Archaeological and Anthropological Sciences (2023) 15:51
https://doi.org/10.1007/s12520-023-01751-2

RESEARCH

Diversified pottery use across 5th and 4th millennium cal BC Neolithic coastal communities along the Strait of Gibraltar

Adrià Breu-Barcons[1] · **Eduardo Vijande-Vila**[2] · **Jesús Cantillo-Duarte**[2] · **Pau Comes**[3] · **Carl Heron**[4] · **Joan Villanueva**[3] · **José Ramos-Muñóz**[2]

Received: 10 October 2022 / Accepted: 13 March 2023 / Published online: 1 April 2023

Abstract

The region around the Strait of Gibraltar offered Neolithic societies a bridge connecting Iberia and North Africa. Using the sea for access to additional resources, Neolithic groups in the area developed close links with this territory as evidenced by its burial rites and storage practices. Nonetheless, the role pottery and its contents may have had in the labour activities of these groups is not well understood. In light of research in neighbouring regions, this study presents an initial analysis using an acidified methanol extraction of 29 pottery vessels from four Neolithic sites (Benzú Cave, Campo de Hockey, SET Parralejos and La Esparragosa) selected with the aim of assessing its potential for organic residue analysis at the point of confluence between southern Iberian and North African historic dynamics. The presence of appreciable lipid residues in 79% of the studied samples and the high variety in the results, including animal fats, dairy products, plant resins and two previously unreported residue types, support further research in the region.

Keywords Neolithic · Strait of Gibraltar · Organic residue analysis · Pottery use

Introduction

The spread of the Neolithic way of life across the Mediterranean Sea was a complex process. Social groups had to adapt new strategies such as agriculture, pastoralism, sedentarism and pottery use to the unique characteristics of different regions and climates. Along the North African coast, the adoption of pottery by 6th millennium BC groups obtaining only a minor percentage of their food from agriculture and pastoralism (Dunne et al. 2020) contrasts with the European dynamics, marked by the arrival of migrants with the complete "Neolithic package" (García-Martínez de Lagrán 2015). Most of the current models explaining the arrival of domesticates and pottery in the region take into account potential evidence of seafaring such as the canoes discovered in La Marmotta, and common stylistic and cultural traits between the African and the European coasts (Fugazzola-Delpino and Mineo 1995; Ramos-Muñoz 2012). At the western limits of this process, the territory surrounding the Strait of Gibraltar offered an easily navigable marine passage less than 20 km wide at its narrowest point across the Holocene and during the maximum interglacial transgression around ca 6500 years BP (Zazo et al. 1997). This potentially connected social groups from both regions and provided access to the Atlantic Ocean (Tarradell 1959; Souville 1988; Ramos-Muñoz 2012, 2013; Otte 2019).

Use-wear patterns indicate that lithic tools were used to process fish, and seashells were used as tools (Cuenca Solana et al. 2013; Clemente-Conte et al. 2020), data which complements the detection of abundant seashell and ichthyofaunal remains (Soriguer et al. 2002) in the area. This evidence suggests that, beyond agriculture and pastoralism, the sea was actively

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Highlights

- Organic residue analysis of 29 pottery vessels from four Neolithic archaeological sites from the Strait of Gibraltar demonstrates good lipid preservation.
- First detection of a pentacyclic triterpenoid methyl ether (PTME) other than miliacin as a residue derived from pottery use.
- Recovery of a wide range of residue types including plant- and animal-based products.
- Compared to previous studies from the Iberian Peninsula and despite the small sample size, the results suggest highly diversified uses of pottery.

✉ Adrià Breu-Barcons
adria.breu@uab.cat

[1] Grup de Recerca en Arqueologia del Mediterrani i El Proper Orient (GRAMPO), Departament de Prehistòria, Facultat de Filosofia i Lletres, Universitat Autònoma de Barcelona, Barcelona, Spain

[2] Universidad de Cádiz, Cádiz, Spain

[3] Institut de Ciència i Tecnologia Ambientals (ICTA-UAB), Universitat Autònoma de Barcelona, Barcelona, Spain

[4] Department of Scientific Research, The British Museum, London WC1B 3DG, UK

exploited as an additional supply of resources. This has not only been detected at the onset of the Neolithisation process at the site of El Retamar, El Estanquillo and the Benzú Cave (Ramos et al. 2003; Cantillo et al. 2010; Vijande-Vila et al. 2019a), but persists as groups developed closer links with the territory in the form of specific burial rites at La Esparragosa and Campo de Hockey (Vijande-Vila et al. 2018, 2022) or refilled underground silos with debris from their marine-related economic activities in SET Parralejos (Villalpando and Montañés 2009; Cantillo et al. 2010). Nonetheless, to date, there is no data on how Neolithic pottery might have related to specific subsistence activities around the Strait of Gibraltar. The study of lipid residues preserved in association with pottery vessels can help fill this gap. This has become a widely applied analytical tool to assess the role pottery played in the Middle Eastern and European Neolithic economic and social systems (Copley et al. 2005a; Evershed et al. 2008; Cramp et al. 2019; Breu et al. 2021a). So far, lipid biomarkers have shown pottery contained ruminant, non-ruminant and dairy fats, plant waxes, oils and resins from C_3 and C_4 organisms, marine products, beeswax and bituminous substances (Evershed et al. 1991; Heron et al. 1994, 2016; Dudd et al. 1999; Regert 2011; Cramp and Evershed 2014; Dunne et al. 2016; Breu et al. 2022; Weber et al. 2020).

Recent organic residue analyses on pottery from archaeological sites in regions neighbouring the Gibraltar strait include the Portuguese Atlantic coast (Cubas et al. 2020) and the European (Sánchez et al. 1998; Tarifa-Mateo et al. 2019; Manzano et al. 2019) and North African Mediterranean seashores (Kherbouche et al. 2016; Dunne et al. 2020). In Ifri Oudadane, Ifri n'Etsedda and Hassi Ouenzga (6th and 5th millennia BC), in Morocco, as well as in Gueldaman cave (6th to 4th millennia BC), and in Algeria, pottery was primarily used to process medium to large ungulates (either domestic or wild) and minor amounts of dairy products. Nonetheless, in the Rif, plant biomarkers (very long-chained fatty acids and odd over even long-chain alkanes) were present in roughly one-quarter of the vessels studied. This, according to Dunne et al. (2020), supports the hypothesis that these groups were flexible broad-spectrum farmers and foragers adapting subsistence strategies to their environment.

Alternatively, results from the south of the Iberian Peninsula present a slightly different picture. Data from Cabeço das Amoreiras, Valada do Mato, São Petro de Canaferrim, Lapiás das Lameiras, Monte da Foz I, Gruta do Caldeirão, Cueva del Toro (6th and 5th millennia) and Cueva Virués-Martínez (4th and 3rd millennia) (Tarifa-Mateo et al. 2019; Manzano et al. 2019; Cubas et al. 2020) is similarly dominated by ruminant and non-ruminant animal fats with minor amounts of dairy products. Although plant sterols and conifer diterpenoids were detected, these were less than 20% of the studied assemblage in Cueva del Toro and almost none was reported from the Portuguese sites. Whilst the Cueva Virués-Martínez presented more extensive evidence of plant processing, analyses partially performed through UPLC-HRMS make the results harder to compare with other sites. The number of published results is still too low to assess whether the detected differences result from true variations in pottery use. Nevertheless, the divergent subsistence strategies between the two regions suggest this question merits further research. The analysis of pottery use amongst the Neolithic populations inhabiting the surroundings of the Strait of Gibraltar can help better understand the social dynamics in southern Iberia and northern Africa.

To explore this further, 29 pottery sherds from four sites in the gulf of Cádiz and the Tingitana Peninsula were studied with the aim to assess the following:

(1) The degree of preservation of lipid residues, and
(2) The range of residue types that could be recovered and interpreted.

We argue that, despite the small sample size, the unprecedented variety of different and unique residue types detected in the assemblage indicates that pottery use was highly diversified.

Materials and methods

Overall, the ceramic assemblages from Benzú, Campo de Hockey, SET Parralejos and La Esparragosa consist of handmade pottery fired in oxidising or reducing atmospheres with smoothed interior and exterior surfaces. The Iberian assemblages tend to present well-levigated tempers with gritty textures whilst the North African vases were made with clays with abundant inorganic temper. The main vessel shapes in the Benzú cave include incurved bowls, straight-walled pots and conical vases. Alternatively, bowls including s-shaped profiles, pots and carinated vases were amongst the main forms in the Iberian sites (see details in SI1), which included some painted and incised sherds, applied cords and handles. Whilst painting could have links with North African productions, incisions were common across southern Iberia. Detailed descriptions of the sites' pottery assemblages can be found in previously published research (Vijande-Vila et al. 2015, 2019a, 2019b, 2022; Sánchez-Barba et al. 2019; Villalpando and Montañés 2009; Pérez et al. 2005).

To maximise the chance of detecting the widest possible range of residues, pots, bowls, cups and carinated vases were sampled. Furthermore, although most samples were taken from rims, three bases from Cueva de Benzú and three body sherds from Campo de Hockey were also studied. These vessels were deposited in different archaeological contexts (pit refills, hearths, burials and habitation layers), possibly correlating with different social activities.

Cueva de Benzú—6th–5th millennium BC

The Benzú Cave is located at the western end of the Autonomous City of Ceuta (Spain), on the North African shore of the Strait of Gibraltar and just 200 m from the current coastline (Fig. 1). It is a small cavity with an area of just 25 m^2 divided into two small rooms containing stratigraphic layers from the Neolithic and Bronze Age.

