Casanova, E. J. A., Knowles, T. J., Ford, C., Cramp, L. J. E., Sharples, N., & Evershed, R. P. (2020). Compound-specific radiocarbon, stable carbon isotope and biomarker analysis of mixed marine/terrestrial lipids preserved in archaeological pottery vessels. *Radiocarbon*. https://doi.org/10.1017/RDC.2020.11

Peer reviewed version

Link to published version (if available):
10.1017/RDC.2020.11

Link to publication record in Explore Bristol Research
PDF-document

University of Bristol - Explore Bristol Research
General rights

1 **Compound-specific radiocarbon, stable carbon isotope and biomarker analysis of mixed**
2 **marine/terrestrial lipids preserved in archaeological pottery vessels**

3

4 Emmanuelle Casanova[1], Timothy D.J. Knowles[1,2], Candice Ford[1,*], Lucy J.E. Cramp[4], Niall
5 Sharples[5] and Richard P. Evershed[1,2]

6

7 [1]Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock's Close BS8 1TS, UK

8 [2]Bristol Accelerator Mass Spectrometry Facility, University of Bristol, 43 Woodland Road, BS8 1UU, UK

9 [3]Department of Anthropology and Archaeology, 43 Woodland Road, University of Bristol, BS8 1UU, UK

10 [4]School of History, Archaeology and Religion, Cardiff University, Humanities Building, Colum Drive, Cardiff
11 CF10 3EU, UK

12

13 *Present address: The University of Nottingham, School of Chemistry, University Park, Nottingham NG7 2RD,
14 14 UK.

15

16 **ABSTRACT**

17 At archaeological sites located on islands or near the coast, the potential exists for lipid

18 extracts of potsherds to contain fatty acids (FA) from both aquatic and terrestrial organisms,

19 meaning that consideration must be given to marine reservoir effects (MRE) in radiocarbon

20 analyses. Here we studied the site of Bornais (Outer Hebrides, UK) where a local MRE, ΔR

21 of -65 ± 45 y was determined through the paired ^{14}C determinations of terrestrial and marine

22 faunal bones. Lipid analysis of 49 potsherds, revealed aquatic biomarkers in 45% of the

23 vessels, and δ^{13}C values of $C_{16:0}$ and $C_{18:0}$ FAs revealed ruminant and marine product mixing

24 for 71% of vessels. Compound-specific radiocarbon analysis (CSRA) of FAs yielded

25 intermediate radiocarbon ages between those of terrestrial and marine bones from the same

26 contexts, confirming an MRE existed. A database containing δ^{13}C values for FAs from

27 reference terrestrial and marine organisms provided endmembers for calculating the

28 percentage marine-derived C ($\%_{marine}$) in FAs. We show that lipid ^{14}C dates can be corrected

29 using determined $\%_{marine}$ and ΔR values, such that pottery vessels from coastal locations can

30 be radiocarbon dated by CSRA of FAs.

31

32 **KEYWORDS:** Pottery vessels, Lipid residues, Compound-specific radiocarbon analysis,

33 Marine reservoir effect, Mixed marine/terrestrial corrections.

34

INTRODUCTION

Due to their central importance to, and survival in the archaeological record, accurate direct

radiocarbon dating of pottery vessels has been one of the "Holy Grails" of archaeology.

Compound-specific radiocarbon dating of lipids preserved within the clay matrix of

archaeological potsherds is technically extremely challenging, with previous attempts failing

to achieve the accuracy and precision required (e.g. Hedges *et al.* 1992, Stott *et al.* 2001,

2003b; Berstan *et al.* 2008). Recently however, we have reported the first accurate dates

achieved for such residues based on compound-specific ^{14}C analyses of $C_{16:0}$ and $C_{18:0}$ fatty

acids (FAs) isolated from the clay walls of Neolithic pottery vessels (Casanova *et al.*, in

press). The preparative-capillary gas chromatography (pcGC) isolation technique required

two major advances, namely a new trap design allowing the solvent-less recovery of the

trapped analytes and a heat-based cleaning method to prevent cross-contamination (Casanova

et al. 2018). These methodological improvements have enabled reliable and accurate dating

of the two FAs characteristic of degraded animal fats. Furthermore, the two independent

radiocarbon dates obtained provide an important internal quality control; the radiocarbon age

of the FAs should agree at the 2σ error level (Casanova *et al.* 2018). The samples used thus

far in the validation of the compound-specific pot lipid dating method, outlined in Casanova

et al. (in press) have originated from archaeological sites located inland where human dietary

subsistence was dominated by domesticated terrestrial animals, such that the target FAs

derived from dairy or carcass fats of ruminant and non-ruminant animals.

None of the pottery dated thus far has originated from coastal areas where the exploitation of

marine products may have occurred. At such locations, FAs preserved in pottery vessels

would likely be affected by a reservoir effect (Heron and Craig 2015), requiring marine

reservoir correction in order to obtain reliable calibrated dates (Cook *et al.* 2015). Particularly

problematic would be potsherds containing mixed marine- and terrestrial-derived FAs

(Cramp and Evershed 2014; Cramp *et al.* 2014a), as this would increase the complexity of

marine reservoir corrections.

Marine product processing in pots can be identified by the presence of specific aquatic

biomarkers alongside the $C_{16:0}$ and $C_{18:0}$ FA, namely: (i) long-chain dihydroxy fatty acids

(DHYAs), (ii) isoprenoid fatty acids (IFAs) and (iii) long-chain ω-(o-alkylphenyl)alkanoic

66 acids (APAAs); (Hansel *et al*. 2004; Evershed *et al*. 2008; Hansel and Evershed 2009;

67 Cramp and Evershed 2014). Furthermore, $\delta^{13}C$ values determined for the $C_{16:0}$ and $C_{18:0}$ FAs

68 can reveal the mixing of both terrestrial and marine commodities in the same vessel (Copley

69 *et al*. 2004, Cramp *et al*. 2014a, 2014b). It is known, however, that the relative abundances of

70 $C_{16:0}$ and $C_{18:0}$ FAs differ between terrestrial and marine organisms and the relationship

71 between their mixing proportions and the resulting $\delta^{13}C$ values is not necessarily linear

72 (Mukherjee *et al*. 2005). It is unclear whether this effect will adversely affect the validity of

73 the internal quality control criteria, such that the ^{14}C dates obtained for $C_{16:0}$ and $C_{18:0}$ FAs in

74 a potsherd are no longer consistent within 2σ (Casanova *et al*. 2018, in press). It is certainly

75 possible that $C_{16:0}$ and $C_{18:0}$ FAs in sherds arising from mixtures of terrestrial- and marine-

76 derived food residues may yield different apparent radiocarbon ages.

77 Generally, MRE corrections require generation of terrestrial/marine mixing curves using

78 dedicated software (e.g. OxCal, CALIB). This requires an understanding of the local

79 deviation (ΔR) from the global marine calibration curve for a specific time period as well as

80 the percentage of marine-derived C (*%marine*) present (Cook *et al*. 2015). The ΔR values can

81 be obtained by radiocarbon dating historical marine specimens (of known date of collection)

82 from museum collections, pairing ^{14}C measurements on terrestrial and marine organisms

83 from secure contexts at the site of interest or by dating tephra layers deposited at sea and on

84 land (Ascough *et al*. 2005). The evaluation of the *%marine*, however, is more challenging. Such

85 considerations are often applied to bone collagen from omnivores which can feed on both

86 terrestrial and marine resources (Cook *et al*. 2015). Typically, $\delta^{13}C$ and $\delta^{15}N$ values are

87 recorded on bulk collagen to understand the local diet and the percentage of marine resources

88 consumed. Preferably, endmembers for pure terrestrial and pure marine organisms are

89 recorded for samples local to the site, but in the majority of cases, more general (non-local)

90 reference values for endmembers are used (Cook *et al*. 2015).

91 Herein, we evaluate whether the approach commonly applied to bone collagen to estimate the

92 contribution of aquatic resources could be applied to FAs extracted from pottery vessels for

93 MRE correction of pot lipids ^{14}C dates. The approach was to undertake radiocarbon dating in

94 order to determine the influence of aquatic resources on CSRA of lipids from potsherds and

95 establish appropriate methods to correct for the MRE. We focussed on lipids preserved in

96 pottery vessels with a clearly mixed marine/terrestrial signal from the site of Bornais (South

97 Uist, UK). Our approach involved: (i) lipid residue analyses on pottery vessels including

98 compound-specific $\delta^{13}C$ determinations on FAs, (ii) calculation of the local deviation from

3

99   the global marine calibration curve at the site using paired marine and terrestrial animal

100   remains, (iii) radiocarbon dating of FAs from a range of pottery vessels, (iv) a multiproxy

101   investigation (i.e. biomarkers, stable isotopes and ^{14}C analyses) to evaluate the proportion of

102   mixing of marine and terrestrial lipids and (v) application of relevant marine reservoir

103   corrections to the radiocarbon dates obtained from pot lipids.

