ELSEVIER

Journal of Chromatography A, 833 (1999) 209–221

JOURNAL OF CHROMATOGRAPHY A

New chromatographic, mass spectrometric and stable isotope approaches to the classification of degraded animal fats preserved in archaeological pottery

H.R. Mottram, S.N. Dudd, G.J. Lawrence, A.W. Stott, R.P. Evershed*

Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Received 19 May 1998; received in revised form 27 November 1998; accepted 30 November 1998

Abstract

A new method is described for distinguishing between animal fats preserved in ancient pottery. Analysis of lipid fractions from two morphologically distinct vessel types (lamps and ''dripping dishes'') using on-line gas chromatography–combustion–isotope ratio mass spectrometry (GC–C–IRMS) showed that they could be distinguished by plotting the $\delta^{13}C$ value for *n*-hexadecanoic acid against that for *n*-octadecanoic acid. The $\delta^{13}C$ values obtained for modern reference fats from domesticated animals likely to have been important in antiquity showed the lamp extracts to correlate with ruminant animal fat, such as sheep or cattle, whereas the ''dripping dishes'' had $\delta^{13}C$ values similar to those of non-ruminant animal fat, such as pig. These findings were entirely consistent with distributional information obtained by GC and with positional isomer information gained from analysis of dimethyldisulphide derivatives of the monounsaturated fatty acids. The results indicate that GC–C–IRMS has considerable potential for the classification of animal fats absorbed in ancient pottery particularly where fatty acid distributions have been altered by degradation during vessel use or burial. $\delta^{13}C$ values were also shown to be of value in detecting the use of vessels in the processing of animal products from more than one source.

Keywords: Fats; Archeology; Ceramics; Lipids; Fatty acids

1. Introduction

Ceramic objects, such as pottery vessels, are amongst the most common class of artefacts found at archaeological sites. Attempts to derive functional and dietary evidence from these vessels have focused on the analysis of organic residues preserved in unglazed pottery, either as charred surface deposits or, more commonly, absorbed within the ceramic fabric [1,2]. Investigations of such residues have revealed a wide range of commodities associated with vessel usage in the past, including epicuticular leaf waxes [3,4], beeswax [5,6] and degraded animal fats [5,7,8]. These studies have utilised a ''biological marker'' or ''biomarker'' approach, attempting to correlate molecular components, particularly lipids, preserved within the organic residues with biomolecules present in modern-day plant and animal tissues.

Although the composition of animal and plant lipids in contemporary materials is well established [9], the effect of degradation, e.g. chemical, microbiological or physical, on these individual lipids and their distributions during vessel use and burial

*Corresponding author. Tel.: +44 117 9287671; fax: +44 117 9293746; e-mail: r.p.evershed@bris.ac.uk

0021-9673/99/$ – see front matter
PII: S0021-9673(98)01041-3

(diagenesis) is still poorly understood [7,8,10]. The complex mixtures which arise from the degradation of lipids, particularly those containing appreciable quantities of unsaturated components, are difficult to interpret and can often lead to the erroneous characterisation of the origin of the residues. Techniques such as nuclear magnetic resonance spectroscopy [11], thin-layer chromatography in conjunction with infrared spectroscopy [12] and high-performance liquid chromatography [2] are useful for providing ''fingerprints'' of organic residues. However, gas chromatography in conjunction with mass spectrometry (GC–MS) is the most useful technique for lipid analysis since it allows structural identification of individual compounds, providing enhanced opportunities for the characterisation of the organic residue [13].

Until recently, most GC and GC–MS studies of lipid extracts from archaeological ceramics have involved the analysis of fatty acids, usually as methyl ester derivatives [14,15]. Since its application to archaeological studies [13], the technique of high-temperature capillary GC, has been routinely used for the analysis of lipids, e.g. fatty acids, mono-, di- and triacylglycerols, of different natural product origin from a range of archaeological ceramics [6,14,17].

Within the last two decades, techniques which make use of the stable isotopes of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) have been widely applied to the investigation of the ancient human diet [18,19]. These studies rely on the fact that the isotopic composition of an organism's tissue depends on the relative contributions of isotopically distinct components of the individual's diet [20,21]. Clear isotopic distinctions are therefore observed between organisms originating from marine or terrestrial sources, specifically in the latter case due to differences between the C_3 (Calvin) and C_4 (Hatch–Slack) photosynthetic pathways. Carbon isotope ratios are expressed relative to the VPDB (Vienna Pee Dee Belemnite) standard (*Bellemnitella americana*), $\delta^{13}C$ (in per mil (%))$=1000\ [(R_{sample}-R_{standard})/R_{standard}]$, where R is $^{13}C/^{12}C$.

Until the relatively recent introduction of on-line techniques, research in this field involved bulk isotopic $\delta^{13}C$ measurements of organic matter. Hastorf and DeNiro [22] applied bulk stable isotope techniques to the analysis of archaeological pottery from South America. Charred organic residues on the surfaces of potsherds retained the isotopic compositions of the contributing foodstuffs. Isotopic analysis of sherds from three historical periods showed how the proportion of legumes, non-leguminous C_3 plants and C_4 plants varied in the prehistoric diet over time. Morton and Schwarcz [23] also used stable carbon isotopes to examine food residues thought to originate from maize.

With the introduction of on-line gas chromatography–combustion–isotope ratio mass spectrometry (GC–C–IRMS), stable carbon isotope ratios of individual components in a mixture can now be measured, providing opportunities to enhance the isotopic analysis of organic residues from archaeological ceramics and indeed other classes of artefact or ecofact [24]. The first application of GC–C–IRMS to archaeological materials was carried out by Evershed et al. [25]. $\delta^{13}C$ values of specific leaf wax compounds (*n*-nonacosane, nonacosan-15-ol and nonacosan-15-one) extracted from potsherds were compared with the equivalent compounds recovered from modern plants. When utilised in conjunction with structural and distributional evidence, these results suggested that the lipids in the potsherds were derived from a *Brassica* species, probably cabbage. Compound-specific stable isotope values have proved to be particularly valuable where distributions or structures of compounds have been altered by human activity in the past, or natural decay processes during burial. One instance of this involved the use of $\delta^{13}C$ values to demonstrate a precursor–product relationship between fatty acid components of ancient pottery and novel plant leaf wax-like long-chain ketones formed by pyrolysis during the use of the vessels [26,27]. Likewise $\delta^{13}C$ values of individual compounds were essential in resolving a question of the presence of beeswax in ceramic lamps and conical cups from Bronze Age Crete [6].

