Radiocarbon (2024), pp. 1–18
doi:10.1017/RDC.2024.61

Selected Papers from the 3rd International Radiocarbon and Diet Conference, Oxford, 20–23 June 2023

CONFERENCE PAPER

Radiocarbon dating of lipids preserved in pottery vessels: guidelines for best-practice in compound-specific ^{14}C analyses

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Received: 12 November 2023; **Revised:** 23 February 2024; **Accepted:** 23 March 2024

Keywords: Compound-specific radiocarbon analyses; fatty acids; paleodiet; pottery vessels

Abstract
Pottery vessels played a central role in the processing, storage and transport of animal and plant products by prehistoric and historic peoples with their chemical residues surviving for thousands of years. Accurate radiocarbon dating of archaeological pottery vessels by isolating reliable sources of carbon relating to the use of pots has long been a major challenge, but is now possible using compound-specific radiocarbon analysis of absorbed organic residues preserved in the ceramic fabric of the vessel wall. This method involves the radiocarbon dating of single fatty acids most commonly derived from degraded animal fats. These compounds are extracted from the ceramic matrix and isolated from potentially interfering compounds using preparative capillary gas chromatography. When coupled with lipid biomarker and compound-specific stable carbon isotope analyses, this method enables the palaeodietary and chronological information contained in archaeological lipids preserved in ceramic vessels to be interpreted together. From a practical perspective the methodology is challenging and for successful application must adhere to rigorous protocols. We present here guidelines which include (i) consideration of pottery selection, (ii) technical parameters for the isolation of fatty acids then their ^{14}C dating and calibration, and (iii) case studies selected to illustrate the best use of this method.

1. Introduction

Direct and accurate radiocarbon dating of archaeological pottery vessels has been challenging due to the rarity of reliable sources of C surviving in sufficient amounts for radiocarbon analysis. In radiocarbon dating, samples must meet three main criteria to provide accurate and reliable dating. First, the carbon in a sample must have been in equilibrium with the atmosphere, or another well-characterised carbon reservoir, during its lifetime. Second, it must not be irretrievably contaminated by other materials containing carbon, and third, it must be securely associated with the event to be dated (Bayliss and Marshall 2022).

Among the sources of carbon available in potsherds, carbon from the clay itself would provide an age older than the manufacture of the pot and is only present in small quantities. The carbon from the temper used in the manufacture of the pot can give accurate results if it is organic, survived the firing and can be

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successfully isolated from other C sources (Messili et al. 2013; Tóth et al. 2023). However, the survival of organic tempers is rare making this method very limited. Charred, or visible, residues adhering to the surface of the potsherds, resulting from the firing (soot residues) or from the cooking (food crusts) are potential candidates for ^{14}C dating but not always reliable due to their exposure to the burial environment requiring separation of exogenous and endogenous C sources. In practice, 1 out of 3 charred residues give non-reproducible results (Bayliss and Marshall 2019), likely related to the presence of contaminants in the bulk fractions that are not food or fuel derived. Finally, the lipids from food residues adsorbed in the vessel wall derive from short-lived organisms, are protected from the burial environment in the clay matrix of the sherd and are associated with the use of the pottery. Dating of total lipid extracts (TLEs) of adsorbed residues has been attempted but found to be problematic (Hedges et al. 1992), emphasising once again the necessity for the source of C to be clearly identified and efficient separation of contaminants from burial or storage undertaken. Furthermore, complete removal of solvent introduced during laboratory processing remains extremely challenging, and often results in apparent age offsets. These limitations led us to consider adopting compound-specific approaches with the use of preparative capillary gas chromatography (pcGC) to remove exogenous contaminants in the 2000s, which although initially promising (Berstan et al. 2008; Stott et al. 2003, 2001), failed to achieve acceptable levels of accuracy due to unidentified methodological problems at the time.

Having established an in-house radiocarbon accelerator facility, we revisited the compound-specific analysis (CSRA) of adsorbed fatty acids residues of animal origin using pcGC for purification (Casanova et al. 2020c, 2018). We undertook the direct identification and quantification of contamination sources (column bleed, residual solvent) demonstrating that their elimination was necessary to achieve the highest levels of purity of single FAs for radiocarbon dating. We demonstrated the accuracy of the method using a range of sites that have independent dates based on dendrochronology or radiocarbon dating of other materials (collagen and charcoals) combined with chronological modelling (Casanova et al. 2020c). We then published a wide range of case studies detailing the utility of the method. These include: the dating of sites that were previously undatable using conventional materials (Casanova et al. 2020c; Stojanovski et al. 2020a), the verification of the age of lipids within pots (Dunne et al. 2019; Fewlass et al. 2020), and the direct dating of specific food commodities such as ruminant dairy products (Casanova et al. 2022a, 2020a; Dunne et al. 2023; Grillo et al. 2020; Manning et al. 2023; Stojanovski et al. 2020b) or equine products (Casanova et al. 2022c). We have also investigated the impact of aquatic resources processing on the age of the lipids and marine reservoir effect corrections and used ^{14}C dating as a tracer for aquatic resources exploitation (Casanova et al. 2022b, 2020b). Despite its reliability, our new method is nonetheless challenging and requires careful sample selection and pretreatment protocols to obtain accurate results.

In order for this method to be routinely and correctly used we present in this paper a set of best-practice guidelines for the CSRA of pottery vessels. We include details of (i) key considerations regarding pottery selection in relation to the archaeological questions to be answered, (ii) technical considerations for the isolation of single compounds, and (iii) the protocols for ^{14}C measurement and the corrections that must be applied before calibration.

2. Selection of potsherds

2.1 Archaeological selection criteria

A primary requirement when selecting potsherds for radiocarbon dating is a detailed understanding of their archaeological context. Sample selection is critically dependent on the objectives of the study and the methodology that will be employed for the interpretation of the results (Bayliss and Marshall 2022, §3).

Sherds may be of intrinsic interest, because they are typologically diagnostic or contain dietary or other information. For instance, if the research question focuses on refining and anchoring relative

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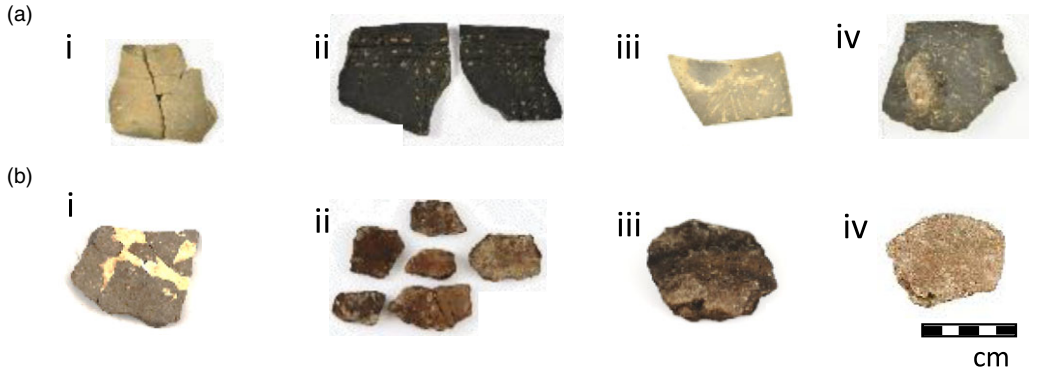

Figure 1. *Photographs of potsherds from the early Neolithic sites of* ***a.*** *Rosheim "Rittergass", France and* ***b.*** *Robin Hood Ball, UK with examples of 1. Refitting potsherds, 2. Non-refitting potsherds judged to be from the same vessel, 3. Single decoratively (a. Linearbandkeramik decoration) or typologically (b. carinated bowl) characteristic potsherds, and 4. Single undecorated potsherds.*

typochronologies to provide calendrical timescales for the occurrence of particular vessel types directly, then sample selection must focus on these typologically characteristic vessels (Casanova et al. 2020c). If the research question focusses on directly dating specific foodstuffs (e.g. dairy products), then potsherds with residues identified as relating to the commodities must be selected (*cf.* part 2.2.2) (Casanova et al. 2022a; Stojanovski et al. 2020b). In these cases, the provenance of the samples is immaterial, as what matters is the quality of the typological or other information that is intrinsic to the sherd.

