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ORGANIC RESIDUES PRESERVED IN ARCHAEOLOGICAL CERAMICS FROM THE EARLY BRONZE AGE SITE OF KHIRBET AL-BATRAWY IN NORTH-CENTRAL JORDAN

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ABSTRACT

Twenty one ceramic shreds, from the Early Bronze Age fortified town of Khirbet Al-Batrawy in Jordan, with known archaeological contexts, were tested concerning the preservation of organic residues using gas chromatography – mass spectrometry (GC-MS) technique. Conventional solvent extraction and alkaline hydrolysis (saponification) were used for the extraction of residues preserved in their fabric. Five of these shreds showed significant preservation of lipid constituents, mainly free fatty acids. The preliminary results of this research provide data on the possible use of plant oil in these vessels and resinous material probably to seal the internal surfaces of the vessels. These results are in conjunction with the archaeological evidence on the availability and use of plant oil in this region, which contribute to the understanding of the usage of ceramic vessels at the site during the Early Bronze Age.

KEYWORDS: Lipids, Fatty acids, ceramic sherds, Gas chromatography – mass spectrometry, Early Bronze Age, Khirbet Al-Batrawy

INTRODUCTION

Chemical analysis of organic residues preserved in ancient ceramic vessels provides useful cultural information on ancient societies. The use of natural materials in unglazed ceramic vessels can result in penetration of organic constituents into the pores of these vessels. These constituents are usually present as complex mixture of organic molecules and can be preserved for long periods of time inside these pores under favorable conditions (Evershed *et al*. 2001: 331-336; Evershed 2008). They can be extracted using organic solvents and then separated, characterized and identified using the common analytical organic chemical technique of gas chromatography – mass spectrometry (GC-MS). This in turn can provide information on ancient materials stored and/or used in these vessels, therefore, on the potential function or usage of these vessels (Heron *et al.* 1991; van Bergen *et al.* 1997; Dudd *et al.* 1999; Regert *et al.* 2001; Stern *et al.* 2003; Evershed 2008; Gregg *et al.* 2009; Baeten *et al.* 2010; Isaksson and Hallgren 2012). This paper presents, for the first time in Jordan, results obtained from the analysis of organic residues preserved in archaeological ceramic vessels excavated at the site of Khirbet Al-Batrawy, an Early Bronze Age (EBA) fortified town (3rd millennium B.C.) in North-Central Jordan. These vessels, however are expected to have had been treated and used in the past for different purposes including storing and transporting natural materials, such as plant oils.

ARCHAEOLOGICAL BACKGROUND

The EBA in Jordan was a period of significant changes in technology, architecture, production of ceramics, arts, social and burial practices. Many EBA sites have been found in Wadi al-Zarqa region (Palumbo *et al.* 1996; Douglas 2006). Very few of these sites have been excavated like Khirbet Al-Batrawy (Nigro 2006 and 2008). The site is located in the northwestern part of the modern city al-Zarqa in North-Central Jordan. It is lying in a prominent geographical location on the northern edge of Wadi al-Zarqa at a strategic spot of the ancient road network. It represents a fortified city built first during the Early Bronze Age II (EBA-II, 3000-2750 B.C.) and flourished in the Early Bronze Age III (EBA-III, 2750-2250 B.C.). At the end of this phase the city was totally destroyed and abandoned. During the Early Bronze Age IV (EBA-IV, 2250-2000 BC) the site was reoccupied as an open village by a nomadic group. Although it is small in size (ca. 4 ha), the city was protected intensively with successive walls, mainly around its main gate.

Between 2005 and 2011 several archaeological excavations were conducted at the site[1] (Nigro 2006, 2008 and 2010). During the second season (2006) ceramic samples were collected from area (D), which is located at the southwestern corner of the site (Douglas and Nigro 2008, Figure 5.1).

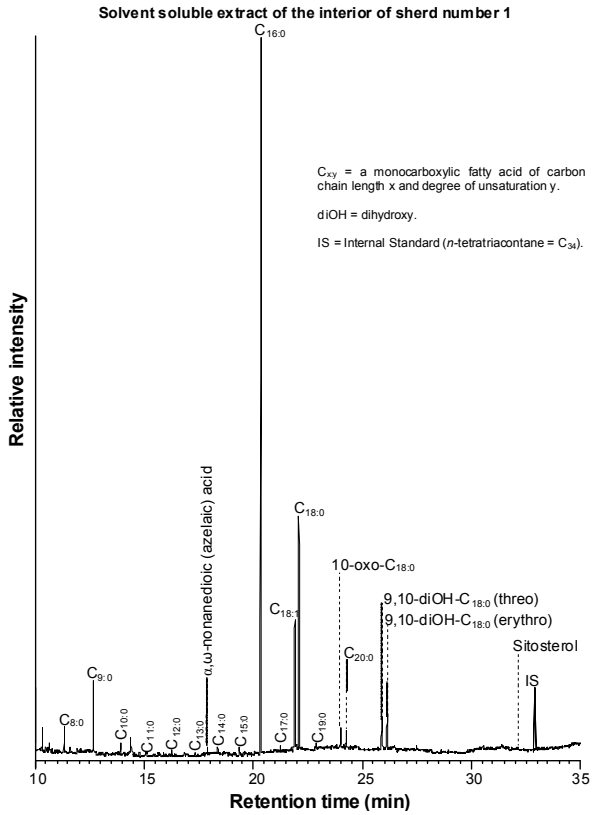

Figure 1. Partial (10-35 min) total-ion-chromatogram (TIC) of the trimethylsilylated total free lipid extract of the absorbed residue from the interior of sherd number 1. ($C_{x:y}$): monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y, (diOH): dihydroxy, and (IS): internal standard (*n*-tetratriacontane = C_{34}).

[1] The first two seasons 2005-2006 excavations were carried out jointly between the Hashemite University represented by Khaled Douglas and La Sapianza/Rome University represented by Lorenzo Nigro and the Department of Antiquities of Jordan. 2007-2011 excavations continued without the Hashemite University.

This area was used at the beginning (EBA-II / EBA-III) for fortification purposes where a huge round tower and a gate system was built. In the EBAIV its function was changed to domestic purposes. Excavations at area (D) however, yielded large variety of ceramic types from both periods (EBAIII and EBAIV) which indicate their domestic use. They included cooking, storage, simple, coarse and fine wares. Samples representing different types of ceramic vessels were chosen for this study.