Archaeological evidence suggests the cave was in use during the 6th–5th millennium BC as shelter for herders. The existence of debitage, lithic tools and ceramic vessels shaped most likely for the preparation and consumption of food suggests these activities might have taken place in the site. The cave's small size suggests it was only temporarily used by a Neolithic occupation dated by thermoluminescence to 7136 ± 433 BP (Vijande-Vila et al. 2019a).

Seven of the pottery sherds analysed belong to the Neolithic phase documented in Strata I and II (Table 1) and were recovered together with numerous lithic, faunal, malacological and botanical remains (Vijande-Vila et al. 2019a).

Campo de Hockey—5th–4th millennium BC

The Campo de Hockey archaeological site is in the town of San Fernando (Cádiz), in the middle of the Gulf of Cádiz (Fig. 1). Studies on the evolution of the coastline indicate that, in the Neolithic, its surrounding territory would have been an island (Arteaga et al. 2008).

The excavation work carried out in 2007 and 2008 documented up to three activity areas in the Neolithic settlement. The western area contained the foundations of two huts; the central sector included five large pits (with diameters between 4 and 5 m) which were interpreted as silos or storage structures, and finally, the lower part (eastern sector) presented a proto-megalithic necropolis including a wide typological variety of tombs and monumental burials with prestigious grave goods (amber, variscite, turquoise, imported axes, etc.) (Vijande-Vila 2009; Vijande-Vila et al. 2015). In total, 53 graves containing 63 individuals were excavated and the disarticulated remains of another 10 individuals were found scattered throughout the necropolis as a result of post-depositional processes.

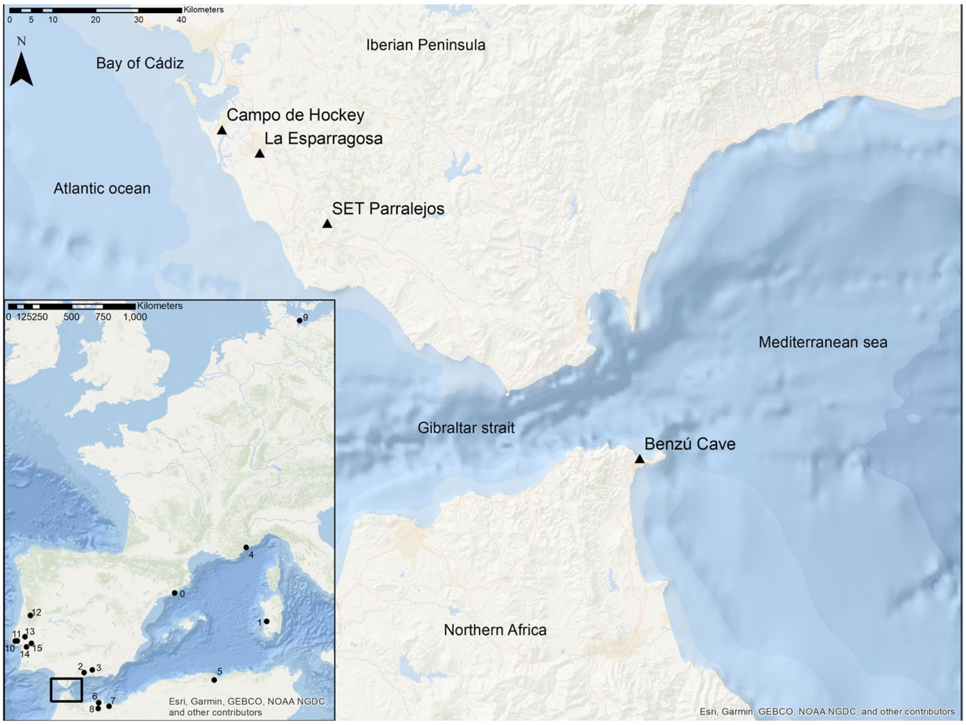

Fig. 1 Map locating the four studied sites and other sites mentioned in the text. (0) Carrer Reina Amàlia-Caserna de Sant Pau (Spain), Can Sadurní and the Gavà Mines, (1) Bau Angius-Gribaia-Su Mulinu Mannu (Sardinia), (2) Cueva del Toro (Spain), (3) Cueva Virués-Martinez (Spain), (4) Abri Pendimoun (France), (5) Gueldaman Cave (Algeria), (6) Ifri Oudadane (Morocco), (7) Ifri n'Etsedda (Morocco), (8) Hassi Ouenzga (Morocco), (9) Wangels LA69 and Oldenburg-Dannau LA77 (Germany), (10) São Petro de Canaferrim, (11) Lapiás das Lameiras, (12) Gruta do Caldeirão, (13) Monte da Foz I, (14) Cabeço das Amoreiras and (15) Valada do Mato (Portugal) (Kherbouche et al. 2016; Fanti et al. 2018; Tarifa-Mateo et al. 2019, 2021; Manzano et al. 2019; Weber et al. 2020; Dunne et al. 2020; Cubas et al. 2020; Drieu et al. 2021; Breu et al. 2021b) (see used coordinates in SI2)

Table 1 Samples analysed from the Benzú Cave

Sample	Year	Context	Find ID	Social space	Sampled part	Vessel type
BZ1	2003	– CXVIII–XIX	[4]–[3]	Habitation	Base	Conical base
BZ2	2003	– DXVIII–XIX	[1]–26	Habitation	Rim	Bowl with incurving rim
BZ3	2003	– CXVIII–XIX	[2]–(3)	Habitation	Rim	Pot with rounded rim
BZ4	2002	– AXVIII–XIX	[2]–(4)	Habitation	Rim	Bowl with incurving rim
BZ5	2002	– AXIX–XX	[2]–(2)	Habitation	Base	Flat-based cup
BZ6	2002	– AXVII–XVIII	[1]–(9)	Habitation	Rim	Open bowl
BZ7	2007	BV1	4A–[148]	Habitation	Base	Flat base

Twenty radiocarbon dates place the site between 4335 and 3515 cal BC (Vijande-Vila et al. 2015, 2022; Sánchez-Barba et al. 2019).

Ten pottery samples from four different contexts were included in this study (Table 2). Five of them had been placed inside a storage structure (Pozo E2-C2-UE205) and correspond to vessel rims from pots and bowls. These storage structures, once abandoned, would have functioned as garbage dumps. The other five fragments were recovered from the necropolis: one body sherd from the megalithic tomb E7T7; a rim from a pot with a fractured handle in a hearth C17-UE1712, located in the middle of the necropolis and possibly associated with ritual activities; a rim from a pot with a fractured handle and a rim from a bowl in the megalithic tomb E11T14, and an amorphous ceramic located in the simple-pit tomb E10T15. All the sherds analysed correspond to ceramic forms likely intended for the preparation and consumption of food.

SET Parralejos—4th millennium BC

The SET Parralejos archaeological site is in the town of Vejer de la Frontera, east from the Gulf of Cádiz and on a hill that dominates part of the Atlantic coastal strip and the Salado River (Fig. 1) (Villalpando and Montañés 2009).

The site was discovered and excavated in 2008 due to the construction of an electrical substation and a second campaign was carried out in 2012 due to additional infrastructure development. It corresponds to one of the archaeological sites traditionally known as “silo fields” (Carrilero et al. 1982; Nocete 1989; Arteaga 2002), which are quite common in the Guadalquivir valley, the Gulf of Cádiz and other areas of the Iberian Peninsula (Molist et al. 2018). They include dozens of negative storage structures which, in the specific case of SET Parralejos, comprise 65 silos, 3 ditches and a concentration of postholes. Four radiocarbon dates place the site between 3522 and 3014 cal BC (Villalpando and Montañés 2009).

The silos present a varied typology both in size and shape. The first type were silos slightly shallower than wide with a cylindrical section and almost vertical walls. The second type were bell-shaped silos, with a mouth diameter smaller than the base diameter. The third were well-type silos, with a cylindrical section, and the fourth type were the so-called false silos or *cubetas*, which corresponded to a depth that in no case exceeded 15 cm. Three twin silos, some of which had traces of postholes, were also excavated (Villalpando and Montañés 2009). The seven analysed pottery fragments (Table 3) correspond to shapes specific to food preparation and consumption activities. All of them were found as secondary depositions in silos 3 and 4.

La Esparragosa—Late 4th millennium BC

The Neolithic settlement of La Esparragosa is in the town of Chiclana de la Frontera (Cádiz), a coastal site east of the

Table 2 Analysed samples from Campo de Hockey

Sample	Structure	Layer	Social space	Sampled part	Vessel type
CH1	E2-C2	205	Refilling debris	Rim	Cooking pot
CH2	E2-C2	205	Refilling debris	Rim	Bowl
CH3	E2-C2	205	Refilling debris	Rim	Stockpot
CH4	E2-C2	205	Refilling debris	Rim	Stockpot
CH5	E2-C2	205	Refilling debris	Rim	Bowl
CH6	C7B E7 Com4	705	Burial	Body	Undetermined
CH7	C17A	1712	Hearth	Body	Stockpot with fractured handle
CH8	E11 T14	1406	Burial	Rim	Stockpot with fractured handle
CH9	E11 T14	1406	Burial	Rim	Bowl
CH10	E10 T15 Com2	1416	Burial	Body	Undetermined

Table 3 Samples analysed from SET Parralejos

Sample	Structure	Find ID	Social space	Sampled part	Vessel type
SET1	E3	125	Refilling debris	Rim	Pot
SET2	E3	137	Refilling debris	Rim	Bowl
SET3	E3	182A	Refilling debris	Rim	Carinated vase
SET4	E3	183A	Refilling debris	Rim	Carinated vase
SET5	E3	184A	Refilling debris	Rim	Carinated vase
SET6	E4	449	Refilling debris	Rim	Stockpot
SET7	E4	453	Refilling debris	Rim	Bowl

Bay of Cádiz (Fig. 1). It is located on a platform 27–30 m above the sea level next to the Iro River, an area with abundant aquifers.

