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Revealing invisible brews: A new approach to the chemical identification of ancient beer

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ABSTRACT

While ancient Near Eastern cuneiform texts and iconography unambiguously demonstrate the social, economic, and ritual significance of beer, direct archaeological evidence for beer production or consumption remains surprisingly rare. This scarcity of material evidence renders it difficult to extrapolate information about the ingredients and production processes of beer, on the one hand, and the paraphernalia and social contexts of its consumption, on the other. In recent decades, organic residue analysis has become an essential tool in the identification of ancient alcoholic beverages, but research on Near Eastern beer has focused largely on production and storage vessels, whose form, archaeological context, and associated macroscopic residues already indicated their use in beer production. In this paper, we present a novel field sampling protocol that prevents contamination along with a refined organic residue analysis methodology that relies on a series of co-occurring compounds to identify confidently beer in ceramic vessels. The same compounds were identified in several modern beer samples and, thus, support our identification of a similar fermented barley-based beverage in archaeological samples from the late second millennium BCE site of Khani Masi in northeastern Iraq. The results presented in this paper allow us, for the first time, to unambiguously link a diverse range of vessel types to the consumption and production of beer, identify a fundamental change in Mesopotamian consumption practices, and shed light on the cultural dimensions of Babylonia's encounter with the Zagros-Mesopotamian borderlands.

1. Introduction

Beer, alongside other alcoholic beverages, was in many past societies a fundamental part of everyday life as well as integral to ritual practices and the expression of social identity and intergroup relations (Dietler and Hayden, 2001). A grain-based fermented beverage, beer has found a range of different geographical and historical expressions: at Jiahu, a Neolithic site in China, chemical analysis revealed that beer was made from rice (McGovern et al., 2005); Peru is known for its corn-based beer or chicha (Hayashida, 2008); while beer in Egypt and the ancient Near East was brewed from cereal grains such as barley (Jennings et al., 2005; Samuel, 1996; Curtis, 2001).

In the ancient Near East, beer and other alcoholic beverages have been investigated largely through textual sources and iconography (Hartman and Oppenheim, 1950). Beer is frequently mentioned in both administrative and ritual cuneiform texts and its consumption is portrayed on a range of media such as seals and ceramic plaques. The beverage suffused all aspects of life in Mesopotamia and the wider Near East both as a highly nutritious dietary staple (O'Connor, 2015) and an essential component of cult festivals and feasting events (Sallaberger, 2015; Otto, 2012). By contrast, archaeological evidence for beer is comparatively limited and mostly confined to ceramic containers used in beer production.

Advances in the field of archaeological organic residue analysis over the past three decades have opened up new ways of exploring ancient diet and the development of subsistence practices such as the case of dairying (Dunne et al., 2012, 2013). Organic residue approaches to alcoholic beverages in the ancient Near East have focused primarily on the documentation of wine (Badler et al., 1996; McGovern et al., 1996; Koh et al., 2014). The chemical identification of beer is to date restricted to a small number of cases in which archaeological context, inferences from textual sources about vessel function or the presence of visible residues (beerstone) in relatively unambiguous terms point to the brewing and storage of beer (Michel et al., 1993; Otto, 2012).

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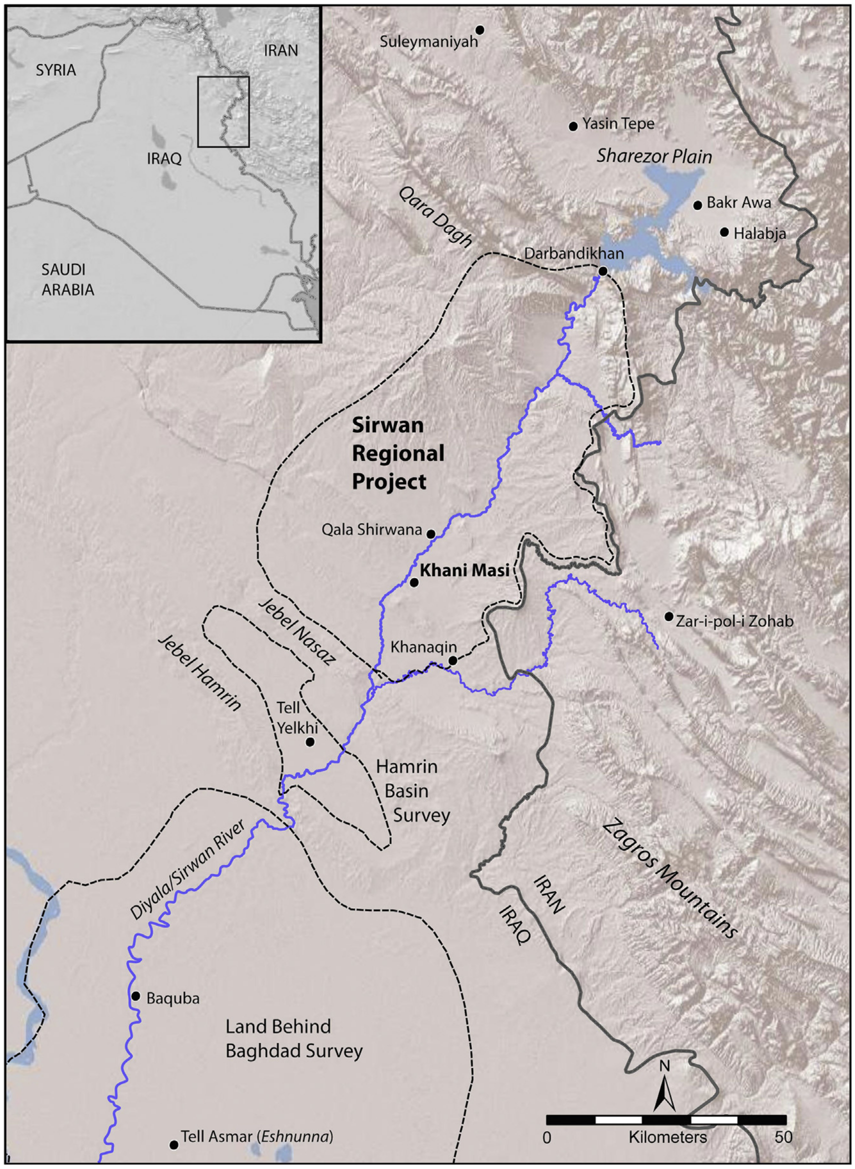

Fig. 1. Map showing the Sirwan Regional Project study region and the location of Khani Masi (after Glatz and Casana, 2016).

Currently lacking is a chemical approach that allows the identification of beer in vessels not directly associated with the brewing process but with its consumption. The identification of the contents of drinking and serving equipment is crucial for the reconstruction of daily and more exceptional consumption practices as well as the social and cultural communities and boundaries that were shaped by the choice of a particular beverage (over alternatives) and through its combination with specific consumption equipment.

In this paper, we lay the methodological groundwork for such a study by presenting a new field-based sampling protocol for archaeological organic residue analysis that prevents the risk of sample contamination, as well as a new analytical approach using gas chromatography and compound co-occurrence for the identification of ancient beer in a series of drinking and serving vessels from the late second millennium BCE site of Khani Masi, northeastern Iraq (Fig. 1). The results of this analysis present a significant advance in the study of ancient Near Eastern beer brewing and consumption practices. They also provide us with unprecedented new insights into the nature of Babylonian cultural expansion into and beyond a politically and economically strategic, yet archaeologically little-known, highland-lowland borderland along the Sirwan/Diyala River. Though much has been written on beer consumption in the ancient Near East on the basis of textual and iconographic sources, proposed associations between consumption containers and types of beverages are educated guesswork. Our results for the first time tie specific types of consumption and serving vessels alongside a long-suspected but never confirmed brewing vessel, unambiguously to the production and consumption of beer. Included in our analysis are several examples of the ubiquitous solid-footed or 'Kassite' goblet, the defining chronological type fossil of the Middle Babylonian Period (c. 1500-1150 BCE) whose temporal and geographical distribution has become synonymous, justifiably or not, with Kassite imperial reach in much of the literature (e.g. Armstrong and Gasche, 2014; Armstrong, 2017; Fuchs, 2017). The function(s) as well as the social and political significance of these vessels, however, remained unexplored until now, with earlier analyses focused on typological development and to a lesser extent also geographical distribution (Bartelmus and Sternitzke, 2017; van As and Jacobs, 1987; Armstrong and Gasche, 2014; Clayden, 1989).

2. Past approaches to beer in the ancient Near East

Archaeological, textual and more recently organic geochemical approaches to beer in the ancient Near East have focused primarily on the contexts and tools used in its production and storage, whilst practices of beer consumption are inferred almost exclusively from cuneiform and iconographic sources.

2.1. Textual and iconographic evidence for beer production

Beer (Sumerian kaš, Akkadian šikaru) is well attested in a range of cuneiform genres from the Uruk period (ca. 4000 - 3100 BCE) onwards. Mid-third millennium BCE administrative records from the Mesopotamian city of Lagash mention a variety of beers including golden beer, sweet dark beer and red beer, alongside differences in beer quality (Michel, 2012). Beer also appears in many texts relating to religion and medicine (Scurlock, 2014). A hymn dedicated to Ninkasi (ca. 1800 BCE), the Babylonian goddess of beer and brewing (Jennings et al., 2005), includes rare instructions for beer brewing involving the use of BAPPIR or 'beer-bread'. Though generally called a recipe, the text is both incomplete and phrased in often very general terms, which leave much room for speculation on the production sequence and ingredients. Lexical and administrative texts also lack more detailed information about the brewing process and how different varieties of beer were produced. Changes in vocabulary associated with beer brewing over time in Mesopotamia, for instance, may indicate changes in production practices. Rosemary Ellison, for example, argued that the evolution of the term 'brewer' from the third millennium BCE LÚ.ŠIM + GAR/LÚ.BAPPIR, which includes the term 'beer-bread' to simply LÚ.ŠIM in the Kassite Period, suggests a change in beer brewing technique that no longer involved the use of beer-bread in most production contexts (Ellison, 1984).

A common practice in attempts to understand more fully the processes involved in the production of ancient Near Eastern beer, therefore, has been to draw on evidence from Egypt (Hartman and Oppenheim, 1950), where brewery scenes are common in Early Dynastic tomb paintings (Samuel, 1993; Curtis, 2001) and archaeological evidence tracks changes in beer brewing from Pre-Dynastic Hierakonpolis to the New Kingdom (ca. 1550-1070 BCE) workers' villages at Deir el-Medina and Amarna (ca. 1350 BCE) (Hornsey, 2003; Samuel, 1996).

2.2. Archaeological evidence for beer production and consumption

Compared to textual and iconographic sources, archaeological attestations of beer brewing are limited in the ancient Near East and their identification for the most part hinges on the presence of cuneiform texts mentioning individuals, ingredients or equipment involved in the brewing process.

