On the beach: new discoveries at Harlyn Bay, Cornwall

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Accepted for publication in the Proceedings of the Prehistoric Society for 2011

Organic residue analysis of a burial urn from Harlyn Bay, Cornwall

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Introduction

The porous nature of unglazed pottery vessels ensures that during the processing of food lipids become absorbed into the vessel wall. These lipids include remnant animal fats, plant oils and plant waxes, which are known to survive in archaeological deposits for several millenia (Evershed et al., 1999). The major compounds present are lipids, i.e. the fats, oils, waxes and resins of the natural world, recoverable by solvent extraction, which are then quantified and identified by high temperature-gas chromatography (HTGC), GC/mass spectrometry (GC/MS; Evershed et al., 1990) and GC-combustion-isotope ratio mass spectrometry (GC-C-IRMS; Evershed et al., 1994; Mottram et al., 1999). Characterisation of lipid extracts to commodity type rests on detailed knowledge of diagnostic compounds and their associated degradation products arising during vessel use or burial. For In archaeological pottery free fatty acids commonly dominate lipid extracts over compounds that are characteristic for fresh fats and oils (i.e. acylglycerol moities). Compound-specific stable carbon isotope determinations, using gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS), allows the carbon stable isotope ($\delta^{13}C$) values of individual compounds to be determined, providing an important complementary criterion for classifying the origins of lipids. $\delta^{13}C$ values of the principal fatty acids ($C_{16:0}$ and $C_{18:0}$) present in degraded animals fats are effective in distinguishing between different animal fats, e.g. ruminant and non-ruminant adipose fats and dairy fats (Evershed et al., 1997a, Dudd and Evershed, 1998), as well as in the identification of the mixing of commodities (Evershed et al., 1999, Copley et al., 2001).

Results and discussion

Analysed pottery sample was taken from a single body potsherd of a Trevisker Urn, which was found to have contained burnt remains of several individuals. The concentration of preserved lipids was rather low in comparison to average lipid concentration observed in Cornish funerary and domestic pottery in the past (Copley et al 2005; Šoberl pers. comment).

Table 1: Summary of the results of the organic residue analyses.

Lipid concentration ($\mu g\ g^{-1}$)	Lipids detected	$\delta^{13}C_{16:0} \pm 0.3$ (‰)	$\delta^{13}C_{18:0} \pm 0.3$ (‰)	Predominant commodity type
9.18	FA(16≈18, 16:1, 18:1), MAG, DAG, TAG	-26.58	-30.82	ruminant dairy fat/ plant oil

Key: FA refers to free fatty acids, MAG to monoacylglycerols; DAG to diacylglycerols; TAG to triacylglycerols.

Figure 1 shows a partial gas chromatogram of the total lipid extract of the Harlyn Bay potsherd that contained free fatty acids – i.e. palmitic ($C_{16:0}$), palmitoleic ($C_{16:1}$), stearic ($C_{18:0}$) and oleic ($C_{18:1}$) acid; together with di- and triacylglycerols (DAGs, TAGs). Free fatty acids represent final products of triacylglycerol hydrolysis, which occurs through time either because of conditions in soil deposits or long-term vessel use. Since TAGs and DAGs are largely present in fresh fat, their presence or absence can be used to asses the extent of degradation the preserved lipids have undergone. Laboratory experiments have shown that certain TAG distributions can be attributed to specific commodities – a narrow TAG distribution with carbon number ranges from C_{48} to C_{52} is indicative of porcine adipose fat, wider TAG distribution with ranges from C_{46} to C_{54} can be attributed to ruminant adipose fat and the widest TAG distribution with ranges from C_{42} to C_{54} can be attributed to ruminant dairy fat. Although the narrow triacylglycerol distribution detected in Harlyn Bay extract (Fig. 2) would indicate the presence of porcine adipose fat according to the criteria mentioned above, we have to be more cautious with our interpretations, especially since the relative abundances of individual TAGs are very atypical with maximum concentrations of TAG 48 and TAG 50. Unsaturated free fatty acids ($C_{16:1}$ and $C_{18:1}$) are most commonly present in plant oils, where the oleic acid ($C_{18:1}$) is the predominant fatty acid.