104

105   **METHODS**

106   **Site description**

107   The site of Bornais is located on the island of South Uist, in the Outer Hebrides, UK

108   (Supplementary material S1). The site comprises 4 mounds with a long duration of

109   occupation defined by 109 radiocarbon dates on seeds and bone collagen, from the late Iron

110   Age (LIA 1 and LIA 2; 5th-6th century AD) to the Early, Middle and Late Norse (EN, MN,

111   LN, respectively; mid-9th-14th century AD) period (Marshall 2005, 2016, forthcoming;

112   Sharples forthcoming). The recovery of plant macrofossils indicates the cultivation of rye and

113   barley, while the faunal assemblage displays a particularly rich diversity of terrestrial animals

114   (*c.*18,000 bones), small vertebrates, birds, fish and molluscs; Sharples and Davis

115   forthcoming, Sharples*, et al.* 2016). Domesticated animals dominate (~ 95 %) the terrestrial

116   faunal assemblage, which comprised cattle (ca 40 %), sheep (ca. 45 %) and pigs (ca. 10%).

117   The mortality profiles derived from the cattle suggest they were exploited for their milk

118   (Sharples*, et al.* 2016). Fish bones (eel, saithe, cod, haddock, ray, turbot, mackerel etc.) and

119   mollusc shells (limpets and winkles) were extremely abundant at the site (*c.* 17,000 identified

120   specimens), while marine mammal bones, e.g. seal, were rare (Sharples, *et al.* 2016).

121   **Lipid residue analysis**

122   Lipid residue analyses of samples of pottery were performed using a methanolic sulphuric

123   acid extraction procedure (Correa-Ascencio and Evershed 2014). The total lipid extracts

124   (TLEs) were analysed by gas chromatography (GC) and GC-Mass spectrometry (GC-MS) for

125   the identification and quantification of biomarkers, including aquatic biomarkers following

126   established procedures (Evershed *et al.* 1990, Cramp and Evershed 2014). Compound-

127   specific δ^{13}C values of fatty acids were determined by GC-Combusted-Isotope ratio MS (GC-

128   C-IRMS; supplementary material S2).

129   **Pretreatment methods for radiocarbon analyses**

130   Approximately 300 mg of coarse bone powder were weighed into a culture tube and pre-

131   treated using a modified Login procedure (Longin 1971) as described in Knowles, *et al.*

132   (2019). Briefly, bone powder was demineralized in HCl (0.5 M, 10 mL, ~ 18h, room

133   temperature (RT)) followed by a wash with NaOH (0.1 M, 10 mL, 30 min, RT) and a second

134   acid wash with HCl (0.5 M, 10 mL, 30 min, RT). The extracted collagen was rinsed with

135   ultrapure MilliQ-water (MQ-water; 3 x 10 mL) in between each acid and base wash and

136   centrifuged (3000 rpm, 5 min). The collagen was then gelatinised at pH 3 with HCl (0.001 M,

137   10 mL, 75 °C, 20 h) and filtered through pre-combusted glass fibre before freeze drying

138   (Knowles, *et al.* 2019).

139   Surface cleaned shells were ultrasonically agitated in MQ-water (5 mL, 5 min) before drying

140   at 60°C. When dried, the shells (~ 30 mg) were crushed roughly before the surface was acid

141   etched (~20 %) with HCl (0.2 M, 10 mL). Samples were rinsed with MQ-water (3 x 10 mL)

142   and dried at 60°C in a drying cabinet (Knowles, *et al.* 2019).

143   Sherds containing lipid concentrations, typically above 500 $\mu g.g^{-1}$, were selected for

144   radiocarbon determinations. Pieces of 2 to 10 g of the potsherd was sampled, depending on

145   the lipid concentrations and size of the potsherds. The lipids were extracted in culture tubes

146   using H_2SO_4/MeOH (4 % *v/v*, 3 x 8 mL, 70°C, 1 h). Samples were centrifuged after each

147   extraction (2500 rpm, 10 min) and the 3 supernatants (methanolic fractions) combined into a

148   second culture tube containing double-distilled water (5 mL). The lipids, including fatty acid

149   methyl esters (FAMEs) created from the reaction of methanol with the FAs during the first

150   step, were extracted from the methanolic solution with *n*-hexane (4 x 5 mL) and blown down

151   to dryness at room temperature under a gentle nitrogen stream. The TLEs were derivatized

152   with BSTFA (20 µL, 70 °C, 1 h). Excess BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide)

153   was removed under a nitrogen stream, then ~180 µL of *n*-hexane was added to obtain a

154   solution containing $C_{16:0}$ and $C_{18:0}$ FAMEs at a concentration at *c.* 5 $\mu g.\mu L^{-1}$ of carbon. The

155   solution was transferred to an autosampler vial for isolation of $C_{16:0}$ and $C_{18:0}$ into individual

156   traps using a preparative capillary gas chromatography (pcGC) instrument following the

157   methods described in Casanova *et al.* (2017, 2018, in press).

158   **Radiocarbon determinations**

159   Organic materials (FAMEs and collagen) were combusted to CO_2 using a Vario Microcube

160   Elemental Analyser (EA, Elementar). The shells (carbonate-based) were digested in H_3PO_4 (1

161 mL, 85 % *v/v*, 70 °C) under a He headspace using a Carbonate Handling System (CHS,

162 Ionplus; Wacker, *et al.* 2013; Knowles, *et al.* 2019) to generate CO_2. Resulting CO_2 was

163 transferred to the Automated Graphitisation Equipment (AGE 3, Ionplus; Wacker *et al.* 2010;

164 Knowles, *et al.* 2019) under a He stream and adsorbed on Zeolite traps before being released

165 into reaction tubes. The CO_2 was reduced to graphite under H_2 (580 °C, 2 h, 420 mbar) on a

166 pre-conditioned iron catalyst. A Pneumatic Sample Press (PSP, Ionplus) was used to press the

167 graphitised samples into Al targets.

168 All ^{14}C determinations were performed at the BRAMS (Bristol Accelerator Mass

169 Spectrometer) facility which is equipped with a mini radiocarbon dating system (BRIS-

170 MICADAS) instrument (ETH Zurich, Zurich, Switzerland; Synal *et al.* 2007). Samples were

171 analysed alongside size-matched processing standards and blanks (Casanova *et al.* 2018;

172 Knowles *et al.* 2019).

Corrections and calibration of ^{14}C measurements

174 Radiocarbon measurement on FAs from single pottery vessels were corrected for the

175 presence of the methyl derivative C (Casanova *et al.* 2017, 2018) and subjected to a 2-sigma

176 equivalency test and, if successful, combined as described in Casanova *et al.* (in press) before

177 testing the validity of calibration on mixed marine/terrestrial resources. Reservoir correction

178 and calibration of the mixed resources was performed in OxCal v 4.3 (Bronk Ramsey 2009)

179 using the 'Marine/mixed curve' tool using the IntCal13 and Marine13 curves (Reimer *et al.*

180 2013). This incorporates the percentage of marine derived resources present in the TLEs and

181 the ΔR value for the site (see results section).

182 The local reservoir effect was calculated for every pair combination of terrestrial/marine

183 organisms in each context using the online ΔR calculation tool (Reimer and Reimer, 2016).

184 These individual ΔR values were subjected to a χ^2 test at the 5 % level (both for each context

185 and all together) to detect potential outliers before calculation of their weighted average, with

186 error calculation as recommended by Russell *et al.* (2010).

187 The mixing of marine/terrestrial commodities was quantified in each potsherd using two

188 independent methods: [14]C dates and $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ FAs (Figure 1). By

189 comparing the mixing ratios obtained by the two methods, it is possible to evaluate whether

190   the FA δ^{13}C values (determined by GC-C-IRMS) can be used to estimate the proportion of

191   marine-derived C in the FAs for use in MRE corrections of their radiocarbon dates. This

192   constitutes an important consideration, especially for sites where terrestrial and marine

193   remains are absent from the archaeological record and so cannot be used to provide reference

194   radiocarbon ages.
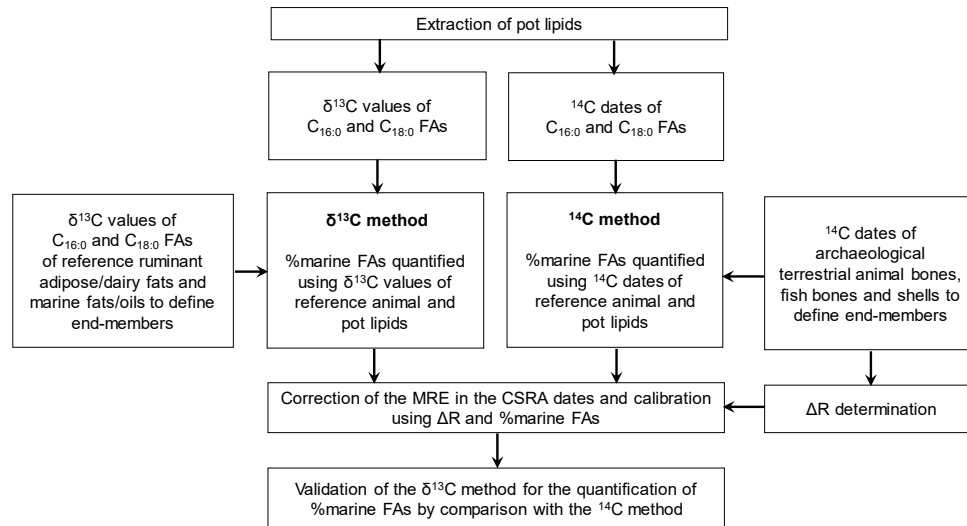
195

196   <u>Figure 1</u>

197   The first method of quantifying the $\%_{marine}$ is based on the weighted average of radiocarbon

198   determinations on the short-lived terrestrial and marine organisms, from the same

199   context/phase as the potsherds dated, as endmembers using Equation (1).