An Early Dynastic III (ca. 2600–2350 BCE) building at Tell al-Hiba, ancient Lagash, in southern Iraq, yielded an assemblage consisting of vats with perforated bases, hearths and ovens. The structure's interpretation as a brewery, however, rests on the presence of an administrative text listing quantities of beer, as well as mentioning the terms BAPPIR and brewery (É-LUNGA) (Hansen, 1980–1983). The early 15th century BCE "Tablet Building" at Tell Hadidi on the Syrian Euphrates, yielded several rooms in which were found a series of storage vessels, cups and jars alongside carbonised grains, grinding stones, a strainer and vessels with perforated bases (Dornemann, 1977, 1981). The latter were identified by Marie Henriette Gates as beer fermenting vats on the basis of cuneiform lexical texts, which refer to such vessels as $^{\text{DUG}}$NÍG.DÚR.BÙR or *namzitu* (Gates, 1988). The identification of the "Tablet Building" as a brewery received further corroboration from a series of sealed cuneiform tablets that indicate that a man named Yaya, the owner of the building, was a large-scale brewer. Further circumstantial evidence of potential brewing activities come from the Late Bronze Age site of Kuşaklı in central Anatolia, where a monumental structure, Building C (ca. 1450-1380 BCE), contained an assemblage of bowls, medium-sized jars, straws and strainers, which the excavators interpreted as a brewery (Müller-Karpe, 1999, 2006).

Since its debut in the 1970s, analysis of organic residues of food and drink that seeped into the porous walls of ceramic containers has emerged as a valuable tool for the exploration of ancient diet (Roffet-Salque et al., 2017), including the production and consumption of alcoholic beverages. In the context of the ancient Near East, however, such research has focused almost exclusively on wine (Badler et al., 1996; McGovern et al., 1996; Koh et al., 2014). Beer has been identified chemically in only three instances, each of which relies on the presence of either contextual archaeological evidence indicative of beer brewing or clearly visible residues of the so-called beerstone, a by-product of barley beer making (Michel et al., 1993).

Beer was identified for the first time using chemical methods in a large Late Uruk Period handled jar at Godin Tepe (ca. 3500-2900 BCE) (Michel et al., 1993), a site with strong cultural ties to lowland Mesopotamia that is located in the Zagros Mountains of western Iran (Rothman and Badler, 2011). Organic residue analysis was carried out on a yellowish-brown resinous-looking material that was preserved on the lip of the Godin Tepe jar. A Feigl spot test (see below) identified the presence of oxalate and likely calcium oxalate, a salt of oxalic acid, principal component of beerstone as well as edible plants such as spinach and rhubarb (Michel et al., 1993; Hornsey, 2003; Gregg, 2009). Beerstone is a precipitate, which tends to settle on the surface of processing and storage vessels used in the brewing of beer. Chemical evidence for beer was also found in a series of household contexts at the 13th century BCE site of Tell Bazi on the Syrian Euphrates (Otto, 2012). Of the 50 or so houses excavated at Tall Bazi, many contained material assemblages indicative of beer brewing such as mills and large vats alongside bronze filter tips to which drinking straws could be attached. Like at Godin Tepe, organic residue analysis at Bazi also focused on the macroscopic remnants of beerstone and the presence of oxalate. Chemical identification of beer in a consumption related context comes from the site of Gordion, the capital of the Iron Age kingdom of Phrygia in central Anatolia. Here, beer was identified as one component of a mixed alcoholic drink (which also included grape wine and possibly honey mead) served at the funeral feast of a Phrygian king in the great tumulus, or Midas' tomb, at Gordion (ca. 700 BCE). The identification of beer at Gordion also rests on the presence of oxalate (Mcgovern et al., 1999).

2.3. Social contexts of beer consumption

With the exception of the possible beer-wine being served at Gordion, our understanding of the specific contexts, equipment and practices of beer consumption derive from iconographic sources, and in less detailed form, also from cuneiform texts and the development of the script itself (Potts, 1997). From the fourth millennium BCE onwards, seals depict the consumption of beer from large piriform jars using straws. A seal impression from Tepe Gawra, for instance, shows human figures drinking from enormous jars with bent straws (Rothman, 2002). A lapis lazuli cylinder seal from the tomb of Queen Pu-abi in the Royal Cemetery at Ur (Early Dynastic III period, ca. 2600-2500 BCE), depicts a banquet scene in two registers (Woolley, 1934, pl. 200, 102). The upper register shows a male and female participant seated on either side of a wide-mouthed jar drinking from long straws or tubes. A couple seated behind them and several more in the second register are drinking their beverages from cups, balanced on their palm or fingertips.

Roughly contemporary limestone plaques depicting feasting events from the third millennium BCE settlement at Tell Khafajah in the Lower Diyala region also attest to a variety of drinking practices (Frankfort, 1939, Plates 105 and 107, 185 and 187). In one of them, a large jar with narrow neck is transported to the feast that takes place in the upper register (Frankfort, 1939, Plate 105, 185). Here, three seated figures drink from small, rounded bowls balanced on their fingertips or grasping the long stems of pedestal cups. Cylinder seals from the same site also depict the consumption of beer in large jars through long

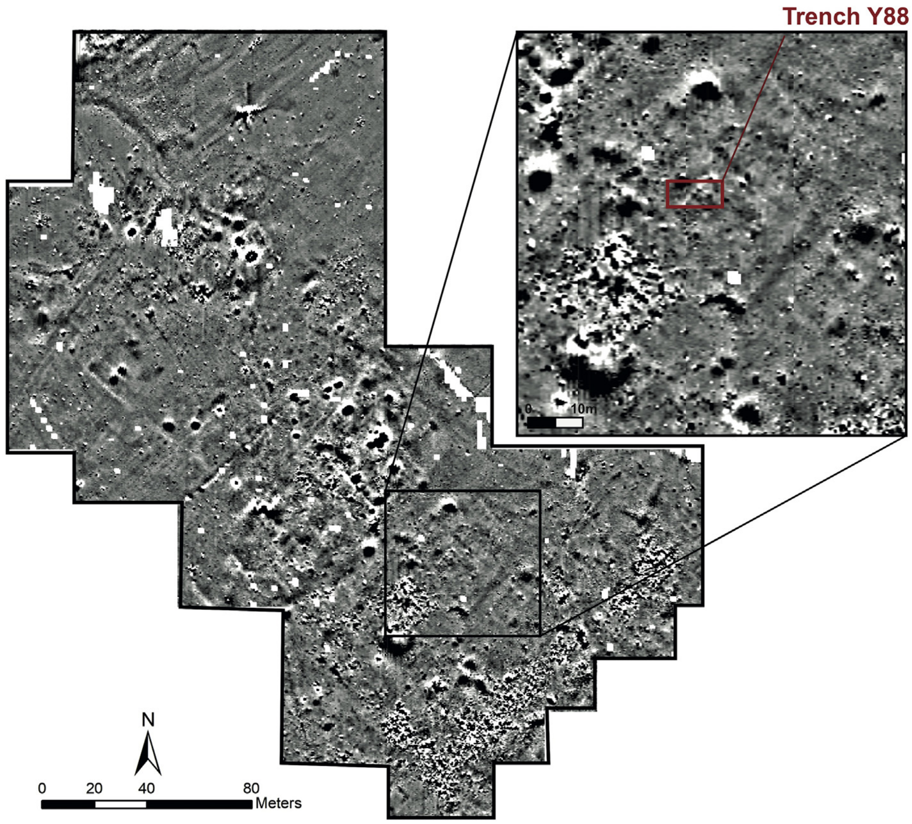

Fig. 2. Results of magnetic gradiometry survey at SRP 46 (Khani Masi) and location of Trench Y88.

straws (Frankfort, 1955). The same drinking practice is attested on a series of Old Babylonian erotic terracotta plaques (ca. 1800 BCE), which depict a copulating couple with the woman bending over to drink beer from a jar through a straw (Bahrani, 2001).

These differences in consumption equipment – bowls and cups versus large jars and straws – have in the past been interpreted as indicating the consumption of different beverages, with bowls commonly associated with wine (McGovern, 2003–2006). However, others have suggested both jars and bowls may have been used for the consumption of beer in the third millennium BCE (Ellison, 1978, 230). Ellison proposed that different drinking equipment may indicate differences in beer brewing techniques. Straws depicted protruding from the beer jars, were used to filter out thick and cloudy beer full of pieces of beer bread and herbs and other impurities. Archaeological evidence, such as from Mari on the Syrian Euphrates, also attest to the use of metal strainers that would have been placed at the tip of the straws to filter the beer (Maeir and Garfinkel, 1992). The use of cups, according to Ellison, suggests a brewing or preparation technique that produced a beer with fewer unpleasant impurities (Ellison, 1978, 146).

Following the Old Babylonian period (ca. 2000-1600 BCE), drinking scenes become rare in the iconographic repertoire of Mesopotamia. Middle Babylonian cylinder seals, stele, wall reliefs and moulded brick façades do not depict banquet or other scenes involving the consumption of food and drink. A drastic reduction in the ceramic repertoire of settlements associated with Middle Babylonian ceramic traditions (Armstrong and Gasche, 2014), which includes the disappearance of large jars of the type depicted on earlier beer-drinking scenes, would suggest a shift in consumption practices, at least as far as the use of ceramic vessels is concerned.

Organic residue analysis holds a special promise here, albeit one as yet little explored in the regional and chronological framework of this paper, in advancing our understanding of food and drink consumption practices through the direct analysis of ceramic vessels. In the remainder of this paper, we present the results of the application of a new organic residue analysis approach to a series of consumption-related vessels from the newly excavated late second millennium BCE site of Khani Masi in northeastern Iraq.

3. Late Bronze Age beer production and consumption in the Zagros-Mesopotamian borderlands

The Khani Masi site is located along the upper reaches of the Sirwan/Diyala River, a tributary of the Tigris in what is today the autonomous Kurdish region of Iraq and, where the Sirwan Regional Project has been carrying out regional-scale archaeological research since 2013 (Glatz and Casana, 2016; Casana and Glatz, 2017) (Fig. 1). Perched between the Zagros piedmonts and the Mesopotamian lowlands, this transitional landscape is located along a series of major corridors of movement, including branches of the later Khorasan Highway and Silk Routes.

Situated atop a relict levee of the Diyala river at the southern tip of a fertile plain and close to a series of perennial springs, the Khani Masi site cluster comprises about a dozen mounded features over a total area of ca. 120 ha and with evidence for occupation from the Neolithic to the modern period. The site's most significant settlement, however, dates to between c. 1500 to 1100 BCE when occupation covered upwards of 40–50 ha[1] (Fig. 2). A strategic thoroughfare and borderland, the region was sought after by a series of Bronze Age imperial polities during the later second millennium BCE, including Kassite-Babylonia (e.g. Fuchs, 2017), and Khani Masi's material culture and associated practices strongly suggest a close cultural link with central Mesopotamia, although definitive evidence for political hegemony is as yet lacking (Glatz and Casana, 2016).

[1] Excavations and a geophysical survey are still ongoing at Khani Masi to determine the site's full extent.