This study however, focuses on analysing organic residues preserved in the fabric of ceramic vessels excavated at the site in order to obtain data concerning the function and use of these vessels. The study comes with the need to increase the knowledge concerning the urban development during the EBA in Jordan. Further similar and related studies focusing on different archaeological sites from different periods in Wadi al-Zarqa region will be following to this preliminary study. As a result data on the interaction of ancient societies with their environment and consequently on the dietary and socio-economic system in this region will be anticipated.

RESEARCH METHODOLOGY

Materials and sampling

All solvents and reagents used in this research were ultrapure or HPLC grade. *n*-tetratriacontane (C_{34}) was used as internal standard and N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) present in 1% v/v trimethylchlorosilane (TMCS) was used as derivatising agent.

Twenty one archaeological ceramic sherds (Table 1) and soil samples adhering onto their surfaces, and one modern ceramic sherd used as a control sample, were sampled and analysed. Two powdered ceramic samples were separately taken from each sherd using a *Dremel* electric drill fitted with a tungsten abrasive bit. The first sample was taken from the interior (between the internal surface and the core) while the second sample was taken from the exterior (between the external surface and the core) of the sherd. Each sample was taken after having scraping and collecting the soil adhering onto the surface using a scalpel blade and after having smoothly cleaned the outer surface from the remaining traces of adhering soil and other deposits, using the electric drill, to avoid contamination. Adhering soil samples were finely ground, sampled and treated similarly alongside the powdered ceramic samples. About 0.1 g of each powder/ground soil was transferred into clean glass vial and extracted three times.

Each time 1 mL mixture of dichloromethane/methanol (DCM/MeOH) solution (2:1 v/v) was added to the powder, ultrasonicated for 5 minutes and centrifuged (2000 rpm × 5 min), and then the supernatant was transferred into a small clean glass vial. The three supernatants from the successive extractions were combined in the glass vial and the solvent was evaporated under a stream of nitrogen gas and mild heat. The residues were left overnight in a vacuum desiccator and then were derivatised by adding BSTFA and leaving the solution in a tightly closed vial for 24 hours at room temperature.

The ceramic residue remained after solvent extraction was dried under a nitrogen gas flow, and then was saponified with 5 ml of 1M methanolic sodium hydroxide (NaOH in MeOH) solution for 3 hours at 70 °C in a water bath. After cooling, the saponified mixture was centrifuged (2000 r.p.m × 5 min). The liquid phase were separated and acidified with 6M hydrochloric acid (HCl) and the liberated lipid components were then extracted three times with *n*-hexane (3 × 5 mL).

The *n*-hexane extracts were combined and the solvent was evaporated under a stream of nitrogen gas and mild heat. The residues were left overnight in a vacuum desiccator. Trimethylsilylation was then performed as described above. Alkaline hydrolysis (saponification) was applied to all ceramic residues remained after solvent extraction of the interiors and exteriors of sherds numbered from 1 to 5 and to soil samples adhering onto the internal surfaces of these five sherds.

The Analytical Technique of GC-MS

Gas chromatography – mass spectrometry (GC-MS) analysis was carried out using Varian 450-GC Gas Chromatograph connected to Varian 320-MS TQ Mass Spectrometer available at

the Princess Haya Biotechnology Center (PHBC) at Jordan University of Science and Technology (JUST), Jordan. The results were confirmed with Agilent 6890N-GC 5975B-MS available at the department of Geology at the University of Mainz, Germany. The GC was equipped with a split/splitless injector. Splitless mode was used. Helium was the carrier gas, with a constant head pressure of 1 psi and a flow rate of 1 ml/min at 50 °C. The injector of the GC and the interface of MS were maintained at 300 °C and 340 °C, respectively.

The temperature of the oven was programmed from 50 °C (2 min isothermal) to 300 °C (30 min isothermal) at a rate of 10 °C/min. HP-5MS fused silica capillary column of 30m length and 0.25mm internal diameter (i.d) coated with a stationary phase film of 0.25μm thickness was used. The column was directly inserted into the ion source. Electron impact (EI) spectra were obtained at 70 eV with full scan from *m*/*z* 50 to 700 amu in the mass spectrometer (MS). Because there were no GC signals in the range of 35 – 52 min retention time in the analysed samples gas chromatograms shown in this paper were displayed in the range of 10 – 35 min retention time in order to expand the chromatogram for clear showing and marking of the identified peaks.

RESULTS AND DISCUSSION

The preservation of organic residues in the fabrics of the archaeological ceramic sherds (Table 1) and their related soil and the modern sherd was tested using gas chromatography – mass spectrometry (GC-MS). Organic extracts of these samples were obtained via conventional solvent extraction of the soluble fraction and alkaline hydrolysis (saponification) of the insoluble fraction of organic residues preserved in these sherds and soil. Among these sherds, only five (numbered with 1, 2, 3, 4 and 5 in Table 1) showed a significant preservation of organic residues compared with the others.

Table 1. General description of the twenty one ceramic sherds tested in this study.

Sherd number	*Sherd code*	*Square*	*Context*	*Part of the vessel analysed*	*Vessel description*	*Chronology*
1.	D624/2	Bh III 14	Compact soil layer / Floor	Rim-neck	Large Pithos with flaring rim and thickened outside. Coarse ware, low fire. Inclusion: Limestone, few flints, red grits, slip outside and inside on the upper rim. Thick sherd.	EBA-III
2.	D626/4	Bj III 13	Plaster floor (L626)	Body	Almost complete medium jar with flaring rim and flat base. Applied rope decoration on the body. Self slip out side. Coarse ware, low fire. Inclusions: limestone, little flint, red grits. Sherd of medium thickness.	EBA-III
3.	D637/4	Bk III 13	Surface floor	Upper body	Medium holemouth jar, cooking pot, coarse ware, low fire, inclusions: flits, quartz, black grits. Thick sherd.	EBA-III
4.	D628/3	Bk III 13	Floor / NW of the city wall	Painted body	Small jar, everted rim, red painted strep outside, coarse ware, medium fire. Inclusions: limestone, red grits. Thick sherd.	EBA-III
5.	D619 + 620/1b	Bi III 14	Soil layer / Fallen stone layer	Upper body	Medium size jar with evetred rim, coarse ware, low fire, yellowish slip outside. Inclusions: basalt, limestone. Small complete jar	EBA-IV