Although degraded animal fats are the most common class of residue observed in archaeological pottery, often in appreciable quantities, their variable composition and decay during burial complicates their identification. The aim of this work was to explore the use of a range of analytical techniques to determine the origin of the acyl lipids present in

Table 1
Medieval pottery samples from Causeway Lane, Leicester, UK

Sample ref.	Vessel type	Burial context
20802	Lamp	Rubbish fills in pit, cess present
21619	Lamp	Rubbish fills in pit, no cess present
23006	Lamp	Rubbish fills in pit, no cess present
20582	Dripping dish	Upper fills of deep pit, no cess present
21449	Dripping dish	Rubbish fills in pit, cess present
21823	Dripping dish	Mixed rubbish and cess fills of deep pit, cess present
21826	Dripping dish	Mixed rubbish and cess fills of deep pit, cess present
21828	Ceramic cauldron	Primary fills of deep pit, probably dug as a well in first instance and later used as a cess pit, cess present

archaeological pottery of medieval date, recovered from the Causeway Lane excavation, Leicester, UK. Lipid analysis was carried out on two types of potsherd, classified as lamps and ''dripping dishes'' (Table 1). One example of a sherd from a ceramic cauldron was also studied. The specific objectives of the study were: (1) to determine whether lipid residues could be used to differentiate types of vessel, and (2) to gain insight into the origin of the lipids by comparison of isotopic ($\delta^{13}C$), structural and distributional data obtained for individual lipids with those of modern reference fats.

2. Experimental

2.1. Materials

Modern reference materials were chosen to represent a range of fat sources which may have been significant in antiquity. Since the potsherds under investigation are dated prior to the introduction of C_4 plants to Europe, where possible the fats analysed were obtained from animals raised from birth on C_3 diets [28]. Samples of subcutaneous adipose tissue from three lambs and two cows were chosen to represent a range of different breeds, ages and other factors and were obtained from local farms. All solvents were of HPLC grade and were obtained from Rathburn (Walkerburn, UK).

2.2. Apparatus

GC analyses were performed on a Hewlett-Packard 5890A gas chromatograph (Palo Alto, CA, USA) coupled to a personal computer equipped with CHEMSTATION software. On-column injections were made manually.

GC–MS was carried out using a Carlo Erba Mega Series gas chromatograph (Milan, Italy) interfaced to a Finnigan MAT 4500 mass spectrometer (San Jose, CA, USA) operated in electron ionisation (EI) mode. Mass spectra were collected over the range m/z 50 to 650 at a frequency of 1 scan/s.

GC–C–IRMS was performed using a Varian gas chromatograph attached to a Finnigan MAT Delta S mass spectrometer (Bremen, Germany) via a Finnigan MAT Mark I combustion interface. The combustion interface comprised a ceramic furnace with a copper oxide and platinum catalyst and was maintained at 850°C. A Nafion membrane prevented water from reaching the ion source. The mass spectrometer source pressure was $7 \cdot 10^{-6}$ Torr (1 Torr 133.322 Pa).

2.3. Lipid extraction

The lipids from the archaeological samples were extracted using chloroform–methanol (2:1, v/v) as the extraction solvent, following a procedure developed by Charters et al. [16]. The lipids from the modern reference materials were extracted as follows. Adipose tissue (≈2 g) was placed in a conical flask with chloroform–methanol (50 ml) and sonicated (2×15 min). The extract was filtered and the bulk of the solvent removed using a rotary evaporator. The remaining solvent was removed under a gentle stream of nitrogen and the resulting lipid extract stored at −20°C until required for analysis.

2.4. Preparation of fatty acid methyl esters

A portion of the total lipid extract was saponified with NaOH (2 *M* in methanol, 2 ml) and heated at 70°C for 1 h. After cooling, the solution was acidified with aqueous HCl (0.5 *M*) and the free fatty acid fraction extracted with cyclohexane (3×5 ml). The solvent was reduced to a small volume by rotary evaporation before the remaining solvent was removed under a gentle stream of nitrogen. The free fatty acids were methylated to their corresponding methyl esters by adding 2 ml of a 14% w/v boron trifluoride–methanol complex (BDH, Poole, UK) to the sample which was heated at 70°C for 1 h. After cooling, water (6 ml) was added and the methyl esters extracted with diethyl ether (3 ml). The solvent was removed under a gentle stream of nitrogen after which the fatty acid methyl esters were redissolved in hexane for analysis by GC, GC–MS and GC–C–IRMS.

2.5. Preparation of dimethyldisulphide derivatives

DMDS (100 μl, Aldrich, Gillingham, UK) and iodine in diethyl ether (6% w/v, 2 drops) were added to the fatty acid methyl esters and allowed to stand at room temperature overnight. The solution was then quenched with aqueous sodium thiosulphate (5% w/v, 500 μl) and the DMDS derivatives extracted with hexane (1 ml). The hexane layer was transferred and used directly for GC–MS analysis.

3. Results and discussion

Since the ''dripping dishes'' are known from pictorial records to have been used to collect the fat form animal carcasses during spit-roasting, the question was posed as to whether the fat from these vessels was used as a fuel for the lamps. A range of analytical techniques was used to compare the compositions of the fats from the two vessel types. Bearing in mind the restricted number of species of domesticated animal that would have been important in the medieval period in the UK, these data can also be used to propose the most likely species of origin for the ancient fats.

3.1. High temperature–GC analyses

Fig. 1 shows typical high-temperature gas chromatograms of the total lipid extracts recovered from a lamp, dripping dish and cauldron. Low abundances of triacylglycerols can be seen at retention times around 30 min, but the majority of the lipid has been hydrolysed, either chemically or enzymatically during use or burial, resulting in a high abundance of free fatty acids. Since di- or monoacylglycerols are only present in very low abundance, this hydrolysis appears to be almost complete. The small amount of triacylglycerol species which remain intact appear to have been absorbed into the matrix of the pot in such a way that they are protected from degradation. The fatty acids present comprise mostly 16:0, 18:0 and 18:1 species and it is possible that shorter chain compounds or oxygenated degradation products which may have been present have been removed through dissolution or are not seen as a result of polymerisation. The high abundance of saturated species in all three vessels suggests animal sources [29]. The distribution of triacylglycerols alone is not sufficiently distinctive to allow different fats to be distinguished.