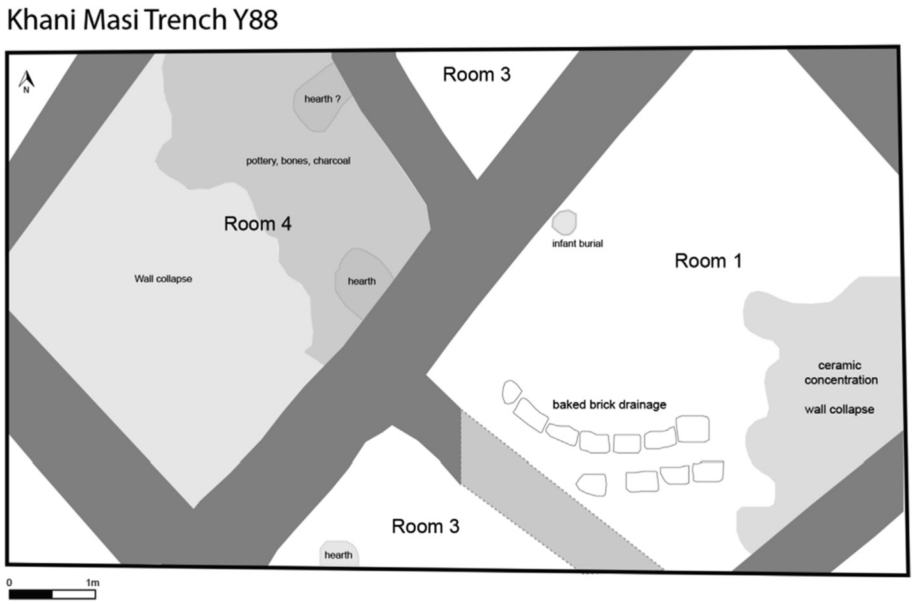

Fig. 3. Plan of Trench Y88 excavated in 2016.

A magnetic gradiometer survey in 2014 revealed a series of large, ca. 30 × 40 m, rectangular and trapezoidal structures in the central and southern portion of the site (Fig. 2). Excavations in Trench Y88 exposed a suite of rooms clustering on the north western side of a monumental courtyard structure built from unbaked mudbricks and with walls up to 1.2 m in width (Fig. 3). In the largest, centrally positioned Room 1 were discovered a large collection of morphologically diverse drinking cups and goblets, which lay strewn across the southeastern floor area and mixed with the wall collapse just above that marks the end of the building's final phase of occupation (Figs. 3 and 4b). The vessels might have been stored on shelves along the southern and eastern walls of Room 1 and were scattered north and westwards into the room when the walls collapsed. A charcoal sample from Room 1 dates the sealed materials under the collapse layer to between 1415 and 1290 cal. BCE (AA109181, X31274). The large number of recovered vessels and their spatial concentration, which is so far unique at Khani Masi, suggest a

Fig. 4. Selection of vessels recovered in Trench Y88: a) two juglets and faience bucket, b) a 'Kassite' goblet and c) a bowl, juglet and faience bucket.

Fig. 5. ***Namzitu*** **or brewing vat from Trench Y88.**

function of Room 1 in the hosting of socially significant consumption events. Two smaller rooms to the west (Rooms 2 and 3) may have served as food preparation areas with several hearths positioned against internal walls.

Following the destruction of the building, its ruins continued to hold significance within Khani Masi's urban fabric as a burial ground and place of ritual. An infant jar burial was dug into the northern wall of Room 1 whilst a wall to the west was cut to deposit – stacked one on top of the other - a bowl, juglet and faience bucket (Fig. 4c), a small open-mouthed vessel made from quartz-derived vitreous material often found in 13th and 12th centuries BCE Kassite-Babylonian funerary contexts (Clayden, 1998). A further collection of offerings was deposited in the centre of the room, which consisted of two identical drinking cups, a further faience bucket and a gold earring (Fig. 4b). A large open-mouthed vessel with a ca. 1 cm wide opening at the bottom, which can be identified as a *namzitu* or beer-brewing vat in textual sources, was placed nearby (Fig. 5). Excavations are still ongoing at Khani Masi, but our current working hypothesis is that these ritual depositions overlap in time with a second phase of large-scale construction at the site (Glatz et al., 2018).

The vessels analysed here are made from medium coarse, usually chaff-tempered clays using a potter's wheel. Surfaces were treated minimally and vessels were fired at high temperatures to buff, greenish-buff or occasionally pinkish colours. The entire Khani Masi ceramic repertoire finds close typological parallels at Late Bronze Age Mesopotamian cities such as Ur, Isin or Nippur and the smaller, mostly agricultural settlements excavated in the Hamrin basin including Tell Yelkhi, Tell Zubeidi and Tell Imlihiye, which are located c. 25 km downstream along the Diyala from Khani Masi. Small footed cups and in a few instances also larger goblets are attested in small quantities at Tell Bakr Awa to the north of Khani Masi in the Sharezor and to the north-east at Tepe Guran in the Mahi Dasht region of western Iran (for distribution maps and bibliography, see Armstrong and Gasche, 2014; Armstrong, 2017). This suggests, as we shall argue below, a selective adoption of Mesopotamian consumption practices at these highland sites.

Systematic sampling for archaeobotanical material has been undertaken across all trenches at Khani Masi, with the purpose of investigating the crop economy of the site. To date, sample sizes of charred grains are relatively small and none have been recovered from the rooms of the monumental structure in Trench Y88. The analysis of charred plant remains sampled from other contemporary contexts, however, show that barley, the most common ingredient in Mesopotamian beer, was one of the major crops at the site, with only few instances of wheat identified to date.

4. Material and method

Organic residue analysis was performed on fifteen samples representing different types of consumption vessels found scattered in the south-eastern portion of Room 1. They include solid-footed or 'Kassite' goblets and smaller footed cups as well as a medium sized bowl, the *namzitu* and one of the juglets deposited as post collapse offerings were also analysed (Figs. 4 and 5). In addition, a sample of malted barley and two samples of modern beers, a wheat beer containing a mixture of wheat malt and barley malt (Erdinger Weißbier, Germany), and a barley beer made from barley malt only (Budweiser original, Czech Republic) were freeze dried for two days, prepared and analysed following the same methodology described below.

No visible residues, such as beerstone, were present in any of the vessels analysed. This, however, is not a disadvantage as the most reliable archaeological information is gained from the absorbed residues in the vessel fabric. Vessel surfaces and visible residues are subject to higher degrees of post-burial and post-excavation contamination (see below) (Evershed, 2008). Our choice of analytical methodology was guided by these factors with a primary objective of identifying archaeologically significant compounds as a first step of analysis.

Lacking visible residues, as well as other clear indicators of a beer-related vessel function (with the exception of the *namzitu*), the Feigl spot test employed in previous studies of ancient Near Eastern beer was not appropriate in our case. The Feigl spot test is a simple qualitative method used to target specific compounds (Feigl, 1956); in the case of

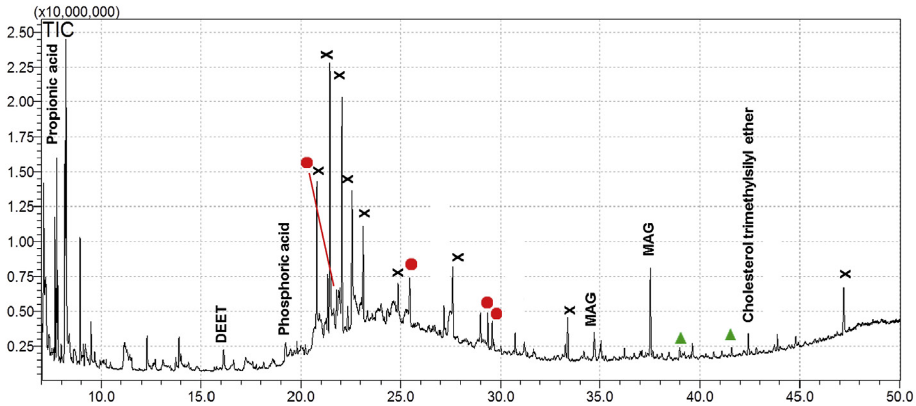

Fig. 6. Partial total ion chromatogram of a 'Kassite' goblet handled without gloves during excavation and stored in a plastic bag before being analysed. Cx:y fatty acids (red circles), Cx alkanes (green triangles), MAG mono-acylglycerols, plasticizers contamination (cross). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

previous organic residue studies of beer it was used to determine the presence of oxalate. After reduction by zinc granules in an acidic medium to glyoxalic acid, samples containing oxalate will give a specific colour reaction (pinkish red colour) with phenylhydrazine and hydrogen peroxide when in contact on a filter paper or a spot plate (McGovern et al., 2008). However, the reliability of the Feigl test has also been called into question (McGovern and Hall, 2015; Rasmussen, 2014). Indeed, some compounds are susceptible to giving false positives and false negatives (Feigl, 1956).

In this study, we opted for the use of gas chromatography, a methodology that allows a large range of compounds to be separated and identified. Gas chromatography has become a valuable part of the archaeological toolkit (e.g., Thornton et al., 1970; Evans and Heron, 1993; Roffet-Salque et al., 2017). Rather than the reliability of the measurement, the central concern in the use of gas chromatography is the contamination of archaeological samples by similar chemical compounds derived from modern sources. For instance, compounds derived from hand oils, plastic, sunscreen and other lotions can be similar to archaeologically significant compounds (Steele, 2013).

Given these potential significant biases, that are always present, especially during the excavation and post-excavation stages of sample recovery, contaminants and sample contamination have received surprisingly little attention in publications on archaeological residue analysis. A basic knowledge of potential contaminants, however, is crucial when seeking to interpret the results of residue analysis and to identify viable samples for analysis and interpretation. In this study we describe practical methods used in each stage of the study from excavation to analysis that allows us to exclude modern contamination as source of archaeologically significant organic residues. In particular, our intention here is to promote a shared methodology that makes the collection of samples for organic residue analysis transparent and more accessible to a wider part of the archaeological community.

Fig. 6 represents an example of a gas chromatogram for a ceramic vessel of the same typological form as those analysed in greater detail below. Unlike the residue samples from this study, the pottery presented in Fig. 6 was handled without gloves during excavation, washed and stored in plastic bags, which is common practice at archaeological excavations. The chromatogram shows clearly contamination by phthalate and phenol peaks that have relative abundances noticeably higher than other compounds. In certain cases, the contaminant peaks were so concentrated that the compounds of interest could not be analysed without the contaminant peaks overloading the detector (both in GC-FID, Gas Chromatograph - Flame Ionization Detector and GC-MS, Gas Chromatograph - Mass Spectrometer). In addition to making analysis difficult or impossible, the dominant presence of contaminants in these two samples makes any results from peaks of potential archaeological interest unreliable. Some contaminants are easily identifiable and can be excluded from consideration since they have no ancient equivalent. This is the case, for instance, for plasticizers that come from plastic storage materials or *N,N-Diethyl-meta-toluamide* or DEET (insect repellent) (Fig. 6). Other compounds, by contrast, could have been present in the past, but distinguishing the modern from the archaeological is often challenging if contaminants are present.