If the objective of the study is to provide dating for an archaeological site or another type of archaeological sequence (e.g. a seriation of grave-assemblages), then stricter archaeological criteria for sampling are required. In these cases, it is important to assess whether potential samples are intrusive or residual in the context from which they were recovered. Evidence that may be used to infer that sherds are not redeposited or intrusive includes (in descending order of reliability; Figure 1):

a. Complete vessels deposited in closed contexts (e.g. graves).
b. Refitting potsherds.
c. Non-refitting sherds judged to be from the same vessel.
d. Vessels where the entire profile survives.
e. Sherds judged to have been deliberately deposited (e.g. to line a pit).
f. Large sherds in fragile fabrics which are likely to have broken further if redeposited.

These criteria are particularly important where it is intended that stratigraphy or other archaeological information will be incorporated with the radiocarbon dates using Bayesian chronological modeling to provide more precise chronologies, or when sampling from multi-period sites. They are also critical when it is not possible to sample typologically distinctive sherds (either on curatorial grounds or because they do not contain sufficient FAs), and so less distinctive material is sampled instead from the same deposits.

2.2. Selection criteria based on organic residue analysis (ORA)

2.2.1 Influence of vessel type and technology on lipid preservation

Prior to any dating, ORA of a pottery assemblage is required as a prescreening process to determine which potsherds contain lipid compositions and concentrations suitable for dating (Evershed et al. 1990). For ORA, analyses a minimum of 30 potsherds per variable (e.g. phase, vessel type), is needed to

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obtain statistically representative results. The selection criteria for ORA are freely available through the Historic England guidance document for good practice in organic residue analysis (Dunne, 2017).

Differential accumulation of lipids in vessels is influenced by vessel type (e.g. bowls, jars, plate) due to the specialisation of different vessels for cooking or storing various commodities (Charters et al. 1993). The use of the same vessel to cook several food commodities can result in an inhomogeneous distribution of lipids from these sources in vessels (Casanova et al. 2020b; Charters et al. 1995). A study using mass spectrometric imaging further highlighted this inhomogeneity and also confirmed the influence of calcium carbonate temper on the preservation of fatty acids as salt precipitates within potsherds (Hammann et al. 2020), explaining the enhanced lipid recoveries achieved with acidified methanol extraction (Correa-Ascencio and Evershed 2014). Quantification of lipids preserved in potsherds is a vital step in identifying potsherds for dating programmes, but due to the inhomogeneous nature of lipid accumulation in vessels, variable concentrations will inevitably be observed between sampling points.

Based on three decades of ORA, cooking vessels have repeatedly been shown to contain the highest concentrations of lipids, often reaching concentrations exceeding one milligram of lipid per gram of sherd fabric, especially in the upper parts of vessels. To maximise the chances of finding potsherds rich in lipids for CSRA dating cooking vessels should be targeted, with sherds taken from the upper part of the vessel. Large potsherds allowing samples of up to 10 g of ceramic to be taken with minimal alteration to the vessel profile are preferred. Different vessel types can also be targeted, such as plates or storage vessels depending on the research question, although they will likely exhibit lower lipid concentrations, but this is site/culture dependent.

2.2.2 Lipid sources and distributions

A critical first step after collection of potsherds is a prescreening using approximately 2 g of potsherd. We recommend that lipid extraction be performed using an acidic extraction ($MeOH/H_2SO_4$) rather than solvent extraction to maximise the lipid recovery and provide effective quantification (Correa-Ascencio and Evershed, 2014). The addition of an internal standard is essential for quantification of lipids (Correa-Ascencio and Evershed, 2014). The TLEs should be prescreened by gas chromatography (GC), GC–mass spectrometry (GC-MS) and GC–combustion–isotope ratio MS (GC-C-IRMS). At present, potsherds which are suitable for dating should be identified based on their lipid distribution according to the following criteria:

a. TLEs should be dominated by palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) fatty acids (FAs) characteristic of degraded animal fats (Figure 2a–d). Sherds with lipids originating from different sources (potentially with reservoir offsets) should be avoided. TLEs showing the presence of other compounds such as long-chain *n*-alkanes or *n*-alkanols in appreciable abundances suggest the mixing of animal fats with other resources. Such samples do not make ideal candidates for CSRA and caution should be exercised (Figure 2e–f).
b. Lipid abundance should be over 500 µg of lipids per gram of sherd, which translates to sampling ~5 g of potsherds for CSRA. Lower concentrations down to 250 µg g^{-1} of sherd can be targeted, but this means up to 10 g of sherd will be required and there is more potential for inhomogeneous lipid partitioning.
c. Ideally, $C_{16:0}$ and $C_{18:0}$ FAs should be present in relatively equal abundances to allow isolation of the same quantity of each compound (Figure 2a–b). This criterion is unlikely to be met for all TLEs, since the relative abundance of the two FAs depends on the source of animal fat and diagenetic state (Figure 2c–d) (Casanova et al. 2022c).
d. FAs must derive from terrestrial animals. This can be determined using the $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values determined by GC-C-IRMS together with screening for aquatic biomarkers by GC/MS with SIM (selective ion monitoring) mode (Casanova et al. 2020b; Cramp and Evershed 2014), examination of faunal remains, and consideration of site location to ensure no reservoir effects will affect the ^{14}C dates.