3.2. FAME analyses

Fig. 2 shows typical gas chromatograms of the FAMEs obtained by saponification and methylation of the total lipid extracts recovered from a lamp (sample 20802) and a ''dripping dish'' (sample 20582). The two types of vessels were clearly grouped according to their fatty acid compositions (Table 2). Although the extracts of all the vessels contained the same major fatty acid components (16:0, 18:0 and 18:1) there were clear differences in the relative proportions. In the lamps, the 18:0 fatty acid was more abundant than the 16:0 component. In contrast, the dripping dishes showed a greater abundance of 16:0. Differences in the minor components could also be seen. The lamps contained significant amounts of branched-chain fatty acids which were only present at low abundance in one of the ''dripping dishes'' (sample 21449) and also displayed a higher abundance of odd carbon-numbered, straight-chain compounds, specifically 17:0 and 19:0. The distinctly different fatty acid profiles of the two

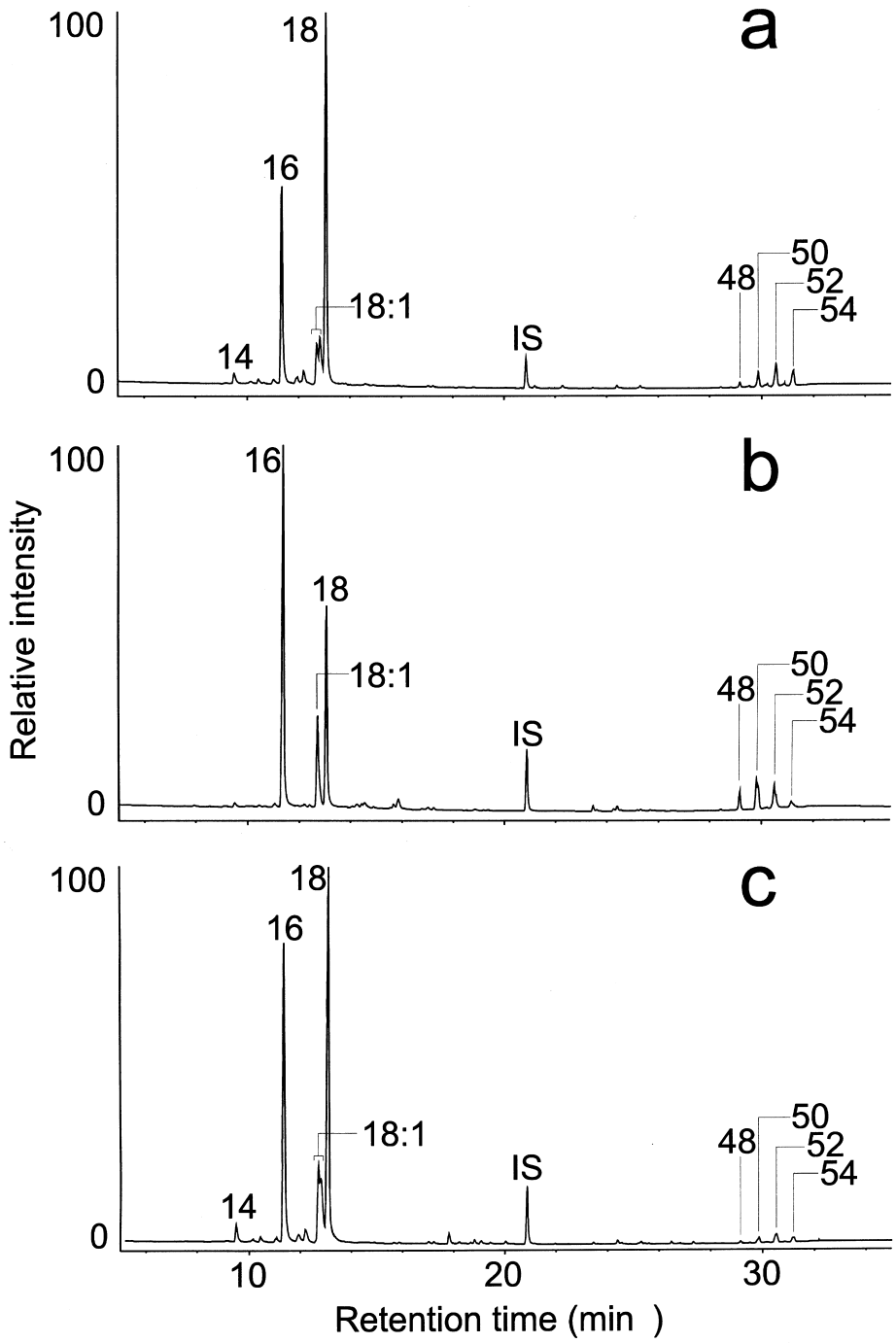

Fig. 1. High-temperature gas chromatograms of the total lipid extracts recovered from a lamp (a), dripping dish (b) and cauldron 21828 (c). Analyses were performed using a 15 m×0.32 mm I.D. fused-silica capillary column coated with DB1 stationary phase (immobilised dimethyl polysiloxane, 0.1 μm film thickness, J&W Scientific, Folsom, CA, USA) and the following temperature program: 50°C (2 min); 50 to 350°C at 10°C min^{-1}; 350°C (10 min). Hydrogen was used as a carrier gas at a column head pressure of 10 p.s.i. (1 p.s.i.=6894.76 Pa). Peak identities are: 14:0, 16:0, 18:0 are *n*-alkanic acids; 18:1 are octadecenoic acids; IS, internal standard of *n*-tetratricontane added at the extraction stage; 48, 50, 52, 54 are triacylglycerols bearing 48, 50, 52, 54 acylcarbon atoms, respectively.

