoctadecenoic acid have been recovered. The suggestion that oxidation products are bound to the ceramic and not simply missing from the record provides some of the first evidence for the ceramic matrix being directly involved in the preservation of organic molecules and not simply a host for their protection.

Condensation/Ketone Formation

One of the best examples of the knowledge of degradation and preservation affecting the interpretation of residues is the identification of ketones. Ketones were once taken to be exclusively a marker for the use of leafy vegetables in antiquity. For example, the epicuticular waxes of cabbage produces a lipid profile containing nonacosane (C_{29} alkane), its oxygenated derivatives (nonacosan-15-one and nonacosan-15-ol), along with other ketones and long-chain alkyl lipids.[131] It is now known that similar ketones are formed through a pyrolytic condensation reaction involving saturated fatty acids from animal fats. The discovery of this set of reactions in an archaeological context arose from two observations. First, a profile containing a consistent ratio of 1:2:1 of $C_{31,}$ C_{33}, C_{35} ketones not known in nature. In addition the asymmetric C_{33} ketone is not normally found in plants. Secondly, when isotope measurements were taken, the $\delta^{13}C$ values more closely reflected that of animals rather than plants.[132]

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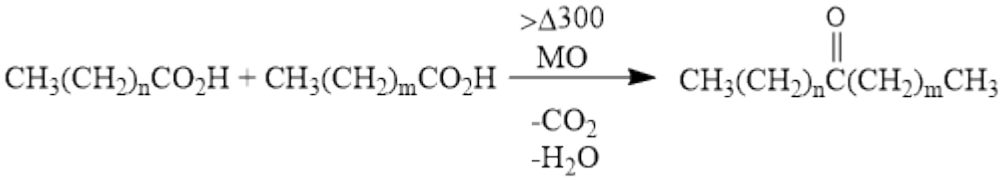
[130] Regert, *et al.* 1998.
[131] Evershed, *et al.* 1991.
[132] Evershed, Stott, *et al.* 1995; Raven, *et al.* 1997.

These ketones are formed by the condensation of fatty acids according to the following mechanism:



$$CH_3(CH_2)_nCO_2H + CH_3(CH_2)_mCO_2H \xrightarrow[-CO_2,\ -H_2O]{>\Delta 300,\ MO} CH_3(CH_2)_nC(=O)(CH_2)_mCH_3$$

This reaction occurs pyrolytically at temperatures in excess of 300C (i.e. cooking situations). It is also important to note that this reaction is a metallic intermediate (generally calcium, iron, thorium, or magnesium). Archaeologically, these metals are found in fired clay sources, meaning that for at least a short time the fatty acids are in a complex with the ceramic. The formation and presence of these long chain ketones are also able to explain the presence of other shorter chain methyl ketones and alkenes, which were before unexplained. Long-chain ketones can undergo a 6-centre rearrangement/condensation reaction according to the mechanism presented in Figure 3-6. This reaction is also dependent on the metals available in the ceramic matrix.

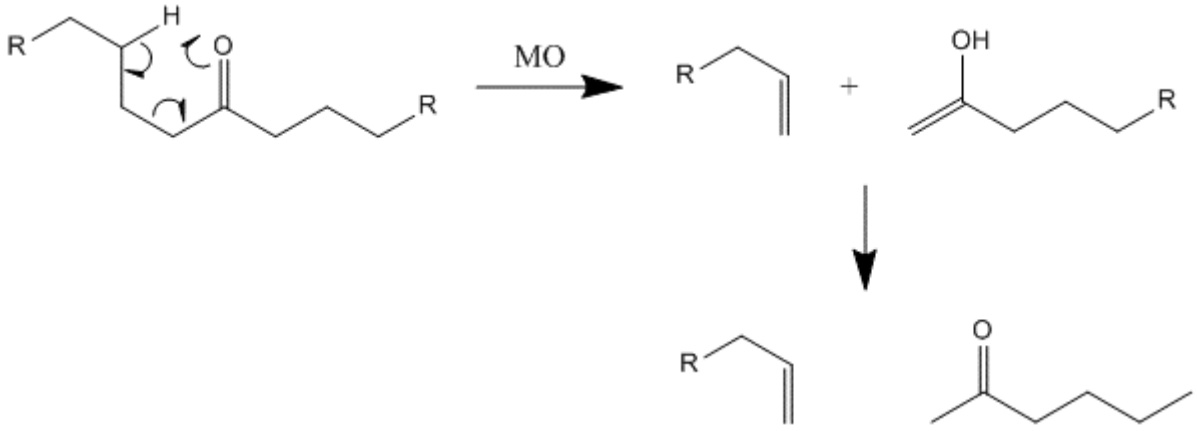


Figure 3-6: Six-Centre Rearrangement and Degradation of Ketones

Microbial Attack and the Burial Environment

The burial environment of an artefact has a significant effect on the preservation of artefacts. Soil chemistry, groundwater, micro-organisms, and the simple change in environment contribute to preservation and degradation. The presence of micro-organisms in the burial environment intensifies normal degradation reactions with bacterial degradation beginning shortly after burial. Simulation experiments involving olive oil and milk samples incubated in mushroom compost under aerobic conditions show that after ten days there is a 90-95% hydrolysis of triacylglycerols into free fatty acids. This degradation, explained above, is most likely both chemically and biologically mediated. Under normal circumstances this hydrolysis does occur, but proceeds at a much faster rate in a highly microbial environment. While it could be expected that the microbial action would leave some trace of a lipid profile unique to these bacteria, the distinction between the hydrolysis profile of microbial accelerated decay and un-accelerated hydrolysis is undistinguishable. The most recognized markers of bacterial action are branched-fatty acids that are the major constituents of membrane lipids. This lipid profile can be identified also in ruminant fats due to the high levels of bacteria in the rumen itself, but in the above study, less than 2% of the degraded lipid concentration were microbial lipid markers.[133]

Removal of organics by groundwater and the alteration of residues by bacteria, along with contamination by soil lipids derived from decaying organic matter, have long been considered to be major sources of alteration and contamination in archaeological residues.[134] The actual impact of these factors, however, does not seem to be as significant to degraded archaeological lipid profiles. Certainly in the case of microbial attack, bacterial and fungal action accelerates the decay of organics, but does not seem to contribute its own set of lipids.[135] The migration of soil lipids also seems to be minimal in archaeological samples. In

[133] Dudd, *et al.* 1998.
[134] e.g. Heron, *et al.* 1991.
[135] Dudd, *et al.* 1998.

studies that compare soil lipids with those extracted from sherds from the same context, significantly different profiles have been observed.[136] This would seem to indicate that the environment is not one in which lipids are freely exchanged but are in some way connected to a specific matrix. The effects of groundwater are hard to define. When an expected organic molecule or its degradation products are absent from a system there are two standard explanations. First, the compound was never there. Second, the compound or its products have leached out of the system. There is very little that can be done to prove either solution.

[136] Heron, *et al.* 1991.

4. The Identification of Residues: A Literature Survey

Building on the overview of lipid chemistry and the chemical challenges in the preservation and degradation of molecular organic materials presented in the previous chapter, the discussion now turns to the recovery and analysis of lipids and other biogenic molecular organics found in the archaeological record. The identification of archaeological residues and the biomarker approach are outlined in light of their chemistry and the analysis of their contexts within the record. Then an overview of the development, history, and current state of archaeological residues is detailed and evaluated.

4a. The Archaeological Biomarker Approach

The analysis of organic residues in archaeological contexts is based on "the archaeological biomarker approach". Formally defined by Richard Evershed, this approach is the comparison of various biomarkers, that is individual compounds or mixtures of compounds, present in archaeological organic substances, to those present in contemporary reference materials in an attempt to recognize the source of the material.[137] On the premise that a compound or ratio of compounds is specific to an individual living thing and tied to particular functions within the original source, one has the potential to reconstruct the materials that were being manipulated in the past. In archaeological samples, the key aspect of these biomarkers is not the identification of the specific original molecule which is indicative of a specific organic substance, but the degradation product(s) that arise from it through predictable reactions and processes. For a number of reasons, the investigation of lipids from archaeological contexts is one of the most common forms of organic residue analysis performed today. As mentioned previously in Chapter 3, lipids are found in many organisms, fulfilling a great number and variety of specialized functions. Triacylglycerols, in the form of fats, provide storage for energy in animals, long chain alkyl compounds give

[137] Evershed, 1993 and 2008b.

structure to plants as the main constituents of natural waxes, terpenoids fill protective roles in plants as natural resins, and phospholipids are the main constituent of cell membranes,[138] and free fatty acids participate in metabolic cycles. Due to the specialized functions of these lipids, they serve as a prime example of the use of the archaeological biomarker approach. Since the nature of each lipid or combination of lipids defines its role, each class of organism will have a different abundance of a wide variety of lipids. If these can be matched and identified as biomarkers in extant species, and the same biomarkers can discovered in archaeological remains, a great deal of information can be garnered about the past. Some of the compounds that have been successfully used as individual biomarkers to identify archaeological organic residues are shown in Figure 4-1.

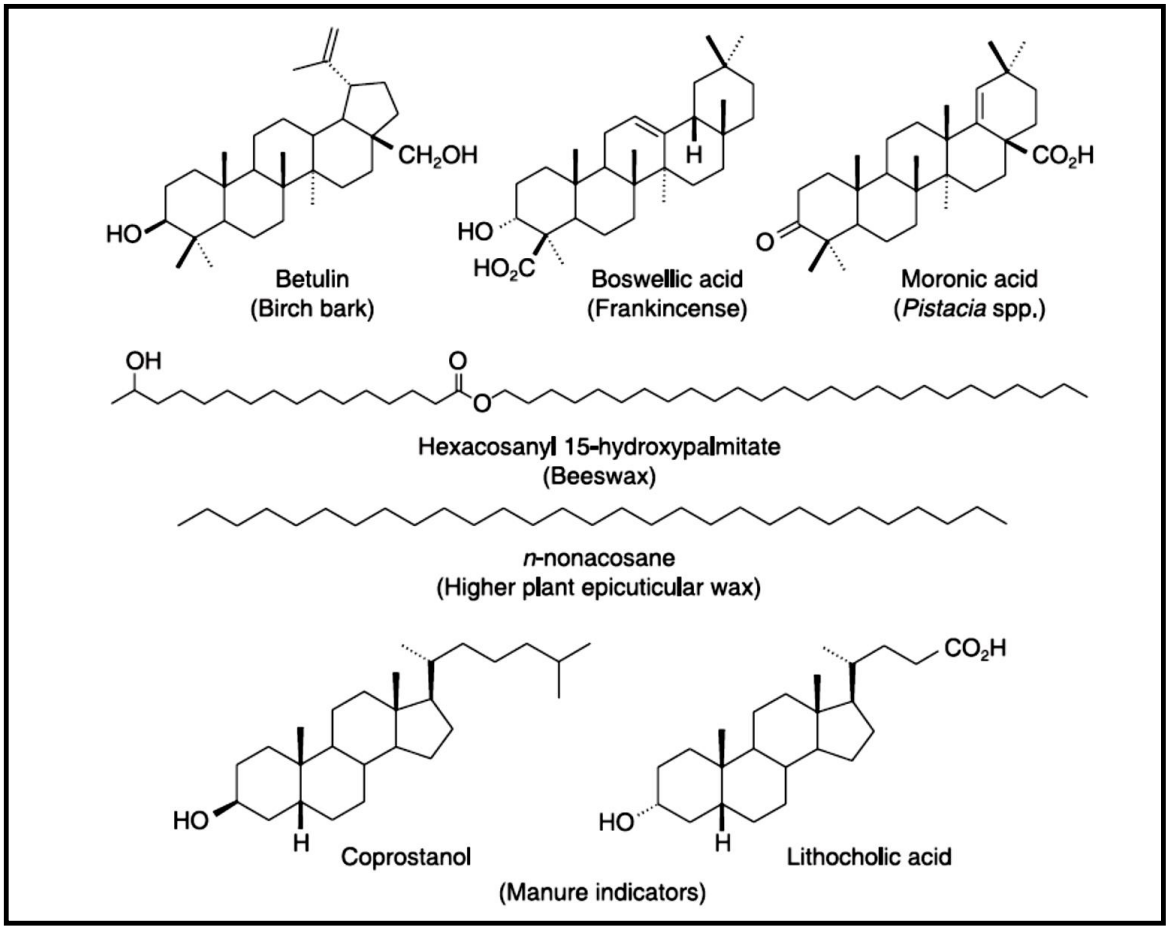


Figure 4-1: Archaeological Biomarkers (Evershed 2008b)

[138] Evershed, 1993.

Beyond the identification of biomarkers and the reconstruction of original substances through their degradation products, residues have been successfully characterized through two other methods to varying degrees of success. Through the use of isotope rationing mass spectrometry, further distinctions between plant, ruminant animal, non-ruminant animal fats, and oils have been able to be distinguished from one another. This has been particularly successful in the differentiation of these substances when the lipid profiles are not solely diagnostic,[139] in the study of early dairying,[140] and the exploitation of marine oils.[141] Isotopic measurements have also been applied to the radiocarbon dating of single compounds isolated from archaeological residues to great effect.[142]

Somewhat more debated in archaeological residue studies has been the identification of original fats and oils based on the ratios of certain fatty acids. Specifically the ratios or comparable amounts of palmitic acid to stearic acid and stearic to oleic acid have been used and correlated to certain lipid sources (Table 4-1).[144]

Table 4-1: Fatty Acid Ratios in Fresh and Degraded Substances[143]

		Meat	Nuts	Berries	Roots	Fish	Greens
C16:0 / C18:0	Fresh	0-4	0-9	2-6	3-12	4-6	5-12
	Degraded	0-7	0-18	4-12	6-24	8-12	10-24
C16:1 / C18:1	Fresh	0.02-0.2	0-0.3	0-0.08	0.05-0.7	0.2-0.5	0-0.7
	Degraded	0.08-0.8	0-1.2	0-0.32	0.3-2.8	0.8-2	0-2.8

The oxidation rates of unsaturated fats are much higher than those for saturated ones.[145] Cooking processes, by design, result in chemical changes and accelerate degradation rates. The question then arises whether the ratios of certain fatty acids which are present in host fats and oils are persistent enough over time to from a secure basis for the identification

[139] Charrie-Duhaut, *et al.* 2009.; Copley, Bland, *et al.* 2005. Craig, *et al.* 2012.; Evershed, 2008a.; Evershed, *et al.* 1994 and 1999.; Evershed, Mottram, *et al.* 1997.; Mottram, *et al.* 1999.; Mukherjee, *et al.* 2007.; Steele, *et al.* 2010.
[140] Copley, Berstan, *et al.* 2005a and 2005b.; Dudd and Evershed, 1998.; Spangenberg, *et al.* 2006.
[141] Craig, *et al.* 2007.
[142] Berstan, *et al.* 2008.; Lampert, *et al.* 2002.; Stott, *et al.* 2001 and 2003.
[143] After Barnard, *et al.* 2007.
[144] Malainy, *et al.* 1999a, 199b, 199c, and 2007.
[145] DeMan, 1992.

of archaeological residues. Another potential problem with this approach lies in extraction efficiencies of methods used to study residues. The solubility of fatty acids and other lipids varies according to molecular size, functional group, and polarity. Some of the differential in extracted lipids is mitigated somewhat by the use of a combination of solvents, however the initial goal of using a combination solvent such as chloroform and methanol or dichloromethane and methanol is to ensure the widest range of lipids extracted, not necessarily equal rates of dissolution and extraction efficiency.

Eerkens argues that the unequal degradation of fatty acids is not as problematic as others would suggest.[146] By looking at experimental decomposition, it has been observed that while a $C_{16:1}$ to $C_{18:1}$ ratio increases overtime, the $C_{15:0}$ and $C_{17:0}$ to $C_{18:0}$ ratios remain relatively the same. Eerkens suggests that by taking into account general increases or decreases in the relative compositions, the biplots of these ratios can be adjusted satisfactorily to account for the differential degradation. When $C_{15:0} + C_{17:0}$ to $C_{18:0}$ ratio is plotted against a $C_{16:1}$ to $C_{18:1}$, and $C_{12:0}$ to $C_{14:0}$ ratio plotted against a $C_{16:0}$ to $C_{18:0}$ ratio, general ellipses begin to form for certain fatty acid sources, namely seed, root, meat, greens, fish, and berries (Figure 4-2).

[146] Eerkens, 2005 and 2007.

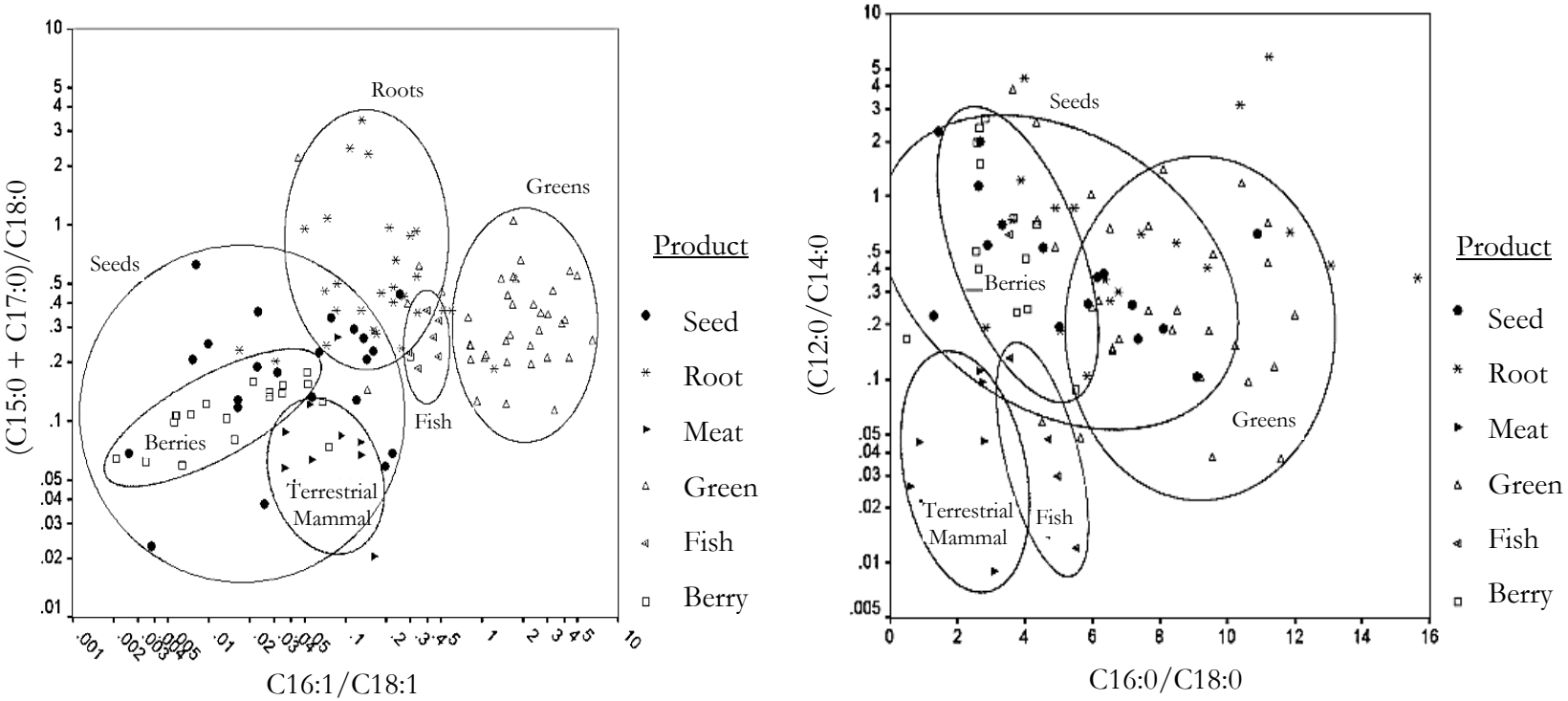


Figure 4-2: Bivariate Plots of Fatty Acid Ratios and Source Correlates
From Eerkens, 2005: Figures 2 and 3.

While these bivariate plots of fatty acid ratios could be useful in the identification of lipid sources, several issues with the technique remain. First, the overlaps of groups remain significant and blur potential correlations. For example, berries lie entirely within the range of seed oils[147]. Secondly, in order to make the securest attributions with this method, fatty acids from C12 to C18 all need to be present as the method depends on comparison of multiple ranges. It is likely that based on one set of ratios, the results from a given residue will fall within an overlapping region, necessitating comparison with a second set of fatty acids. Of course, this is only possible if the residue and its extract contain every fatty acid necessary for comparison. At best, this method can only provide broad categories of original sources, i.e. meat, fish, seed, green, roots, etc. and does very little towards identifying a specific source. Still, when other evidence is lacking and a specific biomarker is not present, such comparisons could be made cautiously to provide information through probable source correlations.

4b. The State of Organic Residue Analysis as Presented in the Literature

The study of residues has always been looked to as an important endeavour in the field of archaeology. However, organic residue analysis has been relatively slow in its development in comparison to other techniques frequently used in archaeological science due to limitations of the pace of technological development. While slow in its development, and despite the intrinsic need for improved methodologies, organic residue analysis has the potential to play a vital role in archaeological pursuits by augmenting our knowledge of diet, ritual practice, economic trends, and technological advancement in antiquity. In a world prolific with living things (fundamentally organic species), the exploitation of organic substances and the evidence of such are of paramount importance in archaeological inquiry.

[147] Eerkens, 2005: Figures 2 and 3.

Crafted and solid state items such as ceramic vessels, tool assemblages, and bones tend to be present ubiquitously in the archaeological record and provide indications of how individuals and societies manipulated their environments and interacted with one another. However, much is missing from the visible archaeological record due to either the nature of the original substance, as in the case of liquids, or cannot be identified or fully understood without chemical analysis. In light of these restrictions to conventional archaeology, the chemical investigation of organic residues is becoming an increasingly valuable and visible aspect of a scientific archaeology.

Archaeological residue analysis seeks to identify organic substances used in the past, whether original vessel contents, adhesives, dyes, or other materials that are now largely absent. The success of such a study relies on and is defined by the archaeological biomarker concept; the idea that substances in nature have unique chemical signatures and these signatures can be identified and related back to the original substance.[148] Organic residues can be found on a variety of materials; including ceramics, bone, stone tools, and fabrics; and due to the wide variety of organic substances and their ubiquitous nature, have the ability to provide information concerning a plethora of different activities. Some of the most commonly studied organic residues in archaeology have been resins (used as adhesives, preservatives, waterproofing), lipids (fats, oils, and waxes in diet, cosmetics, illumination), and other plant extracts (wine, beer, cacao).

Since the late 1800s and the growth in archaeological inquiry, scientists have fostered an interest in the study of molecular organic remains. In one of the earliest studies of residues in archaeological vessels, the French chemist M. Berthelot investigated the possible presence of wine and oils in sealed Gallo-Roman vessels.[149] Similarly around the turn of the twentieth century, Otto Helm began studying amber in an attempt to differentiate between

[148] Evershed 1993, 2008a
[149] Berthelot, 1877a and 1877b

Baltic and non-Baltic ambers based on the concentration of succinic acid present.[150] Early studies, such as Berthelot's study of Gallo-Roman vessel contents and the amber studies of Otto Helm, were severely limited by the chemical knowledge and available instrumentation and, as a result, many of the conclusions drawn by these respected scientists have been since revised. Tests of solubility, density, combustibility, reactivity, and even taste were common place in the pursuit of identifying ancient commodities during this period. In one of the first applications of this form of study to the Bronze Age Mediterranean, Augustus Gill analysed the contents of a Mycenaean stirrup jar which at the time was housed in the Way Collection of Egyptian Antiquities in the Museum of Fine Arts, Boston. Based on the amount of ash resulting from the burning of the residue, the solubility of the residue in various solutions, its melting point, and its resemblance to modern shellacs, Gill concluded that the vase had once contained coconut oil[151]. Certainly the results of this study make very little logical sense since coconuts had not been introduced to the area during the Bronze Age, yet this study and ones like it paved the way for modern studies and the development of science in archaeology.

A resurgence of residue studies occurred in the late 1960s and 1970s along with the advent of a more rigorous scientific approach to archaeology and the study of archaeological materials. With advancements in analytical technologies, such as infrared spectroscopy and gas chromatography, scientists began to take a second look at the properties of archaeological materials. Even though these studies began a renewal of science in archaeology, chemical studies at this time were largely limited to provenance studies such as that of Baltic amber[152] and it was not until the 1990s that organic residue analysis came to the state of which it is known today. The addition of gas chromatography- mass spectrometry (GC-MS) to the repertoire of available analytical techniques revolutionized the way in which scientists approach the study of organic materials. In GC-MS analyses, a substance is

[150] Beck *et al.* 1965; Beck 1995.
[151] Gill, 1906.
[152] Beck, 1995; Beck *et al.* 1965.

volatized and separated into its component compounds based on their affinity for a stationary phase. As each component compound exits the gas chromatographic column, it is subjected to ionization source (usually a reactive chemical ion or electron beam) which breaks it into diagnostic ions. These daughter ions are identified based on their mass to charge ratio and produce spectra unique to the parent compound. The extraction of organic residues from ceramic matrices and their subsequent analysis via GC-MS has been improved upon and routinely implemented for the detection of lipids.[153] While the study of organic residues, even with improvements in GC-MS technology, is still severely limited by detection limits, degradation of organics in the burial environment, and contamination during excavation, treatment, and analysis, it has been instrumental in broadening knowledge of the past.

The understanding of ritual, diet, technology, and economy has been drastically altered and augmented over the last few decades through these types of analysis. The possibility to elucidate the use of ritual vessels has been one of specific interest to archaeologists and in some cases residues have drastically altered prevailing theories. In one study, a set of canopic jars from the Louvre Museum, attributed to Rameses II were re-investigated. Through the identification and dating of the residual remains, the jars, inscribed with the cartouche of Rameses II, were discovered to have been used as unguent vessels during the second Intermediate Period and as canopic jars in the later Ptolemaic Period.[154] This study exemplifies the potential contributions to the elucidation of ritual practice in the past. By studying vessels from ritual contexts, one can gain a picture of what sorts of materials were used in a variety of rituals, from grave offerings (the unguents associated with Rameses II) to feasting.[155] In addition to ritual practice, residues have also

[153] Evershed, *et al.* 1990; Charters, *et al.* 1993b.
[154] Charrie-Dahut, *et al.* 2007.
[155] Hall, *et al.* 1990 gives evidence for cacao use in Mesoamerican ritual vessels.

been used to reconstruct diet,[156] describe technological advances such as illumination,[157] medicinal and cosmetic trends,[158] and trade.[159]

In reference to the Bronze Age Eastern Mediterranean, there have been at least four major study series of organic residues: Canaanite amphora from Amarna, Egypt,[160] the Ulu Burun resin cargo,[161] Mycenaean and Minoan pottery study and exhibition,[162] and a number of wine studies.[163] Each of them has provided archaeologists with insights into specific aspects of life in the Bronze Age Mediterranean. While the study of Mycenaean wares presents a view into the possible contents of cooking and feasting vessels in the localized Aegean world, the study of wines and resins in transported Canaanite jars at the very least provides a glimpse into overseas trade in the Bronze Age. An area of immense interest to archaeologists, residue studies were applied to this area from the beginning[164] and have answered questions concerning diet, ritual, and trade while simultaneously bringing forth new inquiry and challenging conventional notions of life in the eastern Mediterranean during the Bronze Age.

One of the first studies to be undertaken in the modern era of organic residue studies was that of Canaanite trade amphorae. Long assumed to be used for the transport of wine, Canaanite amphorae are found in archaeological contexts around the eastern Mediterranean.[165] The Uluburun shipwreck, one of the most important sources of evidence for international trade in the Late Bronze Age Mediterranean, sank off the coast of Turkey with nearly 150 of these Canaanite amphorae aboard in the late 14th century BCE. Each of these amphorae was a quarter to half full of resin which was determined to be a pistacia

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156 e.g. Mottram, *et al.* 1999; Marshall *et al.*, 2008; Evershed, *et al.* 1991; Kimpe, *et al.* 2002.
157 e.g. Evershed, Vaughn, *et al.* 1997; Romanus, *et al.* 2008; Copley, Bland *et al.* 2005; Kimpe, *et al.*, 2001.
158 e.g. Colombini, *et al.* 2009; Arnott 2008; Fraser, *et al.* 2012.
159 e.g. Stern and Connan *et al.* 2008.
160 Stern, *et al.* 2000 and 2003; Stern and Lampert Moore *et al.* 2008
161 Mills and White, 1989; Stern and Heron *et al.* 2008.
162 Tzedakis, *et al.* 2008.
163 McGovern, Fleming, and Katz, 1996; McGovern, *et al.* 1996; McGovern, 1997; McGovern, *et al.* 2008.
164 Gill, 1906.
165 Leonard, 1996.

resin, most likely the commodity known as Chios turpentine.[166] While it has been recognized that resins were a major trade commodity in the eastern Mediterranean and particularly desired in Egypt for use as incense and sealant, the assumption that these amphorae were used in the transport of wine persisted. In 2008, the group at the University of Bradford analysed a second set of samples from the resin cargo. The study confirmed that the resins were indeed pure and questioned heavily studies that suggested that the resins in these amphorae served the sole purpose of sealing the jars.[167] These conclusions are supported by the presence of Canaanite amphorae in Amarna, Egypt and the detection of pure pistacia resins within them. In addition, the identification of identical resins in Egyptian bowls at the site seems to indicate their use as incense burners[168] and similarly the presence of the same resin used as an embalming agent in the "canopic jars of Rameses II"[169] form a solid argument for a demand for the resin in its own right. In each of these studies, assumptions on the motivation and nature of traded goods and their use upon arrival have been challenged. The relationship between traded resins and those present in ritual contexts provides the opportunity to speculate on the status of imported resins and those individuals who made use of them.

Related to the transport of resins, the trade and consumption of wine has been a repeated subject of inquiry, particularly by P.E. McGovern and the research group at the University of Pennsylvania. The results of an international symposium on the "Origins and Ancient History of Wine", held in Napa Valley in 1991, discuss the earliest evidence of residual wine in jars found in Godin, Tepe, Iran which date to the period between 3500 and 2900 BCE. Throughout the proceedings, arguments largely on the basis of vessel morphologies and distributions in addition to visual and textual evidence were offered for

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[166] Mills and White, 1989.
[167] Stern and Heron, *et al.* 2008.
[168] Stern, *et al.* 2000, 2003; Stern, Heron, *et al.* 2008.
[169] Charrie-Duhaut, *et al.* 2007.

the trade of wine across the Mediterranean.[170] The identification of wine residues has been argued in this volume and elsewhere[171] based on the presence of tartaric acid. While this biomarker is cited as being conclusive for the presence of wine, it is interesting and important to note that in a few cases the detection of the acid has not been reproducible between labs[172] and due to the lack of reproducible results, wine studies have largely been cast in doubt. The continual improvement of instrumentation and chemical analysis, including the application of high pressure – liquid chromatography,[173] holds hope for the continued pursuit of wine biomarkers in archaeological residues, but as of yet fully convincing evidence has not come to fruition.

The final, and possibly most important, study of organic residues in the Bronze Age eastern Mediterranean is that of *Archaeology Meets Science: Biomolecular Investigations in Bronze Age Greece*, conducted by Tzedakis, Martlew, and Jones. Begun as a museum exhibition and initially published as *Minoans and Mycenaeans: Flavours of Their Time*, the study sought to study systematically food production and consumption in Bronze Age Greece. The scientific results, later published in 2008, provide interested parties with a list of contaminants, mass spectral data, and interpretations for each of the catalogued vessels and some additional ceramic samples acquired in the ten year interim. Detailed in its presentation of the results, the study attempts to discuss food remains, the evidence of potential medicinal uses of plants at Chrysokamino, resinated wines and fermented beverages, and the stable isotope ratios of skeletal remains. The study allows for the careful examination of the published data for each sample and the evaluation of the authors' interpretations thereof. While this study filled a substantial gap in the application of residue analysis to the Bronze Age Mediterranean, it is not without flaw. As in many residue studies, the contamination of samples with plastics

[170] McGovern, Fleming, and Katz, 1996
[171] McGovern, 1997; McGovern and Michel 1996; McGovern, *et al.* 2008.
[172] Leonard, 1996.
[173] McGovern, *et al.* 2008

from packaging and oils transferred through handling, the results often list more contaminant species than suspected biomarkers and, as a result, tend to diminish the significance of the relevant compounds. In addition, a systematic analysis of all the samples is lacking, in that each section of the material seems to have been treated in a slightly different manner, preventing a cohesive force in the data. One major issue that arises in this study is the correlation of wine based on the presence of resin biomarkers. As it was common practice during the Bronze Age (and later) to mix resin with wine for its preservative and flavouring properties, this conclusion is not without basis. Also the transport vessels for wines could be lined with resin to reduce the porosity of the interior surface and reduce evaporation of the wine. While these facts lend credence to the correlation of wine and resin, it does not seem a secure conclusion to make consistently, as is seen in the study of Canaanite storage jars above. Despite these flaws that are by no means unique to this study, it will continue to be a starting place for further residue analyses and investigations of ritual and diet in ancient Greece.[174]

It is clear from the current state of residue analysis, as it has been applied to the Bronze Age Mediterranean, that there is a great opportunity for further study and refinement of the technique. Issues of contamination and degradation will have to be overcome or compensated for in order to achieve reliable results. The continual development of analytical techniques also promises to aid in the identification of organic species in archaeological residues, while continuing to complicate researchers' abilities to compare data sets directly. Despite the challenges inherent in this form of analysis, residues also have the ability to challenge conventional assumptions of vessel function based on form. In addition the identification of dietary substances in vessels used for cooking vessels, rituals, and storage has the potential to clarify understanding of day-to-day life of people in the past. The

[174] Tzedakis and Martlew 1999; Tzedakis, *et al.* 2008.

identification of traded commodities, either by correlation with ceramic typologies or the resources known to be available in specific areas, and possible connections to items used in their consumption can lead to conclusions on societal interaction and order. In the end, while still somewhat of an emerging field in archaeology, organic residue analysis continues to have the potential to challenge conventional notions of the manipulation, trade, and consumption of goods and lead archaeologists and scientists to new and significant conclusions about life in the past.

Over the last forty years, organic residue analysis has proven itself to be an immensely useful tool in archaeology, allowing the identification of the use and movement of commodities across the globe. Despite the breadth of knowledge that archaeologists have gained concerning the use of animal fats, plant oils, beeswax, resins, wine, and other commodities, there is still much to be learned. In the following table (Table 4-2), a catalogue compiled to give a picture of organic residue analysis, shows some of the analytical techniques, extraction and derivatisation methods, success rates, and yield data reported in the literature.

Forty-five references are listed here covering a mixture of techniques including GC-MS, FTIR, GC-C-IRMS, and HPLC. These data display a gaping hole in how residues are reported and analysed at present. Only three out of the forty-five groups report failures of their samples to produce residues. Since published overviews of the field are not quite as hopeful as to report an almost 100% success rate,[175] it is assumed that this lack of information is the result of groups only publishing the few samples that work. While this is understandable on some level, it reflects an outlook that does not address whether any differences in the ceramics themselves or their burial environment have any effect on their success. If statistics reported from Richard Evershed are to be taken into account, 60% and

[175] Evershed 1993, 2008b.

nearly all assemblages globally should produce some sort of residue data.[176] This implies that, as displayed in the literature, 40% of results even though negative have been ignored. Science teaches that negative results can many times be as informative as positive. Do these samples not preserve lipids as a result of natural degradation, the burial conditions, the nature of the ceramic, handling during and after excavation, or some other factor? The answers to this question and others must be considered in order to have a full picture of archaeological preservation and, potentially more importantly, the use of these commodities and vessels.

The presentation of yield data is almost as bleak as success rates. Only seventeen report yields with an additional four studying visible residues and thus sample sizes are equivalent to yield. The absence of these yield data is also a problem in that yields vary greatly not only from assemblage to assemblage but from sherd to sherd. The yields presented here range from 1μg/g to 36780μg/g. It is the goal in further research to investigate the different ceramic types presented here in comparison to yield. The difficulty lies in the fact that less than half of writers include such data. As shown here, the extraction methods consist mostly of chloroform or dichloromethane and methanol solvent extractions, confirming the results of experiments done for this project and indicating that this method is the best of the moment. Derivatisation protocols vary between trimethylsilylation and methylation, sometimes a combination of the two, seeming to indicate that there are benefits to both and their use must be defined on the basis of sample set and available materials.

[176] Evershed, Mottram, *et al.* 1997.

