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Caution! Contents were hot: Novel biomarkers to detect the heating of fatty acids in residues from pottery use

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ABSTRACT

Understanding exposure of pottery vessels to fire is an important question in the agenda of researchers studying how prehistoric pottery was used to prepare food and the reasons leading to its widespread adoption across the world. In the case lipid residues from cooking, making sense of the range of biochemical compounds synthesised by the application of significant amounts of heat (i.e > 100 °C) to lipid residues can reveal different use patterns in the repertoires of the earliest pottery productions. While knowledge about the thermal degradation of fats in archaeological pottery has been available since the mid-nineties, this paper presents and describes two previously unreported biomarkers detected during ongoing research on the earliest Mediterranean farming societies: the ketonic decarboxylation of saturated fatty acids and dicarboxylic acids resulting in very long chain oxo fatty acids, and, the cyclisation of monounsaturated fatty acids yielding ω-(2-alkylcyclopentyl)alkanoic acids. Therefore, combining experimentation with the analysis of several sets of Neolithic pottery, this paper aims at updating the available data on the range of known biomarkers for lipid thermal alteration by characterising said unreported compounds and facilitating their detection in further studies.

1. Introduction

Over the past 30 years, the analysis of ancient fats trapped inside ceramic vessels has demonstrated great potential to understand the role pottery played amongst prehistoric societies, even those which used it for the first time (Craig et al., 2013; Drieu et al., 2021; Dunne et al., 2016; Heron et al., 2015; Lantos et al., 2018; Reber and Evershed, 2004; Tükerkul-Bıyık and Özbal, 2008). Its exposure to an element as transformative as fire in activities of cooking and heating food has been repeatedly considered by researchers trying to understand how and why pottery was used for the first time in distinct parts of the world (de Groot et al., 2017; Gündüzalp, 2021; Le Mière and Picon, 1999; Miyake, 2017; Özbal, 2023). Interestingly, evidence for the prolonged heating of ancient fats is widespread amongst hunter-gatherer Jōmon pottery from the 13th millennium BCE and nearby regions (Craig et al., 2013; Junno et al., 2020; Lucquin et al., 2016) but is lacking among the residues from early Holocene African hunter-gatherer vessels dating to the 8th and 7th millennia BCE (Dunne et al., 2012, 2013, 2016). The protracted heating of lipids has also been detected in 7th and 6th millennia BCE vessels from Anatolian and Northern Mesopotamian early farming sites (Breu et al., 2021a; Evershed et al., 2008b; Özbal et al., 2013). However, due to differences in the extraction methods employed and the use of specific SIM methods, it is difficult to ascertain the relevance of cooking amongst the first uses of pottery in these regions. Improving our understanding of the set of biomarkers indicating the application of significant amounts of heat (i.e > 100 °C) to lipids during vessel use can thus help reveal the existence of different cooking techniques, aid in the study of the multiple vessel shapes appearing in the repertoires of the earliest pottery

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productions or better explain the role of pottery in ritual contexts.

While knowledge about the thermally degraded fats in archaeological pottery has been available since the mid-nineties (ex: Evershed et al., 1995) and has been included in most reviews on the practice of organic residue analysis (Budja, 2014; Evershed, 2008; Evershed et al., 1999, 2002; Roffet-Salque et al., 2016), this paper presents experiments validating and archaeological case studies demonstrating two previously unreported types of thermally altered lipids as pottery residues and discuss their implications, limitations, and the analytical procedures necessary for their identification.

1.1. Heating fatty acids, a brief state of the art

An extensive literature describing the thermal degradation of lipids (ex: Nawar, 1989; Simoneit, 2002) has shown how it may yield compounds such as lactones, hydrocarbons, short chain fatty acids or methylated fatty acids amongst others. However, these may be indistinguishable from the results of oxidation and hydrolysis, which commonly affect archaeological residues, or from derivatives created during sample preparation. Thus, the range of compounds qualifying as biomarkers is significantly reduced to specific structures which have been shown to appear only after protracted heating.

The first of them are the results of the ketonic decarboxylation of saturated fatty acids in the ceramic matrix, which can result in a specific range and distribution of ketones placed in the middle of long carbon chains. These, commonly named mid-chain ketones (31K Hentriacontanone, 33K Tritriacontanone, 35K Pentatriacontanone), have been reported across multiple studies (Copley et al., 2005; Cramp et al., 2014; Drieu et al., 2021; Evershed et al., 2008b; Matlova et al., 2017; Nieuwenhuyse et al., 2015; Regert, 2011; Salque et al., 2013). First published by Evershed et al. (1995), and Raven et al. (1997) as evidence for the protractive heating of the palmitic and stearic acids, they are thought to form after repeated episodes of heating clearly above 100 °C (Raven et al., 1997). Baeten et al. (2013) showed the theoretical reconstitution of the ketone's original fatty acyl distribution, further reinforcing the correspondence between the ketone's relative abundances and those of their precursors. Cramp et al. (2012) argued that ketones found only around the rims of cooking pots would be consistent with boiling as water evaporation would keep the lower parts of vessels cooler. Correa-Ascensio and Evershed (2014) validated their recovery by the acidified methanol extraction technique and, recently, Drieu et al. (2020) have highlighted their potential formation during pottery post-firing treatments before the vessel would be effectively used. While experiments indicated that the detected range of ketones resulted from the thermal decarboxylation of all the available fatty acids, archaeological studies have majorly only reported the presence of the 31K, 33K and 35K moieties, as expected by the fact that the palmitic and stearic acids are usually the main recovered compounds in pottery residues, but potentially missing other informative by-products of ketonic decarboxylation. We argue here that elevated temperatures could also affect degraded lipid residues already present in the pottery matrix from previous vessel uses.

Furthermore, ω-(o-alkylphenyl)alkanoic acids (APAAs) are also frequently described as biomarkers of lipid protracted heating in

Table 1
List of experiments performed to validate and demonstrate the formation of several known and previously unreported heating biomarkers.

Original product	Approximate product weight (mg)	Heating time	Heating temperature (°C)	Detected heating biomarkers
Azelaic/Palmitic/Stearic acids	50/25/40	1h	200	No heating markers
Azelaic/Palmitic/Stearic acids	50/40/40	1h	250	No heating markers
Azelaic/Palmitic/Stearic acids	50/30/25	1h	300	ω18oxo-C26:0, ω16oxo-C24:0, 31K, 33K, 35K
Azelaic/Palmitic/Stearic acids	50/25/50	1h	350	No organic matter
Palmitic/Stearic	50/50	1h	300	31K, 33K, 35K
Azelaic/Stearic	50/75	1h	300	ω18oxo-C26:0, 35K
Azelaic acid/Olive oil	40/80	1h	250	ACPAA, APAA
Azelaic acid/Olive oil	25/50	1h	300	ACPAA, APAA
Olive oil	100	1h	300	ACPAA, APAA
Olive oil	100	3h	300	ACPAA, APAA
Oliva europea leaves	50	20 min	350	ACPAA, APAA

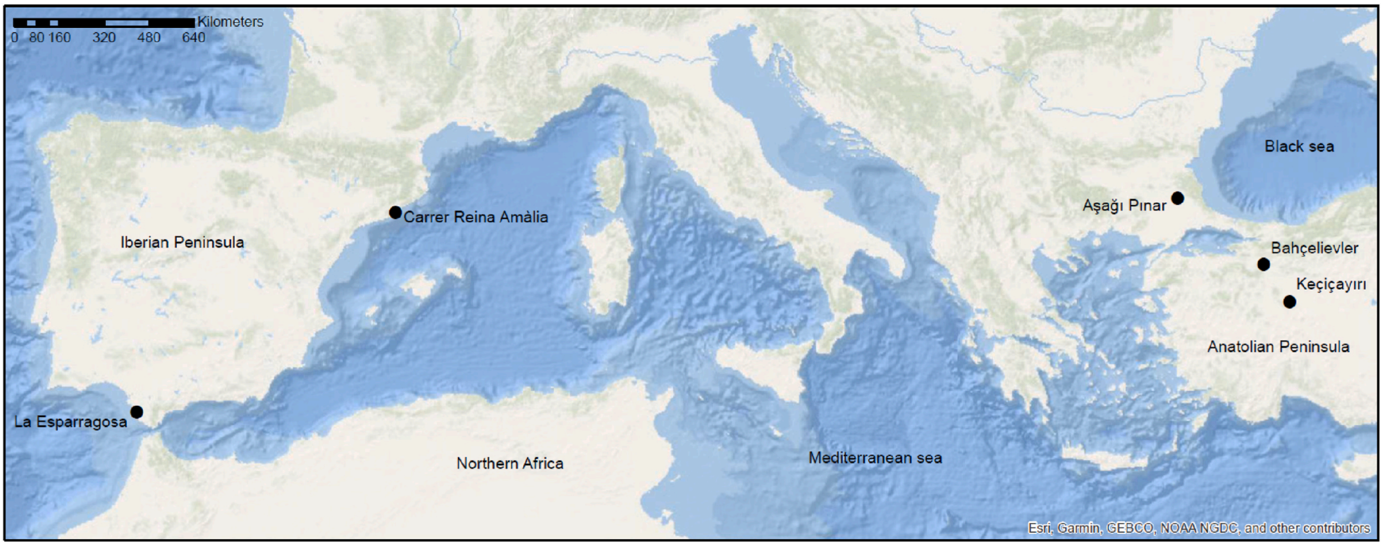


Fig. 1. Map showing the location of the sites mentioned in the text.

Table 2
Number of vessels analysed or revised for each site and number of vessels containing previously unreported heating biomarkers.