For instance, a large range of fatty acids are characteristic biomarkers for degraded fats (e.g., C16 and C18 fatty acids), but are also the most ubiquitous compounds in nature with additional sources from plastics and human skin. Similarly, cholesterol, used as an indicator of animal origins of degraded fats (Charters et al., 1993; Heron and Evershed, 1993), is also present in human skin and residues can be deposited on vessel surfaces through touch (Heron and Evershed, 1993). Washing pottery vessels, a routine practice in the processing stage in archaeological field projects, degrades and often destroys archaeological compounds completely. This is especially the case for biomarker compounds indicative of fermented beverages such as tartaric acid, which possesses a high solubility in water (Rasmussen, 2014).

In order to prevent exogenous contamination from fingerprint residues, sunscreen and contamination from plastic bags in the course of excavation and post-excavation handling, as well as storage and transportation, ceramic vessels selected for sampling at Khani Masi were handled exclusively using cotton gloves (Fig. 7) and manipulated with acetone-sterilized instruments (e.g. tweezers). To protect samples during transportation, the sherds (5 × 5cm) were immediately wrapped in aluminium foil, which had been previously combusted at 450 °C for 8 hours to eliminate potential contaminants (Fig. 7). The sherds were never in contact with plastic as they were protected by aluminium foil from sampling to sample preparation.

Soil samples from the immediate finds contexts as well as from inside sampled vessels were also collected and used as a control to evaluate the likelihood of contamination from the burial environment, such as leaching from decaying plant matter (Brown and Brown, 2011). The soil samples were analysed in the same manner as those extracted from ceramic vessels.

Both the inner and outer surfaces of sampled sherds were drilled using a cordless Dremel 8200 with an abrasive point as grinding tool, which was also sterilized with acetone before use to further reduce the possibility of exogenous or cross sample contamination. The ceramic powders from the inner and outer surfaces were retained for organic residue analysis to identify and assess levels of potential contamination from the burial environment or from handling and storage. The remaining ceramic cores were crushed into powder using a sterilized agate mortar and pestle and stored in 40 ml glass vials, which had been combusted at 450 °C for 8 hours prior to sample storage.

Lipids were extracted from sample matrices using a Dionex Accelerated Solvent Extractor (ASE) 350 in a mixture of dichloromethane and methanol (9:1 v/v DCM:MeOH). The ASE 350 can run 24 samples in 10 ml cells. On average, a 10 ml cell can hold 3 g of sample. This instrument enables better extractions in less time and

Fig. 7. Sampling strategy: vessels were handled exclusively using cotton gloves and immediately wrapped in aluminium foil previously combusted at 450 °C/8 h before use to eliminate potential contaminants.

effort than manual techniques, such as ultrasonication and centrifugation. The possible contamination coming from the lipid extraction process and the laboratory environment were controlled using blanks (combusted sand) analysed in the same manner as the sherd samples and other control samples (soil sample, inner and outer surfaces of samples).

The samples were then transferred into 2 ml vials and derivatised by heating at 80 °C for two hours with addition of 30 µl of the reagent N,O-bis(trimethylsilyl)trifluoroacetamide with 1% Trimethylsilyl chloride and 10 µl of pyridine added as basic catalyst.

Samples were run on the Agilent 7890 GC-FID for biomarker quantification and then on the Agilent 5977 GC-MS for biomarker identification. The analysis time was 63 min (starting at 7 min) using a Rtx-1 Restek column (60 m × 250 µm x 0.25 µm) and an oven temperature program where the temperature was held at 60 °C for 2 min, then increased 30 °C/min up to 120 °C, then increased 5 °C/min up to 300 °C, then increased 5 °C/min up to 340 °C held isothermally for 15 min. Hydrogen was used as the carrier gas for the GC-FID and helium for the GC-MS.

Due to the above sampling regime, organic residues were well-preserved in the Khani Masi samples with only trace amounts of modern contamination such as phthalates and phenols (Fig. 8 and Supplementary Material). Comparisons were made with soil residues and residues extracted from outer and inner vessel surfaces to ensure that identified compounds are of archaeological significance and not the results of contamination (Table 1 and Supplementary Material). The majority of the compounds that were also associated with the burial soils and identified in the outer surfaces of vessels have been excluded from analysis.

5. Results

The analytical sample consists of five typological groups: (1) 'Kassite' goblets (KG), (2) a juglet (J) and (3) footed cups (FC) that are associated with the serving and consumption of liquids and (4) a large vat with perforated base or *namzitu* (N) that can be associated with beer production. (5) A simple, medium-sized bowl (B) from the same context, whose function was not likely associated with the preparation and consumption of alcoholic drinks, serves as a test sample against which the chemical signatures of preparation and consumption vessels can be compared. In addition, a sample of malted barley and two samples of modern beers were also analysed for comparison (Figs. 9 and 10).

The majority of the compounds identified in our ceramic samples were not detected in the control samples (soil samples and outer surfaces of vessels) (Table 1 and Supplementary Material) and thus we interpret these to be of archaeological significance and not the product of contamination. The archaeologically significant compounds are presented below.

All five typological groups yielded residues containing a series of odd ($C_{9:0}$ to $C_{25:0}$) and even-chain fatty acids ($C_{8:0}$ to $C_{28:0}$). Short-chain fatty acids ($C_{8:0}$ and $C_{10:0}$) are found in varying quantities in all animal and plant lipids (Gunstone et al., 1994). All samples also include $C_{16:0}$, palmitic acid, and $C_{18:0}$, stearic acid, the most common and abundant fatty acids in both plant and animal tissues (Evershed et al., 1997; Evershed, 2008; Heron and Evershed, 1993). Unlike the majority of the compounds presented below, $C_{16:0}$ and $C_{18:0}$ were - as might be expected – present in both the inner and outer surfaces of sampled vessels and the surrounding soil samples. As a result, we chose not to include these ubiquitous compounds as significant to our archaeological analysis, but do recognise that they may have ancient origins.

We identified the presence of compounds exclusively in groups N, KG, J and FC such as carboxylic and dicarboxylic acids: benzoic acid, butanedioic acid, pimelic acid, suberic acid and azelaic acid.

The sample residues also contain glycerol in low relative concentration as well as mid-chain monounsaturated and diunsaturated fatty acids ($C_{14:1}$, $C_{16:1}$, $C_{18:1}$ *cis*-9, $C_{18:2}$ and $C_{20:1}$) not identified in control samples, and therefore considered archaeologically significant. $C_{18:1}$, oleic acid, and $C_{16:1}$, palmitoleic acid, can be found in varying quantities in all animal and plant lipids (Gunstone et al., 1994), including cereal grains (Asuman, 2015). The presence of long-chain fatty alcohols (C18 to C30) (Fig. 10 in Supplementary Material) and odd-numbered alkanes (e.g. C27, C29 or C31) are usually associated with plant waxes (Marshall et al., 2008; Baeten et al., 2013; Soberl et al., 2014).

Hydrocinnamic acid and Methoxycinnamic, two phenolic acids, have been identified in plants including pulses and cereal grains such as barley (Kuete, 2013, 227; Nollet, 2004, 696; Hernanz et al., 2001).

A compound from the class terpene is also present. Although, not identified precisely, the mass spectrum shows two predominately high m/z ions 69 and 81 m/z as well as 136/7 m/z and smaller peaks 341 and 410 m/z (Table 2 and Fig. 57 in Supplementary Material). Those are peaks found in the mass spectrum of squalene, a triterpene (Middleditch, 1989, 652). Squalene is a common contaminant and a component in skin sebum, but it has been also identified in germinated grains such as barley (Briggs, 1978, 116). Because this compound 1) was found exclusively in groups N, KG, J and FC, 2) was not identified in soil samples or the outer and inner surfaces and 3) because our vessels were not handled with bare hands and with only sterilized equipment, its presence is interpreted here as archaeologically significant.

In addition, two aldehydes (erucylamide and 9-oxadecenal) were identified recurrently in 6 of the samples and two wax esters were also identified in Group J: Oleyl palmitoleate and oleyl oleate.

Another notable compound was found in Group J, only in the sherd

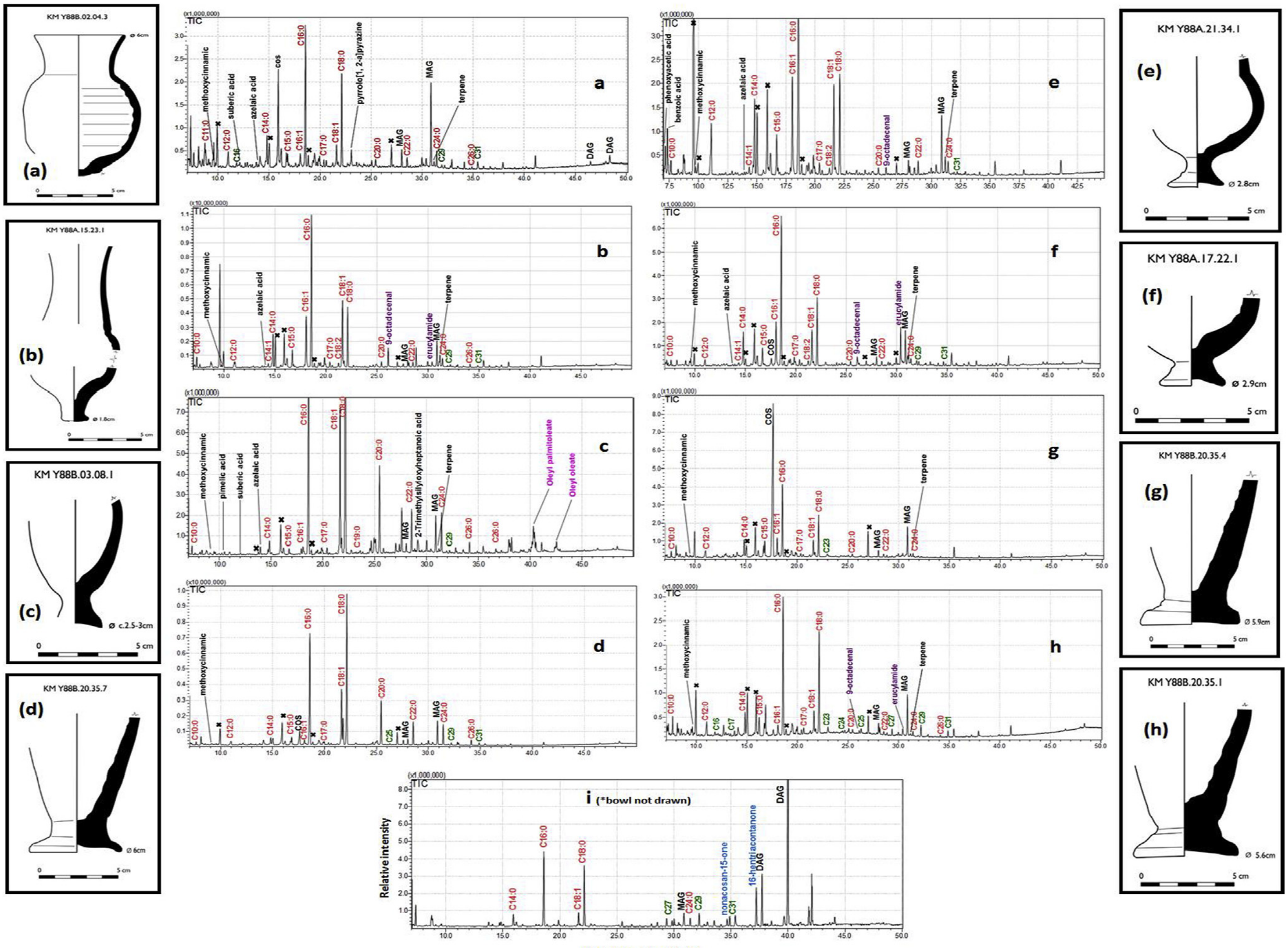

Fig. 8. Partial total ion chromatograms of 9 of the 15 sherd samples: Cx:y fatty acids (red), Cx alkanes (green), aldehydes (purple), ketones (blue), MAG and DAG mono- and diacylglycerols, Wax esters (pink), contamination (cross).