					without base. Thin sherd	
6.	D.600/6	Bj III 13	Floor	Flat base	Medium jar, coarse ware. Inclusions: limestone, flints, red grits, reddish lip outside. Thin sherd.	EBAIII
7.	D.600/13	Bj III 13	Floor	Body	Small Jug, coarse ware, low fire. Inclusions: limestone, flints red burnished slip outside. Thin sherd.	EBAIII
8.	D.608/5	Bi III 13	Compact soil layer	Upper body	Medium holemouth jar, groove on the rim, cooking pot, coarse ware, low fire. Inclusions: flits, quartz, black grits. Thick sherd.	EBAIII
9.	D.622/2	Bi III 14	Wall	Body	Large jar, combed surface, coarse ware. Inclusions: limestone, red grits. Thin sherd.	EBAIII
10.	D.623/1	Bj III 14	Fallen stone layer	Rim	Flaring rim medium jar, coarse ware. Inclusion: limestone, red grits. Thick sherd.	EBAIII
11.	D.623/3	Bj III 14	Fallen stone layer	Flat base	Small Jug, coarse ware, low fire, inclusions: limestone, red grits, self slip outside. Thick sherd.	EBAIII
12.	D.627/1	Bj III 13	Filling layer	Body sherd connected to enveloped ledge handle	Medium jar with enveloped ledge handle, coarse ware, low fire, inclusions: basalt, limestone, flints. Sherd of medium thickness.	EBAIV
13.	D.630/2	Bh III 13	City wall	Body	Medium jar, coarse ware, low fire. Inclusions: limestone, red grits. Sherd of medium thickness.	EBAIII
14.	D.633/4	Bk III 13	Loose soil layer	Body sherd connected to pushed up ledge handle	Large jar with pushed up ledge handle, coarse ware, low fire. Inclusions: limestone, red grits, slip outside. Thick sherd.	EBAIII
15.	D.633/5	Bk III 13	Destruction layer	Body	Small jar, holemouth jar, everted rim, coarse ware, low fire. Inclusions: flints, limestone. Painted vertical lines on the rim and the body. Thin sherd.	EBAIII
16.	D.642/1	Bk III 13	Floor	Body	Medium jar, coarse ware, low fire. Inclusions: limestone, red grits. Knop handle on the surface. Thick sherd.	EBAIII
17.	D.642/7	Bk III 13	Floor	Upper body	Medium holemouth jar, cooking pot, coarse ware, low fire. Inclusions: flits, quartz. Thick sherd.	EBAIII
18.	D.O/2	Bi III 14	Top surface*	Body	Medium jar, flaring rim and vertical neck, flat bas. Coarse ware. Inclusions: basalt, red grits, limestone. Thick sherd.	EBAIII
19.	D.O/4	Bh III 13	Top surface*	Body	Large storage jar, coarse ware, low fire. Inclusions: limestone, red grits. Robe decoration outside. Sherd of medium thickness.	EBAIII
20.	D.O/1a	Bh III 13	Top surface*	Upper body	Medium holemouth jar, cooking pot, coarse ware, low fire. Inclusions: flits, quartz, black grits.	EBAIII

21.	D.O/1b	Bh III 13	Top surface*	Flat base	Thin sherd. Medium jar, coarse ware, low fire. Inclusions: limestone, red grits, self slip outside. Thin sherd.	EBAIII

* This almost complete jar that was found directly under the top surface layer.

GC-MS analysis of the conventional solvent extracts and saponified extracts of the five sherds showed the presence of different classes of organic compounds, most of them being free *n*-alkanoic fatty acids. dioic-, oxo-, hydroxy-, dihydroxy-, abietic, dehydroabietic (DHA), dehydro-7-DHA, 7-oxo-DHA, pimaric and isopimaric acids in addition to sitosterol, campesterol and other minor constituents were also detecte. No acylglycerides were detected in these extracts.

Squalene and cholesterol were also not detected in these extracts or in the extract of the modern ceramic sherd which exclude contamination from handling. It is worth noting that organic constituents obtained via conventional solvent extraction of the five sherds are almost identical. The same is true in case of the saponified extracts. Organic compounds detected in the five sherds and their related soil samples however, are discussed herein.

Organic extracts of the interiors

Organic residues preserved in the interiors (see research methodology) of the five sherds are characterized by preserving high amounts of fatty acids that could have originated from similar natural materials. The only distinction is that solvent extraction of the interiors of sherds 3, 4 or 5 retrieved only $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids and with prominent abundance of $C_{18:1}$ (Fig. 5) compared to the interiors of sherds 1 and 2 (Figs. 1 and 2).

Organic compounds obtained from the interiors of sherds 1 and 2 via simple extraction are saturated $C_{8:0}$ – $C_{20:0}$, monounsaturated $C_{18:1}$ (oleic), α,ω-nonanedioic (azelaic), α,ω-octanedioic (suberic), 10-oxo-octadecanoic (10-oxo-$C_{18:0}$), tentatively identified α,ω-octadecanedioic, and the two isomers, *threo* and *erythro*, of the 9,10-dihydroxyoctadecanoic (9,10-diOH-$C_{18:0}$) acids, in addition to the major plant sterol, sitosterol (Figs. 1 and 2, and Table 2). $C_{x:y}$ is a monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y. The most abundant principal compounds in these extracts, however, are palmitic ($C_{16:0}$), stearic ($C_{18:0}$) and oleic ($C_{18:1}$) fatty acids (Figs. 3 and 4).