Table 4-2: Residue References and Yield Reporting		
Reference	**Technique**	**Success**
Berstan, *et al.* 2008	GC-MS, GC-C-IRMS, AMS	10/13
Boldizsar, *et al.* 2006.	GC-MS, HPLC-MS, Photodiode Array	?
Charrie-Duhaut, *et al.* 2007.	GC-MS, LC-MS	?
Charters, *et al.* 1993.*	GC, GC-MS	?
Charters, *et al.* 1995.*	GC, GC-MS	2
Charters, *et al.* 1997.	GC, GC-MS	2/2
Colombini, *et al.* 2005.	GC-MS, FTIR	3 vis
Colombini, *et al.* 2009.	GC-MS, FTIR, EDX	jar 1/4 vis
Copley, *et al.* 2005.	GC, GC-MS, GC-C-IRMS	10/10
Craig, *et al.* 2004.	Py-GC-MS	2
Dudd, *et al.* 1998.*	GC-MS	
Evershed, *et al.* 1990.*	GC, GC-MS	
Evershed, *et al.* 1994.	GC, GC-MS, IRMS-GC-MS	2
Evershed, *et al.* 1995a.	GC-MS	
Evershed, *et al.* 1995b.	GC, GC-MS	
Evershed, *et al.* 1997a.	GC-MS	
Evershed, *et al.* 1997b.		100 60%
Evershed, *et al.* 1997c.	GC, GC-MS	5
Evershed, *et al.* 2002.	GC	
Evershed, *et al.* 1991.		7
Hansel, *et al.* 2011	GC-MS	12
Heron, *et al.* 1991.	GC-MS	10
Kimpe, *et al.* 2002.	GC, GC-MS, LC-APCI-MS	2
Kimpe, *et al.* 2004.	GC, GC-MS, LC-MS	27
Kimpe, *et al.* 2001*	GC-MS, LC-ACPI-MS	7
Maier, *et al.* 2007.	GC, GC-MS, ATR-IR, FT-Raman, FTIR	2
Mazar, *et al.* 2008.	GC-MS	7
Mottram, *et al.* 1999.	GC, GC-MS, GC-C-IRMS	8
Namdar, *et al.* 2009.	GC-MS	28
Passi, *et al.* 1981.	HPLC, TLC	6
Raven, *et al.* 1997.	GC-MS, pyrolysis	1
Regert, *et al.* 1998.	GC-MS	?
Regert, *et al.* 2001.	GC-MS, FTIR	22
Ribechini, *et al.* 2008.	GC-MS, FTIR	?
Robinson, *et al.* 1987.	GC, GC-MS, IR, NMR, GC, GC-MS	7
Romanus, *et al.* 2007. *	GC-MS, GC-C-IRMS, HPLC-MS	26
Romanus, *et al.* 2008.	PPGC, GC-C-IRMS(4); GC-MS, LC-MS (4)	8
Romanus, *et al.* 2009.	GC, GC-MS, HT-GC, polyphenols	30/31
Shillito, *et al.* 2009.	GC-MS, FTIR	46, vis
Steele, Stern, Stott, 2010.	GC-C-IRMS	2 vis
Stern, *et al.* 2000.	GC, GC-MS	8
Stern, *et al.* 2003.	GC-MS	40
Stott, *et al.* 2001.*	AMS	14
Vazquez, *et al.* 2008.	GC-MS, TXRF, FT-IR	2/2 vis
Wan, *et al.* 2007.	GC, titration against NaOH	
Total		477/521

	Extraction	Yield	Derivatisation
	Soxhlet (large sample >5g)	56-13806 μg/g	base, methylated
	MeOH	10^{-5} g to 10^{-2}g /g	x
	DCM:MeOH		x
	CHCl3:MeOH	1-50, 1-4840μg/g	x
	CHCl3:MeOH		BSTFA, 1% TMCS
	CHCl3:MeOH	8-262μg/g	BSTFA, 1% TMCS
	DCM		BSTFA, 1% TMCS
		n/a	BSTFA, 1% TMCS
	CHCl3:MeOH + 0.5 NaOH/MeOH/H2O	333.3-17764.8 μg/g	BF3 in MeOH or BSTFA, 1% TMCS
	CHCl3:MeOH	0.5-6.0 mg/g	BF3 in MeOH or BSTFA, 1% TMCS
	CHCl3:MeOH		BSTFA
	CHCl3:MeOH		BSTFA
	CHCl3:MeOH		BSTFA, 1% TMCS
		up to 5mg/g	BSTFA
	CHCl3:MeOH	21-172 μg/g	BSTFA, 1% TMCS
		<5 ->750 μg/g	
	solvent		
		40-3140 μg/g (1706 av.)	TMS
	CHCl3:MeOH + 0.5 M NaOH	Dihydroxy 0.05-14.05 μg/g	BF3 in MeOH or BSTFA, 1% TMCS
	CHCl3:MeOH	70μg/g - 4800μg/g	BSTFA
	soxtec (method Kimpe et al)		KOH/MeOH, or MSTFA
	CHCl3:MeOH	10-100μg/g	KOH/MeOH, or MSTFA
	CHCl3:MeOH	10-100 μg/g	KOH/MeOH
	CHCl3:MeOH	160 and 1120 μg/g	HCL/MeOH
	CHCl3:MeOH		BSTFA, 1% TMCS
	CHCl3:MeOH +NaOH/MeOH/H2), HCL		BF3 in MeOH
	CHCl3:MeOH		BSTFA, 1% TMCS
	CHCl3:MeOH	trace, 1.75-15.51 μg/g	KOH, HCL; CH3CN
	CHCl3:MeOH		BSTFA, 1% TMCS
	CHCl3:MeOH or DCM:MeOH		BF3 in MeOH or BSTFA, 1% TMCS
	DCM or CHCl3:MeOH		BSTFA, 1% TMCS
	KOH, HCl		BSTFA, 1% TMCS
	DCM		BF3 in MeOH or BSTFA, 1% TMCS
	CHCl3:MeOH		KOH/MeOH. BF3.
	CHCl3:MeOH	3000-375000μg/g	MSTFA
	CHCl3:MeOH		FAME or MSTFA
	CHCl3:MeOH		
		n/a	BF3
	DCM:MeOH		TMTFTH or diazomethane
	DCM		diazomethane in diethyl ether
	DCM:MeOH	>300μg/g	H2SO4/MeOH
	CHCl3:MeOH	962μg/g and 36780μg/g	HCl/MeOH.
		x	BSTFA, 1% TMCS

Along with laboratory-based study of residues and vessel characteristics, continuation of this literature study must be done. Gathered data on yields and ceramic types need to be compared and analysed to determine if there are any apparent trends. This will be problematic to some degree as a result of the lack of reporting, but that is also one of the reasons why such work must be done. An archaeological residue goes through many processes and interactions throughout time before it reaches an archaeologist and a scientist's laboratory. The manufacture, use, and deposition of a ceramic have significant impacts on the nature of the residue. Many of the degradation reactions that organics undergo are understood but the reasons why they survive at all are not. It seems to be clear that the ceramic matrix plays an important role in that preservation whether it is a mechanical protective or chemical one. The nature of this role certainly has an effect on our understanding of the residue. As researchers are we simply trying to get a substances out of a molecular sieve, reliant on solubility characteristics of the materials or, do we need to be more active in chemical removal? Either way, each technique is selective and could result in altered results that may severely affect the interpretation of the substance's identity and its use by societies in the past.

5. Archaeological Sites, Sample Set, and Historical Relevance

There are a few sampling strategies that could be followed for this project, each having advantages and problematic aspects. Ideally for a project that seeks to investigate the impact of the burial environment on the preservation of organic molecules in ceramic vessels, a specific vessel type would be chosen. This vessel would need to be able to be found in a variety of burial contexts ranging from a dry environment (e.g. a cave), to a waterlogged environment (e.g. a shipwreck). There are a few issues that arise from this strategy. First, it is based on the assumption that the same vessel type has the same intended use and contents across varying cultural contexts. Also, as it is desirable to have unwashed pottery samples for residue analysis, it is exceedingly difficult at times to identify vessels with complete certainty before cleaning. These issues and the practicalities of gaining access to such an assemblage made the selection of such a strategy impossible for this project. In a second strategy, aimed for a comparison of ceramic fabrics, a selection of vessels with same contents, a difficult assumption to make based on morphology and context alone, would be chosen from a single burial context. In this strategy, the use and contents also cannot be absolutely controlled even though the burial context remains mostly the same.

This project took a different view towards the effects of ceramic vessels themselves on preservation by choosing samples from a series of sites (Tel Megiddo, Israel; Tel Kabri, Israel; and Lefkandi, Greece) with overlapping occupational histories, both similar and varied cultural characteristics, and whose societies were in at least indirect contact through known Bronze and Iron Age Eastern Mediterranean trade routes. Each site provides a slightly different archaeological environments (a tell open to tourism, a tell covered with a kibbutz and agricultural growth, and seaside plateau) and a mixture of depositional contexts (funerary, domestic, elite, ritual, and temple). By selecting samples from such a variety of

contexts and burial environments, within a similar "global" culture,[177] it is possible to quantify general preservation rates at each site and then relate the quantitative yields to site characteristics and vessel properties.

A major factor in sampling for residue analysis is the difficulty in obtaining intact vessels. The relatively rare occurrence of intact vessels with respect to sherds makes excavators and antiquities authorities more reluctant to release vessels for analysis. The identification of these vessels, as mentioned before, can also be difficult before cleaning and thus their selection for analysis hesitant. The idea that one cannot be quite sure about vessel contents before the sherd samples are analysed further complicates a strictly methodological sampling strategy. The cultural context of the samples cannot be discounted and the possibility that similar vessels could be used for different purposes within a single cultural framework cannot be ignored. For these reasons, a range of sherd samples and samples drilled from intact vessels were selected, including both fine and coarse wares. One hundred and thirty-three ceramic samples were selected from three sites around the Eastern Mediterranean dating from the Early Bronze age through the Iron Age. The samples from Tel Kabri, Israel; Megiddo, Israel; and Lefkandi, Greece represent sites that overlap in date and have a degree of cultural similarity and contact. These assemblages have the potential to reflect differences of preservation in varying vessel types within the same burial context. They also may reflect differences between the use of vessels of similar types found in varying contexts at the same site, such as a differentiation between burial and domestic function. In addition to the ceramics studied, twenty-two samples of bronze corrosion and mixed corrosion/soil deposits were taken from Roman bronze vessels excavated during the A2 road-scheme project in Kent, to further test the relationships of organic contents with vessel

[177] The sites sampled do reflect different cultures, both "Greek" and "Levantine" and within at least one site suspected changes in cultural identities, but are all part of what can be described as an Eastern Mediterranean network whose contacts, trade influence, and political affinities have been studied in depth. The chronologies of the Aegean, the Levant, Egypt, Anatolia, and Mesopotamia have been constructed on chronological synchronisms and have long been strongly tied to one another.

properties and to investigate potential new contexts for residue preservation. All one hundred and fifty-five samples of pottery and corrosion are catalogued in Part 2, with details of their excavation, typology where available, and analysis.

5a. A Note on Chronology

The dating of the eastern Mediterranean in the second millennium BCE is subject to considerable debate.[178] For the purposes of this study, the Israeli Consensus dates, as published by Mazar, will be used for the Levantine Bronze to Iron Age material.[179] A brief overview of the dating of the Early Bronze Age through the Iron Age in Israel is shown in Table 5-1. It is important to note that Dever and others, including Kenyon and Gerstenblith, use the designation Early Bronze IV (EB IV) for Albright's Middle Bronze I (MB I).[180] As a result, according to Dever, MB I culturally corresponds to MB IIA as defined by Albright and MB II corresponds to MB IIB. EB IV/MB I is also occasionally referred to as the Intermediate Bronze Age, so it is important to note which convention is being used. Here a MB I, MB IIA, and MB IIB-C subdivision (Table 5-2) will be used in accordance with Albright's original designation and the Israeli consensus dates published by Mazar. Table 5-2 shows the chronological subdivisions for the Bronze Age in Canaan and the Aegean. The relative chronologies for the samples from each of the sites can be seen in Table 5-3.

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[178] There exists a substantial corpus of literature on the dating of the 2nd millennium BC Eastern Mediterranean. Ceramic typologies, chronological synchronisms, radiocarbon, dendrochronology, and tephrachronology have all been extensively applied to sites and finds from across the region. The debate continues and the major substance and arguments are not strictly necessary in the development of this project, beyond a rough outline in which to compare materials culturally. (See e.g. Betancourt, 1987; Bruins, 2001; Dever, 1992; Manning, *et al.* 2001; Weinstein, 1991 and 1992.)

[179] Mazar, 1990: 30, Table 2.

[180] Dever, 1992.

Table 5-1: Overview of Dating Schemes for Canaan and Egypt [181]					
Dever (1992)	**Albright**	**Kenyon/ British School**	**Israeli Consensus**	**Egyptian Dynasties**	**Bietak (1991) Tell el-Dab'a**
EB IV 2300-2000 BCE	MB I 2100-1800 BCE	Intermediate EB-MB	MBI 2250-1950 BCE	1st Intermediate Period 6th-11th Dynasties	MB I
MBI 2000-1775 BCE	MB II A 1800-1700 BCE	MB I	MB IIA 1950-1750 BCE	Middle Kingdom 12th Dynasty	MB IIA 1700 BCE
MBI/II 1775-1750 BCE	---	---	---	12th/13th	MB IIA/B
MB II 1750-1650 BCE	MB II B 1700-1575 BCE	MB II	MB IIB-C 1750-1550 BCE	2nd Intermediate Period 13th-14thDynasties	MB IIB 1700-1600 BCE
MB III 1650-1500 BCE	MB IIC 1575-1500 BCE Destructions			Hyksos 15th-16th, 17thDynasties 17th Dynasty	MBIIC 1600-1530 BCE
MB III/LB IA 1500-1450 BCE	LB IA 1550-1450 BCE	"Groups" A, B	LB I 1550-1400 BCE	New Kingdom 18th Dynasty	MB IIC/LB IA 1600-1450 BCE
LB IB 1450-1400 BCE	LB IB 1450-1400 BCE	C (early)			LB IB 1450-1200 BCE
LB IIA 1400-1300 BCE	LB IIA 1400-1300 BCE	C, gap?, D	LB IIA	19th Dynasty	
LB IIB 1300-1225 BCE	LB IIB 1300-1200 BCE	E, F, G	LB IIB		
	Destruction, Disturbance: Israelites, Sea Peoples, Others				
Iron IA 1225 - - Iron IB	Iron IA 1200-1150 BCE Iron IB 1150-1000 BCE	Iron I	Iron I 1200-1000 BCE	20th	

[181] After Dever, 1992:3, Figure 1.

Table 5-2: Dating Conventions Used for Canaan and Their Corresponding Periods in Greece and Egypt			
Canaan (Mazar, 1992)	**Egyptian Periods**	**Aegean (**Warren and Hankey, 1989.)	
EB I 3300-3050		EM I 3650/3500 – 3000/2900	EH I 3650/3500 – 3000/2900
EB II-III 3050-2300		EM II 3000/2900 -2300/2150	EH II 3000/2900-2570/2410
			EH III 2570/2410 – 2050/1950
EB IV/MB I 2300-2000		EM III 2300/2150 – 2160/2025	
		MM IA 2160/2025 – 2050/1950	
MB IIA 2000-1800/1750	Middle Kingdom	MM IB (19th c) MM II (19th c. – 1700/1650)	MH 2050/1950- 1600
MB IIB-C 1800/1750 – 1550	Second Intermediate Period	MM IIIA 1700/1650-1640/1630	
		MM IIIB 1640/1630-1600	
		LM IA 1600-1480	LH I 1600-1500
LB IA 1550-1470	18th Dynasty: Expulsion of Hyksos conquest of Canaan by Tuthmosis III		LH IIA 1500-1440
LB IB 1470 -1400 BCE	18th Dynasty: Tuthmosis III conquest to Amarna Period	LM IB 1480-1425	
		LM II 1425-1390	LH IIB 1440-1390
LB IIA 1400-1300 BCE	Late 18th Dynasty: including Amarna Period	LM IIIA1 (1390-1370/1360)	LH IIIA (1390-1370/1360)
		LM IIIA2 (1370/1360-1340/1330)	LH IIIB 1370/1360-1340/1330
LB IIB 1300-1200 BCE	19th Dynasty	LM IIIB (1340/1330-1190)	LH IIIB (1340/1330-1190)
		LM IIIC/ (1190-1070)	LH IIIC (1190-1070)

Table 5-3: Comparative Chronology of Sites Sampled				
Tel Kabri Israel	**Tel Megiddo Israel**	**Lefkandi Greece**	**A2 Kent, UK**	**Approximate Date**
			Roman	50-70 CE
	Iron Age (Area Q and H)	Protogeometric		1200-1000 BCE
	Late Bronze (Area K)	Late Helladic IIIC *		1550-1200 BCE
Middle Bronze IIB	Middle Bronze (Area K)			2250-1550 BCE
	Early Bronze (Area J)			3000-2250 BCE

5b. Megiddo

Tel Megiddo, also known as Armageddon (Greek from the Hebrew, *'har Megiddo* meaning *mount of Megiddo*) and Tel el-Mutesellim (Arabic, meaning *hill of the commander*), lies on the western fringes of the Esdraelon Valley near the eastern edge of the Carmel Ridge about 30km east of modern Haifa in Israel. The site sits alongside two of the major ancient international highways: the southeast-northwest road which connects coastal Phoenicia and the Acco plain, and the Via Maris (way of the sea) which connects Egypt with Syria and Mesopotamia and served a one of the major trade routes for the ancient Near East. The control of these pathways was crucial to the procurement and maintenance of international economic and political power and thus Megiddo was a naturally key point on the political and economic map of the ancient Levant. In the quest for power amongst the major societies of the Ancient Near East, Megiddo is one of the important type sites for the Levant and provided the stage for numerous battles throughout history.

Megiddo first makes its appearance as an early Canaanite city-state in the Early Bronze Age. During this period, the site was dominated by a series of monumental temples, which can clearly be seen in the modern Area J. The famous round altar dates to this period, stratum J-4, EB III.[182] From the Middle Bronze Age, and especially after the conquest by Thuthmoses III (mid-14th century BCE, c1457BCE; recorded in the Hall of Annals of the Temple at Karnak), the site becomes an outpost for the Egyptian court. Moving into the Late Bronze Age and the Iron Age, the site retained its status through the rise of the Israelite state and the divided kingdoms. The site is mentioned twelve times in the Biblical texts, with ten being direct references to the city. Initially in the Biblical texts, Megiddo is listed as one of King Solomon's chariot cities,[183] and the city retained prominence through the Biblical Kingdom of Israel, when King Josiah rode out in battle against Pharaoh Neco in 609 BCE

[182] Adams in Finkelstein, *et al.* 2000, 2006, and 2013.
[183] 1 Kings 9:15

and was killed (archaeologically near the end of Chicago Stratum III).[184] It is also named as the site of the penultimate battle[185] of the end times which takes the site's name, *Armageddon*. The site is also mentioned in a number of extra-biblical texts including the Amarna Letters to and from Biridiya, the ruler of Megiddo under Amenhotep III, who used chariotry to secure the valley for agriculture, trade, and a military garrison (EA 243). The royal army is also attested to in EA 234.[186] The site was occupied well into the Ottoman period and the Roman camp, Legio, was located at the base of the site. Even in modernity, the site has changed, not only through archaeological excavation and preservation as a national park site, but even as recently as the 1948 War of Independence when soldiers moved exposed archaeological features to create defensive firing platforms.[187]

As an important Biblical site, Megiddo was one of the first sites in Israel to be archaeologically defined. The site was first excavated by Gottleib Schumacher for the Deutsche Palästina-Verein, the German Society for the Study of Palestine, between 1903 and 1905. Schumacher extensively surveyed the tell and the surrounding areas, including the later Roman village of Legio.[188] A lasting reminder of Schumacher's work site is a 20 metre trench that he cut across the centre of the tell from north to south with a few smaller trenches radiating outwards (Figure 5-1).

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[184] 2 Kings 23:29-30; 2 Chronicles 35:20-24
[185] Revelation 16:16.
[186] Halpern, 2000: 545.
[187] Cline and Sutter, 2011.
[188] The area of Legio and the area around Ein el-'Qubbi which Schumacher surveyed has begun to be revaluated and excavated by the Jezreel Valley Regional Project directed by Matthew Adams. Work was begun in 2010 and continues. One of the main aims of this project is to locate the Early Bronze Age settlement that supported the temple complex on the tell. (personal involvement and communication).

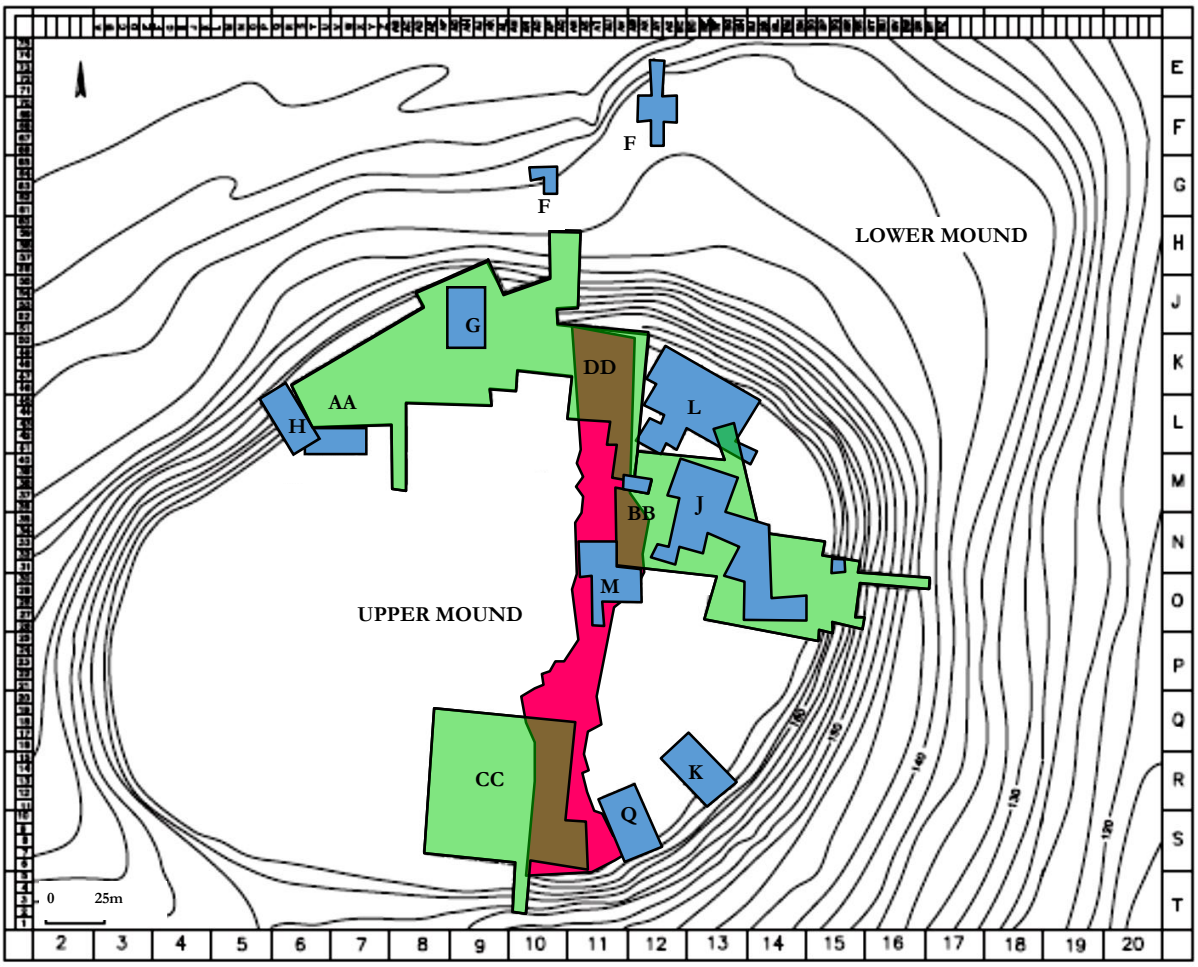

Figure 5-1: Tel Megiddo Excavation Plan
Plan of excavated areas through 2008.
Pink: Schumacher's Trench. Green: University of Chicago Areas. Blue: Current excavations by Tel Aviv University.
(After Finkelstein, *et al.* 2000, 2006, and 2013.)

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Schumacher's goal was to obtain a profile of the entire site, revealing each layer from the surface to bed-rock. Although the excavation of this trench was not completed, the team did reach bedrock in a small area to the North by the time they ceased work in 1905.[189] A portion of the survey and his findings were published in 1908, but many of the field notes and finding were lost with the advent of World War I before full publication.

One of the major advantages of the Schumacher trench is the access to early levels of the site which would not normally be easily reached and studied. The major finds of this era of excavation were the city gates, which would later form some of the basis for the sites identification as Megiddo and as a so-called "chariot-city", the middle and north "palaces", and the *Brandschicht* or "burnt layer".[190] This layer, which has also been identified in the University of Chicago (Stratum VIA) and Tel Aviv excavations, is a thick and easily recognized destruction layer consisting of burnt mudbricks. The exact date of this conflagration and its cause has been the source of much debate. It has been attributed to earthquake[191], the Philistines[192], the Israelites[193], and Shoshenq's invasion of 925 BCE[194]. Unfortunately the dating of this layer has not lent itself to a precise date of destruction nor is the cause conclusive in any manner.

The University of Chicago began an extensive set of excavations at the site in 1925, under the direction of Clarence S. Fisher and then P.L.O. Guy from 1927. From 1925 to 1939, the expedition investigated twenty strata from the Ottoman period down to the Chalcolithic period. Under Fisher, the lower eastern slope of the mound was cleared in preparation for a dump area. Here a substantial number of tombs were uncovered and identified the area as the main cemetery of the site.[195] In 1929, the expedition purchased the

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189 Schumacher and Steuernagel. 1908.
190 Schumacher and Steuernagel, 1908.
191 Cline 2011; Guy 1935: 202-5.; Ussishkin 1980:6; Harrison 2004:8-9.
192 Albright, 1936:38 and 1937:25; Aharoni 1972:308-9, Harrison 2003:60. (Israelite settlement destroyed by the Philistines during northern expansion.)
193 Davies 1986: 46-47.
194 Watzinger 1929:59
195 Guy, 1938.

remaining portions of the mound and extended efforts across the entire tell with the intent to expose each stratum in its entirety. It soon became clear that this was not practical and work was then confined to a few areas (Figure 5-1). In 1935, G. Loud took over the directorship as Fisher began to work towards the publication of *Megiddo I*. At this point, the focus turned to areas AA and DD, along the area of the northern gate. Work ceased in 1939 with the advent of World War II. [196]

Yadin initiated a small excavation at Megiddo in 1960 after the discovery of casemate walls at Hazor and Gezer. Concentrating in the east of the northern gate (Chicago Area DD), he came upon Palace 6000 and casemate walls to the east of the palace. In 1966, 1967, and 1971-1972, the area around Palace 6000 and placed soundings around the city gate were excavated (Chicago Area AA, Figure 5-1). These excavations aimed to clarify the nature of Palace 6000, the city gate, and stables that were attributed to King Solomon and his chariot cities (1 Kings 9:15).[197]

The ongoing Tel Aviv University Megiddo Expedition began in 1992 under the directorship of Israel Finkelstein and David Ussishkin, co-directed by Baruch Halpern from 1992 to 2004 and Eric H Cline from 2006 to 2012. To date, Areas F, J, H, K, M, and Q have been excavated biannually (Figure 5-1). The aim of the renewed excavation is to provide qualitative and scientific archaeological information which significantly contributes to the archaeology of Israel and the Levant. As the excavation seasons have progressed, it has been an aim of the excavators to create a reliable chronological sequence (including scientific dates, pottery typologies, and architectural developments) which can be related to other sites in Israel and the Levant.[198]

A comparative stratigraphy of Megiddo according to Schumacher, the Oriental Institute, and the Tel Aviv Expedition (including Areas K, J, and H) is shown in Table 5-4.

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[196] Lamon, *et al* 1948.; Harrison, 2004.
[197] Yadin, 1970.
[198] Finkelsetin, *et al.* 2000.

Table 5-4: Megiddo Stratigraphy								
University of Chicago Strata	**Period**	**Area K**		**Area J**	**Area H**	**Area F**	**Area L**	**Area M**
-	20th c CE					F-1		
-	Late Roman					F-2		
II	IA IIC					F-3		
III	IA IIB				H-1	F-4a	L-1	
not detected	IA IIB				H-2			
IVA	IA IIB	K-1	city wall 325		H-3	F-4b	L-2	
IVA	IA IIB	K-1			H-4	F-4b	L-2	
VA-IVB	Late IA IIA	K-2	two main phases		H-5		L-3	
VB	Early IA IIA	K-3	two main phases		H8,7,6		L-4	M3,2,1
VIA	Late IA I	K-4	destroyed in violent fire		H-9	F-5	L-5	M-4
VIB	Early IA I	K-5	local Myc IIIC		H-10	F-6		M-5
VIIA?	LB III	K-6	no wholesale destruction			F-7		M-6
VIIB	LB II	K-8,7				F-8		
VIII	LB II	K-9(?)		J-17?		F-9		
IX	LB I			J-14,15,16		F-10		M-7
X (X-IX)	MB III/LB I	K-10 (?)		J-13		F-11		M-8
XI	MB II			J-12				M-9,10
XII	MB II			J-11		F-12		M-11
XIII	MB I			J-10				
XIV	MB I			J-9				
XIV	MB I			J-8				
XV	EB III/IBA			J-7				
XVI	EB III			J-6a				
XVII	EB III			J-5, 6b				
not detected	EB Ib			J-4a				
XVIIII	EB IB			J-4				
XIX	EB IB			J-3				
Phase of XIX	EB IB			J-2				
XX	Chalcolithic/ EB IA			J-1				

Based on his trench cutting through the middle of the tell, Schumacher recorded a sequence consisting of eight superimposed strata with the earliest (Stratum I) on bedrock, reaching to the central part of his trench beneath the northern palace, and the latest (Stratum VIII) corresponding to a medieval Ottoman watchtower on the summit of the tell. The North Palace and the Middle Palace, located on the edge of the trench in what would later become Chicago's Area BB, were assigned to Stratum III, with the upper parts combined with the southern gate to Stratum IV. There are few chronological correlations possible as Schumacher's unpublished notes and field records were lost with the outbreak of World War I. The early levels of the North and central palaces (Stratum II) were dated to the later Middle Bronze Age (1600 BCE), the upper levels to the Late Bronze Age with the central palace lasting until 1400 BCE and the north palace to 1300 BCE. According to this interpretation, Megiddo was abandoned for three centuries until the time of Solomon, the 9th century BCE, at which time the southern gate of stratum IV was in use. A great burnt layer (Brandschicht) was attributed to the destruction of Sheshonq I during his campaign in 925 BCE. This layer covers the entirety of the site and provides an anchor for correlating the stratigraphy of the areas. The Palace attributed to Stratum V was dated to the ninth and eight centuries with a destruction linked to the 733 BCE campaign of Tiglath Pileser III. [199]

The University of Chicago Oriental Institute's expedition identified twenty strata from the Chalcolithic to the modern era. These have now been built upon, modified, and reassigned the periods shown in Table 5-4, by Finkelstein and Ussishkin. Each area of the current excavation is identified with a letter (K, H, J, etc.) and has its own internal gridding system and stratigraphic numbering (Area letter – stratum number) which are then correlated to the University of Chicago strata (Table 5-4).

[199] Finkelstein, *et al.*. 2000.

5b.i. Megiddo Samples

This project included forty-nine samples from ceramic sherd material from each of the Megiddo areas excavated in 2010, including areas J, K, H, and Q (Tables 5-5 and 5-6).

Table 5-5: Megiddo Samples – Areas H, J, and Q

Sample	Area	Locus	Pottery Bucket (Lab No.) Vessel No.	Approx. Date	Context	Sherd Type	Cross-Reference
KRM 092	H	10/H/034	002 (---) 01	LB II	Elite Domestic	Body Sherd	
KRM 093	H	10/H/036	012 (---) 03	LB II	Elite Domestic		
KRM 094	H	10/H/036	012 (---) 02	LB II	Elite Domestic	Body Sherd Bowl	
KRM 095	H	10/H/097	001 (---) 01	LB II	Elite Domestic	Body Sherd	
4 Samples	**Area H**						
KRM 063	J	10/J/113	005 (012)	EB	Temple/Mortuary	Body Sherd Small Juglet	
KRM 064	J	10/J/069	002 (007)	EB	Temple/Mortuary	Body Sherd Juglet	
KRM 065	J	10/J/069	003 (008)	EB	Temple/Mortuary	Body Sherd Juglet	
KRM 066	J	10/J/113	004 (014)	EB	Temple/Mortuary	Body Sherd Globular Juglet	
KRM 067	J	10/J/025	006 (010)	EB	Temple Mortuary	Body Sherd Juglet	
5 Samples	**Area J**						
KRM 133	Q	10/Q/026	012 (002)	IA	Ritual	Rim Sherd Cult Stand?	Two Samples
KRM 134	Q	10/Q/037	028 (035) 02	IA	Ritual	Body Sherd	134-136
KRM 135	Q	10/Q/037	028 (035) 02	IA	Ritual	Base Sherd	134-136
KRM 136	Q	10/Q/037	028 (035) 02	IA	Ritual	Rim Sherd	134-136
KRM 137	Q	10/Q/091	003	IA	Ritual	Body Sherd Cult Stand?	
KRM 138	Q	10/Q/094	002	IA	Ritual	Rim Sherd Bowl	139
KRM 139	Q	10/Q/094	002	IA	Ritual	Body Sherd Bowl	138
KRM 140	Q	10/Q/033	009 (---) 01	IA	Ritual	Rim Sherd	140-142,145
KRM 141	Q	10/Q/033	009 (---) 01	IA	Ritual	Body Sherd	140-142,145
KRM 142	Q	10/Q/033	009 (---) 01	IA	Ritual	Body Sherd	140-142,145
KRM 143	Q	10/Q/050	001 (---) 002	IA	Ritual	Body Sherd	144
KRM 144	Q	10/Q/050	001 (---) 002	IA	Ritual	Soil	143
KRM 145	Q	10/Q/033	009 (---) 01	IA	Ritual	Soil	140-142
14 Samples - Area Q							
23 Samples							

Table 5-6: Megiddo Samples – Area K							
Sample	Area	Locus	Pottery Bucket (Lab No.) Vessel No.	Approx. Date	Context	Sherd Type	Cross-Reference
KRM 013	K	10/K/002	010 (029) 02	LB II	Domestic/ Pit	Body Sherd Bowl	
KRM 068	K	10/K/002	016 (035) 04	LB II	Domestic/ Pit	Body Sherd Painted Jar	068-071
KRM 069	K	10/K/002	016 (035) 04	LB II	Domestic/ Pit	Body Sherd Painted Jar	068-071
KRM 070	K	10/K/002	016 (035) 04	LB II	Domestic/ Pit	Rim Sherd Painted Jar	068-071
KRM 071	K	10/K/002	016 (035) 04	LB II	Domestic/ Pit	Shoulder Sherd Painted Jar	068-071
KRM 074	K	10/K/002	011 (031)	LB II	Domestic/ Pit	Body Sherd	
KRM 075	K	10/K/002	013 (034) 014	LB II	Domestic/ Pit	Rim Sherd Storage Jar	*
KRM 077	K	10/K/002	011 (030) 03	LB II	Domestic/ Pit	Rim Sherd Storage Jar	077-079
KRM 078	K	10/K/002	011 (030) 03	LB II	Domestic/ Pit	Body Sherd Storage Jar	077-079
KRM 079	K	10/K/002	011 (030) 03	LB II	Domestic/ Pit	Base Sherd Storage Jar	077-079
KRM 073	K	10/K/029	010	LB I	Domestic	Body Sherd	
KRM 012	K	10/K/093	6	LB I	Domestic/Mortuary	Base Sherd Storage Jar	
KRM 076	K	10/K/102	007 (028	MB II/ LB I	Domestic/Mortuary	Body Sherd	
KRM 080	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 081	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 082	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 083	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 084	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 085	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 086	K	10/K/102	004	MB II/ LB I	Domestic/Mortuary	Body Sherd	080-086
KRM 087	K	10/K/102	009 (--) 032	MB II/ LB I	Domestic/Mortuary	Body Sherd Storage Jar	087-089
KRM 088	K	10/K/102	009 (--) 032	MB II/ LB I	Domestic/Mortuary	Body Sherd Storage Jar	087-089
KRM 089	K	10/K/102	009 (--) 032	MB II/ LB I	Domestic/Mortuary	Body Sherd Storage Jar	087-089
KRM 090	K	10/K/112	002 (005)	LB I	Domestic/Mortuary	Residue	091
KRM 091	K	10/K/112	002 (005)	LB I	Domestic/Mortuary	Body Sherd	090
KRM 072	K	10/K/118	002 (004)	MB II	Domestic/Mortuary	Body Sherd Pithos	
26 Samples - Area K							
49 TOTAL SAMPLES - MEGIDDO							

Area J samples include five sherds from infant burials within the Early Bronze Age temple complex. Each of these infant burials were found as a vessel containing the remains of the child along with smaller offertory juglets. The fourteen Area Q samples are from a cultic context and include a sample of a cult stand (KRM 137). Four samples were taken from area H, where there is elite domestic accumulation. Three of the Area H samples (KRM092-094) are sherds from what was identified as a "beer jar", the bowl in which the jar was sitting, and an inverted bowl used to cover the jar.

The majority (n=26) of the samples studied from Megiddo were excavated within Area K, dating to the Middle and Late Bronze Age domestic levels. Within this section of the assemblage, there are two categories of context. The first subset consists of sherds found in a vessel deposit during the excavation of a previous baulk between squares N-11 and O-11 (10 samples, locus 10/K/002). The assembage was found directly to the west of wall 06/04, the western wall of K-8 building 06/04, s a roughly square house measuring 9x9m with a large inner courtyard and larger outer work space to the west.[200] A plan indicating the loci from which these samples were taken can be seen in Figure 5-2.

The nature of the vessels indicate that they chronologically correspond to stratum K-8, dating to the LB IIB. The find level of the assemblage is somewhat lower than the elevation attributed to K-8 and therefore must indicate that the vessels were deliberately discarded in a depression or pit. Stratigraphically, the relationship is slightly obscured by the inability to delineate any pit markers. Despite this, the close and isolated nature of this deposit furthers the conclusion that it was a deliberate placement of these vessels. Included in this cache were at least fourteen vessels including a restorable Canaanite storage jar, four imitation Mycenaean stirrup jars, several lamps, bowls, and a Cypriot white-shaved juglet. Examples of these vessel types are shown in Figure 5-3.[201]

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[200] Martin, *et al.* 2013.