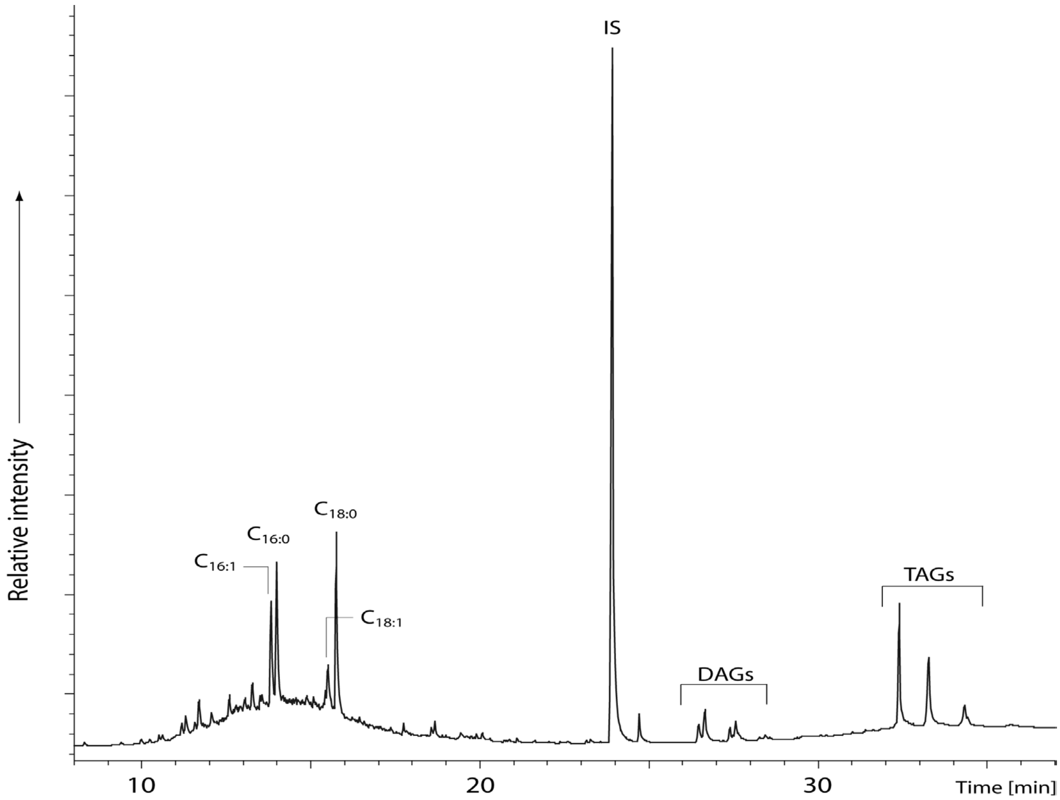

Figure 1. Partial HTGC profile of the trimethylsilylated total lipid extract from Harlyn Bay potsherd, illustrating the distribution of components characteristic of partially degraded fat or oil. Key: $C_{X:Y}$ are saturated free fatty acids of carbon length x and number of double bonds y; IS is the internal standard (C_{34} alkane); DAGs are diacylglycerols; TAGs are triacylglycerols.

The TAG distributions detected in the Harlyn Bay urn is very unusual and is reflecting neither typical ruminant nor non-ruminant animal fat TAG distributions, as can be seen on Figure 2. TAGs and free fatty acids detected in the potsherd resemble more closely a plant oil residue. A similar distribution has been previously observed in pithoi from Isthmia, Greece, which were presumed to contain some kind of unidentified plant oil (Evershed et al. 2003). Major free fatty acids present in plant materials are all saturated or unsaturated straight even-numbered carbon chain (Hitchcock & Nichols 1971). Higher abundance of palmitic acid ($C_{16:0}$) together with presence of unsaturated fatty acids is characteristic for plant remains. Since these fatty acids are ubiquitous in all plant taxa, it is difficult to exactly pinpoint the origin of extracted lipids. Biomarker approach usually exploits the presence of specific compounds like genus specific alkanes, alcohols, ketones and sterols (Charters et al. 1997).

Unfortunately due to the absence of these compounds in Harlyn bay potsherd extracts it is difficult to identify the plant origin more specifically.

