Illuminating the Late Mesolithic: residue analysis of 'blubber' lamps from Northern Europe

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Shallow oval bowls used on the Baltic coast in the Mesolithic have been suggested as oil lamps, burning animal fat. Here researchers confirm the use of four coastal examples as lamps burning blubber, the fat of marine animals, while an inland example burned fat from terrestrial mammals or freshwater aquatics—perhaps eels. The authors use a combination of lipid biomarker and bulk and single-compound carbon isotope analysis to indicate the origin of the residues in these vessels.

Keywords: Baltic, Mesolithic–Neolithic, Ertebølle, pottery, 'blubber lamps', lipid analysis, marine oils

1. The samples

Neustadt

Four of the vessels were excavated at the site of Neustadt, a submerged coastal site spanning the transition to agriculture. Radiocarbon dates fall between 4600 and 3800 cal BC (Hartz *et al*. 2007; Glykou 2010, 2011). Excavations were conducted at Stiftung Schleswig-Holsteinische Landesmuseen, Schloβ Gottorf between 2000 and

2006. The finds include *c*. 7500 pottery sherds including both Ertebølle and funnel beaker styles, typically associated with the Late Mesolithic and Early Neolithic respectively. Only 2.3% of the sherds belong to 'lamps'; the remainder are from pointed-base vessels and funnel beakers. The 'lamps' in this assemblage have an oval shape with pointed or rounded ends. Of the four samples taken, one of the 'lamps' was unblackened and unsooted. Refitting of the vessel fragments from the four vessels recovered at Neustadt and investigated in our study allow estimates of length from 15–26cm.

Tybrind Vig

Tybrind Vig, Denmark was discovered in 1978 on the seabed some 250m from the present day coastline of the island of Fyn. Excavations were conducted by the Institute of Prehistoric Archaeology, University of Aarhus. Radiocarbon dates confirm that the site was occupied throughout the Ertebølle (Andersen 1985) culture. Exceptional preservation of organic remains, including a wide spectrum of organic artefacts and even textiles was found. Many of the pottery vessels had visible surface deposits associated with them. The animal bone assemblage is dominated by fish (cod, flatfish and dogfish). Sea mammal bones include grey seal and porpoise and one killer whale.

Teglgaard-Helligkilde

The sample from Teglgaard-Helligkilde comes from a large, submerged Late Ertebølle coastal settlement off the west coast of Fyn, Denmark (Andersen 2009).

Åkonge

In addition to the six samples from coastal locations, one 'lamp' from the inland site of Åkonge in central Zealand, Denmark, was included in the study. Åkonge is a seasonal fishing and hunting site located in the Åmose mire, approximately 25km from the coast. A test excavation of the site was conducted in 1984–85 by the Danish National Museum in co-operation with Kalundborg Museum and the National Agency for the Protection of Nature, Monuments and Sites. The pottery assemblage is

dominated by thick-walled cooking pots reminiscent of Ertebølle vessels, except for the absence of a pointed base. Small type 0 funnel beakers occur together with bones of domesticated cattle and possibly domestic pig (Enghoff 1995; Gotfredsen 1998; Fischer 2002). Radiocarbon dates of terrestrial samples of negligible biological life age span the interval 5135–4965 BP (3990–3670 cal BC), while the surface deposit on the 'lamp' has been radiocarbon dated to 5260±70 BP (4310–3960 cal BC; AAR-2678). This suggests that the date of the surface deposit from the 'lamp' is affected by a reservoir effect, which Fischer and Heinemeier (2003) have calculated to 175±74 years.

2. Sample preparation

Bulk isotope analysis

Bulk carbon and nitrogen isotope analysis was undertaken on visible surface deposits scraped from the surface of the vessels where present. The samples were dried and weighed into tin capsules and C and N isotope analyses performed on a Europa 20-20 mass spectrometer fitted with a Roboprep combustion unit. All samples were determined in duplicate and the results averaged.

Gas chromatography-mass spectrometry

To avoid contamination nitrile gloves were worn at all times, all glassware and tools were solvent rinsed and all reagents were of Analar or HPLC grade. Visible deposits were sampled by scraping off approximately 20mg of the residue into a clean glass vial. Between 10 and 20mg was then accurately weighed into a clean scintillation vial. The residue was extracted by ultrasonication for 15 minutes with 3 aliquots of 2ml dichloromethane (DCM):methanol (2:1 v/v). After 10 minutes in a centrifuge at 2000 rpm the extracts were pipetted into a clean vial.

To extract absorbed residues approximately 2g was drilled from the surface of the sherd using a Dremel drill fitted with a diamond tipped bit and drilling between 2 and 4mm deep. Approximately 1g of sherd powder was then accurately weighed into a clean scintillation vial. The same extraction procedure was used as that employed for extracting the visible residues but using three 5ml aliquots of the DCM mixture.