In comparison to the bowl (i), the eight drinking/serving vessels (c, d, g and h: Kassite goblets; a: Juglet, b, e and f: Footed cups) exhibit similar chromatogram profile and compounds pointing to the presence of cereals grains and beer; i. Bowl: results interpreted as cooked food of plant origin (Ketones K29 and K31). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

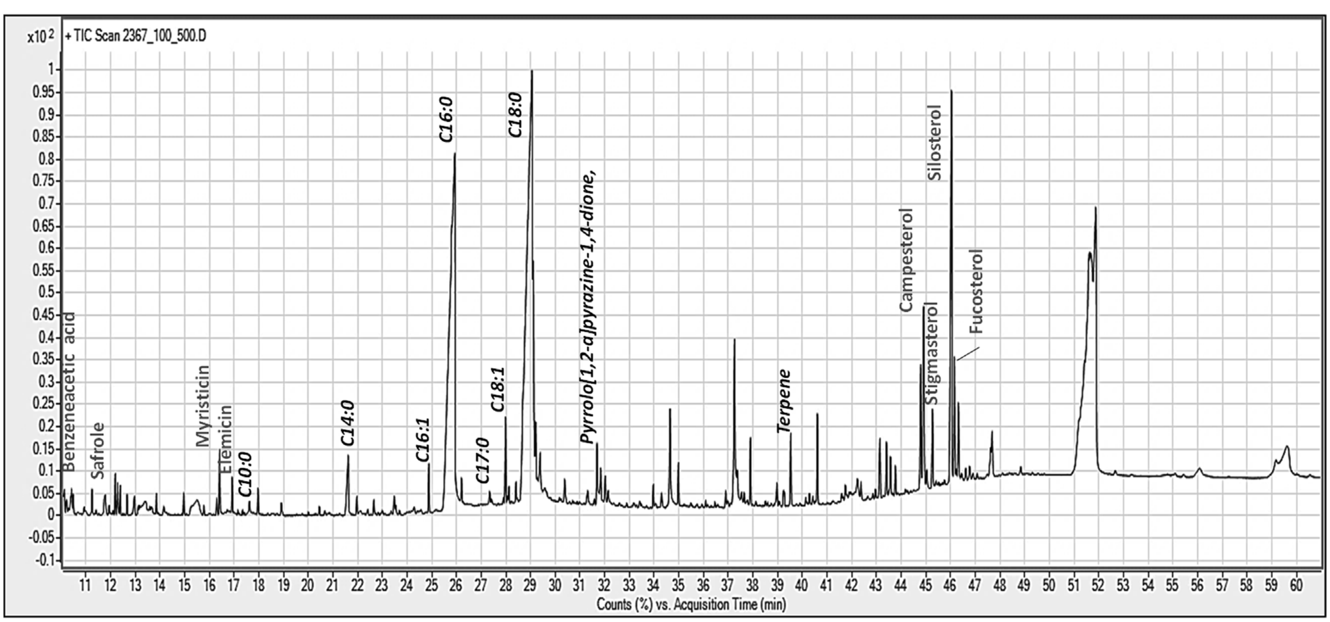

Fig. 9. Partial total ion chromatogram of a sample of modern malted barley. Compounds in *italic* are also found in the sampled drinking vessels.

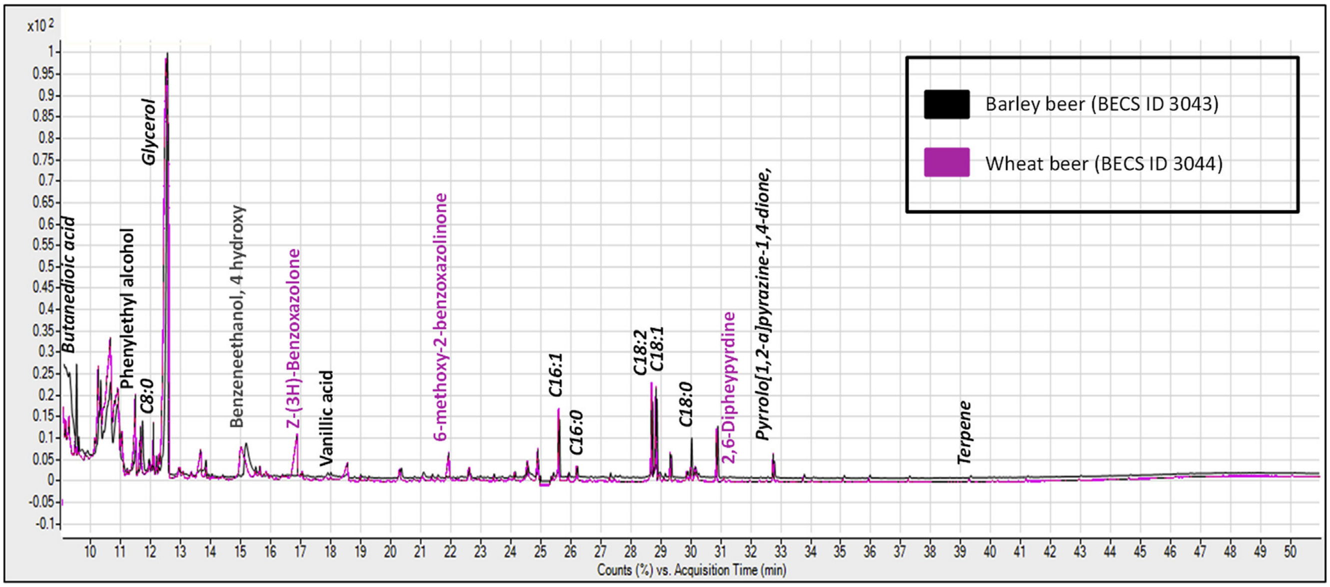

Fig. 10. Combined partial total ion chromatograms of samples of two modern beers: in pink, a sample of wheat beer containing a mixture of wheat malt and barley malt, and in black a sample of barley beer made from barley malt. Compounds in *italic* are found in the sampled drinking vessels. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

sample (and not in the control samples) and thus interpreted here as archaeologically significant (Fig. 8, Tables 1 and 2 and Fig. 55 in Supplementary Material): Pyrrolo[1,2-*a*]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl).

6. Interpretation

Analytical results from the *namzitu* (N), the 'Kassite' goblets (group KG), the juglet (group J) and the footed cups (group FC) show a co-occurrence of ten chemical compounds (highlighted in blue and bold in Tables 1 and 2 and Figs. 50–57 in Supplementary Material), which in concert point to the presence of a cereal-derived fermented beverage, beer.

Among the observed carboxylic and dicarboxylic acids, pimelic acid and butanedioic acid are present in a number of fermented alcoholic beverages such as wine and beer (Klopper et al., 1986; Pecci et al., 2013; Briggs et al., 2004; Nykänen and Suomalainen, 1983). However, no traces of compounds usually associated with wine, such as tartaric acid or polyphenols (e.g. malvidin and syringic acid) were detected (Barnard et al., 2011). Butanedioic acid was identified in our samples of modern beers (Fig. 10) and in the *namzitu* (Fig. 8 and Fig. 27 in Supplementary Material), but not in the drinking vessels, perhaps indicating that there was better preservation and higher concentration in the fermenting vat where beer would have sat longer. Benzoic acid can also be present in smoke and charred materials, a product of plant decay and decomposition; however, it is also a by-product of fermentation processes. Finally, azelaic acid could be, like the hydroxy fatty acids 10-oxo-octadecanoic acid (10-oxo-C18:0), the product of the oxidation of oleic acid (Koh and Birney, 2017; Colombini et al., 2005), however it should be noted that they also occur naturally in cereals grains wheat, rye, and barley (McGovern et al., 2013). Here, in the context of the other compounds identified, our rigorous methodology to avoid contamination, and three controls (soil, inner and outer surfaces), we suggest that the latter is the most likely origin for this compound.

While squalene is a common lipid in many organisms and highly commercialized today for its antioxidant properties (Steele, 2013), it has also been widely reported to occur in germinated grain (Briggs, 1978, 116) and yeast (Blagovic et al., 2001), which is the most important ingredient in brewing beer. Indeed, yeast is a single-cell organism, one of the simplest forms of plant life, which is responsible for the fermentation process in beer. This terpene was identified in our sample of malted barley and two samples of modern beers (Figs. 9 and 10).

Another notable compound consistent with beer was found in Group J (Fig. 8, Tables 1 and 2 and Fig. 55 in Supplementary Material): Pyrrolo[1,2-*a*]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl). Produced by different fungi, pyrazine derivatives have been identified as antioxidants present in roasted barley malt and modern beer (Briggs et al., 2004, 318; Buckingham, 1993, 1226; Gautschi et al., 1997). This compound was indeed identified in our sample of malted barley and our two samples of modern beers containing malted barley (Figs. 9 and 10).

Hydrocinnamic acid and methoxycinnamic acid are cinnamic derivatives that have been in previous studies identified in modern beer (Briggs et al., 2004; Bokulich, 2017), were not identified in our sample of modern beers (Fig. 10). These compounds are also formed by fungi (Guzman, 2014) as well as degradation of wax (Regert et al., 2001) and in honey (Trautvetter et al., 2009). However, these two compounds have not been found in the control samples and no other compounds coherent with the presence of honey were identified in our samples.