200   (1)
$$\%_{marine} = \frac{(Age_{pot} - Age_{terr})}{(Age_{marine} - Age_{terr})} * 100$$

201   Where $\%_{marine}$ is the percentage of aquatic C in the lipid residue and Age_{pot}, Age_{terr}, Age_{marine}

202   are the combined radiocarbon ages on the individual FAs, for terrestrial animals and marine

203   organisms, respectively.

204   The second method uses the δ^{13}C values of the individual FAs of UK reference animals

205   (cattle and sheep raised on a pure C_3 diet; Copley, *et al.* 2003) as the terrestrial endmembers

206   (pigs were hypothesised not to have been processed in potsherds; Sharples, *et al.* 2016, and

207   fish, winkles and limpets captured from UK waters (corrected for the Suess effect; Cramp

208   and Evershed, 2014) to serve as the marine endmembers. The terrestrial endmembers

209   correspond to the average values for both $C_{16:0}$ and $C_{18:0}$ FAs and were found to be

210 $\delta^{13}C_{16:0}$ = -30.0 ± 0.6 ‰ and $\delta^{13}C_{18:0}$ = -32.2 ± 0.6 ‰ for adipose fats and $\delta^{13}C_{16:0}$ = -29.2 ±

211 1.0 ‰ and $\delta^{13}C_{18:0}$ = -34.0 ± 0.9 ‰ for dairy fats. Both ruminant adipose and dairy values

212 were used as endmembers to evaluate whether one should be used over the another. The

213 marine endmembers were $\delta^{13}C_{16:0}$ = -22.7 ± 2.2 ‰ and $\delta^{13}C_{18:0}$ = -21.7 ± 2.5 ‰. The

214 relationship between the relative proportions of marine and terrestrial fats and the $\delta^{13}C$ values

215 is theoretically non-linear, due to the differing relative abundances of the of FAs in the

216 different foodstuffs (Mukherjee, *et al.* 2005), however, the success of the internal quality

217 control on the CSRA dates (see results section) suggests a linear relationship within

218 analytical uncertainty. A linear mixing curve could therefore be employed to estimate the

219 *%marine* contribution and associated uncertainty using the propagation of analytical errors. The

220 *%marine* values obtained on both FAs were then combined as a weighted average with

221 uncertainties calculated according to Russell *et al.* (2010). Such a model is a conservative

222 approach and probably overestimates the uncertainties. Furthermore, it cannot take into

223 account the fact that the true *%marine* values must be constrain between 0 and 100 %.

224 As a comparison, the *%marine* values of the TLEs were also estimated (using the same

225 endmembers) using the software package FRUITS (v2.1). This software employs a Bayesian

226 approach to quantify the contribution of different food sources using isotopic data (Fernandes

227 *et al.* 2014). The output of this software is given both as means and standard deviations

228 (represented by box-and whiskers plots) or as probability distributions constrained to between

229 0 and 100 %. The full range of data points for the probability distributions of the *%marine* after

230 Bayesian modelling was exported and implemented as a prior information file into the mixing

231 marine/terrestrial tool in OxCal.

RESULTS AND DISCUSSION

Characterisation of lipid residues in pottery vessels

234 Forty-nine pottery vessels from layer BCC, Mound 2, MN period were subjected to lipid

235 residue analyses (S2). TLEs with concentrations >5 µg.g^{-1} were recovered from 96 % (*n* =

236 47) of the potsherds, at an average lipid concentration of 1.2 mg.g^{-1} (supplementary material

237 S3). A total of 80 % of the TLEs with residues (*n* = 39) were dominated by the $C_{16:0}$ and $C_{18:0}$

238 fatty acids characteristic of degraded animal fats (Figure 2a). Many of the TLEs (47 % of the

239 sherds with residues; *n* = 22) exhibited marine biomarkers. The long-chain DHYAs (C_{18}, C_{20}

240 and C_{22}) were detectable in 30 % (*n* = 14; Figure 2b), long-chain APAAs (C_{18}, C_{20} and C_{22}) in

241   23 % (n = 11; Figure 2c) and the IFAs (phytanic acid and 4,8,12-trimethyltridecanoic acid

242   (TMTD)) in 30 % (n = 14) of the sherds with residues. In total, only 4 % (n = 2; BN-140,

243   BN-173) of the potsherds with lipid residues contained all 3 classes of aquatic biomarkers, 21

244   % (n = 10) contained 2 aquatic biomarkers and 26 % (n = 12) showed one aquatic biomarker.

245   No aquatic biomarkers were detected in the remainder of the TLEs (n = 25, 53 % of the

246   sherds with organic residues). The $\delta^{13}C$ values of the palmitic and stearic acids were

247   determined by GC-C-IRMS (Figure 2d). Significantly, the $C_{16:0}$ and $C_{18:0}$ fatty acids displayed

248    $\delta^{13}C$ values characteristic of mixtures between ruminant and marine or porcine products

249   (Cramp *et al.* 2014a, 2014b). The extracts yielding the most enriched stable carbon isotope

250   values also contained aquatic biomarkers, strongly suggesting the processing of marine

251   products rather than porcine. Several TLEs were relatively more enriched in ^{13}C, but show no

252   detectable aquatic biomarkers suggesting they did not survive or could denote the processing

253   of marine commodities under conditions not conductive to the formation of thermally-

254   produced aquatic biomarkers (APAAs). The use of $\Delta^{13}C$ (= $\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$) values allows

255   the identification of sherds where FAs are predominantly of dairy product origin (< -3.1 ‰;

256   Copley *et al.* 2003). A total of 22 sherds yielded $\Delta^{13}C$ values below -3.1 ‰, with aquatic

257   biomarker identification for half of them supports the hypothesis of some mixing of dairy

258   products with marine products. The other sherds with higher $\Delta^{13}C$ values of >-3.1 ‰ could

259   result from the mixing of ruminant carcass and marine products.

260   Additionally, 131 potsherds from all the phases and mounds at the site were previously

261   analysed by lipid residue analysis (Cramp *et al.* 2014b, forthcoming). The results suggested a

262   dominance of dairy and ruminant carcass product processing, as well as some mixing of non-

263   ruminant and marine fat/oil (Figure 1d). Only the pottery from the LIA 1 phase lacked

264   aquatic biomarkers.
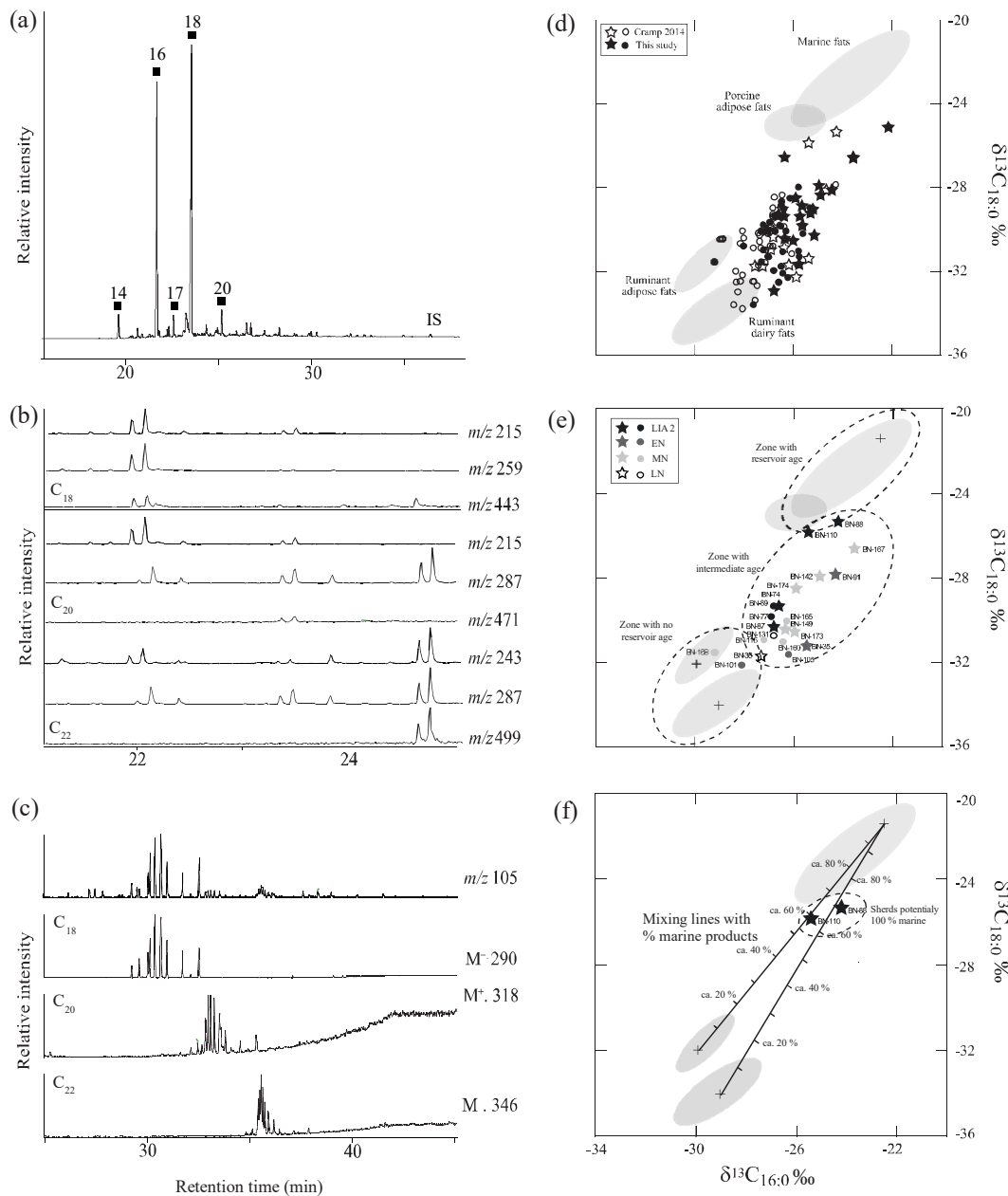
265

266   Figure 2

267   A total of 21 potsherds (from all phases) with sufficient lipid concentrations and containing

268   either none or at least one aquatic biomarker, were subjected to CSRA (Figure 1e).