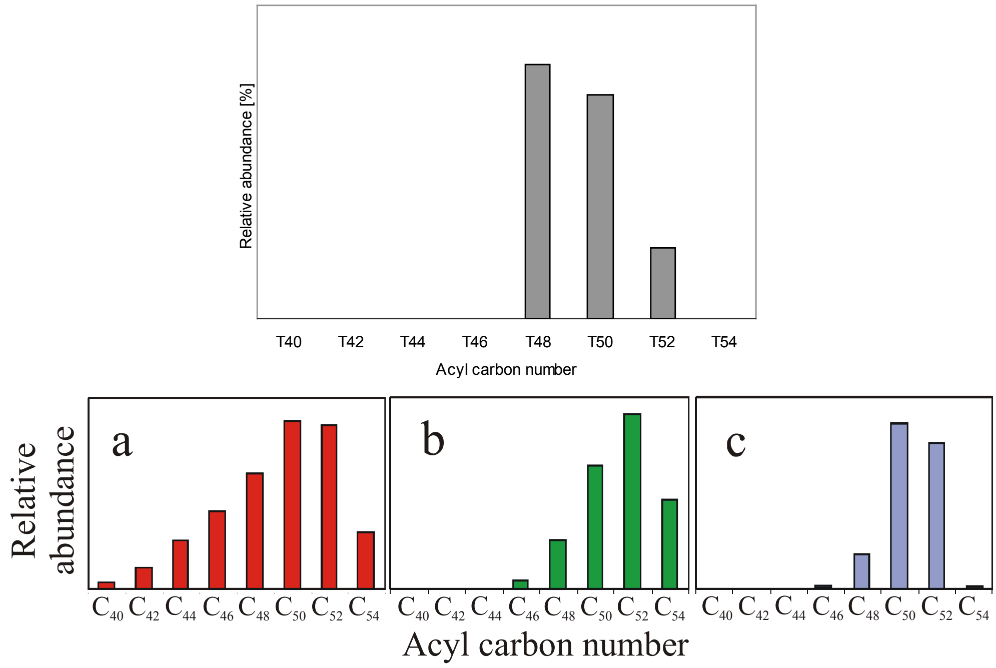

Figure 2. The distribution of triacylglycerols detected in the Harlyn Bay lipid extract compared to TAGs present in modern animal reference fats: a) ruminant dairy fat; b) ruminant adipose fat; c) porcine adipose fat (adapted from Dudd & Evershed 1998)

The Harlyn Bay potsherd extract yielded an appreciable lipid concentration and was thus submitted to further analysis by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) to determine the $\delta^{13}C$ values for the major fatty acids (Figure 3). The $\delta^{13}C$ values for the $C_{18:0}$ fatty acid are more depleted in milk fats than in ruminant adipose fats, thereby enabling distinctions to be drawn between milk and adipose fats from ruminant animals (Dudd & Evershed, 1998). This is witnessed in the *c.* 2.5 ‰ shift between centroids of the reference ruminant adipose fat and ruminant dairy fat ellipses. The $\delta^{13}C$ values for the $C_{16:0}$ and $C_{18:0}$ fatty acids from Harlyn Bay sample plot nearby the ruminant dairy and ruminant adipose fat reference ellipse.

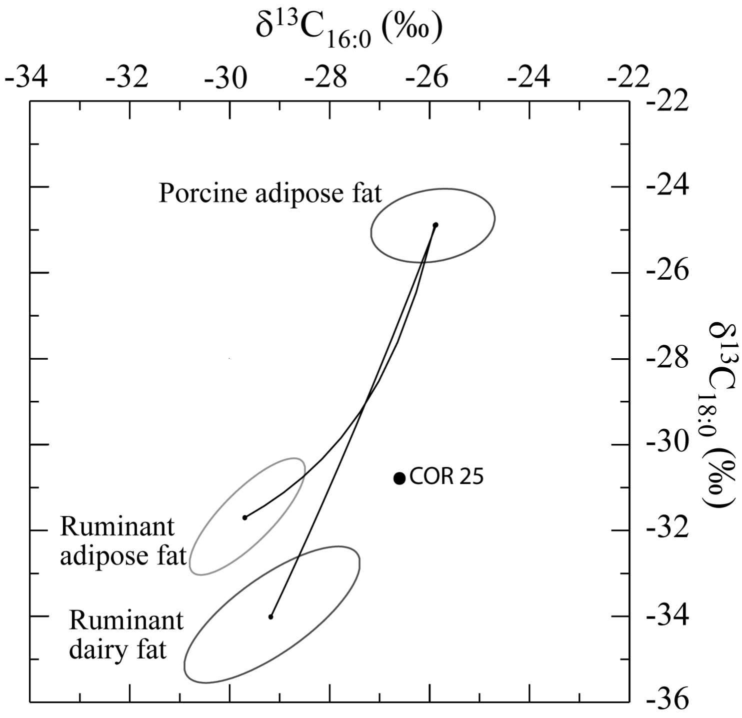

Figure 3. Scatter plot showing the $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids from Harlyn Bay potsherd total lipid extract. The values of modern reference fats are represented by confidence ellipses (1 standard deviation). All $\delta^{13}C$ values obtained for modern reference animal fats have been adjusted for the post-Industrial Revolution effects of fossil fuel burning, by the addition of 1.2 ‰. Lines connecting the ellipses represent theoretical $\delta^{13}C$ values obtained through the mixing of these fats.