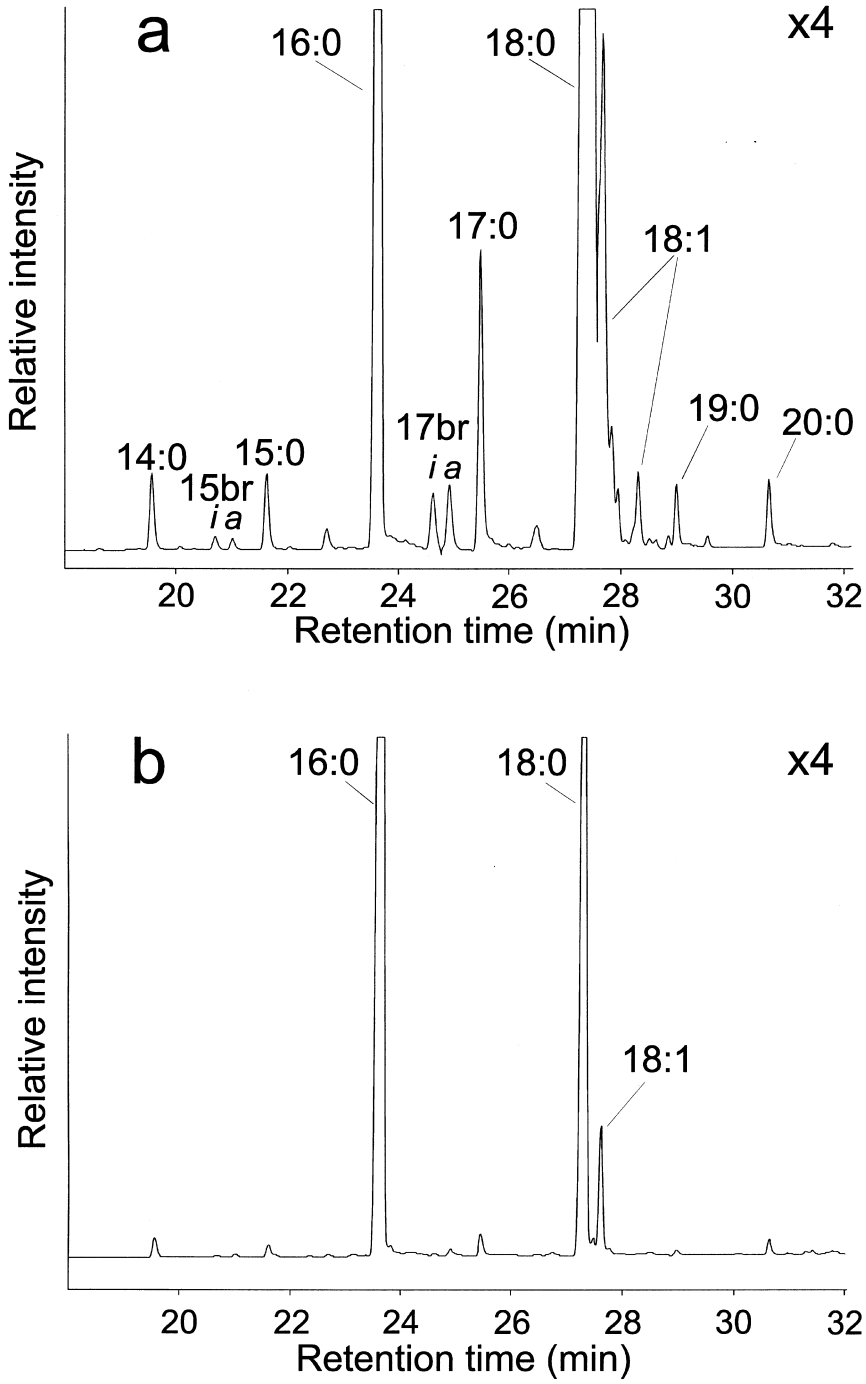

Fig. 2. Gas chromatograms of fatty acid methyl esters recovered from a ''dripping dish'' (a); sample 20582) and a lamp (b); sample 20802). Analyses were performed using a 25 m×0.32 mm I.D. fused-silica capillary column coated with BPX70 stationary phase (immobilised 70% cyanopropyl equivalent modified siloxane; 0.12 μm film thickness; SGE, Milton Keynes, UK). The temperature program was as follows: 40°C (2 min); 40–200°C at 4°C min^{-1}; 200°C (10 min). Helium was used as a carrier gas at a column head pressure of 10 p.s.i. Peak identities are as for Fig. 1 in addition to 15 br and 17 br; i- and a- are iso- and anteiso-isomers of branched C_{15} and C_{17} alkanoic acids.

Table 2
Fatty acid compositions of the total lipid extracts of archaeological pottery vessels

Fatty acid	Archaeological pottery							
	Lamps			Dripping dishes				Cauldron 21828
	20802	21619	23006	20582	21449	21823	21826	
14:0	6.9	2.5	0.7	0.5	1.3	0.9	0.6	2.4
15:0	0.7	1.2	0.6	0.4	0.5	0.7	0.4	1.0
15br	0.2	0.6	0.2	–	0.2	–	–	0.5
16:0	21.5	29.9	18.4	58.6	61.0	57.4	63.0	42.5
17:0	3.2	2.7	2.6	0.6	0.7	1.0	0.6	1.1
17br	1.5	1.5	0.8	–	0.4	–	–	1.0
18:0	59.8	51.9	71.0	32.2	19.5	20.2	26.9	38.3
18:1	8.7	6.5	2.2	3.3	9.8	16.4	1.4	8.8
19:0	1.3	0.3	0.7	–	–	–	–	0.2
20:0	0.6	0.5	1.1	–	0.4	0.5	1.3	0.4
21:0	–	–	0.2	–	–	–	–	0.2
22:0	–	0.4	–	0.4	–	–	–	–
24:0	–	0.8	–	–	–	0.3	–	–
26:0	–	0.7	–	–	–	–	–	–

The compositions are expressed as a percentage of the total. Only those components comprising >0.1% of the total have been reported. Chromatographic conditions as in Fig. 2.

vessel types clearly indicated that the absorbed lipid residues had different origins. The branched-chain compounds observed in the lamps could be due to microbial contamination, but are also characteristic of the fats of ruminant animals, including sheep and cattle [30].

3.3. GC–C–IRMS analyses

Results obtained from duplicate injections were corrected to allow for the extra carbon atom introduced to the molecule during methylation. A correction factor, specific to the batch of reagent, was obtained by comparison of the $\delta^{13}C$ values obtained for standard fatty acids of known isotopic composition (palmitic acid, Sigma, Sigma grade 99%; stearic acid, Aldrich, 99+%) with those of their methyl esters, using the equation of Jones et al. [31]. Fig. 3 shows typical data for the GC–C–IRMS analysis of degraded animal fats from archaeological ceramics. The inset shows the region in which the major fatty acids elute expanded to reveal the resolution that is attained. Since polyunsaturated fatty acids are absent and $\delta^{13}C$ values were only required for the 16:0 and 18:0 components a dimethylpolysiloxane stationary phase was deemed appropriate for this type of analysis. For GC–C–IRMS analyses of fresh animal fats (and plant oils) polar stationary phases, e.g. polyethylene glycol or cyanopropyl polysiloxane phases, are essential to achieve the baseline resolution required for deriving reliable $\delta^{13}C$ values from more complex mixtures [32–35]. It is clear from the high quality of the GC resolution shown in Fig. 3 that high precision $\delta^{13}C$ values are readily obtainable. All our GC–C–IRMS data are manually edited with the result that precisions of better than ±0.3‰ are routinely obtained.