269   **ΔR value determination**

270   In order to determine the age of the structures associated with the pots, and the local reservoir

271   effect at the site of Bornais a range of fish bones ($n = 13$), marine mollusc shells ($n = 14$) and

272   terrestrial animal bones ($n = 8$) were radiocarbon dated (Table 1). These were assessed

273   together with other available radiocarbon measurements on terrestrial animal bones and

274 grains (layer BCC, *n* = 7; Marshall *et al*. forthcoming-b). All these materials derive from the

275 LIA2, EN, MN and LN settlement structures. On a context-by-context basis, marine and

276 terrestrial organisms were subjected to χ^2 statistical testing to detect outliers for exclusion

277 (Table 1). Two marine samples from context BAF and two terrestrial animal bones from

278 context BCC were, therefore, excluded from ΔR determination. The ΔR values calculated

279 using all the pairs of terrestrial/marine organism (80 in total) per context are reported in Table

280 1. No ΔR was calculated for contexts BBA and BBD as they were dated based on only one

281 material type, and for AG, the two marine organisms from this context failed the χ^2 test.

282 With the exception of context BCC, all the contexts demonstrated a negative ΔR, varying

283 from -214 ± 26 to -45 ± 21. Interestingly, layer BCC (MN phase) shows a ΔR of 28 ± 150;

284 the large uncertainty associated with this value results from high variability in the

285 radiocarbon ages of the marine organisms, which could be classified into three distinct

286 groups. Group (a) gave a ΔR of -107 ± 54, Group (b) 242 ± 55 and Group (c) -31 ± 56. The

287 MRE of Group (c), comprised only fish bones and likely reflects the mobility of the fish

288 species (Russell*, et al.* 2011). Groups (a) and (b) comprise both winkles and limpets and their

289 MREs do not appear to be species dependent. The grouping could, therefore, either

290 correspond to two different collection points of the mollusc shells (likely collection points

291 nearby are either completely coastal, or sea lochs with the potential for substantial terrestrial

292 runoff) or simply the introduction of older material into a later context (although, this offset

293 was only observed for some limpet and winkle shells, but not fish bones).

294

295 Table 1: Radiocarbon determinations on terrestrial and marine organisms at Bornais and ΔR
296 calculated for the diverse contexts based on the multiple paired terrestrial/marine organisms. *refer to
297 statistical outliers that have been excluded from ΔR calculation.

Phase	Layer	Terrestrial organisms			Marine organisms			ΔR
		Material	Laboratory#	Conventional ^{14}C age	Material	Laboratory#	Conventional ^{14}C age	
LIA 2	BAC	Cattle	BRAMS-1710	1,272 ± 25	Limpet-1	BRAMS-1727	1,624 ± 26	-47 ± 23
		Caprine	BRAMS-1711	1,298 ± 25	Limpet-2	BRAMS-1728	1,627 ± 26	
		Unidentified	BRAMS-1713.1	1,258 ± 25	Limpet-5	BRAMS-1731	1,642 ± 26	
			BRAMS-1713.2	1,264 ± 25	Limpet-6	BRAMS-1732	1,616 ± 26	
	BAF	Cattle	BRAMS-1712	1,348 ± 25	Fish-9	BRAMS-1725*	1,651 ± 25	-165 ± 26
					Fish-10	BRAMS-1726*	1,294 ± 25	
					Limpet-3	BRAMS-1729	1,565 ± 26	
					Limpet-4	BRAMS-1730	1,584 ± 26	
	BAG	Cattle	BRAMS-1708	1,320 ± 25	Fish-1	BRAMS-1717	1,509 ± 25	-214 ± 26
		Cattle	BRAMS-1709	1,320 ± 25				
EN	BBD	Cattle	BRAMS-1715*	1,082 ± 25	-			-
		Cattle	BRAMS-1719*	945 ± 25				
	BBA	-			Limpet-7	BRAMS-1733	1,622 ± 26	-

MN	BCC	Cattle	SUERC-2684	925 ± 35	Fish-11	BRAMS-2049 (c)	1,306 ± 25	-102 ± 35 (a)
		Red deer	SUERC-22894*	875 ± 30	Fish-12	BRAMS-2050 (c)	1,318 ± 25	248 ± 37 (b)
		Pig	SUERC-22890*	1,035 ± 30	Fish-13	BRAMS-205.1 (c)	1,323 ± 25	-26± 40 (c)
		Seed	GU-18290	-	Fish-14	BRAMS-2052 (c)	1,365 ± 25	35 ± 150 (all)
		Cattle	SUERC-22896	970 ± 30	Fish-15	BRAMS-2053 (c)	1,308 ± 25	
		Cattle	SUERC-22897	975 ± 25	Limpet-8	BRAMS-2041*	1,380 ± 24	
		Sheep	OxA-15420	903 ± 27	Limpet-9	BRAMS-2042.1 (a)	1,263 ± 25	
		Cattle	OxA-15522	985 ± 26		BRAMS-2042.2 (a)	1,236 ± 24	
					Limpet-10	BRAMS-2043(b)*	1,575 ± 24	
					Limpet-11	BRAMS-2044 (b)*	1,593 ± 25	
					Winkle-1	BRAMS-2045 (a)	1,257 ± 24	
					Winkle-2	BRAMS-2046 (b)*	1,614 ± 25	
					Winkle-3	BRAMS-2047 (a)	1,243 ± 24	
					Winkle-4	BRAMS-2048 (b)*	1,613 ± 25	
	AD	Cattle	BRAMS-1716	956 ± 25	Fish-4	BRAMS-1720	1,167 ± 25	-84 ± 34
					Fish-5	BRAMS-1721	1,261 ± 25	
					Fish-6	BRAMS-1722	1,257 ± 25	
LN	AG	Sheep	BRAMS-1714	930 ± 25	Fish-7	BRAMS-1723.1*	1,268 ± 25	-
						BRAMS-1723.2*	1,237 ± 25	
					Fish-8	BRAMS-1724*	1,183 ± 25	
Overall site								-65 ± 46

298 The MREs calculated from Groups (a) and (c) gave statistically indistinguishable [14]C

299 determinations and are in good agreement with ΔR values calculated for the other contexts.

300 Only shells from Group (b) were excluded from the overall ΔR determination due to

301 uncertainty in the security of the context in light of its high ΔR value. The remaining 56 ΔRs

302 failed the statistical identicality test, therefore layer BAG (ΔR = -214 ± 26), showing the

303 lowest ΔR and the pairs BN-F-14/SUERC-2684, BN-F-14/OxA15420 which showed the

304 highest ΔR values were excluded from the calculation. With the removal of the organisms

305 and terrestrial/marine pairs identified as outliers the remaining 53 ΔR values are statistically

306 identical (T' = 69.3, T'(5 %) = 71.0, υ = 53) and average to -65 ± 46. These data suggest

307 there is no significant difference in the reservoir effect from the LIA2to LN period at the site.

308 This ΔR value of -65 ± 46 is also consistent with the previously reported ΔR values for the

309 North Atlantic, including the (Inner, and Outer) Hebrides Island of -47 ± 52 for the period

310 3500 BC-1450 cal AD (Reimer, *et al.* 2002; Ascough, *et al.* 2004, 2005, 2006, 2007, 2009,

311 2017; Russel, *et al.* 2010, 2015; see supplementary material S4).

312

Radiocarbon dating of pottery vessels

314 $C_{16:0}$ and $C_{18:0}$ FAs from 21 sherds were dated, of which six were dated in duplicate. This

315 includes potsherds from all phases present at Bornais, both with and without aquatic

316 biomarkers present. Of these, 17 sherds successfully passed the internal quality control

317 criterion, whereby the radiocarbon dates of the $C_{16:0}$ and $C_{18:0}$ FAs must agree within 95 %

318 confidence. Three failed, and seven did not yield sufficient C for both FAs to be dated

independently. These last ten sherds were therefore not further considered as no internal

control on the $C_{16:0}$ and $C_{18:0}$ FAs was present to ensure the security of the dates

(Supplementary materials S5).