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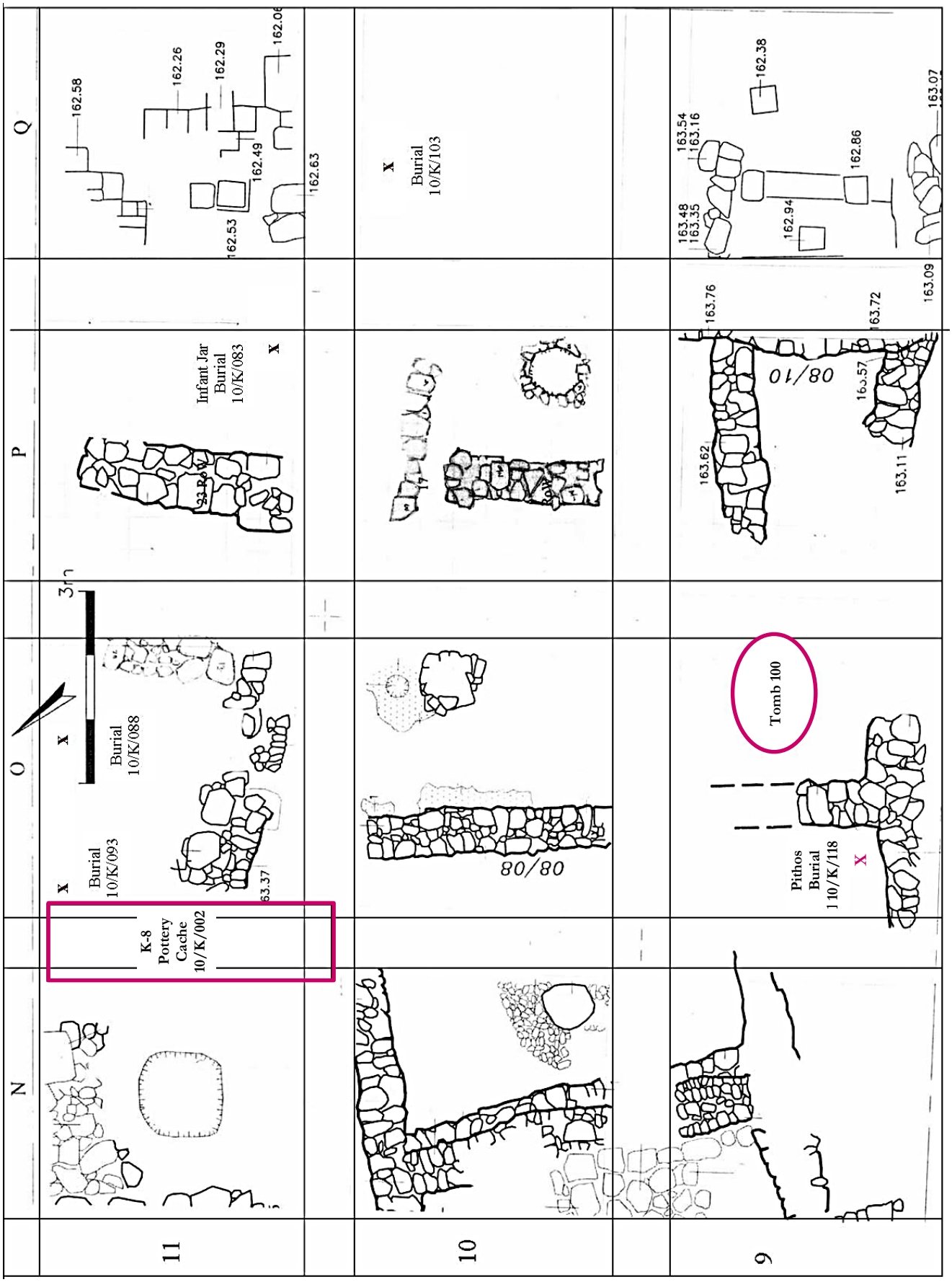

Figure 5-2: Area K Plan

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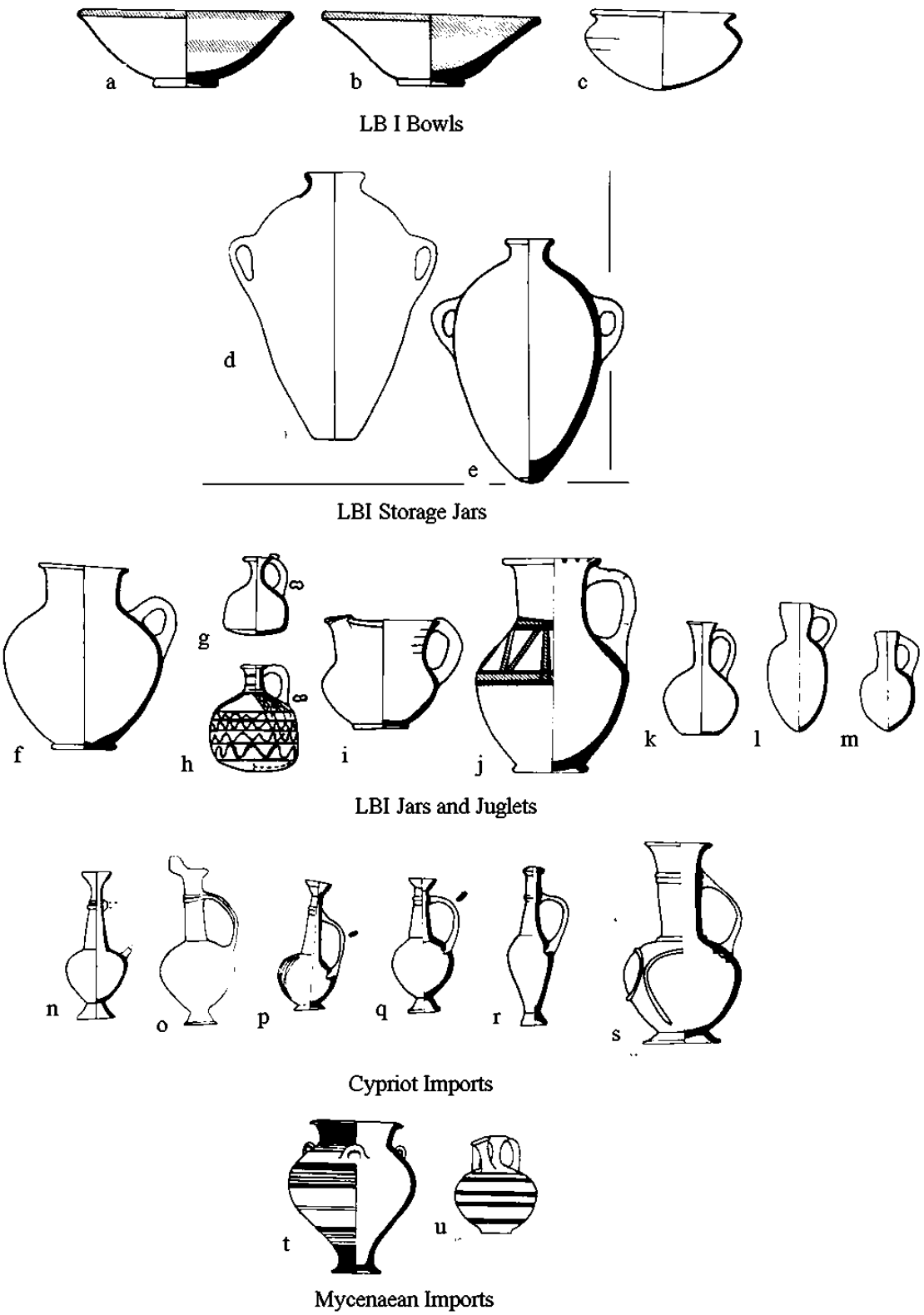

Figure 5-3: Late Bronze I Canaanite Ceramic Forms
(after Amiran 1969)

The international character makes it particularly interesting assemblage for the study of vessel use and imports in a urban domestic context.

The second category of the Area K samples are vessels associated with burials (16 samples). Three types of burials were excavated in this area during the 2010 season. The first, Tomb 100, is a structural stone tomb found under domestic accumulation in the southern section of the area. Measuring approximately 1.8m by 1.4m, the tomb contained a significant quantity of disarticulated skeletal material and copious finds (Table 5-7). Within the tomb, approximately 50 intact vessels were found, including lamps, jugs, juglets, bowls, a platter, and a storage jar. Imports include a Syrian juglet, a Cypriot base-ring juglet, and several lustrous wares in a quantity higher than most other MB II/LB I burials (~9%). Other finds included a bronze dagger, various animal teeth, two scarabs, an amethyst amulet, bronze leaves, and a great deal of incised bone fragments. This tomb represents the seventh structural tomb in Bronze Age Canaan to be excavated. It is also the only structural tomb at Megiddo to have its contents undisturbed since antiquity. As such it provides a wealth of information on the burial type as a whole. Fourteen sherds corresponding to a storage jar and other unidentified sherd material were studied in this project, the complete vessels not being able to be studied at the time.

Table 5-7: Tel Megiddo Tomb 2010/K/100 Contents

Complete Vessels			
Platters	2	Juglets	18
Lamps	13	Dipper	15
Bowls	3	Double Stranded	2
Jugs	9	Flat-Bottom Juglets	1
Bichrome	3	Red Lustrous Wheel Made	2
Bi-conical	3	Black Lustrous	1
		Cypriot Base Ring	1

Non Ceramic Objects	
Bronze Dagger	Amethyst Amulet
Bone Inlay (Box/Boxes?)	Metal Rings (>2)
Bronze Pins (> 7)	Scarabs (2)
Bronze Leaves	

In addition to Tomb 100, six other burials were excavated in the 2010 season (Figure 5-2). The first of these burials was dug down from the top of the Middle Bronze Age mudbrick rampart wall and sealed with stone. The burial consists of two adults, one almost fully articulated in a contracted position and oriented from east to west. Offerings included two juglets located to the west of the fully articulated individual and another juglet and platter near the feet. Based on the pottery, this burial dates the mudbrick wall to the MB IIA, about 100 years earlier than the University of Chicago thought (MB IIB). An infant jar burial, 10/K/083, was interred below the floors of a small room close to the edge of the tell. Inside, a complete juglet and a well preserved infant skeleton were found. Above in potentially unrelated context was a large amount of pottery and two large tablet-shaped grinding stones. In subsequent levels, the pottery assemblage seemed to be richer in this room than in the rest of the area for an unknown reason and potentially unrelated reason.

In the room directly to the west, two further burials were encountered. Burial 10/K/088 consisted of rather poorly articulated remains of a child oriented from east to west. Two small juglets and a number of beads were excavated near the skull which seemed to be surrounded with fieldstones. In burial 10/K/093, the partial remains of multiple individuals was encircled with a line of mudbricks. One sample of a vessel was taken from this grave. Offerings included a jug, a bowl, and two juglets. The sixth burial, 10/K/118, is an adult pithos burial with three juglets. One sherd was taken from the pithos itself. The jar was smashed up against one of the room walls and the bone heap nearby seems to correspond to the original burial contents. This burial is located in the southern section of the area in the same square in which the tomb was found. The walls against which the pithos was smashed relates in some way to the tomb architecture, the exact nature of this relationship is not yet clear. These burials represent a range of intramural burials dating from MB IIA through LB I and provide an avenue for the study of mortuary practices as well mortuary and domestic vessel use during the MBA-LBA transition.

The samples from Tel Megiddo (n=49) have the potential to answer several questions related to the archaeology of the site, vessel use and function, and the preservation of residues. First, the pottery cache of 10/K/002 has the potential to inform on vessels/commodities traded internationally. The few samples from area H could provide confirmation of the identification of the jar as a "beer" jar. Particularly, the samples from Megiddo are an ideal assemblage to study the potential differences in contents of burial vessels and how they compare to contents of similar vessels used domestically. In particular, Area K provides an even closer point of comparison as opposed to the burials in Area J (religious context) as the burials are found within the domestic accumulation. Lastly, these samples represent four different contexts of use at the same site providing the basis for any potential differences in preservation rates across the site or vessel function across time and context.

5c. Kabri

Tel Kabri is a 32 ha. (80 acre) site in the Western Galilee 5 km east of modern Nahariya. The tell is surrounded by a Middle Bronze Age rampart centred around a natural spring, the 'Ein Giah Spring. There is a functioning kibbutz on the site which predominantly farms avocados. In the early twentieth century, there were several small Arab villages near to the site and spring, most having been abandoned in 1948. The archaeological site of Tel Kabri was first discovered in the 1950s by the members of Kibbutz Kabri. Some of the first archaeological materials that were found were Late Neolithic stone implements near the 'Ein Giah Spring.[202] Between 1957 and 1958 Prausntiz conducted salvage excavations on behalf of the Israel Department of Antiquities and Museums. During these excavations, the Middle Bronze Age rampart wall was identified.[203] Throughout the 1960s and 1970s, the Israel

[202] Stekelis 1958.
[203] Prausnitz, 1959.

Department of Antiquities and Tel Aviv University conducted short salvage excavations finding some MB IIA vessels (1969), dating the rampart, and looking into the Neolithic occupation at the site.[204]

From 1986 to 1993, Aharon Kempinski directed excavations at Kabri under the auspices of Tel Aviv University. He was assisted by Eli Miron as deputy director from 1986-1998 and Wolf-Dietrich Niemeier as co-director from 1989. These excavations aimed to investigate further the findings of the previous salvage work at the site and evaluate the size of the Middle Bronze Age settlement. The major find of these excavations was the MB IIB palace. What is striking about the palace and site, other than its large size in relationship to its neighbours, is the marked international flavour of the site. Kempinski and Niemeier, discovered that the palace had a high quantity of Aegean imports and the ceremonial hall produced the remains of a Minoan-style fresco the likes of which are not commonly seen outside of the Aegean islands during this time.[205]

In 2005, Assaf Yasur-Landau (Tel Aviv University) and Eric Cline (The George Washington University) renewed excavations at Kabri. In six seasons from 2005-2013, the team started excavations in the area around the Middle Bronze Age palace (Area D-West), the area north of the palace (D-North), and to the South and East (Area D-South). Some of the main goals were to establish the extent of the palace, investigate the palatial destruction layers and determine any additional areas of plaster floor to elucidate the origin and extent of Minoan style frescoes found previously, and locate the residential and support buildings associated with the palace.[206] Area D-South was initially excavated as Area F by Kempinski and Niemier but was identified as a southern section of Area D in the final publications.[207] Here a monumental wall of differing construction than the palace walls was found being of

[204] Kempinski, 2002:2.
[205] The major exception to this trend being the frescoes at Tel el-'Daba.
[206] Yasur-Landau and Cline, Preliminary Reports: digkabri.worpress.com and personal communication. Personally involved in the 2005 season.
[207] Kempinski, 2002.

burnt and collapsed mudbrick. Investigations continue in this area with the goal to determine its nature.

At the eastern edge of the main MB IIB palace, and to the northwest of Ceremonial Hall 611, room 740 was further delineated. Kempinski originally thought that this room may have served as a throne room as it had thick walls, direct access from the ceremonial hall, and a thick plaster floor. The south-western wall of this room was excavated in 2005 to reveal mudbricks over a stone socle and covered with further wall plaster. In subsequent seasons, work was done around the ceremonial hall and the edges of the previously excavated palace. It was quickly discovered that the palace, while sizeable in first estimation, was actually bigger than previously thought and probably covered an area of 3-4,000 square meters rather than only 2,000 square meters.[208] At the height of its power, Kabri would have probably ruled over the territory from the Carmel ridge to the Sulam ridge with at least 31 smaller sites and ca. 30, 000 inhabitants.

Throughout the excavations, both under Kempinski and Yasur-Landau and Cline, the international character of the site has been abundantly clear. The presence of Minoan-style miniature frescoes at Kabri makes the site an incredibly important site in the analysis of contact between the Aegean and the Levant during the Middle Bronze Age. Miniature frescoes have been found at only four sites in the Aegean, namely, Knossos (Grandstand, Sacred Grove, and Dance), Tylissos House A, Akrotiri West House, and Ayia Irini.[209] Outside of the Aegean these sorts of frescoes are even less common. The fresco at Tel Kabri is the first to be found outside of the Aegean and predates those found later at Tel-Dab'a and Alalakh.[210] These frescoes are rare outside of the Aegean and, while well-known, not particularly common even within the Aegean.

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[208] Cline and Yasur-Landau, 2007.
[209] Cline and Yasur-Landau, 2007.
[210] Niemeier and Niemeier 2002:281.

It appears that at Kabri, the Syrian artistic tradition (king glorification) was abandoned in favour of the Aegean style (implication/invisibility of rulers). At the Palace at Mari, the iconography is very much tied up in the relationship between the ruler and the divine.[211] The surrounding of the palace and paintings within it provide an environment which is predominantly focused and descriptive of the King. Much of the iconography throughout Middle Bronze Age Palestine is similar to that of the Syrian tradition with clear portrayals of the power and the central figure. The departure of this king-centric Syrian-tradition in the Levant in exchange for a more "Aegean" style iconography is a significant indication that a closer connection existed between the Aegean and the rulers at Kabri, and potentially even a difference in ethnicity for these people inhabiting the site and ruling the surrounding area.

[211] Magueron in Cline and Yasur-Landau, 2007.

5c.i. The Kabri Samples

Fifty-five ceramic samples were taken from Tel Kabri during the 2008 excavation season (Tables 5-8 and 5-9). Twenty-one of them originated from area D-South and the remaining thirty-four from D-West. The thirty-four samples from D-West were found in a pottery cache or suspected drain to the north of the Ceremonial Hall. Most of these samples are sherds from typical Canaanite storage jars (examples of typology in Figure 5-4). These samples provide a significantly different burial environment due to the agricultural activity that has been present over the archaeological remains since at least the 1950s. The alteration of the natural top soil, addition of fertilizers and pesticides, and constant irrigation drastically change the environment of the remains. The palatial context of these sherds also has the potential to inform on ritual feasting and elite palatial practice during the Middle Bronze Age.

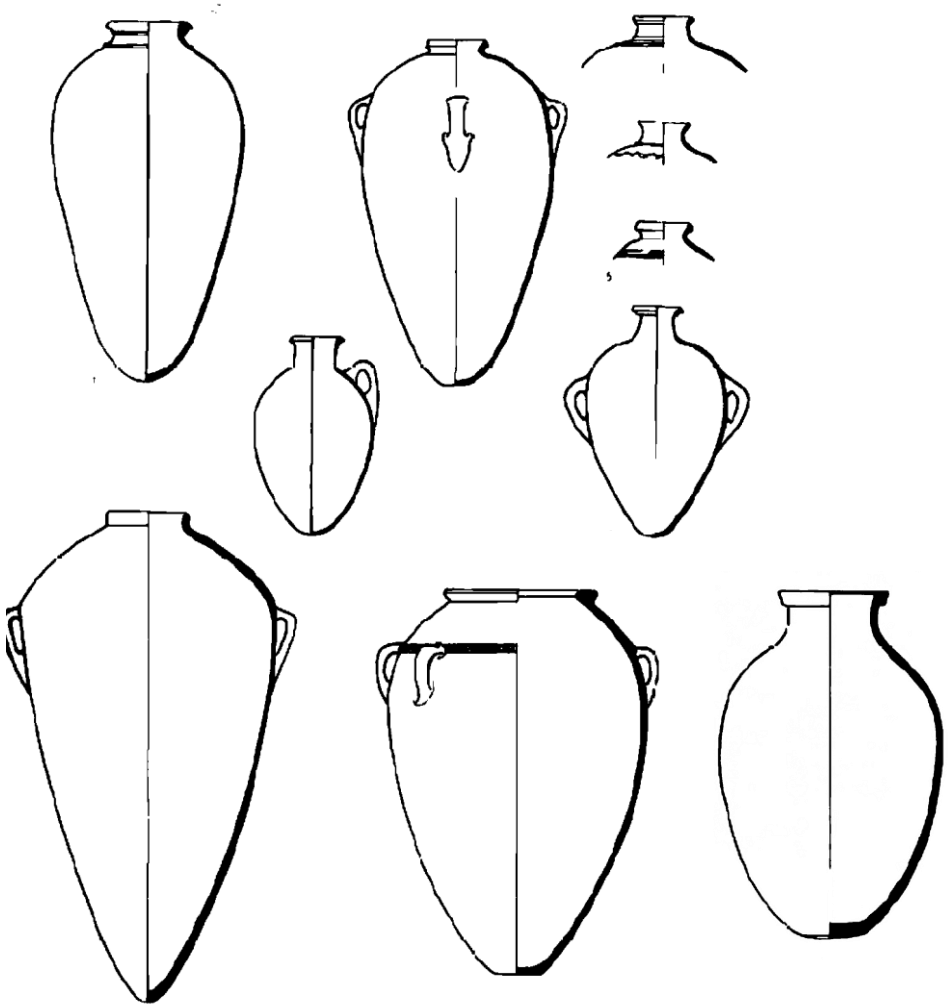

Figure 5-4: MB II Storage Jars (After Amiran 1969: Plates 31-32

Table 5-8: Kabri Samples – Area DW							
Sample	Area	Locus	Pottery Bucket (Lab No.) Vessel No.	Approx. Date	Context	Sherd Type	Cross-Reference
KRM 003	DW-W	2161	2161-8 (17)	MB II	Palace	Body Sherd	
KRM 005	DW-W	2161	2161-8 (24)	MB II	Palace	Rim Sherd	
KRM 006	DW-W	2161	2161-8 (28)	MB II	Palace	Rim Sherd	
KRM 008	DW-W	2161	2161-6 (48)	MB II	Palace	Base Sherd	Koh 3338
KRM 018	DW-W	2161	2161-6 (32)	MB II	Palace	Base Sherd	Koh 3337
KRM 022	DW-W	2161	2161-6 (33)	MB II	Palace	Rim Sherd	
KRM 023	DW-W	2161	2161-10 (21)	MB II	Palace	Body Sherd	
KRM 025	DW-W	2161	2161-6 (31)	MB II	Palace	Rim Sherd Red Slip	
KRM 028	DW-W	2161	2161-6 (23)	MB II	Palace	Body Sherd	
KRM 029	DW-W	2161	2161-6 (29)	MB II	Palace	Rim Sherd	
KRM 031	DW-W	2161	2161-10 (19)	MB II	Palace	Rim Sherd	
KRM 046	DW-W	2161	2161-9	MB II	Palace	Body Sherd	
KRM 050	DW-W	2161	2161-7 (18)	MB II	Palace	Body Sherd	
KRM 014	DW-W	2167	2167-1 (30)	MB II	Palace	Rim Sherd	
KRM 015	DW-W	2167	2167-1 (25)	MB II	Palace	Base Sherd	
KRM 024	DW-W	2167	2167-2 (20)	MB II	Palace	Rim Sherd	
KRM 026	DW-W	2167	2167-1 (26)	MB II	Palace	Rim Sherd	
KRM 030	DW-W	2173	2173-2 (16)	MB II	Palace	Body Sherd Chocolate on White	
18 Samples	**DW-W (except locus 2197)**						
KRM 009	DW-W	2197	2197-1 (43)	MB II	Drainage Deposit	Body Sherd	Koh 3332
KRM 017	DW-W	2197	2197-1 (40)	MB II	Drainage Deposit	Base Sherd	Koh 3333
KRM 019	DW-W	2197	2197-8	MB II	Palace	Rim Sherd Kabri Cup	
KRM 032	DW-W	2197	2197(61)	MB II	Drainage Deposit	Body Sherd	
KRM 034	DW-W	2197	2197 (62)	MB II	Drainage Deposit	Body Sherd	
KRM 036	DW-W	2197	2197 (58)	MB II	Drainage Deposit	Rim Sherd	
KRM 037	DW-W	2197	2197 (56)	MB II	Drainage Deposit	Body Sherd	
KRM 038	DW-W	2197	2197 (52)	MB II	Drainage Deposit	Body Sherd	
KRM 042	DW-W	2197	2197 (53)	MB II	Drainage Deposit	Body Sherd	
KRM 043	DW-W	2197	2197 (54)	MB II	Drainage Deposit	Body Sherd	
KRM 049	DW-W	2197	2197 (51)	MB II	Drainage Deposit	Body Sherd	
KRM 051	DW-W	2197	2197 (60)	MB II	Drainage Deposit	Body Sherd	
KRM 052	DW-W	2197	2197 (60)	MB II	Drainage Deposit	Body Sherd	
KRM 055	DW-W	2197	2197 (59)	MB II	Drainage Deposit	Body Sherd	
KRM 056	DW-W	2197	2197 (55)	MB II	Drainage Deposit	Body Sherd	
KRM 058	DW-W	2197	2197 (57)	MB II	Drainage Deposit	Body Sherd	
16 Samples	**DW-W, locus 2197**						
34 Samples	**Kabri DW-W**						

Table 5-9: Kabri Samples – Area DS							
Sample	Area	Locus	Pottery Bucket (Lab No.) Vessel No.	Approx. Date	Context	Sherd Type	Cross-Reference
KRM 007	DS-1	3033	3033-6 (1)	MB II	Floor	Body Sherd	
KRM 010	DS-1	3039	3039-2 (3)	MB II	Installation	Body Sherd Tabun?	
KRM 033	DS-1	3061	3061-2 (49)	MB II		Base Sherd	
KRM 035	DS-1	3061	3061-1 (37)	MB II	Floor	Body Sherd	039
KRM 039	DS-1	3061	3061-1 (36)	MB II	Floor	Body Sherd	035
KRM 044	DS-1	3033	3033-6 (8)	MB II		Body Sherd	
KRM 047	DS-1	3049	3049-16 (38)	MB II	Floor	Body Sherd	
KRM 053	DS-1	3019	3019-8 (5)	MB II		Rim Sherd	
KRM 054	DS-1	3019	3019-7 (7)	MB II	Floor	Rim Sherd	
KRM 057	DS-1	3049	3049-1 (2)	MB II	Floor	Body Sherd Cooking Pot	
KRM 059	DS-1	3055	3055-6 (39)	MB II	Floor	Rim Sherd	
KRM 060	DS-1	3049	3049-4 (4)	MB II	Floor	Body Sherd	
KRM 061	DS-1	3061	3061-1	MB II		Body Sherd	
KRM 062	DS-1	3049	3049-1 (6)	MB II	Floor	Body Sherd Painted	
14 Samples	**DS-1**						
KRM 004	DS-2	3060	3060-11 (11)	MB II		Rim Sherd	040-1,045
KRM 020	DS-2	3054	3054-2 (47)	MB II		Rim Sherd Cypriot	
KRM 021	DS-2	3060	3060-11 (9)	MB II		Body Sherd Carinated Bowl	
KRM 040	DS-2	3060	3060-11 (10)	MB II		Rim Sherd	04, 41, 45
KRM 041	DS-2	3060	3060-11 (11)	MB II		Rim Sherd	4, 40, 45
KRM 045	DS-2	3060	3060-11 (13)	MB II		Rim Sherd	4, 40, 41
KRM 048	DS-2	3060	3060-15 (14)	MB II		Base Sherd	
7 Samples	**DS-2**						
21 Samples	**Kabri, DS**						
55 TOTAL SAMPLES - KABRI							

5d. Lefkandi

Excavations since the 1960s near the modern town of Lefkandi on the island of Euboea, Greece have provided major insights into the history of the Late Bronze Age and Early Iron Age Aegean. The British School at Athens began excavations at the site in 1964 under the direction of Mervyn Popham, and Hugh Sackett continued work throughout the 1970s, 80s, and 90s.[212] Since 2003, the new set of excavations have been under the direction of Irene Lemos, with work ongoing.[213] Lefkandi located on the island of Euboea directly across from Boeotia where the Southern Gulf of Euboea meets the narrow Euripus Strait. The excavations at Lefkandi have investigated the ancient settlement of Xeropolis and the nearby cemeteries of Skoubris, Toumba, and Palia Perivolia. The ancient settlement, Xeropolis, sits just east of the modern town on a coastal promontory plateau of about 500 metres in length and 120 metres in breadth. (Figure 5-5)

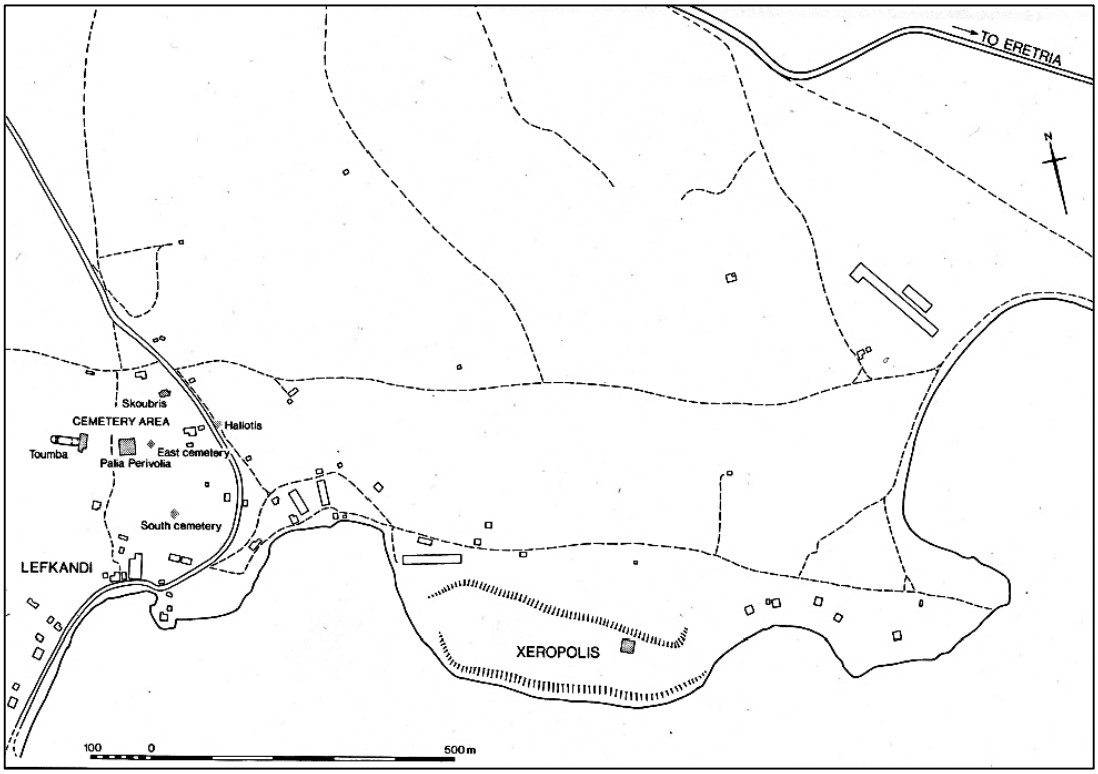

Figure 5-5: Lefkandi – Xeropolis and Cemetery Area
(Lemos 2006a: Figure 27.2)

[212] Popham, *et al.* 1980; Popham, *et al.* 1990; Popham and Lemos, 1996; and Evely 2006.
[213] Website of the current excavations (2003-): http://lefkandi.classics.ox.ac.uk, last accessed 20 August 2014.

The plateau itself is preserved to about 17 metres above sea level with sharp abrupt cliffs which drop off into the sea and a steep incline towards the inland.[214]

The one of the primary initial aims[215] of the project was to investigate the nature of Euboea's role in early trade contacts with the Near East after a suggestion that some of the ceramics that Woolley identified at Al Mina might be more closely comparable to Euboean ceramics than that of other areas of the Aegean world.[216] The site would have been an important port with two harbours along the maritime trade routes of the Western Aegean in antiquity just as Chalcis is still an important port today.

The ancient name of the site is unknown. Based on the location of Xeropolis in the Lelantine plain between the cities of Chalcis and Eretria, two of the most important city-states in the early Iron Age, it has been suggested that the settlement at Xeropolis may be Old Eretria or Old Chalcis. There is no mention of the site in the accounts of the Lelantine War which was fought between Eretria and Chalcis during the early Archaic period (c. 710-650 BCE). Thucydides notes that this war was *the one in which most cities belonging to the rest of Greece were divided up into alliances with one side or the other,*[217] as such alliances were not common between the Trojan and Peloponnesian wars. As the control of the Lelantine plain was a significant motivator for this conflict, if the site was still active one would think it would have been mentioned. By the time of Strabo, the greatest cities in Euboea were Chalcis and Eretria. This echoes their listing in the Catalogue of Ships,[218] along with several other places with no identifiable links to the settlement at Lefkandi. Strabo mentions that the foundations of Old Eretria were still visible from when the Persians destroyed the city and exiled the inhabitants.[219] This evidence could point to Old Eretria being the settlement at

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[214] Popham, *et al.* 1980.
[215] Popham, *et al.* 1980:3-4.
[216] Boardman, 1952, 1957.
[217] Thucydides, *History of the Peloponnesian War*, I.15.3
[218] Homer, *Iliad,* II. 493-759.
[219] Strabo, *Geography*, X.1.11.

Xeropolis. Popham notes, however, that described location of Old Eretria by Strabo would place the site east of Eretria, while Xeropolis is to the west, however this could be an error. It has also been suggested that the site could be Old Chalcis. There is no literary support for this and the suggestion arises purely from geographical speculation. The last speculated ancient name for Xeropolis is Lelanton as it sits in the middle of the fertile Lelantine plain and could be the origin of the regional designation.[220] In any case, the original name was lost in antiquity and the settlement at Xeropolis would have been in decline by the time that either the archaeological settlements known now as Eretria or Chalcis would have been "founded" before rising to prominence around 750 BCE.

Regardless of its ancient identity, Lefkandi/Xeropolis was a significant settlement in the Aegean from the Early Bronze Age through the Iron Age and is important in the archaeological and historical understanding of particularly the Late Helladic IIIC through Protogeometric periods. Settlement at Lefkandi begins around 2000 BCE at the end of the Early Bronze Age when people arrived with an alien pottery style which is unrelated to the native Early Helladic pottery styles of Euboea and mainland Greece. These generally undecorated but burnished wares are of a typology that is closed to that of Western Anatolia. The site was fortified from around the Middle Helladic/Late Helladic transition until the Late Helladic IIIB. The LH IIIC brings about a significant population increase and either fortification was no longer as pressing of a need or the need was eclipsed by the need for housing space as the remnants of the fortification walls were used as housing walls. The LIIIC (12th century BCE) settlement provided the first continuous sequence of settlement architecture covering the much of the Bronze Age. It also signifies the first continuous sequence of LH IIIC pottery which is closely associated with structures in and around it was used.[221]

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[220] Popham, *et al.* 1980: Appendix B.
[221] Sherratt, 2006.

It was once believed that Greece descended into "Dark Ages" following the collapse of the Mycenaean palaces in the LH IIC, but the excavations at Lefkandi show that the site was expanding during this period.[222] This has now been seen at other Aegean sites such as the former palatial city of Tiryns. The phrase *Dark Age of Greece* was used to describe the period between the fall of the Mycenaean palatial system c 1200 BCE and the rise of the Greek city-states around 770 BCE. For a long time in the study of the Aegean, this period was thought to mark the decline of Mycenaean society and a loss of continuity in many Greek sites in addition to limited contact with the rest of the Eastern Mediterranean world.[223] The "Dark Ages" incorporate the Late Helladic IIIC, the Sub-Mycenaean, Protogeometric, and Early/Middle Geometric (c 1200-1100, 1100-1025, 1025-900, 900-770). The Late Geometric period was believed to and is considered the beginning of the Greek world's recovery, by which time, the Greeks had adopted their alphabet. It has been discovered, however, that while there was a sharp decline in population and a breakdown of the Mycenaean culture, some of the palatial sites continued to be occupied. At Tiryns for example, local rulers took the place of the Mycenaean wanaktes and the megaron was remodelled into a smaller space. It is at this point that other sites which were not as significant or consequential during the Mycenaean period gained greater importance. One of the key sites for this transition is Lefkandi. Changes in social and political conditions can be seen in burial practices of which the evidence is strong for the Early Iron Age in the Aegean. Settlements that provide clear evidence for this period are few, and one of the clearest is Lefkandi, especially as it did not have a strong Mycenaean tradition and grew in the LH IIC, sub-Mycenaean, and Protogeometric periods.[224]

Three phases constitute the LH IIIC levels at Xeropolis. Phase 1 consists of mostly domestic buildings of varying size which cut down slightly into the previous LH IIIB

[222] Lemos, 2006a and 2006b.
[223] Snodgrass, 1971; Desborough, 1964, 1972.
[224] Lemos, 2006b.

structures. All of these houses were likely two-storied structures with the living rooms on the upper floors. This phase was destroyed in a conflagration. During this phase, it was also common to practice intramural burial, in addition to or rather than burial in one of the nearby cemeteries. Infant, juvenile, and adult burials within the walls or under living floors are attested throughout this phase.[225] The second phase of the LH IIIC settlement was built on the flattened and burned remains of phase 1 soon after its destruction. The inhabitants of Xeropolis paid little attention to the housing pattern of the previous phase, completely ignoring the prior wall lines. These new buildings were of mostly consistent size having approximately 5 metre square rooms and open spaces.[226] Phase three is the last of the Bronze Age layers at Xeropolis. Following the destruction of this building phase, reoccupation of the site is not seen until the late Protogeometric. The few sherds dating to the middle Protogeometric are attributed to later contamination. Burials in the nearby cemetery areas begin in the sub-Mycenaean period and continue throughout the Iron Age.[227]

The LH IIIC pottery assemblage at Lefkandi contains not only implements and vessels for normal domestic activities such as grinding grain, tools for butchering, and cooking pots, but also a significant quantity of decorated craters and a relatively high proportion of cups and drinking vessels.[228] This seems to indicate that feasting and convivial drinking was common at Lefkandi as it was at other sites in the Bronze Age Aegean. In further support of this argument, ritualized drinking is depicted on at least one of the craters excavated at Xeropolis.[229]

Evidence of international trade imports include Base Ring II bowls[230] and a Late Minoan IIIB octopus stirrup jar[231] which point to connections with Cyprus and Crete at the

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[225] Evely, 2006:1.
[226] Evely, 2006:1.
[227] Evely, 2006:1.
[228] Sherratt, 2006.
[229] Evely, 2006: Ch. 3 pp 240-241.
[230] Evely, 2006: Ch. 1 pp 131
[231] Evely, 2006: Ch. 2 pp 140.

beginning of LH IIIC and possibly earlier. The local wares standard to Lefkandi are wheel-made from Levantine clays found nearby. These clays from the Lelantine valley are still exploited on an industrial scale today.[232]

5.d.i. The Lefkandi Samples

The majority of the samples from Lefkandi taken for this project were excavated during the 2008 season, with only one of the samples coming from the 2007 season. All of the samples were part of the area excavated in Region 2 on the western side of the plateau where work began during the 2004 season and continued from 2006-present. In all, twenty-nine samples were drilled with a hand drill from sherd material and intact vases in the summer of 2010 (Table 5-10).

Area Q is to the southeast where rooms of one or more houses were uncovered which dated to the late stages of LH IIIC and the sub-Mycenaean periods (period not well represented elsewhere in the Aegean. During the 2006 and 2007 seasons a large "wall" was uncovered which was not a building wall, but resembles a terrace or city wall. This suggests that Xeropolis may have a more complex fortification system. The dating of this feature extends through the Late Bronze and Early Iron Ages. Further to the west of the "wall" in Area T, new structures were discovered considered to be atypical of the general Aegean architecture, dating to the LH IIIC to early Protogeometric. It is suggested that these building were non-domestic and tentatively identified as ritual. One of the features of one of these structures is a number of circular platforms along the central North/South axis. The largest of these is 2m in diameter and the smallest about 1m in diameter. They are similar in construction to some of those found in the Toumba cemetery building[233]. The soils of the structure are bereft of any bone, ash, or domestic debris, but vase fragments are common

[232] Sherratt, 2006.
[233] Popham, *et al.* 1990, and Lemos, 2009.

Table 5-10: Lefkandi Samples						
Sample	Area	Locus	Pottery Bucket (Lab No.) Vessel No.	Approximate Date	Sherd Type	Cross-Reference
KRM 113	Area Q-NE	Λ58	4600	LH III/IA	Vessel Body	
KRM 123	Area Q-NE	Λ58	4600	LH III/IA	Vessel Body	
2 Samples	**Area Q-NE**					
KRM 105	Area T-N	Λ11	956	LH III/IA	Vessel Base Bowl	
KRM 118	Area T-N	Λ11	883	LH III/IA	Body Sherd Decorated Jug	
2 Samples	**Area T-N**					
KRM 096	Area T-S	Λ56	2674	LH III/IA	Rim Sherd	
KRM 097	Area T-S	Λ55	3668	LH III/IA	Base Sherd	
KRM 098	Area T-S	Λ55	2667	LH III/IA	Rim Sherd Krater	
KRM 099	Area T-S	Λ55	3668	LH III/IA	Handle Sherd	
KRM 100	Area T-S	Λ56	2662	LH III/IA	Base Sherd	
KRM 101	Area T-S	Λ56	2662	LH III/IA	Base Sherd	
KRM 102	Area T-S	Λ	2659	LH III/IA	Base Sherd	
KRM 103	Area T-S	Λ56	2674	LH III/IA	Base Sherd	
KRM 104	Area T-S	Λ56	2662	LH III/IA	Body Sherd Storage Jar	
KRM 106	Area T-S	Λ55	3668	LH III/IA	Body Sherd	
KRM 107	Area T-S	Λ	2659	LH III/IA	Body Sherd Bowl/Juglet	
KRM 108	Area T-S	Λ56	2662	LH III/IA	Rim Sherd	
KRM 109	Area T-S	Λ55	3668	LH III/IA	Base Sherd	
KRM 110	Area T-S	Λ	2659	LH III/IA	Base Sherd Jar	
KRM 111	Area T-S	Λ57	2675	LH III/IA	Rim Sherd	
KRM 112	Area T-S	Λ56	2669	LH III/IA	Base Sherd Juglet	
KRM 114	Area T-S	Λ56	2665	LH III/IA	Base Sherd	
KRM 115	Area T-S	Λ	2666	LH III/IA	Rim Sherd Krater	
KRM 116	Area T-S	Λ	2661	LH III/IA	Body Sherd	
KRM 117	Area T-S	Λ56	2665	LH III/IA	Body Sherd	
KRM 119	Area T-S	Λ55	2667	LH III/IA	Handle Sherd	
KRM 120	Area T-S	Λ	2666	LH III/IA	Body Sherd Juglet	
KRM 121	Area T-S	Λ56	2665	LH III/IA	Base Sherd Juglet	
KRM 122	Area T-S	Λ1,2	2533	LH III/IA	Rim Sherd Cup	
KRM 124	Area T-S	Λ56	2673	LH III/IA	Base Sherd	
25 Samples	**Area T-S**					
29 TOTAL SAMPLES - LEFKANDI						

especially that of craters. Based on pottery typology, the structures and the surround area belongs to the early Protogeometric period (end of the 11th and early 10th centuries BCE).