The archaeological site is a "silo field" resembling that of SET Parralejos where, to date, nine silos and a burial pit have been excavated. The silos had been dug in Tertiary loam and presented a diameter from 1 to 1.20 m and a bell-shaped section. Their depth varied between 1 and 1.40 m, and their bases had diameters between 1.60 and 2 m and a subcircular shape. Furthermore, a circular structure 60 cm deep and 2.5 m wide dug on the Tertiary loam was identified as a female burial (AV). The body had been placed in a supine position with bent legs and covered by 477 clam shells (*Ruditapes decussatus*) and a domestic dog (Vijande-Vila et al. 2019b). Five radiocarbon dates and two thermoluminescence dates place the site between 3092 and 2854 cal BC (Fernández-Sánchez et al. 2019).

The five vessels analysed (Table 4) correspond to the first excavation campaign carried out by the University of Cádiz in 2002–2003 (Pérez et al. 2005; Vijande-Vila et al. 2019b). Four sherds were selected from the secondary refilling of silos AIV (3) and CIII (1), whilst the remaining sample belonged to burial AV. All ceramic shapes correspond to characteristic forms related to activities of food preparation and consumption.

Analytical approach

Using a sterilised drill and after removal of the vessel's interior surface (1–2 mm), around 1 g of powdered pottery was spiked with 10 µg of *n*-tetratriacontane (C34) and prepared using an acidified methanol extraction (Craig et al. 2013; Correa-Ascencio and Evershed 2014) to maximise the extraction yield. After addition of 10 µg of *n*-hexatriacontane (C36), lipid extracts were analysed by gas chromatography-mass spectrometry (GC–MS) to identify the presence of lipid biomarkers (see analytical details in SI2). Selected samples were further derivatised with BSTFA and analysed again. All chromatograms produced for this study are available in SI3 and a summary of all results can be found in SI4.

To characterise further the nature of the recovered animal fats, compound-specific δ^{13}C values from stearic and palmitic acids were obtained from samples with a total lipid extract (TLE) above 5 $\mu g \cdot g^{-1}$ and absence of co-eluting interfering peaks with the targeted analytes. According to modern lipid reference values, the Δ^{13}C proxy ($\delta^{13}C_{18:0}$-$\delta^{13}C_{16:0}$) detecting physiological differences in fatty acid biosynthesis between tissues (Mukherjee et al. 2005) was used to discriminate between non-ruminant adipose ($>0‰$), ruminant adipose ($<0‰, > -3‰$) and ruminant dairy ($< -3‰$) products (Fig. 4).

Results: molecular and isotopic data

Cueva de Benzú

The preservation of the lipid residues at the Benzú Cave was the best within this study as all samples presented a TLE higher than 5 $\mu g\ g^{-1}$. The mean concentration was 189.3 $\mu g\ g^{-1}$ and the median was placed at 170.4 $\mu g\ g^{-1}$. Only sample BZ3 contained a lipid amount significantly lower than that of its counterparts, and close to the 5 $\mu g\ g^{-1}$ threshold (Table 5). Within this limited sample size, lipids

Table 4 Analysed samples from La Esparragosa

Sample	Context code	Find ID	Social space	Sampled part	Vessel type
LE1	AIV	7–1	Refilling debris	Rim	Bowl
LE2	AIV	7–2	Refilling debris	Rim	Carinated vase
LE3	AV	-	Burial	Rim	Straight-walled vessel
LE4	CIII	-	Refilling debris	Rim	Carinated vase
LE5	AIV	3–15	Refilling debris	Rim	Carinated vase

were equally abundant in rim and base fragments. Alternatively, TLEs seemed to correlate with the vessel's position within the cave's grid, as samples from the A and -A rows consistently contained an order of magnitude higher amount of lipids than samples from the -C and -D rows (see SI1). All extracts presented dicarboxylic acids and keto acids coherent with the oxidation of unsaturated fatty acids (Regert et al. 1998). Trace amounts of phthalate plasticisers were also detected due to the storage of the samples in plastic bags, but they did not affect the overall interpretation of the residues.

A set of saturated even chained free fatty acids (FFA) dominated the extracts of all seven samples. These ranged from dodecanoic ($C_{12:0}$) to eicosanoic ($C_{20:0}$) acid and were accompanied by minor amounts of docosanoic ($C_{22:0}$) to octacosanoic ($C_{28:0}$) acid in samples 4 to 7. The hexadecanoic ($C_{16:0}$) and octadecanoic ($C_{18:0}$) acids were the most abundant compounds and were detected in similar abundance, which strongly suggested that FFAs originated from hydrolysed animal triacylglycerols. The presence of trace amounts of cholesterol methyl ether in samples 5 and 6 and the absence of squalene are consistent with an animal fat origin. However, given that other cholesterol degradation products could not be detected (Hammann et al. 2018), the possibility that this compound does not originate from pottery use cannot be fully rejected. Phytanic acid, resulting from the bacterial oxidation and hydrogenation of phytol (Lucquin et al. 2016a), a constituent of chlorophyll, was detected in samples 4, 5 and 6. No evidence for the presence of aquatic biomarkers was detected. Nonetheless, several compounds indicated the existence of a plant input.

Similar to analyses of reference standards and prehistoric pottery (Heron et al. 2016), samples BZ4, 5 and 6, presented peaks containing the M^+ *m/z* 440 parent ion characteristic of pentacyclic triterpenoid methyl ethers (PTMEs) eluting slightly before the C34 and C36 alkane standards. Further inspection of its corresponding mass spectra did not support the presence of miliacin due to the absence of a strong *m/z* 189 ion. Alternatively, the dominating ions were *m/z* 425, 393, 273 and 241, which are specific to fernane- and arborane-type PTMEs such as fern-9(11)-en-3β-ol methyl ether (arundoin) or Arbor-9(11)-en-3β-ol methyl ether (cylindrin) (Fig. 2) (Bryce et al. 1967; Jacob et al. 2005). The detection of only one PTME in the samples prevented the use of relative retention times to distinguish between arundoin and cylindrin, a limitation that increases the potential range of plant species from which the compound originates. Although PTMEs are rare in nature, several archaeological studies have successfully detected and used them as biomarkers for specific plant products (Heron et al. 2016; Ganzarolli et al. 2018; Rageot et al. 2019; Junno et al. 2020; Taché et al. 2021).

In sample BZ5, the additional detection of a clear range of ω-(o-alkylphenyl)alkanoic acids with 18 carbon atoms (APAA-C_{18}) indicated that unsaturated fats were subjected to protracted heating. Integration of the *m/z* 290 ion at the retention times corresponding with the E and H isomers (Fig. 2) was used to evaluate the possible plant/animal origin of APAAs before heating (Bondetti et al. 2020b). Values higher than 4 have been so far accompanied by either plant or aquatic biomarkers in archaeological samples. BZ5's value of 4.3, with co-occurrence of the PTME, thus further supports the presence of a plant residue.

Finally, trace amounts of dehydroabietic acid (DHA) (BZ1, 2, 3 and 5), didehydroabietic acid (DDA) (BZ2) and 7-oxodehydroabietic acid (7ODA) (BZ2 and 5) point to a possible input of conifer resins in a limited number of samples. Potential origins for these diterpenoids in sample BZ2 include the association of resins with pottery vessel use (e.g. storage), the application of resin-based post-firing treatments (Drieu et al. 2020) or the exposure to conifer firewood during firing or cooking (Reber et al. 2018). A discussion considering the relevance of conifers in the botanical record is necessary before accepting or rejecting any of these possibilities (Breu et al. 2023).