Fig. 4 shows a plot of the $\delta^{13}C$ values of the 16:0 fatty acid versus those of the 18:0 fatty acid. The values show a distinct grouping of the vessels, reflecting that indicated by the fatty acid distributions (Table 2). In the lamps the 16:0 was enriched in ^{13}C relative to the 18:0, whereas in the dripping dishes it was relatively depleted. The discrete groupings indicated by the isotope ratios provide further evidence for the different origins of the lipids absorbed in the pottery. The $\delta^{13}C$ values obtained for sheep and cattle (grass fed ruminants) correlated well with the data obtained for the lamps and were consistent with the fatty acid distributions obtained by GC analysis. The isotope values obtained for the pig fat (non-ruminant) coincided very closely with those obtained

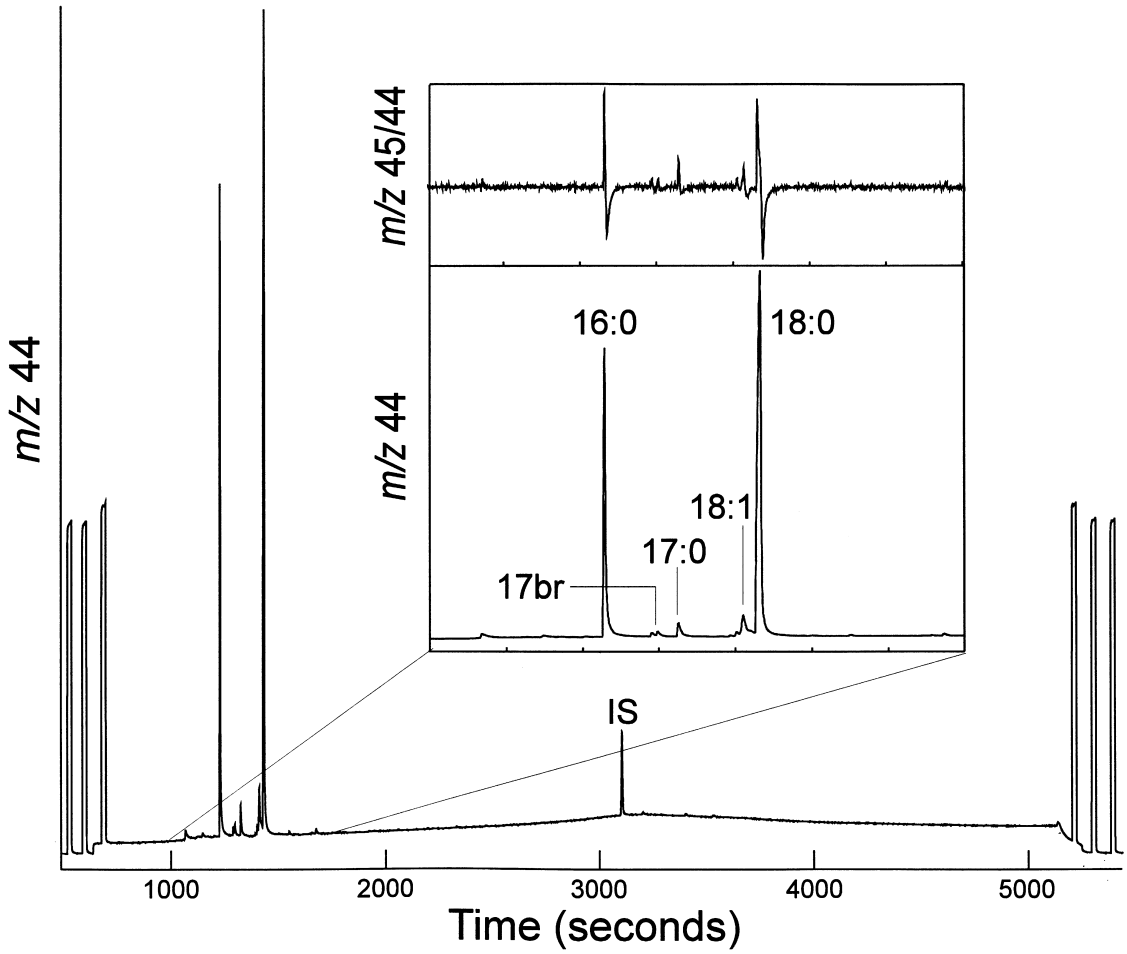

Fig. 3. Partial m/z 44 chromatogram obtained for the GC–C–IRMS analysis of the fatty acid methyl esters recovered from a medieval lamp (sample 21619). Analyses were performed using a 50 m×0.32 mm I.D. fused-silica capillary column coated with CPSil-5CB stationary phase (immobilised dimethyl polysiloxane; 0.12 μm film thickness; Chrompack, Middelburg, The Netherlands), using a SPI injector. The temperature program was as follows: 40°C (2 min); 40–200°C at 10°C min^{-1}; 200–300°C at 3°C min^{-1}; 300°C (15 min). Helium was used as the carrier gas at a column head pressure of 10 p.s.i. The groups of three signals at the beginning and end of the analytical run are replicate samples of reference CO_2 gas used for standardisation purposes. The inset shows an expansion of the region of elution of the fatty acid methyl esters emphasising the baseline resolution required for obtaining reliable $\delta^{13}C$ values. The upper chromatogram in the inset shows the instantaneous ratio of m/z 45/44. I.S. is *n*-tetratricontane, the internal standard used for quantification in standalone GC analyses. The peak identities are as given in Figs. 1 and 2.

for the ''dripping dishes''. Again this was consistent with the fatty acid composition data obtained by GC and GC–MS analysis.

3.4. Analysis of dimethyldisulphide derivatives

Addition of DMDS across the double bonds of monounsaturated fatty acid methyl esters results in bis-methylthio compounds, which when analysed by GC–MS give rise to fragment ions corresponding to cleavage of the molecule between the two methylthio groups. These fragment ions allow the position of the methylthio groups to be determined and hence give information on the position of the double bonds in the original fatty acids (Table 3) [36].