Structure C is the latest of the structures to be excavated to date. This structure contains circular platforms of stones and pebbles rather than the clay drums of structures A and B. The associated pottery indicates that this structure was in use between the Late Helladic IIIC and Middle Protogeometric period. Evidence of quite large craters and cooking pots with animal bones is found to the East of Structure C where cooking, eating and drinking seem to have taken place outside of but near to the structure. In an alternative suggestion to a ritual area, it has been suggested that the area might have been industrial for the processing of oil or wine. The suggestion relies on the clay drums and platforms as rests for vessels for the crushing of olives or grapes. The difficulty with this interpretation is that the spaces seem to be too small for this type of activity and the platforms are at ground or floor level. The samples from both areas have the potential to elucidate the identification of these areas as ritual or in the case of Area T as a possible oil or wine processing area. If taken as ritual spaces, residue analysis has the potential to inform on feasting practices at the site.

5e. A2 Pepperhill to Cobham

The A2 Pepperhill to Cobham road-scheme project was conducted by Oxford Archaeology on behalf of The National Highways Agency for Skanska Construction Limited from 2006 to 2007. The excavations along the A2 roadway uncovered materials and features from every period between the Mesolithic (10,000-4,000 BCE) and the post-Medieval period (1485-2000 CE).[234] The twenty-two corrosion and mixed corrosion and soil samples were taken from five copper alloy vessels including one cauldron, two ewers, and two paterae, found in high-status Roman burials dating to between 43 and 70 CE. The list of these samples, the vessels from which they were taken, and their context is presented in Table 5-11.

Table 5-11: Copper Alloy Corrosion Samples from A2: Pepperhill to Cobham

Vessel No.	Context	Vessel Types	Sample Numbers
681	6231 (grave 6260)	Cauldron/Wine-Mixing Bowl (Eggers Form 33)	KRM146-147
683	6232 (grave 6260)	Ewer (Nuber's Hagenow Service)	KRM157
689	6262 (grave 6260)	Patera (Nuber's Millingen Service)	KRM152-154
1549	6661 (grave 6635)	Patera (Nuber's Hagenow Service)	KRM148-151,158-167
1550	6663 (grave 6635)	Ewer (Nuber's Millingen Service)	KRM155-156

During the Roman period the focus of settlement moved away from the Iron Age ditched settlement, metaled trackway, and associated enclosures to a location further east which overlooked the Tollgate dry valley. During the Oxford Archaeology excavations, the northern section of the Roman enclosures was uncovered. Based on the pottery accumulation, this new settlement predominantly dates to the 1st and 2nd centuries CE. Along with the settlement evidence, several burials were excavated, including a large high-status cremation (grave 6260), two high-status graves (grave 6635 and grave 6645), and six other cremation burials to the north-west.[235] The samples studied in this project were taken from finds within graves 6260 and 6635.

[234] Allen, *et al.* 2012: xxi, summary of period accumulations.
[235] Allen, *et al.* 2012: Chapter 4: The Roman Evidence. pp. 319-484.

Grave 6260[236]

The first high-status burial, 6260, consists of a square pit, oriented from north-northeast to south-southwest and measuring 2.4 metres across by 0.7 metres deep. The assemblage associated with this high-status cremation burial included: a gaming board evidenced by two copper-alloy drop handles, some copper-alloy edging strips, hinges, and a small amount of degraded wood; glass counters; bone or antler dice; scattered nails and a line of bronze tacks which are taken to represent the decoration of a table; eighteen pottery vessels; three bronze vessels, including a cauldron and a ewer inverted over a patera; and a copper alloy brooch. The grave was organized thematically: the south-west quadrant for individual and personal adornments (cremated bone and brooch), the south-east for feasting implements (table, vessels for eating, drinking, and ritual washing, and pig remains), and the north-west for entertainment pieces (gaming board, counters and dice). It appears that the majority of the vessels were placed upon a side-table, which was decorated with bronze roundels and fittings. The caldron, patera, and flagon were laid on the floor of the grave beneath it. There is evidence that at least a portion of the grave was lined before the deposition of the remains and vessels, in that straw was found in the corrosion material beneath the patera and cauldron. Eight of the eighteen ceramic vessels were Gallo-Belgic imports, one a North Gaulish import, one a south Gaulish import, and the remaining eight local vessels only one of which is a local Iron Age form. The bronze vessels and the bronze brooch are assumed to be of Italian origin. The Rearhook brooch is the most secure piece of dating evidence for this grave, dated to the mid-1st century CE. Balancing the metalwork evidence, the excavators suggest that the burial was made about or shortly after the time of the Claudian conquest in 43 CE. Each of the bronze vessels from 6260, including those from which the corrosion samples were taken, will be discussed in turn below.

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[236] Allen, *et al.* 2012: 325-354. Details of grave 6260 and its contents.

The cauldron or wine-mixing bowl, vessel number 681, is of Eggers Form 33[237] and listed as likely to be contemporary with Nuber's Hagenow service[238] (Figure 5-6). There are very few northern European examples of this form, but similar features are seen in Italy until the late 1st century CE. This three-knob-footed vessel measures 267 mm in diameter (198 mm in diameter at the rim) and 200 mm in height. The hemispherical lower body shoulders sharply in to a square rim which is adorned with an eye motif. The attachment plates are cast in the shape of vine leaves engraved with fine lines and finished with a horizontal border echoing the eye-motif of the rim. The plates, which were soldered on to the hammered bronze, end in rings in which to hold the handle. The cast handle has hooked ends, formed as duck heads emerging from calyx mouldings. Finally there is a ring towards the top of the handle from which the vessel could have been hung.[239]

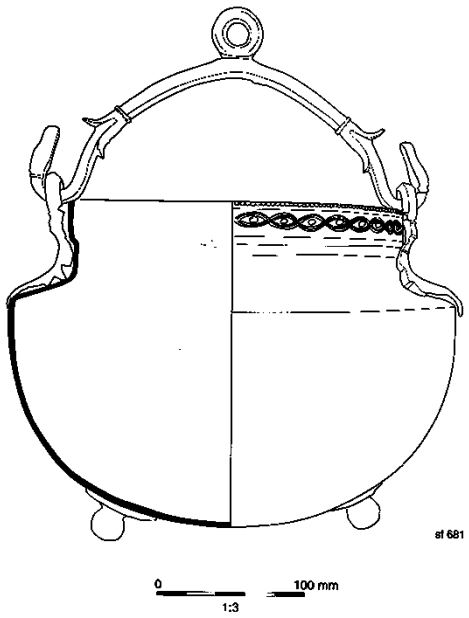

Figure 5-6: Cauldron/Wine Mixing Bowl 681
(Allen, *et al* 2012: Figures 4.7)

[237] Eggers 1951.
[238] Nuber 1972.
[239] Scott, 2012a: Description on pp 334-335 and plates on pp 336-338.

Two corrosion samples were taken from cauldron 681 (KRM146 and KRM147). Sample KRM146 corresponds to corrosion from the interior of the vessel, and KRM147 to corrosion, consolidant, and grass/textile fibres from the exterior. It is remarked by the excavator that this cauldron bears markings and impressions of the grass flooring and a textile cover, some of which may be present in sample KRM147.

The patera, vessel number 689, typologically corresponds to Nuber's Millingen service, dating to the reign of Claudius (41-54 CE) and continuing in use through the 2nd century CE[240]. This vessel is a wide, shallow dish with a low base ring and strongly curved sides. It has a leaded bronze handle, hollow cast in the shape of a ram's head. The patera measures 210x220 mm in diameter and 67 mm in height with a handle length of 142 mm (Figure 5-7).[241]

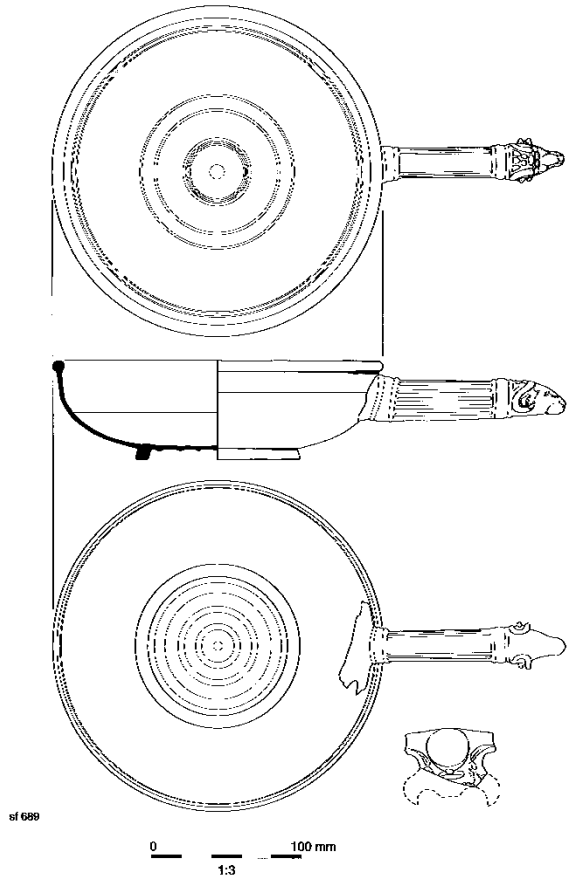

Figure 5-7: Patera 689
(Allen, *et al.* 2012: Figure 4.11)

[240] Nuber 1972: 53-54.
[241] Scott, 2012a: Description on pp 335,338-340 and plates on pp 339-341.

Three corrosion samples were taken from this vessel: KRM152, a mixed soil and corrosion sample from the interior of the patera; KRM153, a corrosion sample from the interior; and KRM154, a corrosion sample from the exterior possibly including some consolidant. The exterior corrosion products of patera 689 show evidence of the grass or material that once covered the bottom of the grave, but none of this material is present in the external sample.

A trilobite ewer or jug, vessel number 683, was inverted over patera 689 and typologically belongs to Nuber's Hagenow service (Figure 5-8). The ewer has a brass base and a leaded bronze handle attached with lead/tin solder. The top of the handle is in the form of a female bust whose arms are outstretched to grasp the rim of the jug. The base of the handle finishes with a face mask escutcheon adorned with curled hair and a diadem. The vessel measures 167 mm in height, 124x130 mm in diameter at its widest, and 69 mm in diameter at the base. Based on a similar vessel at Stanfordbury A, it could date to the very end of the Pre-Roman Iron Age or the immediate aftermath of the Claudian invasion of 43 CE.[242] The Hagenow service was the earliest type of Italian service to appear in the western provinces and Free Germany following the Augustan conquest and continued until the reign of Claudius.[243] One corrosion sample, KRM157, was taken from the exterior of this ewer near the brass base.

[242] Scott, 2012a: Description on pp 340-342 and plates on pp 342-343.
[243] Nuber 1972:38.

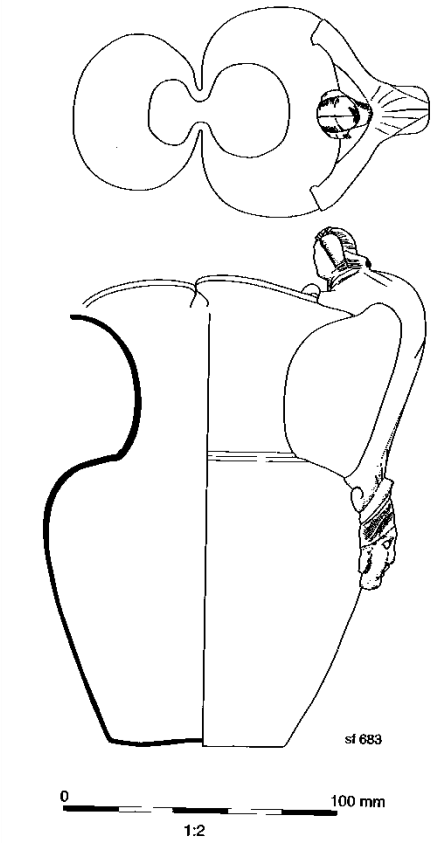

Figure 5-8: Ewer 683
(Allen, *et al.* 2012: Figure 4.14)

Grave 6635[244]

To the north-west of the main settlement enclosure, there is a cemetery containing nine further burials. The central two graves are high-status cremation burials (graves 6635 and 6645), both of which consist of square pits just over 1 metre across. The remaining six burials include three cremation burial pits and three inhumations. Sixteen bronze corrosion samples were taken from vessels found in the richest of these graves, grave 6635. This grave survived to a depth of approximately 0.30 meters and contained the cremated remains of what was probably an adult female. Within the grave there were fourteen pottery vessels including two lagenae, a beaker, a cup, a decorated samian bowl, and nine platters. Only two

[244] Scott, 2012b.

of these vessels are non-local wares. Overlaying the majority of the ceramic materials, were two bronze objects, a patera (vessel 1549) and a ewer (vessel 1550). A pharmaceutical or cosmetic set and a bronze brooch overlay the cremation deposit, which included a copper-alloy-sheathed small box, a stone mixing palette encased in a copper-alloy sheathe, and a spatula probe. The two bronze vessels suggest that the burial dates to the mid-first century CE and the typology of the brooch confirms this conclusion.

The patera, vessel number 1549, typologically belongs to Nuber's Hagenow service (Figure 5-9).[245] At one point this vessel would have had three cast feet, but these were lost in antiquity. The shallow main body of the vessel was beaten out and incised with a decorative pattern. The incised decoration displays a small eight-petaled flower surrounded by two concentric bands consisting of alternating large and small sections. The handle, cast out of leaded bronze in two sections and soldered to the dish, is formed in the shape of a ram's head. The pieces measures 233 mm x 235 mm in diameter with a handle length of 121 mm.[246] Fourteen corrosion and mixed samples from the interior and exterior of this patera were analysed for their organic content (KRM148-151, KRM158-167).

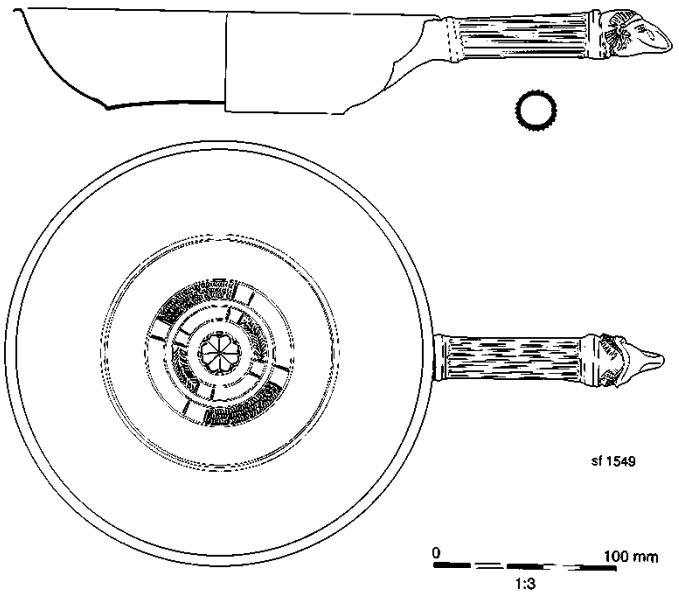

Figure 5-9: Patera 1549
(Allen, *et al.* 2012: Figure 4.25)

[245] Nuber 1972: 39.
[246] Scott, 2012b: Description on pp 363 & 366 and plates on pp 363-365.

The trilobite ewer or jug, vessel number 1550, belongs to the Millingen service (Figure 5-10).[247] This vessel is also made of hammered bronze with a cast leaded bronze handle. The handle boasts the face of lion which looks into the vessel and whose front legs encircle the rim. The handle tapers down to a face mask escutcheon at the lower attachment point. The outer face of the handle is decorated with a snake, its tail ending directly above the face mask and its head at the top curve of the handle before the lion's head. The vessel measures 133 mm in height and 127 mm in diameter (82 mm diameter at the base). The handle measures 135 mm in length and 75mm in width.[248] Two corrosion samples were taken from the interior and exterior of this vessel (KRM 155-156).

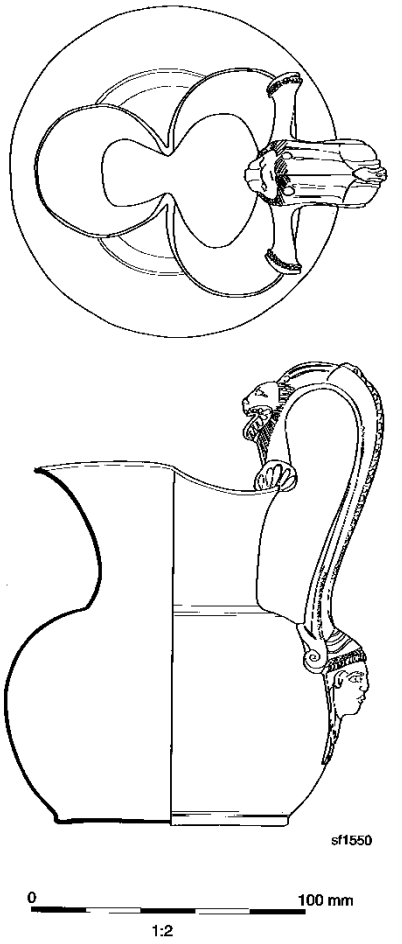

Figure 5-10: Ewer 1550
(Allen, *et al.* 2012: Figure 4.28)

[247] Nuber 1972: 45, 48
[248] Scott, 2012b: Description on pp 366 & 368 and plates on pp 366-367.

6. METHODOLOGY: DEVELOPMENT AND IMPLEMENTATION

In this chapter, building on what has been previously achieved in residue analysis of archaeological materials, the materials and methodologies used in this study are discussed. First, the methods used will be outlined in detail and then the justification and evaluation of these methods will be presented in light of the literature and analytical theory.

6a. Materials and Methods

One hundred and seventy-six samples of pottery, bronze corrosion, and modern reference materials were evaluated for their fatty acid content (Table 6-1).

Table 6-1: Samples for Residue Analysis

Site	**Sample Type**	**No. of Samples**		
Tel Kabri, Israel	Whole Sherd	55	104	133
Tel Megiddo, Israel	Whole Sherd	49		
Lefkandi, Greece	Drilled Powder from Vessel	29		
A2 Kent, UK	Bronze Corrosion	22		22
Modern Reference	Fat/Oil	21		21
Total				**176**

Samples from Kabri and Megiddo were in large part collected personally, either in whole sherd form or broken from a larger sherd with ceramic tile nippers. The sherds were labelled, packaged (paper and plastic bags for Kabri, aluminium foil and plastic bags for Megiddo), and stored in a dry location until analysis. The samples from Lefkandi were drilled from intact vessels or sherd material with a hand drill on location. The powdered samples, each weighing approximately one gram, were kept in glass vials until analysis. Bronze corrosion samples were taken and provided by Dana Goodburn-Brown. Each of the samples was removed from the surface of the bronze vessel with a scalpel and stored in acid free paper and aluminium foil until analysis. A range of modern commercial foodstuffs (olive oil, sunflower oil, grapeseed oil, butter, lard, milk, lip balm, wine) were studied directly. Once in the laboratory, each sample was subjected to an extraction, derivatisation, and analytical protocol, shown in Figure 6-1 and described in detail below.

The first step in the analytical protocol is the preparation of the sample for analysis. In the case of whole sherds, the surface dirt was mechanically removed with a scalpel and the sherd was weighed. In the case of large sherds, some were broken again to achieve a manageable size and weight. The powdered samples, both ceramic and corrosion, were weighed into new vials ready for extraction. In this study each sample was subjected to a sequential extraction protocol which consisted of a conventional solvent extraction phase and a direct methylation extraction phase. For the conventional solvent extraction, each sample was placed in a clean[249] beaker or test tube of appropriate size and covered in 2:1 (v:v) dichloromethane: methanol[250] and sonicated for 20 minutes. The solvent was decanted, centrifuged, and re-decanted into a pre-weighed test tube to remove suspended material and the extraction process was repeated. This solvent with any extracted residue was placed in a reweighed vial and the solvent allowed to evaporate. Any remaining solvent was removed by a gentle stream of nitrogen until the residue was dry and then the residue weighed.

Each residue was then derivatised according to a FAME protocol developed after O'Fallon, *et al.* 2004. 0.8mL of 10N potassium hydroxide (KOH) and 5.3 mL of methanol (MeOH) were added to the weighed residue. This mixture was agitated and heated at 55°C for an hour and a half, shaking vigorously every twenty minutes. After cooling to below room temperature in a cold water bath, 0.7mL of 24N sulphuric acid (H_2SO_4) was added and heated again to 55°C for an hour and a half, shaking vigorously every 20 minutes. The sample was again cooled and 3mL of hexane added, agitated thoroughly and the precipitate allowed to settle. Once the precipitate settled and the layers separated, the hexane layer was removed with a glass pipette and placed in a small vial for GC-MS analysis. This sample constituted the series of analysed sample labelled KRM XXX-001.

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[249] All glassware was either baked out at 500°C or rinsed three times with concentrated nitric acid, followed with milli-q water, and lastly chloroform:methanol.

[250] Chemicals obtained from Sigma-Aldrich, GC-MS grade where appropriate.

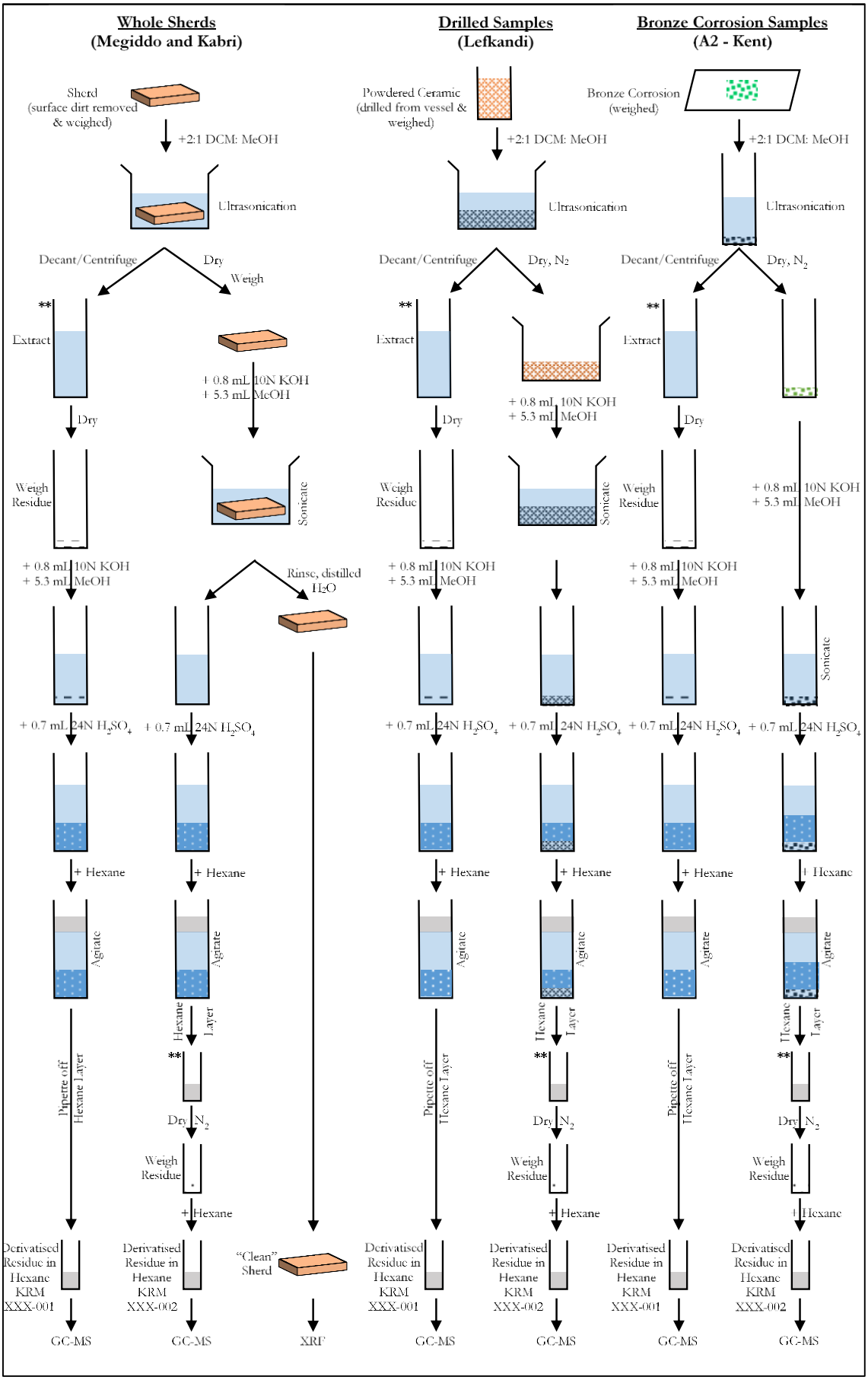

Figure 6-1: Analytical Protocol
** indicate pre-weighed vials

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After this conventional solvent extraction and derivatisation, the original sample was dried in a low temperature oven (sherd) or dried under a gentle stream of nitrogen (powdered ceramic and bronze) and reweighed in preparation for the direct extraction/derivatisation phase. In this phase, each sample was covered with 0.8mL of 10N KOH and 5.3ML of MeOH and sonicated for 20 minutes and then heated to 55°C for an hour and a half, sonicating again half way through. The extract was then decanted off the original sample for the intact sherds and cooled, or cooled in its entirety if containing a powdered sample. Once cool, 0.7mL of 24N H_2SO_4 was added to the mixture, agitated, and heated to 55°C for an hour and a half, shaking every 20 minutes. Once cooled again, 3mL of hexane was added, the sample thoroughly agitated and allowed to settle. The hexane layer was then removed with a glass pipette and placed in a pre-weighed vial to dry. The residue was then weighed, and re-dissolved in hexane for analysis. This extraction and derivatisation phase resulted in the series of samples labelled KRM XXX-002. At this point the powdered ceramic and bronze corrosion samples were discarded as they were inextricably mixed with precipitate potassium sulfate. The intact sherds were rinsed with milli-q water and dried in a low temperature oven in preparation for x-ray fluorescence.

The weights of the original samples and the dried residues were used to calculate residual extraction yield simply as follows:

$$TLY = \frac{m_r}{m_s}$$

where *TLY* is total lipid yield, m_r is the weight of the residue, and m_s is the original weight of the sample. The resulting extracted and derivatised samples in hexane were then analysed on an Agilent GC/MSD with auto-sampler, fitted with a RXi-5MS column (30m, 0.25mm id, 0.25 μm d_f). The GC-MS conditions were as follows: injection volume, 1μL; 20:1 or 5:1 split as necessary, generally 20:1 for series KRMXXX-1 and 5:1 for series KRMXXX-2); inlet

temperature, 300°C; inlet pressure, 11.681psi; flow rate; 1.2mL/min; temperature ramp, 80°C for 2 minutes, then 10°C/minute to 300°C, hold for 2 minutes; solvent delay, 4 minutes.

Finally, the intact sherd samples that survived the sequential extraction process were rinsed with milli-q water in order to rinse away any potassium sulfate precipitate and were dried for elemental analysis via energy dispersive x-ray fluorescence. The samples were placed with their internal surface perpendicular to the x-ray source and supported with various props to ensure stability during testing. The instrument was run in open air at 40 kV and 0.3 mA, with as spot size of approximately 2mm and count time of 180 seconds. As this simple set up was performed in open air, it was unable to record light elements (below potassium atomic number 19) and only provide general chemical characterization of the sherds based on relative and not absolute quantities.

In order to obtain reference information on the effectiveness of the extraction and derivatisation protocols and comparable fatty acid methyl ester data, modern reference materials were also sampled. These included commercially available olive oil, grapeseed oil, sunflower oil, lard, milk, butter, butter spread, mayonnaise, red wine, white wine, liqueur, whiskey, gin, lip balm, and conservation consolidant (Table 6-2). For each reference material between 0.14000 g and 0.18000 g was weighed out and treated with the FAME derivatisation and analytical protocols outlined above. Two samples of commercial olive oil on modern ceramic were also prepared by soaking a piece of terra cotta plant pot in olive oil for several days at room temperature. The sherds were then extracted and analysed in the same manner as the intact archaeological sherd materials from Megiddo and Kabri.

Table 6-2: Modern Reference Materials			
Class	**Type**	**Brand**	**Sample Number**
Oil on Ceramic	Olive Oil	Sainsbury's Basic	KRM 001, 002
Oil	Olive Oil	Sainsbury's Basic	KRM 171
	Grapeseed Oil	Tesco	KRM 016, 170
	Sunflower Oil	Flora	KRM 169
Fat	Lard	Tesco Everyday	KRM 011, 172
	Butter	Tesco Everyday	KRM 131
Mixed Oil/Fat	Lip Balm	Burt's Bees	KRM 027
	Milk	Tesco Reduced Fat	KRM 173
	Butter Spread	Lurpak	KRM 132
	Mayonnaise	Hellman's	KRM 130
Alcohol	Gin	Hendrick's	KRM 174
		Tanqueray	KRM 175
	Whiskey	Buffalo Trace	KRM 123
		Talisker	KRM 128
	Red Wine	McGuigan Estate Shiraz	KRM 129
	White Wine	Isla Negra Sauvignon Blanc	KRM 126
	Elderflower Liqueur	Chase Distillery	KRM 127
Conservation Material	Consolidant	Cyclododecane	KRM 168

Throughout the study, several steps were taken to control for error in the method and the introduction of experimental contaminants. The first step was to ensure that all reagents were GC-MS grade and that all glassware was clean. All glassware in the study was either baked out at 500°C or rinsed three times with concentrated nitric acid, then milli-q water, and finally chloroform/methanol. Where possible, the use of any material containing plasticizers was avoided. One of the most significant ways in which error was controlled, was in the inclusion of method blanks at every step of the protocol. To expedite sample preparation times, in general five to ten samples were extracted and derivatised simultaneously. For each batch of samples, a method blank was prepared without a sample. For this blank, an empty piece of clean glassware was filled with the solvents and reagents used for the samples according to the protocol. These method blanks were then run through

the GC-MS along with the corresponding samples. In this way, the cleanliness of the glassware, continued purity of reagents, and introduction of experimental error was controlled. Between every one to three samples run through the GC-MS, reagents blanks were also run to ensure that no residual material was caught in the column or inlet.

6b. Methodological Concerns

There are four areas of concern in the development of a methodology for the analysis of archaeological organic residues: the recovery of residual organics from the matrix on/in which they are preserved (extraction), the preparation of the residue for analysis (including derivatisation), the evaluation of yields and preservation rates, and the instrumentation used for analysis. Many residues in the archaeological record are absorbed or adsorbed within the ceramic matrix and must be recovered. When choosing a sampling and extraction procedure, the sample type must be first taken into account and the merits of destructive testing weighed. Secondly, the extraction procedure impacts the interpretation of a residue and the chemistry behind how it may have been preserved, such as trapped within the pore or bonded to the ceramic. As the presumption is that most archaeological residues are absorbed species within the ceramic vessel walls, the percentage of the total amount that is extracted is not always specifically known. Determining yield values provides a basis for determining effective methodologies, reducing error by exclusion of trace/minimal residues, and interpreting vessel use in addition to content[251].

The instrumentation, its benefits and limitations, is dependent on the research questions and also defines the sample preparation protocols. For GC-MS work, derivatisation of organic molecules is generally required. While it is possible to analyse highly polar molecules using columns with highly polar stationary phases such as FFAP-CB and

[251] Charters, *et al.* 1993b; Stern, *et al.* 2000 use concentration gradients and distributions of lipids in order to differentiate roasting and boiling techniques.

Chrompack, these columns are generally limited to lower temperatures ranges (~250 °C) which leads to long analysis times, broad peaks, and reduced resolution, particularly for large numbered carbon atoms (>24).[252] In light of this, derivatisation protocols are chosen on the basis of instrument conditions, the nature of the sample, and inherent characteristics concerning the resulting materials.

Each of these concerns must be taken in light of both the aims of the project and the available laboratory conditions and each has several avenues by which it can be addressed. The methods chosen for this project are outlined above, but the reasoning behind choosing these protocols over other potential protocols will be discussed in turn below according to relevant methodological concerns. An evaluation of each of the concerns, including the reasons behind them and the potential resolutions, is presented below in light of analytical theory and the goals of archaeological residue analysis. Considering this evaluation and the results of methodological testing, the methods chosen for this project as outlined in the previous section are justified.

6c. Sample Preparation: Sample Recovery and Residue Extraction

6c.i. Destructive vs Non-Destructive Analysis

Much of organic residue analysis in archaeology is destructive in nature, in that it most often a sherd is crushed or a small portion drilled in preparation for analysis. Destruction is typical in archaeology and archaeological science, as excavation itself is inherently destructive in the pursuit of investigating the past with the aim to preserve the information that results and the objects uncovered to a great extent. It is possible that the acknowledgement that archaeological excavation is a destructive art in itself drives the desire to preserve as much as possible. Most often in the field and the laboratory, a researcher

[252] Rieley, 1994.

must maintain a careful balance between the preservation of an object and its partial or total destruction in order to gain further information and answer research questions. Even in the realm of conservation, the line between preservation and inherently changing the character of an object can be blurred. With so many cultural materials lost and at risk through natural degradation processes, environmental conditions, human activity, display and public access, prior conservation efforts, negligence, looting, and war, the instinct of the archaeologist to attempt to minimize these factors is understandable and laudable. However, it must be decided, particularly with many analytical techniques, what intentional destruction for information is prudent, achievable, necessary, and desirable. To minimize this conflict between the conservation of materials and the need for analysis, there is a constant push to develop new non-destructive or minimally-destructive[253] analytical techniques for archaeological and historical materials which cannot be replaced.

In the analysis of organic residues in archaeological contexts, there are a number of benefits to both destructive analysis and non-destructive analysis in terms of access to materials and the research questions that can be answered. On one hand, non-diagnostic or semi-diagnostic, non-restorable sherd material is abundant in the archaeological record globally. This type of material is ideal for destructive testing, however it can be difficult to make meaningful interpretations based on vessel types. Anecdotally, a researcher may enter the field intending to collect a significant sample set of sherds corresponding to a specific vessel type to discover later upon removal of surface material and extraction that a large portion of the sample set is not what originally believed. Ceramic material is routinely washed in the field prior to reading, sorting, and determining what is restorable. A research paradigm that involves specific vessel types must be integrated into the initial excavation plan so sherds can be set aside prior to the rest of pottery processing and analysis. If this is done,

[253] The term *non-destructive* is generally used by scientists for techniques that make no change to an object (truly non-destructive), those that consume only a few picoliters of material (micro-destructive), or those that do not require a sample to be removed from the object (non-invasive).

issues accessing material and obtaining permits for its analysis (and export, if necessary) are somewhat easier to obtain. This framework does leave a void in the potential research questions and information to be gained in organic residue analysis. Sherds from restorable vessels and intact vessels begin to propose new problems.

It is not commonly true that an excavator, pottery restorer or specialist, conservator, or curator is willing to sacrifice a sherd of a restorable vessel or allow a hole to be drilled in a vessel that could otherwise be of museum display quality. Herein lies the attractiveness of a non-destructive approach. One could not only study whole vessels to which access would otherwise be limited as a result of excavator reluctance, export permit issues, museum regulations, or permissions, but also sherd material which could be used for restoration post-analysis. Such material could also be available for subsequent analyses of other forms. It is recognized that, even with a non-destructive approach, access to materials and permissions for analysis can be difficult to obtain and maintain, so one must be careful when designing such a project.

Non-destructive organic residue analysis has been tested by a few laboratories with mixed success and credibility of results. Some of the first work on non-crushed sherd material was done on two fragments of cooking vessels and one Dressel 20 amphora fragment excavated in the Roman village of Grand Loou, France. These sherds were passively extracted with methanol for 32 hours or three nights.[254] One major proponent of non-destructive extraction of archaeological organic residues is Andrew Koh, director of the ARCHEM project. His extraction method involves shortly heating a sherd in dichloromethane followed by ethanol.[255] Using this method, the ARCHEM project has claimed to find residues of wine, olive oil, resins, perfumes, honey, and herbs.[256] This technique closely follows the solvent swirling technique attempted by MASCA in the early

[254] Lecarpentier, *et al.* 1987
[255] Koh and Betancourt, 2010.
[256] Koh, 2008; Koh and Betancourt, 2010; and Koh, *et al* 2014.

1990s on Corinthian "plastic" vases using methylene chloride then methanol at room temperature.[257] Similarly, Garner non-destructively studied samples from Chania Kastelli Kalamaki, Salamis, and Sykia as part of the large Minoan and Mycenaean vessel study overseen by Tzedakis, Martlew, and Jones. In this study, sherds were flooded with methanol or dichloromethane and left to equilibrate for several minutes before drawing off the solvent.[258] Each of these extraction protocols involve passive flooding of the intact sherds with various solvents either at room temperature or slightly warmed.

A major drawback of these studies is the fact that several have noted the removal of only surface contaminants, particularly in the case of the swirling of solvent in whole vessels.[259] Environmental and excavation contaminants appear to be particularly rife in these projects, especially nicotine from cigarette smoke, suntan lotions, oils from handling, perfumes, and insecticides/repellents.[260] With the exception of the ARCHEM studies, non-destructive residue analysis has not yet been seen to give secure results with clear interpretations. In the case of ARCHEM, the investigators have reported excessively high success rates (100% of all sherds sampled at Tel Kabri resulting in residue), in addition to uncommonly reported residual components (spices, wine – tartaric acid, etc.).[261] It also seems that, while heating the solvent does increase the solubility of organics, passive flooding is unlikely to be entirely effective when even drilled or crushed materials require sonication to remove significant quantities of organics from a ceramic medium.

It has been suggested that drilling or crushing of sherds releases further material for analysis. This arises from the porous nature of the ceramic, which when drilled, removes the protective spaces in which a residue is preserved. If the preservation of residues in ceramics is predominantly driven by absorption and the physical protection, restricted access to the

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[257] Gerhardt, *et al.* 1990; Biers, 1994: 19.
[258] Garner, 2008; Tzedakis, Martlew, and Jones, 2008.
[259] Gerhardt, *et al.* 1990; Biers, 1994.
[260] Biers, 1994.
[261] Koh, *et al.* 2014.

molecular organic material is what has protected it from leaching, microbial attack, and other environmental factors which would otherwise remove it from the system and this would similarly restrict laboratory removal. Even if there are other mechanisms at play, access is nonetheless important. One crucial difference between the above passive flooding extractions and the protocol used for this study, is the addition of ultrasonication. The most that the other teams using non-destructive analysis have done to increase extraction yield is the heating of the solvents to increase the solubility of the residual molecular organics.[262] By ultrasonicating the intact sherds in the solvents, it is ensured that the maximum contact is made between the solvent and the materials caught within the ceramic matrix. It also ensures constant movement of the solvent, so that it not only reaches all of the pores but also prevents localized saturation. Noting that problems with the removal of only surface contaminants has occurred in other studies,[263] surface material was gently scraped from the surface with a scalpel or carefully brushed away. It has been shown elsewhere that the bulk of organic material is held in the first 2mm of a sherd,[264] so removal of the surface of a sherd prior to extraction[265] has a high probability of removing a great deal of preserved molecular organics. In addition, the removal of a drilling step takes with it the increased probability introduction of analytical artefacts from the drilling process and handling. Generally, this step is controlled for in the preparation of a method blank of clean modern ceramic, prepared, extracted, and analysed according to the method chosen. This step was not taken in this study due to the fact that minimal drilling was performed in the field, where if contamination from the area was introduced, it could have been introduced in the laboratory, in the transport of the clean sample to Greece, or in the drilling process itself.

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[262] Koh, 2008; Koh and Betancourt, 2010; and Koh, *et al* 2014.
[263] e.g. Biers, 1994.
[264] Stern, *et al.* 2000.
[265] e.g. Charters *et al.*1995; Copley *et al.* 2005; cleaning the surface of sherds with a hand drill prior to extraction.