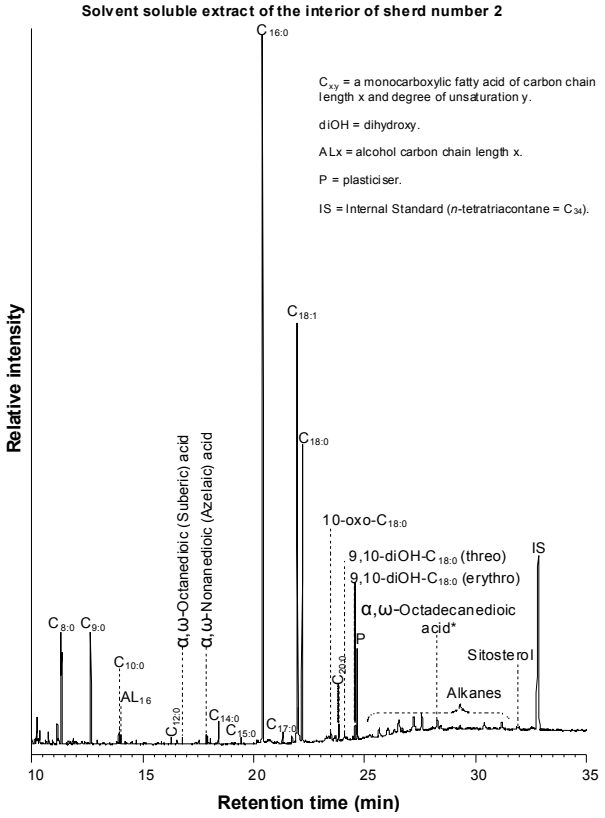

Figure 2. Partial (10-35 min) total-ion-chromatogram (TIC) of the trimethylsilylated total free lipid extract of the absorbed residue from the interior of sherd number 2. ($C_{x:y}$): monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y, (diOH): dihydroxy, (AL_x) alcohol carbon chain length x, (P): plasticiser, and (IS) internal standard (*n*-tetratriacontane = C_{34}), and (*): tentatively identified.

Table 2. Organic constituents retrieved via simple extraction and alkaline hydrolysis from the interiors of the five ceramic sherds numbered from 1 to 5.

Sherd number	*Sherd Code*	*Organic constituents* obtained via simple extraction of the interiors***					
		Fatty acids	Dioic acids	Oxo-acids	Hydroxy acids	Sterols	*n*-alkanes
		(TMS)	**(TMS)**	**(TMS)**	**(TMS)**	**(TMS)**	**(Neutrals)**
1	D624/2	$C_{8:0}$ $C_{9:0}$ $C_{10:0}$ $C_{11:0}$ $C_{12:0}$ $C_{13:0}$ $C_{14:0}$ $C_{15:0}$ **$C_{16:0}$** $C_{17:0}$ **$C_{18:0}$** **$C_{18:1}$** $C_{19:0}$ $C_{20:0}$	α,ω-nonanedioic (azelaic)	10-oxo-octadecanoic	*threo* and *erythro* of 9,10-dihydroxyoctadecanoic	Sitosterol	X
2	D626/4	$C_{8:0}$ $C_{9:0}$ $C_{10:0}$ $C_{11:0}$ $C_{12:0}$ $C_{13:0}$ $C_{14:0}$ $C_{15:0}$ **$C_{16:0}$** $C_{17:0}$ **$C_{18:0}$** **$C_{18:1}$** $C_{19:0}$ $C_{20:0}$	α,ω-octanedioic (suberic) α,ω-nonanedioic (azelaic) α,ω-octadecane dioic	10-oxo-octadecanoic acid	*threo* and *erythro* of 9,10-dihydroxyoctadecanoic	Sitosterol	Un-identified
3	D637/4	**$C_{16:0}$** **$C_{18:0}$** **$C_{18:1}$**	X	X	X	X	X
4	D628/3	**$C_{18:0}$** **$C_{18:1}$**	X	X	X	X	X
5	D619 + 620/1b	**$C_{16:0}$** **$C_{18:0}$** **$C_{18:1}$**	X	X	X	X	X

Organic constituents obtained via alkaline hydrolysis of the interiors***							
Fatty acids		Diterpenoic acids		Dioic acids	Hydroxy acids	Sterols	*n*-alkanes
(TMS)	**(Me)**	**(TMS)**	**(Me)**	**(Me)**	**(Me)**	**(TMS)**	**(Neutrals)**
$C_{9:0}$	$C_{9:0}$	DHA	DHA	α,ω-hexanedioic	12-	Campesterol	C_8
$C_{16:0}$	**$C_{16:0}$**			(adipic)	hydroxyoctadecanoic		C_9
$C_{18:0}$	**$C_{18:0}$**	Dehydro-7-					C_{12}
$C_{18:1}$	**$C_{18:1}$**	DHA					C_{13}
(2 isomers)	(2 isomers)						C_{24}
		Pimaric					C_{25}
	$C_{24:0}$						C_{26}
	$C_{26:0}$	Isopimaric					C_{27}
							C_{28}
		7-oxo-DHA					C_{29}
							C_{30}
							C_{31}
							C_{32}
							C_{33}
						Campesterol	C_8
$C_{9:0}$		DHA	DHA	α,ω-hexanedioic	12-		C_9
$C_{10:0}$				(adipic)	hydroxyoctadecanoic		C_{12}
$C_{12:0}$		Dehydro-7-					C_{13}
$C_{14:0}$		DHA					C_{24}
$C_{16:0}$	**$C_{16:0}$**						C_{25}
$C_{18:0}$	**$C_{18:0}$**	Pimaric					C_{26}
$C_{18:1}$	**$C_{18:1}$**						C_{27}
(2 isomers)	(2 isomers)	Isopimaric					C_{28}
							C_{29}
	$C_{24:0}$	7-oxo-DHA					C_{30}
	$C_{26:0}$						C_{31}
							C_{32}
							C_{33}
$C_{9:0}$		DHA	X	α,ω-hexanedioic	X		C_{24}
$C_{10:0}$				(adipic)			C_{25}
$C_{12:0}$		Isopimaric					C_{26}
$C_{14:0}$							C_{27}
$C_{16:0}$	**$C_{16:0}$,**						C_{28}
$C_{18:0}$	**$C_{18:0}$, $C_{18:1}$**						C_{29}
$C_{18:1}$							C_{30}
	$C_{24:0}$						C_{31}
	$C_{26:0}$						C_{32}
							C_{33}
$C_{9:0}$		DHA	X	X	X		C_{24}
$C_{10:0}$							C_{25}
$C_{14:0}$		Isopimaric					C_{26}
$C_{16:0}$							C_{27}
$C_{18:0}$							C_{28}
$C_{18:1}$							C_{29}
							C_{30}
	$C_{24:0}$						C_{31}
	$C_{26:0}$						C_{32}
							C_{33}

$C_{9:0}$		DHA	X	X	X	C_{24}
$C_{10:0}$						C_{25}
$C_{12:0}$		Isopimaric				C_{26}
$C_{14:0}$						C_{27}
$C_{16:0}$	**$C_{16:0}$**					C_{28}
$C_{18:0}$	**$C_{18:0}$**					C_{29}
$C_{18:1}$	**$C_{18:1}$**					C_{30}
						C_{31}
	$C_{24:0}$					C_{32}
	$C_{26:0}$					C_{33}

TMS = Trimethylsilylated derivative, Me = Methylated derivative, DHA = Dehydroabietic acid, $C_{x:y}$ = monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y, C_x = *n*-alkane of carbon chain length x, * = Retention time is shown in figures 1 and 6, ** = Exteriors lack to constituents, and X = Nothing.