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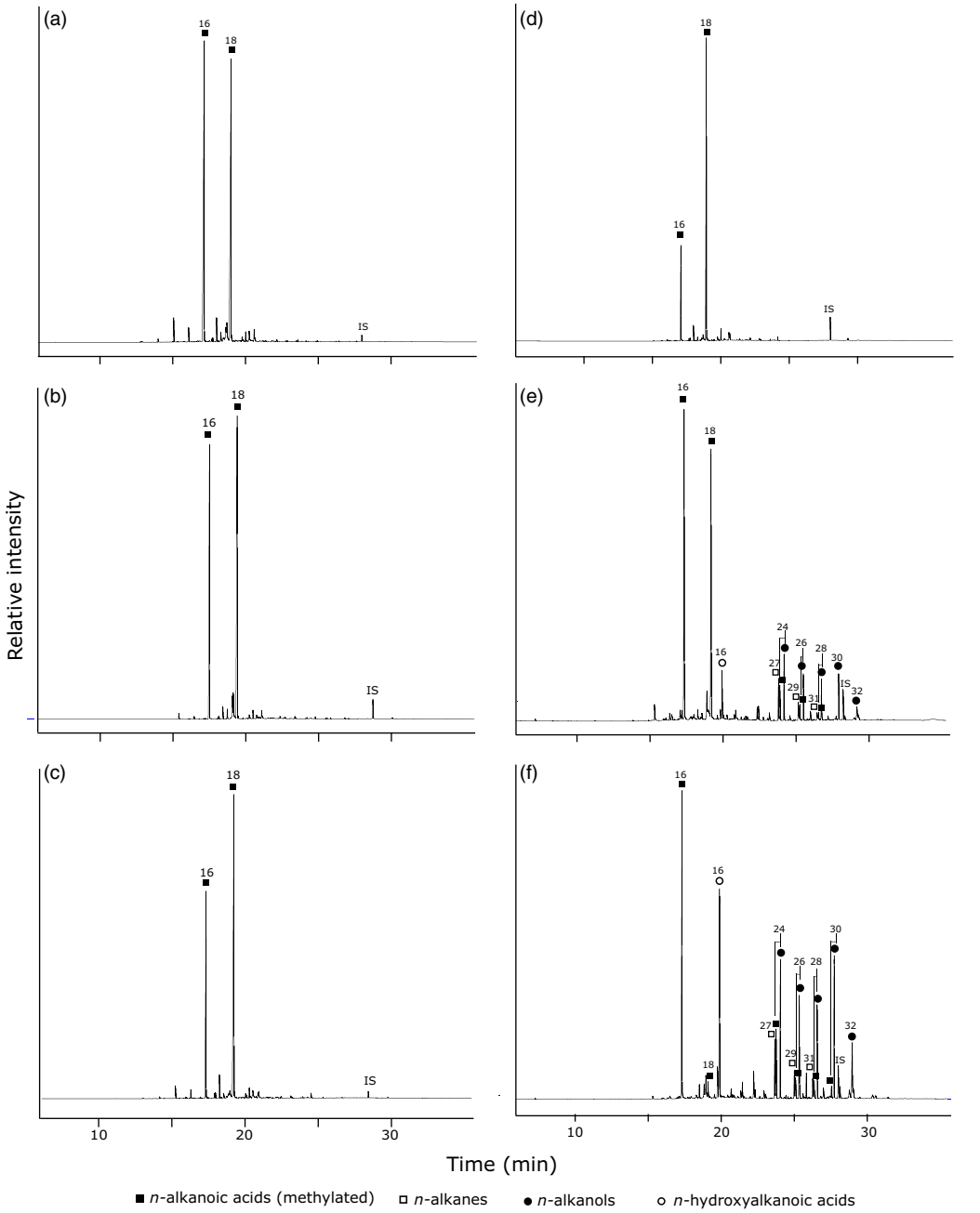

Figure 2. *Partial gas chromatograms of potsherds with concentrations suitable for ^{14}C dating for* ***a.*** *ROS-C-4694* ***b.*** *ROS-C-4682* ***c.*** *ROS-C-4701* ***d.*** *ROS-C-4677 exhibiting "pure" animal fats and various ratios of the $C_{16:0}$ and $C_{18:0}$ fatty acids,* ***e.*** *ROS-C-4615 showing a mixture of animal fat and beeswax and* ***f.*** *ROS-C-4617 showing a dominance of beeswax. IS is the internal standard and numbers corresponds to the carbon chain lengths of the various alkyl lipids.*

Pottery used to process aquatic resources only or the mixing of terrestrial and aquatic resources can also be CSRA dated but this adds complexity compared to FAs of terrestrial origin as it requires quantification and correction for aquatic reservoir effects (cf. part 5.2). It is also possible to target biomarker lipids other than FAs, such as *n*-alkanes in the case of the presence beeswax (Figure 2f) or

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plant residues. The compound(s) of interest need to be present at high enough concentrations for CSRA. Furthermore, targeting other classes of compounds will necessitate making changes to the chromatographic and trapping parameters required for the isolation of new compounds (cf. part 3.3). These modified methods will require full re-validation as they may affect factors such as trapping efficiency, cross-contamination in the pcGC (notably, the syringe and trapping capillaries), and column bleed etc.

2.3 Case Study 1: Consideration of the number of required potsherds for CSRA

We provide here an example of a "typical" application of CSRA using a regional collection of pottery from seven sites dating from the 6th to 4th millennium BC in Alsace, France (Casanova et al. 2020a). Table 1 summarises ORA results of 871 potsherds indicating the lipid profiles defined as 'pure' terrestrial animal fats, the sherds from refined decorated vessels and undecorated vessels, including refitting sherds, containing lipid concentrations >500 $\mu g.g^{-1}$. This level of evaluation is essential for assessing the suitability of pottery assemblages and pinpointing specific potsherds, for CSRA (Table 1).

Of the 871 potsherds analyzed, a total of 88 sherds, or 10%, were regarded as suitable for ^{14}C dating if sherd size allowed. The proportion of potsherds datable from each site varies between 2% and 28%. Overall, the frequency of undecorated vessels was found to be better than decorated pottery vessels in meeting the criteria for CSRA, i.e. 83 undecorated versus 5 decorated potsherds. The highest lipid concentrations defined as "pure" animal products were recovered predominantly from undecorated pottery vessels, while decorated vessels showed lower lipid concentrations and more complex mixed animal and plant/beeswax lipid profiles. This difference supports hypotheses surrounding vessel specialisation, with undecorated vessels being most commonly used as utilitarian cooking pots while the decorated vessels were more likely used as table wares. Focussing only on the undecorated (cooking vessels) then 15% of sherds from this category were suitable for dating using CSRA, which is typical for many prehistoric assemblages.

Variations in the proportion of datable potsherds in assemblages derived from contemporaneous sites, even those in close proximity and of the same cultural group (Linearbandkermik (LBK) culture), highlight the influence of the burial and diagenesis on lipid preservation. For example, the site of Colmar showed poor lipid preservation with 3% of the undecorated sherds being datable, while other LBK settlements reached up to 17%. There is also temporal variation for lipid preservation from the same locality as illustrated by Rosheim. The proportion of datable undecorated potsherds is 17% for the LBK (ca. 5500 BC), 33% for the Grossgartach (ca. 4600 BC) and 32% for the Roessen (ca. 4400 BC). The higher proportion of sherds suitable for CSRA in the younger deposits may point to differences in cooking practices between the cultural groups.

The overall dataset shows that cooking vessels are the best candidates for CSRA. The results also suggest that, ca. 3 to 10 times the number of potsherds targeted for radiocarbon dating should be analyzed by ORA to identify sufficient suitable samples for a dating programme.