All samples were then desulphured using activated, cleaned copper turnings. The extracts were blown to dryness using a gentle flow of dry nitrogen and gentle warmth (40°C). One portion (10%) of each sample was stored for silylation and analysis by gas chromatography-mass spectrometry (GC-MS). Silylation was carried out by heating for 30 minutes at 60%with an excess of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% TMCS. The excess BSTFA was removed by evaporation under dry nitrogen before analysis. The other portion was methylated by heating in a closed tube at 70°C for 20 minutes with boron trifluoride methanol complex (BF_3), 14% w/v. The reaction was quenched immediately with a few drops of de-ionised water and after cooling the fatty acid methyl esters (FAMEs) were extracted with three 2ml aliquots hexane. The FAME extracts were then partitioned (10/90): 10% retained for GC-MS analysis; 90% sent for compound specific carbon stable isotope analysis by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS). A mixed $C_{16:0}$ and $C_{18:0}$ standard was methylated with each batch of samples to allow correction of the GC-C-IRMS results for the carbon atom added to each molecule during methylation. The carbon isotopic value of unmethylated samples of the same $C_{16:0}$ and $C_{18:0}$ fatty acids had previously been measured.

Further portions of both visible residues and ceramic powders were also extracted by alkaline saponification. A measured amount of residue or powder was heated for 3 hours at 70°C with 3ml 0.5M methanolic sodium hydroxide with 10% water in a closed vial. The neutral fractions were extracted with 3 aliquots of 2ml hexane and the extracts stored for futher analysis. The remaining solution was acidified with 1M hydrochloric acid and extracted as above. The samples were then redissolved in DCM and desulphured with activated copper turnings. The acidic fraction was derivatised with BSTFA before analysis by GC-MS

GC-MS analysis was carried out using an Agilent 7890A Series GC connected to a 5975C Inert XL mass selective detector. The splitless injector and interface were maintained at 300°C and 340°C, respectively. Helium was the carrier gas at constant inlet pressure. The column was inserted directly into the ion source of the mass spectrometer. The ionisation energy was 70eV and spectra were obtained by scanning

between *m/*z 50 and 800. All samples were analysed using an Agilent DB5-ms 15m × 2.5mm × 2.5μm column. The oven temperature was programmed to be isothermal at 50°C for 2 minutes, followed by a rise of 10°C per minute up to 340°C and an isothermal hold for 10 minutes. Methylated samples were also analysed using an Agilent DB23 60 m × 2.5 mm × 2.5μm column to achieve optimum separation of the FAMEs. The oven temperature was programmed to be isothermal at 50°C for 2 minutes, rise at 10°C per minute to 100°C, then at 4°C per minute to 240°C with an isothermal hold for 15 minutes.

Compound specific analysis was carried out on all residues which yielded sufficient $C_{16:0}$ and $C_{18:0}$ fatty acids. Analyses were carried out on Thermo Trace GC connected to a Thermo Delta V IRMS. The GC was fitted with a DB1-Mms (60m × 0.2.5mm × 0.25μm) column. The injector temperature was set at 50°C. The oven was initially held at 50°C for 1 minute, then ramped at 10°C per minute to 120°C, and finally increased to 250°C at 4°C minute and an isothermal hold 20 minutes. Helium was used as the carrier gas. The combustion reactor was set at 940°C.

3. Biomarker identification

The presence of the isoprenoid fatty acids 4,8,12-trimethyltridecanoic acid (4,8,12-TMTD) and 3,7,11,25-tetramethylhexadecanoic acid (phytanic acid) is consistent with aquatic resources. These acyclic isoprenoids are degradation products of phytol (Rontani & Volkman 2003). TMTD has been described as "a compound exclusive to the marine environment…." Corr *et al*. (2008: 2106) although it is also found in freshwater tissues (e.g. Ackman & Hooper 1970). Phytanic acid is found in the tissues of ruminant animals but in combination with TMTD supports the use of aquatic resources in the 'lamps'.

The abundance of cholesterol and cholesterol oxidation products is consistent with lipid of animal origin. Cholesterol has been reported in lipid residues recovered from pottery vessels although the diversity of oxidation products seen in these samples is unusual (Evershed 2008; Regert 2011). An exception is the lipid residue from *c*. 250-year-old soapstone lamp from a coastal Inuit settlement in Alaska which shows a similar suite of cholesterol oxidation products (Solazzo & Erhardt 2007).