Two of the pottery vessels dated in duplicate failed the internal quality control the first time,

but either passed it the second time (BN-35) or yielded insufficient C for two targets (BN-

101). Three pot dates that were duplicated gave indistinguishable dates for both extracts. The

duplicate analysis of potsherd BN-74 produced statistically non-identical results between the

two extractions. The CSRA dates successfully passed the internal criterion for both

extractions and as the $C_{16:0}$ and $C_{18:0}$ dates are essentially independent, it is unlikely that both

FAs in one extraction could be contaminated to the same degree (giving rise to identical, but

inaccurate, dates; Casanova, *et al.* 2018). This difference could, therefore, reflect an

inhomogeneous partitioning of the marine and terrestrial products in the same potsherd (due

to different filling levels during cooking for example), and could potentially be monitored

and corrected for in the future by recording $\delta^{13}C$ values on the two different TLEs (not

performed in this case). Table 2 reports the combined measurements on the potsherds which

passed the internal control.

These results suggest that the internal quality control is valid in this case of mixed

marine/terrestrial resources and can be used as evidence for the reliability of the CSRA

measurements. The error introduced by mixing the FAs of different abundances is likely

below the AMS error, justifying the hold of the internal criteria.

Table 2: Summary of radiocarbon dated potsherds from Bornais, including the presence of aquatic
biomarkers, $\delta^{13}C$ values of individual FAs, combined radiocarbon determinations of $C_{16:0}$ and $C_{18:0}$
FAs (which passed the internal criterion) and the percentage of marine fat/oil within the TLEs. The
%marine were calculated using reference ^{14}C measurements on marine-terrestrial samples (*%marine* ^{14}C),
using a linear mixing with $\delta^{13}C$ values on ruminant adipose products (*%marine* $\delta^{13}C_{adipose}$) and $\delta^{13}C$
values on ruminant dairy products (*%marine* $\delta^{13}C_{milk}$) as endmembers and finally using $\delta^{13}C$ values
implemented in FRUITS (*%marine* $\delta^{13}C$ FRUITS). *refers to the preferred endmembers for the
terrestrial fats based on the $\Delta^{13}C$ value (i.e. milk if $\Delta^{13}C < -3.1‰$, ruminant adipose otherwise) and
used for the *%marine* calculation using FRUITS (v2.1; here the mean and standard deviation are
presented and the full probability distribution are in supplementary material S6).

Phase	Layer	Pot#	Aquatic biomarkers	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Laboratory#	Age ± 1 σ (BP)	*%marine* ^{14}C	*%marine* $\delta^{13}C_{adipose}$	*%marine* $\delta^{13}C_{milk}$	*%marine* $\delta^{13}C$ FRUITS
LIA 2	BAC	BN89 (1)	-		-26.8	-29.4	BRAMS-1549.1	1,368 ± 25	27 ± 12	30 ± 22*	37 ± 22	35 ± 10
		BN89 (2)					BRAMS-1549.2	1,365 ± 25	26 ± 12			
		BN74 (1)	APAAs	-26.6	-29.4	BRAMS-1551.1	1,383 ± 30	31 ± 12	31 ± 23*	39 ± 16	36 ± 10
		BN74 (2)					BRAMS-1551.2	1,286 ± 25	4 ± 11			
	BAF	BN77	-		-26.9	-29.9	BRAMS-1605	1,370 ± 24	-	26 ±23*	34± 14	32 ± 10
		BN87	APAAs	-26.8	-30.4	BRAMS-1604	1,304 ± 24	-	21 ± 25	33 ± 15*	32 ± 12
	BAG	BN88 (1)	APAAs,	-24.2	-25.4	BRAMS-1548	1,757 ± 25	-	69 ± 31*	73 ± 27	71 ± 12

		BN88 (2)	DHYAs			BRAMS-1548	1,762 ± 25	-			
EN	BBD	BN35	APAAs, DHYAs	-25.4	-31.4	BRAMS-1552	1,156 ± 27	-	12 ±12	31 ±31*	33 ± 10
		BN105 (1)	-	-26.2	-31.7	BRAMS-1547.1	1,268 ± 25	-	8 ±36	28± 24*	27 ± 10
		BN105 (2)				BRAMS-1547.2	1,327 ±27	-			
	BBA	BN110	APAAs	-25.4	-25.9	BRAMS-1608	1,326 ± 25	-	64 ± 28*	63 ± 24	63 ± 13
MN	BCA	BN115	-	-27.2	-31.0	BRAMS-1609	987 ± 24	-	15 ± 24	28 ± 13*	27 ± 9
	BCC	BN160	-	-26.4	-31.0	BRAMS-2066	1,201 ± 25	74 ± 16	16 ± 31	32 ± 20*	29 ± 10
		BN165	-	-26.3	-30.1	BRAMS-2063	1,060 ± 25	32 ± 14	25 ± 28	38 ± 18*	36 ± 10
		BN174	APAAs	-25.9	-28.5	BRAMS-2062	1,115 ± 26	49 ± 15	40 ± 26*	48 ± 20	46 ± 12
LN	AG	BN36	APAAs, DHYAs	-27.3	-31.8	BRAMS-1607	786 ± 25	-	7 ± 26	24 ±14*	21 ± 8

350

351 The four sherds from the BAC and BAF contexts of phase LIA2, the three from the EN phase

352 and the three from the BCC context of the MN phase were shown to have radiocarbon ages

353 between the age of the terrestrial organisms and their contemporaneous marine analogues

354 (Table 1 and 2). These include the five sherds (BN-89, BN-77, BN-105, BN160 and BN-165)

355 which did not exhibit aquatic biomarkers. These dates suggest, therefore, mixing of terrestrial

356 and marine resources in all the sherds.

357 The sherd BN-88 from the BAG context LIA2 phase exhibited not only the most enriched

358 $\delta^{13}C$ values but also the oldest age obtained in this investigation. This date is older than the

359 marine reference fish bone from this context and, indeed the reference fish bones from other

360 LIA 2 contexts. The second dating of the potsherd confirmed the accuracy of the compound-

361 specific ^{14}C measurement, suggesting the FAs likely derived from a pure marine fat/oil

362 residue and that the MRE (based on only one pair) was underestimated in this case, unless the

363 potsherd was residual and corresponds to the LIA1 phase, although no aquatic biomarkers

364 were detected in potsherds extracts from this particular phase.

365 The potsherd BN-115 (987 ± 24 BP) from context BCA (not dated) of the MN phase, which

366 lacked aquatic biomarkers exhibited an age consistent with the MN phase, and thus is likely

367 to be entirely composed of terrestrial animal fats.

368 For the LN phase, the FA date on the pot BN-36 (786 ± 25 BP) is younger than that of the

369 terrestrial organisms (BN-MB-7: 930 ± 25 BP). Based on the $\delta^{13}C$ values, the sherd plots

370 close to the reference dairy fat ellipses despite containing aquatic biomarkers. This result is

371 surprising and suggests that the dating of this phase, based on only one terrestrial organism

372 could be erroneous. Younger ages from other LN contexts from Bornais were obtained in a

373 range of 900 to 650 radiocarbon years BP (uncalibrated), which would support this

374 hypothesis (Marshall *et al.* 2016, forthcoming).

375 These measurements clearly confirm that lipid dates can be affected by the marine reservoir

376 effect and such dates will therefore require calibration using relevant ΔR values and

377 proportionately mixed terrestrial/marine curves. The mixing of marine and terrestrial

378 products influences the determined δ^{13}C values and radiocarbon dates of FAs and this does

379 not appear to have an adverse effect on the internal quality control criteria. Interestingly,

380 MREs are evident in TLEs from potsherds lacking detectable aquatic biomarkers. The results

381 therefore suggest that ^{14}C dates could be used to detect a (low-)level of marine organism

382 processing in pots where aquatic biomarkers are undetectable. This would be especially

383 relevant for sites where potential exists for processing of non-ruminant products or where

384 aridity effects are possible, shifting the δ^{13}C values away from the ruminant products ellipses.

385 **Correction of the MRE and calibration**

386 The *%marine* in the lipid residues was quantified for the sherds which passed the internal

387 quality control criterion (Table 2; Supplementary material S5, S6). To ensure a fair

388 evaluation of the use of FA δ^{13}C values for determination of the degree of marine/terrestrial

389 product mixing, only potsherds from contexts which were securely dated using more than one

390 marine/terrestrial organism were used for validating the correction and calibration (BAC and

391 BCC). The validity of using δ^{13}C values of FAs for the quantification of marine-derived C

392 was evaluated by comparison with reference values obtained by ^{14}C dates.

393 Overall, no significant differences in *%marine* were noted in the use of δ^{13}C values from

394 ruminant adipose or milk fats as terrestrial end members in a simple linear mixing model

395 (Table 2, Figure 2f). Therefore, only the one most representative of the terrestrial

396 endmembers was used for MRE corrections (i.e. milk if Δ^{13}C < -3.1‰, ruminant adipose if

397 Δ^{13}C > -3.1‰).