The reference fats that were used to construct the reference isotope plot came from animals that were reared on a strict C_3 diet of fodders and cereals. The slight displacement of $\delta^{13}C$ isotopic values outside the confidence ellipses may be due to the fact that the animals in prehistory were reared on diets, which varied in $\delta^{13}C$ values compared to today's values of environmental influences. $\Delta^{13}C$ values ($\delta^{13}C_{16:0}$ - $\delta^{13}C_{18:0}$) are therefore a useful indicator of lipid origin when such variations in isotope values occur. Figure 4 displays the $\Delta^{13}C$ values plotted against $\delta^{13}C_{16:0}$ values for the Harlyn bay potsherd extract. The ranges on the left side of the plot are from the modern reference fats. $\Delta^{13}C$ values obtained for the Harlyn bay potsherd indicate the presence of ruminant dairy lipids.

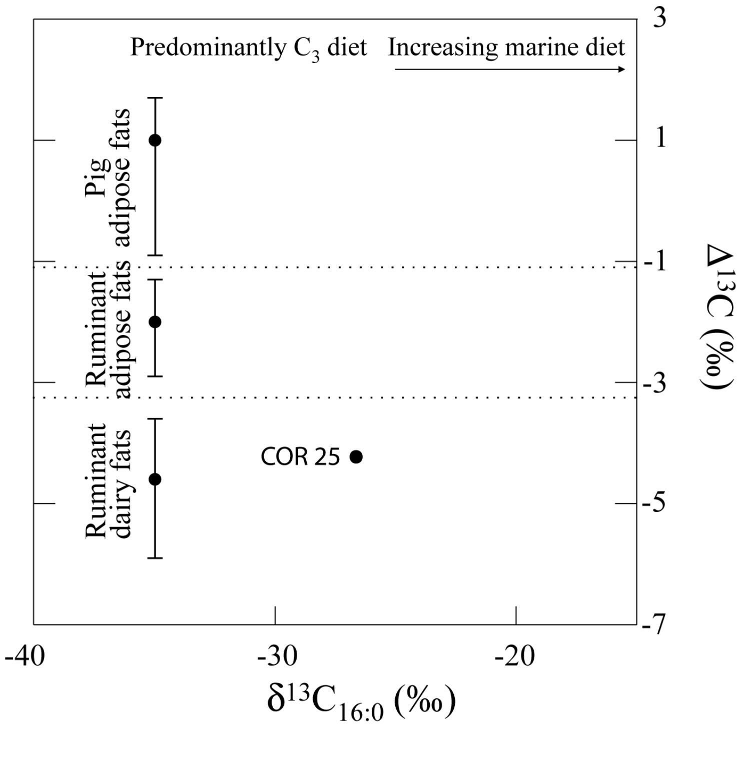

Figure 4. A plot showing the $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$) and $\delta^{13}C$ values obtained from the Harlyn Bay potsherd exract. The values for the modern reference fats are plotted to the left of the diagram and displayed with the 2.s.d. ranges.

4. Discussion

The lipid residue analysis of the Harlyn Bay urn has shown that the sherd had appreciable lipid residues preserved (> 5μg g^{-1} sherd), although the overall concentration is low in comparison to average lipid concentration observed in other Cornish Early Bronze Age pottery. The measured $\delta^{13}C$ values of the potsherd extract fall within the ruminant dairy fat reference area. The presence of partially degraded triglycerides indicates good preservation, however their distribution appears to be atypical of animal fat and more closely resembling plant oil profile, especially due to the presence of mono-unsaturated fatty acids i.e. palmitoleic and oleic acid. The $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ fatty acids indicate that the source of the preserved lipids is ruminant dairy fat. Due to various degradation processes which can skew the TAG distributions, the $\delta^{13}C$ values usually offer the most reliable identification of the lipids' source. In the Harlyn bay urn however, the isotope results have to be interpreted with caution. It has been known that the presence of unsaturated fatty acids can also be due to the modern contamination that occurs due to the post-excavation handling of the potsherds. Palmitoleic acid ($C_{16:1}$) is the most common unsaturated fatty acid present in the human skin and is commonly found in various cosmetic products like deodorants, lipstick, handcreams and sunscreen lotions, due to its antimicrobial properties and increasing the lipid barrier of the skin (Morello & Downing 1976; Nicollier et al. 1986; Asano et al. 2002). We try to eliminate these modern contaminants with the pre-extraction cleaning process, however sometimes modern lipids can be absorbed into the ceramic matrix itself during the pottery classification, illustration and general post-excavation handling.

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