The remaining compounds identified in the ceramic vessels (presented in Fig. 8 and Table 1) though not directly contributing further evidence to the identification of beer, by no means contradict it. Indeed, our samples of malted barley and modern beers contain, like our archaeological samples, mid-chain monounsaturated and diunsaturated fatty acids ($C_{16:1}$, $C_{18:1}$ *cis*-9, $C_{18:2}$) as well as glycerol in high concentrations (Figs. 9 and 10). Glycerol has been identified in previous studies in high quantities in different kinds of beers, even alcohol-free ones (Klopper et al., 1986). The reliability of the above results and interpretation are further corroborated by the similar chromatogram obtained for group N associated with beer production and groups KG, FC and J. On the contrary, we obtained a distinct chromatographic profile of the test sample, a medium-sized bowl (B), which contains different compounds such as long-chain ketones: nonacosan-15-one and 16-hentriacontanone (Table 1, Fig. 8 and Fig. 33 in Supplementary Material). Long-chain ketones have been widely reported as evidence of higher plants as well as compounds produced by pyrolysis of fatty acids or cooking (Evershed et al., 1995). Most significantly, the sample derived from the bowl contained none of the chemical compounds that are associated directly with cereal-grains and alcoholic beverages, suggesting a very different function to the vat (N) and consumption vessels

Table 1

Summary of the major compounds found in the samples of malted barley (MB), modern barley beer (BB) and modern wheat beer (WB) as well as in the 15 vessel samples and comparison with soil samples as well as inner and outer surfaces. **X**: Drilled Sample, X: Inner surface sample, X: Outer surface sample, X: Soil.

	Benzoic	**Pimelic**	**Suberic**	**Butanedioic**	Pentanoic acid, 2,2,4-trimethyl-3-carboxyisopropyl, isobutyl ester	Propanoic	Phosphoric	Acetic	**Pyrrolo[1,2-a]pyrazine-1,4-dione**	**Terpene**	**Azelaic**	Aldehydes	**Hydrocinnamic**	Wax esters	Straight-chain alcohols	Ketones	Even-numbered Alkanes	Odd-numbered Alkanes	DAG	**Glycerol, TMS**	**Methoxycinnamic**	10-oxo-C18:0
N KM11	X, X (inner), X (outer)			X	X		X, X (inner), X (outer)			X			X					X				
B KM19																X		X	X			
J KM2			X			X, X (inner), X (outer), X (soil)	X, X (inner), X (outer)		X	X	X, X (inner)							X	X		X	
FC KM38						X, X (inner), X (outer), X (soil)				X	X	X						X			X	
FC KM29						X, X (inner), X (outer), N/A (soil)				X, N/A (soil)		X						X, N/A (soil)			X, X (inner), N/A (soil)	
FC KM34	X, X (soil)					X, X (inner), X (outer), X (soil)		X		X	X, X (inner), X (soil)	X						X			X	
KG KM20		X	X							X	X, X (inner), X (soil)			X				X			X, X (inner)	
KG KM55						X, X (inner), X (outer), X (soil)				X							X, X (inner)	X			X, X (inner)	
KG KM49						X, X (inner), X (outer), X (soil)				X		X					X, X (inner)	X, X (inner)			X	
KG KM56						X, X (inner), X (outer), X (soil)												X			X, X (inner)	
KG KM54					X					X		X			X			X		X		
KG KM66	X, X (inner), X (outer), X (soil)									X									X			X
KG KM70										X		X	X, X (inner)					X		X		
KG KM18										X, N/A (soil)									X, N/A (soil)			
KG KM17						X, X (inner), X (outer), X (soil)		X		X	X, X (inner), X (soil)	X		X, X (inner), X (outer)					X, X (inner), X (outer)		X, X (inner)	
MB									X	X										X		
BB				X					X	X										X		
WB				X					X	X										X		

(continued on next page)

Table 1 (*continued*)

	C8:0	C9:0	C10:0	C11:0	C12:0	C14:0	C15:0	C16:0	C17:0	C18:0	C19:0	C20:0	C22:0	C23:0	C24:0	C25:0	C26:0	C28:0	C14:1	C16:1	C18:1	C18:2	C20:1
N KM11	XXXX	XXX	X		XXXX	XXXX	XXXX	XXXX	XX	XXXX		X	XX							X	X		
B KM19						XXX		XXX		XXX											X		
J KM2	XXXX	XXX		X	XXXX	XX	XXXX	XXXX	X	XXXX			XX		X		X			X	X	X	
FC KM38			XXXX		XXXX	XXXX	XXXX	XXXX	XX	XXXX		X	XX		X				X	X	X	X	
FC KM29			XXN/A		XXXXN/A	XXXXN/A	XN/A	XXXXN/A	XN/A	XXXXN/A		XN/A	XN/A		XN/A		XN/A		XN/A	XN/A	XN/A	XN/A	
FC KM34			XXXX			XXXX	XX	XXXX	XX	XXXX		X	XX		X				X	X	X	X	
KG KM20			XXXX		XXXX	XXXX	XXXX	XXXX	XX	XXXX	X	XX	XX		X		X			X	X		
KG KM55			XXXX		XXXX	XX	XX	XXXX	XX	XXXX		X	XX							X	X		
KG KM49			XXXX		XXXX	XXXX	XXXX	XXXX	XX	XXXX		X	XX		X		X			X	X		
KG KM56			XXXX		XXXX	XX	XXXX	XXXX	XX	XXXX		X	XX		X		X			X	X		
KG KM54	XXXX	XXXX	XXXX		XXXX	XXXX	XXXX	XXXX	XX	XXXX		X	XXXX		X					X	X		
KG KM66	XX	X	XX		XXXX	XXX	XX	XXXX	XX	XXXX		X	XXXX		X	X	X	X		X	X		
KG KM70						XXXX		XXXX	XX	XXXX		X	XXXX		X					X	X		
KG KM18	XXXXN/A	XXXXN/A				XXXXN/A	XXXXN/A	XXXXN/A	XN/A	XXXXN/A	XN/A	XN/A	XN/A		XN/A	XN/A	XN/A	XN/A		XN/A	XN/A		XN/A
KG KM17			XXXX			XXXX	XX	XXXX	XX	XXXX		X	XX						X	X	X		
MB			X			X		X		X										X	X		
BB	X							X		X										X	X	X	
WB	X							X		X		X								X	X	X	

(KG, J, FC). The organic residue analysis of further bowls and other vessel types is currently underway.

7. Discussion

Analyses of organic residues from ceramic vessels excavated from the site of Khani Masi in northeastern Iraq enable us to draw several significant and entirely novel conclusions regarding the production and consumption of beer in the ancient Near East. Firstly, we are now able to confirm the function of the large vessels with perforated bases as beer fermenting vats, which had long been suspected on the basis of textual sources, but not chemically confirmed. The chromatographic profile and compounds recovered from the fermenting vat or *namzitu* sample (Group N) analysed in this study is the same as those of the samples from drinking/serving vessels (Groups KG, J and FC) and consistent with the presence of beer.

Our analytical results also allow us, for the first time and with confidence, to ascribe a diverse range of drinking equipment to the consumption of beer and in so doing track a significant transformation in Mesopotamian drinking practices.

Most studies of ancient Mesopotamian beer have associated its consumption with medium to large jars, from which the beverage was collectively sipped using long straws, sometimes with metal filters attached to the top. Daintier goblets and cups have tended to be associated with wine (McGovern, 2003–2006); although some have suggested a more varied range of beer-drinking equipment (Ellison, 1978).

Table 2
Summary table of the ten compounds identified in our samples and consistent with beer, presenting their common name, molecular formula, molecular weight and key m/z(s) found in our mass spectra that helped us identify the compounds.

Compounds	Molecular formula	Molecular weight	Key m/z(s) in our mass spectra
Hydrocinnamic	C9H10O2	150.177 g/mol	91, 104, 150
Methoxycinnamic	C10H10O3	178.187 g/mol	75, 133, 161, 175, 178, 191, 235, 250
Benzoic	C10H14O2Si	194.3025 g/mol	77, 105, 135, 179
Butanedioic	C10H22O4Si2	262.105661 g/mol	45,55,56,73,74,75,147,148,149,247
Pimelic	C13H28O4Si2	304.152613 g/mol	44,45,55,69,73,75,125,147,155,173
Suberic	C14H30O4Si2	318.1682262 g/mol	45,55,73,75,83,117,129,169,187,303
Azelaic	C15H32O4Si2	332.183912 g/mol	45, 55, 73, 75, 55, 117, 129, 147, 149, 201, 317
Squalene	C30H50	410.73 g/mol	41, 69, 81, 136, 137, 341, 410
Pyrrolo[1,2-*a*]pyrazine-1,4-dione	C14H16N2O2	244.2890 g/mol	70, 91, 125, 153, 173, 201, 244
Glycerol	C12H32O3Si3	308.64 g/mol	73, 103, 133, 147, 205

In line with changes in the Middle Babylonian ceramic repertoire, our results not only confirm a change in beer consumption equipment but allow us to unambiguously link several widely attested vessel types, including the iconic 'Kassite' goblet, with its consumption. Both cups and goblets are ubiquitous at excavated urban sites and their monumental precincts in the Mesopotamian heartland but are also attested in rural agricultural contexts both in excavations and in the survey record. There is, thus, nothing intrinsically prestigious about either these objects or their contents, although their concentration in the monumental structure at Khani Masi points to their use in socially significant consumption events.

In social terms the association of both small to very small drinking cups and the medium-sized solid-footed goblets with beer suggests a shift from late third and early second millennium BCE collective beer drinking experiences to more individualised ones. The small drinking vessels recovered from the floor and destruction debris in the monumental structure in Trench Y88 take a variety of shapes ranging from squatter to slender, elongated shapes; sizes and the shape of footed stems also varies a great deal (Groups 195, 205 and 210 in Armstrong and Gasche, 2014). Vessel volumes, based on a pilot study, however, appear to cluster around 100–200 ml, the latter of which is comparable to a small glass of wine. The larger solid-footed goblets (Group 215 in Armstrong and Gasche, 2014) also vary in shape with some smaller, more rounded varieties and others tall and elongated. Vessel volumes vary between 300 and 600 ml, which is just under the standard volume of a bottle of wine. This relatively restricted capacity and the open, outward tapering rims of the goblets make their use as storage container unlikely. They are also not well suited to pouring, spilling a lot of liquid in the process. Beer may, thus, have been consumed from them directly or through straws. Unlike the large jars shown on earlier depictions, neither the footed cups nor the goblets are very stable when placed on the ground or a table, and so would have had to be held while full; the larger vessels lending themselves to sharing by passing the vessel among participants. The presence of beer residues in one of the juglets deposited as part of a ritual offering in the destruction debris of Room 1 at Khani Masi also sheds a new light on local ritual practice, pointing to either the drinking, libation or both of beer as part of funerary and commemorative ceremonies, which are frequently associated with abandoned structures at Middle Babylonian sites (Sternitzke, 2017).

Our findings also provide us with new insights into the cultural and social dimensions of the encounter between Mesopotamian imperial powers and the landscapes and people of the strategic, but as yet archaeologically little understood, highland-lowland borderland of the Upper Diyala River valley and adjacent Zagros uplands. The site of Khani Masi displays cultural similarities across a wide range of material categories with central and southern Mesopotamia during the later second millennium BCE. It is tempting, as a result, to place it under at least nominal Kassite-Babylonian sovereignty and see the latter's performance and material reproduction in the commensal paraphernalia excavated in the monumental structure in Y88 and through the consumption of Mesopotamia's alcoholic beverage of choice.