According to the USDA National Nutrient Database for Standard Reference, cholesterol levels in fish oils exceed those found in terrestrial adipose tissues. Significant amounts of cholesterol are found in marine mammal blubbers including minke whale, harbour seal, common seal and hooded seal (Stern, unpublished results) and some marine and freshwater tissues, in particular eel and shellfish, are also reported as being rich in cholesterol (Holland *et al*. 1991: 190–221).

The presence of ω-(o-alkylphenyl)alkanoic acids (Evershed *et al*. 2008) and ketones (Evershed *et al*. 1995) is strong evidence for heating of the contents. The presence of C_{16}–C_{22} ω-(o-alkylphenyl)alkanoic acids is indicative of the prolonged heating of tri-, di- and/or monounsaturated fatty acids at high temperatures (270°C or above; Evershed *et al*. 2008). The chain length of these thermal alteration products corresponds to the length of the carbon chain in the precursor unsaturated fatty acids. Unsaturated fatty acids with longer carbon chain lengths (especially C_{20} and C_{22}) are particularly concentrated in fresh tissues of aquatic organisms.

Vicinal dihydroxyfatty acids (C_{16}–C_{20}) were also detected in several 'lamp' extracts. These arise from the oxidative degradation of unsaturated fatty acids in the samples (Hansel and Evershed 2009). This study demonstrated convincingly that the positions of the hydroxyl groups identify the position of the double bond in the precursor fatty acid. Unfortunately no C_{22} dihydroxyfatty acid was detected in the samples even after alkaline hydrolysis. This biomarker can help in distinguishing aquatic from terrestrial resources (Hansel & Evershed 2009; Heron *et al*. 2010). The diagnostic quality of the shorter chain dihydroxyfatty acids components in the 'lamp' extracts is limited. It is possible that the temperatures reached in the burning of the oil in these vessels was insufficient to convert unsaturated fatty acids to ω-(o-alkylphenyl)alkanoic acids. This is supported by the good preservation of the long-chain unsaturated fatty acids in the lipid extracts.

Table S1. 'Lamp' samples analysed.

Vessel no.	Site	Vessel description	Sample code	Sample description	GC-MS	Bulk isotopic	GC-C-IRMS
110	Neustadt	Fragment – base, body and rim. No evidence of surface deposits	N338i	Drilled ceramic (interior)	Y	N	Y
112	Neustadt	Fragment – base, body and rim.	N1009i	Drilled ceramic (interior)	Y	N	Y
		Thin, blackened deposit on the exterior surface of the rim	N1009s	Exterior surface deposit	Y	Y	N
111	Neustadt	Fragment – body and rim	N1682i	Drilled ceramic (interior)	Y	N	Y
		Thin, blackened deposit on the exterior surface of the rim	N1682s	Exterior surface deposit	Y	Y	N
18	Neustadt	Fragment – body and rim. Evidence of thick interior deposit and traces of exterior deposit	N2285i	Drilled ceramic (interior)	Y	N	Y
		Thick black deposit on the interior	N2285f	Interior surface deposit	Y	Y	Y
TH1	Teglgaard Helligkilde	'Lamp' with black interior deposit	TH1i	Drilled ceramic (interior)	Y	N	Y
		Thin, blackened deposit on the interior surface of the rim	TH1f	Interior surface deposit	Y	Y	Y
TV-2033-E	Tybrind Vig	No evidence of surface deposits	TV-2033-Ei	Drilled ceramic (interior surface)	Y	N	N

KML 49.5/75.5:20	Åkonge	Surface deposit sampled for ^{14}C dating (Fischer & Heinemeier 2003)	KML 49.5/75.5:20i	Drilled ceramic (interior)	Y	Y*	Y

Table S2. Carbon and nitrogen isotope measurements obtained on charred surface deposits associated with Ertebølle 'lamps'. Samples with low (<2%) nitrogen by weight indicate that the $\delta^{15}N$ may be unreliable and are shaded. Not determined (nd). Key: (s) exterior surface deposit; (f) interior surface deposit.

Site	Sample	%N	$\delta^{15}N$ (‰)	%C	$\delta^{13}C$ (‰)	C/N ratio
Neustadt	N1009s	4.0	8.98	53	-18.1	15.5
Neustadt	N1682s	1.2	10.99	27	-22.8	25.2
Neustadt	N2285f	0.6	8.49	10	-23.4	19.0
Teglgaard-Helligkilde	TH1f	1.1	4.67	29.7	-19.0	34.0
Åkonge	KML 49.5/75.5:20*	nd	nd	nd	-32.5	nd

* This value is reported in Fischer and Heinemeier (2003).

Table S3. Summary of GC-MS data for all samples.