Site	Period	Sample N	Samples with oxoVLCFAs	Samples with ACPAAs	References
La Esparragosa	Late Neolithic 4th millennium	5	1	1	Breu et al., 2023
Carrer Reina Amàlia	Epicardial first half of the 5th millennium	53	2	7	Breu et al., 2021
Aşağı Pınar	Karanovo I to IV: 6th and early 5th millennia	26	0	6	This paper
Bahçelievler	Early neolithic 7th millennium	24	1	1	This paper
Keçiçayırı	Early neolithic 7th millennium	5	0	3	This paper
Total	7th to 4th millennia	113	4	18	

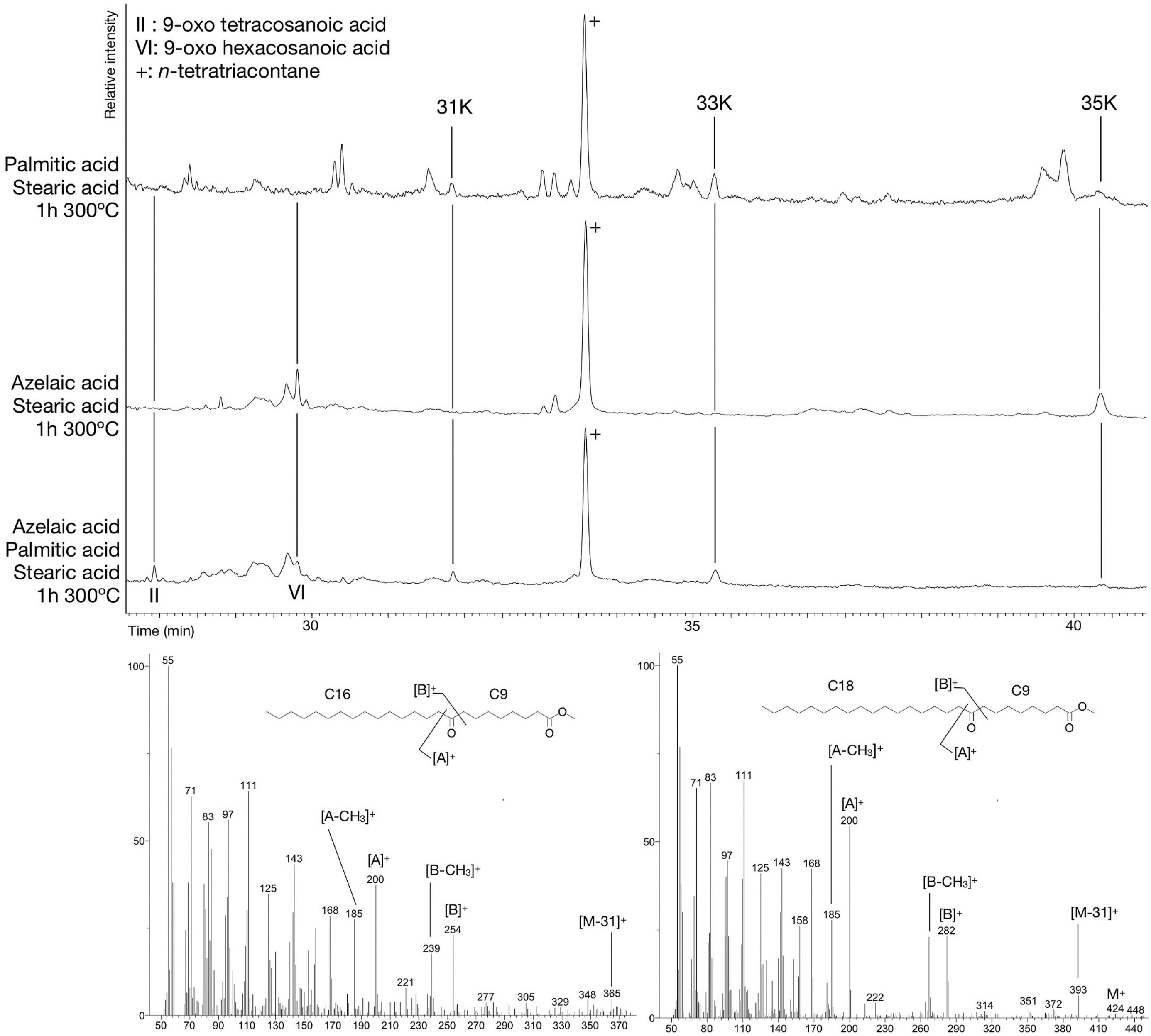


Fig. 2. GC-MS chromatograms and mass spectra of the experimental samples demonstrating the formation of 9-oxo tetracosanoic and 9-oxo hexacosanoic acids through thermal decarboxylation.

archaeological vessels. First reported by Hansel et al. (2004), APAAs were described as potential proxies for very long chain polyunsaturated fatty acids. Experimental research has revealed that they could be produced via alkali isomerization (Evershed et al., 2008a; Hansel et al., 2004) or possibly via allylic radical intermediates (Bondetti et al., 2020; Matikainen et al., 2003), indicating that the presence of a pottery matrix greatly assists their formation. The range of APAA precursors, potentially tri- di- and mono-unsaturated fatty acids, has been shown to

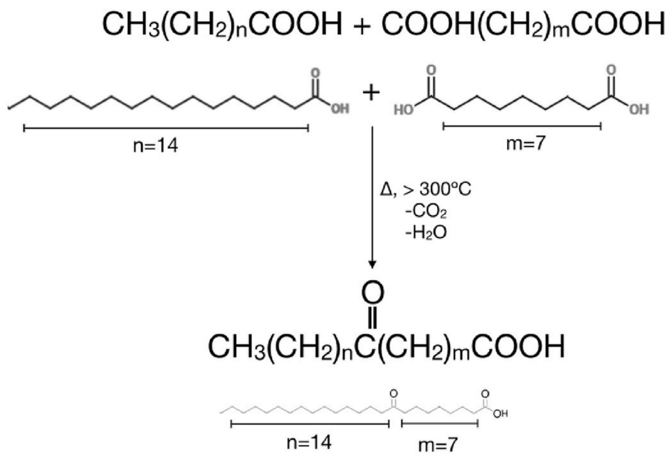


Fig. 3. Proposed formation process of very long chain oxo fatty acids.

correspond with the range and abundance of APAA isomers synthesised after heating. Recent experiments have also shown that the ratio between the E and H isomers is an effective proxy to distinguish cereals/fruits/non-leafy vegetables from animal fats and leafy plants. However, a high thermal impact could also produce the values typically found in leafy vegetables (Bondetti et al., 2020). APAAs are thought to be formed after episodes of heating pottery to temperatures clearly exceeding 100 °C (Bondetti et al., 2020; Evershed et al., 2008a), as well as when heating/boiling liquid contents (Bondetti et al., 2020). Nonetheless, in modern experiments, heating cooking oils used in the fast-food industry (Sébédio et al., 1991) have shown that, in addition to APAAs, other cyclic compounds such as cyclopentyl and cyclohexyl fatty acids can be generated (Sebedio et al., 1987a, 1987b, 1989). We argue here that these are easily formed under the same conditions creating APAAs in pottery vessels and that their presence might be widespread in ancient pottery as their precursors, monounsaturated fatty acids, are usually present in higher abundances than polyunsaturated fatty acids in certain everyday foods.

Beyond fatty acids, heating in pottery residues has also been detected through the presence of smoke condensates (Reber et al., 2018) such as polyaromatic hydrocarbons and benzenepolycarboxylic acids (BPCAs) (Admiraal et al., 2020; Wiedemeier et al., 2015) or through diterpenoid and triterpenoid by-products formed during the preparation of tars (Marchand-Geneste and Carpy, 2003; Rageot et al., 2019).

2. Materials and methods

Experimental samples to reproduce the thermal decarboxylation of degraded lipids and the formation of cyclopentyl and cyclohexyl fatty acids were prepared by mixing pure standards (Azelaic acid, Palmitic acid, Stearic acid) or commercially available natural products (Olive oil and *Oliva europaea* leaves) in 1g of ancient pottery powder inherently composed of clay and metal oxides/salts and muffled at 450 °C for 8h. A blank consisting of 1g of the same pottery powder was extracted along the experimental samples and validated the absence of lipids in the clay matrix. After homogenization, eleven samples were placed in open glass vials and heated in an oven for specific times and temperatures (Table 1). To compare with the archaeological lipids in this study, all experimental samples were extracted using an acidified methanol extraction and analysed following simmilar instruments and parameters.

Samples from five Neolithic sites at opposite ends of the Mediterranean were studied to validate the presence of novel heating biomarkers in prehistoric pottery. These included 5 vessels from the Neolithic layers in Keçiçayırı (Eskişehir, Turkey; Sari and Akyol, 2019), 24 vessels from the site of Bahçelievler (Bilecik, Turkey; Fidan, 2020; Fidan et al., 2022) and 26 vessels from layers 2 to 7 in Aşağı Pınar (Kırklareli, Turkey; Özdoğan, 2011b; Özdoğan, 2011a), which are being studied within the scope of the project AN_SÜT (Anatolian Neolithic Studies of Unique Technologies for food preparation; see supplementary materials 1 for a detailed list of relevant samples). Additionally, 5 vessels from La Esparragosa (Chiclana de la Frontera, Cádiz, Spain) (Breu, 2019a; Breu et al., 2023) and 53 lipid extracts from pottery vessels in Carrer Reina Amàlia 31–33 (Barcelona, Spain; Breu et al., 2021b), both published elsewhere, were reviewed to assess the full range of heating biomarkers present at the sites (Fig. 1 and Table 2). The recovery and analysis of lipids followed commonly applied procedures (Correa-Ascencio and Evershed, 2014; Craig et al., 2013). Briefly, after removal of the first 2 mm of the vessel's interior surface in the sampling area, 1g of pottery powder was collected and prepared using the acidified methanol procedure and analysed through Gas Chromatography-Flame Ionisation Detector and Gas Chromatography-Mass Spectrometry to identify potential biomarkers for thermal alteration either in full scan or SIM mode

Table 3
Range of potential fatty acid and dicarboxylic acid combinations, its expected resulting compounds, and diagnostic ions. All compounds have been detected in multiple archaeological samples.