3. Pretreatment of fatty acids for CSRA

3.1 Extraction of FAs from potsherds

Once the potsherds have been selected for CSRA, lipids are extracted from the ceramic matrix using an acidified solution of methanol (Correa-Ascencio and Evershed, 2014) employing a protocol optimised for larger ceramic samples, up to 10 g (Casanova et al. 2020c). The processing of potsherds proceeds as follows:

a. Removal of surface contaminants from the exterior of the potsherd using a modeling drill (Figure 3ai). The cleaned piece is handled with tweezers (to avoid contamination from fingers or gloves),

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Table 1. *Table showing the numbers of potsherds: analyzed per site, containing animal fats, with concentration >500 μg.g^{-1}, and suitable for ^{14}C dating for the overall assemblage, refitted, decorated and undecorated sherds. The percentages are calculated for the total number of sherds per category except for the bold values that are the percentage of the total number of sherds analyzed per site. BIS = Bischoffsheim, ROS = Rosheim, COL = Colmar, ENS = Ensisheim, SIE = Sierentz, LBK = Linearbandkeramik (early Neolithic), Gro. = Grossgartach (Middle Neolithic), Roe. = Roessen (Middle Neolithic)*

		Total sherds		Refitted sherds		Decorated sherds		Undecorated sherds	
Site	Characteristic	#	%	#	%	#	%	#	%
BIS	# analyzed	**287**	**100**	**29**	**10**	**134**	**47**	**153**	**53**
LBK	'Pure' animal fats	68	24	3	10	12	9	56	37
	Lipid conc. > 500 μg.g^{-1}	29	10	0	0	3	2	26	17
	Datable	28	10	0	0	2	1	26	17
ROS	# analyzed	**102**	**100**	**18**	**18**	**37**	**36**	**65**	**64**
LBK	'Pure' animal fats	34	33	4	22	5	14	29	44
	Lipid conc. > 500 μg.g^{-1}	13	13	1	6	1	3	12	18
	Datable	12	12	1	6	1	3	11	17
ROS	# analyzed	**57**	**100**	**15**	**26**	**14**	**25**	**43**	**75**
Gro.	'Pure' animal fats	26	46	8	53	6	43	20	47
	Lipid conc. > 500 μg.g^{-1}	18	32	6	40	2	14	16	34
	Datable	15	26	5	33	1	7	14	33
ROS	# analyzed	**29**	**100**	**8**	**28**	**7**	**24**	**22**	**76**
Roe.	'Pure' animal fats	10	34	5	63	1	14	9	41
	Lipid conc. > 500 μg.g^{-1}	11	38	1	13	2	28	9	45
	Datable	8	28	1	13	1	14	7	32
COL	# analyzed	**192**	**100**	**22**	**11**	**68**	**35**	**124**	**65**
LBK	'Pure' animal fats	17	9	2	9	2	3	15	12
	Lipid conc. > 500 μg.g^{-1}	5	3	0	0	0	0	5	4
	Datable	4	2	0	0	0	0	4	3
ENS	# analyzed	**101**	**100**	**7**	**7**	**43**	**43**	**58**	**57**
LBK	'Pure' animal fats	40	40	3	42	20	47	20	34
	Lipid conc. > 500 μg.g^{-1}	8	8	0	0	0	0	8	14
	Datable	8	8	0	0	0	0	8	14
SIE	# analyzed	**102**	**100**	**16**	**16**	**22**	**22**	**80**	**78**
LBK	'Pure' animal fats	46	45	4	25	6	27	40	50
	Lipid conc. > 500 μg.g^{-1}	14	14	2	13	1	5	13	16
	Datable	13	13	1	6	0	0	13	14
Total	# analyzed	**871**	**100**	**115**	**13**	**325**	**37**	**545**	**63**
	'Pure' animal fats	241	27	29	25	52	16	189	35
	Lipid conc. > 500 μg.g^{-1}	98	11	10	9	9	3	89	16
	Datable	88	10	8	7	5	2	83	15

sub-sampled using a hammer and chisel, crushed to a fine powder using a pestle and mortar then transferred to one or several culture tubes depending on the mass of ceramic powder.

b. The lipids are simultaneously extracted, and the FAs methylated to fatty acid methyl esters (FAMEs) using a methanolic solution of sulphuric acid (4% *v/v*, 3 × 8 mL, 1 hr, 70ºC; Figure 3aii). To ensure all lipids are recovered, especially when extracting large amounts of clay regular mixing is performed and the extraction performed three times in total.

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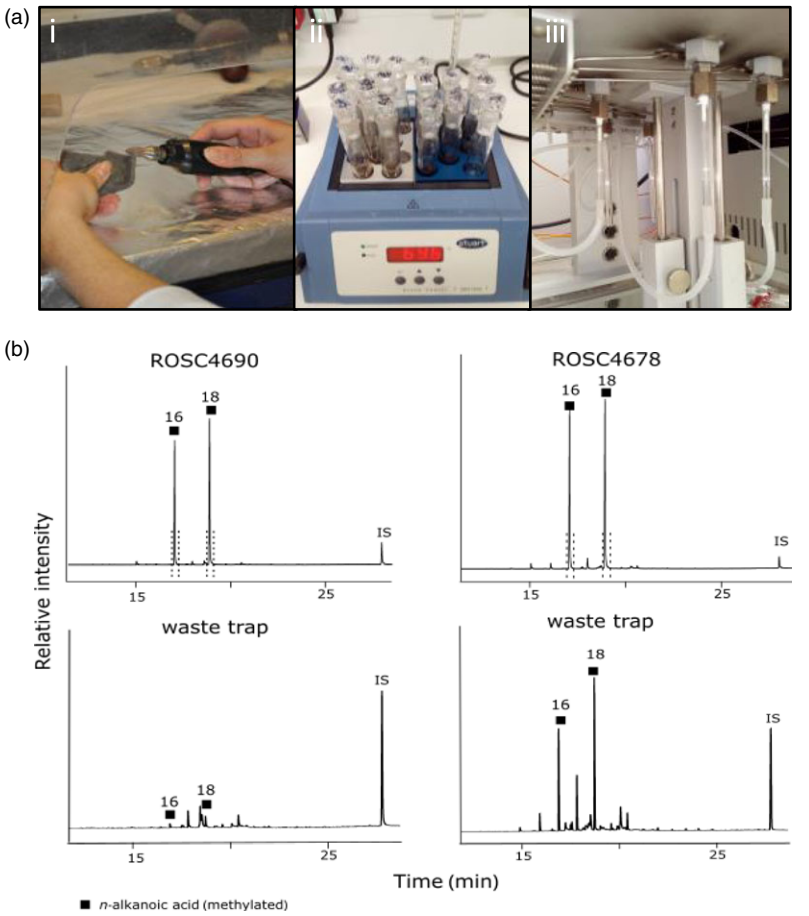

Figure 3. ***a****. Main steps of the pretreatment procedure:* ***i.*** *Cleaning of potsherd surface* ***ii.*** *Extraction of lipids from powdered ceramic on heating block* ***iii.*** *Solventless trapping system for isolation of single compounds by pcGC.* ***b.*** *Gas chromatograms of potsherd lipid extracts suitable for* ^{14}C *dating (upper) with the dashed lines indicating the trapping windows required to isolate* $C_{16:0}$ *and* $C_{18:0}$ *fatty acids, and the contents of the waste traps after isolation by pcGC (lower).*

c. The three acid extracts are transferred to a test tube, centrifuged (10 min, 2500 rpm) and combined in a larger culture tube containing 5mL of MQ-water. The lipids are then extracted from the acidic aqueous phase using *n*-hexane (4 × 5 mL), which is transferred into 3.5 mL vials, and blown down to dryness under a gentle N_2 stream. If an emulsion is visible in the centrifuge tubes further centrifugation is undertaken (5 min, 2000 rpm) before decanting the *n*-hexane fractions for evaporation.
d. The vials are weighed empty, and after concentration of the lipids extracted to roughly estimate the recovery of lipids. TLEs are stored dried and sealed with PTFE tape in the fridge before pcGC isolation.