Compound-specific $\delta^{13}C$ values from $C_{16:0}$ and $C_{18:0}$ were used to further characterise the origin of the

Table 5 Detected lipid concentrations (TLE), fatty acid palmitic and stearic ratios (P/S), biomarkers and compound-specific isotopic values at the Benzú Cave

ID	TLE (μg g^{-1})	P/S	Biomarkers	$\delta\ ^{13}C_{16:0}$	$\delta\ ^{13}C_{18:0}$	$\Delta\ ^{13}C$
BZ1	29	0.9	DA	−25.3	−25.2	0.1
BZ2	56	0.9	DA, DDA, 7ODA	−27.1	−28.8	−1.8
BZ3	7	1.2	DA	-	-	-
BZ4	173	1.3	Phy. PTME	−26.9	−29.1	−2.2
BZ5	219	1.1	Chol. Phy. DA, 7ODA, PTME, APAA-C_{18}, CFAM	−28.2	−30.4	−2.2
BZ6	669	1.4	Chol. Phy. PTME	−26.1	−29.2	−3.2
BZ7	170	1.1	-	−27.4	−29.5	−2.1

Abbreviations: *Chol.*, cholesterol methyl ether; *Phy*, phytanic acid; *DA*, dehydroabietic acid; *DDA*, didehydroabietic acid; *7ODA*, 7-oxodehydroabietic acid; *R*, retene; *APAA*, ω-(o-alkylphenyl)alkanoic acids; *CFAM*, cyclopentyl fatty acid methyl ester; *PTME*, pentacyclic triterpenoid methyl ether; *VLCA*, very long-chained alcohols, *VLCFA*, very long chained fatty acids

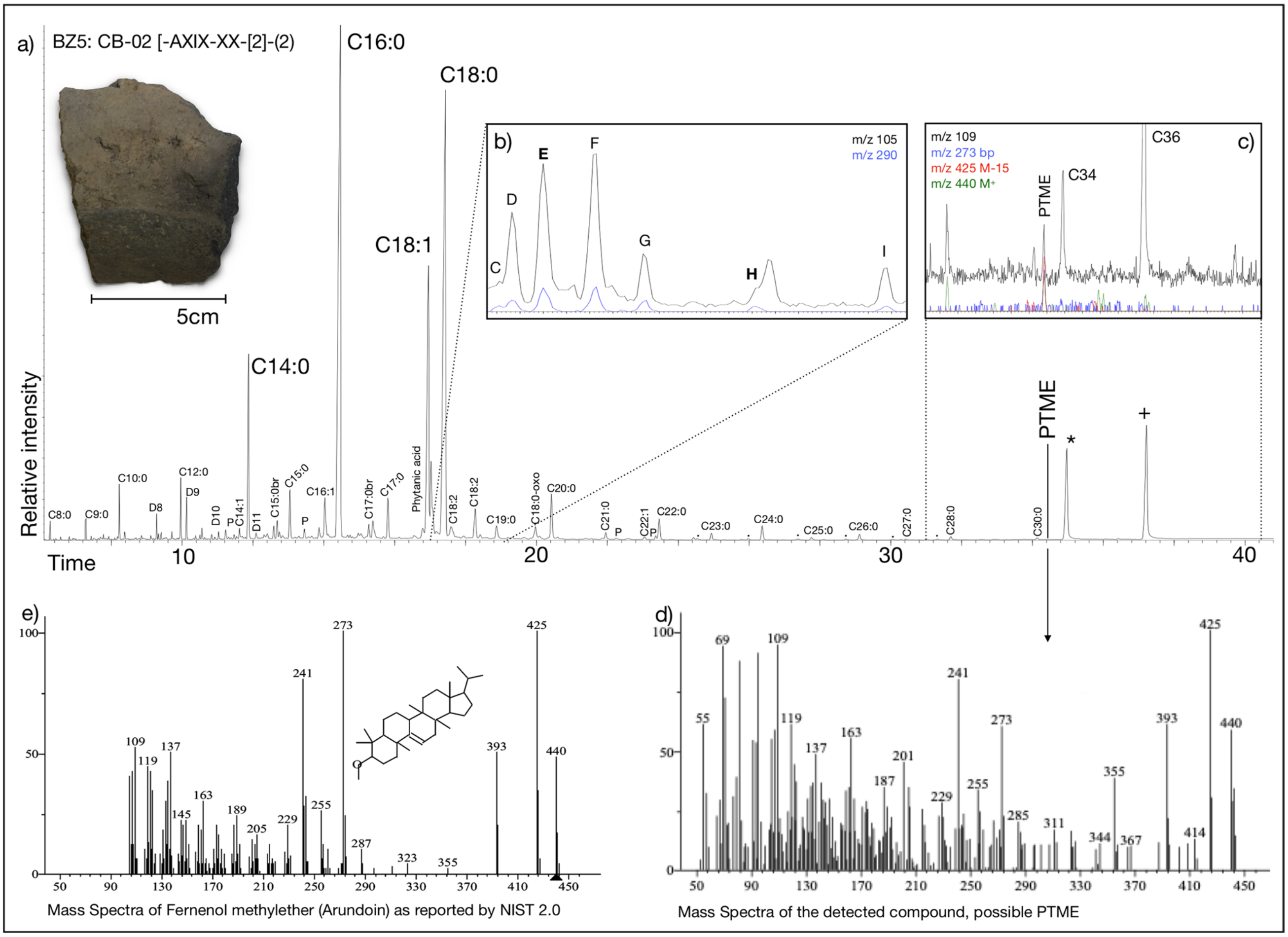

Fig. 2 (**a**) Chromatogram from sample BZ5 detailing the detected range of (**b**) ω-(o-alkylphenyl)alkanoic acid isomers and the (**c**) partial ion chromatograms and (**d**) mass spectra identifying the presence of a PTME and its correspondence with (**e**) its NIST reference. Internal standards: * tetratriacontane, + hexatriacontane

recovered animal fats. At Benzú Cave, $\delta^{13}C_{16:0}$ values ranged between − 25.3 and − 28.2‰ whilst $\delta^{13}C_{18:0}$ values varied between − 25.2 and − 30.4‰ (Fig. 4). The $\Delta^{13}C$ values from 66% of the vessels were grouped between − 3 and 0, which is indicative of the presence of ruminant adipose fats (Table 5). Sample BZ6 has a $\Delta^{13}C$ value of − 3.2‰, which is coherent with the presence of dairy lipids or their mix with ruminant adipose fats. In the case of BZ1 ($\delta^{13}C_{16:0} = -25.3$‰; $\delta^{13}C_{18:0} = -25.2$‰), the values are consistent with porcine fats and marine products (Copley et al. 2003; Lucquin et al. 2016b; Choy et al. 2016; Colonese et al. 2017). Although the study of the bone, seashell and lithic tool remains from the Benzú Cave suggests the site was used as a base for hunting and shellfish gathering, the absence of other aquatic biomarkers prevents the secure identification of marine products. Alternatively, the presence of wild boar amongst the faunal remains indicates that porcine adipose fats are a more likely interpretation for this residue.

Campo de Hockey

At Campo de Hockey, seven samples (70%) had a TLE higher than 5 μg g^{-1}. The mean concentration was 33 μg g^{-1} and the median value was 8.5 μg g^{-1} (Table 6). Although there is a slight difference in the mean concentrations recovered from vessels in funerary and non-funerary contexts (median 19 μg g^{-1} and 41 μg g^{-1} respectively), these do not seem to result from different use-patterns (Mann–Whitney $U = 12$, $N = 10$, $p = 0.92$). The effects of post-depositional degradation on the residue through oxidation could be detected in all samples due to the widespread presence of dicarboxylic acids such as azelaic acid, the occasional detection of keto acids in samples with the highest TLE (CH3 and 8) and the identification of 9,10-dihydroxyoctadecanoic acid (sample CH8) (Regert et al. 1998). Although trace amounts of phthalate plasticisers were found in all vessels, modern post-excavation contamination due to storage in plastic bags

Table 6 Detected lipid concentrations (TLE), fatty acid palmitic and stearic ratios (P/S), biomarkers and compound-specific isotopic values at Campo de Hockey. Abbreviations follow Table 5

ID	TLE (μg g^{-1})	P/S	Biomarkers	δ $^{13}C_{16:0}$	δ $^{13}C_{18:0}$	Δ ^{13}C
CH1	4	1.1	DA, 7ODA	-	-	-
CH2	7	0.6	DA	−28.9	−30.4	−1.5
CH3	132	0.5	Phy. APAA-C_{18} (traces)	−27.2	−32.8	−5.5
CH4	88	0.9	Chol	−28.5	−29.0	−0.4
CH5	4	1.1	-	-	-	-
CH6	8	2.0	-	-	-	-
CH7	14	1.0	DA	−31.2	−29.7	1.5
CH8	55	2.0	Chol. VLCA, VLCFA(0.16)	−29.2	−29.4	−0.2
CH9	9	1.5	Chol	−27.7	−30.8	−3.1
CH10	4	1.3	-	-	-	-

was minimal and did not hinder the study of the recovered archaeological residues.

All samples were dominated by a range of long-chain free fatty acids from $C_{12:0}$ to $C_{20:0}$. The overall high abundance of $C_{18:0}$, almost equal or higher than the quantity of $C_{16:0}$, and a very long-chain fatty acid (VLCFA) ratio below 0.08 for all samples except for CH8 suggest that FFAs most likely originated from the complete hydrolysis of animal fat triacylglycerols (Dolbunova et al. 2022). The detection of traces of cholesterol methyl ether in samples CH4 and 9 supports this interpretation but the absence of additional degradation products indicates that other origins are also possible. Furthermore, the tentative detection of trace amounts of APAA-C_{18} in CH3 suggests that the degraded animal fat might have been significantly heated.

Several compounds hint at the presence of products other than terrestrial animal fats. CH6, a vessel from burial 7, exhibits an unusually high amount of hexadecenoic acid ($C_{16:1}$) when compared with other vessels at Campo de Hockey. Given the co-occurrence of several methoxy fatty acids, it cannot be ruled out that this vessel could have contained minimal quantities some type of product resembling the oils found in SET Parralejos (see the “SET Parralejos” section). In sample CH8, a range of very long-chain fatty acids ($C_{20:0}$ to $C_{28:0}$) with a VLCFA ratio of 0.16 (Dolbunova et al. 2022) and the presence of trace amounts of three very long-chained alcohols (VLCA) (hexacosanol, octacosanol and triacontanol) suggest the presence of hydrolysed wax esters (Fig. 3). Given the trace nature of VLCAs including triacontanol, the absence of dotriacontanol and 15-hydroxyhexadecanoic acid, and the higher abundance of long-chain fatty acids, this pattern is consistent with a hydrolysed plant epicuticular wax rather than beeswax. Furthermore, the greater abundance of $C_{16:0}$ relative to $C_{18:0}$ and the detection of two isomers of octadecadienoic acid ($C_{18:2}$) make a plant origin more likely. Its abundance, however, is not high enough to exclude its accidental incorporation when processing any plant part including leaves, seeds, nuts, grains and its oils (Dunne et al. 2020). It does seem likely that this residue was the result of a mixture incorporating degraded animal fat with a minor input from a plant product.