398 The range of calibrated terrestrial dates on mammals for BRAMS-1710, BRAMS-1711,

399 BRAMS-1713, in the LIA 2 phase, BAC context, were 672 - 773 cal AD, 662 - 769 cal AD

400 and 685 - 772 cal AD, respectively (95% probability, Figure 3a). The *%marine* within the FAs

401 in pot BN-89 was determined to be 27 ± 12 % using ^{14}C dates, 30 ± 22 % using δ^{13}C values

402 of adipose endmembers in the simple linear mixing and 35 ± 10 % (mean and standard

403 deviation) when implemented in FRUITS (Table 2). All these estimates are statistically

404   indistinguishable and the calibrated ages after MRE correction agrees with the reference age

405   of the terrestrial organisms (Figure 3a).

406   Turning to potsherd BN-74, the first extract yielded estimates of 31 ± 12 % marine fat/oil

407   using ^{14}C dates, and 31 ± 23 % and 36 ± 10 % using $\delta^{13}C$ values of adipose FAs endmembers

408   on the mixing lines and FRUITS, respectively. The calibrated age from pot BN-74 (1st

409   extract) agrees with the age of terrestrial organisms (Figure 3a). Nonetheless, the 2nd extract

410   of the pot BN-74, which yielded results statistically different to the 1st extract, showed a

411    $\%_{marine}$ of 4 ± 11 % using ^{14}C as end-members, suggesting an underestimation of the

412   proportion of marine products in the TLE based on the $\delta^{13}C$ values in this case. As mentioned

413   previously, this potsherd is likely affected by a differential deposition of the marine fats in

414   certain areas of the vessel, implying that determination of $\delta^{13}C$ values and ^{14}C dates on the

415   same TLE is required for a satisfactory quantification of the $\%_{marine}$ using $\delta^{13}C$ values.
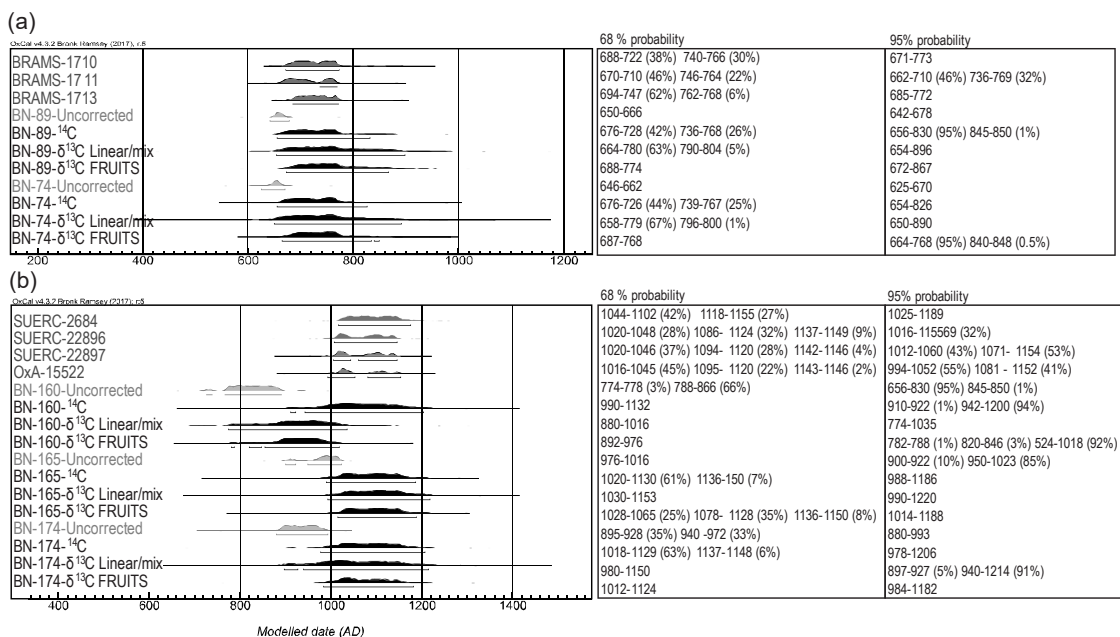
416

417   <u>Figure 3</u>

418   The range of calibrated terrestrial dates (excluding outliers, Table 1) varies from 993 – 1,052

419   cal AD (55 % probability) and 1,081 – 1,152 cal AD (OxA-15522; 41% probability) to 1,039

420   – 1,206 cal AD (OxA-1540, 95 % probability) for the MN phase, BCC context (Figure 3b).

421   The results for potsherds BN-165 using $\delta^{13}C$ values of milk fatty acids and BN174 using $\delta^{13}C$

422   values of adipose fatty acids showed, similarly to BN-89 and BN-74 (1[rst] extraction), a good

16

423   agreement with the age of reference terrestrial animals using the different methods (Figure

424   3b).

425   The $\%_{marine}$ in the pot BN-160 is, however, estimated to be 74 ± 16 % with the use of ^{14}C

426   dates, 26 ± 34 % and 29 ± 10 % with the use of δ^{13}C values milk endmembers in the linear

427   mixing curve and FRUITS, respectively (Table 2). These results are not identical within a 1 σ

428   error but are within 2 σ. The potsherd BN-160 was calibrated to 908 – 1,212 cal AD by

429   radiocarbon estimates, 730 – 1,044 cal AD and to 780 – 1,016 cal AD (95 % probability for

430   all) by dairy endmember in linear mixing and FRUITS, respectively. The end of the last two

431   distributions overlap only at the start of the calibration of the reference terrestrial organisms

432   (Figure 3b). It should be noted that for potsherd BN-160, the ^{14}C dates suggest that marine

433   fat/oil are dominate in the TLE whereas the δ^{13}C values suggest a dominance of dairy

434   products. Unless the CSRA date is inaccurate, this implies that this potsherd, like BN-74,

435   could be affected by a differential partitioning of the marine products and that δ^{13}C values

436   recorded on another TLE are not representative of the TLE used for ^{14}C dating.

437   Overall, MRE corrections of lipid residues, using δ^{13}C calculations using the simple linear

438   mixing model showed a wider probability distribution than those obtained using radiocarbon

439   dates and δ^{13}C values used in the software FRUITS. However, the calibrated range of the

440   corrected CSRA determinations on pot lipids using both methods clearly overlaps the

441   calibrated range of the reference terrestrial organisms. The precision of the calibrated ages

442   depends almost entirely on the uncertainties associated with the calculated $\%_{marine}$, as

443   illustrated with reduced errors obtained using FRUITS software instead of the simple linear

444   mixing curve. The results demonstrate no significant difference in the use of ruminant

445   adipose or dairy δ^{13}C values as end members for the quantification of the $\%_{marine}$. In practice,

446   however, one should be chosen over the other based on the Δ^{13}C values to ensure that the

447   terrestrial endmember is representative of the animal products processed in the vessels at the

448   time (i.e. dairy if Δ^{13}C < -3.1‰ or adipose if Δ^{13}C > -3.1‰). On the other hand, the ^{14}C dates

449   provide an accurate estimate of the $\%_{marine}$ present in the FAs and could be used for

450   quantification of marine products in TLEs instead of a calendar age. The $\%_{marine}$ in potsherds

451   BN-74 (2nd extraction) and BN-160 were underestimated, leading to inappropriate

452   corrections. However, this could be accounted for in the future if the ^{14}C measurements and

453   δ^{13}C values are recorded on the same lipid extract to avoid potential inconsistencies

454   associated with inhomogeneous deposition of the lipids within vessels and use more reliable

455    $\delta^{13}C$ values for the quantification of marine products.

456   One limitation of the $\delta^{13}C$ approach is the estimation of %*marine* due to the wide range of

457   reference values (from ca. -26 ‰ to -20 ‰) observed in modern marine organisms. The

458   reference ellipses commonly plotted comprise only 68 % of the reference values (i.e. 1-σ).

459   The average values used to generate an endmember here are not centred in the ellipses

460   (Figure 2f). Therefore, potsherds with individual FAs $\delta^{13}C$ values plotting at the edge of the

461   reference marine ellipse can be purely marine but, the %*marine* deposited in the sherd can be

462   underestimated using the linear mixing curves (Table 2, Figure 2f). This phenomenon is

463   illustrated in the case of potsherd BN-88 which is likely to contain predominantly marine fats

464   based on the CSRA dates. The $\delta^{13}C$ values plotted just outside the marine reference ellipse

465   and marine-derived C was quantified to be 69 ± 31 % with adipose endmember, and the

466   %*marine* appeared to be underestimated in this case. Potsherd BN-110 could also contain a

467   dominance of marine products based on fatty acid $\delta^{13}C$ values (i.e. 63 ± 28 % with adipose

468   used as endmembers; Table 2, Figure 2f). This suggests that the linear mixing does not

469   account particularly well for the dominance of marine products at the boundaries. Therefore,

470   the use of the mean and standard deviation for the reported %*marine* products would lead to

471   some underestimation when applying MRE corrections in the case of dominance of marine

472   products. This would be overcome using the full probability distribution calculated in

473   FRUITS as prior information on the percentage marine.

474   We suggest that a linear mixing curve can give valid corrections if marine products are not

475   dominant in the TLE, however, the FRUITS software would deal more adequately with the

476   boundaries (if probability distribution are used) and should be used preferably to access the

477   %*marine* in the TLEs.