$C_{16:0}$ and $C_{18:0}$ are ubiquitous and abundant in plant oils and animal fats (Dudd and Evershed 1998). $C_{18:1}$ is the most common monounsaturated fatty acid and is present in most plant and animal lipids as it is the most widely distributed of all the natural fatty acids (Dey and Harborne 1997: 238; Copley *et al.* 2005a; Gunstone *et al.* 2007: 4). Very small proportions of $C_{18:0}$ and higher contents of $C_{18:1}$ are present in vegetable oils (Kimpe *et al.* 2004).

The presence of α,ω-nonanedioic and 10-oxo-octadecanoic acids in addition to the two isomers, *threo* and *erythro*, of the 9,10-dihydroxyoctadecanoic acid in the two lipid extracts is attributed to the oxidation process of the unsaturated moieties of fatty acids (Evershed *et al.* 1999; Reber and Evershed 2004a and 2004b; Colombini *et al.* 2005; Copley *et al.* 2005b; Boran *et al.* 2006; Spangenberg *et al.* 2006). These Dioic-, oxo- and hydroxy- acids most probably have originated via oxidation of the C=C double bond between the two carbons (numbered 9 and 10) of the $C_{18:1}$ fatty acid present in the original lipid. The variation of the concentration of $C_{18:1}$ compared to that of $C_{16:0}$ and $C_{18:0}$ and the higher concentration of $C_{9:0}$ compared to these of the short chain fatty acids ($C_{8:0}$ – $C_{15:0}$) in the two extracts of sherds 1 and 2 (Figs. 3 and 4) can be attributed to the oxidation degree of $C_{18:1}$ into these oxidative products and into $C_{9:0}$ during burial (Shimoyama *et al.* 1995).

However, the oxidation has not yet been completed. Therefore, the occurrence of $C_{9:0}$, $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, dioic-, oxo- and hydroxy- acids in the lipid extracts of the interiors of sherds 1 and 2 may suggest a plant origin of these residues, possibly plant oil. The major plant sterol, sitosterol, detected in the two sherds supports the plant origin of the residues. These results can be compared and supported with the results obtained by Copley *et al.* 2005a; Colombini *et al.* 2005 and 2009; Ribechini *et al.* 2009 and Giorgi *et al.* 2010.

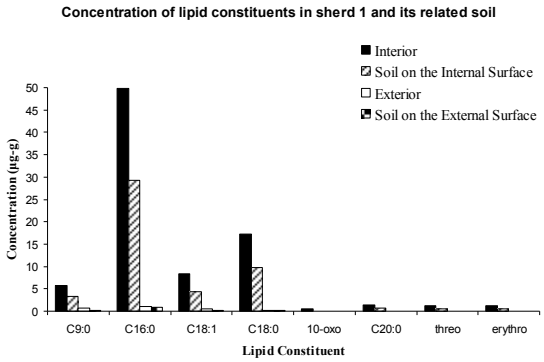

Figure 3. A comparison showing the relative concentration of main lipid constituents obtained via solvent extraction from sherd number 1 and its related soil. ($C_{x:y}$): monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y, and (*threo* and *erythro*): two isomers of the 9,10-dihydroxyoctadecanoic.

Threo and *erythro* isomers were observed in the replica olive and seed oil lamps upon burning (Regert *et al.* 1998). Similar profiles of fatty acids and oxidation products were also obtained from ceramic vessels tested by Knappett *et al.* (2005) and Giorgi *et al.* (2010). Their investigations suggest that the lipid profiles of the residues obtained from these vessels have originated from plant materials, possibly plant oil. Although the high concentration of $C_{16:0}$ and $C_{18:0}$ compared to that of $C_{18:1}$ in the residue of

sherd 1 (Fig. 3) could be attributed to animal fat input the lower concentration of $C_{18:1}$ could have resulted from the oxidation of this fatty acid during burial, leading to the decrease in its concentration and increase in the concentrations of the oxidation products, such as $C_{9:0}$. It is known that $C_{12:0}$ and $C_{14:0}$ are major short-chain fatty acids in fresh animal milk (Copley *et al.* 2003), but in sherd 1 the shorter fatty acid, $C_{9:0}$, which is more vulnerable to degradation, is present with abundance higher than that of $C_{12:0}$ and $C_{14:0}$. This may confirm the decrease of the concentration of $C_{18:1}$ and increase in the concentration of $C_{9:0}$ as a result of oxidation during burial. However, animal fat as a source of this residue can not be absolutely excluded.

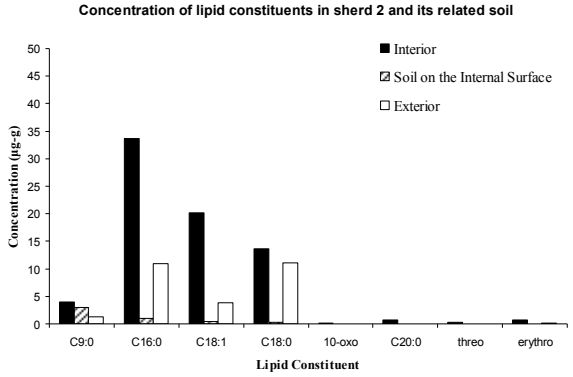

Figure 4. A comparison showing the relative concentration of main lipid constituents obtained via solvent extraction from sherd number 2 and its related soil. ($C_{x:y}$) monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y, and (*threo* and *erythro*): two isomers of the 9,10-dihydroxyoctadecanoic.