The detection of dehydroabietic acid in samples CH1, CH3 and CH7 and 7-oxodehydroabietic acid in sample CH1 was considered insufficient for conifer resins to be a potential content of these vessels. Higher abundances and the presence of additional compounds commonly detected in archaeological conifer resins such as didehydroabietic acid, isopimaric acid and retene are necessary to support this interpretation (Bondetti et al. 2020a; Breu et al. 2023; Croft et al. 2018).

The nature of the animal fats was explored further through the study of compound-specific $\delta^{13}C$ values from $C_{16:0}$ and $C_{18:0}$. At Campo de Hockey, $\delta^{13}C_{16:0}$ values ranged between −27.2 and −31.2‰ whilst $\delta^{13}C_{18:0}$ values varied between −29.0 and −30.8‰. This resulted in a wide range of $\Delta^{13}C$ values, from −5.5 to 1.5 (Table 6), implying the presence of dairy residues (CH3), a mixture of dairy with ruminant adipose fats (CH9), ruminant (CH2, CH4 and CH8) and non-ruminant adipose fats (CH7). In the latter case, the $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values (−31.2‰ and −29.7‰ respectively) were significantly lower than expected for porcine fats, suggesting its origin could be related to non-ruminant animals with an herbivorous diet (Fig. 4) as observed in compound-specific studies of their modern authentic fats (Gregg et al. 2009; Taché and Craig 2015; Carrer et al. 2016; Choy et al. 2016). Although this sample has no biomarkers for plant lipids and its high abundance of stearic acid might be more consistent with animal fats, the observed isotopic values could also correspond with oils from C3 plants (see SI5) (Spangenberg and Ogrinc 2001).

The range of results is thus dominated by terrestrial animal fats with a possible small contribution of plant oils. The imbalance between these two products is not surprising as plants tend to produce lower amounts of fats and, due to their higher degree of unsaturation, they are more readily affected by oxidation and further loss of alteration products by groundwater leaching (Regert et al. 1998; Craig et al. 2019, p. 84).

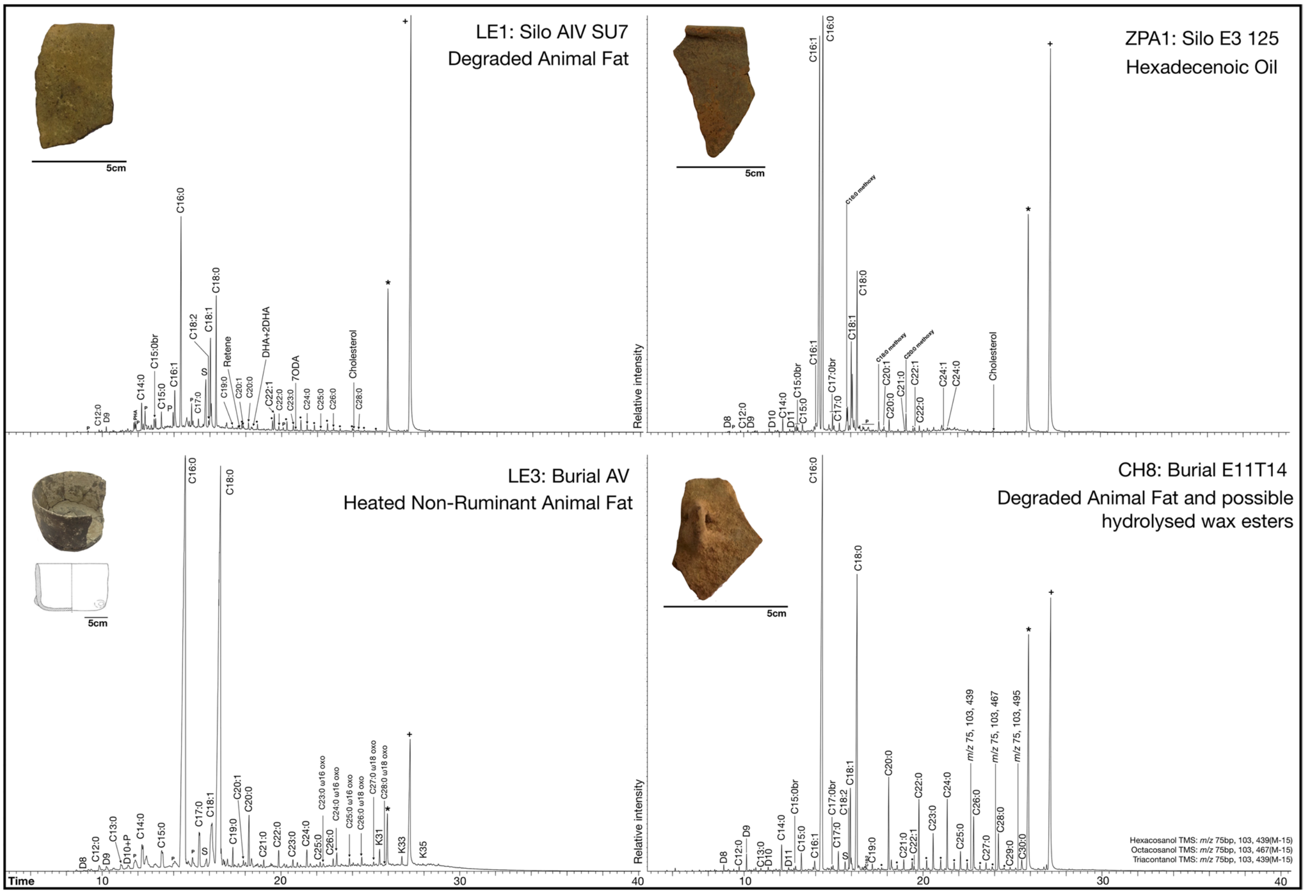

Fig. 3 Selection of chromatograms representative of the range of products detected in the study: LE1 ruminant adipose fat, SET1 hexadecenoic acid oil, LE3 protracted heating on a non-ruminant animal fat, CH8 ruminant adipose fat and traces of TMS-derivatised fatty alcohols pointing at plant hydrolysed wax esters. Internal standards: * tetratriacontane, + hexatriacontane

SET Parralejos

At SET Parralejos, TLEs higher than 5 μg g^{-1} were detected in six out of the seven analysed samples (85%). The mean concentration was 52.8 μg g^{-1} and the median was placed at 41 μg g^{-1} (Table 7). The widespread presence of dicarboxylic acids was consistent with the post-depositional oxidation of unsaturated fatty acids (Regert et al. 1998). Although trace amounts of phthalate plasticisers were present in all samples, this did not affect the interpretation of the residues.

At SET Parralejos, the vessels were characterised by a set of long-chain fatty acids ranging between $C_{12:0}$ and $C_{20:0}$ with significant variations in the quantity of unsaturated compounds. Three of the analysed samples (vessels SET3, 4 and 5) showed a clear predominance of $C_{18:0}$ and $C_{16:0}$ acids in similar abundances, which is consistent with the presence of hydrolysed triacylglycerols from animal fats. Although dehydroabietic acid was detected in sample SET7, the absence of other diterpenoids prevented any further archaeological interpretation of the compound. Additionally, traces of cholesterol methyl ether were detected in SET 1, 2, 3, 4 and 6.

SET1 and 2 presented an unusual fatty acid profile only seldomly reported within the study of organic residues in Neolithic pottery vessels (Fig. 3) (Fanti et al. 2018; Weber et al. 2020). $C_{16:0}$ was roughly four times more abundant than $C_{18:0}$, a distribution common in both plant and marine oils (Copley et al. 2005b; Heron et al. 2010; Cramp and Evershed 2014; Dunne et al. 2016). Secondly, although unsaturated fats are highly susceptible to postpositional degradation, the abundance of $C_{16:1}$ and $C_{18:1}$ is either equal or greater than its saturated counterparts ($C_{16:0}$ and $C_{18:0}$). This suggests a lipid source with abundant unsaturation. A closer look at the unsaturated fatty acid oxidation products provided further insight as to the double bond positions. Dicarboxylic acid chain lengths spanned from C_7 to C_{13}. Furthermore, a series of methoxy acids, commonly reported as extraction artefacts (Lough 1964; Rojo and Perkins 1987; Aldai et al. 2005), were also identified: 7-methoxy to 13-methoxy C16:0 and 8-methoxy to 14-methoxy C18:0 (Table 8). A detailed interpretation of