	Combination		Resulting compound		Characteristic ions (*m/z*)					
	Fatty acid	Dicarboxylic acid	IUPAC name	Shorthand notation	**A-CH_3**	**A**	**B–CH_3**	**B**	**M-31**	**M+**
I	C16:0	C8:0	8-oxo tricosanoic acid	C23:0 ω16-oxo	171	186	239	254	351	385
II	C16:0	C9:0	9-oxo tetracosanoic acid	C24:0 ω16-oxo	185	200	239	254	365	396
III	C16:0	C10:0	10-oxo pentaconsanoic acid	C25:0 ω16-oxo	171	186	267	282	379	410
IV	C18:0	C8:0	8-oxo pentacosanoic acid	C25:0 ω18-oxo	199	214	239	254	379	410
V	C16:0	C11:0	11-oxo hexacosanoic acid	C26:0 ω16-oxo	185	200	267	282	393	424
VI	C18:0	C9:0	9-oxo hexacosanoic acid	C26:0 ω18-oxo	213	228	239	254	393	424
VII	C18:0	C10:0	10-oxo heptacosanoic acid	C27:0 ω18-oxo	199	214	267	282	407	438
VIII	C18:0	C11:0	11-oxo octacosanoic acid	C28:0 ω18-oxo	213	228	267	282	421	452

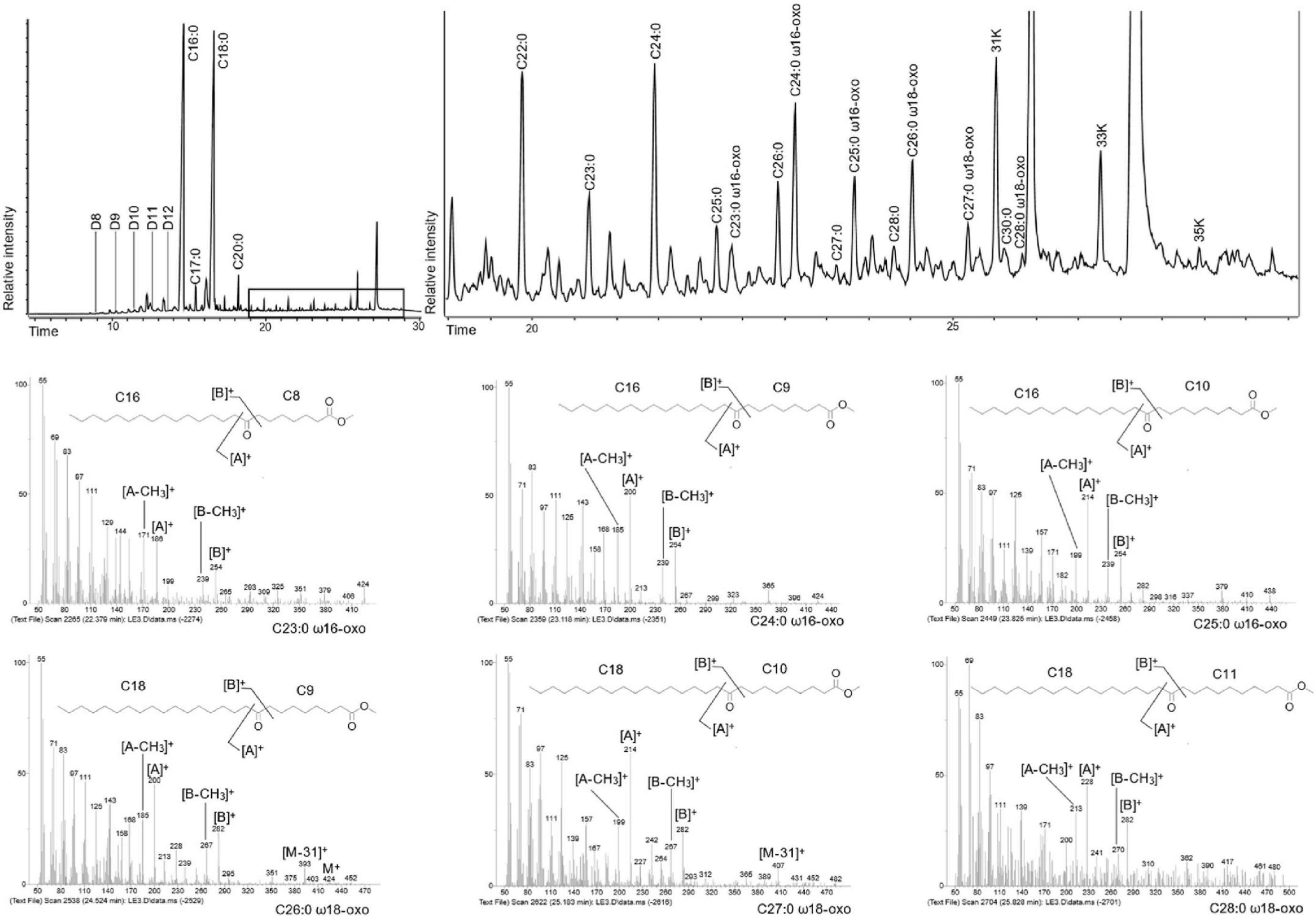


Fig. 4. GC-MS chromatograms and mass spectra of six of the eight detected oxoVLCFAs in sample LE3 from La Esparragosa. Diagnostic A and B fragments are related to their corresponding *m/z* ions. Dx: Dicarboxylic acids of x carbon chain length. Cx:0: Fatty acids of x carbon chain length. xK: mid chain ketones.

(see supplementary 2 for full analytical details). All chromatograms shown in the figures of this paper were obtained from GC-MS analyses.

3. Results and discussion: expanding the biomolecular toolset

3.1. Ketonic decarboxylation of dicarboxylic acids and saturated fatty acids

Experiments studying the formation of ketones from thermal decarboxylation and studies of ancient pottery vessels have reported that, while Hentriacontan-16-one (31K), Tritriacontan-16-one (33K) and Pentatriacontan-18-one (35K) are the most abundant resulting compounds when palmitic and stearic acid are involved, the range of synthesised ketones usually result from the combination of all the available carboxylic acids in their respective abundances (Baeten et al., 2013; Raven et al., 1997).

The experiments presented here successfully reproduced the formation of the 31K, 33K and 35K ketones only when temperatures were around 300 °C and failed to yield any organic matter at 350 °C. When only stearic acid was present in a mix with azelaic acid, the 31K and 33K ketones were not produced and a peak at retention time 27.9 min presented the mass spectra of 9-oxo hexacosanoic acid (II). In the sample where palmitic acid, stearic acid and azelaic acid were present, the characteristic 31K, 33K and 35K ketones were accompanied by II and a new peak at retention time 29.8 min identified as 9-oxo tetracosanoic acid (VI) (Fig. 2).

These results validate that, when present in sufficient abundances, dicarboxylic and saturated fatty acids can undergo thermal decarboxylation yielding very long chain oxo fatty acids (oxoVLCFAs) whose chain lengths and position of the keto group result from their precursors (Fig. 3). Given that pottery lipid extracts tend to present multiple dicarboxylic acids resulting from the oxidation of unsaturated fatty acids with varied double-bond positions, the range of oxoVLCFAs expected after protracted heating may include from 8-oxo tricosanoic acid to 11-oxo octacosanoic acid and beyond. If at least three different dicarboxylic acids were present before the heating event, this could result in the formation of VLCFAs with different oxo positions but the same chain length (Table 3, III-VI and V-VI). These isomers may elute at the same

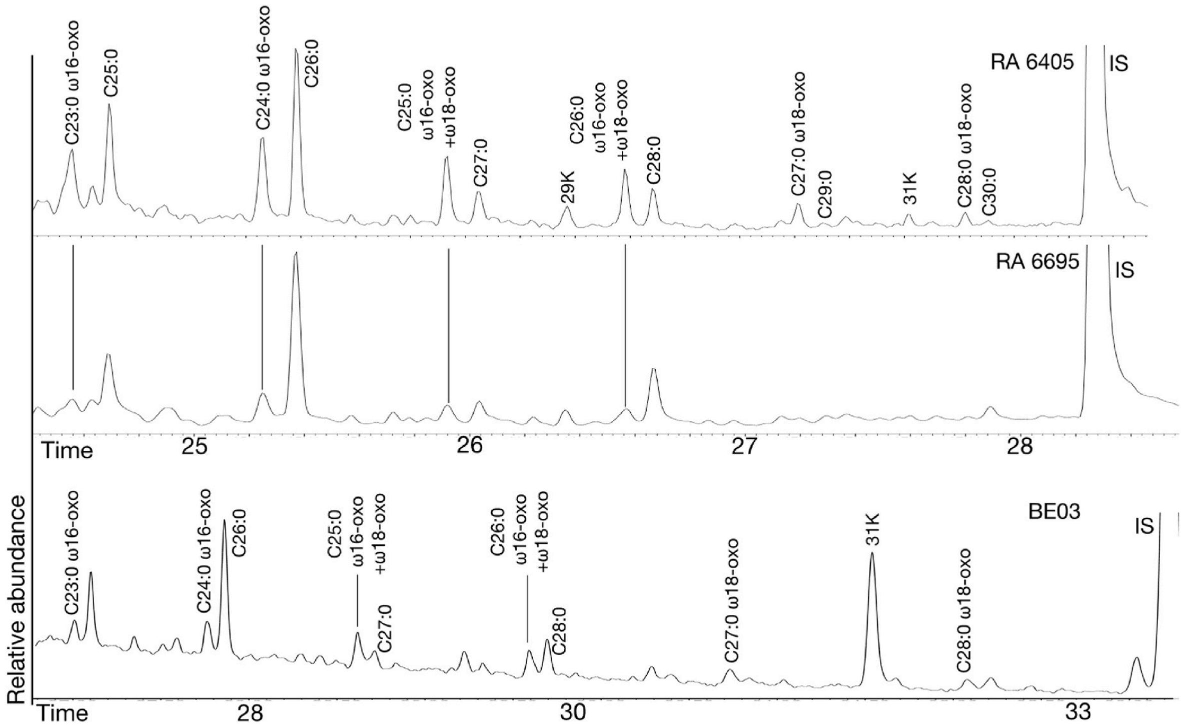


Fig. 5. GC-MS chromatograms showing the presence of oxoVLCFAs in samples from Carrer Reina Amàlia. Retention times in BE03 differ due to the use of different instrumentation (see SI2).

time when analysed using the most frequent GC-MS parameters reported in the literature for archaeological organic residue analysis, thus adding difficulty in its identification, but may be distinguished by their characteristic ions (Table 3).

To consider oxoVLCFAs a secure biomarker for thermal alteration, other potential competing causes explaining their presence in archaeological samples should be considered. Hitherto only 9-oxo hexacosanoic acid has been described as a by-product of natamycin (an antifungal medication; Cope et al., 1966) and in the roots of plants resisting fungal attack (Rozlianah et al., 2015). Other oxoVLCFAs neither seem to be abundant in nature nor commonly available in animal or plant fats. Furthermore, ketones in the chain of shorter free fatty acids could originate from the extensive oxidation of unsaturated fatty acids (Evershed et al., 1992; Passi et al., 1993; Regert, 2011). Was that the case, archaeological samples should present traces of precursor very long chain unsaturated fatty acids and other oxidation compounds such as but not necessarily hydroxy acids, hemialdehydes and dicarboxylic acids. In consequence, oxoVLCFAs should only be considered a reliable biomarker of thermal alteration when their chain lengths and oxo positions are coherent with the thermal decarboxylation of fatty acids and dicarboxylic acids, in presence of their respective saturated fatty acid precursors, and, in absence of very long chain unsaturated fatty acids.