Plant origin, however, could also be supported with the higher content of $C_{18:1}$ fatty acid compared to the contents of $C_{16:0}$ and $C_{18:0}$ in the extract of sherds 3, 4 and 5 (Fig. 5). The phthalate plasticizers (P) with m/z 149 are modern contaminants resulting from plastic bags used for storing the ceramic sherds.

Organic extracts of the exteriors

The exteriors (see research methodology) of sherds 1 and 2 preserve only $C_{9:0}$, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids but with lower concentrations compared with their counterparts present in the interiors (Figs. 3 and 4). This can be attributed to that lipid constituents had permeated from the interior of the sherd toward the exterior during usage and burial. No lipid constituents where retrieved from the exteriors of sherds 3, 4 and 5, except $C_{18:1}$ with low abundance.

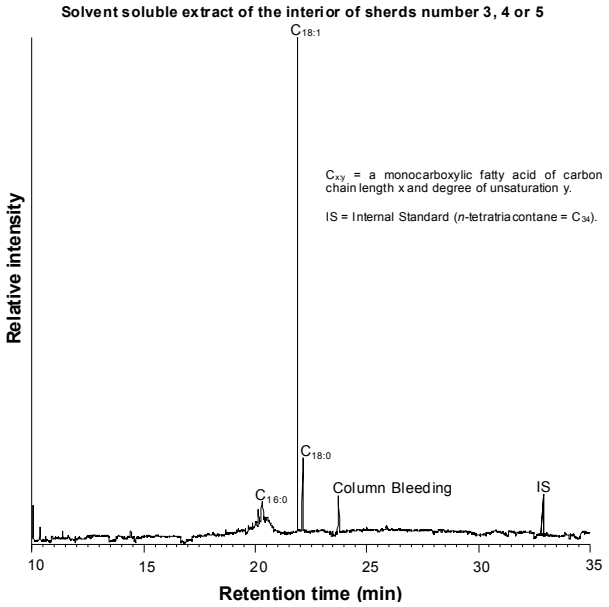

Figure 5. Partial (10-35 min) total-ion-chromatogram (TIC) of the trimethylsilylated total free lipid extract of the absorbed residue from the interior of sherds number 3, 4 or 5. (Cx:y): monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y and (IS): internal standard (n-tetratriacontane = C34).

Organic extracts of the adhering soil

The possible contamination from soil can be excluded and the migration of lipid residue from the interiors of ceramic sherds 1 and 2 to the attached soil on their surfaces can be proved. Soil sample adhering onto the internal surface of sherd 1 preserves $C_{9:0}$, $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$, $C_{18:1}$ and $C_{20:0}$ fatty acids in addition to the azelaic acid, while that adhering onto the external surface of the same sherd preserves only $C_{9:0}$, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids. On the other hand, soil sample adhering onto the internal surface of sherd 2 preserves only $C_{9:0}$, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ fatty acids, while that adhering onto the external surface of the same sherd has no lipid constituents. However, the concentrations of the significant lipid constituents detected in soil extracts were compared with those detected in the lipid extracts of the interior and exterior of each sherd (Figs. 3 and 4). The comparison clearly

shows that concentrations of the lipid constituents preserved in the interior of each sherd are higher than those preserved in the exterior or in the soil adhering onto the internal or external surface of that sherd. This demonstrates that lipid constituents were originally present in the ceramic fabric of the sherd, mainly in the interior, and after that, they had permeated toward the external surface during usage and burial and even to the soil attached to both surfaces during burial. No lipid constituents were detected in the soil adhering onto the external surfaces of sherds 3, 4 and 5. The only constituent detected in the soil adhering onto the interiors of these sherds is $C_{18:1}$ and with low abundance, and this supports the fact of the lipid permeation which was demonstrated above.

Organic extracts of the alkaline hydrolysis

This method is able to retrieve organic constituents that are weakly bound to the ceramic matrix or to the insoluble organic moiety. It provides further data on the residues preserved in the fabric of ceramic sherds. GC-MS analysis of the insoluble residue obtained via alkaline treatment from sherds number 1 and 2 revealed the preservation of other profiles of lipid constituents (Fig. 6). $C_{9:0}$, $C_{16:0}$, $C_{18:0}$ and two isomers of $C_{18:1}$ fatty acids, campesterol and diterpenoic acids, including abietic, dehydroabietic (DHA), dehydro-7-DHA, 7-oxo-DHA with very low abundance, pimaric and isopimaric acids, were retrieved as trimethylsilylated (TMS) derivatives. Moreover, $C_{16:0}$, $C_{18:0}$, two isomers of $C_{18:1}$, 12-hydroxyoctadecanoic (12-OH-$C_{18:0}$), α,ω-hexanedioic (adipic) and DHA acids, in addition to the tentatively identified $C_{24:0}$ and $C_{26:0}$ acids were retrieved as methyl esters using this method. Retrieving these acids as methyl esters could be attributed to the rather over-vigorous saponification that has caused transmethylation within the sample. The occurrence of these acids and the plant sterol, campesterol, in this extract may imply the plant origin of the lipid residue. On the other hand, the high abundance of $C_{16:0}$ and $C_{18:0}$ compared with $C_{18:1}$ (present in two isomers) could be attributed to animal fat. The vessel could have had a prior use for animal fat, such as milk or its derivatives. Therefore, animal fat as a source of this residue cannot be absolutely excluded. However, plant origin could be supported with the occurrence of the plant sterol, campesterol, and with the results obtained in the solvent extracts, which were discussed above.