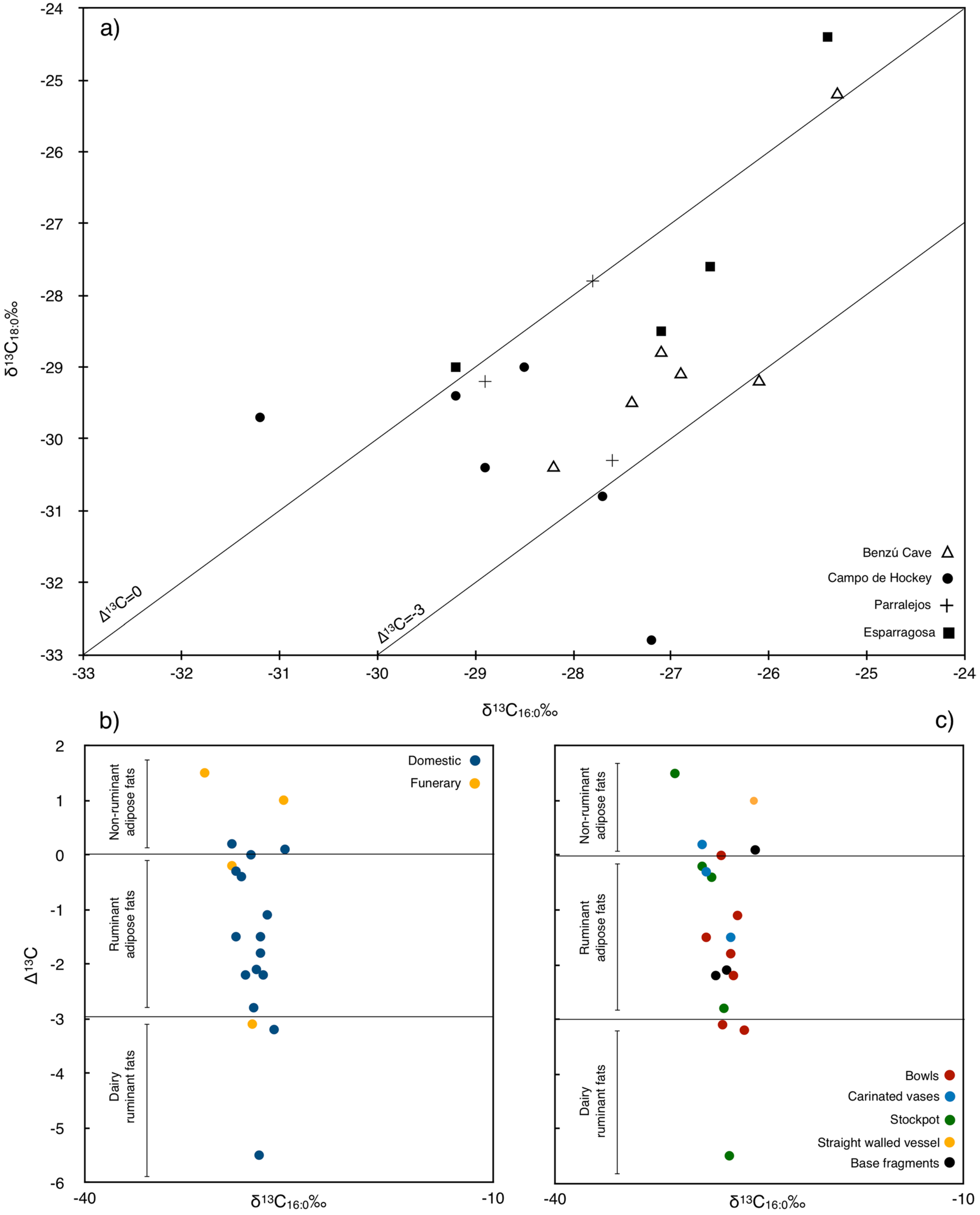

Fig. 4 Plots presenting the compound-specific isotopic analysis of palmitic and stearic acids. **a** Results from the Benzú Cave, Campo de Hockey, La Esparragosa and SET Parralejos. **b** Comparison between funerary and domestic contexts. **c** Comparison between vessel shapes

Table 7 Detected lipid concentrations (TLE), fatty acid palmitic and stearic ratios (P/S), biomarkers and compound-specific isotopic values at SET Parralejos. *MeFA*, methoxy fatty acids. Other abbreviations follow Table 5

ID	TLE (μg g^{-1})	P/S	Biomarkers	δ $^{13}C_{16:0}$	δ $^{13}C_{18:0}$	Δ ^{13}C
SET1	61	4.0	Chol. MeFA	– 27.6	– 30.3	– 2.8
SET2	63	4.1	Chol. MeFA	– 27.8	– 27.8	0.0
SET3	41	1.0	Chol	– 28.9	– 29.2	– 0.3
SET4	14	1.3	Chol	-	-	-
SET5	13	0.8	-	-	-	-
SET6	3	1.0	Chol	-	-	-
SET7	175	2.3	DA, MeFA	-	-	-

the mass spectra used to identify the position of methoxy moieties is included in SI5.

In both samples, these fatty acid profiles were accompanied by trace amounts of cholesterol methyl ether, but the absence of other degradation products prevents using this compound as an animal fat biomarker. This and the absence of phytosterols, isoprenoid acids and APAAs motivated further compound-specific isotope analyses to assess the origin of the residue.

For samples SET1 and SET2, δ$^{13}C_{16:0}$ values at – 27.6‰ and – 27.8‰ and δ$^{13}C_{18:0}$ at values – 30.3‰ and – 27.8‰ respectively were incompatible with inputs from marine products. Nonetheless, the isotopic values from SET2 resembled reference values from both plant oils and freshwater organisms (Spangenberg and Ogrinc 2001; Steele et al. 2010; Craig et al. 2011; Taché and Craig 2015; Lucquin et al. 2016b; Choy et al. 2016). In the case of sample SET3, which presented a fatty acid profile coherent with animal fats, a Δ^{13}C value of – 0.3 suggested the residue would have been composed by degraded ruminant adipose fats (Fig. 4). Due to the singularity of samples SET1 and SET2, we provide a detailed discussion of their potential origin in the "Hexadecenoic acid oils" section.

La Esparragosa

Lipid quantities significantly above 5 μg g^{-1} were recovered in all five samples from La Esparragosa. The mean concentration was 183.1 μg g^{-1} and the median was 88.0 μg g^{-1}. Nonetheless, LE2 contained a significantly lower TLE compared to other vessels from the site, which may suggest its contact with fatty substances was minimal (Table 9). The widespread presence of dicarboxylic acids, keto acids and, in LE1, hydroxy acids is consistent with the post-depositional oxidation of the residues (Regert et al. 1998). Additionally, phthalate plasticisers were detected in trace amounts in all samples due to the post-excavation storage of the pottery fragments in plastic bags. Their presence did not affect the interpretation of the overall residue.

The samples were characterised by a set of even-chain and saturated long-chain free fatty acids ranging from $C_{12:0}$ to $C_{20:0}$ with $C_{16:0}$ and $C_{18:0}$ acids again the most abundant (Breu 2019). No biomarkers supporting the presence of plant oils were detected. Sample LE5 contained higher amounts of very long-chain fatty acids ($C_{20:0}$–$C_{26:0}$) than their counterparts at the site, but their origin is unclear as alkanols from hydrolysed wax esters might have been preferentially degraded. Furthermore, the VLCFA ratio (0.14) is just below the recommended 0.15 threshold to consider a wax ester input (Dolbunova et al. 2022). Dehydroabietic acid was detected in samples LE1, 2, 4 and 5; retene and didehydroabietic acid were identified in samples LE1 and 4; whilst LE1 was the only case containing 7-oxodehydroabietic acid. Apart from LE1 and LE4, with four and three distinct diterpenoid biomarkers, respectively, the low levels of conifer diterpenoids may not be associated with the use of the vessels (Breu et al. 2023). Nonetheless, the potential input of plant products in sample LE1 was reinforced by a slightly higher abundance of the odd over the even chain alkanes (CPI: 1.3, ACL: 26.9), which was amongst the highest in the study (see SI4 for the alkane distributions).

Table 8 Diagnostic ions and relative abundances of methoxy fatty acids detected in samples SET1 and SET2. See further details in SI5

Methoxy position	Diagnostic ions (m/z)	SET 1 relative abundance	SET 2 relative abundance
14-Me C16:0	73/271	0%	0%
13-Me C16:0	87/257	8%	7%
12-Me C16:0	101/243	43%	42%
11-Me C16:0	115/229	38%	37%
10-Me C16:0	129/215	7%	6%
9-Me C16:0	143/201	3%	5%
8-Me C16:0	157/187	1%	2%
7-Me C16:0	171/173	1%	2%
6-Me C16:0	185/159	0%	0%
14-Me C18:0	101/271	5%	4%
13-Me C18:0	115/257	7%	10%
12-Me C18:0	129/243	16%	13%
11-Me C18:0	143/229	18%	14%
10-Me C18:0	157/215	26%	27%
9-Me C18:0	171/201	23%	26%
8-Me C18:0	185/187	5%	6%
7-Me C18:0	199/173	0%	0%

Table 9 Detected lipid concentrations (TLE), fatty acid palmitic and stearic ratios (P/S), biomarkers and compound-specific isotopic values at La Esparragosa. Keto, mid-chain ketones. Abbreviations follow Table 5

ID	TLE ($\mu g\ g^{-1}$)	P/S	Biomarkers	$\delta\ ^{13}C_{16:0}$	$\delta\ ^{13}C_{18:0}$	$\Delta\ ^{13}C$
LE1	61	1.8	Chol. DA, DDA, 7ODA, R	−26.6	−27.6	−1.1
LE2	11	0.9	DA	-	-	-
LE3	593	1.2	APAA-C_{18} (traces), Keto, CFAM	−25.4	−24.4	1.0
LE4	162	1.4	Chol. DA, DDA, R	−29.2	−29.0	0.2
LE5	88	1.6	DA	−27.1	−28.5	−1.5