478

479   **CONCLUSION**

480   The processing of mixed terrestrial/marine fats in pottery vessels at the site of Bornais was

481   revealed through lipid biomarker and CSRA analyses. CSRA and comparison with the

482   radiocarbon dates of associated marine and terrestrial samples also enabled the detection of

483   marine product processing in cases were no aquatic biomarkers were detected. We therefore

484   suggest that in such circumstances, ^{14}C measurements could be used as a tracer for the

485 detection and quantification of marine products processing in pots. Compound-specific dates

486 from potsherds from Bornais were successfully subjected to MRE correction, and assessed

487 against independent ages determined for contemporaneous terrestrial organisms using:

488   (i)   An appropriate ΔR (-65 ± 45) for the site and time period.

489   (ii)   An estimate of the proportion of marine resource processed in the pots calculated

490   using $\delta^{13}C$ values on individual pot FAs and from a modern reference database

491   (linear mixing or implementation in FRUITS).

492   (iii)   A mixed calibration approach in OxCal software.

493 These corrected ages agreed well with the calibrated age of terrestrial samples which

494 confirmed the efficacy of using FA $\delta^{13}C$ values to estimate the *%marine*, meaning that an

495 approach similar to that commonly adopted for bone collagen can be used to correct for MRE

496 present in lipids. For future MRE corrections and calibration on lipids dates, we recommend:

497   (i)   Calculating a ΔR for the site using a paired terrestrial/marine sample approach or

498   using a previously published ΔR relevant for the spatiotemporal area.

499   (ii)   Recording $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values from the same TLE as that used for ^{14}C

500   dating to determine the *%marine*, avoiding the negative impact of potential

501   inhomogeneity of lipid distribution in vessels.

502

503   (iii)   Using mixing model endmembers calculated from modern reference values valid

504   for the location of interest, by using either those of the database for UK animals

505   (excluding the species not present at the site; Copley, *et al.* 2003; Cramp and

506   Evershed 2014) or $\delta^{13}C$ values recorded from reference animals, representative of

507   other locations and environmental conditions (e.g. arid environments, Dunne *et al.*

508   2012).

509   (iv)   Using endmembers from dairy reference fats in the case of potsherds with $\Delta^{13}C < -$

510   3.1 ‰ or using endmembers from the reference ruminant adipose fats values for

511   potsherds with $\Delta^{13}C > -$ 3.1 ‰, to determine *%marine* in the TLEs.

512   (v)   Employ FRUITS or other Bayesian approaches (if available) to quantify $\%_{marine}$ in
513   the TLEs using a probability density function.

514   (vi)   Correct CSRA dates for the MRE using mixed atmospheric and marine calibration
515   curves (e.g. in OxCal).

516

524

525   **REFERENCES**

526   Ascough, P.L, Cook, G.T. and Dugmore, A.J. 2005. Methodological approaches to determining the
527   marine radiocarbon reservoir effect. *Progress in Physical Geography* 29 (4): 532-547.

528   Ascough, P.L., Dugmore, A.J., Cook, G.T., Higney,E., Barber, J. and Scott, E.M. 2004. Holocene
529   variations in the Scottish marine radiocarbon reservoir effect. *Radiocarbon* 46 (2): 611-620.

530   Ascough, P.L., Cook, G.T., Church, M.J., Dugmore, A.J., Arge, S.V. and McGovern, T.H. 2006.
531   Variability in North Atlantic marine radiocarbon reservoir effects at c. AD 1000. *The Holocene* 16
532   (1): 131-136.

533   Ascough, P.L., Cook, G.T., Dugmore, A.J. and Scott, E.M. 2007. The North Atlantic marine reservoir
534   effect in the Early Holocene: Implications for defining and understanding MRE values. *Nuclear*
535   *Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and*
536   *Atoms* 259 (1): 438-447.

537   Ascough, P.L., Cook, G.T. and Dugmore, A.J. 2009. North Atlantic marine 14C reservoir effects:
538   implications for late-Holocene chronological studies. *Quaternary Geochronology* 4 (3): 171-180.

539   Ascough, P.L., Church, M.J. and Cook, G.T. 2017. Marine radiocarbon reservoir effects for the
540   Mesolithic and Medieval periods in the Western Isles of Scotland. *Radiocarbon* 59 (1): 17-31.

541   Berstan, R., Stott, A.W., Minnitt, S., Bronk Ramsey, C., Hedges, R.E.M. and Evershed, R.P. 2008.

542   Direct dating of pottery from its organic residues: new precision using compound-specific carbon

543   isotopes. *Antiquity* 82 (317): 702-713.

544   Bronk Ramsey, C. 2009. Dealing with outliers and offsets in radiocarbon dating. *Radiocarbon* 51 (3):

545   1025-1045.

546   Casanova, E., Knowles, T.D.J., Williams, C., Crump, M.P. and Evershed, R.P. 2017. Use of a 700

547   MHz NMR microcryoprobe for the identification and quantification of exogenous carbon in

548   compounds purified by preparative capillary gas chromatography for radiocarbon determinations.

549   *Analytical Chemistry* 89 (13): 7090-7098.

550   Casanova, E., Knowles, T.D.J., Williams, C., Crump, M.P. and Evershed, R.P. 2018. Practical

551   considerations in high precision compound-specific radiocarbon dating: Eliminating the effects of

552   solvent and sample cross-contamination on accuracy and precision. *Analytical Chemistry* 90 (18):

553   11025-11032.

554   Casanova, E., Knowles T.D.J., Bayliss A., Dunne J., Barański M.Z., Denaire A., Lefranc P., di Lernia

555   S., Roffet-Salque M., Smyth J., Gillard T., Claßen E., Coles B.J., Illet M., Jeunesse C., Krueger M.,

556   Marciniak A., Minnitt, Rotunno R., Van De Velde P., van Wijk I., MOLA and Evershed R.P. In press.

557   Accurate compound-specific radiocarbon dating of archaeological pottery vessels. *Nature.*

558   Cook, G.T., Ascough, P.L., Bonsall, C., Hamilton, W.D., Russell, N., Sayle, K.L., Scott, E.M. and

559   Bownes, J.M. 2015. Best practice methodology for ^{14}C calibration of marine and mixed

560   terrestrial/marine samples. *Quaternary Geochronology* 27: 164-171.

561   Copley, M.S., Berstan, R., Dudd, S.N., Docherty, G., Mukherjee, A.J., Straker, V., Payne, S. and

562   Evershed, R.P. 2003. Direct chemical evidence for widespread dairying in prehistoric Britain.

563   *Proceedings of the National Academy of Sciences* 100 (4): 1524-1529.

564   Copley, M.S., Hansel, F.A., Sadr, K. and Evershed, R.P. 2004. Organic residue evidence for the

565   processing of marine animal products in pottery vessels from the pre-colonial archaeological site of

566   Kasteelberg D east, South Africa. *South African Journal of Science* 100 (5-6): 279-283.

567   Correa-Ascencio, M. and Evershed, R.P. 2014. High throughput screening of organic residues in

568   archaeological potsherds using direct acidified methanol extraction. *Analytical Methods* 6 (5): 1330-

569   1340.

570   Cramp, L.J.E. and Evershed, R.P. 2014. "Reconstructing aquatic resource exploitation in human

571   prehistory using lipid biomarkers and stable isotope". *Treatise on Geochemistry: Archaeology and*

572   *Anthropology* Amsterdam: Elsevier Oxford 12: 319-339.

573 Cramp, L.J.E., Evershed, R.P., Lavento, M., Halinen, P., Mannermaa, K., Oinonen, M., Kettunen, J.,
574 Perola, M., Onkamo, P. and Heyd, V. 2014a. Neolithic dairy farming at the extreme of agriculture in
575 northern Europe. *Proceedings of the Royal Society B: Biological Sciences* 281 (1791): 20140819.

576 Cramp, L.J.E., Jones, J., Sheridan, A., Smyth, J., Whelton, H., Mulville, J., Sharples, N. and
577 Evershed, R.P. 2014b. Immediate replacement of fishing with dairying by the earliest farmers of the
578 northeast Atlantic archipelagos. *Proceedings of the Royal Society of London B: Biological Sciences*
579 281 (1780): 20132372.

580 Cramp, L.J.E., Casanova E. and Evershed R.P. Forthcoming. "Organic residues from Late Iron Age
581 and Norse pottery. A Norse settlement in the Outer Hebrides". *Excavation on Mounds 2 and 2A,*
582 *Bornais, South Uist*. Oxbow Books, Oxford.

583 Dunne, J., Evershed, R.P., Salque, M., Cramp, L.J.E., Bruni, S., Ryan, K., Biagetti, S. and di Lernia,
584 S. 2012. First dairying in green Saharan Africa in the fifth millennium BC. *Nature* 486 (7403): 390-
585 394.

586 Evershed, R.P., Heron, C. and Goad, L.J. 1990. Analysis of organic residues of archaeological origin
587 by high-temperature gas chromatography and gas chromatography-mass spectrometry. *Analyst* 115
588 (10): 1339-1342.

589 Evershed, R.P., Copley, M. S., Dickson, L. and Hansel, F.A. 2008. Experimental evidence for the
590 processing of marine animal products and other commodities containing polyunsaturated fatty acids in
591 pottery vessels. *Archaeometry* 50 (1): 101-113.

592 Fernandes, R., Millard, A.R., Brabec, M., Nadeau, M.-J., Grootes, P., 2014. Food Reconstruction
593 Using Isotopic Transferred Signals (FRUITS): A Bayesian Model for Diet Reconstruction, PLOS
594 ONE 9(2), e87436.