Analysis of the DMDS derivatives of the monoun-

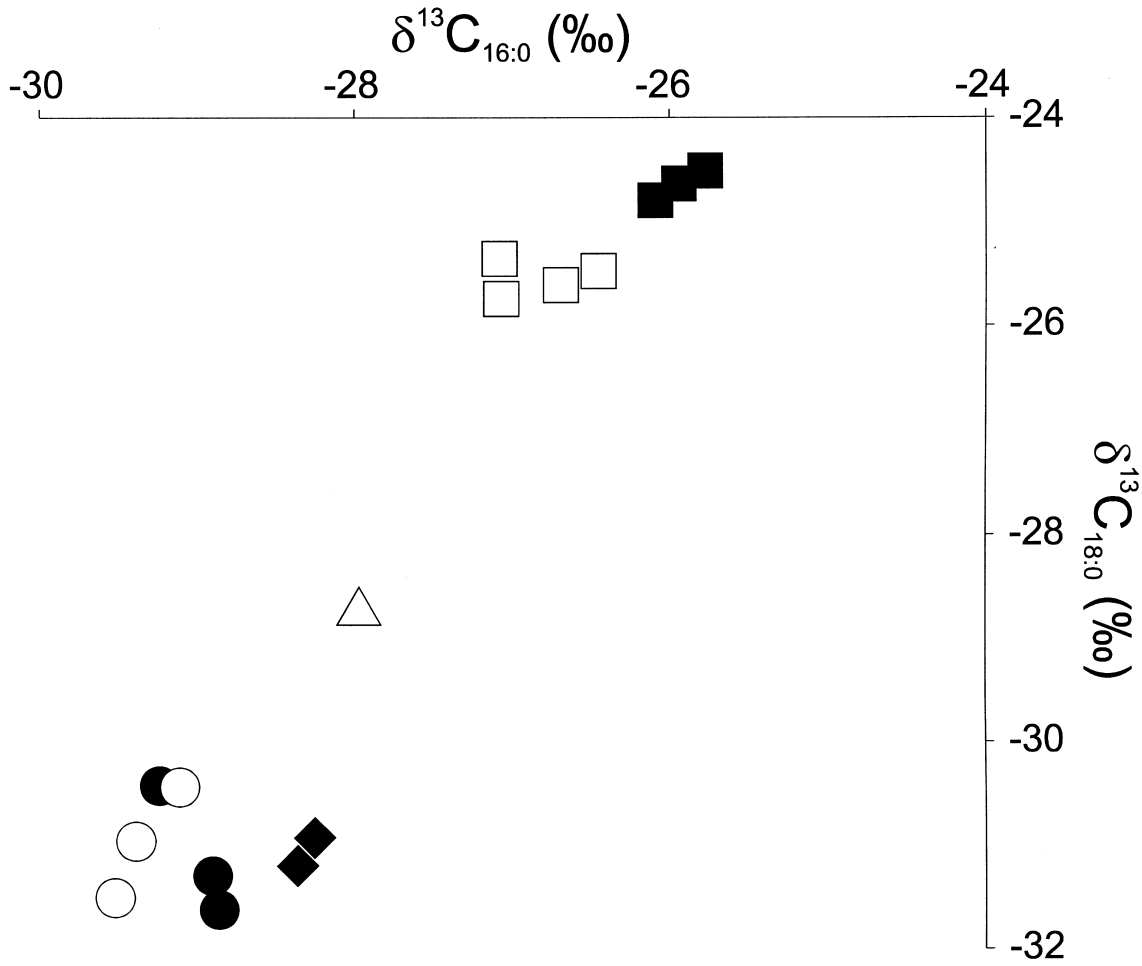

Fig. 4. Plot showing the $\delta^{13}C$ values of the 16:0 and 18:0 fatty acids from archaeological vessels [lamps (○), ''dripping dishes'' (□) and cauldron (△)] and from modern reference fats [cattle (♦), sheep (●) and pig (■)]. Analyses of pottery lipid extracts were carried out using the chromatographic conditions described in Fig. 3. The modern reference fats were analysed according to the chromatographic conditions given in the caption to Fig. 2.

Table 3
Diagnostic fragment ions arising from DMDS derivatives of octadecenoic acid positional isomers

Positional isomer	Fragment ions (m/z)
Δ^{9}	173, 217
Δ^{10}	159, 231
Δ^{11}	145, 245
Δ^{12}	131, 259
Δ^{13}	117, 273
Δ^{14}	103, 287
Δ^{15}	89, 301
Δ^{16}	75, 315

saturated fatty acids extracted from the lamps (Fig. 5a) showed a complex mixture of positional isomers ($18{:}1\Delta^{9,10,11,13,14,15,16}$). The same mixture of isomers is found in the fats of ruminant animals, such as sheep and cattle, due to biohydrogenation of unsaturated dietary fats in the rumen [29]. Such mixtures of monounsaturated fatty acids are not found in the fats of monogastric animals, such as pigs, where a single isomer ($18{:}1\Delta^{9}$) is observed. The presence of this isomer alone in the dripping dishes (Fig. 5b) implies a monogastric or non-ruminant animal origin, whereas the mixture of isomers observed in the lamps