One major benefit to non-destructive analysis in terms of the goals of this project is the ability to compare directly residue results with information concerning the characteristics of its immediate context. It also allows for the characterization of the vessel without any competing information from the residues. For example, if one need to do scanning electron microscopy or take thin-sections for petrography, the sample would be clear of any residue prior to this characterization. An important decision with regards to the initial goal to take porosity measurements, taking a porosity measurement of a sherd with the absorbed residue already removed, would allow for direct comparison of the volume of space in which the residue was occupying to the amount of residue itself. In the long term, not only does the characterization of the same sherds that are tested for residues allow for the most direct comparison, it reduces the amount of material needed for analysis and eliminates errors caused by variations in any given ceramic fabric. For the majority of the sherd material tested in this project, the samples survived and could be subjected to further analytical methods in the future to obtain additional data.

6c.ii. Extraction

Only in a few circumstances is some sort of extraction protocol unnecessary for the analysis of organics preserved in pottery. One example of this is the analysis of charred visible residues by Curie-point pyrolysis coupled with gas chromatography and mass spectrometry (CuPy-MS and CuPy-GC-MS).[266] This technique has benefits in that it does not require preparation of a sample outside of grinding; it requires only small samples sizes; and it allows for the direct comparison of samples in varying matrices (e.g. visible residues, pottery fragments, and soil samples). However, it has not yet been seen to provide more information than conventional gas chromatography-mass spectrometry and it is unable to

[266] Oudemans and Boon, 1991.

quantify the conversion of sample into analysable components.[267] Archaeological lipid residues are by nature altered, degraded, and manipulated, resulting in a complex mixture that is only reminiscent of the original substance. The choice of extraction method depends on the nature of the matrix (ceramic, metal, tissue, lithics, etc.), the composition and chemical nature of the residue, and the presence of any forces which may bind the residue to its matrix. There are two main types of extraction used in organic residue analysis: conventional solvent extraction and base assisted extraction, both were used in this project.

Conventional solvent extraction, using either chloroform or dichloromethane and methanol in a 2:1 by volume combination is the most frequently used extraction protocol for archaeological residues.[268] This method is solely dependent on the solubility of residual organics, namely lipids, in the chosen solvent and depending on the composition of the residue, the choice of solvent significantly impacts the efficiency of extraction. The class of organic compounds referred to as *lipids* is defined by the solubility of these compounds in organic solvents. What complicates pure solvent extraction of archaeological lipid-containing residues is their degradation, chemical interactions, and slight differences in solubility. For example, the solubility of saturated fatty acids in water, chloroform, and methanol changes significantly with the addition or subtraction of a carbon centre (Table 6-3). While the difference in water solubility of C12-C18 fatty acids is relatively small, all being relatively insoluble, the solubility of $C_{12:0}$ and $C_{18:0}$ in methanol differs by a factor of six hundred and five.

Table 6-3: Solubility of Fatty Acids in Various Solvents at 20°C (g fatty acid/100g solvent)

Fatty Acid	Water	Chloroform	Methanol	Acetone
$C_{12:0}$	0.0055	120	60.5	15.9
$C_{14:0}$	0.0020	83	17.3	5.38
$C_{16:0}$	0.00072	32.5	15.1	3.7
$C_{18:0}$	0.00029	6.0	0.1	1.54

[267] Riedo, *et al.* 2011.
[268] Evershed, 1993.

Other compounds are also formed by the reaction of the initial substances components with the environment, other substances, and potentially its matrix. These compounds can differ greatly in their solubility in various solvents and their absence from conventional solvent extracts could significantly affect interpretation of a given residue. Fatty acids salts in particular are temperamental to extract and less soluble than their fatty acid precursors. In solution, carboxylic acids are weakly acid and available to participate in ionic reactions. Salts of these acids can be formed with alkaline metals, and amines with pronounced ionic character which are commonly present in water:

$$RCO_2H + NaHCO_3 \rightarrow RCO_2^- Na^+ + CO_2 + H_2O$$

$$RCO_2H + (CH_3)_3N \rightarrow RCO_2^- (CH_3)_3NH^+$$

$$RCO_2H + AgOH \rightarrow RCO_2^- Ag^+ + H_2O$$

When these salts form with fatty acids containing 10 carbon centres or more, these salts become amphilic (both hydrophilic and hydrophobic) in nature making them good surfactants and can be commonly found as "soap salts". The most soluble of these fatty acid salts are those formed with potassium. Conversely, calcium fatty acid salts are insoluble and create what is commonly known as soap scum.

To counter wide ranges of solubility in polar solvents, a mixture of solvents is usually employed in the extraction of fatty acids and other lipids. The most common mixture of these solvents is chloroform or dichloromethane (similar solvent abilities) with methanol 2:1 (v:v). Even so, it must be noted that absolute concentrations of extracted fatty acids is not only altered by the degradation reactions but also by preferential extraction by the chosen solvent. This makes a big difference in the efficiency of simple solvent extraction via sonication or Soxhlet as it depends solely on the solubility of the organic in the chosen solvent and assumes that organics are only trapped within the matrix. Using a reflux apparatus such as Soxhlet allows for repeated clean rinsing of the sample to release a greater amount of trapped residue ensuring that the possibility reaching the absorption capacity of

the solvent is minimized and the yield is increased. Sonication helps to ensure that the solvent enters as many of the pores as possible and achieves contact with as much of the organic as possible. In the case of samples containing very little organic material, Soxhlet extraction is helpful, but it is generally not preferred as it is much more time consuming and limiting in scope.

One of the pieces of evidence that seems to indicate that organic molecules may interact with the ceramic matrix itself over short range bonds is that, in some cases, base treatment of a sample will release further organic species after conventional solvent extraction. Regert and colleagues discovered the presence of fatty acid oxidation products such as α,ω-dicarboxylic acids and α-hydroxy carboxylic acids, previously undetected with solvent extraction.[269] Similarly, vicinal dihydroxy acids have been recovered and linked to their monounsaturated fatty acid precursors.[270] The suggestion that these smaller oxidation products are linked via ester linkages[271] to the mineral surface is a relevant one. It has been suggested previously that the oxidation products, which are most certainly created during use and in the burial environment, may be missing from the corpus of studied archaeological residues due to ground water leaching as their small size would make them more susceptible. Yet, these two examples produce some convincing evidence that despite their higher solubility, these oxidation products are not easily removed by solvents so therefore must be strongly bound in some way.

Craig and Collins followed this suggestion by investigating the possibility of proteins preserved on mineral surfaces (i.e. ceramic) and showed that they too were not absent in absorbed residues as previously assumed, but could be released by sodium dodecyl sulphate which would disrupt non-covalent bonds and bind to hydrophobic regions of the protein.[272]

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[269] Regert, *et al.* 1998.
[270] Hansel, *et al.* 2011.
[271] Regert, *et al.* 1998; Stern *et al.* 2000.
[272] Craig and Collins 2002.

While this marks a significant step towards understanding potential interactions between minerals and organics, it is important to note that they did not achieve good detection limits in 16 of 19 samples. Proteins are more complicated in their recovery as their identification is usually based on their activity which is dependent on them keeping a specific stereochemistry, however the fact that oxygenated degradation products have been released by strong base hydrolysis and not by polar solvents seems to support strongly the idea that these compounds are chemically linked to their matrix. It has also been suggested based on the fact that fatty acids are released by direct methylation or base catalysed saponification reactions, but to a lesser extent when acid catalysed, that the fatty acids released are not fatty acid salts but cross-linked macromolecules.[273]

During the write-up of this thesis, a paper was published with new data concerning the application of direct acidified methanol extraction to archaeological residues.[274] Correa-Ascencio and Evershed used methanolic sulphuric acid to treat crushed sherd materials that had previously studied via conventional solvent extraction and derivatisation. They had great success with this new method and show that acidic extraction was able to produce residues where conventional extraction could not. They suggest that the acidified extraction opens up the clay surfaces. They also compared the porosity via scanning electron micrograph to show that sherds with macropores allow deep penetration of lipids and high absorptive capacities. They also observe the accumulation of inorganic salts on the surface of Mesoamerican cooking vessels, but not that the strong acidified solution dissolved this surface deposit and allowed the reagents to penetrate the surface and release further lipids. They promote this new technique as a faster, more efficient, and in many cases more effective extraction protocol for the extraction of residues from archaeological ceramics.[275]

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[273] Stern, *et al.* 2000.
[274] Correa-Ascencio and Evershed, 2014.
[275] Correa-Ascencio and Evershed, 2014.

In development of an effective methodology for the sample set and one that produced the best results under current laboratory conditions, two extraction methods were tested on modern ceramic material (terra cotta flower pot). Four ceramic samples were weighed placed in a small Petrie dishes and submerged in olive oil (Sainsbury's Extra Virgin Olive Oil, packaged in Spain). Two samples were left on the bench top and the other two placed in a 40°C oven for a week. One heated and one non-heated sample were subjected to extraction with dichloromethane: methanol 2:1. The other set was subjected to direct extraction and creation of fatty acid methyl esters with methanolic potassium hydroxide. The results are presented in Table 6-4.

Table 6-4: Results of Solvent Extraction vs. Direct Methylation for Modern Samples of Olive Oil Absorbed in Reference Ceramic

Sample	Oil Absorbed mg/g	% Extracted	Yield mg/g
Heated, DCM:MeOH	121	49.89	53.97
Heated, FAME	122	14.21	15.46
Unheated, DCM:MeOH	116	54.42	63.46
Unheated, FAME	118	14.31	15.15

It is clear from these results that the direct treatment of absorbed residues with aqueous methanolic potassium hydroxide is less than half as effective as extraction with dichloromethane and methanol. Neither method completely removed the absorbed oil, but even taking into account any mass change due to methylation and experimental error (e.g. solvent not fully evaporated, loss in transfer), a comparison of sherd weights (dry before addition of oil, and dry after extraction) shows that the alkaline treatment left behind 60-77% of the absorbed oil, while dichloromethane and methanol left behind only 46-48%. It is also worth commenting that the absorption of olive oil increased by nearly 4% over room temperature values upon heating the sample to 40°C. These results confirm the need to perform conventional solvent extractions in analysing archaeological samples. The results

also confirm that convention solvent extractions are not 100% efficient in removing residual compounds from ceramics and that sequential extractions might release further species.

Interestingly, these data differ from the published literature on base-catalysed extractions, as most have found that yield figures are higher with base-catalysed extractions over conventional extraction, despite the fact that it continues to be used less frequently. This may reflect time or degradation components to the interaction between ceramics and organics or a divergence the identity of the residue measured in various yield calculations.[276] A possible explanation for this divergence, also seen in the archaeological sample results, lies in the sample preparation and supports an argument for a dual mechanism of preservation. In other studies using base and acid hydrolysis, the samples have been crushed prior to extraction. If cross-linkages are in existence between some of the lipid material and ceramic matrix, these lipids would be those held closest to the crystalline surfaces deepest within the porous matrix. The limited release of lipids with base may indicate that for these particular lipids, physical inhibition of the solvent is more of a factor than easily soluble lipids extracted conventionally. This theory needs to be tested further by comparison extractions of crushed and intact reference ceramic and archaeological sherds.

For the purposes of this project, it was decided to perform sequential chloroform: methanol (2:1, v:v) and direct FAME extractions for all of the samples in order to measure residual yields quantitatively and qualitatively and compare them across the sample set with regard to other vessel characteristics. The choice of specific FAME protocol and its mechanism are discussed further in the next section. Ideally, if there is a direct relationship between the ratios of conventional extract yield to direct FAME extract yields and specific characteristics such as fabric type, it would provide some evidence as to the presence or absence of a chemical preservation mechanism between a vessel and its contents. If there is

[276] Several ways of calculating yields is discussed in section 6f. This is an important factor in the comparability of results and potential explanations of any deviation.

no interaction, a tapering off of extraction efficiency would be expected as the direct FAME extraction would be removing only what was beyond the solubility of the constituents in the initial solute and if the quantities of residue were lower than their concentrated solubility in chloroform: methanol, there would be no remaining residue for the direct FAME solvents to extract.

6d. Derivatisation

One of the primary concerns in developing a preparative methodology for the GC-MS analysis of lipids in archaeological residues is derivatisation. Derivatisation is defined as *the transformation of a chemical compound into another chemical compound, by altering one or more of its functional groups. Derivatisation is generally performed to alter reactivity or change a physical property such as solubility, boiling point, melting point, thermal stability, etc.*[277] In general, lipids and biomolecules must be derivatised before instrumental analysis in order to make them more suitable for the desired analytical method. The type of derivatisation is dependent on the form of analysis, but rarely can one analyse these compounds directly without alteration. The range in polarity and masses of the analytes must be taken into account, particularly for chromatography. Figure 6-2 indicates some of the types of biomolecules that can be analysed by mass spectrometry, specifically gas chromatography – mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LCMS), and matrix assisted laser desorption ionization mass spectrometry (MALDI). The classes of compounds are graphed according to their mass and polarity. Arrows A and B show how derivatisation allows for the analysis of a larger range of molecules for GC-MS and LCMS/MALDI/LDI, respectively.

[277] Definition according to the Royal Society of Chemistry, http://www.rsc.org/publishing/journals/prospect/ontology.asp?id=CMO:0001485.

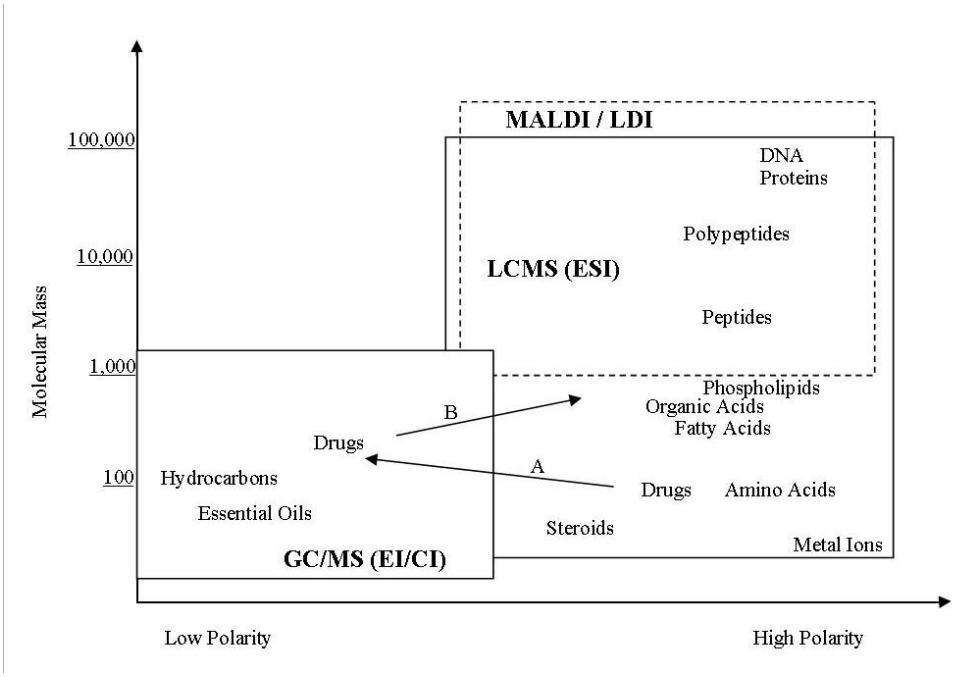

Figure 6-2: Approximate Analyte Polarity and Molecular Ranges for Mass Spectrometry (GC/MS, LC/MS, and MALDI).
The effects of derivatisation reactions are also indicated. Arrow A indicates derivatisation required for analysis of specified compounds via GC/MS and arrow B indicates that required for analysis via LCMS and MALDI/LDI. (after Zaikin & Halket 2009)

The main aims of derivatisation for GC-MS are the following: to increase the volatility of an analyte by decreasing its polarity, to improve the chromatographic properties of the sample, to improve sensitivity and selectivity, and to increase the amount of structural information available. In gas chromatography, analytes are separated based on their affinity for a solid phase lining, which is proportional to their polarity. Chemical derivatisation reactions can reduce intermolecular and ionic compounds or break apart large bulky molecules and thus increase their volatility and improve chromatographic separation. As the compounds flow more easily through the column, they separate more effectively and produce sharp distinct chromatographic peaks. These sharp and defined peaks are essential for quantitative and qualitative determinations. Finally, derivatisation is able to improve sensitivity and selectivity of GC-MS measurements by making abundant high mass fragment ions and increasing structural information based on reactions over specific functional groups and linkages. Ultimately, the limits of detection are improved and result in more accurate

and diagnostic mass spectra.[278] Common derivatisation mechanisms in the study of lipids both within and outside of the context of archaeological residues include silylation and esterification. Both of these reaction mechanisms target the active hydrogen in hydroxyl (-OH), carboxyl (-COOH), amino (-NH2), and thiol (-SH) groups. Each mechanism will be dealt with individually below.

Silylation

Silylation is one of the most common and universal derivatisation methods used in the study of organics. In this type of derivatisation, a silyl group ($-SiR_3$) replaces an active hydrogen such as that present in hydroxy groups (alcohols, phenols, carboxylic acids, oximes, sulphic acids, borous acids, phosphorous acids, and enols) and amino groups (amines, amides, and imines).[279] Due to the large range of hydrogen-containing functional groups that can undergo silylation, this method is commonly applied to the study of organics and trace compounds analyses in forensics, pharmacology, archaeology, and other areas. A number of reagents can be used to silate a sample, but due to commercial availability and ease of use, trimethylsilyl derivatives of acetamide and trifluoroacetamide are the most common.

In the study of triacylglycerols and fatty acids present in oils, fats, and waxes, silylation has several benefits. First, it does not hydrolyse glycerols allowing for analysis of intact mono-, di-, and tri-acylglycerols. This provides more specific information on the location of specific fatty acids on the glycerol backbone, their breakdown, and leading to more specific identifications.[280] Silylation reactions also do not proceed around a carbon centre contained in the final derivative, minimizing kinetic isotope effects in GC-C-IRMS measurements[281]. The detraction of this method is relative instability of trimethylsilyl

[278] Zaikin and Halket 2009: Introduction.
[279] Zaikin and Halket 2009: xxi.
[280] Wan, *et al.* 2007.
[281] Rieley, 1994.

derivatives and their high sensitivity to hydrolysis. The hydrolysis reaction reverses the derivatisation potentially not only affecting the analytical timeframe post-derivatisation but also the shelf-life of reagents.

Esterification: Methylation, Acetylation, and Transesterification

In esterification reactions, also known as alkylation reactions, reactive hydrogens are replaced by an alkyl group. It is an effective derivatisation technique for carboxylic acids, sulphonic acids, alcohols, phenols, mercaptans, primary and secondary amines, and amides. They can occur in acid or basic solutions, or combination of the two allowing for collection of both acidic and basic solution. One mechanism by which esterification of a carboxylic acid in acidic solution is presented here in Figure 6-3.[282]

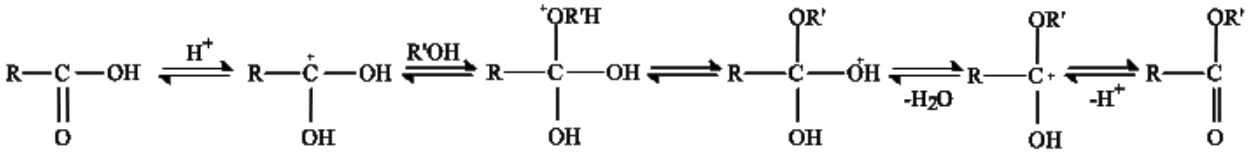

Figure 6-3: Esterification of a Carboxylic Acid in Acidic Solution

A significant trait of these reactions in the derivatisation of lipid samples is the hydrolysis of acylglycerols into their component fatty acids as methyl esters (FAMEs). Triacylglycerols can also be saponified through base hydrolysis and then acidified to create methyl esters. Saponification occurs by the following mechanism in Figure 6-4.

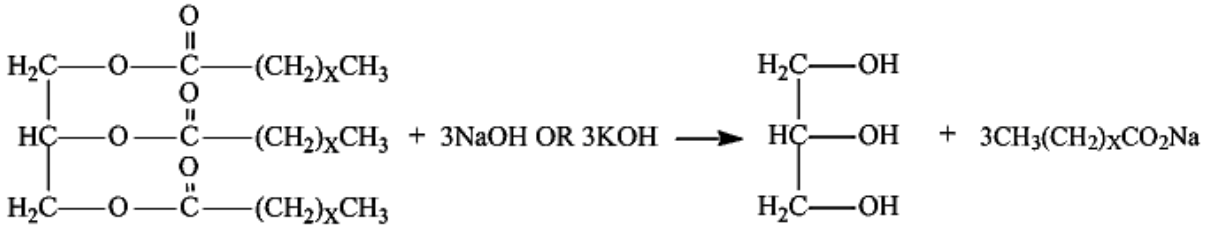

Figure 6-4: Saponification of a Triacylglycerol by Sodium or Potassium Hydroxide

[282] Rieley, 1994.

The attraction of esterification reactions is an increased stability over trimethylsilyl derivatives and the creation of smaller derivative molecules. Also, esterification reactions that proceed in the presence of an acid and base catalyst are fully quantitative and can easily be driven to completion. It has been suggested that fatty acid ratios are not enough alone to indicate origin of archaeological residues. One major reason for this is the inherent alteration in these ratios due to differential solubility during the extraction process (see above). For this reason, FAME analysis is sometimes done in conjunction with other derivatisation methods or with single-compound isotope analysis. However it should be noted that in the case of using GC-C-IRMS to confirm plant and animal lipid identifications, the results can be altered. Transesterification generally proceeds around a carbon centre contained in the final derivative product and introduces the possibility of a kinetic isotope effect[283].

Derivatisation: Experimental Results

Three derivatisation reactions have been tested in the development of a working methodology for the purpose of this thesis. The first is a silylation reaction involving N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). This method has been reported repeatedly in the literature with good success, generally referring to work done at the University of Bristol.[284] Originating in food science, the second and third methods result in the formation of FAMEs using two techniques originating in food science. The first of these methods was developed by Chemical Standards for Supelco in order to analyse modern reference oils, particularly corn oil.[285] In this set of reactions, methanolic hydrochloric acid (HCl) is first used to break apart triacylglycerols into constituent fatty acids and glycerol (Figure 6-5).

[283] Rieley, 1994.
[284] Charters, *et al.* 1993b, 1995. Evershed, *et al.* 1990.
[285] Kiefer, 1997.

Then 2,2-dimethoxypropane serves to drive the transesterification to completion by reacting with glycerol to form isopropylidine glycerol and methanol, preventing the transesterification reaction from going backwards (Figure 6- 6).

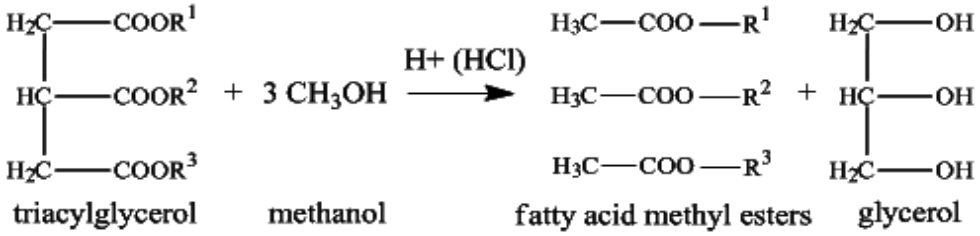

Figure 6-5: Methylation of Triacylglycerol (Transesterification Reaction)

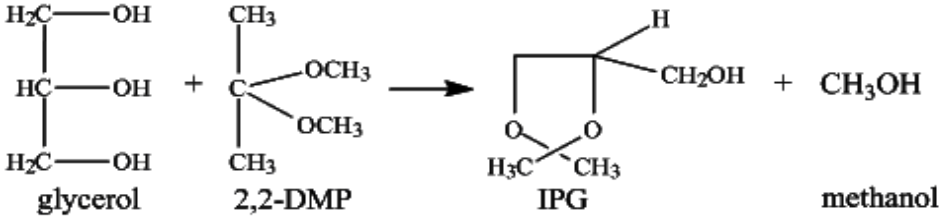

Figure 6-6: 2,2 Dimethoxypropane Reaction with Glycerol to form Isoproylidine Glycerol.

The third method tested for its success in analysing lipid residues originates in animal science studies for the analysis of lipid content in tissues. O'Fallon and his colleagues compare a traditional method for creating fatty acid methyl esters using boron trifluoride in methanol or sodium methanol with a new method. They show that by saponifying the sample with potassium hydroxide in water and methanol and then acidifying the sample with sulphuric acid to complete methylation, that one could obtain reliable FAME results in the presence of water without risking quick hydrolysis and alteration of the sample. The fact that this reaction can proceed in the presence of water is a significant contribution to the study of lipids from a wide range of contexts. This two-step method was also shown to be more effective in the complete hydrolysis, methylation, and recovery of FAMES than boron

trifluoride and sodium methoxide. It allows for ease of sampling, and reduces the chances of incomplete derivatisation via hydrolysis. [286]

Each technique was tested on a number of modern fats and oils (olive, safflower, grapeseed, corn, lard). There were some problems encountered with the trimethylsilyl derivatisation method encountered in reproducibility and stability of reagents. In a few of the tests it is expected that the derivatisation did not work as a result of either excess solvents that allowed for some hydrolysis or inactive derivatisation reagent. Previous work had success with BTSFA as a derivatisation agent,[287] but it was found over the time scale of the project that the FAME derivatisation was just as simply performed, did not rely on the complete dryness of a the sample, was more consistent from sample to sample, and was stable over long periods of time, allowing for the bulk preparation of samples in advance of scheduled time on the GC-MS. TMS derivatisation with BSTFA seems also to leave analytical artefacts within the GC column from time to time increasing the wear on the column, as it was observed during this project after runs of TMS derivatised samples by another user in the laboratory. The two-step FAME protocol using KOH/MeOH and H_2SO_4 was chosen over methanolic HCl as the reagents were easier to prepare and in initial testing, there seemed to be little benefit of the methanolic HCl chromatograph over the one from the two-step protocol. For the lab set up, FAME derivatisation was extremely reproducible and the continued quality of GC-MS spectra testable as samples could be retested if necessary weeks after the initial derivatisation. Such re-testing is not possible for the TMS derivatives as they are unstable and susceptible to polymerization and reversal by moisture. Overall, the FAME protocol is far more forgiving in terms of error, measurement, and timescale. It is also not a worry that any of the reagents used in the FAME protocol will

[286] O'Fallon, *et al.* 2007.
[287] Merriman, 2009.

become inactive, reducing costs and reducing time pressure, especially under shared laboratory conditions.

The two FAME derivatisation methods provided clearer and more consistent results. Good $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$ peaks were seen in each of the chromatograms. Cholesterol was identified in the lard sample treated with KOH but not methanolic HCl. In addition squalene was identified in both olive oil samples, but the signal was much clearer for the saponified sample. Both FAME methods produced similar profiles for the major fatty acid components; however in each case, saponification produced larger and clearer signals. In addition to providing better results for each of the oils and fats, the saponified samples proved to be much more stable, still producing identical chromatograms after seven and ten days, while the methanolic HCl derived FAMEs began to alter around day five.

In the development of extraction and derivatisation protocols for the analysis of archaeological residues by GC-MS, a few conclusions have been made apparent. First, it is clear that the derivatisation method (after O'Fallon, *et al.* 2007) is the best suited to current laboratory conditions. In addition to the best and most informative GC-MS results, this method produces the most stable and consistent derivatives providing a distinct advantage over unstable TMS derivatives. While there is a loss of some potential information with FAME over TMS due to the hydrolysis of triacylglycerols in particular, the ease and small margin of execution error is preferential. By choosing the two-step FAME method, theoretically the extraction yield is increased over methanolic HCl derivatisation and the presence of water does not endanger the mechanism. While TMS and diazomethane derivatisations are routine, both require nearly immediate processing of derivatives and constant turnover of reagents to keep them active, in addition to the toxicity and explosivity of diazomethane raising concerns. Both catalysed methylation methods require cheaper reagents, but methanolic HCl must also be kept carefully to maintain its anhydrous nature. The two-step approach demands reagents that are easily acquired, prepared, and stored, thus

it is quicker, cheaper, less likely to encounter failures, and produces the most stable derivative. Lastly, the FAME protocol was used for the study of residues in this study to evaluate the mechanism of preservation and the possibility of bonding of molecular organic residues to the ceramic matrix in a direct extraction/derivatisation setting. This accords with previous and current research into the bonding of materials to ceramic and the development and evaluation of methods for archaeological organic residue analysis.

6e. Modern Fats and Oils

In order to test the established methodologies for extraction, derivatisation, and analysis by GC-MS, a number of modern foodstuffs were tested for lipid content. Items tested include commercial olive oil (Sainsbury's Olive Oil, Spain), sunflower oil (Flora), grapeseed oil (Tesco), butter (Tesco unsalted butter), milk (Tesco, semi-skim), butter and vegetable spread (Lurpak spreadable), mayonnaise (Tesco), red and white wines (McGuigan estate Shiraz and Isla Negra sauvignon blanc), bourbon (Buffalo Trace), single malt whisky (Talisker, 10-year), two varieties of gin (Hendrik's and Tanqueray), elderflower liquor (Chase Distilleries), and lip balm (Burt's Bees). Each of the fat, oil, or liquid samples were dissolved in chloroform: methanol (2:1, v:v), derivatised using the direct FAME protocol, and the hexane fraction analysed via GC-MS. In the predominantly triacylglycerol-containing fats and oils, namely the butter, milk, spread, mayonnaise, and all of the seed oils, the expected fatty acid concentrations were also observed. In the sample of lip balm (KRM 027) which is advertised to be predominantly beeswax, with vitamin E, and aromatics, the expected compounds were observed. Menthone and its derivatives, Levomenthol, fatty acids from C8 to C20, longer chain alkanes, and vitamin E were observed in the chromatograph.

Somewhat problematically, none of the alcohol-based modern reference materials were successful in the detection of molecular constituents. It is possible that the extraction process was not sensitive enough and that the solvents did not come into enough contact

with the lipid and acidic constituents due to water content. Studies on the aromatic compounds of bourbon, indicate the presence of small chain lipids (i.e. butanoate, hexanoate) and lactones.[288] It is noted, however, that this study was primarily looking for odour producing compounds and odour activity values and thus could use a mixtures of ethanol and water to analyse their samples. In the future, dehydrated samples of water-based or alcoholic substances could provide better comparative materials. The second conclusion that could be drawn from this evidence is that the extraction technique and set-up used are simply not suited to the detection of volatiles and non-lipid or non-terpenoid compounds. The compounds observed in the referenced study of American whiskey, if present in the extracts for this project, would not have been seen due to solvent delays and the peaks associated with the hexane solvent.

Two of the modern olive oil samples were extracted from modern ceramic sherds. (KRM 001 and KRM 002.) Two pieces of a modern terra cotta plant pot were covered with olive oil for several days. When removed from the oil, excess oil was dabbed from the surface with a paper towel and the sample left to dry. The sherds were then extracted and analysed in the same fashion as the archaeological sherds. These sherds, in contrast to the extracted pure olive oil samples, produced better chromatographs. The minor entities in the oils were detected along with the major oleic acid peaks. There could be two reasons for this: first the natural oxidative degradations that occur as thin films of oil are left to the air for several days, or to a mediated reaction involving the ceramic. In the pure extracted samples, a indistinct oleic acid peak results with lack of derivatisation. In several of the modern fat/oil samples, indistinct peaks were observed where components were not distinctly separated by the GC column (eg. KRM 131, 172). These samples were too concentrated and thus not completely derivatised by the quantity of reagents added. These

[288] Poisson and Schieberle, 2008.

samples clearly show the requirement of derivatisation for the analysis of fats and oils and the benefits of a completely derivatised sample.

6f. A Note on Internal Standards and Yield Calculations

In this study, internal standards were not used in order to calculate yields as it has been done elsewhere.[289] Based on the inclusion of a specified amount of internal standard and the GC-MS profile, the yield of a given residue is then calculated as delineated below:[290] Relative Molar Response, F(R Molar), the relative amount of a component x necessary to obtain the same response GC signal as the internal standard, is determined according to the following equation, where ECN is the effective carbon number:

$$F(Rmolar)_x = \frac{ECN_{is}}{ECN_x}$$

The calculation of relative molar response allows for the comparison of peak areas as a representation of quantity. Then the amount of every compound, x, in a total sample, q, can be determined as:

$$q_x = q_{is} \times F(Rmolar)_x \times \frac{A_x}{A_{is}} \text{ (mol)}$$

where q is the amount of compound, and A is the relative peak area (%). The percentage by weight of each component represented in the chromatograph can then be calculated as a normalized weight percentage (WP):

$$WP_x = \frac{q_x \times MW_{x\,(underivatised)}}{\sum_{x=1}^{n}(q_x \times MW_{x\,(underivatized)}} \times 100\%$$

where n is the number of compounds in the sample and MW is the molecular weight of compound. The total lipid yield can then be calculated as:

$$TLY = \frac{\sum_{x=1}^{n}(q_x \times MW_{x,(underivatised)})}{W_s}$$

[289] Tetratriacontane ($C_{34}H_{70}$) is the most frequently used, such as Evershed 1993
[290] Oudemans and Boon, 2007.

where W_s is the original weight of the sample.

The second method of quantification method is direct weight comparisons prior to analysis. This, rather than giving an indirect original weight based on comparable data, gives a direct measure of extracted material. In this quantification method, the extracted residue is dried and weighed and then compared to the original sherd weight.

$$TLY = \frac{m_r}{m_s}$$

Where m_r is the mass of the residue and m_s is the weight of the original extracted sherd.

There are several reasons behind this choice not to employ an internal standard calibration protocol. While GC-MS can be used for quantitative analysis, its primary function is qualitative, in providing structural data for the identification of constituent structures. In order to gain a quantitative profile from the GC-MS, one should carefully calibrate the GC-MS with known reference compounds to produce a calibration curve that accurately represents the signal variation of each instrument. Then the calculation is dependent on the comparison of these calibration signals with the unknown compounds and internal standard within a sample. A flame ionization detector is desirable when using calibration curves and internal standards as the source is less susceptible to contamination and produces more consistent signals than other ionization sources. The GC-MS used for this study was fitted with an electron ionization source, in itself requiring careful monitoring with blank runs to ensure its proper maintenance much less able to maintain a constant signal to concentration ratio.

One of the primary issues that arises when attempting to quantify archaeological residues based on a GC-MS profile with an internal standard is the timing of the addition of the standard and the extent to which measured substance resembles the original residue in quantity and quality. The first question that should be asked when deciding upon a

quantification method is what exactly needs to be quantified to answer the research questions. In the case of archaeological residues there are two potential answers to this question. The first is the quantified composition of a residue, i.e. precisely how much of each residual component (stearic acid, oleic acid, cholesterol, etc.) is in a given extracted residue. This can be answered by the addition of an internal standard before analysis via GC-MS. The resulting chromatograph can analysed by measuring peak areas. As the exact quantity of the internal standard is known, the relationship between peak area and quantity is directly measured for each sample and can be applied to determine the quantity of each compound represented in the GC-MS profile.[291] As a result, the exact quantity of each compound present in the analysed sample and identifiable by GC-MS is known.

In terms of an archaeological residue and the calculation of yields, a few problems are inherent in this method. To relate these figures back to the bulk residue is problematic in that it assumes that the residue is quantitatively and qualitatively constant through extraction, derivatisation, and analysis. The correlation of the residue yield based on the quantified GC-MS profile relies on the assumption that the extraction was completely effective in removing the residue from the ceramic sample and the constituents represented on the chromatograph are measurable and identifiable. I would suggest that this would also rely on theory that a residue is only mechanically preserved within the pores of a given sherd and not bound in any way as in conventional analysis the removal of these residues is purely based on the solubility of the residue. This method of yield calculation is also reliant on the assumption that all of the compounds are equally characterized and identifiable via GC-MS and nothing is lost in the analytical protocol, or at the very least equally so.

It has already been seen in the method testing that extraction is not 100% efficient, so then the question arises of the true proportionality of the residue constituents and the

[291] e.g. Heron, *et al.* 1991.

completeness of the extracted sample. The question then arises: what is left behind and how much? This leads to the next possible question, not the quantification of residue for residue sake, but quantification to elucidate the relationship of the residue to the matrix and the quantification of extraction efficiency/preservation rate. This relies less on the chromatograph being complete, signal to noise ratios being consistent, and the internal standard behaving in the same manner throughout the analytical protocol. In this study the two extraction yields were added to give a composite number and relative percentage data for each extraction. This has the major advantage of being the quantification of all aspects of a residue and not solely those that are identifiable via GC-MS (i.e. non-organics, underivatised species, or those too bulky to be ionized by the source and flow through the GC column).

6g. X-Ray Fluorescence

In x-ray fluorescence analysis (XRF), x-rays excite electrons in the sample to an elevated energy state. When these electrons fall from their higher energy state to the ground level state, they emit energy in the form of a wave. The energy and thus the wavelength of this radiation (referred to as fluorescence) are characteristic of the atom with which the electron is associated. The wavelengths and the relative intensities of the resulting fluorescence are measured. These data result in a profile of the elemental composition of the sample. The purpose of including XRF analysis in this study was primarily to evaluate a theorized correlation between elemental components of the ceramic matrix and the preservation of organic material. As the primary alkaline and metallic components of most ceramic, calcium and iron concentrations were identified for comparison. Both of these elements have the potential to provide cations to weak carboxylic acids to form ionic bonds or form other linkages.

7. RESULTS FROM GAS CHROMATOGRAPHY- MASS SPECTROMETRY

One hundred and thirty-three samples of pottery sherds and associated soils were studied from the three sites, Megiddo, Kabri, and Lefkandi. The twenty-two samples of bronze corrosion from the A2 Pepperhill to Cobham road-scheme are be discussed separately in Chapter 8.

7a. Overview

Of the one hundred and thirty-three ceramic samples studied from Kabri, Lefkandi, and Megiddo, only four samples failed to produce over 0.20 mg/g of total residue. Fifty-eight of the one hundred and thirty-three produced quantifiable residues with GC-MS detectable lipid fractions, a 43.61% success rate, with the remaining seventy-five resulting in seemingly lipid-free residues or predominantly plasticiser contamination. The success rates and average yields for each of the sites and sub-areas are presented in Table 7-1, 7-2, and 7-3.