To validate their occurrence in neolithic pottery, we present new analytical results from the site of Bahçelievler (Bilecik, Turkey) and reviewed GCMS spectra of a set of recently published vessels from the site of Carrer Reina Amàlia (Barcelona, Spain) and La Esparragosa (Chiclana de la Frontera, Spain; Breu et al., 2021b; 2023). In the latter, sample LE3 contained, in descending order of abundance, 31K, 33K and 35K ketones, indicative of the exposure of fats to protracted heating. Additionally, eight very long chain fatty acids with an oxo group in the ω16 and ω18 positions were also identified (Figs. 4 and 5, Table 2, I-VIII). Furthermore, samples 6405 and 6695 at Carrer Reina Amàlia also contained sets of oxoVLCFAs, from 8-oxo tricosanoic acid to 11-oxo octacosanoic acid (Figs. 5 and 6).

The absence of tricosenoic acid, tetracosenoic acid, pentacosenoic acid, hexacosenoic acid and heptacosenoic acid and its related hydroxy acids in these lipid extracts suggests that the detected compounds are best explained as the result of the ketonic decarboxylation of palmitic or stearic acid and short chain dicarboxylic acids; either octanedioic acid, nonanedioic acid, decanedioic acid or undecanedioic acid, which are present in the samples. Furthermore, the relative contributions of the dicarboxylic acids detected in the sample are coherent with those of the very long chain oxo acids (Fig. 6).

The formation of oxoVLCFAs directly from unsaturated and saturated fatty acids in a single heating event seems unlikely as they were neither reported by Copley et al. (2005b) in their experiments burning plant oils in replica lamps nor where detected here when heating olive oil (containing both palmitic and oleic acid) at 300 °C for 1 and 3h. Instead, we posit that unsaturated fatty acids must be subject to extensive oxidation or heating yielding dicarboxylic acids (Hammann et al., 2018) before oxoVLCFAs can be formed. Furthermore, the concentration of dicarboxylic acids in the sample must be sufficiently high to produce oxoVLCFAs in enough quantities to allow its detection after burial and degradation. This suggests that, in archaeological contexts without evidence of post-depositional fires such as La Esparragosa, Carrer Reina Amàlia and Bahçelievler, this could be indicative of the existence of two

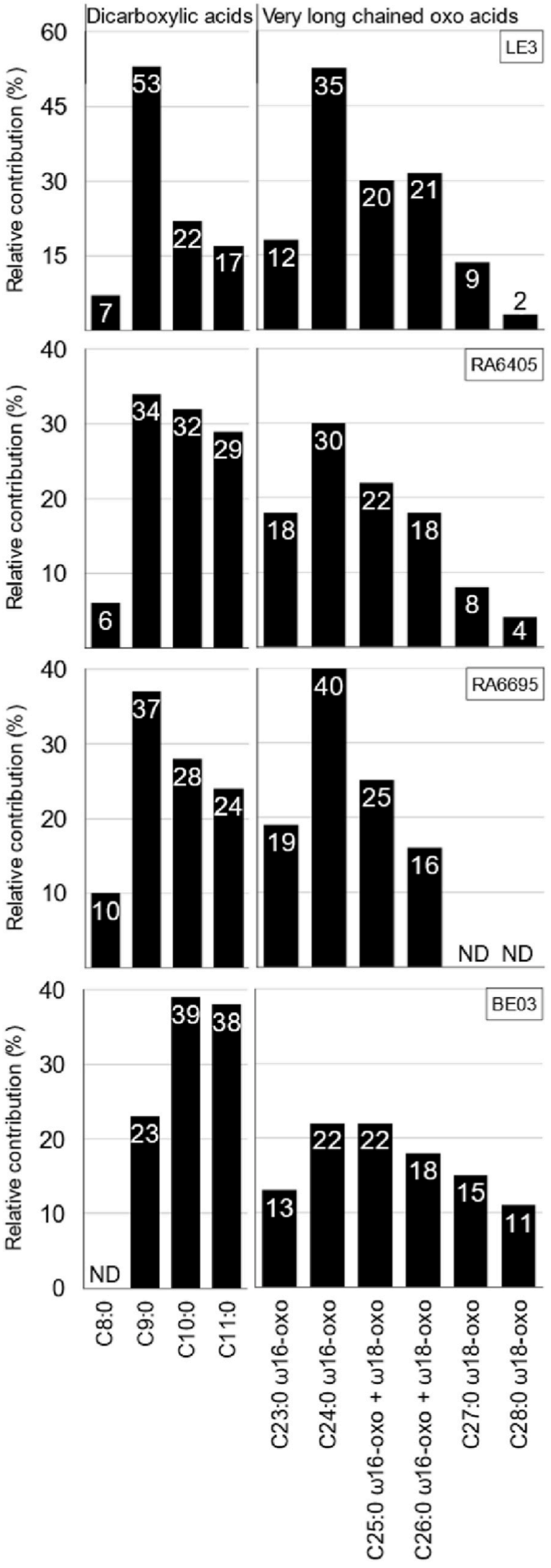


Fig. 6. A comparison of the detected relative contributions of different dicarboxylic acids and very long chained oxo fatty acids in four archaeological samples.

episodes of residue formation. The first, incorporating unsaturated fatty acids into the clay matrix and forming dicarboxylic acids, and not long after, the second, performing the ketonic decarboxylation of fatty acids and dicarboxylic acids.

The detection of oxoVLCFAs in 4 out of 84 samples from three different archaeological sites suggests that these compounds were less frequently formed than the 31K, 33K and 35K ketones (found in 7 out of 84 samples). Thus, although scarce, oxoVLCFAs may be the result of specific use cases were pottery had long use-lives or was thermally altered after a period of inactivity because of a re-use or a cleaning strategy. Dicarboxylic acids could also originate from a degraded post-firing treatment (Drieu et al., 2020), indicating that additional experimentation is needed to clarify which events may be conducive to the formation of oxoVLCFAs. The fact that LE3 is a grave good and that samples 6405 and 6695 in layer 59 from CRA are contemporary with two burials placed in the same hut seems coherent with this hypothesis. However, exploring whether vessels presenting oxoVLCFAs might have been differently used should consider additional information such as the vessel's context of deposition or its shape.

3.2. *The cyclysation of monounsaturated fatty acids to cyclopentyl alkanoic acids*

Experimental and methodological research on archaeological organic residues has previously taken into account that ω-(o-alkylphenyl)alkanoic acids (APAAs) are not the only cyclic acids formed though protracted heating (Evershed et al., 2008a; Hansel et al., 2004; Rojo and Perkins, 1987; Sébédio and Juaneda, 2007). The new experiments reported here were successful in reproducing the formation of APAAs 18 carbons long (APAA-C18) and showing that other cyclic alkanoic acids were indeed created alongside them.

This is the case of several experiments heating *Oliva europaea* leaves and olive oil and at a range of temperatures (250–300 °C) and times (1–3h), which yielded mainly methyl *trans* 4-(2-nonylcyclopentyl)-butanoic acid. At 300 °C for 3h (Fig. 7 and Table 4), the first detected ω-(2-alkylcyclopentyl)alkanoic acid (ACPAA) (I) is the most abundant and corresponds again with methyl *trans* 4-(2-nonylcyclopentyl)-butanoic acid. Peak II, showing strong m/z 148 and 220 ions could correspond with methyl 5-(2-octylcyclopentyl)pentanoic acid (Vatèla et al., 1988), however a strong m/z 164 ion suggests it could be co-eluting with an unidentified peak detected by Romero et al. (2000). According to its characteristic m/z 130, 143 and 189 ions, methyl *trans* 9-(2-butylcylocpentyl)-nonanoic acid (III) appears in co-elusion with the beginning of the oleic acid *trans* isomer peak and methyl *cis* 4-(2-nonylcyclopentyl)-butanoic acid (IV) elutes just after the oleic acid *cis* isomer. Finally, in agreement with results obtained by Romero et al. (2000), an unidentified peak containing an intense ion at m/z 223 (V) and a peak with the characteristic ions of methyl 9-(2-propylcyclohexyl) nonanoic acid (VI) (Rojo and Perkins, 1987) were also detected in our experimental sample. These results are, thus, in agreement with previous findings and validate the formation of ω-(2-alkylcyclopentyl)alkanoic acids in events analogous to cooking with prehistoric pottery.

There doesn't seem to be any competing causes potentially explaining the presence of ACPAAs in prehistoric pottery. While some tropical plant seeds have been shown to contain traces of ω-cyclopentyl fatty acids 16 and 18 carbons long (Christie et al., 1989), none of the compounds detected here presented the cyclopentyl ring at the end of the carbon chain. Alternatively, experimental research (Sebedio et al., 1989; Sebedio and Grandgirard, 1989) has demonstrated that ACPAAs are a by-product of frying oil, resulting from chemical reactions similar to those of ω-(o-alkylphenyl)alkanoic acids. To explain their formation, Dobson et al. (1996a, 1996b) proposed that ACPAAs could be formed via radical intermediates and 1.5 or 1.6 hydrogen shifts (Fig. 8). For cyclopentyls, this hypothesised mechanism would yield *cis* and *trans* isomers with rings in the 5–9 and 10–14 positions, which is coherent with compounds I, III, IV and VI. Furthermore, experiments focusing on