This broad spectrum of Babylonian cultural connections diminishes rapidly to the north and east of Khani Masi, which alongside several other large contemporary settlements newly discovered by the Sirwan Regional Project, marks an emergent cultural boundary zone between intensive Mesopotamian connectivity and shared practice and the highland regions to the north and east of the Upper Diyala valley (Glatz et al., 2018). The exception to this general trend is the commensal sphere, where evidence from Tepe Guran in western Iran, for instance, includes a limited range of locally produced Babylonian-style ceramic vessels (Thrane, 1999), among them the same range of drinking equipment that we have analysed in this paper. This points to the selective and no doubt socially strategic local adoption of Babylonian drinking paraphernalia and practices into an otherwise distinct west Iranian cultural sphere. Evidence not of political integration as such (Fuchs, 2017), but of a shared arena of social and cultural production that connected culturally otherwise distinct communities across a large, topographically challenging and ecologically diverse region, whose further analysis presents one of the key foci of the Sirwan Regional Project's ongoing research.

8. Conclusions

While textual sources and iconographic representations from the ancient Near East show that beer formed a central component of both daily meals and ritual practices, our research using organic residue analysis demonstrates the potential of this approach to provide a much more nuanced understanding of beer production processes and consumption behaviours in the Near East and the ancient world more broadly.

This paper makes two key methodological contributions to this field of research and sheds light on a series of important regional and period-specific socio-cultural practices, their transformation and adoption. The first is a rigorous field-based sampling strategy that successfully minimises sample contamination from excavation and post-excavation handling and enables a straight-forward distinction to be made between archaeologically significant chemical compounds and others likely presenting contamination.

The use of gas chromatography, which allows us to identify co-occurring chemical compounds consistent with both the ingredients, including cereal grains (e.g. Pyrrolo[1,2-*a*]pyrazine-1,4-dione, terpene and monounsaturated fatty acids), and the fermentation processes (e.g. butanedioic acid, and glycerol) involved in the production of beer presents a second significant methodological advance. Those same compounds have been identified in analysed samples of modern malted barley and modern beers. Previous studies of ancient beer have relied on a combination of visible residues, beerstone, and analytical approaches suitable only in scenarios where the result can be anticipated with some degree of certainty. The methodology presented in this paper allows the identification of beer in ceramic vessels whose content and function is unknown or difficult to discern from archaeological contexts alone. Going forward, we plan to further refine this methodology through compound quantification, which will provide more information on complex mixture and possible flavourings of beer.

Based on the organic residue results from the late second millennium BCE site of Khani Masi, we were able to ascribe a broad range of drinking equipment to the consumption of beer, identify substantial changes in regional drinking practice and begin to sketch their behavioural and social implications. This in turn has allowed us to contribute significant new knowledge to the study of the, to-date little explored, cultural and political dimensions of early highland-lowland encounters in the Zagros-Mesopotamian interface.

In conclusion, the sampling strategy and analytical approach presented in this paper provides us with the ability to understand the contents and, hence, the function(s) of particular ceramic vessels, and consumption vessels more specifically, independently of textual sources, iconographic evidence and archaeological context. As such it has the potential to transform the study of ancient food and drink as well as its contexts and practices of consumption in the Near East and elsewhere.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jas.2018.05.010.

References

Armstrong, J.A., 2017. Babylonian pottery in the Kassite Period. In: Sternitzke, K., Bartelmus, A., Roaf, M. (Eds.), Karduniaš: Babylonien in der Kassitenzeit. The Proceedings of the Symposium held in Munich 30 June to 2 July 2011, vol. 2. De Gruyter, Berlin, pp. 437–478.
Armstrong, J.A., Gasche, H., 2014. Mesopotamian Pottery: a Guide to the Babylonian Tradition in the Second Millennium B.C. Ghent, Chicago.
van As, A., Jacobs, L., 1987. Second millennium B.C. goblet bases from Tell ed-Deir - the relationship between form and technique. Newsl. Dep. Pottery Technol. 5, 39–53.
Asuman, K., 2015. Characterization of the fatty acid and mineral compositions of selected cereal cultivars from Turkey. Record Nat. Prod. 9 (1), 124–134.
Badler, R.V., Mcgovern, P.E., Glusker, D.L., 1996. Chemical evidence for a wine residue from Warka (Uruk) inside a late Uruk period spouted jar. Baghdader Mittl. 27, 39–43.
Baeten, J., Jervis, B., De Vos, D., Waelkens, M., 2013. Molecular evidence for the mixing of meat, fish and vegetables in Anglo-Saxon coarseware from Hamwick, UK. Archaeometry 55 (6), 1150–1174.
Bahrani, Z., 2001. Women of Babylon: Gender and Representation in Mesopotamia. Routledge, Londres-New York.
Barnard, H., Dooley, A.N., Areshian, G., Gasparyan, B., Faull, K.F., 2011. Chemical evidence for wine production around 4000 BCE in the Late Chalcolithic Near Eastern highlands. J. Archaeol. Sci. 38, 977–984.
Bartelmus, A., Sternitzke, K. (Eds.), 2017. Karduniaš, vol. 2 De Gruyter, Boston.
Blagovic, B., Rupcic, J., Mesaric, M., Georgiu, K., Maric, V., 2001. Lipid composition of brewer's yeast. Food Technol. Biotechnol. 39 (3), 175–181.
Bokulich, N.A., 2017. Brewing Microbiology. Caister Academic Press, Norfolk.
Briggs, D.E., 1978. Barley. Chapman & Hall, London.
Briggs, D.E., Brookes, P.A., Stevens, R., Boulton, C.A., 2004. Brewing: Science and Practice. Woodhead Publishing, Cambridge.
Brown, T.A., Brown, K., 2011. Biomolecular Archaeology: an Introduction. John Wiley & Sons, Chichester, West Sussex.
Buckingham, J., 1993. Dictionary of Natural Products. Taylor & Francis Ltd/CRC Press, London.
Casana, J., Glatz, C., 2017. The land behind the land behind Baghdad: archaeological landscapes of the Upper Diyala (Sirwan) River Valley, Iraq. 79, 1–23.
Charters, S., Evershed, R.P., Goad, L.J., Heron, C., Blinkhorn, P., 1993. Identification of an adhesive used to repair a Roman jar. Archaeometry 35, 91–101.
Clayden, T., 1989. Aspects of the Early History of the Kassites and the Archaeology of the Kassite Period in Iraq (c. 1600-1150 BC). Doctoral thesis. Wolfson College, Oxford.
Clayden, T., 1998. Faience buckets. Baghdader Mittl. 29, 47–79.
Colombini, M.P., Giachi, G., Modugno, F., Ribechini, E., 2005. Characterisation of organic residues in pottery vessels of the Roman Age from Antinoe (Egypt). Microchem. J. 79 (1–2), 83–90. https://doi.org/10.1016/j.microc.2004.05.004.
Curtis, R.I., 2001. Ancient food Technology. Brill, Boston.
Dietler, M., Hayden, B., 2001. Digesting the feast – good to eat, good to drink, good to think: an introduction. In: Dietler, M., Hayden, B. (Eds.), Feasts: Archaeological and Ethnographic Perspectives on Food, Politics and Power. Smithsonian, Washington DC, pp. 1–20.
Dornemann, R.H., 1977. Tell Hadidi: a millennium of Bronze Age City occupation. Ann. Am. Sch. Orient. Res. 44, 113–150.
Dornemann, R.H., 1981. The Late Bronze Age pottery tradition at Tell Hadidi, Syria. Bull. Am. Sch. Orient. Res. 241, 29–47.
Dunne, J., Evershed, R.P., Cramp, L.J.E., Bruni, S., Biagetti, S., di Lernia, S., 2013. The beginnings of dairying as practised by Pastoralists in 'Green' Saharan Africa in the 5th Millennium BC. Doc. Praehistorica 40, 118–130.
Dunne, J., Evershed, R.P., Salque, M., Cramp, L., Bruni, S., Ryan, K., Biagetti, S., di Lernia, S., 2012. First dairying in green Saharan Africa in the fifth millennium BC. Nature 486, 390–394.
Ellison, E.R., 1978. A Study of Diet in Mesopotamia (c.3000-600 BC) and Associated Agricultural Techniques and Methods of Food Preparation. Doctoral thesis. University of London, London.
Ellison, E.R., 1984. Methods of food preparation in Mesopotamia (c. 3000-600 BC). J. Econ. Soc. Hist. Orient 27 (1), 89–98. http://dx.doi.org/10.2307/3631938.
Evans, K., Heron, C., 1993. Glue, disinfectant and chewing gum: natural products chemistry in archaeology. Chem. Ind. 12, 446–449.
Evershed, R.P., 2008. Organic residue analysis in archaeology: the archaeological biomarker revolution. Archaeometry 50, 895–924.
Evershed, R.P., Mottram, H.R., Dudd, S.N., Charters, S., Stott, A.W., Lawrence, G.J., Gibson, A.M., Conner, A., Blinkhorn, P.W., Reeves, V., 1997. New criteria for the identification of animal fats preserved in archaeological pottery. Naturwissenschaften 84, 402–406.
Evershed, R.P., Scott, A.W., Raven, A., Dudd, S.N., Charters, S., Leyden, A., 1995. Formation of long-chain ketones in ancient pottery vessels by pyrolysis of acyl lipids. Tetrahedron Lett. 36 (48), 8875–8878.
Feigl, F., 1956. Spot Tests in Organic Analysis. Elsevier Publishing Co., Amsterdam.
Frankfort, H., 1939. Sculpture of the Third Millennium B.C. From Tell Asmar and Khafājah, vol. 44 Oriental Institute Publications, University of Chicago Press, Chicago.
Frankfort, H., 1955. Stratified Cylinder Seals from the Diyala Region, vol. 72 Oriental Institute Publications, University of Chicago Press, Chicago.
Fuchs, A., 2017. Die Kassiten, das mittelbabylonische Reich und der Zagros. In: Bartelmus, A., Sternitzke, K. (Eds.), Karduniaš. Babylonia under the Kassites, The Proceedings of the Symposium Held in Munich 30 June to 2 July 2011, vol. 1. De Gruyter, Boston, pp. 123–165.
Gates, M.-H., 1988. Dialogues between ancient near eastern texts and the archaeological record: test cases from Bronze Age Syria. Bull. Am. Sch. Orient. Res. 270, 63–91.
Gautschi, M., Schmid, J.P., Peppard, T.L., Ryan, T.P., Tuorto, R.M., Xiaogen, Y., 1997. Chemical characterization of Diketopiperazines in beer. J. Agric. Food Chem. 45, 3183–3189.
Glatz, C., Casana, J., 2016. Of highland-lowland borderlands: local societies and foreign power in the Zagros-Mesopotamian interface. J. Anthropol. Archaeol. 44, 127–147.
Glatz, C., et al., 2018. Babylonian Encounters in the Upper Diyala Valley: Kassite Imperialism and the Khani Masi Site Cluster, c. 1500-1100 BCE. (in preparation).
Gregg, M.W., 2009. Organic Residue Analysis and the Earliest Uses of Pottery in the Ancient Middle East. Doctoral Thesis. University of Toronto, Toronto.
Gunstone, F.D., Harwood, J.L., Padley, F.B., 1994. The Lipid Handbook, second ed. Chapman and Hall, London.
Guzman, J.D., 2014. Natural cinnamic acids, synthetic derivatives and hybrids with antimicrobial activity. Molecules 19 (12), 19292–19349.
Hansen, D.P., 1980–1983. Lagaš B Archäologisch. RIA VI, Berlin, pp. 422–430.
Hartman, L.F., Oppenheim, A.L., 1950. On beer and brewing techniques in Ancient Mesopotamia: according to the XXIIIrd tablet of the Series HAR.ra = hubullu. Supp.

