6.2 Organic residue analysis of pottery from Warren Field timber hall and the Crathes Castle Overflow Car Park site

Lucija Šoberl and Richard P. Evershed

Introduction

The porous nature of unglazed pottery vessels ensures that, during the processing of food and other organic materials, 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 thousand years (Evershed *et al*., 1999). They are 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).

Identifying from lipid extracts the types of commodity processed in the pottery vessels rests on detailed knowledge of diagnostic compounds and their associated degradation products arising during the use or burial of the pot. For example, triacylglycerols, which are the major constituents of modern animal fats and vegetable oils, are degraded to diacylglycerols, monoacylglycerols and free fatty acids during burial/vessel use. In archaeological pottery free fatty acids commonly dominate lipid extracts (Evershed 1993), with their origins having been verified through laboratory degradation experiments (*e.g*. Charters *et al*., 1997, Dudd and Evershed, 1998; Evershed, 2008).

Compound-specific stable carbon isotope determinations, using gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS), allow the carbon stable isotope ($\delta^{13}C$) values of individual compounds (within a mixture) 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 (body) fats and dairy fats (Evershed *et al*., 1997a, 1997b, Dudd and Evershed, 1998), as well as in the identification of the mixing of commodities (Evershed *et al*., 1999, Copley *et al*., 2001).

Lipid residue analyses were undertaken on eighteen sherds of pottery from Warren Field and two from the Crathes Castle Overflow Car Park site in order to provide insights into vessel use, food processing and on animal husbandry at the settlements. The latter is of particular importance in light of the poor survival of animal bone on the sites.

Materials and Methods

Lipid analyses were performed using established protocols which are described in detail elsewhere (Evershed *et al*., 1990; Charters *et al*., 1993). HTGC and GC/MS analyses were undertaken to quantify and identify compounds in the lipid extracts, seeking to determine the presence of: (i) an animal fat or plant oil, and/or (ii) plant epicuticular waxes, and/or (iii) beeswax, and/or (iv) mid-chain ketones indicative of vessel heating (Evershed *et al.*, 1995, Raven *et al.*, 1997). GC-C-IRMS analyses were used distinguish between ruminant and non-ruminant adipose fats and dairy fats by investigating their $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values.

Results

The results of HTGC screening are summarised in Table 8 on a sample-by-sample basis, giving the total lipid concentration per gram of powdered sherd, and a brief description of the composition of the preserved lipids. Where sufficient lipid was present, the samples were further analysed by GC-C-IRMS; Seven of the twenty sherds sampled (35%) yielded significant lipids ($> 5\ \mu g\ g^{-1}$).

The presence of degraded animal fat residues was indicated in seven sherds, characterised by a distribution of free fatty acids exhibiting a high abundance of the $C_{18:0}$ fatty acids, together with mono-, di- and triacylglycerols. Other compounds present were mono-unsaturated ($C_{18:1}$), saturated odd carbon chain number ($C_{15:0,}$ $C_{17:0}$) and *iso*- and *anteiso*- branched odd carbon number fatty acids ($C_{15:0br}$, $C_{17:0br}$), which suggest a

ruminant source of extracted lipids (Evershed *et al*., 1997a, 1997b, 2002; Mottram *et al*. 1999). Triacylglycerols are the major constituent of fresh animal fat but they degrade with time through hydrolysis into di- and monoacylglycerols and free fatty acids. Mono- and diacylglycerols were detected in six of the samples lipid extracts together with high abundances of $C_{16:0}$ and $C_{18:0}$ free fatty acids. The intact triacylglycerol distributions observed in the extracts from sherds CRA01, 02, 06, 15, 16 and 19 were attributable to ruminant adipose and dairy fat, while narrower distributions typical of porcine fats were not observed. Although laboratory experiments have shown that such distributions become skewed to higher carbon numbers by degradation, sufficient of the lower carbon number triacylglycerols are often preserved to allow dairy fats to remain recognisable; the parent C_{40} to C_{54} TAG range narrows to C_{44} to C_{54}.