Table 7-1: Sequential Extraction Results – Ceramics, Kabri							
Sample	**Site/Year**	**Area (Locus)**	**Weight**	**Total Extract**	**Total Yield**	**% CHCl3**	**% FAME**
KRM 053	Kabri 09	DS-1 (3019)	10.81980 g	0.04206 g	3.89 mg/g	3.23 %	96.77 %
KRM 054	Kabri 09	DS-1 (3019)	4.52960 g	0.00373 g	0.82 mg/g	75.07 %	24.93 %
KRM 007	Kabri 09	DS-1 (3033)	25.37618 g	0.03342 g	1.20 mg/g	93.72 %	6.28 %
KRM 044	Kabri 09	DS-1 (3033)	13.67025 g	0.01071 g	0.78 mg/g	97.48 %	2.52 %
KRM 010	Kabri 09	DS-1 (3039)	13.59826 g	0.05186 g	3.81 mg/g	99.63 %	0.37 %
KRM 047	Kabri 09	DS-1 (3049)	8.62229 g	0.00848 g	0.98 mg/g	99.06 %	0.94 %
KRM 057	Kabri 09	DS-1 (3049)	6.25093 g	0.00541 g	0.87 mg/g	89.83 %	10.17 %
KRM 060	Kabri 09	DS-1 (3049)	9.77168 g	0.00351 g	0.36 mg/g	90.88 %	9.12 %
KRM 062	Kabri 09	DS-1 (3049)	15.38765 g	0.00309 g	0.20 mg/g	91.91 %	8.09 %
KRM 059	Kabri 09	DS-1 (3055)	9.33507 g	0.01972 g	2.11 mg/g	21.50 %	78.50 %
KRM 033	Kabri 09	DS-1 (3061)	2.52146 g	0.00521 g	2.07 mg/g	100.00 %	0.00 %
KRM 035	Kabri 09	DS-1 (3061)	6.56752 g	0.01580 g	2.41 mg/g	94.37 %	5.63 %
KRM 039	Kabri 09	DS-1 (3061)	3.99201 g	0.02078 g	5.21 mg/g	97.16 %	2.84 %
KRM 061	Kabri 09	DS-1 (3061)	4.39800 g	0.00433 g	0.94 mg/g	85.22 %	14.78 %
Average: DS-1 (n=14)			**9.63148 g**	**0.01629 g**	**1.83 mg/g**	**81.31 %**	**18.64 %**
KRM 004	Kabri 09	DS-2 (3054)	3.22250 g				
KRM 020	Kabri 09	DS-2 (3060)	10.37091 g	0.01585 g	1.53 mg/g	99.56 %	0.44 %
KRM 021	Kabri 09	DS-2 (3060)	6.27337 g	0.00641 g	1.04 mg/g	99.06 %	0.94 %
KRM 040	Kabri 09	DS-2 (3060)	4.86526 g	0.01105 g	2.27 mg/g	76.65 %	23.35 %
KRM 041	Kabri 09	DS-2 (3060)	4.17315 g	0.00854 g	2.04 mg/g	99.18 %	0.82 %
KRM 045	Kabri 09	DS-2 (3060)	2.55724 g	0.00577 g	2.26 mg/g	98.79 %	1.21 %
KRM 048	Kabri 09	DS-2 (3060)	7.41653 g	0.00381 g	0.51 mg/g	50.39 %	49.61 %
Average: DS-2 (n=7)			**5.55414 g**	**0.00857 g**	**1.61 mg/g**	**87.27 %**	**12.73 %**
KRM 003	Kabri 09	DW-W (2161)	11.83000 g	0.00628 g	0.53 mg/g		
KRM 005	Kabri 09	DW-W (2161)	6.70281 g	0.01241 g	1.85 mg/g	67.69 %	32.31 %
KRM 006	Kabri 09	DW-W (2161)	4.55701 g	0.07319 g	16.06 mg/g	54.95 %	45.05 %
KRM 008	Kabri 09	DW-W (2161)	3.27733 g	0.00773 g	2.30 mg/g	96.38 %	3.62 %
KRM 018	Kabri 09	DW-W (2161)	3.02668 g	0.01093 g	3.61 mg/g	78.96 %	21.04 %
KRM 022	Kabri 09	DW-W (2161)	1.63117 g	0.03476 g	2.13 mg/g	100.00 %	0.00 %

Table 7-1: Sequential Extraction Results – Ceramics, Kabri (Cont.)							
Sample	**Site/Year**	**Area (Locus)**	**Weight**	**Total Extract**	**Total Yield**	**% CHCl3**	**% FAME**
KRM 023	Kabri 09	DW-W (2161)	8.54733 g	0.03110 g	3.64 mg/g	99.58 %	0.42 %
KRM 025	Kabri 09	DW-W (2161)	4.14700 g	0.02321 g	5.60 mg/g	99.83 %	0.17 %
KRM 029	Kabri 09	DW-W (2161)	3.09418 g	0.00399 g	1.29 mg/g	96.24 %	3.76 %
KRM 031	Kabri 09	DW-W (2161)	11.08077 g	0.00885 g	0.80 mg/g	66.10 %	33.90 %
KRM 046	Kabri 09	DW-W (2161)	2.91959 g	0.00557 g	1.91 mg/g	78.99 %	21.01 %
KRM 050	Kabri 09	DW-W (2161)	6.25263 g	0.00399 g	0.64 mg/g	87.72 %	12.28 %
KRM 014	Kabri 09	DW-W (2167)	6.12719 g	0.01340 g	2.19 mg/g	98.58 %	1.42 %
KRM 015	Kabri 09	DW-W (2167)	7.70208 g	0.01052 g	1.37 mg/g	73.19 %	26.81 %
KRM 024	Kabri 09	DW-W (2167)	7.40579 g	0.03275 g	4.42 mg/g	100.00 %	0.00 %
KRM 026	Kabri 09	DW-W (2167)	2.99558 g	0.02888 g	9.64 mg/g	99.93 %	0.07 %
KRM 030	Kabri 09	DW-W (2173)	5.11714 g	0.00867 g	1.69 mg/g	99.31 %	0.69 %
KRM 009	Kabri 09	DW-W (2197)	1.81442 g	0.03623 g	19.97 mg/g	88.16 %	11.84 %
KRM 017	Kabri 09	DW-W (2197)	6.46795 g	0.01524 g	2.36 mg/g	99.61 %	0.39 %
KRM 019	Kabri 09	DW-W (2197)	1.85117 g	0.00923 g	4.99 mg/g	99.02 %	0.98 %
KRM 032	Kabri 09	DW-W (2197)	6.79094 g	0.00946 g	1.39 mg/g	100.00 %	0.00 %
KRM 034	Kabri 09	DW-W (2197)	6.00319 g	0.01772 g	2.95 mg/g	42.10 %	57.90 %
KRM 036	Kabri 09	DW-W (2197)	4.57848 g	0.01225 g	2.68 mg/g	98.45 %	1.55 %
KRM 037	Kabri 09	DW-W (2197)	7.19211 g	0.03843 g	5.34 mg/g	99.69 %	0.31 %
KRM 038	Kabri 09	DW-W (2197)	12.29261 g	0.05505 g	4.48 mg/g	99.53 %	0.47 %
KRM 042	Kabri 09	DW-W (2197)	6.43243 g	0.00716 g	1.11 mg/g	99.16 %	0.84 %
KRM 043	Kabri 09	DW-W (2197)	3.26929 g	0.00898 g	2.75 mg/g	99.00 %	1.00 %
KRM 049	Kabri 09	DW-W (2197)	4.40243 g	0.00772 g	1.75 mg/g	68.39 %	31.61 %
KRM 051	Kabri 09	DW-W (2197)	6.02838 g	0.00650 g	1.08 mg/g	74.31 %	25.69 %
KRM 052	Kabri 09	DW-W (2197)	2.91826 g	0.00424 g	1.45 mg/g	87.26 %	12.74 %
KRM 055	Kabri 09	DW-W (2197)	11.90259 g	0.03604 g	3.03 mg/g	9.41 %	90.59
KRM 056	Kabri 09	DW-W (2197)	8.38687 g	0.01154 g	1.38 mg/g	91.94 %	8.06 %
KRM 058	Kabri 09	DW-W (2197)	5.95928 g	0.00871 g	1.46 mg/g	70.72 %	29.28 %
Average DW-W (n=34)			**5.80163 g**	**0.01794 g**	**3.53 mg/g**	**85.50 %**	**14.50 %**
Average Kabri (n=55)			**6.74500 g**	**0.01648 g**	**2.87 mg/g**	**84.60 %**	**15.40 %**

Table 7-2: Sequential Extraction Results- Ceramics, Lefkandi							
Sample	**Site/Year**	**Area (Locus)**	**Weight**	**Total Extract**	**Total Yield**	**% CHCl3**	**% FAME**
KRM 122	Lefkandi 07	T-S	1.91830 g	0.00069 g	0.36 mg/g	100.00 %	0.00 %
KRM 096	Lefkandi 08	T-S	1.22760 g	0.00197 g	1.60 mg/g	92.39 %	7.61 %
KRM 097	Lefkandi 08	T-S	1.32787 g	0.00288 g	2.17 mg/g	100.00 %	0.00 %
KRM 098	Lefkandi 08	T-S	1.17075 g	0.00616 g	5.26 mg/g	99.35 %	0.65 %
KRM 099	Lefkandi 08	T-S	0.34194 g	0.00343 g	10.03 mg/g	100.00 %	0.00 %
KRM 100	Lefkandi 08	T-S	1.15720 g	0.00208 g	1.80 mg/g	100.00 %	0.00 %
KRM 101	Lefkandi 08	T-S	0.79063 g	0.00277 g	3.50 mg/g	96.03 %	3.97 %
KRM 102	Lefkandi 08	T-S	0.57776 g	0.00464 g	8.03 mg/g	99.35 %	0.65 %
KRM 103	Lefkandi 08	T-S	0.94163 g	0.00128 g	1.36 mg/g	100.00 %	0.00 %
KRM 104	Lefkandi 08	T-S	1.39141 g	0.00034 g	0.24 mg/g	100.00 %	0.00 %
KRM 105	Lefkandi 08	T-N	1.48051 g	0.00316 g	2.13 mg/g	98.10 %	1.90 %
KRM 106	Lefkandi 08	T-S	1.35067 g	0.00125 g	0.93 mg/g	100.00 %	0.00 %
KRM 107	Lefkandi 08	T-S	1.18091 g	0.00230 g	1.95 mg/g	100.00 %	0.00 %
KRM 108	Lefkandi 08	T-S	0.86889 g	0.01055 g	12.14 mg/g	99.34 %	0.66 %
KRM 109	Lefkandi 08	T-S	0.54363 g	0.00110 g	2.02 mg/g	100.00 %	0.00 %
KRM 110	Lefkandi 08	T-S	1.37661 g	0.00263 g	1.91 mg/g	100.00 %	0.00 %
KRM 111	Lefkandi 08	T-S	1.39171 g	0.00403 g	2.90 mg/g	100.00 %	0.00 %
KRM 112	Lefkandi 08	T-S	0.52849 g	0.00214 g	4.05 mg/g	100.00 %	0.00 %
KRM 113	Lefkandi 08	Q-NE	1.83874 g	0.00135 g	0.73 mg/g	82.96 %	17.04 %
KRM 114	Lefkandi 08	T-S	0.63102 g	0.00062 g	0.98 mg/g	88.71 %	11.29 %
KRM 115	Lefkandi 08	T-S	1.59097 g	0.00187 g	1.18 mg/g	92.51 %	7.49 %
KRM 116	Lefkandi 08	T-S	1.30998 g	0.00315 g	2.40 mg/g	25.08 %	74.92 %
KRM 117	Lefkandi 08	T-S	1.36980 g	0.00105 g	0.77 mg/g	85.71 %	14.29 %
KRM 118	Lefkandi 08	T-N	1.88509 g	0.00114 g	0.60 mg/g	83.33 %	16.67 %
KRM 119	Lefkandi 08	T-S	0.67819 g	0.00265 g	3.91 mg/g	93.21 %	6.79 %
KRM 120	Lefkandi 08	T-S	1.19734 g	0.00210 g	1.75 mg/g	74.76 %	25.24 %
KRM 121	Lefkandi 08	T-S	1.04780 g	0.00168 g	1.60 mg/g	100.00 %	0.00 %
KRM 123	Lefkandi 08	Q-NE	1.77592 g	0.00266 g	1.50 mg/g	92.48 %	7.52 %
KRM 124	Lefkandi 08	T-S	0.41267 g	0.00163 g	3.95 mg/g	93.25 %	6.75 %
Average Lefkandi (n=29)			**1.14841 g**	**0.00253 g**	**2.82 mg/g**	**92.99 %**	**7.01 %**

Table 7-3: Sequential Extraction Results – Ceramics, Megiddo							
Sample	**Site/Year**	**Area (Locus)**	**Weight**	**Total Extract**	**Total Yield**	**% CHCl3**	**% FAME**
KRM 092	Megiddo 10	H (034)	5.04470 g	0.00232 g	0.46 mg/g	100.00 %	0.00 %
KRM 093	Megiddo 10	H (036)	8.79593 g	0.02340 g	2.66 mg/g	96.45 %	3.55 %
KRM 094	Megiddo 10	H (036)	7.46469 g	0.00169 g	0.22 mg/g	54.44 %	45.56 %
KRM 095	Megiddo 10	H (097)	3.58000 g	0.00390 g	1.09 mg/g	100.00 %	0.00 %
Average Area H (n=4)			**6.22133 g**	**0.00783 g**	**1.11 mg/g**	**87.72 %**	**12.28 %**
KRM 067	Megiddo 10	J (025)	13.54453 g	0.00503 g	0.37 mg/g	100.00 %	0.00 %
KRM 064	Megiddo 10	J (069)	6.12834 g	0.00548 g	0.89 mg/g	99.09 %	0.91 %
KRM 065	Megiddo 10	J (069)	6.05411 g	0.00598 g	0.99 mg/g	98.83 %	1.17 %
KRM 063	Megiddo 10	J (113)	2.46233 g	0.02678 g	10.88 mg/g	20.58 %	79.42 %
KRM 066	Megiddo 10	J (113)	4.88163 g	0.00273 g	0.56 mg/g	100.00 %	0.00 %
Average Area J (n=5)			**6.61419 g**	**0.00920 g**	**2.74 mg/g**	**83.70 %**	**16.30 %**
KRM 133	Megiddo 10	Q (026)	2.90698 g	0.00618 g	2.13 mg/g	50.49 %	49.51 %
KRM 133	Megiddo 10	Q (026)	0.99393 g	0.10960 g	116.68 mg/g	1.32 %	98.68 %
KRM 140	Megiddo 10	Q (033)	10.36457 g	0.00798 g	0.77 mg/g	98.62 %	1.38 %
KRM 141	Megiddo 10	Q (033)	9.46037 g	0.00711 g	0.75 mg/g	100.00 %	0.00 %
KRM 142	Megiddo 10	Q (033)	4.89936 g	0.00686 g	1.40 mg/g	100.00 %	0.00 %
KRM 145	Megiddo 10	Q (033)	4.80279 g	0.00043 g	0.09 mg/g	90.70 %	9.30 %
KRM 134	Megiddo 10	Q (037)	6.51496 g	0.01184 g	1.82 mg/g	26.01 %	73.99 %
KRM 135	Megiddo 10	Q (037)	2.87625 g	0.02466 g	8.57 mg/g	25.79 %	74.21 %
KRM 136	Megiddo 10	Q (037)	5.00637 g	0.00692 g	1.38 mg/g	99.42 %	0.58 %
KRM 143	Megiddo 10	Q (050)	4.24406 g	0.00977 g	2.30 mg/g	65.71 %	34.29 %
KRM 144	Megiddo 10	Q (050)	2.27911 g	0.00037 g	0.16 mg/g	100.00 %	0.00 %
KRM 137	Megiddo 10	Q (091)	8.77450 g	0.01064 g	1.21 mg/g	56.11 %	43.89 %
KRM 138	Megiddo 10	Q (094)	4.85218 g	0.00661 g	1.36 mg/g	85.33 %	14.67
KRM 139	Megiddo 10	Q (094)	4.99244 g	0.01266 g	2.54 mg/g	100.00 %	0.00 %
Average, Area Q (n=14)			**5.21199 g**	**0.01583 g**	**10.08 mg/g**	**71.39 %**	**28.61 %**

Table 7-3: Sequential Extraction Results – Ceramics, Megiddo (Cont.)							
Sample	**Site/Year**	**Area (Locus)**	**Weight**	**Total Extract**	**Total Yield**	**% CHCl3**	**% FAME**
KRM 013	Megiddo 10	K (002)	5.62466 g	0.06654 g	1.18 mg/g	99.71 %	0.29 %
KRM 068	Megiddo 10	K (002)	7.57228 g	0.00685 g	0.90 mg/g	100.00 %	0.00 %
KRM 069	Megiddo 10	K (002)	9.89539 g	0.00331 g	0.33 mg/g	100.00 %	0.00 %
KRM 070	Megiddo 10	K (002)	17.81692 g	0.00660 g	0.37 mg/g	100.00 %	0.00 %
KRM 071	Megiddo 10	K (002)	10.58348 g	0.00584 g	0.55 mg/g	38.18 %	61.82 %
KRM 074	Megiddo 10	K (002)	7.56089 g	0.00379 g	0.50 mg/g	100.00 %	0.00 %
KRM 075	Megiddo 10	K (002)	13.52360 g	0.00637 g	0.47 mg/g	100.00 %	0.00 %
KRM 077	Megiddo 10	K (002)	11.66030 g	0.00359 g	0.31 mg/g	100.00 %	0.00 %
KRM 078	Megiddo 10	K (002)	9.51652 g	0.00716 g	0.75 mg/g	100.00 %	0.00 %
KRM 079	Megiddo 10	K (002)	12.13899 g	0.00492 g	0.41 mg/g	100.00 %	0.00 %
KRM 073	Megiddo 10	K (029)	15.88996 g	0.00763 g	0.48 mg/g	100.00 %	0.00 %
KRM 012	Megiddo 10	K (093)	4.16631 g	0.00083 g	0.20 mg/g	80.72 %	19.28 %
KRM 076	Megiddo 10	K (102)	4.12619 g	0.00743 g	1.80 mg/g	100.00 %	0.00 %
KRM 080	Megiddo 10	K (102)	4.59253 g	0.02089 g	4.55 mg/g		
KRM 081	Megiddo 10	K (102)	3.66947 g	0.00958 g	2.61 mg/g	93.84 %	6.16 %
KRM 082	Megiddo 10	K (102)	7.49489 g	0.00865 g	1.15 mg/g	100.00 %	0.00 %
KRM 083	Megiddo 10	K (102)	5.84587 g	0.02076 g	3.55 mg/g	17.49	82.51 %
KRM 084	Megiddo 10	K (102)	7.03429 g	0.01884 g	2.68 mg/g	23.83 %	76.17 %
KRM 085	Megiddo 10	K (102)	4.97594 g	0.00150 g	0.30 mg/g	100.00 %	0.00 %
KRM 086	Megiddo 10	K (102)	5.36721 g	0.00408 g	0.76 mg/g	93.63 %	6.37 %
KRM 087	Megiddo 10	K (102)	5.09054 g	0.00249 g	0.49 mg/g	93.57 %	6.43 %
KRM 088	Megiddo 10	K (102)	7.15927 g	0.01665 g	2.33 mg/g	8.41 %	91.59 %
KRM 089	Megiddo 10	K (102)	5.68315 g	0.00458 g	0.81 mg/g	100.00 %	0.00 %
KRM 090	Megiddo 10	K (112)	0.88442 g	0.01449 g	16.38 mg/g	80.75 %	19.25 %
KRM 091	Megiddo 10	K (112)	5.46084 g	0.00248 g	0.45 mg/g	79.03 %	20.97 %
KRM 072	Megiddo 10	K (118)	5.04850 g	0.00386 g	0.76 mg/g	100.00 %	0.00 %
Average, Area K (n=26)			**7.63009 g**	**0.00999 g**	**10.08 mg/g**	**84.37 %**	**15.63 %**
Average, Megiddo (n=49)			**6.72054 g**	**0.001140 g**	**3.34 mg/g**	**80.79 %**	**19.21 %**

The average yield figures from all samples are much higher than reported elsewhere (mg/g range rather than μg/g range). This is in large part the result of the choice to calculate yield based on weight determinations rather than the inclusion of an internal standard. This makes the distinction between samples that resulted in a measurable yield and those that resulted in a lipid-fraction that was detectable via GC-MS. One reason for the extraction of a residue of measurable mass but which does not contain any lipid, could be the inclusion of microscopic ceramic dust or dirt that was separated from the sherd during sonication. This explanation is possible, but minimized in most of the samples due to the fact that centrifuging the extract would remove this material from suspension prior to decanting. The fact that the method blanks run with each batch of archaeological samples (every 8-12 samples) were clear of contamination generally rules out other sources. A more likely reason for this phenomenon is the extraction or removal of non-lipid species or species that are not represented for one of two reasons. Either they are not derivatised and dissolved in the hexane layer during sample preparation, or they are not easily volatised in the gas-chromatograph during analysis and left out of the profile. The use of internal standards would naturally produce lower yield figures because they exclude any such species that do not survive sample preparation or do not make it through the gas-chromatography column. The internal standard is compared only to those compounds reflected in the chromatograph, potentially as these results suggest, a small fraction of an extracted residue.

The second issue that arises in the yield numbers when compared to what is present in the literature, is that the direct FAME extraction/derivatisation released smaller amounts of lipid than conventional extraction. In other studies, this trend is reversed with base-catalysed or acid-catalysed extractions releasing greater amounts of lipid.[292] This discrepancy is somewhat difficult to directly address as a result of the use of different yield calculation

[292] Oudemans and Boon, 1991; Stern, *et al.* 2000; Mills, 1966; Correa-Ascencio and Evershed, 2014.

techniques as discussed above. In other studies there is no direct measurement of everything that may be extracted from the sherd but not derivatised or volatised in the GC. One thing that can be considered as a potential explanation for this trend arises in the use of non-destructive methodology. It could be argued that the first solvent extraction is the most effective in removing the vast majority of the residue from the surface under ultrasonication. The second-extraction also could be more inhibited by the porosity of the sherd in that the bound material is held deeper within the matrix and harder to remove. This explanation requires further testing, but as the modern samples also reflected higher solvent extraction rates than FAME extraction rates, it is unlikely that is result of a degraded residue composition. The Lefkandi samples also seem to follow this trend, somewhat problematically. One of the suggestions that Correa-Ascencio and Evershed make regarding the release of lipids with acid-catalysed materials, is that the acid opens up the mineral surface to release minimal lipid preserved in micropores.[293] This seems to suggest that porosity is the predominant factor in the preservation of these lipids and they remain difficult to reach even when the sample is crushed. In terms of this study, the KOH would not equally open up these spaces and the surface area would not be not increased enough in the intact sherd to release the compounds.

It seems from this discussion that it is more likely that the differences in yield and opposite results from the literature arise from the calculation of yield. To test this in the future, a yield calculation based on weights and based on internal standards for the same samples should be tested and evaluated. If it is the case that a significant portion of the material that is extracted from a sherd with solvent is not identifiable by conventional means, the exact nature of this remaining material needs to be investigated. There are several things that this material could be: dissolvable inorganic material, organic complexes, metals, or even

[293] Correa-Ascencio and Evershed, 2014.

fatty acid salts. Analysis via Fourier transform infrared spectroscopy could provide data concerning their nature as inorganic or organic substance as it profiles compounds based on bond length. Loss on ignition analysis is commonly used in inorganic mineral analysis and would successfully characterise any inorganic compounds present in the sample but underivatised or detected by GC-MS.

Despite these discrepancies with published results, the methodology chosen for this project proves to be useful. First, it shows that non-destructive analysis of whole sherd materials is possible and effective. The method tests show that for modern olive oil, ultrasonication and the sequential extraction protocol can remove up to 75-80% of absorbed oil from a piece of pottery. The success rate for lipid detectable residues from archaeological contexts is well within the desirable and expected range. The diminished comparability of results from the yield calculation and non-destructive analysis is offset by the success of non-destructive analysis and the suggestion that are further species that may be extractable from archaeological vessels, bearing the need for further study.

As mentioned above, fifty-eight of the one hundred and thirty-three produced quantifiable residues with GC-MS detectable lipid fractions (43.61% success rate), with the remaining seventy-five resulting in seemingly lipid-free residues or predominantly plasticiser contamination. Table 7-4 provides a summary of the total residue yields for the complete ceramic sample set and the sub-set of lipid containing sherds organized by site and area. The higher average total residue yield for the Megiddo samples is due to the lipid content of sample KRM 133 from Area Q at 116.68 mg/g. Without this sample, the average yield lowers considerably to 2.53 mg/g, a number more reflective of the other sites and the majority of samples. It is reasonable to exclude this value for the comparison of averages as this sample greatly exceeds all of the other samples in its yield (sample 133 is nearly 6 times bigger than the next largest residue from a ceramic, sample KRM 009 with 19.97 mg/g). In addition to this identification of KRM 133 as an outlier, a second sample from KRM 133

was evaluated for its residue content and resulted in a yield value of 2.13 mg/g, a value that lies closer to the average and is a better marker for this sample. If the average for the Megiddo samples is recalculated based on the classification of KRM 133 as an outlier, the result is 2.54 mg/g.

Table 7-4: Total Residue Yields and Success Rates – Ceramics					
Site	**Area**	**No. Samples**	**Average Total Residue Yield All Samples**	**No. Samples with Lipid Fraction**	**Average Total Residue Yield Lipid Fraction**
Kabri	DS-1	14	1.83 mg/g	7	2.45 mg/g
	DS-2	7	1.61 mg/g	2	1.04 mg/g
	DW-W	34	3.53 mg/g	15	4.11 mg/g
	Total	**55**	**2.87 m/g**	**24 (43.64%)**	**3.47 mg/g**
Lefkandi	Q-NE	2	1.15 mg/g	2	1.15 mg/g
	T-N	2	1.37 mg/g	2	1.37 mg/g
	T-S	25	3.07 mg/g	15	3.21 mg/g
	Total	**29**	**2.82 mg/g**	**19 (65.52%)**	**2.80 mg/g**
Megiddo	H	4	1.11 mg/g	2	1.44 mg/g
	J	5	2.74 mg/g	0	-
	K	26	1.73 mg/g	5	3.98 mg/g
	Q	14	10.08 mg/g	8	16.18 mg/g
	Total	**49**	**4.17 mg/g**	**15 (30.61%)**	**10.14 mg/g (2.54 mg/g)*[294]**
TOTAL		**133**	**3.34 mg/g**	**58 (43.61%)**	**5.01 mg/g (3.01 mg/g)***

The samples from Kabri closely reflect the success rate for this study, while the samples from Lefkandi reflect a much higher rate at 65.52% and those from Megiddo a much lower one with only 30.61% of samples resulting in a lipid-containing residue.

[294] * indicates the exclusion of sample KRM133, a clear outlier in terms of yield, see discussion above.

Considering all of the samples, the average extraction yield is 3.34 mg per gram of ceramic sample. The distribution of samples according to their total residual yield and the percentage of those samples have lipid constituents is presented in Figure 7-1.

For one sample, KRM 004, the weight measurements were lost or inconsistent and thus yield data are not available. The other one hundred and thirty-two samples can be separated into categories that were randomly assigned to produce a profile. The success rate of lipid fraction does not increase linearly with the overall total yield, nor is the relationship exponential. Even though the majority of ceramic samples resulted in yields between 1 and 5 mg/g, the success rate peaks at 54.56% between 1 and 2 mg/g, before rising sharply over 80% for yields over 10mg/g. The majority of the samples (n=73) contained between 1 and 5 mg/g of total residue. Both of the two samples with yields below 0.2 mg/g both failed to contain any materials detectable by GC-MS. In all of the yield categories between 0.2 m/g and 1 mg/g, the samples had at least a 26 percent success rate for the detection of lipids (26.92% for samples yielding 0.5-1.0 mg/g). The rate of success increases between 1 and 5 mg/g to around 50%, decreases for samples between 5 and 10 mg/g and then sharply increases for samples over 10 mg/g. Interestingly in each category, with the exception of KRM 133 yielding 116 mg/g which will be discussed individually below, there were samples which failed to contain lipid material across the range of total residue yield values. This trend seems to contradict the notion that the greater residual yield results is a greater amount of information and that exclusion or inclusion of a sample purely based on yield is not secure. In Figure 7-2, the distributions of yields are graphically depicted. The central box and whisker plots show the distributions by number of samples into their respective quartiles. The coloured boxes indicate the central 50% of samples with the whiskers indicating the minimum and maximum yield values. The outer boxes signify the average values and the yields which fall within one standard deviation (grey area) and two deviations (white boxes). As seen in the figure, the majority of samples fall within two standard deviations of the

average values. Only five samples exceed the value. The Lefkandi samples are also the only sub-set whose average value actually lies within the central distribution. For the complete sample set as well as the Kabri sub-set and Megiddo sub-set, the averages lie within the 4th quartile.

The relationship of total yield weights to the weight of the original ceramic sample are depicted in Figure 7-3, all 133 ceramic samples, and Figure 7-4, the 55 samples with lipid fractions. As can be seen in these graphs, the overall distribution of samples changes little when the samples without lipids are excluded. The averages of total residue yields for each sample rises slightly (refer back to Table 7-4). These figures indicate that there is not only no direct relationship between residue weight and success in preserving a lipid fraction; nor is there a direct relationship between residual yield and sample weight.

Despite the fact that the residue yields were slightly below the average of the total sample set, the rate of lipid detection is highest in the samples from Lefkandi. As all of these samples were drilled on site, the range of sample weights is deliberately low. Based on the success rate of preserved lipid, it can be seen that drilling samples is as effective if not more so than non-destructive extraction of whole sherds. The break-down of the protective ceramic matrix in drilling does not seem to enable the further release of lipids from the sample. The residual yield averages are the highest for the samples from Kabri and the samples from Megiddo across the board seem to be less successful in preserving any molecular organic, or at least lipid material.

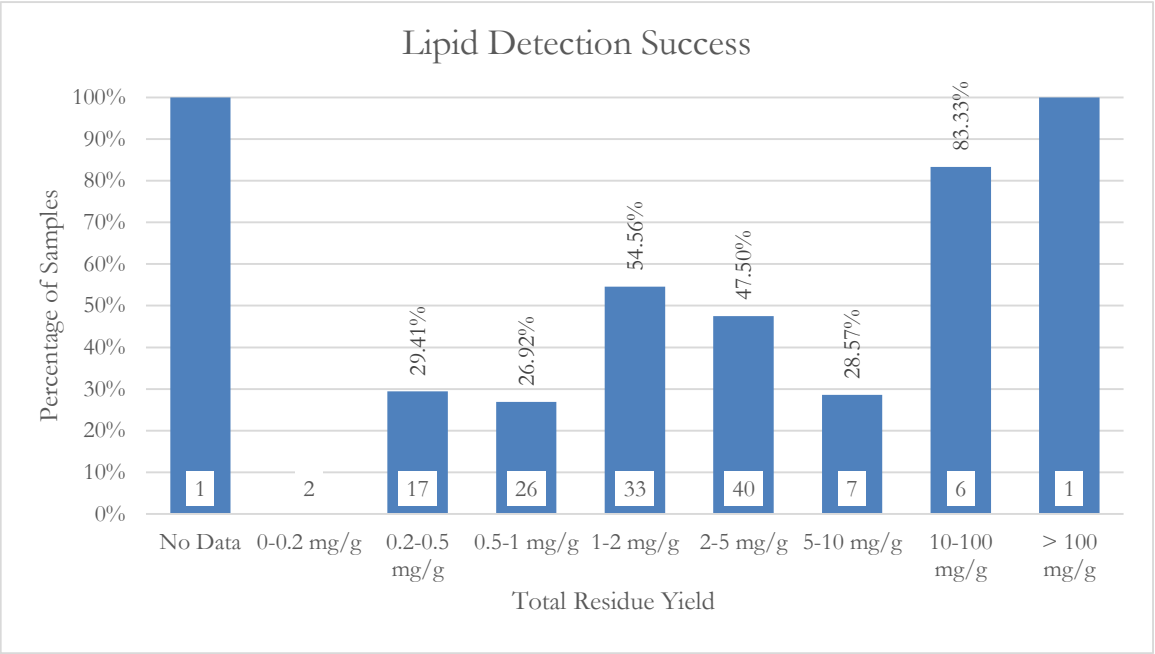

Figure 7-1: Lipid Detection Success in Archaeological Ceramics
The percentage of samples in which lipids were detected according to categories of residual yield. The number of total samples is indicated at the bottom of each bar.

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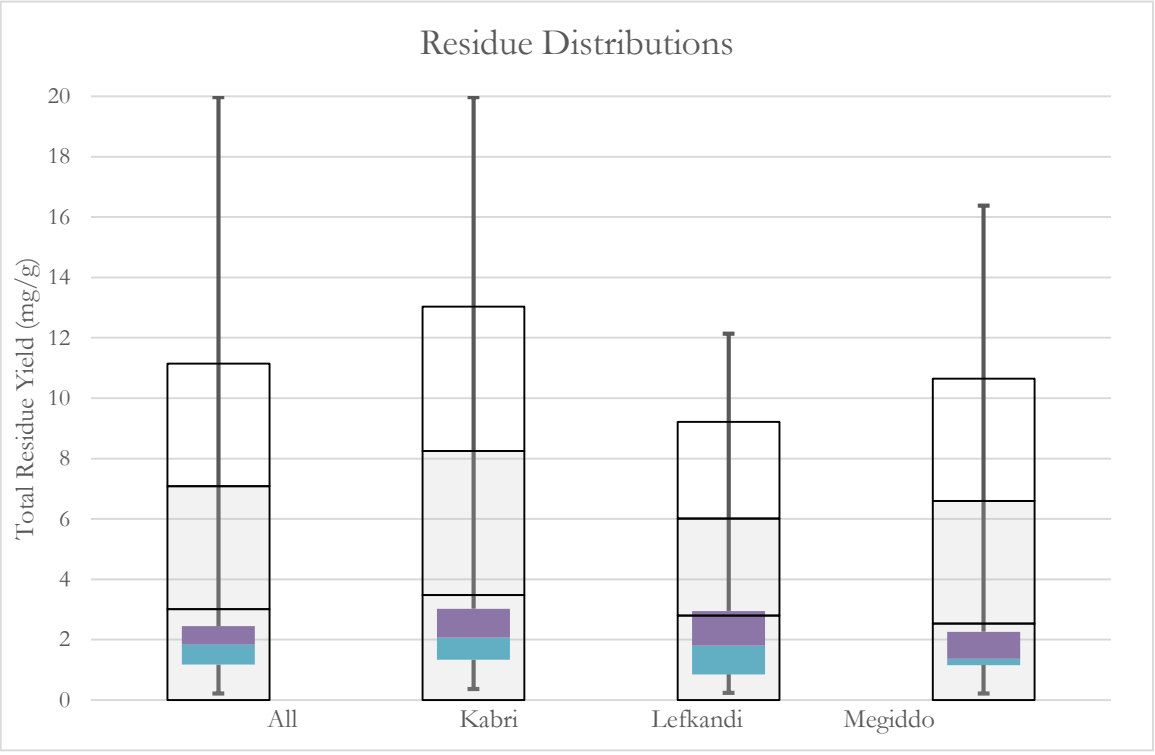

Figure 7-2: Residue Yield Distributions
The 2nd and 3rd quartile values are indicated by coloured boxes along with the minimum and maximum values. The average values with the area covered by a single standard deviation are indicated by the large grey boxes. The range covered by a second standard deviation is signified by the white box. These figures show that the vast majority of the samples fall within 1σ of the average value.

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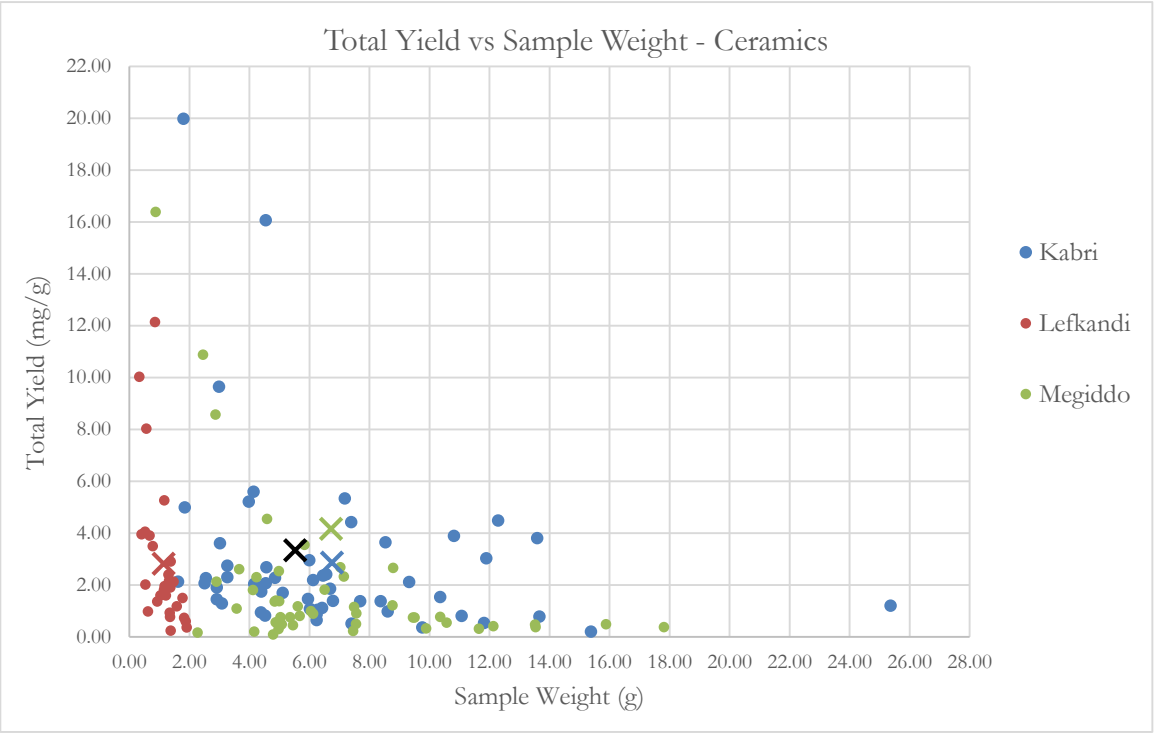

Figure 7-3: Total Yield vs. Sample Weight – Ceramics
This graph excludes sample KRM 133, an outlier with residue yield of 116.68 mg/g and sample weight of 0.99393g (Megiddo). Averages for each site are indicated as follows: Kabri (X), Lefkandi (X), Megiddo (X), and all ceramic samples (**X**).

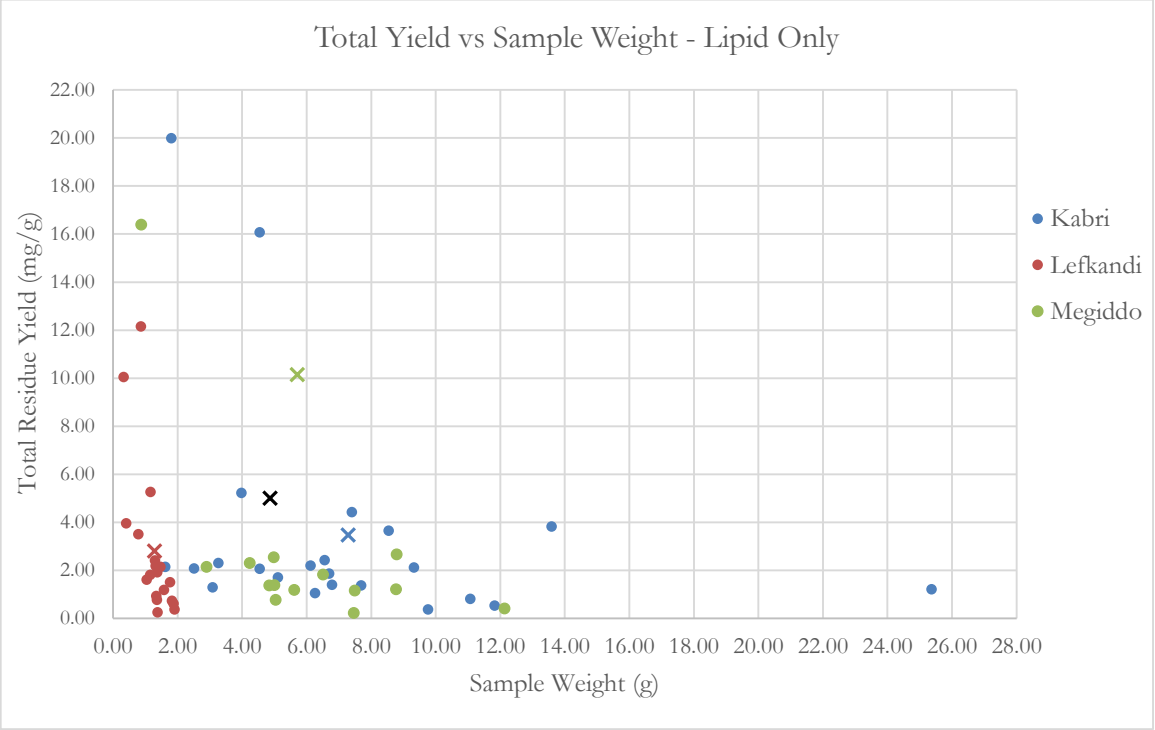

Figure 7-4: Residue Yield vs Sample Weight: Ceramics with Lipid Content Only.
Also excludes sample 133, see above. Averages marked with x.