3.2 Assessing and eliminating contamination in the PCGC instrument

Prior to the isolation of the FAs in the pcGC instrument, sources of contamination should be quantified and suppressed. To achieve this, we recommend the following:

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a. Verifying that the GC column stationary phase "bleed" is not contributing significant C to samples by its quantification. This can be achieved using the method described in Casanova et al. (2017). This should be performed every time a new column is fitted, and when changing the trapping parameters to isolate higher molecular weight compounds. For FAME isolation, we utilise a non-polar column (100% dimethylpolysiloxane, 1.5 µm film thickness, 30 m, Restek) as it allows injection of concentrated lipid extracts and demonstrates minimal column "bleed". Other "low bleed" columns from other suppliers are likely also suitable for the method, but have not been tested by us.
b. Use of our solventless trapping system (STS; Figure 3aiii) consisting of a plug of furnaced glass wool (~1 cm) held in a glass capillary tube (Casanova et al. 2018). The standard U-tube trap design should be avoided as it requires use of organic solvent to recover the trapped compounds. Our NMR studies have shown this solvent remains trapped within the isolated FAME sample, which introduces offsets in the ^{14}C results. In addition, we showed the average FAME recovery with the STS is 95.7% (Casanova et al. 2018).
c. Elimination of carryover effects between samples in the instrument by cleaning the syringe, changing the waste solvent, and baking the column at 300°C for 20 min. The residual FAs in the capillaries connecting the preparative unit to the traps must be cleaned using a heat gun then wiped with ethanol. If further contamination is visible (e.g. particulate graphite from ferrules) after cleaning, then the capillaries must be trimmed or replaced before proceeding.
d. In the absence of standards and blanks of the same compounds (with the same chromatographic and trapping parameters), pseudo-processing standards and blanks should be employed. This is achieved by injection of *n*-hexane, and trapping the same chromatographic elution "windows" as for the analyte compounds ($C_{16:0}$ and $C_{18:0}$ FAMEs). After transfer of the glass wool (containing any column bleed or other contamination arising from processing that would be present in samples) to foil capsules, a standard or blank (e.g. IAEA C-7, phthalic anhydride blank etc.) is added to the same capsule to obtain the pseudo processed standards. We have also created $C_{16:0}$ and $C_{18:0}$ FA ^{14}C standards from bog butter for use as full processing standards for CSRA (Casanova et al. 2021). Once the, current intercomparison exercise on these materials is completed, these standards will be made available to the scientific dating community upon request to the National Museum of Ireland.

3.3 Isolation of FAs by PCGC

Successful isolation of FAMEs requires rigorous assessment of (i) chromatographic quality, (ii) the concentration of FAs in the extract solutions, and (iii) retention times of the FAs under the pcGC conditions, before setting up a trapping sequence. A short GC method of just over 20 min for each run means that one pot extract can be completed in 24 h. The critical steps in the workflow are as follows:

a. The TLEs must be derivatised with *N,O*-Bis(trimethylsilyl)trifluoroacetamide (20 µL, 1 h, 70°C) as *n*-alkanols are often present (even in low concentrations) and clog the injector if not derivatised. After removal of the excess of BSTFA under a stream of N_2, the TLE is redissolved in a minimum of 80 µL *n*-hexane and transferred to an auto-sampler vial using a clean syringe.
b. Furnaced traps need to be fitted on the fraction collector, one per compound to be isolated and one for use as a "waste"' trap. This way, if isolation is not successful, FAMEs can be recovered from the waste trap and re-isolated.
c. The TLE should be run once in the pcGC to assess the chromatography, allow the concentration to be adjusted to ~5 $\mu g.\mu L^{-1}$ of individual FAMEs, and to define the trapping windows for the isolation of FAMEs based on their retention times.
d. A trapping sequence should be set up to isolate ~200 µg of C per compound in 40 consecutive injections. If the relative proportion of $C_{16:0}$ and $C_{18:0}$ FAs is uneven adjust the dilution to ensure a

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minimum of 200 µg of C is isolated for the compound with the lowest abundance in 40 injections. If the relative proportion of the two FAs is over four, the most concentrated FAME should be isolated for fewer runs (10, for example), the trap replaced with a new one to complete the isolation of the second FAME (Casanova et al. 2022c). This will prevent the isolation of substantially different amounts of FAMEs, but also ensure that no more than the maximum amount of C required for graphitisation is used (1 mg in our case). Pseudo-processing standards and blanks can be run using these parameters for blank correction and quality control purposes.

e. Once isolated, the traps should be removed, wrapped in aluminium foil, and stored in the fridge until graphitization, as the FAMEs can demethylate under high temperatures.

3.4 Case Study 2: Trapping efficiency

The PGC trapping efficiencies of solventless trap design have been rigorously assessed using a standard solution of $C_{16:0}$ and $C_{18:0}$ FAMEs (Casanova et al. 2018). The study showed that using a 1 min trapping window across the two peaks resulted in ca. 1% of the FAMEs going into the waste trap, probably as a result of the tailing of the peaks. The remainder of each FAME, on average 98% of the total, was trapped onto the glass wool plug with 1% deposited on the glass wall. When applied to more complex FAME extracts of potsherds the trapping windows were reduced to about 30 s to avoid co-trapping of compounds eluting just after (<1 min) after the FAMEs.

Efficiency of FAME trapping is illustrated in Figure 3b. The extraction of 1.8 g and 2.3 g of powdered potsherd yielded total lipid concentrations of 2.1 $mg.g^{-1}$ and 5.3 $mg.g^{-1}$, respectively, of potsherds ROSC4690 and ROSC4678. The concentrations of the TLEs were adjusted to ~5 $\mu g.\mu L^{-1}$ of individual FAMEs for their isolation in the pcGC. In order to evaluate the trapping efficiency, the contents of the waste trap were analyzed by GC as the trapped $C_{16:0}$ and $C_{18:0}$ were required for the ^{14}C measurements. For sherd TLE ROSC4690 the amounts of $C_{16:0}$ and $C_{18:0}$ present in waste trap were 5.1 µg and 11.3 µg, respectively, corresponding to 1 and 2% of the FAME injected supporting the average 98% trapping efficiencies determined using standards. For the TLE of ROSC4678 the waste trap contained 15.2 µg and 21.9 µg, respectively, of $C_{16:0}$ and $C_{18:0}$ which corresponds to 8 and 10% of the FAME injected. In this case the peak tail was longer due to the higher amounts of FAMEs injected with the result that a lower proportion of the chromatographic peaks were captured by the narrower trapping windows.

This case study emphasises the importance of carefully considering the width of trapping windows in relation to the amounts of FAME injected, as trapping efficiencies will be reduced due to peak tailing, with the chromatographic peak tails transferred to the waste trap following switching. The critical judgement in trapping compounds from complex mixtures is balancing the need for peak purity (avoiding co-trapping) against trapping efficiency.

4. Radiocarbon determinations

4.1 Graphitization and AMS measurements

Once the FAMEs are trapped, the glass wool plug containing the FAMEs is directly transferred into an Al foil capsule using a clean glass pipette, plunger or a wire. Graphitization and AMS analysis is carried out as described in Knowles et al. (2019). Briefly, we use an elemental analyser for the combustion coupled to an automated graphitization equipment (EA-AGE 3) (Wacker et al. 2010b), but this could also be performed using semi-automatic or manual lines depending on individual laboratory capabilities. For the pseudo-processing standards (*cf* part 3.2), the standard is weighed into the Al capsule then the glass wool from the trap is added prior to combustion. The FAME processing standards (bog butters) are treated in exactly the same way as a pot lipid extract.