Site	Sample code	Saturated fatty acids*	Unsaturated fatty acids	Isoprenoid fatty acids	ω-(*o*-alkylphenyl) alkanoic acids	Other lipids present
Neustadt	N338i	$C_{12:0}$–$C_{20:0}$	$C_{16:1}$–$C_{26:1}$	TMTD, phytanic	nd	mono- and dihydroxy fatty acids (C18)
Neustadt	N1009i	$C_{7:0}$–$C_{30:0}$	$C_{14:1}$–$C_{26:1}$	TMTD, phytanic	C18	cholesterol and cholesterol-oxidation products, mono and dihydroxy fatty acids (C18 and C20), MAGs (C16, C18), DAGs
Neustadt	N1009s	$C_{8:0}$–$C_{24:0}$	$C_{14:1}$–$C_{20:1}$	phytanic	C16, C18, C20	cholesterol and cholesterol oxidation products, mono- and dihydroxy fatty acids (C18), ketones (C31, C33)
Neustadt	N1682i	$C_{8:0}$–$C_{26:0}$	$C_{16:1}$–$C_{20:1}$, $C_{18:2}$	TMTD, phytanic	C18	cholesterol and cholesterol oxidation products, diacids (C_{4di}–C_{10di}), mono- and dihydroxy fatty acids (C16, C18, C20), MAGs (C16, C18), C27 and C29 alkanes
Neustadt	N1682s	$C_{10:0}$–$C_{22:0}$	$C_{16:1}$–$C_{18:1}$, $C_{18:2}$	phytanic	C16, C18	cholesterol
Neustadt	N2285i	$C_{7:0}$–$C_{26:0}$	$C_{16:1}$–$C_{18:1}$	TMTD, phytanic	C18, C20	cholesterol and cholesterol oxidation products, mono- and dihydroxy fatty acids (C16, C18, C20), diacids ($C_{4:0di}$–$C_{12:0di}$), ketones (C29, C31, C33)

Neustadt	N2285f	$C_{8:0}$–$C_{26:0}$	$C_{16:1}$–$C_{20:1}$	TMTD, phytanic	C18	cholesterol, dihydroxy fatty acids (C16, C18)
Teglgaard-Helligkilde	TH1i	$C_{6:0}$–$C_{32:0}$	$C_{16:1}$–$C_{24:1}$, $C_{18:2}$–$C_{20:2}$	TMTD, phytanic	C16, C18, C20, C22	cholesterol and cholesterol oxidation products, mono-and dihydroxy fatty acids (C16, C18, C20), diacids ($C_{4:0di}$–$C_{10:0di}$)
Teglgaard-Helligkilde	TH1f	$C_{6:0}$–$C_{26:0}$	$C_{16:1}$–$C_{24:1}$, $C_{18:2}$	TMTD, phytanic	C16, C18, C20, C22	cholesterol and cholesterol oxidation products, mono- and dihydroxy fatty acids (C16, C18, C20), diacids ($C_{4:0di}$–$C_{9:0di}$)
Tybrind Vig	TV-2033-Ei	$C_{8:0}$–$C_{24:0}$	$C_{16:1}$–$C_{18:1}$, $C_{18:2}$	nd	nd	cholesterol, dihydroxy fatty acid (C18), diacid (C_{9di}), dehydroabietic acid
Åkonge	KML 49.5/75.5:20i	$C_{7:0}$–$C_{32:0}$	$C_{14:1}$–$C_{24:1}$, $C_{18:2}$	phytanic	nd	cholesterol and cholesterol oxidation products, mono- and di-hydroxy fatty acids (C16, C18), diacids ($C_{8:0di}$–$C_{10:0di}$), MAGs (C14–C20), ketones (C29–C35)

* Includes low levels of odd-carbon number fatty acids.

Table S4. Single-compound isotope data obtained on $C_{16:0}$ and $C_{18:0}$ fatty acids. Where determined bulk carbon isotope values are shown for comparison. Key: (i) powdered ceramic sample; (s) exterior surface deposit; (f) interior surface deposit.

Site	Sample	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Bulk $\delta^{13}C$ (‰)
Neustadt	N338i	-22.9	-22.9	-
Neustadt	N1009i	-20.3	-21.6	-
Neustadt	N1009s	nd	nd	-18.1
Neustadt	N1682i	-23.6	-23.3	-
Neustadt	N1682s	nd	nd	-22.8
Neustadt	N2285i	-21.4	-22.2	-
Neustadt	N2285f	-22.5	-22.2	-23.4
Teglgaard-Helligkilde	NTH1i	-17.3	-17.2	-
Teglgaard-Helligkilde	TH1f	-15.7	-15.1	-19.0
Åkonge	KML 49.5/75.5:20i	-30.4	-33.1	-32.5

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