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7b. Archaeological Ceramic Samples – Contextual Analysis

None of the sherds from burial contexts produced a lipid fraction or any appreciable amount of residue. This could indicate one or a combination of the following factors. Either the burial environment in these graves is not conducive to molecular organic and specifically lipid preservation, the vessels were empty upon burial or at least did not contain lipid matter. As each of these sherds were sampled non-destructively, any residual weight in the extract could either be a substance which is not lipid based, or more probably is other inorganic material such as clay dust. The small vessels from Area J were samples from vessels associated with infantile burials. These small juglets are of the type that are commonly associated with more precious substances such as perfumed oils. It is noteworthy that in the samples studied here there is no evidence of such a purpose. As they are small and closed, some of the more common assumed vessel purposes such as other food stuffs, liquids, or grains are highly unlikely. It is tempting to suggest that these offerings were made for the vessels themselves and not for any presumed content.

The samples from Tomb 100 may represent another preservation phenomena or challenge to residue analysis. It is recalled that upon excavation much of the material appeared slightly crystallized. This crystalline material was not characterised in this project as it was no longer visible on the sherds that were sampled. It is possible that this material was a salt of some sort and may have been an organic salt, which may have inhibited extraction of material if present. The remains in the tomb were heavily degraded and did not display the same level of preservation as other burials across the site. This indicates that the environment in the tomb was distinctly different from the standard burial environment at the site and most likely had a significant impact on the preservation of organic material. This said, the samples tested here from the burial in Area J and the three burials in Area K do not provide clear indications of use based on residue profiles and are not sufficient in number to fully conclude that these vessels were not filled.

The majority of samples from Megiddo were taken from a pottery cache found during the dismantling of a baulk. The assemblage in this cache represent a fairly typical array of Late Bronze Age vessels consistent with the rest of the Levant and its Eastern Mediterranean contacts. Included in the assemblage were a Canaanite storage jar, a large painted jar, several bowls, and a number of imitation Mycenaean stirrup jars. The identification of this deposit as a cache is based on the dense arrangement of the sherds which is not reflective of the rest of the domestic assemblage in Area K. The deposit is at a slightly lower elevation from the correlated layers in the stratigraphic plan. That said, no markings of a pit or demarcations of the deposit were able to be identified in the section or during its excavation. Based on this evidence it can be concluded that this deposit was intentional and rather than a hoard more of a refuse area. The organic residue results from this locus and deposit are sparse in terms of yield and hit rate. It is probable that as these were discarded vessels, very little of the original contents were remaining within the vessels or remains of these vessels upon deposition. Any traces seem to have vanished from the record through degradation and removal from the system.

Unfortunately, while producing small ranges of lipid material, mostly predominant in palmitic and stearic acids, very few of the sherds resulted in the detection of any specific biomarkers. Sample KRM 140, a rim sherd from Area Q at Megiddo, contained a phenolic compound, squalene, along with palmitic acid, eicosane, hexacosanoic acid, heineicosanoic acid, and octacosanoic acid. Squalene in olive oils as well as human skin oils and the combination of these particular compounds are not singularly diagnostic. Both the conventional and FAME extracts were low yielding 0.76mg/g and 0.01 mg/g, so despite the fact that the FAME extract appears to have a wider range of constituent acids, the residue on this sherd is also mostly contamination.

Phthalates were singularly difficult to avoid during this project despite care in the field and in the lab. Most all of the samples did have some quantity of contamination and

even some of the sherds that did not display any other lipids, still showed signs of plastic. As for the application of fatty acid ratios to clarify source materials, this also proved difficult with the ceramic material. As mentioned previously, the successful application of such a technique depends on a core set of fatty acids. Frequently the only basis of comparison for these samples was palmitic and stearic acids. The quantities of the two acids were generally similar, making it only possible to give some very broad categories of plant or animal fats, a conclusion that is tenuous at best.

None of the samples at Kabri produced a diagnostic GC-MS profile. The exact nature of the pit within the palace is unknown so conclusions based on the area's precise function are unable to be formed. Upon comparison to data published from the same site and in a nearby context within the palace,[295] a few discrepancies arise. First, the other study reports a 100% success rate for 40 samples taken from one area. In addition, the preservation rate is cited as high enough to preserve aromatic and volatile compounds associated with wine that are not well attested elsewhere. These other samples were extracted intact at the site in heated ethanol and the extracts transported for analysis. The reported success of the vessels preserving wine far exceeds the success rates reported in the remaining of the literature. This fact, combined with the data presented here, calls into question the accuracy of the study. In all probability, if preservation was as high in one location at the site as Koh reports, at least some of the samples studied here would have produced a clear lipid signal.

The Lefkandi samples present the highest hit rates for lipids from the study. The natural environment of the promontory near the sea seems to be conducive to molecular organic preservation. In one of the samples, KRM 110, additional alkanes and a high

[295] Koh, *et al.* 2014.

percentage of oleic acid were observed, but were not completely diagnostic of a specific source, although an animal source seems probable.

7c. Archaeological Ceramic Samples – Vessel Characteristics

The thickness of ninety-six of the sherds from Kabri and Megiddo was measured with a digital calliper with a reading accuracy of ± 0.01 mm. Thirty-four of these samples produced a residue containing a GC-MS detectable lipid fraction. A graph of the thickness measurements and with residual yields are presented in Figure 7-5 (all samples) and Figure 7-6 (samples with lipid fractions). The results from this comparison show no real correlation between thickness and yield. This relates to previous work on the quantification of lipid profiles within a vessel.[296] In these studies, it was found that the majority of the lipid is preserved within the interior 2mm of a sherd. The thickness data along with the results above which show no increase of residual yield with weight supports the notion that regardless of size and thickness, residue preservation is relatively a surface phenomenon. When only the sherds with detectable lipids are graphed along, the yield distribution compared with thickness is relatively consistent showing that the extraction is effective to a unspecified depth without crushing.

[296] Charters, *et al.* 1993; Charters and Evershed, *1997.*

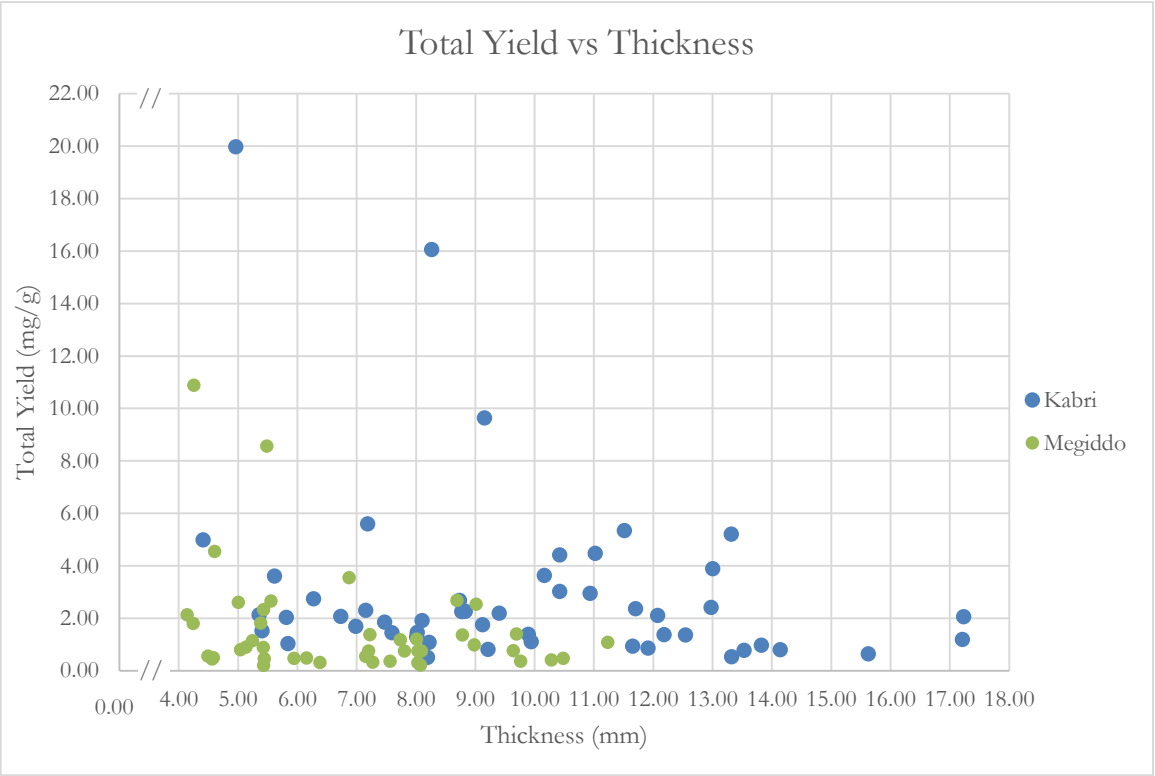

Figure 7-5: Total Residue Yield and Thickness Measurements – Ceramics
Relationship between total residue yield and thickness of sherd for samples from Kabri and Megiddo. Excludes outlier sample KRM 133.

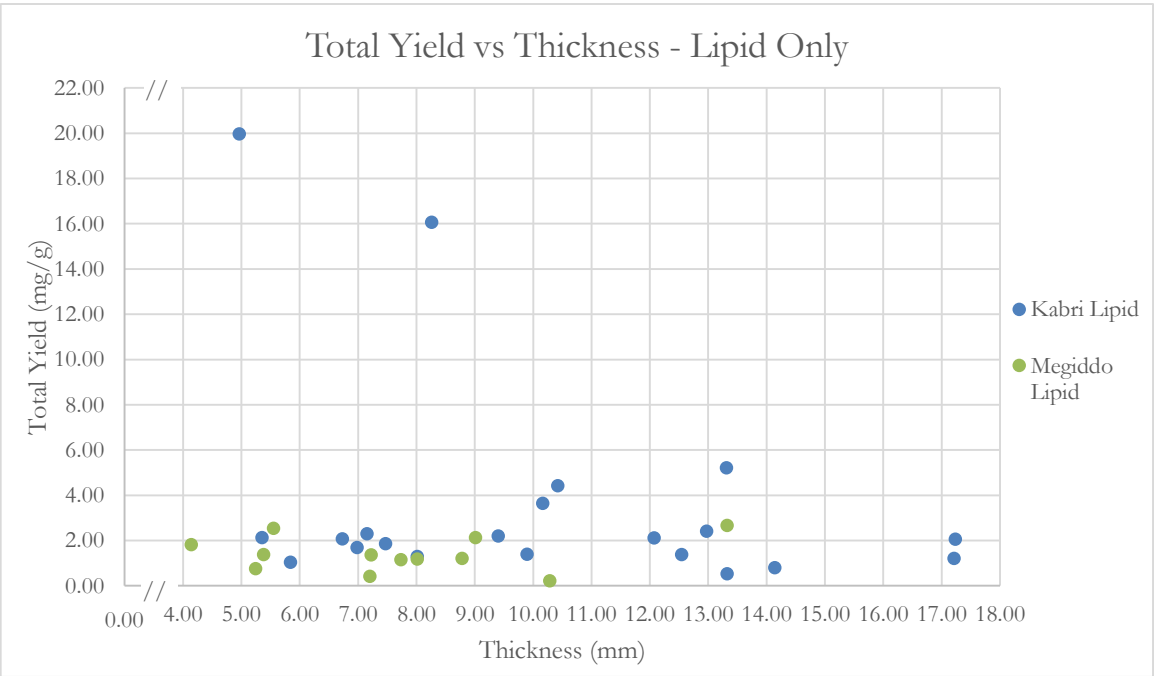

Figure 7-6: Total Residue Yield and Sherd Thickness – Ceramics with Lipid Fraction

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Table 7-5 shows success rates and total residue yields by morphology. The success rates for rim and base sherds is higher than that of body sherds from all of the sites. In terms of average yield, the rim sherds seem to contain the most lipid material per gram of ceramic. These data are consistent with findings in studying concerning lipid profiles.[297] Unlike other sherds that seem not to follow any discernible trend, the rim sherds from Kabri seem to produce greater residual yields with increasing sample weight (Figure 7-7).

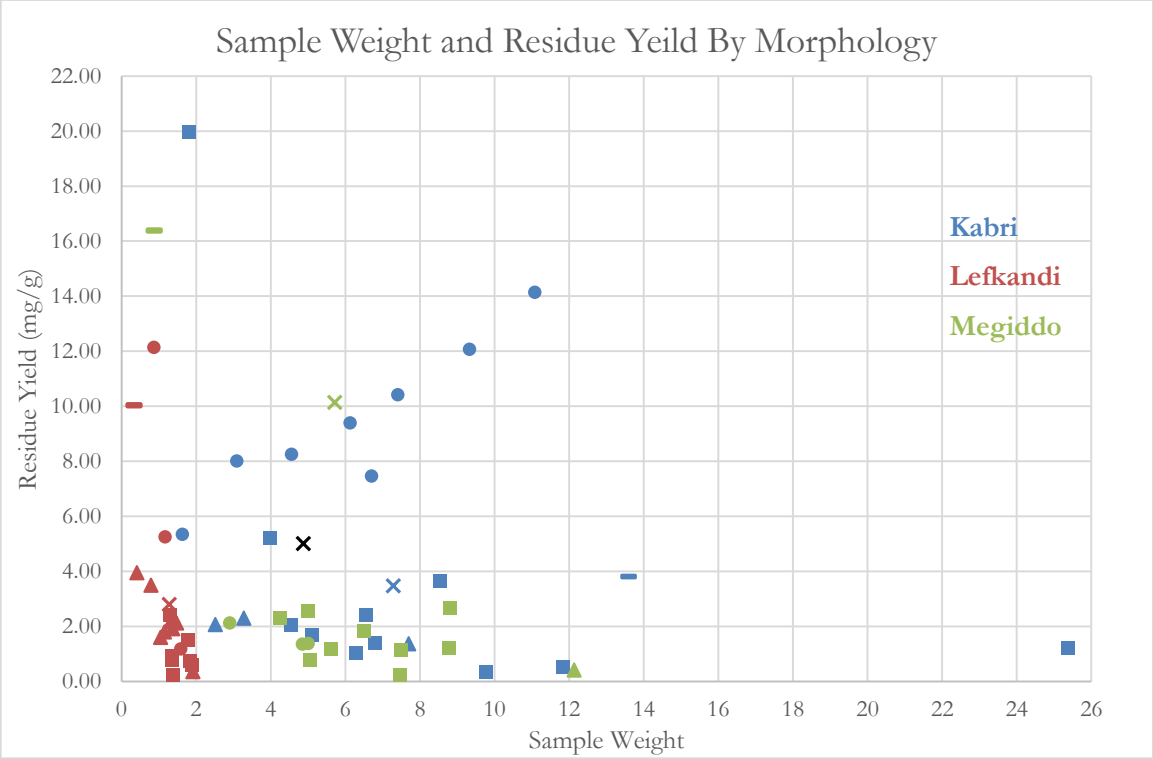

Figure 7-7: Residue Yield by Sherd Type.
Morphology is divided into base sherds (▲), body sherds (■), rim sherds (●), and others (▬). The averages for each site and totals are also indicated by the symbol (**x**).

[297] Charters, *et al.* 1993b.; Charters and Evershed, 1997.

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7d. Archaeological Ceramic Samples: Chemical Composition

Ninety-three of the ceramic samples from Kabri and Lefkandi were subjected to x-ray fluorescence testing (XRF) after being studied for their molecular organic residue content. The elemental composition of the remaining eleven samples from these two sites were not able to be determined due to decomposition of the samples during residue extraction. The ceramic samples from Lefkandi were also not included in this analysis as they were drilled on-site and thus the extraction process was complete destructive for these powdered samples. Each ceramic sherd was studied in its entirety mounting the sherd so that the interior was parallel to the x-ray source. The sample was exposed to the source for three minutes and the fluorescence counts measured. Calcium (Ca) and Iron (Fe) were chosen for comparison as they are primary constituents of clay minerals that have cation exchange properties. As the analysis was performed under atmospheric conditions, light elements are not able to be fully investigated, but the silicon (Si) concentration serves as good background signal for comparison.

Figure 7-8 shows the relationship between residual yield and the relative calcium concentrations in the sherds. The first thing that is apparent from these data is that Kabri clays are generally more calcareous than Megiddo clays. As the success rates for extracting preserved lipids are higher at Kabri, it would seem to follow that the calcareousness of a clay may influence preservation. From the evidence presented here, it is not a clear relationship but the study of a larger corpus of material could clarify this possibility. Figures 7-9 and 7-10 show the relative iron concentrations with relationship to silicon and calcium. Neither one of these seems to provide a clear answer to the question of organo-clay complexes having an impact on the preservation of lipid material. The distributions are widespread which could have two possible interpretations: the chemical composition of the clay has no effect on the preservation of organics or not enough material has been thus far tested to allow a trend to emerge. In either case, the XRF analysis performed here is admittedly only cursory. The

Table 7-5 Total Residue Yields and Success Rates – Vessel Morphology					
Site	**Sherd Type**	**No. Samples**	**Average Total Residue Yield All Samples**	**No. Samples with Lipid Fraction**	**Average Total Residue Yield Lipid Fraction**
Kabri	Base	6	2.04 mg/g	3	1.91 mg/g
	Body	29	2.50 mg/g	11	3.59 mg/g
	Rim	19	3.70 mg/g	9	3.86 mg/g
	Other	1	3.81 mg/g	1	3.81 mg/g
	Total	**55**	**2.87 m/g**	**24 (43.64%)**	**3.47 mg/g**
Lefkandi	Base	12	2.79 mg/g	7	2.44 mg/g
	Body	9	1.21 mg/g	7	1.02 mg/g
	Rim	6	3.91 mg/g	4	4.74 mg/g
	Handle	2	6.97 mg/g	1	10.03 mg/g
	Total	**29**	**2.82 mg/g**	**19 (65.52%)**	**2.80 mg/g**
Megiddo	Base	3	3.06 mg/g	1	0.41 mg/g
	Body	34	5.02 mg/g	10	13.05 mg/g 1.53 mg/g *[298]
	Rim	8	0.91 mg/g	3	1.62 mg/g
	Shoulder	1	0.55 mg/g	0	-
	Residue	1	16.38 mg/g	1	16.38 mg/g
	Soil	2	0.13 mg/g	0	-
	Total	**49**	**4.17 mg/g**	**15 (30.61%)**	**10.14 mg/g (2.54 mg/g)***
Total	**Base**	**21**	**2.61 mg/g**	**11 (52.38%)**	**2.11 mg/g**
	Body	**72**	**3.53 mg/g**	**28 (38.88%)**	**6.34mg/g (2.24 mg/g)***
	Rim	**33**	**3.06 mg/g**	**16 (48.48%)**	**3.66 mg/g**
	Other	**4**	**13.42 mg/g**	**2 (50.00%)**	**6.92 mg/g**
	Residue	**1**	**16.38 mg/g**	**1 (1.000%)**	**16.38mg/g**
	Soil	**2**	**0.13 mg/g**	**-**	**-**
	Total	**133**	**3.34 mg/g**	**58 (43.61%)**	**5.01 mg/g (3.01 mg/g)***

[298] * Exclusion of KRM133, a clear outlier. See discussion above.

measurements of these elements is only a potential proxy for the cation exchange capacity of a material as while they would be directly involved, they are present in the materials as larger minerals with other interactions that define the ceramic. Ideally, in the future direct measurement of the exchange capacity can be compared to residual results providing a higher potential to inform upon any relationship in a more meaningful way. In the interim, this analysis did not rule out the usefulness of such further study.

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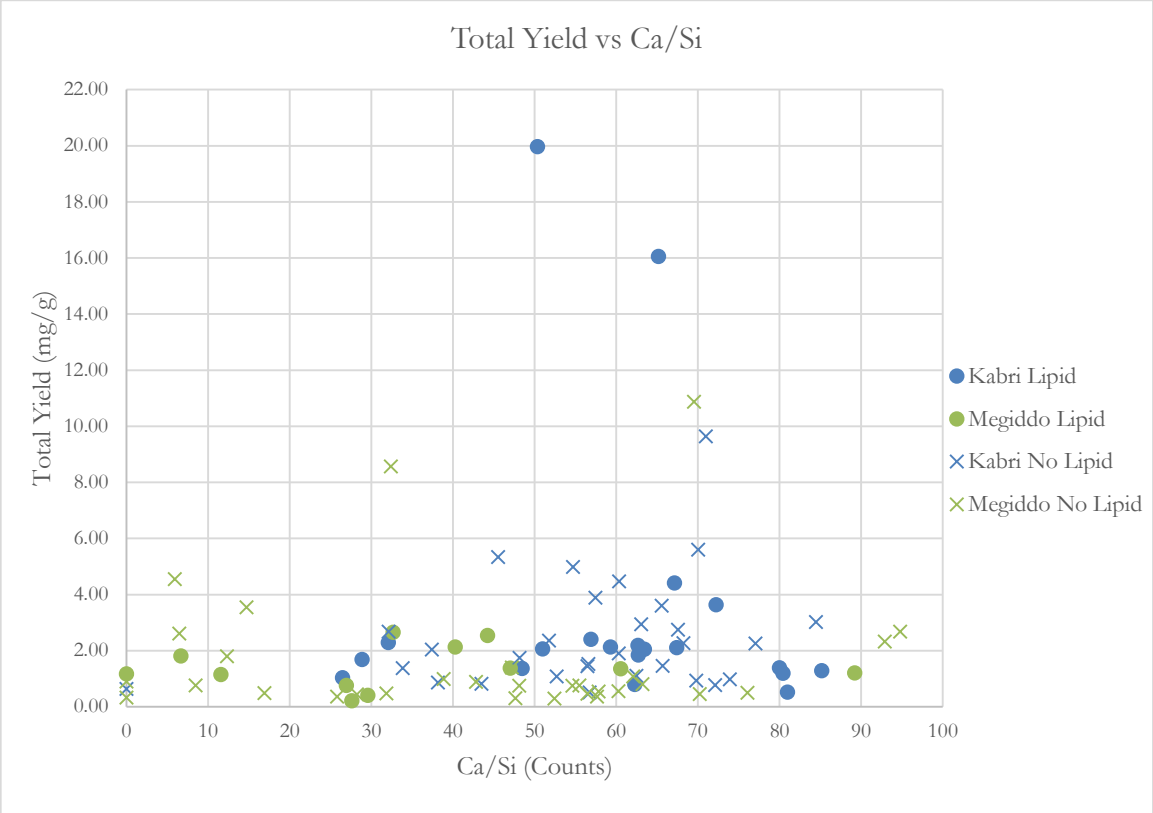

Figure 7-8: Total Residue Yield vs Calcium to Silicon Ratio
Results of XRF analysis compared to residue yield for ceramic samples from Kabri and Megiddo. Both sample that contained GC-MS detectable lipids (•) and those that do not (x) are indicated. The outlier sample KRM 133 is excluded. The calcium to silicon ratio is calculated using maximum count values.

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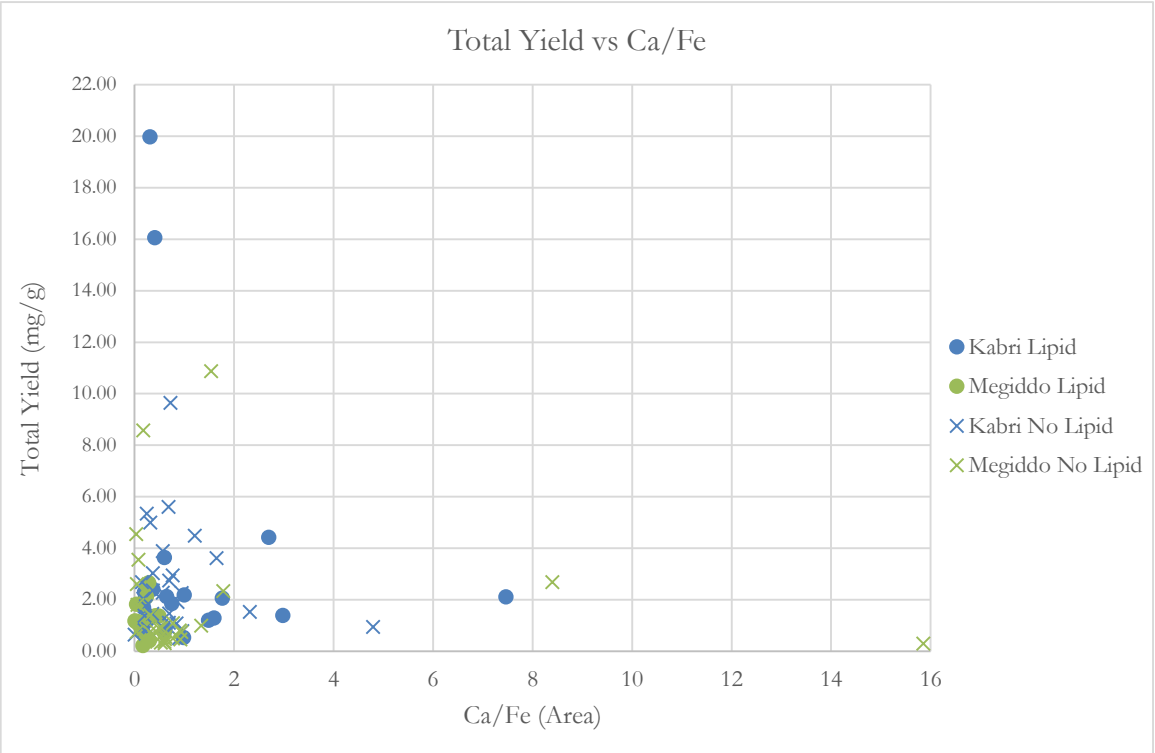

Figure 7-9: Total Residue Yield and Calcium to Iron Ratio
Results of XRF analysis compared to total residue yield from ceramic samples from Kabri and Megiddo. Those samples with a GC-MS detectable lipid fraction (•) and those that do not (x) are indicated. The Calcium to Iron ratio is calculated on approximate area

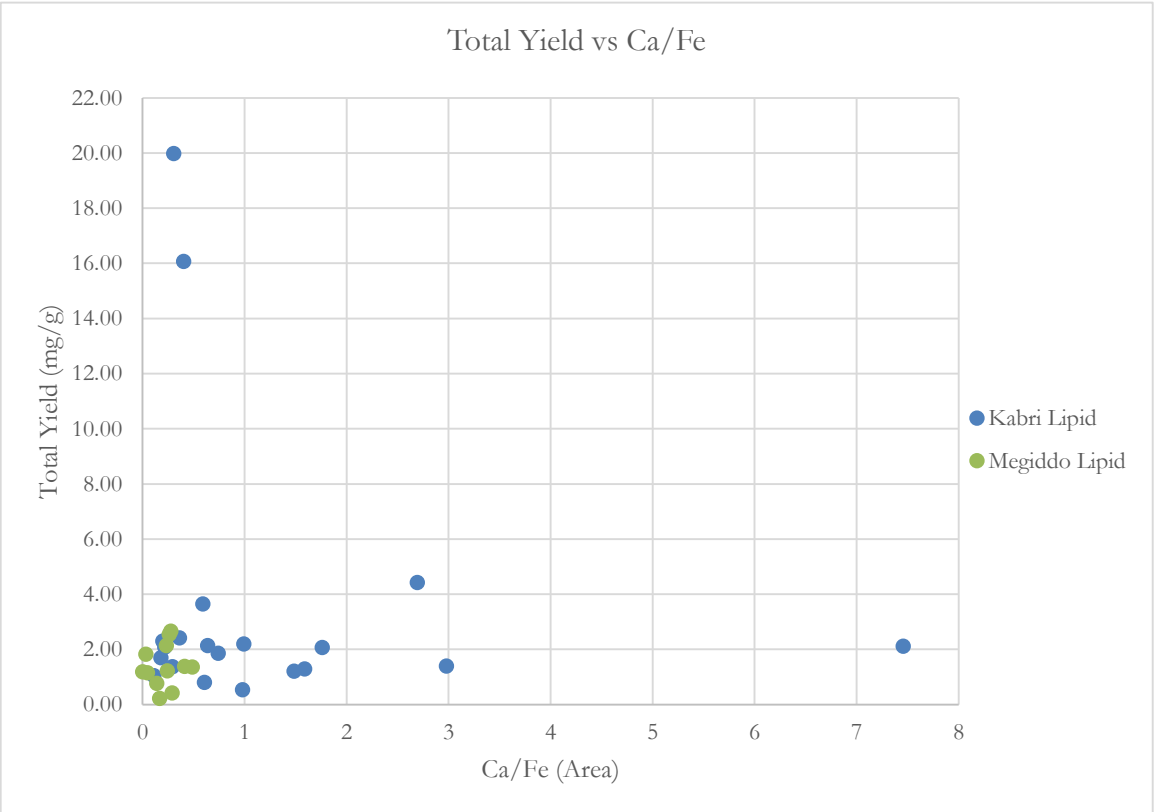

Figure 7-10: Total Residue Yield and Calcium to Iron Ratio
Results of XRF analysis compared to total residue yield from ceramic samples from Kabri and Megiddo. Only those samples that produced a GC-MS detectable lipid fraction are included. The Calcium to Iron ratio is calculated on approximate area under the curve for each peak.

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8. Bronze Corrosion: A New Context for Organic Residue Preservation?

In the development of this project and the discussion of the factors which may or may not influence the preservation of molecular organics in archaeological vessels, the question of organic residue preservation in vessels composed of materials other than fired clay arose. Specifically, it is hypothesized that bronze and copper alloy vessels could preserve organic substances either by encasing them within corrosion products or by forming organometallic complexes. If copper alloy vessels do indeed preserve the residues of their organic contents, this would not only be an important contribution to the understanding of feasting and ritual activities in the past, but also to the understanding of the preservation of molecular organics in archaeological vessels. In order to test this hypothesis concerning organics and copper alloy corrosion, twenty-two samples of corrosion, associated soil and deposits from five copper alloy vessels excavated in the A2 Pepperhill to Cobham project in Kent were evaluated for organic content.

8a. Bronze Corrosion – A Matrix for Organic Materials?

The corrosion of copper alloys[299] is defined by electrochemical reactions between the metal and its environment. Typical copper and copper alloy corrosion is a mixture of inorganic copper salts including oxides, sulphides, sulphates, chlorides, nitrates, and carbonates in addition to organic copper salts which include formate, acetate, and oxalate.[300] These corrosion products form in the atmosphere and the process continues in the burial environment. Immediately when copper is exposed to the environment, a layer of copper (I) oxide, or cuprite, forms and is oxidized to form copper (II) oxides. In the atmosphere, the presence of water allows for the dissolution of atmospheric species into a surface film where

[299] Bronze is a specific copper alloy, but for the purposes of this discussion of corrosion, the term *copper alloy* is used as the focus is the reactions of metallic copper with substances in the environment. While it is noted that the alloying materials will have an effect on the chemistry of bronze and other alloys of copper, the major component is copper and most likely responsibly for the majority of the corrosion products.
[300] Graedel, *et al.* 1987.

hydroxide provides the major building block for many of the standard corrosion products. The diffusion of Cu^{+} and Cu^{2+} through the material allows for reactions with anions and molecules in the surface film.[301] A schematic for the formation of copper patinas is shown in Figure 8-1. In this schematic, the effects of different environments on the inorganic copper salts formed are represented in addition to one thought for the inclusion of organics.

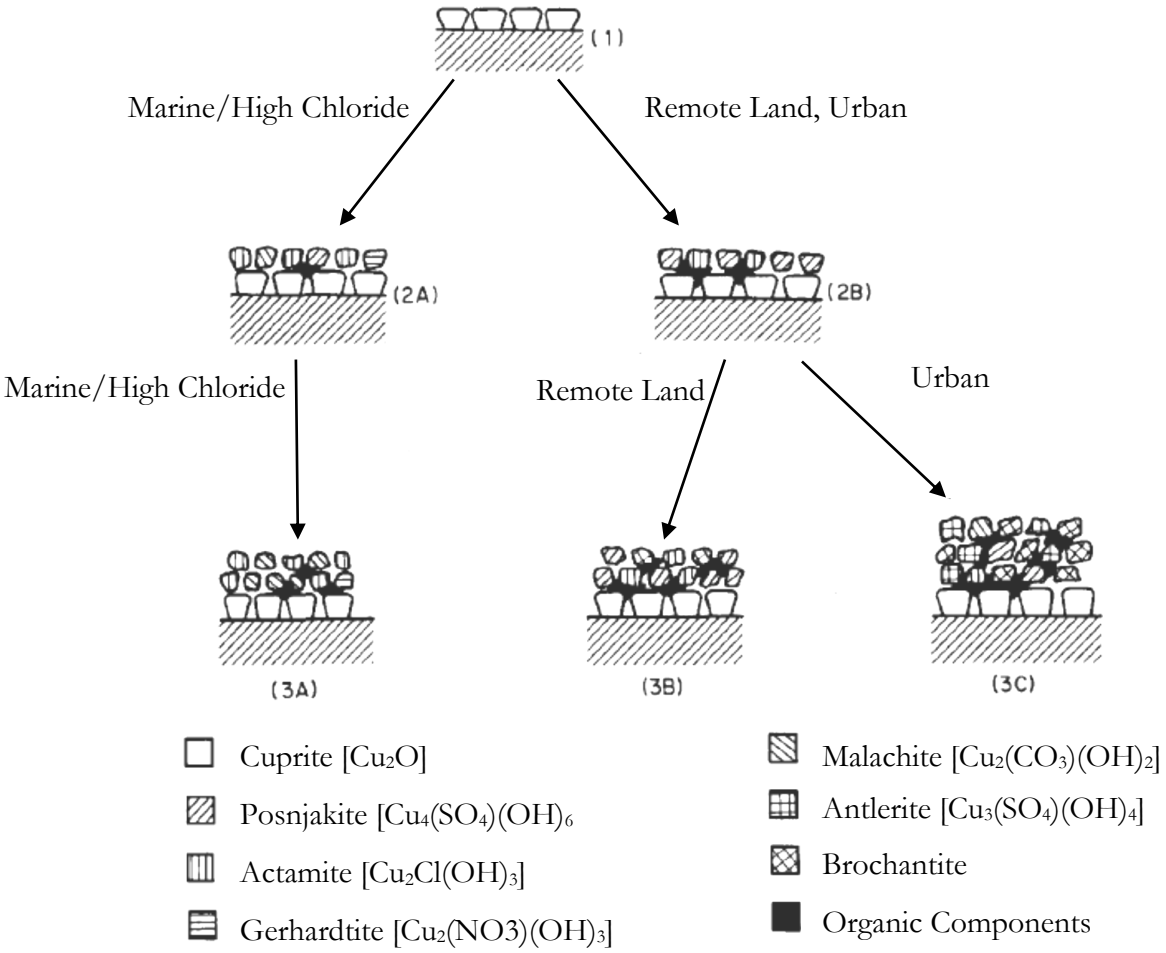

Figure 8-1: Schematic of Copper Patina Formation.
Crystalline minerals are shown according to the environments in which they are formed. Marine: high chloride, low acidity, reduced and oxidized sulphur. Remote Land: Moderate acidity, chloride, reduced and oxidized sulphur. Urban: moderate chloride and reduced sulphur, high acidity and oxidized sulphur.
(After Graedel 1987a)

[301] Graedel, 1987a.

Through these electrochemical reactions, a patina is formed. This layer is strongly bound to the object and generally impervious to abrasive removal and predominantly insoluble in water. It has been suggested, due to the ability to remove some copper patina with acetone soaked abrasives that organics may act as a binder during the cementation of copper corrosion during patination. This incorporation and potential binding action is also hinted at in Figure 8-1.[302] The exact nature of this binder and its mechanism is poorly understood. In early studies of copper corrosion, it was thought that the presence of carboxylic acids may be the precursor to malachite formation [$Cu_2(CO_3)(OH)_2$].[303] This suggestion was made when it was generally thought that malachite was the principal component of copper corrosion, however the compound now is known to be only a trace component of copper corrosion and the suggestion the interactions with carboxylic acids has not been re-evaluated.

The possibility of organic compounds preserved in copper alloy corrosion is not one that has been investigated thoroughly in the past, certainly not in an archaeological context. The limited evidence for organics in bronze is limited to the study of patinas on statues and monuments. By using pyrolysis/gas chromatography-mass spectrometry, Chiavari *et al.* cite limited organic materials in the corrosion patinas of bronze statues and portals dating to the Italian Renaissance.[304] Among the compounds the group identified are mono- and di-carboxylic acids, including a predominance of palmitic acid, and a series of aliphatic hydrocarbons. In both cases, the organic content of the patinas in question are attributed to applied protective coatings and atmospheric pollutants.

As mentioned above, it has been noted by researchers at AT&T Bell Laboratories that while patinas are resistant to removal via abrasion and water, in some cases the patina can be partially removed with acetone soaked abrasives and is thus acetone-soluble. Their

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[302] Graedel, *et al.*, 1987.
[303] Vernon, 1933.
[304] Chiavari, *et al.* 1991 & 1999.

conclusion based on this observation is polar organic substances must be involved in the formation and durability of copper patinas.[305] In the study of the copper patina from the Statue of Liberty in New York Harbour and from the copper roof of the AT&T Bell Laboratories Building in New Jersey, acetone-soluble organic species were removed from the bound patina and studied. The removed organics included small carboxylic acids (formic and acetic – also reflected in copper salts from rainwater runoff), the common palmitic, oleic, and stearic acids, predominantly odd-numbered alkanes, and several polynuclear cyclic compounds. The composition and proportions of the carboxylic acids and alkanes are consistent with biogenic lipid sources deposited through rain, fog, and atmospheric pollution. The polynuclear cyclic compounds are attributed to fossil fuel combustion products or to the petroleum based adhesives used in the construction of the AT&T Bell Laboratories roof[306].

As evidenced by these studies of Renaissance monuments and portals, the Statue of Liberty, and the AT&T Bell Laboratories Building, organic molecules can be found in copper alloy corrosion and bronze patinas. The question arises, however, in at least these two studies, the extent to which the organics are surface deposits, contaminating the object so to speak, or an integral part of the corrosion material itself. Certainly in the case of the statues and portals from the Italian Renaissance, the organics can be linked to protective coatings, such as wax and polishing materials. By definition, these materials are designed to cover the surface and protect it from corrosion and the environment. Whether or not these materials are preserved in the corrosion as a residue or are preserved as a coating unrelated to the corrosion process is undefined.