The graphite targets are analyzed by AMS (MICADAS; Synal et al. 2007) alongside size-matched standards. It is commonly the case that the $C_{16:0}$ and $C_{18:0}$ FA of individual potsherds differ in

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abundance resulting in differing amounts being trapped. In such instances data reduction for the different sample sizes is performed in different calculation sets, so that appropriate corrections can be applied.

4.2 Correction for the derivatising methyl carbon

The FAs are converted to FAMEs during their extraction, making them amenable for GC isolation using a non-polar GC column. The methylation adds a single C atom (of fossil origin, from the methanol) to the FA that affects the measured radiocarbon date and thus requires correction. Two types of correction can be applied (Stott et al. 2003): (i) a simple mass balance correction (Equation 1, referred as $F^{14}C_{FA.1}$), or (ii) a more refined correction, which considers the fractionation occurring during the methylation reaction (Equation 2, referred as $F^{14}C_{FA.2}$).

$$F^{14}C_{FA.1} = \frac{No.C_{FAME} * F^{14}C_{measured}}{No.C_{FA}} \tag{1}$$

$$F^{14}C_{FA.2} = F^{14}C_{FA.1} * \left(\frac{1 + \left[\frac{-25 + \delta^{13}C_{FAME}}{1000} \right]}{1 + \left[\frac{-25 + \delta^{13}C_{FA}}{1000} \right]} \right) \tag{2}$$

Where $F^{14}C_{FA.x}$ is the fraction modern of the FA corrected for the derivative C, $F^{14}C_{measured}$ the fraction modern of the measured FAME, $No.C_{FA\ or\ FAME}$ is the total number of C atoms in the FA or FAME and $\delta^{13}C_{FA\ or\ FAME}$ the $\delta^{13}C$ value of the FA or FAME (‰) recorded by GC-C-IRMS.

The efficiency of such corrections was verified by ^{14}C dating two modern FA standards before and after methylation (no PCGC isolation). The direct measurements on the FA (Table 2) passed the χ^2 test at the 5% level and the weighted average is $F^{14}C_{FA} = 1.0430 \pm 0.0015$ ($T' = 1.5$, $T'(5\%) = 9.5$, $\nu = 4$) for the $C_{16:0}$ FA and $F^{14}C_{FA} = 1.5037 \pm 0.0015$ ($T' = 0.3$, $T'(5\%) = 9.5$, $\nu = 4$) for the $C_{18:0}$ FA. The measurements of the methylated FA passed the χ^2 test at the 5% level for the $C_{16:0}$ ($T' = 7.6$, $T'(5\%) = 9.5$, $\nu = 4$) and the $C_{18:0}$ ($T' = 4.6$, $T'(5\%) = 9.5$, $\nu = 4$). This demonstrates a good reproducibility of the methylation process within statistical expectations.

When applying the mass balance correction (Equation 1) then $F^{14}C_{FA.1} = 1.0434 \pm 0.0020$ for the $C_{16:0}$ and $F^{14}C_{FA.1} = 1.0528 \pm 0.002$ for the $C_{18:0}$ FA. The values were all identical within error to the weighted mean of direct measurements (with the exception of BRAMS-1086.2.1 which is just outside the 2-σ range) demonstrating the accuracy of the radiocarbon determinations after correction. When applying the correction including fractionation (Equation 2) then $F^{14}C_{FA.2} = 1.0428 \pm 000.20$ for the $C_{16:0}$ and $F^{14}C_{FA.2} = 1.0521 \pm 0.0020$ for the $C_{18:0}$ FA. These values are identical within error to the weighted average of the direct measurements, demonstrating the accuracy of the radiocarbon determinations after correction.

A difference was observed of 0.5‰ from the weighted average value of $F^{14}C_{FA}$ and $F^{14}C_{FA.1}$, and of 0.2‰ from the average value of $F^{14}C_{FA}$ and $F^{14}C_{FA.2}$ for the $C_{16:0}$ FA. The difference between the two corrections is 0.7‰ (i.e. 5-6 y with fossil C). For the $C_{18:0}$ FA the difference between the average values of $F^{14}C_{FA}$ and $F^{14}C_{FA.1}$ is 0.9‰ and that between $F^{14}C_{FA}$ and $F^{14}C_{FA.2}$ is 1.6‰. The difference between the two corrections is also 0.7‰.

Both corrections met the accuracy expected after correction as the results are statistically indistinguishable from the direct measurements. The $F^{14}C_{FA.2}$ measure for the $C_{18:0}$ FA being above 1‰ difference from the bulk date, we suggest the simple mass balance approach (Equation 1, $F^{14}C_{FA.1}$) introduces less variability and is sufficient in obtaining an accurate correction for the derivatising methyl group added during the extraction of lipids and we therefore adopt this one routinely.

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Table 2. *$F^{14}C$ of $C_{16:0}$ and $C_{18:0}$ FA dated directly and after methylation and pcGC isolation. $F^{14}C_{FA}$ corresponds to the fatty acid, $F^{14}C_{FAME}$ to the fatty acid after methylation, $F^{14}C_{FA.1}$ to the correction of additional methyl group using mass balance calculation, and $F^{14}C_{FA.2}$ to the correction of the methyl group using the refined correction to account for fractionation*

	Direct measurement		Measurement after methylation			
Sample	BRAMS #	$F^{14}C_{FA} \pm 1\ \sigma$	BRAMS #	$F^{14}C_{FAME} \pm 1\ \sigma$	$F^{14}C_{FA.1} \pm 1\ \sigma$	$F^{14}C_{FA.2} \pm 1\ \sigma$
$C_{16:0}$ FA	1086.1.1	1.0458 ± 0.0035	1086.2.1	0.9715 ± 0.0046	1.0322 ± 0.0046	1.0315 ± 0.0046
	1086.1.2	1.0418 ± 0.0034	1086.2.2	0.9847 ± 0.0045	1.0462 ± 0.0045	1.0455 ± 0.0045
	1086.1.3	1.0423 ± 0.0034	1086.2.3	0.9845 ± 0.0045	1.0461 ± 0.0045	1.0454 ± 0.0045
	1086.1.4	1.0406 ± 0.0034	1086.2.4	0.9858 ± 0.0045	1.0475 ± 0.0045	1.0467 ± 0.0045
	1086.1.5	1.0445 ± 0.0034	1086.2.5	0.9837 ± 0.0045	1.0451 ± 0.0045	1.0444 ± 0.0045
	Weighted mean	**1.0430 ± 0.0015**	**Weighted mean**	**0.9847 ± 0.0022**	**1.0435 ± 0.0020**	**1.0428 ± 0.0020**
$C_{18:0}$ FA	1085.1.1	1.0527 ± 0.0035	1085.2.1	1.0018 ± 0.0045	1.0575 ± 0.0045	1.0568 ± 0.0045
	1085.1.2	1.0545 ± 0.0035	1085.2.2	0.9914 ± 0.0046	1.0464 ± 0.0046	1.0458 ± 0.0046
	1085.1.3	1.0526 ± 0.0035	1085.2.3	0.9974 ± 0.0044	1.0529 ± 0.0044	1.0522 ± 0.0044
	1085.1.4	1.0545 ± 0.0035	1085.2.4	1.0016 ± 0.0045	1.0573 ± 0.0045	1.0566 ± 0.0045
	1085.1.5	1.0540 ± 0.0035	1085.2.5	0.9946 ± 0.0045	1.0499 ± 0.0045	1.0492 ± 0.0045
	Weighted mean	**1.0537 ± 0.0015**	**Weighted mean**	**0.9974 ± 0.0022**	**1.0528 ± 0.0022**	**1.0521 ± 0.0022**

4.3. Internal quality control and combination

Each pottery vessel produces two ^{14}C dates: one per FA. There is therefore, an internal quality control criterion based on the identicality of the $C_{16:0}$ and $C_{18:0}$ FA radiocarbon ages after correction for the methanol (Casanova et al. 2020c). If the measurements are statistically indistinguishable at the 5% level, the two results should be combined before any calibration.