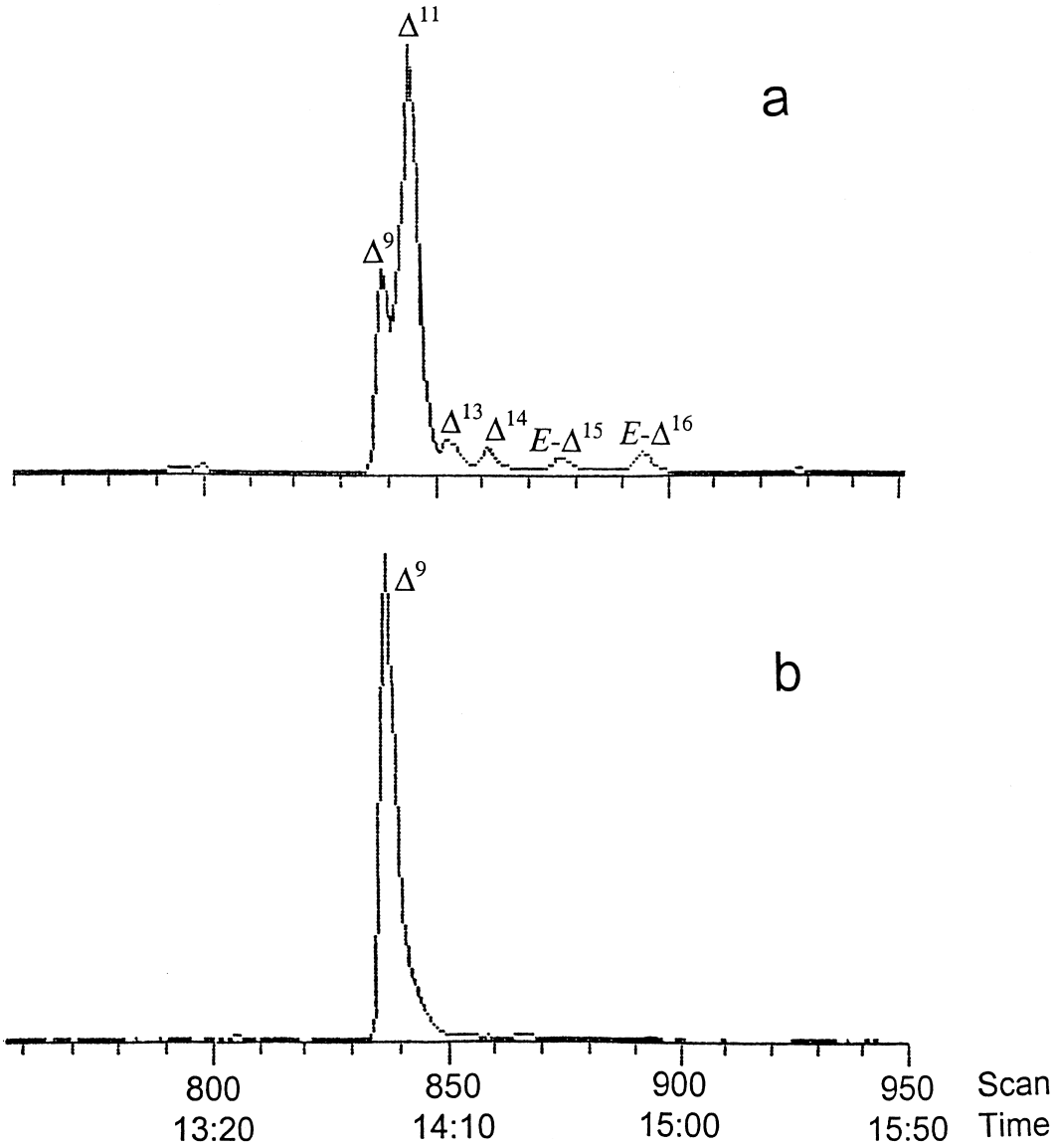

Fig. 5. Partial ion chromatograms from the GC–MS analysis (70 eV electron ionisation) of the dimethyldisulphide derivatives of octadecenoic acid obtained from lamp (a) and dripping dish (b). Analyses performed under the conditions given the caption to Fig. 2.

indicates a ruminant origin. The geometry of the positional isomers of the octadecenoic acid was deduced from the elution orders of the *erythro*- and *threo*-forms of the bis-methylthio derivative [37]. The presence of appreciable abundances of the *E*-isomers is consistent with an origin from biohydrogenated dietary unsaturated fatty acids, i.e. 18:2 and 18:3 [29,30]. These data fully corroborate the information gained from the $\delta^{13}C$ measurements and from the fatty acid analyses.

3.5. Analysis of lipids extracted from the cauldron

Since the lamps and the ''dripping dishes'' had specific purposes in antiquity it is not surprising that they were found to contain residues which originate

from a single fat source. However, general purpose cooking vessels, such as cauldrons, would have been used to process a variety of foodstuffs, so would contain lipid residues of mixed origin. This is confirmed by the HT–GC trace (Fig. 1) in which the fatty acid composition appears to be intermediate between that of the lamps, with the 18:0 fatty acid dominant, and that of the ''dripping dishes''. The assignment of residues of mixed origin by GC alone would be a complex task due to the incomplete knowledge of the effects of long term degradation processes which occur, however the use of $\delta^{13}C$ values provides another criteria for their detection.

The gas chromatogram of the fatty acid methyl esters obtained from the cauldron is shown in Fig. 6. Both branched chain and odd-numbered straight chain fatty acids were detected, in abundances lower than those observed in the lamps (Table 2). Analysis of the DMDS derivatives of the fatty acids from the cauldron showed that the unsaturated fatty acids were present as a mixture of positional isomers ($\Delta^{9,11,13}$). Initially, these results could be indicative of ruminant fat. However, when the isotope values obtained for the 16:0 and 18:0 fatty acids were plotted in Fig. 4, they were clearly distinct from those representing ruminant fat. This could be due to the lipid residue originating from a lipid source which has not been included in this study. More likely in the case of a general purpose cooking vessel, the lipid residue appears to have derived from more than one source, since the mixing of fats would cause the $\delta^{13}C$ values of the resulting lipid residue to be different from those of pure end members. This demonstrates that the stable isotope technique provides a valuable means of detecting mixed origin lipid residues in archaeological pottery.

In summary, GC–C–IRMS has been used to obtain $\delta^{13}C$ values for individual lipid components obtained from a range of archaeological pottery types. Comparison of these values with those from

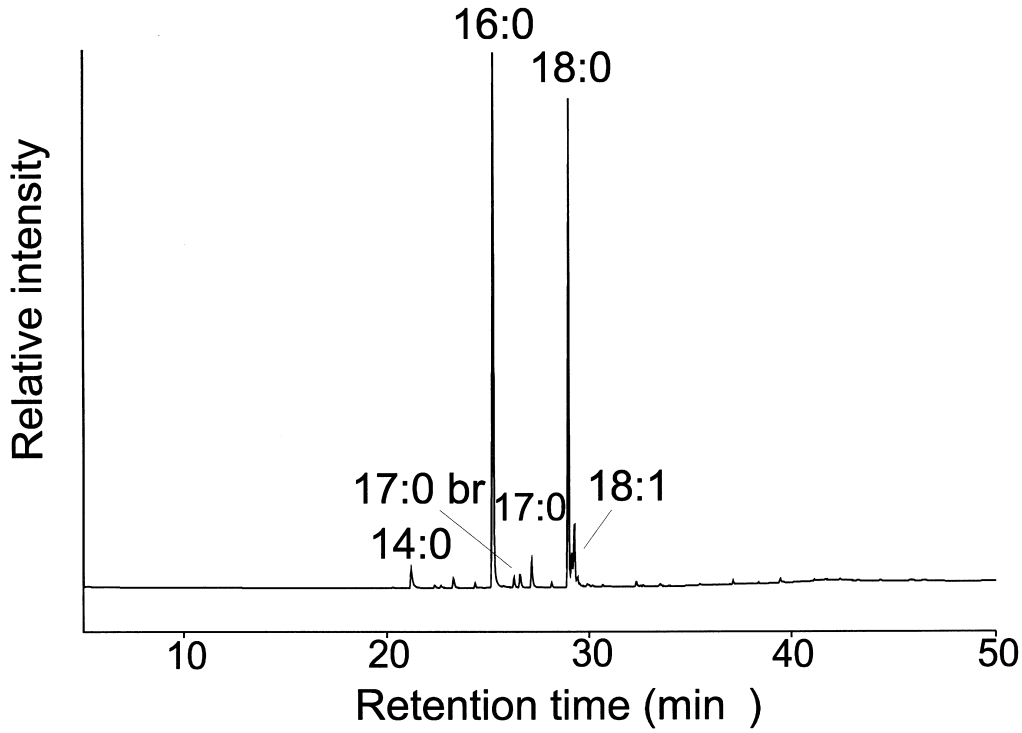

Fig. 6. Gas chromatogram of fatty acid methyl esters recovered from the cauldron (sample 21828). Chromatographic conditions as in Fig. 2. Slight differences in retention times arise from the analyses not being performed on the same day and using a different column of similar dimensions. Peak identities are as given in the captions to Figs. 1 and 2.

modern reference samples has allowed conclusions to be drawn about the function of the vessels in antiquity. These conclusions are substantiated by the use of fatty acid profiling and by determination of the positional isomers of the unsaturated components in the lipid extracts. The data are consistent with the expectation that the fuel burned in the ancient lamps was a ruminant tallow, whilst the ''dripping dishes'' had been used for the collection of fat(s) from non-ruminant animals. The results support the hypothesis that fat collected in the ''dripping dishes'' was not recycled into the lamps as fuel. The compound-specific isotope analyses of fats from a general purpose cooking vessel points to the usefulness of this approach for detecting the use of ancient vessels in the processing of a range of different animal products. A recent development has been the application of this approach in detecting the use of pottery vessels in connection with the processing of dairy products thus providing for the first time a direct means of detecting the exploitation of domesticated animals for milk by early farmers [38,39].