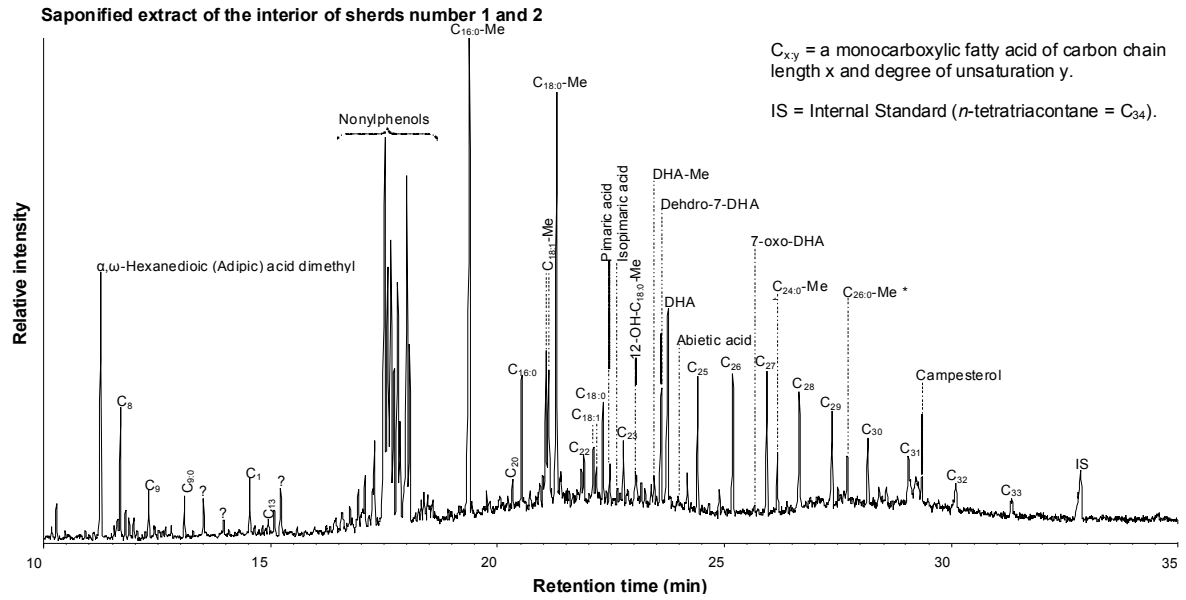

Figure 6. Partial (10-35 min) total-ion-chromatogram (TIC) of the trimethylsilylated total lipid extract of the alkaline hydrolysed insoluble fraction of organic residues preserved in the interior of sherds number 1 and 2. (C_x): *n*-alkane of carbon chain length x, (OH): hydroxy group, ($C_{x:y}$): monocarboxylic fatty acid of carbon chain length x and degree of unsaturation y, ($C_{x:y}$-Me): methylated fatty acid, (DHA): dehydroabietic acid, (DHA-Me): methylated dehydroabietic acid, (IS): the internal standard (*n*-tetratriacontane = C_{34}), (?): unknown, and (*): tentatively identified.

Long chain fatty acids including $C_{24:0}$ and $C_{26:0}$ are present in plant/seeds oils (Stern *et al.* 2000; Puah *et al*. 2006; Romanus et al. 2007; Řezanka and Sigler 2007 and 2009). They are also present in plant wax esters and beeswax (Garnier *et al.* 2002; Regert 2004). A wide range of fatty acids ($C_{8:0}$ – $C_{26:0}$) were detected by Shimoyama *et al.* (1995) in archaeological lamp residue that is expected to have originated from olive oil. Adipic acid could be contaminant as it is used extensively in the manufacturing of many modern materials including plastics.

The two diterpenoids, abietanoic and DHA acids belong to the abietane skeletal group. DHA could produce from the oxidation of abietane and pimarane diterpenoids (Eerkens 2002). It is known as a coniferous biomarker and a specific pine resin signal (Regert *et al.* 2003; Reber and Hart 2008; Giorgi *et al.* 2010). In addition to DHA, the occurrence of dehydro-7-DHA and 7-oxo-DHA acids are interpreted as degradation products of abietic acid, the major constituent of the fresh pine resin (Regert and Rolando 2002; Otto *et al.* 2003; Regert *et al.* 2006; Pollard and Heron 2008: 242; Reber and Hart 2008; Colombini and Modugno 2009: 15).

The low abundance of abietic acid and the high abundances of DHA and dehydro-7-DHA acids are attributed to the oxidative dehydrogenation of abietic acid (Otto *et al.* 2002 and 2003). This oxidation however, could be attributed to anthropogenic heating of the resinous material to an extent that is not high enough to produce pitch (Garnier *et al.* 2003; Reber and Hart 2008), and/or to ageing of the resinous material (Stern *et al.* 2003 and 2008; Assimopoulou and Papageorgiou 2005; Burger *et al.* 2009).

The two diterpenoids, pimaric and isopimaric acids belong to the pimarane skeletal groups and present in pine resin (Eerkens 2002; Regert 2004; Reber and Hart 2008). Isopimaric acid was detected with very low abundance in this extract providing mean that the resin is relatively well preserved. The occurrence of these diterpenes in the saponified extract is attributed to the possible use of resinous material in these ceramic vessels, possibly pine resin. Data obtained from this extract can be compared and supported with the results obtained by Colombini *et al.* 2005 and 2009; Ribechini *et al.* 2009 and Giorgi *et al.* 2010. Solvent and saponified extracts of the soil adhering onto the internal surfaces of sherds 1 and 2 do not contain any resinous biomarkers. Also, ceramic sherds were stored in plastic bags and were not exposed to any material made of wood. Therefore, the occurrence of these diterpenoic acids in the saponified extracts of the interiors of sherds 1 and 2 may confirms the higher plant origin of the residues and excludes contamination from burial environment and laboratory.

The odd and even-numbered *n*-alkanes with chain lengths in the range of C_{19} – C_{33} (Fig. 7) are contaminants. They could have introduced to the samples during laboratory preparations.

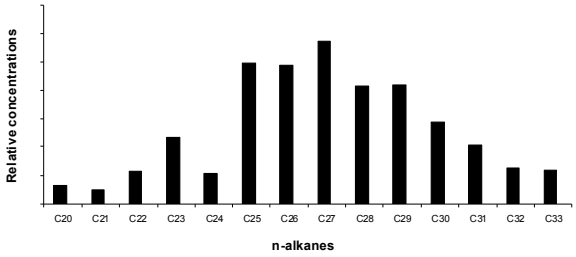

Figure 7. A comparison showing the relative concentration of odd and even *n*-alkanes obtained via alkaline hydrolysis of the insoluble fraction of organic residues preserved in the interior of sherd number 1. (C_x): *n*-alkane of carbon chain length x.