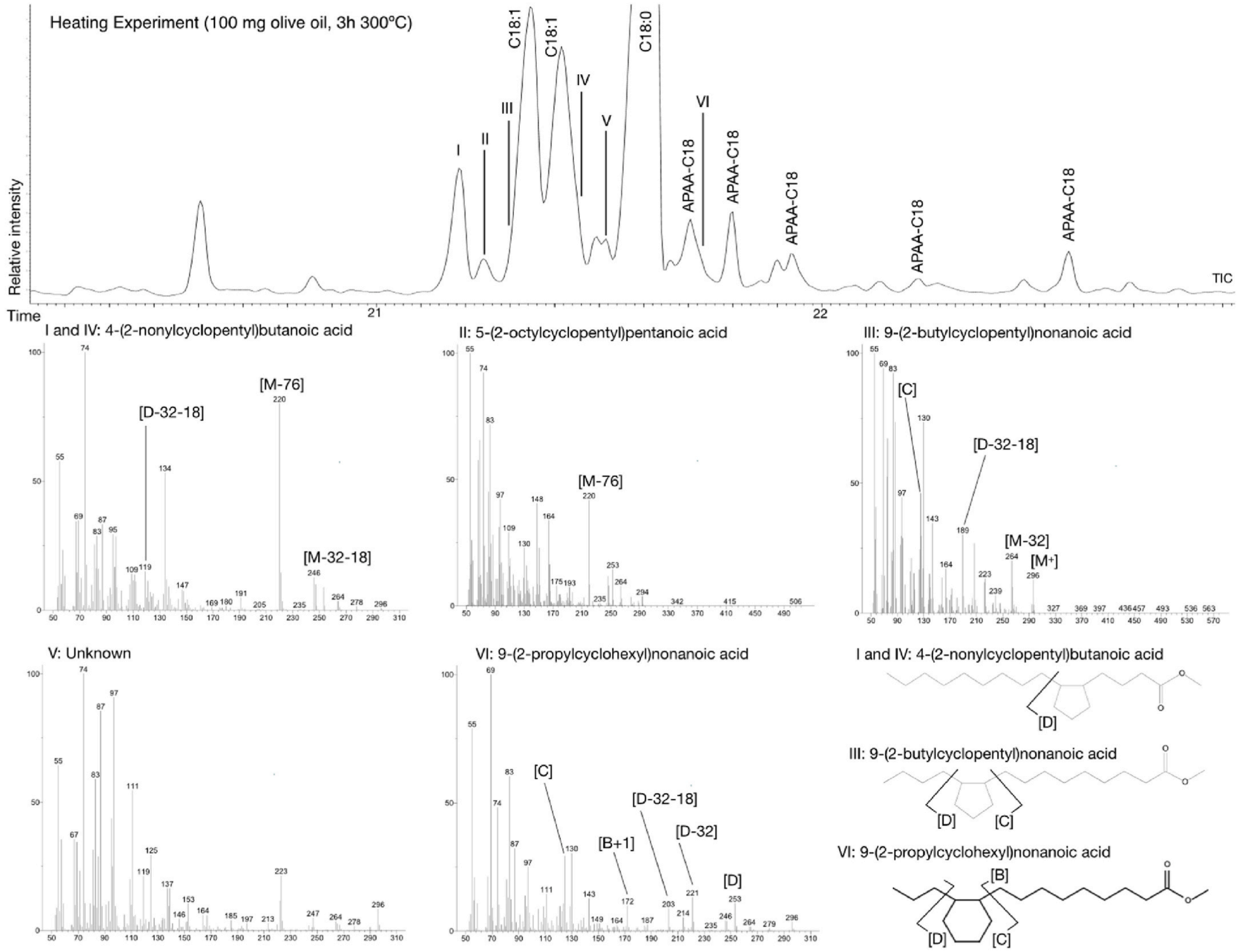


Fig. 7. GC-MS chromatograms and mass spectra of the six detected cyclopentyl and cyclohexyl structures in a heating experiment with olive oil in a pottery matrix at 300 °C for 3h. M-76 is attributed to a rearrangement ion with successive loss of CH3OH and CH2=CHOH by Sebedio et al. (1989). In spectrum III, the relative abundances of ions M+ and M-32 are not reliable due to co-elusion with C18:1.

Table 4
Characteristic ions and references to the published mass spectra of the 6 detected compounds. All were identified as their methyl esters.

	IUPAC name	Characteristic ions	References
I	*trans* 4-(2-nonylcyclopentyl)-butanoic acid	134, 220, 246	Sebedio et al., 1989
II	5-(2-octylcyclopentyl)pentanoic acid	148, 220, 246	Vatèla et al. (1988)
III	*trans* 9-(2-butylcylocpentyl)-nonanoic acid	130, 189, 296	Sebedio et al., 1989
IV	*cis* 4-(2-nonylcyclopentyl)-butanoic acid	134, 220, 246	Sebedio et al., 1989
V	Unidentified	223	Romero et al. (2000)
VI	9-(2-propylcyclohexyl)nonanoic acid	125, 203, 221, 256	Rojo and Perkins (1987)

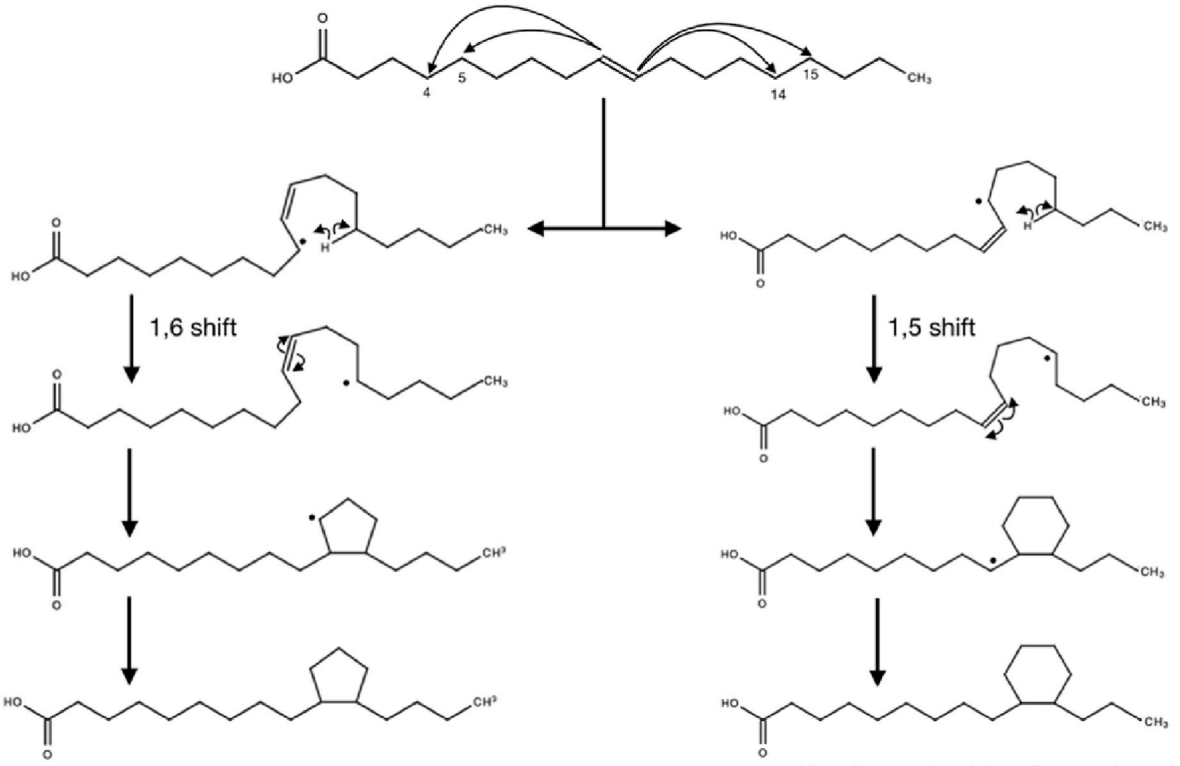
oils with high monounsaturated acids (Romero et al., 2000, 2003, 2006) demonstrated that cyclopentyl structures appeared in larger amounts than their cyclohexyl counterparts. Given that APAAs are commonly identified as pottery lipid residues, this suggests that, when present, cyclopentyl structures should be detectable too.

After study of ACPAA's characteristic ions, sample AP167B from Aşağı Pınar and sample 272-1 from Keçiayırı (Fig. 9) were shown to contain several cyclopentyl fatty acids dominated by methyl *trans* 4-(2-nonylcyclopentyl)butanoic acid (I) with minor amounts of other cyclic fatty acids (II, III, VI)(Fig. 7). However, these were not visible in the total ion chromatograms when operating the GC-MS in the standard parameters for organic residue analysis as their retention times are similar to more abundant compounds such as phytanic acid, octadecenoic and octadecanoic acids. To mitigate potential difficulties to detect ACPAAs in additional samples, SIM analyses were used to target the most abundant ACPAA (I) with ions 134, 220 and 246. In a total of 31 vessels from the two aforementioned sites, 6 out of 26 (23%) and 3 out of 5 (60%) samples respectively were found to contain ACPAAs. This is coherent with previous research on Neolithic pottery in the strait of Gibraltar (Breu et al., 2023) and in the northeast of the Iberian Peninsula (Breu, 2019b), also reporting their presence.

Notably distinct from other biomarkers for thermal alteration, the formation of ACPAAs through radical intermediates has not been shown to be catalysed by the presence of inorganic salts or a clay matrix (Dobson et al., 1996b), a point which may merit further research. Therefore, they could have been formed before their absorption into the vessel matrix and thus be the result of the protracted heating of fats elsewhere. In the absence of other biomarkers for elevated temperatures, their detection should, thus, be interpreted with caution as they do provide unequivocal evidence of the practice of food preparation with heat, but this one might have not involved pottery.

Although most of the vessels hitherto reported present both ACPAAs and APAAs, cyclopentyl structures have also been detected in absence of other heating biomarkers in sample AP112 from Aşağı Pınar and samples 9734 and 5531 from Carrer Reina Amàlia. These could be best explained as the result of heating products where monounsaturated fatty acids dominate over their polyunsaturated counterparts, such as animal fats and some plant oils. Their higher yield of cyclopentyl structures over other ring types could explain the sole identification of ACPAAs and suggests that evaluating their presence is indispensable to fully assess the number of vessels containing heat-altered fats in any archaeological pottery assemblage.

Finally, ACPAAs and oxoVLCFAs are not without limitations (Table 5). A clear understanding of the archaeological context surrounding the analysed pottery is necessary to consider potential post-depositional fires which could have formed these heating biomarkers after the vessel had been discarded. Furthermore, the temperatures achieved by pottery in reproduction experiments may not correspond with the actual temperatures achieved by the contents. The ω-(o-



III: 9-(2-butylcyclopentyl)nonanoic acid

VI: 9-(2-propylcyclohexyl)nonanoic acid

Fig. 8. Mechanism proposed in the literature for the formation of cyclopentyl and cyclohexyl rings from *cis* and *trans* monounsaturated fatty acids (only the *trans* isomer is depicted in the figure). Adapted from Dobson et al., 1996a, Dobson et al., 1996b and Destaillats and Angers (2005).