LE3, the vessel with the highest quantity of lipids at this site (593 $\mu g\ g^{-1}$), contained, in descending order of abundance, hentriacontanone, tritriacontanone and pentatriacontanone, ketones indicative of the exposure of fats to protracted heating (Evershed et al. 1995; Raven et al. 1997). Additionally, six very long-chain fatty acids with an oxo group in the ω16 and ω18 positions were also identified. Rather than resulting from the oxidation of a double bond, the possibility that they result from the ketonic decarboxylation of palmitic or stearic acid and a short-chained dicarboxylic acid (either octanedioic acid, nonanedioic acid, decanedioic acid or undecanedioic acid) (see SI5 for the proposed chemical mechanism) should be also taken into account. The presence of these dicarboxylic acids in relative abundances consistent with the detected amounts of ω16-oxotricosanoic acid, ω16-oxotetracosanoic acid, ω16-oxopentacosanoic acid, ω18-oxohexacosanoic acid, ω18-oxoheptacosanoic acid and ω18-oxooctacosanoic acid (Fig. 3) seems to support this hypothesis. Should this be the case, it would imply that the saturated fats were heated after unsaturated fatty acids had been subject to extensive oxidation. Ketonic decarboxylation is a well-known reaction shown to affect dicarboxylic acids and demonstrated to occur in analogues of archaeological vessels between lipids other than palmitic and stearic acids (Evershed et al. 1995; Raven et al. 1997). To our knowledge, the lipid fingerprint in LE3 has not been described in prehistoric pottery before and experimental research is underway to support or reject the interpretation presented here.

The range of $\delta^{13}C_{16:0}$ values from La Esparragosa varied between −25.4 and −29.7‰ whilst $\delta^{13}C_{18:0}$ values ranged between −24.4 and −29‰. In this case, the resulting $\Delta^{13}C$ values were consistent with ruminant adipose fats (LE1 and LE5) and porcine fats (LE3). In the case of LE4, the isotopic ratios could be associated with a non-ruminant adipose fat (Fig. 4).

Discussion

Hexadecenoic acid oils

Free fatty acid profiles with dominant $C_{16:1}$ signals are not unprecedented in the study of organic residues from Neolithic pottery vessels. On the Wagrian Peninsula, in north-west Germany (Weber et al. 2020), sea buckthorn (*Hippophae rhamnoides*) was considered the most likely explanation for the elevated $C_{16:1}$ concentration. Additionally, in a study of Middle Neolithic B pottery from Sardinia (Fanti et al. 2018), these residues were interpreted as probably originating from an unknown plant source.

An alternative explanation considered in both investigations was that this profile resulted from modern human sebum contamination. The Δ6 desaturase enzyme is the major desaturase found in the human sebaceous gland that converts $C_{16:0}$ to $C_{16:1\ \Delta 6}$ (sapienic acid), which is considered unique to humans (Picardo et al. 2009). Should that be the case for $C_{16:1}$ in the SET Parralejos residues (SET1 and SET2), the dicarboxylic acid range resulting from the oxidation of monounsaturated compounds should contain hexanedioic acid and methoxy acids resulting from extraction artefacts should comprise 6-methoxyhexadecanoic acid and 7-methoxyhexadecanoic acid. As detailed in the "SET Parralejos" section and in SI5, these compounds were not detected neither in SET1 nor in SET2. Furthermore, other abundant molecules in the human sebum such as squalene were absent and safeguards including the removal of exterior pottery surfaces were put into place to minimise modern sources of contamination. Therefore, the range of possible natural products which could have generated the fatty acid profiles in samples SET1 and SET2 must be considered further.

When compared to results from Sardinia and the Wagrian Peninsula, the samples from SET Parralejos present several unique features. Firstly, β-sitosterol was not present, but trace amounts of cholesterol methyl ether were detected. The recovery of similar amounts of hexadecenoic acid and hexadecanoic acid ($C_{16:1}/C_{16:0}=0.95$) is complemented by the fact that $C_{18:0}$ was four times less abundant than $C_{16:0}$. These fatty acid distributions are markedly different than those reported by Weber et al. (2020) and Fanti et al. (2018), who described P/S ratios below 3.3 and $C_{16:1}/C_{16:0}<0.50$. Although inputs of *Hippophae rhamnoides* could account for the observed SET1 and SET2 fatty acid profiles, the modern geographical distribution of this plant does not extend south of the Pyrenees (Uzquiano 2006, 2008). Moreover, there is no archaeological evidence supporting its presence during the 4th millennium BC in the south of the Iberian Peninsula (Uzquiano et al. 2021). Pollen analyses carried out in La Esparragosa (Ruiz-Zapata and Gil-García 2019) detected a landscape composed of shrubs from the Rosaceae and Ericaceae families. To the best of our knowledge, species within these families do not produce oils with fatty acid profiles similar to the ones found in SET1 and SET2.

Well-established biomarkers of marine products such as isoprenoid acids and APAAs supporting the original presence of polyunsaturated fatty acids are not present in samples SET1 and SET2 either. Another source of high $C_{16:1}$ in foodstuffs are grey mullets (*Mugilidae* sp.), a preferentially herbivorous fish (Persic et al. 2004). Indeed, $C_{16:1}$ has been reported to compose up to 19% of the glycerolipids of grey mullets, this being the second most abundant fatty acid after $C_{16:0}$. Furthermore, grey mullets present significantly reduced quantities of polyunsaturated fatty acids (PUFAs), especially the C_{20} and C_{22} moieties, and minor amounts of $C_{18:0}$ and cholesterol (Özogul and Özogul 2007; Özogul et al. 2007, 2009). This suggests that the formation of APAAs with carbon numbers higher than C_{18} could be less frequent in heated oils from this species. The composition of the fatty acid profiles and isotopic values of mugilids can vary significantly depending on its dietary sources as some species migrate into brackish (Koussoroplis et al. 2010) or freshwater environments during their life and significantly modify their diets. This might explain the compound-specific isotopic values obtained from SET2 but does not fit the results from $C_{18:0}$ in SET1. Mullet fishing is attested in the Iberian Peninsula at Palaeolithic and Mesolithic sites such as in Cueva de Nerja (Aura et al. 2001), the site of Santa Maria in the province of Alicante (Salazar-García et al. 2014), at Neolithic sites such as the Cendres cave and at Bronze age sites in the Balearic Islands such as the Cova dels Riuets (López et al. 2012; Marlasca 2013). In the case of Cádiz, sites with ichthyofaunal remains such as El Retamar do not include mullet bones (Ramos et al. 2006) but the processing of marine resources is attested at the nearby site of La Esparragosa by evidence of fish filleting in the lithic industry (Cantillo et al. 2010).

Having considered both a plant and a fish origin, the current molecular and isotopic evidence is insufficient to clearly determine the source of these relatively high concentrations of hexadecenoic acid. Nonetheless, its scarce but repeated presence in the Neolithic archaeological record suggests it was a distinct product different to the usually detected animal, plant and marine residues in pottery.

Pentacyclic triterpene methyl ethers

PTMEs have been used as biomarkers of higher plant species in several studies of lacustrine sediments (Oyo-Ita et al. 2010) and prehistoric paleosols (Courel et al. 2017). Miliacin, a PTME, has been recently reported in several analyses of organic residues from prehistoric and mediaeval pottery in both Europe and Asia (Heron et al. 2016; Ganzarolli et al. 2018; Rageot et al. 2019; Junno et al. 2020; Taché et al. 2021). Hitherto, no other PTMEs have been reported from archaeological vessels given that miliacin is the sole PTME produced by *Panicum miliaceum*. Nonetheless, the same mechanisms facilitating the mobilisation and absorption of miliacin into ceramic vessels (Heron et al. 2016) could be expected to affect other PTMEs. Although fernane and arborane compounds have been recovered from well-preserved fossils, the complete combustion of organic matter in clay during vessel firing (Reber et al. 2018) suggests that the incorporation of PTMEs to the vessel must have occurred during its use.

Pentacyclic triterpenes bearing a methyl ether functional group at C-3, which includes fernanes and arboranes, are mainly constrained to Gramineae (Ohmoto et al. 1970; Bossard et al. 2013; Courel et al. 2017). More specifically, whilst arundoin has only been reported in Gramineae, cylindrin can also be found within the Arecaceae (palms) and Rubicaceae families (Ohmoto et al. 1970; Connor and Purdie 1976; Jacob et al. 2005; Oyo-Ita et al. 2010). Hitherto, arundoin has been reported in sediments from the Guadalquivir delta, suggesting Gramineae generating this PTME can be expected in regions around the Strait of Gibraltar (Grimalt et al. 1991). In light of this evidence, it seems probable that the detected PTMEs in the Benzú cave originated from the processing of plants from the Gramineae family, as their pollen was detected in the cave sediments too (Vijande-Vila et al. 2019a, b).

Diterpenoids

Diterpenoid biomarkers for conifer resins, namely derivatives of abietic acid, have been detected in 12 samples in this study. Whilst most contained only one or two distinct diterpenoids and should thus be treated with caution (Breu et al. 2023), only three vessels, BZ2, LE4 and LE1, contained three or more compounds (retene, dehydroabietic acid, didehydroabietic acid and 7-oxodehydroabietic acid) characteristic of degraded conifer resins (Croft et al. 2018; Bondetti et al. 2020a).