In both studies, the predominant organics identified were pollutants from smog and rain. Such substances can be distinguished from other coatings and other substances used in

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[305] Muller and McCrory-Joy, 1987; Graedel, *et al.*, 1987.
[306] Muller and McCrory-Joy, 1987.

pre-Modern manufacturing because of their high levels of odd-numbered carbon chain fatty acids and polynuclear cyclic compounds. The organic content of acid rain and smog has been studied repeatedly in the past and the composition of the organics from these exposed structures are consistent with air and rain pollutant profiles[307]. Deposited pollutants are also mostly a surface phenomenon. The extent to which the molecular organics deposited on the surfaces of bronze monuments interact with the bronze and become part of the corrosion, beyond that of the formation of copper salts with formate, acetate, and oxalate ions, is unknown. Degradation of bronze and copper monuments is an ongoing concern for conservators and it is possible maybe even probable that the majority of the degradative effects of pollution are more intrinsically tied to the properties of acid rain and smog rather than the organic content. More research in the attempt to understand the interaction of copper and copper alloys with organics is needed. In the context of residues in bronze and copper alloy vessels, however, these studies do not contribute significantly to the hypothesis that copper alloy vessels in archaeological contexts may preserve organic substances through the reaction with or entrapment of these substances within corrosion products.

[307] Organic Content of Precipitation: e.g. Meyers and Hites, 1982; Gill, *et al.*, 1983.
Organic Content of Airborne Particulates: e.g. Weschler and Fong, 1986; Graeves, *et al.*, 1985.; Cautreels and van Cauwenberghe, 1978.

8b. Results from the Study of Organics in Bronze Corrosion

Twenty-two samples of corrosion and mixed soil-corrosion encrustations were taken from five copper alloy vessels by Danna Goodburn-Brown and submitted to the Research Laboratory for Archaeology and the History of Art for analysis. Each sample was submitted to the protocol outlined in Chapter 5. The results of each of the sequential extractions and the yield values are presented in Table 8-1.

Table 8-1: Sequential Extraction Results- Roman Copper Alloy Corrosion Samples								
Sample	**Type**	**Vessel**	**Location**	**Weight**	**Total Extract**	**Total Yield**	**% $CHCl_3$**	**% FAME**
KRM 146	Corrosion	681 (Cauldron)	Interior	0.06010 g	0.00029 g	4.83 mg/g	100.00 %	0 %
KRM 147	Corrosion	681 (Cauldron)	Exterior (+CDD)	0.00741 g	0.00025 g	33.74 mg/g	84.00 %	16.00%
KRM 148	Corrosion	1549 (Patera)	Interior	0.03280 g	0.01375 g	419.21 mg/g	99.35 %	0.65 %
KRM 149	Corrosion	1549 (Patera)	Interior	0.05667 g	0.00183 g	32.29 mg/g	97.27 %	2.73 %
KRM 150	Corrosion	1549 (Patera)	Exterior *btw vessels	0.00006 g	failed			
KRM 151	Corrosion	1549 (Patera)	Exterior *deposit	0.00486 g	0.00287 g	590.53 mg/g	21.60 %	78.40 %
KRM 152	Soil/Corrosion	689 (Patera)	Interior	2.77372 g	0.00373 g	1.34 mg/g	54.96 %	45.04 %
KRM 153	Corrosion	689 (Patera)	Interior	0.53361 g	0.00932 g	17.47 mg/g	99.03 %	0.97 %
KRM 154	Corrosion	689 (Patera)	Exterior (+CDD)	0.00416 g	0.00118 g	283.65 mg/g	81.36 %	18.64 %
KRM 155	Corrosion	1550 (Ewer)	Interior	0.15555 g	0.00056 g	3.60 mg/g	87.50 %	12.50 %
KRM 156	Corrosion	1550 (Ewer)	Exterior	0.03934 g	0.00011 g	0.79 mg/g	72.73 %	27.27 %
KRM 157	Corrosion	683 (Ewer)	Exterior –brass base	0.01835 g	0.00381 g	207.63 mg/g	3.94 %	96.06 %
KRM 158	Soil/Corrosion	1549 (Patera)	Interior	0.53938 g	0.00578 g	10.72 mg/g	92.39 %	7.61 %
KRM 159	Soil/Corrosion	1549 (Patera)	Interior	2.44891 g	0.01800 g	7.35 mg/g	48.11 %	51.89 %
KRM 160	Soil/Corrosion	1549 (Patera)	Interior	0.36184 g	0.00709 g	19.59 mg/g	96.33 %	3.67 %
KRM 161	Soil/Corrosion	1549 (Patera)	Interior	1.19642 g	0.01297 g	10.84 mg/g	72.17 %	27.83 %
KRM 162	Soil/Corrosion	1549 (Patera)	Exterior *btw vessels	0.19477 g	0.01139 g	58.48 mg/g	97.54 %	2.46 %
KRM 163	Soil/Corrosion	1549 (Patera)	Exterior *btw vessels	0.91464 g	0.00934 g	10.21 mg/g	90.58 %	9.42 %
KRM 164	Corrosion	1549 (Patera)	Exterior *deposit	0.00065 g	0.00026 g	384.62 mg/g	76.00 %	24.00 %
KRM 165	Corrosion	1549 (Patera)	Exterior *deposit	0.00649 g	failed			
KRM 166	Soil/Corrosion	1549 (Patera)	Exterior	2.24249 g	0.00093 g	0.41 mg/g	80.65 %	19.35 %
KRM 167	Soil/Corrosion	1549 (Patera)	Interior	1.42412 g	0.00349 g	2.45 mg/g	82.52 %	17.48 %

*note that "exterior" samples of patera 1549 are exterior corrosion of the vessel but are not purely external samples as they are also in contact with the vessels below and above the vessel and thus potentially in contact with other substances.

Of the twenty-two samples, only two failed to produce any residual yield (KRM150 and 165). The successful samples (n=20) averaged a total extract yield of 104.99 mg/g, a much higher value than the ceramic samples in the study which average a yield of only 3.34 mg/g. Within the copper alloy samples, the extractions of the pure corrosion samples displayed much higher yield rates than the corresponding mixed soil and corrosion samples (an average of 13.49 mg/g for mixed samples compared to an average of 179.85 mg/g for corrosion samples). The results for each vessel will be discussed in turn below.

Two corrosion samples were analysed from cauldron 681, one from the interior (KRM146) and one from the exterior (KRM147). The samples, although seemingly significant in their residual yield compared to sample weight (4.83 mg/g and 33.74 mg/g, respectively) the residue weights themselves were quite small (0.00029 g ± 0.00001 g and 0.00025 g ± 0.00001 g). In both cases, the GC-MS results of the FAME-extracts show only contaminants including a plasticiser and small amount of $C_{16:0}$, $C_{18:0}$, and $C_{18:1}$, all of which could come from plastic contamination (Catalogue pp. 294-297). The information provided by the conservator indicated that the external sample most likely was adulterated by consolidant (cyclododecane, from henceforth referred to as CDD). This compound was not observed in the GC-MS profile, so either the vessel was not covered by the consolidant at the sampling location or the extraction was not effective. It was initially thought that the yield value for the external corrosion sample was much higher than the interior sample due to the presence of CDD, but on closer inspection the absolute weights are similar and the higher yield value is the direct result of a much smaller sample size. These results suggest that yield calculations may not be the best standard for the determination and comparison of significant results and that absolute residue weights must be evaluated alongside yield calculations.

Three samples were taken from patera 689, two from the interior (mixed soil and corrosion sample KRM152 and corrosion sample KRM153) and one from the exterior

(KRM154). As in the case of cauldron 681, the comparative yield of the external sample is much higher than the internal samples, but the absolute weight of the residue is smaller and produced only plasticisers and siloxanes. However, in contrast with cauldron 681, the two internal samples produced residues that were three (KRM152) and eight times (KRM153) the absolute weight of the external sample. In other words, although the external yield value is higher than that of the internal samples, the weight of the external residue is much less and therefore less successful than the internal samples, indicating that the residual content of the internal corrosion samples is a reflective of content. The GC-MS profiles of both KRM152 and KRM153 show a series of straight chain alkanoic methyl esters with even-numbered carbon chain lengths ranging from 12 to 28, the unsaturated palmitic and oleic acids, and a number of dicarboxylic acids with 16, 18, 20, and 22 carbons. (Catalogue pp. 306-311) In addition, KRM 152 produced methyl dehydroabietate, a resin biomarker. These compounds suggest that this patera once contained a cosmetic.

The single sample from ewer 683 consists of a small amount of external corrosion (KRM157). Though the yield is relatively high at 207.62 mg/g and the absolute weight of the extracted residue was 0.000381 g ± 0.00001 g, the majority of the residue was the result of the second direct FAME extraction. There is a strong probability that the increased weight is in large part due to non-systematic experimental contamination. The GC-MS profile neither confirms nor denies this conclusion, only displaying small amounts of $C_{16:0}$ and $C_{18:0}$ (Catalogue pp. 316-317).

Two corrosion samples from ewer 1550, internal sample KRM155 and external sample KRM156, show a marked difference in yield. The external sample had a low yield of 0.79 mg/g (0.00011 g ± 0.00001 g absolute) and its GC-MS profile only contained small amounts of $C_{16:0}$ and $C_{18:0}$ (Catalogue pp. 314-315). Due to the combined evidence of low yield and absolute weight of this sample, these two compounds can be attributed to small levels of experimental contamination. The internal sample, KRM155 conversely produced a

yield over four times that of the external corrosion. The GC-MS profile of the internal corrosion is also distinct from that of the exterior sample (Catalogue pp. 312-313). The sample contained a series of alkanoic acids with even numbered carbon chains ranging from 16 to 26 carbons and shows evidence of both a dicarboxylic acid (hexadecanedioic acid) and the CDD consolidant. The success of this sample is not so much in the yield values themselves, but in the external/internal differential. In this case, the exterior shows no evidence of the organics found in the interior and thus rules out the possibility of organic contributions from the burial environment, treatments, and microbial action.

The majority of the bronze samples analysed for this project were taken from patera 1549. These samples include two samples of internal corrosion (KRM148 and 149), five mixed internal samples (KRM158, 159, 160, 161, and 167), four external corrosion samples (KRM150, 151, 164, and 165), and three mixed external samples (KRM162, 163, and 166). It is important to note in the case of this patera, the "external" samples cannot necessarily be assumed to be clean since several of the samples correspond the area between the patera and ceramic vessels beneath (vessels 1553, 1555, 1598). This is especially true in the case of the mixed samples which would potentially contain soil and other remnants from the vessels beneath. Of the four external corrosion samples, two of them failed in the extraction of any residue (KRM150 and 165). The other two samples both produced comparatively high yields, 590.53 mg/g for sample KRM151 and 384.62 mg/g for sample KRM164. In the case of sample KRM164, the absolute weight is low as in the cases of samples KRM146 and KRM147. The GC-MS profiles of both KRM 151 and KRM 164 are both clear of any organic materials other than plasticisers. Devoid of significant organic residues, as evidenced in their qualitative GC-MS profiles as opposed to their quantitative yields, these four external corrosion samples provide a test blank of sorts for the mixed samples between the vessels and the internal samples. It is also note-worthy that samples, KRM 151, 164, and 165 are all

surface deposits that are visually distinguishable from the main body of the vessel and its corrosion. (Catalogue pp. 302-305, 330-333)

The mixed external samples from patera 1549, KRM162, 163, and 166, provide a different set of results from that of the external corrosion deposits just discussed. Ranging in yield from 0.41 mg/g to 58.48 mg/g and in absolute weight from 0.00093 g to 0.01139 g, each of the samples gave rise to a GC-MS profile containing a series of alkanoic acid methyl esters ranging in carbon chain length from C12 to C28, stearic acid, and one dicarboxylic acid. The CDD consolidant is also present in sample KRM163 (Catalogue pp. 326-329, 334-335). It is important to note that these mixed samples unlike the deposits do preserve molecular organics. It is unclear whether or not these organics arise from the vessels beneath the patera or the burial environment as the one external corrosion sample that was not directly attributed to a deposit was one that failed. However, it does suggest that there is a soil contribution of the organic profile. It can be concluded that the deposits are not phenomena originating in the presence of organic materials or at least ones that are detectable via this method.

All of the internal samples, both corrosion and mixed corrosion and soil, from patera 1549 resulted in significant yield numbers (average 225.75 mg/g for corrosion and 10.19 mg/g, for mixed), absolute residue weights (average 0.00779 g for corrosion and 0.00947 g for mixed), and GC-MS profiles (Catalogue pp. 298-301, 318-325). Each of these samples contained a series of alkanes ranging in carbon chain length from C20 to C31. These samples mark a significant difference in the contents of the patera from that of the vessels beneath it and its exterior.

8d. Discussion

Based on the results presented here, there is good initial evidence for the presence of molecular organics preserved in association with bronze and copper alloy vessels, and several conclusions. Figure 8-2 shows a graphical analysis of the bronze samples by vessel, location,

residue weight, and sample weight. First, based on the fact that samples KRM146, 147, and 164 all failed to produce any materials evident in their GC/MS spectra, it is suggested that a threshold of significance of at least 0.00030 g in absolute residue weight should be set. It has been seen that, at least in the case of bronzes, a significance value based on yield is not sufficient for the identification of a useful residue. This is in contrast to the suggested level of significance for ceramic samples as greater than 5μg/g[308]. If this new value is taken to be the minimum significant residue weight, several samples can then be excluded and then the average yields can be re-calculated as the following: 13.49mg/g for mixed samples, 222.05 mg/g for corrosion samples, and 104.99 mg/g total. These average yield values actually change very little from the values calculated with the total number of samples (same value for mixed samples, 179.85 mg/g for corrosion samples and 104.74 mg/g total).

A comparison of the yields and residues weights of each class of sample and each vessel can be seen in Figures 8-3 and 8-4. Overall, the yields for the corrosion samples were much higher than that of the mixed samples. Without data on the percentage of corrosion in the samples of soil, corrosion, and other materials, it cannot be concluded firmly as to whether this is the result of the dilution of the residue present in the mixed samples or the increased preservation of molecular organics in the corrosion itself. When the residue weights from the internal and external samples are compared, the average weight of the internal samples are nearly double that of the external samples, 0.00765 g vs. 0.00492 g, lending credence to the hypothesis that bronze does indeed preserve its organic content. This general trend can also clearly be seen in Figure 8-2.

[308] Copley, Berstan, *et al.*, 2005b.

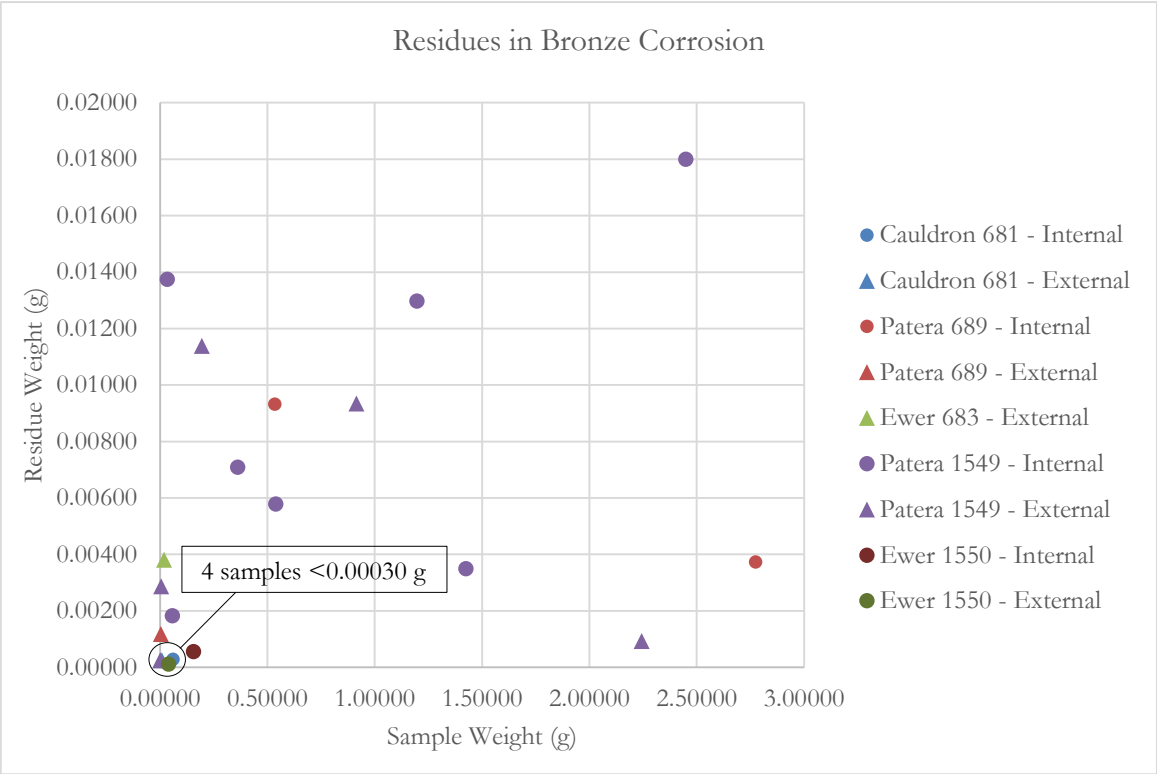

Figure 8-2: Residues in Bronze Corrosion.
Residue weight compared with sample weight and classified by vessel and sampling location.

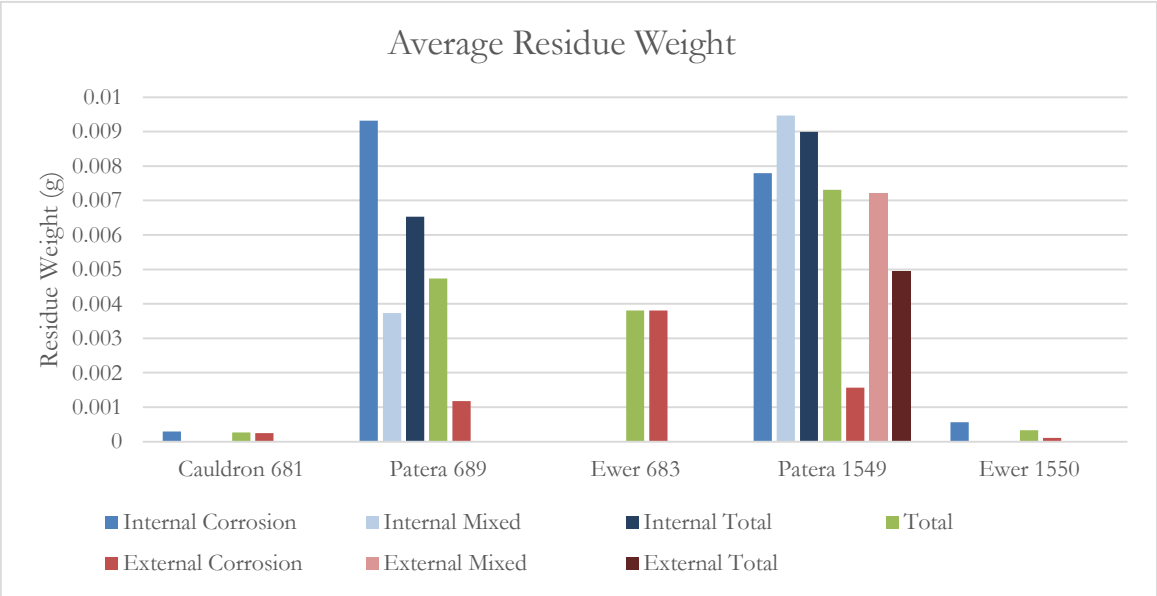

Figure 8-3: Average Residue Weight by Vessel

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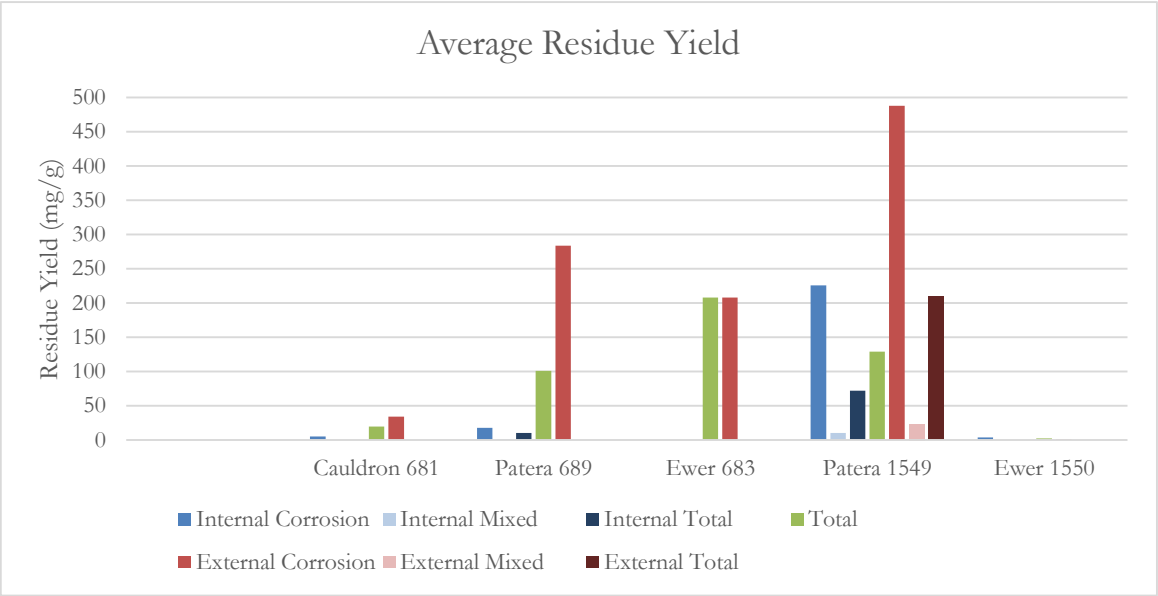

Figure 8-4: Average Residue Yield by Vessel

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Lipid analysis was carried out by Heron and Spiteri on eleven ceramic vessels including flagons, beakers, and cups found in cremation graves at the site.[309] This study serves as an excellent point of comparison for the preservation levels and the contents of both vessel materials. Five of these vessels were found from grave 6260, including one flagon, vessel 682, being found between cauldron 681 and ewer 683 which were studied here. Three of the vessels were found in gave 6635, none of which were those vessels directly beneath or in close proximity to the bronze vessels studied from the same grave. The saturated fatty acids $C_{14:0}$, $C_{16:0}$, and $C_{18:0}$ are reported in most of the ceramic samples alongside low levels of odd and even-chained alkanes. The investigators attribute these alkanes to bacterial sources and suggest that soil microorganisms have infiltrated the sherds. In addition, flagons 633 and 1539 from graves 6260 and 6635, show the presence of triterpenoids typical of a birch bark tar mixed with a fat or oil. One sample was submitted for isotope analysis to discover that the $\delta^{13}C$ values were consistent with those of ruminant adipose fat. While the odd and even-chained alkanes were present in soil samples studied, these same samples were devoid of any acyl lipids and triterpenoids allowing for the clarification of organic species from the environment and those from potential content.[310]

On comparison of the samples taken from bronze vessels with their ceramic counterparts studied by Heron and Spiteri, a few conclusions can be drawn regarding the molecular content of these samples and the potential sources of that content. The samples from cauldron 681, both internal (KRM146) and external (KRM147), failed to produce any significant amount of residue. They contained only small amounts of contaminants in their FAME extracted residues and neither extract contained any of the alkanes observed in the ceramics. In the literature, cauldrons of this type from the Roman period are frequently referred to as "wine-mixing bowls". The evidence from this study neither confirms nor

[309] Heron and Spiteri 2012a.
[310] Ibid.

denies this possibility. The principal compounds of wines and beers are difficult to detect due to their volatile nature. That said, there is no evidence of the components that were frequently mixed with ancient wines such as resins and flavourings.

The external sample of ewer 683 also failed to produce any materials detectable by GC-MS. As this ewer was inverted over patera 689, it is worth discussing the two vessels together. The external sample from patera 689 also failed to produce any organic material, including the alkanes seen in the ceramic samples. In contrast, the both the internal samples from this patera were successful in the preservation of predominantly even-chained acyl lipids, dicarboxylic acids, and dehydroabietate. Notably, these samples show none of the alkanes elsewhere attributed to microbial action. In the direct-FAME extract of sample KRM152, there are two odd-chained acyl lipids, $C_{15:0}$ and $C_{23:0}$, which most likely originate from microbial degradation. These compounds are not seen in the $CHCl_3$MeOH extracts which constitute the majority of the residue and contain all of the even-chained alkanoic acids from C14 to C28, in addition to the alkenoic acids $C_{18:1}$ and $C_{18:2}$. These compounds suggest that this patera contained a pine resin mixed with an oil.

The identification of the contents of patera 689 as a pine resin mixed with an oil suggests that this patera held some sort of cosmetic. Paterae are well known from religious/ritual contexts in the Roman Empire, though their use can be varied. Part of the confusion of the use of patera in roman culture is due to the combination of three similar vessel types which are generally conflated under the Latin term *patera*: the patera, the *Griffschale*, and the saucepan. Each of these vessels are shallow, open vessels with the distinctions based on adornment and the presence of a handle. It has been argued that the term patera should only be used for those vessels without a handle and used for pouring wine on an altar or on a sacrificial animal. Separately, the term *griffschale* ("grip plate")should be used for those vessels with a handle which represents part of the hand-washing set in the votive milieu as well as daily activity. The last distinction, *saucepan* and elsewhere termed

skillet, should be used for those undecorated utilitarian vessels used for cooking in a predominantly military context.[311] By this designation, the patera from the A2 project should be more correctly labelled as *Griffschale*, the term that Nuber used in the identification of service types to which these vessels belong. The argument made by Mustaţă is one that is based in practicality for a scholar to be able to identify the function of a vessel by its name. Typologically this argument has merit, but in reality the romans would have known all of these vessels as *paterae*, and should have known their intended use from their form and context. It is apparent, however, in the corpus of roman literature that the separations between these forms were not so distinct. Cicero condemns that shameless romans without religious scruples would stoop so low as to eat off of paterae themselves.[312] While this type of behaviour would have appeared barbaric to those in Rome, it is known that the undecorated "saucepan" forms were common in the tool kit of a roman soldier, though this food-preparation use seems to be confined only to military contexts. [313]

Here we can see three particular known uses for the patera: libation, cleansing, and cooking. Patera 689 from the elite does not fit seamlessly into these accounted uses, in its apparent use to contain a cosmetic composed of fat/oil and resin. While not attested in the context of paterae, the chemical content of roman cosmetics has been studied. There are two notable instances of residue studies conducted on cosmetic-like materials dating to the roman period in Britain. The first of these cosmetics was found mostly preserved in a tin canister excavated in London in the context of a temple precinct. Analysis of the "slightly granular" cream paste showed that the substance was a mixture of ruminant adipose fat C (~ 40%), starch (~ 40%), and tin oxide (~15%).[314] The second study was performed on a visible hard black resinous residue found within an enamelled jar from the Roman levels at

[311] Mustaţă, 2012.
[312] Cicero, *De Finibus*, II.7.
[313] Allason-Jones, 2011: 163-164; Bennett and Young, 1981.
[314] Evershed, *et al.* 2004.

Catterick, North Yorkshire, United Kingdom. Based on the isotopic signature of the fatty acids present in the substance and the presence of betulin and its derivatives, the investigators concluded that the substance was composed of ruminant animal fat and birch bark tar. This formulation was apparently heated to produce a modified resin, the resulting reactions producing unusual triterpene fatty acyl esters (acid-catalysed condensation).[315] There is one more comparable substance to that found in patera 689 dating to the Roman Empire. The content of a glass unguentaria found in Naples was shown to contain a mixture of pine resin and beeswax.[316] The cosmetics/unguents from Naples and Catterick show the closest analogies for the contents of patera 689. It can be surmised that the substances was intended for personal hygiene purposes. The cosmetic from London is similar to the white cosmetics that Pliny describes roman women using to lighten their complexion.[317] It is unclear from the evidence here whether the substance in patera 689 is something akin to this cosmetic or an unguent cream that would have had particular scent qualities and may have been heated as that in the enamel jar from Catterick.

The samples from patera 1549, as mentioned above, present the clearest picture of organic preservation in bronzes. The external mixed samples show a mixture of odd and even-chained alkanoic molecules which are probably the result of microbial contributions, similar to those observed in the soil samples and ceramic samples from the same grave. The external corrosion samples, interestingly, do not preserve these contributions. The internal samples differ from the external samples in yield as seen in Figure 8-2 and in composition, indicating that the contents of the patera are preserved or at least had a direct influence on the corrosion products. The internal mixed samples, unsurprisingly, contain higher levels of the microbial odd and even-chained alkanes as portions of the soil were extracted with the rest of the sample. The internal corrosion products also preserve these soil contributions,

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[315] Dudd and Evershed, 1999.
[316] Ribechini, *et al.* 2008.
[317] Pliny, *Natural History:* 9

but at lower levels than the mixed samples indicating that the soil fraction of these samples are the major source of these compounds. In addition to the odd and even-chained alkanes, the internal samples also show the acyl lipids $C_{14:0}$, $C_{16:0}$, and $C_{18:0}$. The comparative quantities of these compounds are higher in the pure corrosion samples than the mixed samples, indicating that they signify the content of the vessel. In all of the samples, the amount of stearic acid is nearly equal, but slightly less than the amount of palmitic acid.

The corrosion samples either preserve these compounds on a surface level or incorporate the compounds in the corrosion process. In all of the bronze vessels, the external corrosion products were devoid of odd and even-chained alkanes attributed to soil microorganisms. Of the external mixed samples, some produced these compounds and some did not. In the case of the internal samples, the relative quantities of the alkanes were lower than that of the compounds attributed to original content. This suggests that the presence of organic matter has some effect on the corrosion process of copper alloys. When organic material is already present, organics from the burial environment seem to be more readily taken up by the corrosion products. In the case of the external deposit samples, it is surmised that these deposits form due to non-organic substances in the burial environment or substances with which the vessel came into contact during use as there is no evidence of them containing any organic content. At the very least, they do not preserve GC-MS detectable organics.

From this results of this project, it can be concluded that bronze and copper alloy vessels do have the capacity to preserve organic materials at least as well as ceramics in the same burial environment. Differences in the organic profiles of external and internal samples prove that the contents are preserved within corrosion materials and probably influence the ways in which the corrosion process proceeds and the ways in which the corrosion products interact with the burial environment. It seems that the suggestion that organic materials have a direct impact on the cementation of copper patinas is a credible one.

Certainly the internal corrosion that incorporates constituents of the original contents react differently from external corrosion, in that the interior incorporates further organics from the burial environment while the exterior does not. The fact that this phenomenon occurs in bronze vessels and is not documented in ceramics, indicates a slightly more complicated mechanism for the preservation of residues in copper alloy vessels. Further research into the mechanisms of reaction between copper alloys and lipid contents is needed. The influence of lipid content on the corrosion of copper alloys and the impact of these reactions on the interaction of archaeological vessels with their burial environments needs to be further understood in order to clarify the interpretation of residues in such vessels. Finally, it is noted that the results here are limited to solvent-extracted lipid components preserved in copper corrosion. The possibility of organic copper complexes and compounds other than copper salts and trapped organics is not addressed here and merits further research.

9. Vessel Properties and their Impact on Residue Preservation

Here I have presented the results of the organic residue analysis of one hundred and fifty five samples of archaeological vessels, both ceramic and bronze. In the presentation of these results there a number of conclusions made based on the varying success of lipid preservation and extraction from these two vessel types as related to the aims of the project.

First, the trial of a new methodology has proven merits and disadvantages. The application of sequential extraction protocols are deemed to be relevant in the removal of further organic materials even if the results differ somewhat from that presented elsewhere. It is clear that solvent extraction in and of itself is not effective in the removal of all lipid materials and there is some linkage between a lipid and its matrix. Upon comparison of the data presented here with initial data concerning acid-catalysed extraction, it appears that acid-extraction could be more effective in altering ceramic surfaces, pointing to porosity being a determining factor in the preservation of organic materials in vessels.

Non-destructive organic residue analysis of sherd material has been seen here to be as effective in releasing at least a significant amount of material when combined with ultrasonication. This is promising for future studies as it has the potential to free a wider range of ceramic material for analysis while reducing sampling load and reducing effort and time required for preparation. The comparison of thickness and weight with residual yield appears to suggest that ultrasonication is penetrating a critical volume of pores consistently without crushing. One particular question of interest that remains is that, if the conclusion that has been made concerning acid treatment alteration the surface to provide greater surface area for extraction and thus the release of lipids not seen in other extractions stands, are these lipids are truly where they are completely inaccessible even with drilling, more strongly bound, or pulled deeper into the matrix. If bound materials are held within smaller pores than their unbound counterparts, it would lend some explanation as to why non-destructive analysis coupled with FAME extraction proved less successful in producing

greater yields than conventional extraction as expected. Supercritical fluid extraction, which would effectively reach all of these spaces and force materials out of the matrix, could provide more insight to this theory.

It was noted in a previous chapter that the corpus of archaeological residue analysis is lacking in the rigorous reporting of yields and success rates with a few major exceptions including the Bradford and Bristol labs. It is clear in this study and in a review of the literature, that it is of utmost importance that such data be published in order to gain a deeper understanding of residues and their relationships with their containers, surfaces, and depositional history. Issues were encountered here in the comparability of yield data. The relative merits of yield calculation methods have been discussed above and more work needs to be done to relate the two. Specifically, the fact that in many cases residues were extracted which did not result in a lipid profile when analysed by GC-MS suggests that residues are more complicated than previously attested and there may be other organic or inorganic materials present which need to be characterised by the application of other methods such as FTIR, loss-on-ignition analysis, SEM, and direct pyrolysis. Regardless, based on the data from this study and the literature, rigorous reporting of yields and thespecific details of how they are calculated is of utmost importance in the interpretation of residues and the understanding of how they are preserved.

9a. Ceramic Vessels

The organic residue analysis of the one hundred and thirty-three ceramic vessels from Lefkandi, Greece, Kabri, Israel, and Megiddo, Israel presented mixed results. While there is a disappointing lack of evidence of typical biomarkers or collections of compounds for any source determinations to be made for this material, there is some success in working toward understanding why molecular organic residues are preserved in archaeological vessels.

By recording yields from each sample in this project, several things were able to be determined. First, the exact success rates for each site and the overall assemblage were able to be compared directly. In terms of morphology, it was confirmed that rim sherds are more successful in preservation of lipid materials not just in cooking vessels[318] but in all vessels regardless of use or fabric composition. The other important observation is that none of the vessels associated with any of the burials at Megiddo seemed to have any lipid content upon deposition. These vessels may have been used for grains or other substances, but no evidence of this was observed in the excavation or during laboratory analysis. Both of these conclusions could impact the way residue analysis is carried out in the future. In the selection of sherds for analysis it would follow that diagnostic rim and base sherds should be a priority. Also, in the grand scale of worldwide archaeology, site profiles could be developed in order to estimate more accurately these locations where residue analysis might be more successful and build the analysis further into the grant-seeking and excavation-planning processes.

The second major reason for including a rigorous examination of yield figures was the elucidation of the mechanisms responsible for molecular organic preservation in vessels. Here an attempt has been made to investigate initially some of the potential pathways for this preservation including chemical composition. This is only one step into further understanding the *chaîne opératoire* of vessels and their contents and the interactions they have with one another. As one of the defining characteristics of ceramic materials is their porosity and as there has been general success in the reconstruction of "absorbed" resides, porosity has been one of the main reasons cited for the preservation and minimization of degradation reactions and other environmental forces that would otherwise remove these organic species from their depositional context. However, that is not the only potential mechanism. The

[318] Charters, *et al.* 1993b; Charters and Evereshed, 1997.

correlation of chemical characteristics with preservation, potential formation of organo-clay complexes based on cation exchange properties, the prevention of microbial action, and the effect of micropores and micropores, all seem to have significance in the preservation of organic materials within a ceramic. Similar to the prevention of microbial action due to toxicity in copper corrosion, the ceramic seems to provide mechanical protection of its own, particularly in its smaller pores. It could be argued that there is a critical pore size that could allow for the entry of organic material and prevent microbial access. Future work addressing porosity of a sherd, particularly its microporosity, will be able to confirm this hypothesis and evaluate the suggestion of bound lipids trapped deeper in the matrix within smaller, more protected spaces.

Further to the cursory XRF analysis presented here, cation exchange capacities could be measured directly to evaluate the influence of these forces on the formation of macromolecules and cross-linkages between clay minerals and lipids. This mode of inquiry could then provide further insight into the best manner to extract and study residues.

9b. Bronze Vessels.

Possibly the most ground-breaking results of this project is some of the first evidence for the preservation of organic residues in the corrosion products of archaeological bronze vessels. The results from the bronze corrosion products display clearly that bronze corrosion products can preserve lipids, both fatty acids and terpenoid compounds, opening up an entirely new context for the application of residue analysis. As this was a trial, it is only beginning to investigate this new source of information. Several issues still arise with these data and several opportunities overlooked, which future work can strive to eliminate and to make this truly applicable to other fields of inquiry. First, as small samples were provided by the conservator, it was difficult to characterize the material further than a designation of "bronze corrosion". It still seems to be apparent that the corrosion process

helps to incorporate the original contents of the vessel and once this process begins, other contaminants and degradative forces are kept at bay. In the samples studied, none of the microbial lipids that were prevalent in ceramic samples from the same graves were identified.[319] The profiles of the external samples, even those mixed with some soil deposits, were bereft of any GC-MS detectable species.

Without the ability to characterize the corrosion products on these vessels rigorously as they were tested for residual content, it is difficult to make a conclusion as to the mechanism(s) behind this phenomenon. However, the story is much the same as with ceramic vessels, rigorous yield data must combined with characterization of the specific corrosion products of a vessel to elucidate how the levels of structure interact and survive the archaeological environment. It is sensible to suggest that the primary reasons for the preservation of organics in bronze is twofold and each could be tested in the future. The encapsulation of molecular organics within corrosion products appears to occur and based on the data presented here, can be extracted from this corrosion. The organics would appear to mediate the formation of strong patinas in copper and copper alloys and in the process can become trapped. While they are in contact with the surface and the burial environment, but not yet surrounded in the protective corrosion, there is a strong possibility that there is a buffer zone where microbial action and other environmental degradation forces are diminished. In significant concentrations copper is toxic to may microbes and bacteria and thus the toxicity prevents the removal of organics by these species. In light of this conclusion, as well as the protective nature of ceramics in the potential to provide a "filter" for microorganisms, the prevention of microbial action may be more significant in the preservation of molecular organics in vessels than previously thought. It is known that extreme environments that reduce microbial action and oxidation such as arid or frozen

[319] Heron and Spiteri, 2009 and 2012.

systems, organic preservation is increased. If the vessel matrix contributes to this making a smaller "extreme" context within the overall burial environment, smaller changes in aridity or temperature could have a larger impact on the preservation of organics in vessels than organics in the rest of the system.

Despite the fact that the bronze vessels from this study only represent a few vessels from a singular context, these data remain promising for the study of residues in bronze vessels and vessels composed of other materials which may provide a unique environment separated from the environment of the surrounding larger context.

9c. Conclusions and Future Implications

In conclusion, several last remarks can be made. First, a 46% average lipid detection rate in ceramics from these three sites in the Eastern Mediterranean and encouraging data for the preservation of organics at Lefkandi. Second, it is clear from the literature and the state of the field currently, that rigorous quantification must be combined with qualitative analysis to understand the use of fats, oils, resins, and other organic substances in antiquity. Without the clarification of the interactions of these substances with the surfaces on which or in which they are found and studied, the field is limited to the reconstruction of complicated sets of degradative forces and sparse evidence. Such correlations between a substance and its containers can also lead to more informed planning and decision making when approaching organic residue analysis in the future. Finally, it is exciting to note that another potential source of information regarding vessel and organic uses and functions in the past has been found.

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