Nonylphenols within the retention time range of 16 – 19 min (Fig. 3) are also contaminants. They come from many modern materials including detergents and insecticides. They could also have introduced into the samples during laboratory preparations. Although these two components did not appear in the saponified extract of the modern ceramic sherd used as a control sample in this research project they have recently appeared in two saponified extracts, one of a blank and the other of modern ceramic sherd used as a control sample in a research project applied by us on ceramic samples from another site. This result however, confirms that contamination with *n*-alkanes and nonylphenols was picked up in the laboratory. The occurrence of the resin markers, fatty acids including hydroxy- acids mentioned above in the alkaline extract perhaps indicates that the vessels contain materials of animal and plant origin, including oil and resin.

Organic constituents obtained via alkaline hydrolysis of the insoluble residues of the interiors of sherds 3, 4 and 5 are shown in Table 2. These constituents are almost identical to those obtained from sherd 1 and 2 via alkaline hydrolysis. Alkaline hydrolysis of the insoluble residues of the soil adhering onto the internal surfaces of the five sherds numbered from 1 to 5, however did not retrieve organic constituents.

The results of organic residues, retrieved via conventional solvent extraction and alkaline hydrolysis show that two types of plant materials, oil and resin, were introduced into the interiors of five of the tested vessels. These five vessels however, could have been used for storing (vessel 1), storing and transporting (vessels 2, 4 and 5) and cooking/processing (vessel 3). It is commonly known that vessels of the EBA are coarse, i.e. porous. Therefore, the internal surfaces of these vessels could have been sealed with resinous material during this period in order to reduce their porosity.

Archaeologically, several evidences show that olives were cultivated during the Chalcolithic period and continued in a larger scale in the EBA in the southern Levant (Stager 1985; Neef 1990; Genz 2002: 92). All sherds analysed in this research belong to the EBA. Therefore, the results obtained in this research may support the use of plant oil, possibly olive oil. This can be supported by many studies discussing the function of similar vessels from the same period. For example, some studies inform that vessels like the ones tested in this study (numbered with 2, 4 and 5 in Table 1) have two, and in some cases four, handles on their sides, and they were usually used for storing and transporting (Esse and Hopke 1986: 332-339; Esse 1991: 114-123).

The relatively narrow openings of these vessels and the presence of handles may support that they were used for storing and transporting liquids (Fargo 1979: 240; Mazzoni 1988: 87; Joffe 1998: 301). These vessels were made during the EBA-II and EBA-III in large, medium and small sizes that can hold 28, 10 and 8 liters respectively (Zemer 1978: 4-8; Genz 2002: 93), and were used for storing and transporting both olive oil and wine (Fargo 1979: 240; Mazzoni 1988: 87; Joffe 1998: 301).

Sherd 3 with burning markers on its external surface clearly belongs to a type of vessels that were commonly used during the EBA for cooking (Genz 2002: 93). Chemically, the occurrence of resinous material and plant oil in the interior of this vessel could be attributed to that the resinous material was processed in this vessel in order to be applied later as a sealant on other vessels or to be used for other purposes. After that the vessel was used to keep plant oil. On the other hand, this vessel may have been exploited for cooking with olive oil before it was used later for processing resinous material.

Concerning sherd 1, it belongs to a large Pithos with flaring rim. This kind of vessels was used commonly during the EBA-II and EBA-III for storage purpose but not transportation from one place to another due to their large size. Therefore, it is expected that Pithoi were used mainly for storing. Most vessels of this kind were made without handles, which confirm the storing function of these vessels that can retain about 141 liter. The narrow opening of this kind of vessels could have been used for storing liquids (Genz 2002: 93). This study revealed the preservation of plant material, possibly olive oil and resinous material in the interior of this vessel proposing that it was sealed with resinous material in order to keep plant oil.

The absence of significant organic constituents in the other sixteen sherds analysed in this study can be attributed to that organic materials were not used in these vessels, or have degraded during burial, or were used in somehow in which organic constituents were not able to survive in their pores.

Concerning the methodology adopted in this study, GC-MS settings were applied on the extracts of ceramic samples from other sites where mono- and di- acylglycerides were detected. However, triacylglycerides were not detected in this research which could be attributed to the inability of the MS technique to detect such heavy molecules. The absence of other diagnostic lipid constituents, such as mono- and diacylglycerides, in the extracts analysed in this research and the absence of the analytical technique of compound specific carbon isotope analysis (^{13}C analysis) precluded us to ensure the origin of organic residues. Future research

should focus on more ceramic and soil samples freshly excavated and stored from different contexts from the same site and from other contemporary archaeological sites located in different regions in Jordan.

On the other hand, some points in the methodology should be considered. The sample size of the ceramic powder will be larger than 0.1 g in order to overcome the effect of contamination and for more clear results. The method of alkaline hydrolysis will be changed to avoid transmethylation within the sample. Furthermore, the extracts obtained via conventional solvent extraction method should be subjected to alkaline hydrolysis in order to retrieve more fatty acids from acylglycerides that could have been present in these extracts, particularly, the higher molecular weight triacylglycerides that could not be detected by the MS technique.

CONCLUSIONS

This research project represents a preliminary study focusing on identifying organic residues preserved in EBA ceramic sherds and their related soil excavated at the site of Khirbet Al-Batrawy in Jordan. Conventional solvent extraction and alkaline hydrolysis were used for the extraction of residues preserved in the fabrics of twenty one sherds from different vessels, while gas chromatography – mass spectrometry (GC-MS) technique was used for separation and analyzing organic residues.

The preliminary results inform that plant material, oil and resin, have been preserved in the fabrics of five of these sherds. These five sherds belong to belong to five vessels described in Table 1. One was used for storing, three were used for storing and transporting, and one was used for cooking.

These vessels were made of coarse ware of high porosity. Therefore, the occurrence of a resinous material in the interiors of these vessels indicates that their internal surfaces were sealed with resinous material to reduce their porosity, and thereby, to reduce the permeation and loss of liquid material stored in them.

The occurrence of plant oil, possibly olive oil in these vessels, however, is attributed to that these vessels were used for storing (vessel 1) and storing/transporting (vessels 2, 4 and 5) plant oil and for cooking (vessel 3) with the use of plant oil. These results are in conjunction with the archaeological evidences on the cultivation and use of olive oil in this region during the EBA.

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