The measurements on the $C_{16:0}$ and $C_{18:0}$ FAs are not fully independent as they are extracted and methylated from the same vessel and trapped by GC at the same time, so the combination of their dates should not be calculated as a simple weighted average using their quoted uncertainties, as would be done for two independent replicates. Given the uncertainties introduced during the FA preparation are not statistically independent we calculate the uncertainty of the combined date as follows (Casanova et al. 2020b):

$$\sigma_f = \sqrt{{\sigma_{wm}}^2 + {\sigma_{ss}}^2} \tag{3}$$

Where σ_f is the final overall uncertainty associated with the combined measurements of the FAs, σ_{wm} is the combined (reduced) uncertainty from the weighted mean of measurements using only the AMS uncertainty (equivalent to $\sigma_{<Rmol,bl,f>}$ in Wacker et al. (2010a) and σ_{ss} is the sample scatter to account for additional uncertainties associated with sample preparation (equivalent to σ_{ex}). The value for σ_{wm} is calculated by combining the two dates after removing the sample scatter factor from their respective uncertainties.

Any two measurements that are not statistically indistinguishable should be treated with caution as this could denote contamination occurred during pretreatment or isolation. Possible causes would be deterioration of graphite ferrules in the preparative unit or inadvertent deposition of dust in the traps during the fitting/release of the traps. If a significant difference is still observed between the two FA ages in a second analysis of lipids from the same pot, this would more likely be a result of different sources of C (with different relative abundances and radiocarbon ages) contributing to the two FAs, such as the mixing of aquatic and terrestrial fats in the same vessel (see section 5.2. below for further discussion of this). If remeasurement is not possible then these values should be treated with caution.

5 Calibration of radiocarbon dates

5.1 Calibration of terrestrial animal lipid dates

For the calibration of terrestrial fats, we use the combined $C_{16:0}$ and $C_{18:0}$ measurements in calibration software such as OxCal (Bronk Ramsey 2009). The potsherd dates are calibrated against the latest calibration curve available for the Northern or Southern hemisphere based on the location of the site.

If the potsherd dates are integrated into chronological models for Bayesian analyses of radiocarbon dates their position in the models is defined based on the site stratigraphy or seriation on a case-by-case basis. For instance, the CSRA of FAs from potsherds from Çatalhöyük were integrated in the model in a position defined by the stratigraphy, while the potsherds from the Grossgartach were integrated into a model based on seriation (Casanova et al. 2020c).

5.2 Calibration of mixed marine/terrestrial lipid dates

In some cases, the ^{14}C dated FAs are not purely of terrestrial origin but present as mixtures with fats of marine origin. In such cases corrections for marine reservoir effects (MRE) are necessary. For calibration and correction, similar considerations to those applicable to bone collagen are applied. This means using the local deviation from the global marine curve (ΔR,) and calculating the percentage of marine products in the dated fraction (Cook et al. 2015). These considerations are published in detail in Casanova et al. (2020b), so we only provide a summary here. The following steps must be undertaken:

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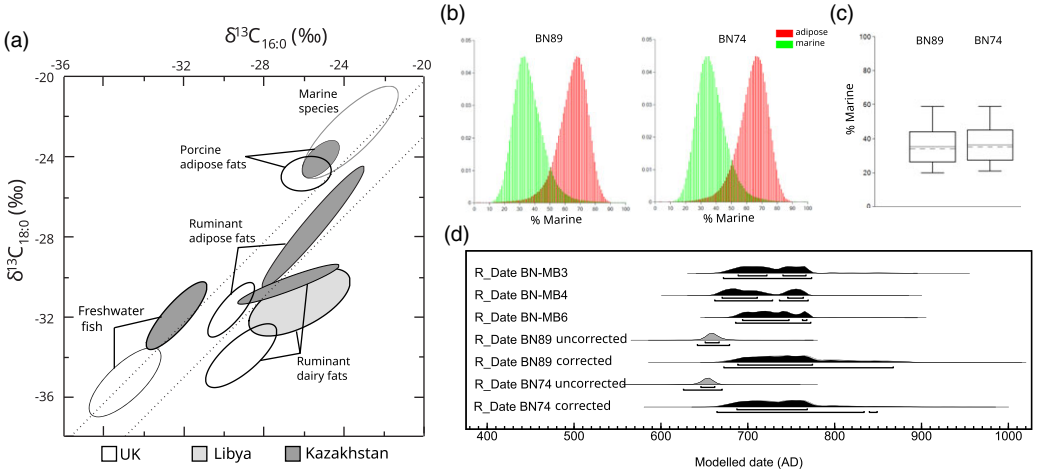

Figure 4. a. *Compilation of reference values of modern ruminant adipose, ruminant dairy, porcine adipose fats, marine and freshwater species from the UK, Libya and Kazakhstan (Copley et al. 2003; Cramp and Evershed 2014; Dunne et al. 2012; Outram et al. 2009). Ellipses represent the 68% (1σ) of the values.* ***b,c.*** *Percentage of marine products in the lipid extracts expressed as probability distributions (b) box and whisker plots (c) for the potsherds BN74 and BN89.* ***d.*** *Calibration of reference terrestrial animal bone dates and the dates on the lipids from potsherd BN74 and BN89 uncorrected and corrected for the marine reservoir effect (From Casanova et al. 2020b).*

a. Identification of the likely presence of marine product processing in potsherds based on the presence of aquatic biomarkers in the TLEs, $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values, and faunal assessments.
b. Evaluation of the local ΔR using paired marine/terrestrial specimens at the site or using the published ΔR relevant for the spatiotemporal area.
c. Evaluation of $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ end-member values for modern reference terrestrial and marine species relevant to the local area. There is now a large database of reference animals for the UK, north Africa and Kazakhstan e.g. (Copley et al. 2003; Cramp and Evershed 2014; Dunne et al. 2012; Outram et al. 2009) allowing selection of values appropriate to the local range and animal species present at archaeological sites as endmembers (Figure 4a). If no published reference animals are available for the area, local modern reference values should be recorded on animals with feeding practices relevant to prehistory (Roffet-Salque et al. 2017).
d. Calculation of the percentage of marine products ($\%_{marine}$) using $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values and those of the local and relevant endmembers. The percentage of marine products could be simply evaluated with linear mixing of the $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values of marine and terrestrial endmembers, however, we recommend implementing the $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values in the software FRUITS (Fernandes et al. 2014) or the ReSources IsoMemo package (https://github.com/Pandora-IsoMemo/resources).
e. Correction for the marine reservoir effects in the software OxCal using the *Marine/mixed curve* tool and the ΔR and $\%_{marine}$ determined. We recommend implementing the full probability distribution of the $\%_{marine}$ calculated in FRUITS or ReSources as a *Prior* file rather than the mean and standard deviation as the percentage marine.