Acknowledgements

The NERC are acknowledged for financial support for mass spectrometry facilities (GR3/2951, GR3/3758 and F60G6/36/01) and a research grant to R.P.E. (GR3/10153). Mr. A. Gledhill is thanked for technical assistance and Ms. A. Conner for provision of archaeological samples and valuable discussions. Julian and Eliza Ridge are thanked for provision of reference animal fats. Drs. M. Enser and J.B. Rossell are thanked for valuable discussions.

References

[1] T.F. Oudemans, J.J. Boon, J. Anal. Appl. Pyrol. 20 (1991) 197.
[2] S. Passi, M.C. Rothschild-Boros, P. Fasella, M. Nazarro-Porro, D.J. Whitehouse, J. Lipid Res. 22 (1981) 778.
[3] R.P. Evershed, C. Heron, L.J. Goad, Antiquity 65 (1991) 540.
[4] S. Charters, R.P. Evershed, A. Quye, P.W. Blinkhorn, V.J.N. Reeves, J. Arch. Sci. 24 (1997) 1.
[5] S. Charters, R.P. Evershed, P.W. Blinkhorn, V. Denham, Archaeometry 37 (1995) 113.
[6] R.P. Evershed, S.J. Vaughan, S.N. Dudd, J.S. Soles, Antiquity 71 (1997) 979.
[7] R.P. Evershed, C. Heron, S. Charters, L.J. Goad, Proc. Br. Acad. 77 (1992) 187.
[8] R.P. Evershed, S. Charters, A. Quye, Mat. Res. Soc. Symp. Proc. 352 (1995) 85.
[9] F.D. Gunstone, J.L. Harwood, F.D. Padley (Eds.), The Lipid Handbook, Chapman and Hall, London, 1986.
[10] S.N. Dudd, M. Regert, R.P. Evershed, Organic Geochemistry 29 (1998) 1345–1354.
[11] B.L. Sherriff, M.A. Tilsdale, B.G. Sayer, H.P. Schwarcz, M. Knyf, Archaeometry 37 (1995) 95.
[12] H.E. Hill, J. Evans, in: D.R. Harris, G.C. Hillman (Eds.), Foraging and Farming: the Evolution of Plant Exploitation, Unwin Hyman, London, 1989, p. 418.
[13] R.P. Evershed, C. Heron, L.J. Goad, Analyst (London) 115 (1990) 1339.
[14] J. Condamin, F. Formenti, M.O. Metais, M. Michel, P. Blond, Archaeometry 18 (1976) 195.
[15] M. Patrick, A.J. de Koning, A.B. Smith, Archaeometry 27 (1985) 231.
[16] S. Charters, R.P. Evershed, L.J. Goad, A. Leyden, P.W. Blinkhorn, V. Denham, Archaeometry 35 (1993) 211.
[17] R.P. Evershed, C. Heron, S. Charters, L.J. Goad, in: R. White, H. Page (Eds.), Organic Residues: Their Identification and Analysis, UKIC Archaeology Section, London, 1990, p. 11.
[18] N.J. van der Merwe, Am. Sci. 75 (1987) 182.
[19] M.J. deNiro, Proc. Br. Acad. 77 (1992) 247.
[20] M.J. deNiro, S. Epstein, Geochim. Cosmochim. 42 (1978) 495.
[21] M.J. deNiro, S. Epstein, Geochim. Cosmochim. 45 (1981) 341.
[22] C.A. Hastorf, M.J. deNiro, Nature (London) 315 (1985) 489.
[23] J.D. Morton, H.P. Schwarcz, in: R. Farquarhar, R.G.V. Hancock, L. Pavlish (Eds.), Proceedings of the 26th International Archaeometry Symposium, University of Toronto, Toronto, 1985, p. 89.
[24] A.W. Stott, R.P. Evershed, Anal. Chem. 68 (1996) 4402.
[25] R.P. Evershed, K.I. Arnot, J. Collister, G. Eglinton, S. Charters, Analyst (London) 119 (1994) 909.
[26] R.P. Evershed, A.W. Stott, A. Raven, S.N. Dudd, S. Charters, A. Leyden, Tetrahed. Lett. 36 (1995) 8875.
[27] A.M. Raven, P.F. van Bergen, A.W. Stott, S.N. Dudd, R.P. Evershed, J. Anal. App. Pyrol. 40 (1997) 267.
[28] P.E. Hare, M.L. Fogel, T.W. Stafford Jr., A.D. Mitchell, T.C. Hoering, J. Archaeol. Sci. 18 (1991) 277.
[29] M. Enser, in: J.B. Rossell, J.L.R. Pritchard (Eds.), Analysis of Oilseeds, Fats and Fatty Foods, Elsevier, London, 1991, p. 329.
[30] W.W. Christie, Prog. Lipid Res. 17 (1978) 111.
[31] D.M. Jones, J.F. Carter, G. Eglinton, E.J. Jumeau, C.S. Fenwick, Biolog. Mass Spectrom. 20 (1991) 641.
[32] S.E. Woodbury, R.P. Evershed, J.B. Rossell, R.E. Griffiths, P. Farnell, Anal. Chem. 67 (1995) 2685–2690.
[33] A.W. Stott, E. Davies, R.P. Evershed, N. Tuross, Naturwissen 84 (1996) 82–86.

[34] S.E. Woodbury, R.P. Evershed, J.B. Rossell, J. Am. Oil Chem. Soc. 75 (1998) 371–379.
[35] S.E. Woodbury, R.P. Evershed, J.B. Rossell, J. Chromatogr. A 805 (1998) 249–257.
[36] G.W. Francis, Chem. Phys. Lipids 29 (1981) 369.
[37] P. Scribe, J. Guezennec, J. Dagaut, C. Pepe, A. Saliot, Anal. Chem. 60 (1988) 928.
[38] R.P. Evershed, S.N. Dudd, S. Charters, H. Mottram, A.W. Stott, A. Raven, P.F. van Bergen, H.A. Bland, Phil. Trans. Roy. Soc., 1998, in press.
[39] S.N. Dudd, R.P. Evershed, Science 282 (1998) 1478–1481.