J. Am. Orient. Soc 10, Baltimore.
Hayashida, F.M., 2008. Ancient beer and modern brewers: ethnoarchaeological observations of chicha production in two regions of the North Coast of Peru. J. Anthropol. Archaeol. 27 (2), 161–174. https://doi.org/10.1016/J.JAA.2008.03.003.
Hernanz, D., Nuñez, V., Sancho, A.I., Faulds, C.B., Williams, G., Bartolome, R., Gomez-Cordoves, C., 2001. Hydrocinnamic acids and ferulic acid dehydrodimers in barley and processed barley. J. Agric. Food Chem. 49, 4884–4888.
Heron, C., Evershed, R.P., 1993. The analysis of organic residues and the study of pottery use. Archaeol. Meth. Theor. 5, 247–284.
Hornsey, I.S., 2003. History of Beer Making and Brewing. Royal Society of Chemistry, London.
Jennings, J., Antrobus, K.L., Atencio, S.J., Glavich, E., Johnson, R., Loffler, G., Luu, C., 2005. Drinking beer in a blissful mood. Curr. Anthropol. 46 (2), 275–294.
Klopper, W.J., Angelino, S.A.G.F., Tuning, B., Vermeire, H.A., 1986. Organic acids and glycerol in beer. J. Inst. Brew. 92, 225–228.
Koh, A.J., Birney, K.J., 2017. Organic compounds and cultural continuity: the Penn Museum Late Minoan IIIC stirrup jar from Tourloti. Mediterr. Archaeol. Archaeometry 17 (2), 19–33. https://doi.org/10.5281/zenodo.581717.
Koh, A.J., Yasur-Landau, A., Cline, E.H., 2014. Characterizing a middle bronze palatial wine cellar from Tel Kabri, Israel. PLoS One 9 (8). https://doi.org/10.1371/journal.pone.0106406.
Kuete, V., 2013. Medicinal Plant Research in Africa: Pharmacology and Chemistry. Elsevier, London.
Maeir, A.M., Garfinkel, Y., 1992. Bone and metal straw-tip beer-strainers from the Ancient Near East. Levant 24, 218–223.
Marshall, L.-J., Cook, S.R., Almond, M.J., Fulford, M.G., 2008. Roman diet and trade : evidence from organic residues on pottery sherds. Brittania 39, 245–253.
McGovern, P.E., 2003–2006. Ancient Wine: the Search for the Origins of Viniculture. Princeton University Press, Princeton, New Jersey.
McGovern, P.E., Fleming, S., Katz, S.H. (Eds.), 1996. The Origins and Ancient History of Wine. Gordon and Breach Publishers, Amsterdam.
McGovern, P.E., Glusker, D.L., Exner, L.J., Hall, G.R., 2008. The chemical identification of resinated wine and a fermented beverage in Bronze-Age pottery vessels of Greece. In: Tzedakis, Y., Martlew, H., Jones, M. (Eds.), Archaeology Meets Science: Biomolecular Investigation in Bronze Age Greece. Oxbow, Oxford, pp. 169–218.
Mcgovern, P.E., Glusker, D.L., Moreau, R.A., Nunez, A., Beck, C.W., Simpson, E., Butrym, E.D., Exner, L.J., Stout, E.C., 1999. A funerary feast fit for King Midas: a royal banquet has been reconstructed from residues in pots found inside the tomb. Nature 402, 863–864.
McGovern, P.E., Hall, G.R., 2015. Charting a future course for organic residue analysis in archaeology. J. Archaeol. Meth. Theor 22 (86), 1–31. https://doi.org/10.1007/s10816-015-9253-z.
McGovern, P.E., Hall, G.R., Mirzoian, A., 2013. A biomolecular archaeological approach to Nordic grog. Dan. J. Archaeol. 2 (2), 112–131.
McGovern, P.E., Underhill, A.P., Fang, H., Luan, F., Hall, G.R., Yu, H., Wang, C.-s., Cai, F., Zhao, Z., Feinman, G.M., 2005. Chemical identification and cultural implications of a mixed fermented beverage from Late Prehistoric China. Asian Perspect. 44, 249–275.
Michel, C., 2012. L'alimentation au Proche-Orient ancien: les sources et leur exploitation. Dialogues d'Histoire Ancienne 7, 17–45.
Michel, R.H., Mcgovern, P.E., Badler, V.R., 1993. The first wine & beer: chemical detection of ancient fermented beverages. Anal. Chem. 65 (8), 408–413.
Middleditch, B.S., 1989. Analytical Artifacts. Elsevier, New York and Amsterdam.
Müller-Karpe, V., 1999. Untersuchungen in Kuşaklı 1998. Mittl. Dtsch. Orient-Ges. 135, 57–113.
Müller-Karpe, V., 2006. Tempelinventare in Kuşaklı und Boğazköy im Vergleich: Ein Beitrag zur hethitischen Chronologie. In: Mielke, D.P., Schoop, U.-D., Seeher, J. (Eds.), Strukturierung und Datierung in der Hethitischen Archäologie, Byzas 4. Ege Yayınları, Istanbul, pp. 241–249.
Nollet, L.M.L., 2004. Handbook of Food Analysis: Physical Characterization. Marcel Dekker, New-York.
Nykänen, L., Suomalainen, H., 1983. Aroma of Beer, Wine and Distilled Alcoholic Beverages, Handbook of Aroma Research. Springer Science & Business Media, Berlin.
O'Connor, K., 2015. Mesopotamia: the pursuit of abundance. In: O'Connor, K. (Ed.), The Never-ending Feast: The Anthropology and Archaeology of Feasting. Bloomsbury Publishing, London, pp. 21–52.
Otto, A., 2012. Defining and transgressing the boundaries between ritual commensality and daily commensal practices: the case of Late Bronze Age Tall Bazi. eTopoi J. Ancient Stud. 2, 179–195.
Pecci, A., Giorgi, G., Salvini, L., Cau Ontiveros, M.A., 2013. Identifying wine markers in ceramics and plasters using gas chromatography-mass spectrometry: experimental and archaeological materials. J. Archaeol. Sci. 40, 109–115.
Potts, D.T., 1997. Mesopotamian Civilization: the Material Foundations. Cornell University Press, Ithaca, New York.
Rasmussen, S.C., 2014. The Quest for Aqua Vitae: the History and Chemistry of Alcohol from Antiquity to the Middle Ages. Springer, New York, pp. 29–48.
Regert, M., Colinart, S., Degrand, L., Decavallas, O., 2001. Chemical alteration and use of beeswax through time: accelerated ageing tests and analysis of archaeological samples from various environmental contexts. Archaeometry 43 (4), 549–569.
Roffet-Salque, M., Dunne, J., Altoft, D.T., Casanova, E., Cramp, L.J.E., Smyth, J., Whelton, H.L., Evershed, R.P., 2017. From the inside out: upscaling organic residue analyses of archaeological ceramics. J. Archaeol. Sci. Reports 16, 627–640. https://doi.org/10.1016/j.jasrep.2016.04.005.
Rothman, M.S., 2002. Tepe Gawra: the Evolution of a Small, Prehistoric Center in Northern Iraq. University of Pennsylvania, Museum of Archaeology and Anthropology, Philadelphia.
Rothman, M.S., Badler, V., 2011. Contact and development in Godin VI. In: Gopnik, H., Rothman, M. (Eds.), On the High Road: The History of Godin Tepe, Iran. Royal Ontario Museum and Mazda Press, Toronto, pp. 67–138.
Sallaberger, W., 2015. Home-made bread, municipal mutton, royal wine. Establishing social relations during the preparation and consumption of food in religious festivals at Late Bronze Age Emar. In: Pollock, S. (Ed.), Between Feasts and Daily Meals. Towards an Archaeology of Commensal Spaces. Edition Topoi, Berlin, pp. 181–204.
Samuel, D., 1993. Ancient Egyptian bread and beer: an interdisciplinary approach. In: Davies, W.V., Walker, R. (Eds.), Biological Anthropology and the Study of Ancient Egypt. British Museum Press, London, pp. 156–164.
Samuel, D., 1996. Archaeology of ancient Egyptian beer. J. Am. Soc. Brew. Chem. 54, 3–11.
Scurlock, J.A., 2014. Sourcebook for Ancient Mesopotamian Medicine. Writings from the Ancient World. Society of Biblical Literature, Atlanta.
Soberl, L., Horvat, M., Gasparic, A.Z., Sraka, M., Evershed, R.P., Budja, M., 2014. Neolithic and Eneolithic activities inferred from organic residue analysis of pottery from Mala Triglavca, Moverna vas and Ajdovska jama, Slovenia. Doc. Praehist. 41, 149–179. https://doi.org/10.4312/dp.41.9.
Steele, V., 2013. Organic residues in archaeology – the highs and lows of recent research. In: Armitage, R.A., Burton, J. (Eds.), Archaeological Chemistry VIII. American Chemical Society, pp. 89–108.
Sternitzke, K., 2017. Bestattungen in der Kassiten- und Isin II-Zeit. In: Sternitzke, K., Bartelmus, A., Roaf, M. (Eds.), Karduniaš: Babylonien in der Kassitenzeit. The Proceedings of the Symposium held in Munich 30 June to 2 July 2011, vol. 1. De Gruyter, Berlin, pp. 351–420.
Thornton, M.D., Morgan, E.D., Celoria, F., 1970. The composition of bog butter. Sci. Archaeol. 2/3, 20–25.
Thrane, H., 1999. Pots and peoples - once again. The goblets from the Bronze Age settlement at Tepe Guran, Lurestan. Iran. Antiq. 34, 21–40.
Trautvetter, S., Koelling-Speer, I., Speer, K., 2009. Confirmation of phenolic acids and flavonoids in honeys by UPLC-MS. Apidologie 40 (2), 140–150 Springer Verlag.
Woolley, C.L., 1934. The Royal Cemetery, vol. II British Museum, London.