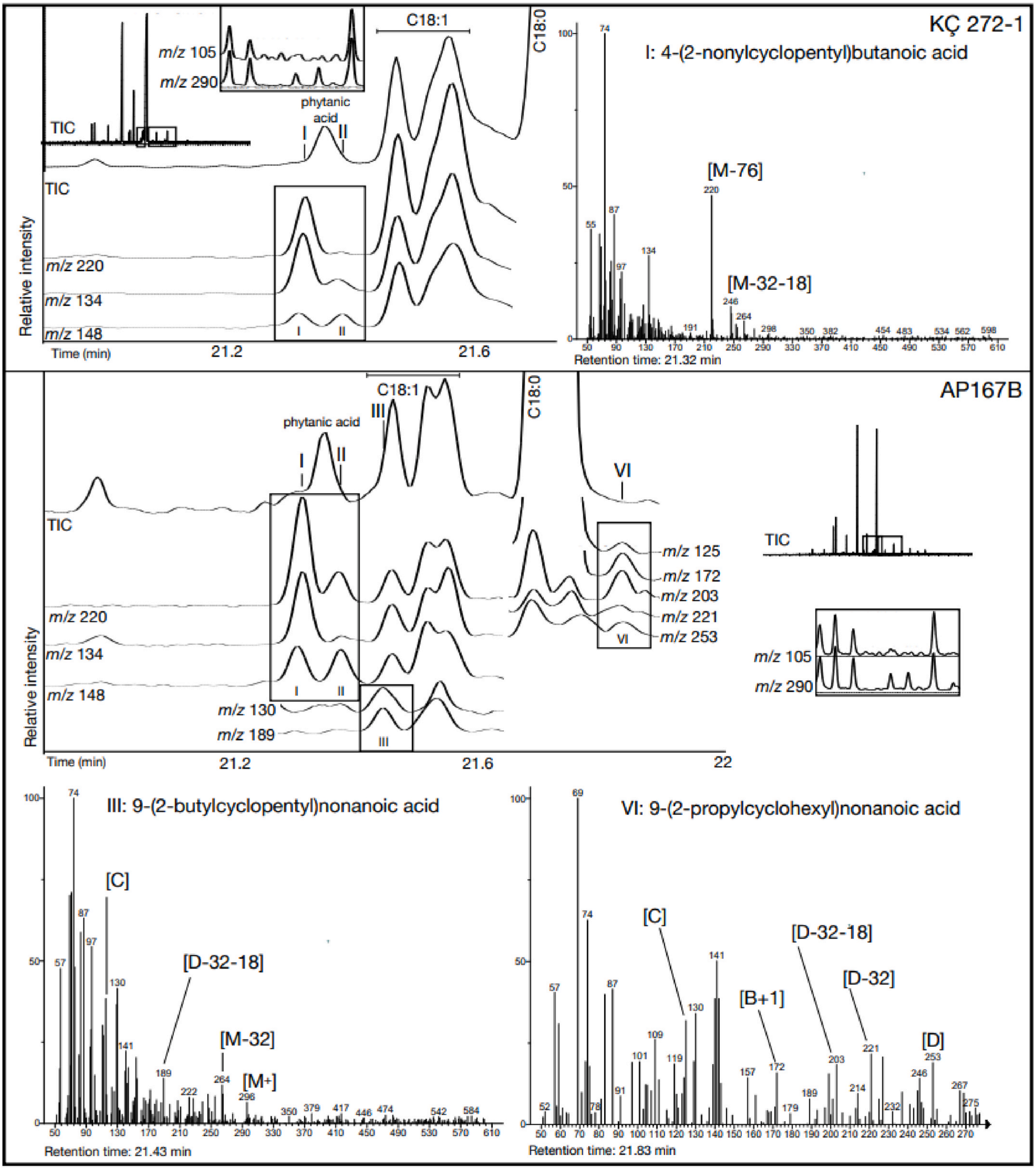


Fig. 9. Total ion chromatograms (TIC) and extracted ion chromatograms (EIC) from GC-MS analyses showing the presence of APAAs (*m/z* 105, 290), cyclopentyl (I: 134, 220; II: 148; III: 130, 189) and cyclohexyl (VI: 125, 172, 203, 221, 253) structures. EIC are not to scale.

alkylphenyl)alkanoic acids have been shown to appear from boiling (Bondetti et al., 2020) and therefore this should also be expected for ω-(2-alkylcyclopentyl)alkanoic acids. Compounds formed at higher temperatures also seem to be less frequent. In Aşağı Pınar, only one case of ketones contrasts with 6 cases of ACPAAs and in Keçiçayırı none of the former were detected while 60% of the samples contained cyclic fatty acids. In Carrer Reina Amàlia, 7 samples presented ACPAAs while only 2 had ketones. Given that the 31K, 33K and 35K ketones and oxoVLCFAs are only formed at around 300 °C, which falls outside of the most common cooking temperature ranges, their formation could be limited to specific cases, including infrequent food preparation practices, cooking accidents or the reuse of vessels for other activities where high

Table 5
Summary of compounds arising from the protracted heating of lipid residues in pottery.

Compounds	Conditions of experimental reproduction	Precursors	Potential considerations	References
Hentiacontan-16-one (31K) Tritriacontan-16-one (33K) Pentatriacontan-18-one (35K)	>350 °C for 10–20s and 300 °C for 1h	Saturated fatty acids (mainly palmitic and stearic acid)	Observed in the interior surfaces of modern vessels with organic post-firing treatments	Evershed et al., (1995); Raven et al., (1997); Drieu et al., (2020); This paper
Very long chain oxo fatty acids	300 °C for 1h	Palmitic acid, stearic acid and C8 to C11 dicarboxylic acids	Might indicate two episodes of use or exceptionally long pottery live	This paper
ω-(o-alkylphenyl) alkanoic acids	270 °C for 1h and 200 °C for 5h	Mono and polyunsaturated fatty acids	E/H isomer ratios are indicative of their origin and their thermal impact	Hansel et al., (2004); Evershed et al., 2008a; Bondetti et al., (2020)
ω-(2-alkylcyclopentyl) alkanoic acids	250 °C for 1h and 300 °C for 1–3h	Monounsaturated fatty acids	Thermal alteration need not occur inside the pottery vessel	Vatèla et al., (1988); This paper

temperatures are involved, amongst others.

4. Conclusion

The detection of lipids formed after protracted heating is a powerful tool for archaeologists to assess differences in pottery use beyond the taxonomic classification of the vessel's surviving fatty residues. In this paper, the ketonic decarboxylation of saturated fatty acids is suggested to also involve dicarboxylic acids when vessels had exceptionally long lives or were reused after a period of inactivity. This coincides with their first detection amongst vessels placed in ritual contexts such as La Esparragosa, although more analyses will be needed before this can be considered a strong association.

Supported by experimentation, the cyclisation products of monounsaturated fatty acids, favouring the formation of cyclopentyl over cyclohexyl or phenyl structures, may be better differentiated from the thermal alteration of products rich in polyunsaturated fats such as marine products and some plant oils. This opens new opportunities to better detect the thermal alteration of animal fats and highly monounsaturated plant oils, products which have been shown to be highly intertwined with pottery use by the first farmers of Europe and Southwestern Asia. Further determining the processes forming these compounds and links to their original food groups will require more experimentation and improved chromatographic techniques.

In conclusion, understanding the consequences of the prolonged heating of pottery organic residues along with its caveats and limitations will only help clarify how pottery was used and how its contents were transformed and preserved, potentially shedding new light into the unique cooking technologies available to societies adopting pottery for the first time and beyond.

5. Author contributions (CRediT author statement)

Adrià Breu: Conceptualisation, Methodology, Formal analysis, Investigation, Writing – Original draft, Writing – Review and Editing, Funding acquisition. **Ayla Türkekul**: Methodology, Validation, Investigation, Writing – Review and Editing. **Şemsettin Akyol**: Resources, Writing – Review and Editing. **Anna Bach-Gómez**: Resources, Writing – Review and Editing. **Cafer Çakal**: Validation, Resources, Writing – Review and Editing. **Mehmet Fırat İlker**: Resources, Writing – Review and Editing. **Deniz Sarı**: Resources, Writing – Review and Editing. **Savaş Sarıaltun**: Resources, Writing – Review and Editing. **Eduardo Vijande-Vila**: Resources, Writing – Review and Editing. **Rana Özbal**: Conceptualisation, Resources, Writing – Review and Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

All the authors declare that they have no established conflicting financial interests or personal relationships that may have influenced the research presented in the paper with the following title: Caution! Contents were hot: novel biomarkers to detect the heating of fatty acids in residues from pottery use.

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Appendix A. Supplementary data

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References

Admiraal, M., Lucquin, A., Drieu, L., Casale, S., Jordan, P.D., Craig, O.E., 2020. Leftovers: the presence of manufacture-derived aquatic lipids in Alaskan pottery. Archaeometry 62, 346–361. https://doi.org/10.1111/arcm.12515.

Baeten, J., Jervis, B., De Vos, D., Waelkens, M., 2013. Molecular evidence for the mixing of meat, fish and vegetables in anglo-saxon coarseware from hamwic, UK. Archaeometry 55, 1150–1174. https://doi.org/10.1111/j.1475-4754.2012.00731.x.

Bondetti, M., Scott, E., Courel, B., Lucquin, A., Shoda, S., Lundy, J., Labra-Odde, C., Drieu, L., Craig, O.E., 2020. Investigating the formation and diagnostic value of ω-(o-alkylphenyl)alkanoic acids in ancient pottery. Archaeometry. https://doi.org/10.1111/arcm.12631.

Breu, A., 2019a. Capítulo XVIII. Residuos orgánicos en cerámica de contexto funerario y doméstico. Resultados preliminares. In: Vijande, E., Ramos-Muñoz, J., Fernández Sánchez, D., Cantillo Duarte, J.J., Pérez Rodríguez, M. (Eds.), La Esparragosa (Chiclana de La Frontera, Cádiz). Un Campo de Silos Neolítico Del IV Milenio ANE. Cádiz, pp. 201–207.

Breu, A., 2019b. Earliest pottery uses in north-eastern Iberia. In: Organic Residue Analysis on Vessels from the First Farmers and Herders. Autonomous University of Barcelona.

Breu, A., Gómez-Bach, A., Faura, J.M., Rosell, A., Molist, M.A., 2021a. Animal residues from the seventh and sixth millennia BCE pottery at tell halula. In: Neolithic Pottery from the Near East: Production, Distribution and Use. AKMED. Koç University, pp. 199–212.