5.3 Calibration of mixed freshwater/terrestrial lipid dates

Animal fat residues in pottery can also originate from freshwater environments such as lakes or rivers. In such systems these residues will be affected by a freshwater reservoir effect (FRE). FREs generally arise due to the introduction of old C to the aquatic system, most notably as a result of the dissolution of

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carbonates, known as the hard water effect (Philippsen, 2013) or the ebullition of CO_2 from close volcanic activity. The measurement of such reservoir effects is time, depth, and species dependent for a given site, with high variability observed (Hajdas et al. 2021; Keaveney and Reimer 2012). It is therefore extremely complex, making it essential to properly estimate the FRE at sites. It is also extremely difficult to quantify the FRE of lipids preserved in potsherds if freshwater resources were mixed with terrestrial resources.

There is currently no published example of a dataset where correction of ^{14}C dates of lipid residues affected by a FRE has been performed. However, if such study is to be contemplated, we recommend the following:

a. Identification of the presence of freshwater resource processing in potsherds using combination of the specific aquatic biomarkers, stable carbon isotope values and faunal evidence. This should be done for every site in a freshwater catchment using the whole ceramic assemblage studied for ORA.
b. Assessment of the local geology to determine whether the water bodies are closed or open systems and if possibilities exist for dissolution of "old" C from carbonates or volcanic activity. This will give preliminary indications of whether FRE are likely to be present at sites. The FRE can then be evaluated, as before, by dating paired aquatic and terrestrial archaeological samples from the same contexts.
c. Evaluation the percentage of freshwater products using the using $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values of the individual fatty acids of the pots (recorded on the same TLE submitted for dating) and those of endmember values derived from modern references relevant for the site catchment.
d. Correction of the FA radiocarbon dates for the FRE prior to calibration using the calculated reservoir effect and the percentage of aquatic products processed in the vessels.

5.4 Case Study 3: Calibrating and modeling mixed terrestrial and aquatic lipid dates

We illustrate here the correction for marine reservoir effects affecting lipids from two potsherds for the site of Bornais in the Outer Hebrides, UK. For this site ~170 pottery vessels were analyzed by ORA, which revealed extensive processing of ruminant carcass, ruminant dairy and marine products in the pottery vessels. Aquatic biomarkers were identified in approximatively 50% of the vessels analyzed (Casanova et al. 2020c; Cramp et al. 2020). We applied the paired dating approach to terrestrial and marine products from the same contexts to calculate the local ΔR of –65 ± 46.

We calculated the $\%_{marine}$ using $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values of the pottery and those of modern reference animal species from the UK land and coastal waters as endmembers (Copley et al. 2003; Cramp and Evershed, 2014). We hypothesised that pigs and other non-ruminants had not contributed significantly to the fat residues in the pottery due to their relatively low representation in the faunal record compared to other species, and only considered marine species present at the site (e.g. limpets, winkles, cod, saith etc.). We therefore, used the mean values of $\delta^{13}C_{16:0} = -30.0 \pm 0.6‰$ and $\delta^{13}C_{18:0} = -32.2 \pm 0.6‰$ for ruminant adipose fats, $\delta^{13}C_{16:0} = -29.2 \pm 1.0‰$ and $\delta^{13}C_{18:0} = -34.0 \pm 0.9‰$ for dairy fats and $\delta^{13}C_{16:0} = -22.7 \pm 2.2‰$ and $\delta^{13}C_{18:0} = -21.7 \pm 2.5‰$ for marine fats as end-members. These values were input into the FRUITS model alongside the $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values recorded for the FAs extracted from two potsherds to obtain the proportion of marine products present in pots (Figure 4b,c). This value, alongside the percentage marine (full probability distribution file extracted from FRUITS), were inputted into OxCal using the Mix/Marine function for MRE corrections. The corrected ^{14}C measurements give probability distributions entirely compatible with the calendar ages of terrestrial organisms from the same context (Figure 4d).

In another case study of inland sites across central Europe, we found aquatic biomarkers in lipid extracts identified as ruminant adipose and ruminant dairy products based on $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values (Casanova et al. 2022a). Because these sites are inland but rather close to freshwater streams and

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lakes, FREs were possible. The absence of aquatic remains in the faunal record meant it was not possible to evaluate the FRE for the sites, hence, the ^{14}C dates were not corrected but rather modeled in OxCal as *TPQ* dates (*Terminus Post Quem*, i.e. "date after which"). This was a cautionary approach which recognised the potential for FREs affecting the CSRA measurements.

Conclusions

CSRA dating of pottery vessels is a powerful new method that we have validated and applied to numerous case studies allowing us to begin two establish its potential and limitations. It should not be underestimated how challenging this CSRA is to perform on a routine basis. The ^{14}C dating of two FAs from the same sample matrix provides a unique quality control criterion for assessing the ^{14}C age of pottery lipids, which if applied correctly adds considerable confidence to this dating approach compared to conventional materials. As should always be the case in selecting archaeological materials for ^{14}C dating, pottery selection is extremely important in answering meaningful archaeological questions. Critically, prescreening of pottery for lipid content is vital, especially the identification and quantification of the FA components of residues. The assessment of aquatic biomarkers is also key in avoiding the confounding effects of marine and freshwater reservoir effects and achieving accurate ^{14}C dates.

In summary, we recommend the following:

a. Systematic selection of potsherds based on clearly defined research questions or hypotheses, prioritising larger (ca. 20 to 30 g) refitting and/or typologically characteristic potsherds.
b. Performing prescreening of sherds for lipid residue preservation on 3 to 10 times the total number of pottery vessels required for dating.
c. Selecting sherds with lipid residues interpreted as originating from the processing of products of animals consuming a terrestrial diet.
d. Using a solventless trapping system and rigorous cleaning approach to remove contamination during the pcGC pretreatment.
e. Measuring processing, pseudo-processing and sized-matched standards alongside every batch of isolated compounds.
f. Evaluating the compatibility of the $C_{16:0}$ and $C_{18:0}$ radiocarbon results, and combining them before calibration where appropriate.
g. Correct, or consider, the potential for reservoir effects in calibration and modeling of ^{14}C dates.

Compound-specific ^{14}C dating of fatty acids preserved in other matrices such as bones, cosmetics, soils etc. as well as other class of compounds preserved in archaeological or environmental matrices, can also be achieved using these methods. These are, however, not yet a standard procedure and will in most cases require adapting and re-assessment of the pretreatment and isolation steps we developed specifically for FAs preserved in pottery vessels.

Acknowledgments. We acknowledge the European research council for funding the NeoMilk advanced project (FP7-IDEAS-ERC/324202) and the LipDat proof of concept project (H2020 ERC-2018-PoC/812917) to RPE financing respectively the doctoral and postdoctoral positions of EC. We thank the BRAMS facility where method development was performed.

Competing interests. The authors declare no competing interests.

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Cite this article: Casanova E, Knowles TDJ, Bayliss A, and Evershed RP. Radiocarbon dating of lipids preserved in pottery vessels: guidelines for best-practice in compound-specific ^{14}C analyses. *Radiocarbon*. https://doi.org/10.1017/RDC.2024.61