Mid-chain ketones (in the range of C_{31} to C_{35}) were detected in the extracts of four samples (CRA01, CRA02, CRA15 and CRA16). The presence of ketones can be attributed to two possible sources: either the absorption of epicuticular leaf waxes into the pottery fabric during the cooking of leafy vegetables (Evershed *et al*., 1991; Charters *et al*., 1997), or as a consequence of the ketonic decarboxylation reaction which occurs in unglazed ceramic vessels during heating, when the temperature exceeds 300˚C, which leads to the condensation of two fatty acids (Evershed *et al*. 1995; Raven *et al*., 1997). The latter compounds provide direct evidence for the heating of animal fats/plant oils to temperatures, greater than might be expected in cooking.

The seven samples that yielded appreciable prehistoric lipid concentrations were submitted to further analysis by GC-C-IRMS to determine the $\delta^{13}C$ values for the major fatty acids; these values are plotted in Fig. 45. The $\delta^{13}C$ values obtained for modern reference animal fats from the major domesticated animals exploited in prehistoric Britain and Ireland are grouped within confidence ellipses, onto which the values from the Crathes pottery samples have been plotted. 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 less depleted $\delta^{13}C$ values seen for the fatty acids in non-ruminant fats compared to equivalent components in ruminant fat are

due to differences in diet and in the metabolic and biochemical processes involved in the formation of body fats in ruminant and non-ruminant animals. The $\delta^{13}C$ values from six of the Crathes samples plot within or adjacent to the ruminant dairy fat reference confidence ellipse, while only one sample (CRA 20) plots in the region of the porcine adipose fat ellipse.

The modern fats used to construct the reference isotope plot were derived from animals reared on strict C_3 diets of forage/fodder 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 modern diets affected by today's different environmental influences. $\Delta^{13}C$ values ($\delta^{13}C_{16:0} - \delta^{13}C_{18:0}$) are also useful indicators of lipid origin when such variations in isotope values occur. Fig. 46 displays the $\Delta^{13}C$ values plotted against $\delta^{13}C_{16:0}$ values for the Crathes samples. The ranges on the left side of the plot are from the modern reference fats. $\Delta^{13}C$ values obtained for the Crathes samples again strongly confirm the presence of ruminant dairy lipids in six pottery samples and also the presence of porcine adipose fat in sample CRA20.

Discussion

The analyses of the twenty early Neolithic pottery samples from Crathes have shown 35% of the sherds to contain appreciable contemporary lipid residues (>5μg g^{-1} sherd), higher than often observed for British Neolithic pottery (Copley *et al*., 2005b). The high degree of preservation overall was also reflected in the survival of acylglycerol components (monoacylglycerols, diacylglycerols, triacylglycerols) in a significant proportion of lipid extracts. Mid-chain ketones were identified in extracts of four sherds, which confirmed extensive heating of the vessels or sherds from which they derived.

Most of the extracts containing preserved triacylglycerols displayed a wide acyl carbon number distribution, including lower molecular weight species diagnostic of milk fats, which was confirmed by GC-C-IRMS analyses. Although none of the samples contained TAGs distributions typical of porcine fats, the extract of CRA20, which lacked

TAGs, contained fatty acids exhibiting $\delta^{13}C$ values consistent with processing pig products.

Recently it has been demonstrated that dairy products were important commodities in prehistoric southern Britain, established through the survival of residues of dairy fats preserved in cooking vessels (Copley *et al*., 2003, 2005). The vast majority of southern British prehistoric sites showing dairy fat residues yielded faunal assemblages dominated by cattle. Notable examples of early Neolithic sites yielding high proportions of cattle bones and abundant dairy fats include: Eton Rowing Lake, Windmill Hill and Hambeldon Hill (Copley *et al*., 2003, 2005).

In summary, while acidic soil conditions meant that the faunal remains at Crathes were poor, precluding their use in the reconstruction of the settlement subsistence strategies, the lipids preserved in the pottery from both the Warren Field timber hall and the Crathes Castle Overflow Car Park site provide strong evidence for the processing of dairy products (from either cattle or sheep/goat). A single sample from the timber hall suggests some use of pig meat, although this could be from wild or domesticated animals (Mukherjee *et al*. 2007, 2008).

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