Breu, A., Gómez-Bach, A., Heron, C., Rosell-Melé, A., Molist, M., 2021b. Variation in pottery use across the early neolithic in the Barcelona plain. Archaeol. Anthropol. Sci. 13, 53. https://doi.org/10.1007/s12520-021-01296-2.

Breu, A., Vijande-Vila, E., Cantillo-Duarte, J., Comes, P., Heron, C., Villanueva, J., Ramos-Muñóz, J., 2023. Diversified pottery use across 5th and 4th millennium cal BC Neolithic coastal communities along the Strait of Gibraltar. Archaeol. Anthropol. Sci. 15, 51. https://doi.org/10.1007/s12520-023-01751-2.

Budja, M., 2014. Neolithic pottery and the biomolecular archaeology of lipids. Doc. Praehist. 41, 196. https://doi.org/10.4312/dp.41.11.

Christie, W.W., Brechany, E.Y., Shukla, V.K.S., 1989. Analysis of seed oils containing cyclopentenyl fatty acids by combined chromatographic procedures. Lipids 24, 116–120. https://doi.org/10.1007/BF02535247.

Cope, A.C., Axen, U., Burrows, E.P., 1966. Rimocidin. II. Oxygenation pattern of the aglycone. J. Am. Chem. Soc. 88, 4221–4227.

Copley, M.S., Berstan, R., Dudd, S.N., Aillaud, S., Mukherjee, A.J., Straker, V., Payne, S., Evershed, R.P., 2005a. Processing of milk products in pottery vessels through British prehistory. Antiquity 79, 895–908.

Copley, M.S., Bland, H.A., Rose, P., Horton, M.C.M., Evershed, R.P., 2005b. Gas chromatographic, mass spectrometric and stable carbon isotopic investigations of organic residues of plant oils and animal fats employed as illuminants in archaeological lamps from Egypt. Analyst 130, 860–871. https://doi.org/10.1039/B500403A.

Correa-Ascencio, M., Evershed, R.P., 2014. High throughput screening of organic residues in archaeological potsherds using direct acidified methanol extraction. Anal. Methods 6, 1330–1340. https://doi.org/10.1039/C3AY41678J.

Craig, O.E., Saul, H., Lucquin, A., Nishida, Y., Taché, K., Clarke, L., Thompson, A., Altoft, D.T., Uchiyama, J., Ajimoto, M., Gibbs, K., Isaksson, S., Heron, C.P., Jordan, P., 2013. Earliest evidence for the use of pottery. Nature 496, 351–354. https://doi.org/10.1038/nature12109 nature/journal/v496/n7445/abs/nature12109.html#supplementary-information.

Cramp, L.J.E., Evershed, R.P., Eckardt, H., 2012. Are you what you grind? A comparison of organic residues from ceramics at two Roman British sites. In: Schruefer-Kolb, I. (Ed.), Journal of Roman Archaeology Supplementary Series. Vol 91. More than Just Numbers? the Role of Science in Roman Archaeology. Portsmouth, Rhode Island, pp. 93–110.

Cramp, L.J.E., Jones, J., Sheridan, A., Smyth, J., Whelton, H.L., Mulville, J., Sharples, N., Evershed, R.P., E, C.L.J., Jennifer, J., Alison, S., Jessica, S., Helen, W., Jacqui, M., Niall, S., P, E.R., 2014. Immediate replacement of fishing with dairying by the earliest farmers of the Northeast Atlantic archipelagos. Proc. R. Soc. B Biol. Sci. 281, 20132372 https://doi.org/10.1098/rspb.2013.2372.

de Groot, B., Thissen, L., Özbal, R., Gerritsen, F., 2017. Clay preparation and function of the first ceramics in north-west Anatolia: a case study from Neolithic Barcın Höyük. J. Archaeol. Sci. Reports 16, 542–552. https://doi.org/10.1016/j.jasrep.2017.06.028.

Destaillats, F., Angers, P., 2005. On the mechanisms of cyclic and bicyclic fatty acid monomer formation in heated edible oils. Eur. J. Lipid Sci. Technol. 107, 767–772. https://doi.org/10.1002/ejlt.200501159.

Dobson, G, Christie, WW, Louis, J, 1996a. Monocyclic saturated fatty acids formed from oleic acid in heated sunflower oils. Chem Phys Lipids 82, 101–110.

Dobson, G., Christie, W.W., Sebedio, J.L., 1996b. The nature of cyclic fatty acids formed in heated vegetable oils. Grasas Aceites 47, 26–33.

Drieu, L., Lepère, C., Regert, M., 2020. The missing step of pottery chaîne opératoire: considering post-firing treatments on ceramic vessels using macro- and microscopic observation and molecular analysis. J. Archaeol. Method Theor 27, 302–326. https://doi.org/10.1007/s10816-019-09428-8.

Drieu, L., Lucquin, A., Cassard, L., Sorin, S., Craig, O.E., Binder, D., Regert, M., 2021. A Neolithic without dairy? Chemical evidence from the content of ceramics from the Pendimoun rock-shelter (Castellar, France, 5750–5150 BCE). J. Archaeol. Sci. Reports 35. https://doi.org/10.1016/j.jasrep.2020.102682.

Dunne, J., Evershed, R.P., Cramp, L., Bruni, S., Biagetti, S., Di Lernia, S., 2013. The beginnings of dairying as practised by pastoralists in 'green' Saharan Africa in the 5th millennium BC. Doc. Praehist. 40, 118–130. https://doi.org/10.4312/dp.40.10.

Dunne, J., Evershed, R.P., Salque, M., Cramp, L.J.E., Bruni, S., Ryan, K., Biagetti, S., Di Lernia, S., 2012. First dairying in green Saharan Africa in the fifth millennium bc. Nature 486, 390–394 v486/n7403/abs/nature11186.html#supplementary-information.

Dunne, J., Mercuri, A.M., Evershed, R.P., Bruni, S., di Lernia, S., 2016. Earliest direct evidence of plant processing in prehistoric Saharan pottery. Nat. Plants 3, 16194. https://doi.org/10.1038/nplants.2016.194.

Evershed, R.P., 2008. Organic residue analysis in archaeology: the archaeological biomarker revolution. Archaeometry 50, 895–924. https://doi.org/10.1111/j.1475-4754.2008.00446.x.

Evershed, R.P., Copley, M.S., Dickson, L., Hansel, F.A., 2008a. Experimental evidence for the processing of marine animal products and other commodities containing polyunsaturated fatty acids in pottery vessels. Archaeometry 50, 101–113. https://doi.org/10.1111/j.1475-4754.2007.00368.x.

Evershed, R.P., Dudd, S.N., Charters, S., Mottram, H., Stott, A.W., Raven, A., van Bergen, P.F., Bland, H.A., 1999. Lipids as carriers of anthropogenic signals from prehistory. Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci. 354, 19–31. https://doi.org/10.1098/rstb.1999.0357.

Evershed, R.P., Dudd, S.N., Copley, M.S., Berstan, R., Stott, A.W., Mottram, H.R., Buckley, S.A., Crossman, Z., 2002. Chemistry of archaeological animal fats. Acc. Chem. Res. 35, 660–668. https://doi.org/10.1021/ar000200f.

Evershed, R.P., Heron, C., Charters, S., Goad, L.J., 1992. The survival of food residues: new methdos of analysis, interpretation and application. Proc. Br. Acad. 77, 187–208.

Evershed, Richard P., Payne, S., Sherratt, A.G., Copley, M.S., Coolidge, J., Urem-Kotsu, D., Kotsakis, K., Özdoğan, M., Özdoğan, A.E., Nieuwenhuyse, O., Akkermans, P.M.M.G., Bailey, D., Andeescu, R.-R., Campbell, S., Farid, S., Hodder, I., Yalman, N., Özbaşaran, M., Bıçakcı, E., Garfinkel, Y., Levy, T., Burton, M.M., 2008b. Earliest date for milk use in the Near East and southeastern Europe linked to cattle herding. Nature 455, 528–531. https://doi.org/10.1038/nature07180.

Evershed, R.P., Stott, A.W., Raven, A., Dudd, S.N., Charters, S., Leyden, A., 1995. Formation of long-chain ketones in ancient pottery vessels by pyrolysis of acyl lipids. Tetrahedron Lett. 36, 8875–8878. https://doi.org/10.1016/0040-4039(95)01844-8.

Fidan, E., 2020. Fikirtepe kültürü ve öncesi: bilecik bahçelievler kurtarma kazısı'nın. Arkeol. ve Sanat 29–38.

Fidan, E., Sarıaltun, S., Doğan, T., Seçer-Fidan, S., İlkmen, E., 2022. Radiocarbon dating evidence and cultural sequencing in chronology of neolithic settlement at bilecik-bahçelievler from northwest anatolia. Mediterr. Archaeol. Archaeom. 22, 133–148. https://doi.org/10.5281/zenodo.7306042.

Gündüzalp, S., 2021. Beginning and development of pottery use in upper mesopotamia in the light of sumaki höyük data. Neo-lithics 1/2021, 29–31. https://doi.org/10.48632/nl.2021.1.84912.

Hammann, S., Cramp, L.J.E., Whittle, M., Evershed, R.P., 2018. Cholesterol degradation in archaeological pottery mediated by fired clay and fatty acid pro-oxidants. Tetrahedron Lett. 59, 4401–4404. https://doi.org/10.1016/j.tetlet.2018.10.071.

Hansel, F.A., Copley, M.S., Madureira, L.A.S., Evershed, R.P., 2004. Thermally produced ω-(o-alkylphenyl)alkanoic acids provide evidence for the processing of marine products in archaeological pottery vessels. Tetrahedron Lett. 45, 2999–3002. https://doi.org/10.1016/j.tetlet.2004.01.111.

Heron, C., Craig, O.E., Luquin, A., Steele, V.J., Thompson, A., Piličiauskas, G., 2015. Cooking fish and drinking milk? Patterns in pottery use in the southeastern Baltic, 3300–2400 cal BC. J. Archaeol. Sci. 63, 33–43. https://doi.org/10.1016/j.jas.2015.08.002.

Junno, A., Isaksson, S., Hirasawa, Y., Kato, H., Jordan, P.D., 2020. Evidence of increasing functional differentiation in pottery use among Late Holocene maritime foragers in northern Japan. Archaeol. Res. Asia 22, 100194. https://doi.org/10.1016/j.ara.2020.100194.

Lantos, I., Palamarczuk, V., Orgaz, M., Ratto, N., Maier, M., 2018. Exploring the culinary uses of santa maría and belén painted vessels from the late intermediate period in catamarca, Argentina. J. Archaeol. Sci. Reports 18, 660–667. https://doi.org/10.1016/j.jasrep.2017.03.019.