The presence of these compounds in archaeological containers may respond to a multiplicity of indistinguishable activities (Rageot et al. 2016; Steele and Stern 2017) such as the collection, storage and transformation of resins or their application as a waterproofing or post-firing treatment (Drieu et al. 2020). Moreover, the presence of resinous material in firewoods can also transfer diterpenoids into the ceramic matrix (Reber et al. 2018). Only minor amounts of pine charcoal have been reported from Campo de Hockey (Uzquiano et al. 2021), and none was found at the Benzú Cave. The available data indicates that hearths were fuelled with wood from species that did not produce resins, such as *Quercus* spp., *Arbutus unedo* and *Fabaceae* spp.

(Vijande-Vila et al. 2019a). Furthermore, pollen analysis performed at La Esparragosa detected a dry Mediterranean climate where the extent of forests was limited, and pines were probably not part of the flora at the site (Ruiz-Zapata and Gil-García 2019), but a component of the vegetation cover across the territory. Therefore, inputs related to the use of pine as firewood for either cooking or firing pottery are unlikely. Alternatively, the coincidence of several biomarkers in samples BZ2, LE1 and LE4 in low quantities may be indicative of the sporadic presence of this plant exudate inside the vessels, but, in the absence of additional evidence, the detected signal could equally correspond to a surface treatment.

Archaeological relevance

Organic residue analysis of 29 pottery vessels from four Neolithic archaeological sites located across the Strait of Gibraltar successfully recovered significant quantities of lipids from 23 samples (79% of the total). This demonstrates the potential of organic residue analysis to explore the uses of Neolithic pottery in the regions neighbouring the Gibraltar strait.

Eight different inputs could be inferred from the lipid compositions of the vessels (Table 10): ruminant and non-ruminant adipose fats; ruminant dairy fats; conifer resins; Gramineae plants; a possible plant wax; hexadecenoic acid oils, and contents resulting only in negligible amounts of fats (< 5 µg g^{-1}). This is a high variety of results for such a small sample size, which includes some products hitherto unrecognised in the Iberian Neolithic. In this study, whilst vessels with negligible lipid and animal adipose residues are consistently present at all sites, plant products are more diverse and infrequent. Across southwestern Europe, animal fats are the most common lipid residues in Neolithic pottery (Debono Spiteri et al. 2016; Tarifa-Mateo et al. 2019; Manzano et al. 2019; Cubas et al. 2020; Francés-Negro et al. 2021; Breu et al. 2021b). Diterpenoids likely originating from conifer resins have been reported from the Pendimoun rock-shelter, Cueva del Toro and sites at the northeast of the Iberian Peninsula such as Can Sardurní (Tarifa-Mateo et al. 2019; Drieu et al. 2021; Breu et al. 2021b, 2023). Hexadecenoic acid oils have only been reported in two sites from Sardinia (Fanti et al. 2018) whilst plant waxes have been detected in Pendimoun, Sardinia and the Atlas (Kherbouche et al. 2016; Fanti et al. 2018; Dunne et al. 2020; Drieu et al. 2021). Interestingly, evidence for protracted heating is not widespread, only being reported in the Barcelona plain, Can Sadurní, the Gavà Mines, Pendimoun and Sardinia (Debono Spiteri et al. 2016; Fanti et al. 2018; Drieu et al. 2021; Breu et al. 2021b). Beeswax has been reported in Pendimoun, the Gavà Mines and in the Gueldaman Cave in Algeria (Kherbouche et al. 2016; Drieu et al. 2021; Tarifa-Mateo et al. 2021) but was not detected in this study. PTMEs pointing at residues from the Gramineae family have only been identified at Benzú Cave.

Table 10 Synthesis of all detected products in each of the studied archaeological sites. Protracted heating is not counted towards the total number of distinct types

Sites	BZ	CH	SET	LE	Total
Number of samples	7	10	7	5	29
Preservation rate	85%	70%	86%	80%	79%
Absence of lipids	1	3	1	1	6
Ruminant adipose fat	4	4	1	1	10
Non-ruminant adipose fat	1	1	-	2	4
Ruminant dairy fat	1	2	-	-	3
Conifer resins	1	-	-	2	3
Gramineae family	3	-	-	-	3
Hexadecenoic acid oil	-	-	2	-	2
Possible plant wax	-	1	-	-	1
Protracted heating	1	-	-	1	2
Number of distinct types	6	5	3	4	8

When pottery shapes are considered, neither cooking pots nor bowls seem to be associated with any specific residue type and, whilst carinated dishes have only been found to contain degraded animal fats from either ruminant or non-ruminant adipose tissue (Fig. 4c), further analysis could significantly revise these associations. Vessels used as grave goods mainly contained non-ruminant animal fats (Fig. 4b). Nonetheless, the presence of very long-chain alcohols in sample CH8 pointing at hydrolysed wax esters and, in L3, evidence of ketonic decarboxylation possibly affecting both saturated carboxylic and dicarboxylic acids suggests specific use-cases which could be tied with the burial ritual. So far, organic residue analyses of grave goods from the 4th millennium have only been reported from the Gavà Mines (Tarifa-Mateo et al. 2021), containing animal fats and another product, beeswax.

The end of 5th millennium cal BC and the beginning of the 4th millennium cal BC saw a significant increase in the appearance of necropolises in a wide range of territories across the Iberian Peninsula, at the same time as high quantities of labour were invested in pottery and other grave goods deposited in these highly ritualised contexts. It is still too early to know whether the contents of mortuary vessels were different from those involved in the everyday transformation of foodstuffs. Nonetheless, as more samples from grave goods such as CH8, LE3 or MIG18 (Tarifa-Mateo et al. 2021) are shown to present infrequent types of lipid residues, it will become necessary to develop new analytical programmes to assess the differences in pottery contents between domestic and funerary contexts.

Whilst the results indicate that Neolithic societies across the Strait of Gibraltar incorporated the use of pottery in a wide range of processes, it is impossible to evaluate trends and diachronic changes in uses with the present sample size and the diversity of residues. Due to the wide chronological span of the selected samples and the examined archaeological sites, this study reaffirms the potential for wider research in this region and the connections between southern European and North African Neolithic groups.

Conclusion

The study of 29 pottery samples from the sites of Benzú Cave, Campo de Hockey, SET Parralejos and La Esparragosa has recovered interpretable amounts of lipids from 79% of the vessels. When compared with other studies from the western Mediterranean and despite the extremely low sample size, pottery used around the Gibraltar Strait has yielded a diverse range of residue types, including animal fats, dairy products, plant resins some possibly from the Gramineae family and an hexadecenoic acid–dominated oil with a conflicting interpretation.

Subject to confirmation from further studies including both acidified methanol and organic solvent extractions, it seems clear that 5th and 4th millennium Neolithic communities used pottery in a wide variety of labour processes. These contained both domestic and wild products, both animals and plants, and were used both for those alive and to accompany those recently dead. The success of this first study in the region thus strengthens potential future research in the Strait and confirms that organic residue analyses can help clarify the role of Neolithic pottery in the exploitation and transformation of Holocene environments. The potential detection of plant and animal, and terrestrial and aquatic products, in a range of vessel types, as demonstrated with this preliminary dataset, will help assess how stylistically similar pottery vessels were used in both shores, thus better understanding the social dynamics developed in a unique world historical region directly connecting Africa and Europe.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s12520-023-01751-2.

Acknowledgements GC-C-IRMS analyses have been performed at the ICTA-UAB laboratories and we thank Nuria Moraleda for her support. Rebecca Stacey and Christopher Mussell at The British Museum are thanked for their support whilst performing laboratory work. We also thank the excavation teams from all four archaeological sites.

Author contribution ABB, EVV, JRM and JCD designed the project, provided samples and funded the research, ABB and PC performed the analyses, JV and CH provided analytical support, ABB wrote the main manuscript text and all authors reviewed and contributed to the manuscript.

Funding This research has been partially funded by the following projects: "Análisis interdisciplinar para el conocimiento del poblamiento humano de la Bahía de Cadiz durante la Prehistoria Reciente (VI-II milenios a.n.e.)", funded by 2014–2020 ERDF Operational Programme and the Department of Economy, Knowledge, Business and University of the Regional Government of Andalusia (Ref.: FEDER-UCA18-106917 (2020–2023)); "Analysis of prehistoric societies from the Middle Palaeolithic to the Late Neolithic at both sides of the Strait of Gibraltar: relations and contacts", funded by the State Research Agency (SRA) and the European Regional Development Fund (ERDF) (Ref.: HAR2017-87324-P. (2018–2021)); and Análisis de las sociedades prehistóricas (del Paleolítico medio al Neolítico final) en las dos orillas del estrecho de Gibraltar.Acrónimo: PALEOGIB Ministerio de Ciencia e Innovacion (Ref.: HAR2017-87324-P). Adrià Breu has been funded by a FPU grant (2014/00957) and is a member of the 2017 SGR 1302 Grup de Recerca en Arqueologia del Mediterrani i el Proper Orient (GRAMPO). Carl Heron thanks the Wellcome Trust for support (Grant Ref: 097365/Z/11/Z).

Data availability All data generated or analysed during this study are included in this published article (and its supplementary information files).

Code availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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