Le Mière, M., Picon, M., 1999. Les débuts de la céramique au Proche-Orient. Paleorient 24, 5–26.

Lucquin, A., Gibbs, K., Uchiyama, J., Saul, H., Ajimoto, M., Eley, Y., Radini, A., Heron, C. P., Shoda, S., Nishida, Y., Lundy, J., Jordan, P., Isaksson, S., Craig, O.E., 2016. Ancient lipids document continuity in the use of early hunter–gatherer pottery through 9,000 years of Japanese prehistory. Proc. Natl. Acad. Sci. USA 113, 3991–3996. https://doi.org/10.1073/pnas.1522908113.

Marchand-Geneste, N., Carpy, A., 2003. Theoretical study of the thermal degradation pathways of abietane skeleton diterpenoids: aromatization to retene. J. Mol. Struct. Theochem. 635, 55–82. https://doi.org/10.1016/S0166-1280(03)00401-9.

Matikainen, J., Kaltia, S., Ala-Peijari, M., Petit-Gras, N., Harju, K., Heikkilä, J., Yksjärvi, R., Hase, T., 2003. A study of 1,5-hydrogen shift and cyclization reactions of an alkali isomerized methyl linolenoate. Tetrahedron 59, 567–573. https://doi.org/10.1016/S0040-4020(02)01513-2.

Matlova, V., Roffet-Salque, M., Pavlu, I., Kyselka, J., Sedlarova, I., Filip, V., Evershed, R. P., 2017. Defining pottery use and animal management at the Neolithic site of Bylany (Czech Republic). J. Archaeol. Sci. Reports 14, 262–274. https://doi.org/10.1016/j.jasrep.2017.05.028.

Miyake, Y., 2017. The Earliest Pottery of Salat Camii Yanı. Emerg. Pottery West. Asia 55–58.

Nawar, W.W., 1989. Thermal Decomposition of Lipids 94–104. https://doi.org/10.1021/bk-1989-0409.ch009.

Nieuwenhuyse, O., Salque, M., Evershed, R.P., Akkermans, P.M.M.G., Russell, A., 2015. Tracing pottery use and the emergence of secondary product exploitation through lipid residue analysis at Late Neolithic Tell Sabi Abyad (Syria). J. Archaeol. Sci. 64, 54–66. https://doi.org/10.1016/j.jas.2015.10.002.

Özbal, H., Thissen, L., Doğan, T., Gerritsen, F., Özbal, R., Türkekul-Bıyık, A., 2013. Neolitik batı anadolu ve marmara yerlesimleri ĉanak çomleklerinde Organi̇k kalıntı Anali̇zleri̇. Arkeom. Sonuc. Toplantısı 28, 105–114.

Özbal, R., 2023. Early pottery and 'displaced' cooking pots. In: Düring, B.S., Akkermans, P.M.M. (Eds.), Style and Society in the Prehistory of West Asia: Essays in Honour of Olivier P. Nieuwenhuyse. PALMA 29: Papers on Archaeology of the Leiden Museum of Antiquities. Sidestone Press., Leiden, pp. 173–182.

Özdoğan, E., 2011a. Settlement organization and architecture in Aşağı pınar. Early neolithic layer 6. In: Krauss, R. (Ed.), Beginnings - New Research in the Appearance of the Neolithic between Northwest Anatolia and the Carpathian Basin. Papers of the International Workshop 8th-9th April 2009, Istanbul, pp. 213–223.

Özdoğan, M., 2011b. Polychrome early Neolithic painted pottery at Aşağı Pınar. Stud. Praehist. 14, 83–90.

Passi, S., Picardo, M., De Luca, C., Nazzaro-Porro, M., Rossi, L., Rotilio, G., 1993. Saturated dicarboxylic acids as products of unsaturated fatty acid oxidation. Biochim. Biophys. Acta Lipids Lipid. Metabol. 1168, 190–198. https://doi.org/10.1016/0005-2760(93)90124-R.

Rageot, M., Théry-Parisot, I., Beyries, S., Lepère, C., Carré, A., Mazuy, A., Filippi, J.J., Fernandez, X., Binder, D., Regert, M., 2019. Birch bark tar production: experimental and biomolecular approaches to the study of a common and widely used prehistoric adhesive. J. Archaeol. Method Theor 26, 276–312. https://doi.org/10.1007/s10816-018-9372-4.

Raven, A.M., van Bergen, P.F., Stott, A.W., Dudd, S.N., Evershed, R.P., 1997. Formation of long-chain ketones in archaeological pottery vessels by pyrolysis of acyl lipids. J. Anal. Appl. Pyrolysis 40–41, 267–285. https://doi.org/10.1016/S0165-2370(97)00036-3.

Reber, E.A., Evershed, R.P., 2004. How did mississippians prepare maize? The application of compound-specific carbon isotope analysis to absorbed pottery residues from several Mississippi valley sites. Archaeometry 46, 19–33. https://doi.org/10.1111/j.1475-4754.2004.00141.x.

Reber, EA, Kerr, MT, Whelton, HL, Evershed, RP, 2018. Lipid Residues from Low-Fired Pottery. Archaeometry 61, 131–144. https://doi.org/10.1111/arcm.12403.

Regert, M., 2011. Analytical strategies for discriminating archaeological fatty substances from animal origin. Mass Spectrom. Rev. 30, 177–220.

Roffet-Salque, M., Dunne, J., Altoft, D.T., Casanova, E., Cramp, L.J.E., Smyth, J., Whelton, H., Evershed, R.P., 2016. From the inside out: upscaling organic residue analyses of archaeological ceramics. J. Archaeol. Sci. Reports. https://doi.org/10.1016/j.jasrep.2016.04.005.

Rojo, J.A., Perkins, E.G., 1987. Cyclic fatty acid monomer formation in frying fats. I. Determination and structural study. J. Am. Oil Chem. Soc. 64, 414–421. https://doi.org/10.1007/BF02549306.

Romero, A., Bastida, S., Sánchez-Muniz, F.J., 2006. Cyclic fatty acid monomer formation in domestic frying of frozen foods in sunflower oil and high oleic acid sunflower oil without oil replenishment. Food Chem. Toxicol. 44, 1674–1681. https://doi.org/10.1016/j.fct.2006.05.003.

Romero, A., Cuesta, C., Sánchez-Muniz, F.J., 2003. Cyclic FA monomers in high-oleic acid sunflower oil and extra virgin olive oil used in repeated frying of fresh potatoes. JAOCS, J. Am. Oil Chem. Soc. 80, 437–442. https://doi.org/10.1007/s11746-003-0717-x.

Romero, A., Cuesta, C., Snchez-Muniz, F.J., 2000. Cyclic fatty acid monomers and thermoxidative alteration compounds formed during frying of frozen foods in extra virgin olive oil. JAOCS, J. Am. Oil Chem. Soc. 77, 1169–1175. https://doi.org/10.1007/s11746-000-0183-5.

Rozlianah, F.S., Jualang, A.G., Chong, K.P., 2015. Fatty acids and phenols involved in resistance of oil palm to ganoderma boninense. Adv. Environ. Biol. 9, 11–16.

Salque, M., Bogucki, P.I., Pyzel, J., Sobkowiak-Tabaka, I., Grygiel, R., Szmyt, M., Evershed, R.P., 2013. Earliest evidence for cheese making in the sixth millennium BC in northern Europe. Nature 493, 522–525. https://doi.org/10.1038/nature11698.

Sari, D., Akyol, Ş., 2019. The early neolithic pottery of keçiçayiri and its place in the north-western anatolian neolithisation process. Doc. Praehist. 46, 138–156. https://doi.org/10.4312/dp.46.9.

Sébédio, J.-L., Juaneda, P., 2007. Isomeric and cyclic fatty acids as a result of frying. In: Deep Frying. Elsevier, pp. 57–86. https://doi.org/10.1016/B978-1-893997-92-9.50011-6.

Sebedio, J.L., Grandgirard, A., 1989. Cyclic fatty acids: natural sources, formation durin heat treatment, synthesis and biological properties. Prog. Lipid Res. 28, 303–336. https://doi.org/10.1016/0163-7827(89)90003-9.

Sébédio, J.L., Kaitaranta, J., Grandgirarda, A., Malkk, Y., 1991. Quality assessment of industrial prefried French fries. J. Am. Oil Chem. Soc. 68, 299–302. https://doi.org/10.1007/BF02657680.

Sebedio, J.L., Le Quere, J.L., Semon, E., Morin, O., Prevost, J., Grandgirard, A., 1987a. Heat treatment of vegetable oils. II. GC-MS and GC-FTIR spectra of some isolated cyclic fatty acid monomers. J. Am. Oil Chem. Soc. 64, 1324–1333. https://doi.org/10.1007/BF02540791.

Sebedio, J.L., LeQuere, J.L., Morin, O., Vatele, J.M., Grandgirard, A., 1989. Heat treatment of vegetable oils III. GC-MS characterization of cyclic fatty acid monomers in heated sunflower and linseed oils after total hydrogenation. J. Am. Oil Chem. Soc. 66, 704–709.

Sebedio, J.L., Prevost, J., Grandgirard, A., 1987b. Heat treatment of vegetable oils I. Isolation of the cyclic fatty acid monomers from heated sunflower and linseed oils. J. Am. Oil Chem. Soc. 64, 1026–1032. https://doi.org/10.1007/BF02542443.

Simoneit, B.R., 2002. Biomass burning — a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 17, 129–162. https://doi.org/10.1016/S0883-2927(01)00061-0.

Tükerkul-Bıyık, A., Özbal, H., 2008. Arkeolojik çanak çomleklerde organik kalıntıların belirlenmesi: anadolu’dan bazı örnekler. Arkeom. Sonuc. Toplantısı 23, 249–264.

Vatèla, J.M., Sébédio, J.L., Le Quéré, J.L., 1988. Cyclic fatty acid monomers: synthesis and characterization of methyl ω-(2-alkylcyclopentyl) alkenoates and alkanoates. Chem. Phys. Lipids 48, 119–128. https://doi.org/10.1016/0009-3084(88)90139-9.

Wiedemeier, D.B., Brodowski, S., Wiesenberg, G.L.B., 2015. Pyrogenic molecular markers: linking PAH with BPCA analysis. Chemosphere 119, 432–437. https://doi.org/10.1016/j.chemosphere.2014.06.046.