595 Hansel, F.A., Copley, M. S., Madureira, L.A.S. and Evershed, R.P. 2004. Thermally produced ω-(*o*-
596 alkylphenyl) alkanoic acids provide evidence for the processing of marine products in archaeological
597 pottery vessels. *Tetrahedron Letters* 45 (14): 2999-3002.

598 Hansel, F.A. and Evershed, R.P. 2009. Formation of dihydroxy acids from Z-monounsaturated
599 alkenoic acids and their use as biomarkers for the processing of marine commodities in archaeological
600 pottery vessels. *Tetrahedron Letters* 50 (40): 5562-5564.

601 Hedges, R.M., Tiemei, C. and Housley, R.A. 1992. Results and methods in the radiocarbon dating of
602 pottery. *Radiocarbon* 34 (3): 906-915.

603 Heron, C. and Craig, O. E. 2015. Aquatic Resources in Foodcrusts: Identification and Implication.
604 *Radiocarbon* 57 (4): 707-719.

605 Knowles, T.D.J., Monaghan P.S. and Evershed R.P. 2019. Radiocarbon sample preparation
606 procedures and the first status report from the Bristol radiocarbon AMS (BRAMS) facility.
607 *Radiocarbon*: 1-10.

608 Longin, R. 1971. New method of collagen extraction for radiocarbon dating. *Nature* 230(5291): 241.

609 Marshall, P. 2005. "The Chronology". In *A Norse farmstead in the Outer Hebrides: Excavations at*
610 *Mound 3, Bornais, South Uist* Oxbow Books (8): 153-156.

611 Marshall, P., Bronk Ramsey, C. and Cook, G. 2016. "Chronology". In *A late Iron Age farmstead in*
612 *the Outer Hebrides: Excavations at Mound 1, Bornais, South Uist* Oxbow Books: 211-223

613 Marshall, P., Bronk Ramsey, C. and Cook, G. forthcoming. "The chronology". In *A Norse settlement*
614 *in the Outer Hebrides. Excavation on Mounds 2 and 2A, Bornais, South Uist* Oxbow Books, Oxford.

615 Mukherjee, A.J., Copley, M. S., Berstan, R., Clark, K.A. and Evershed, R.P. 2005. Interpretation of
616 δ13C values of fatty acids in relation to animal husbandry, food processing and consumption in
617 prehistory. *9th ICAZ Conference* Oxbow Books Durham: 77-93

618 Reimer, P.J., McCormac, F. G., Moore, J., McCormick, F. and Murray, E.V. 2002. Marine
619 radiocarbon reservoir corrections for the mid to late Holocene in the eastern subpolar North Atlantic.
620 *The Holocene* 12 (2): 129-135.

621 Reimer, P.J., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P. G., Bronk Ramsey, C., Buck, C.E.,
622 Cheng, H., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Haflidason, H., Hajdas, I.,
623 Hatté, C., Heaton, T.J., Hoffmann, D.L., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B.,
624 Manning, S.W., Niu, M., Reimer, R.W., Richards, D.A., Scott, E.M., Southon, J.R., Staff, R.A.,
625 Turney, C.S.M. and van der Plicht, J. 2013. IntCal13 and Marine13 radiocarbon age calibration curves
626 0–50,000 years cal BP. *Radiocarbon* 55 (4): 1869-1887.

627 Reimer, R.W., Reimer, P.J., 2016. An online application for ΔR calculation. *Radiocarbon* 59, 1623-
628 1627.

629 Russell, N., Cook, G. T., Ascough, P. L. and Dugmore, A. J. 2010. Spatial variation in the marine
630 radiocarbon reservoir effect throughout the Scottish post-Roman to late Medieval period: North Sea
631 values (500-1350 BP). *Radiocarbon* 52 (3): 1166-1181.

632 Russell, N., Cook, G. T., Ascough, P., Barrett, J. H. and Dugmore, A. 2011. Species specific marine
633 radiocarbon reservoir effect: a comparison of ΔR values between Patella vulgata (limpet) shell
634 carbonate and Gadus morhua (Atlantic cod) bone collagen. *Journal of Archaeological Science* 38 (5):
635 1008-1015.

636   Russell, N., Cook, G. T., Ascough, P. L. and Scott, E. M. 2015. A period of calm in Scottish seas: A
637   comprehensive study of ΔR values for the northern British Isles coast and the consequent implications
638   for archaeology and oceanography. *Quaternary Geochronology* 30: 34-41.

639   Sharples, N., Ingrem, C., Marshall, P., Mulville, J., Powell, A. and Reed, K. 2016. "The Viking
640   occupation of the Herbides: evidence from the excavations at Bornais, South Uist". In *Maritime*
641   *societies of the Viking and medieval world* (James Barrett and Sara-Jane Gibbon) Chapter 17, pp. 247-
642   268, Monograph 37, Maney, Leeds.

643   Sharples, N. Forthcoming. "A Norse settlement in the Outer Hebrides". In *Excavation on Mounds 2*
644   *and 2A, Bornais, South Uist* Oxbow Books, Oxford.

645   Sharples, N. and Davis O. Forthcoming. "The Middle Norse house on Mound 2 (BC)". In *Excavation*
646   *on Mounds 2 and 2A, Bornais, South Uist* Oxbow Books, Oxford.

647   Stott, A. W., Berstan, R., Evershed, P., Hedges, R. E. M., Ramsey, C. B. and Humm, M. J. 2001.
648   Radiocarbon dating of single compounds isolated from pottery cooking vessel residues. *Radiocarbon*
649   43 (2A): 191-197.

650   Stott, A. W., Berstan, R., Evershed, R. P., Bronk-Ramsey, C., Hedges, R. E. M. and Humm, M. J.
651   2003. Direct dating of archaeological pottery by compound-specific ^{14}C analysis of preserved lipids.
652   *Analytical Chemistry* 75 (19): 5037-5045.

653   Synal, H.-A., Stocker, M. and Suter, M. 2007. MICADAS: A new compact radiocarbon AMS system.
654   *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials*
655   *and Atoms* 259 (1): 7-13.

656   Wacker, L., Němec, M. and Bourquin, J. 2010. A revolutionary graphitisation system: Fully
657   automated, compact and simple. *Nuclear Instruments and Methods in Physics Research Section B:*
658   *Beam Interactions with Materials and Atoms* 268 (7–8): 931-934.

659   Wacker, L., Fülöp, R. H., Hajdas, I., Molnár, M. and Rethemeyer, J. 2013. A novel approach to
660   process carbonate samples for radiocarbon measurements with helium carrier gas. *Nuclear*
661   *Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and*
662   *Atoms* B 294: 214-217.

663

664   **Figure captions:**

665   Figure 1: Flowchart showing the method used to assess the validity of the δ^{13}C values method for the
666   estimation of the *%marine* products and correction of the CSRA dates on the FAs.

667

668   Figure 2: Partial gas chromatogram of the TLE (a), and GC/MS SIM mass chromatograms showing
669   detection of DHYAs (b) and APAAs (c), for potsherd BN-173. Scatter plots of δ^{13}C$_{16:0}$ plotted against
670   δ^{13}C$_{18:0}$ from lipid residues characteristic of animal fats at Bornais for all the TLEs (Cramp *et al.,*
671   2014b, forthcoming and this study), (d) for the 22 potsherd extracts selected for ^{14}C dating by CSRA
672   and position of the average reference values (crosses) (e), and the theoretical mixing lines of
673   terrestrial and marine end-members with the approximate percentage of marine fat/oil marked on the
674   lines (f). Stars denote the detection of aquatic biomarkers. Shaded areas indicate the reference ellipses
675   for δ^{13}C values on modern animals and the crosses are the values used as endmembers. The dashed
676   lines correspond to the areas where lipid residues are hypothesised to be affected to varying degrees
677   by the MRE.

678

679   Figure 3: Corrections and calibration for potsherds of the (a) LIA phase, (b) MN phase in OxCal v4.3
680   against the IntCal13 calibration curve (Bronk Ramsey 2009, Reimer *et al.* 2013). The distributions
681   plotted in dark grey correspond to the reference age of terrestrial animal bones, in light grey the
682   uncorrected determinations on pot lipids and in black the corrected determinations on pot lipids using
683   either the ^{14}C or δ^{13}C methods using adipose or milk as endmembers.

684

Supporting Materials

Compound-specific radiocarbon, stable carbon isotope and biomarker analysis of mixed marine/terrestrial lipids preserved in archaeological pottery vessels

Emmanuelle Casanova[1], Timothy D.J. Knowles[1,2], Candice Ford[1,*], Lucy J.E. Cramp[4], Niall Sharples[5] and Richard P. Evershed[1,2]

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

[2]Bristol Accelerator Mass Spectrometry Facility, University of Bristol, 43 Woodland Road, BS8 1UU, UK

[3]Department of Anthropology and Archaeology, 43 Woodland Road, University of Bristol, BS8 1UU, UK

[4]School of History, Archaeology and Religion, Cardiff University, Humanities Building, Colum Drive, Cardiff CF10 3EU, UK

*Present address: The University of Nottingham, School of Chemistry, University Park, Nottingham NG7 2RD, 14 UK.

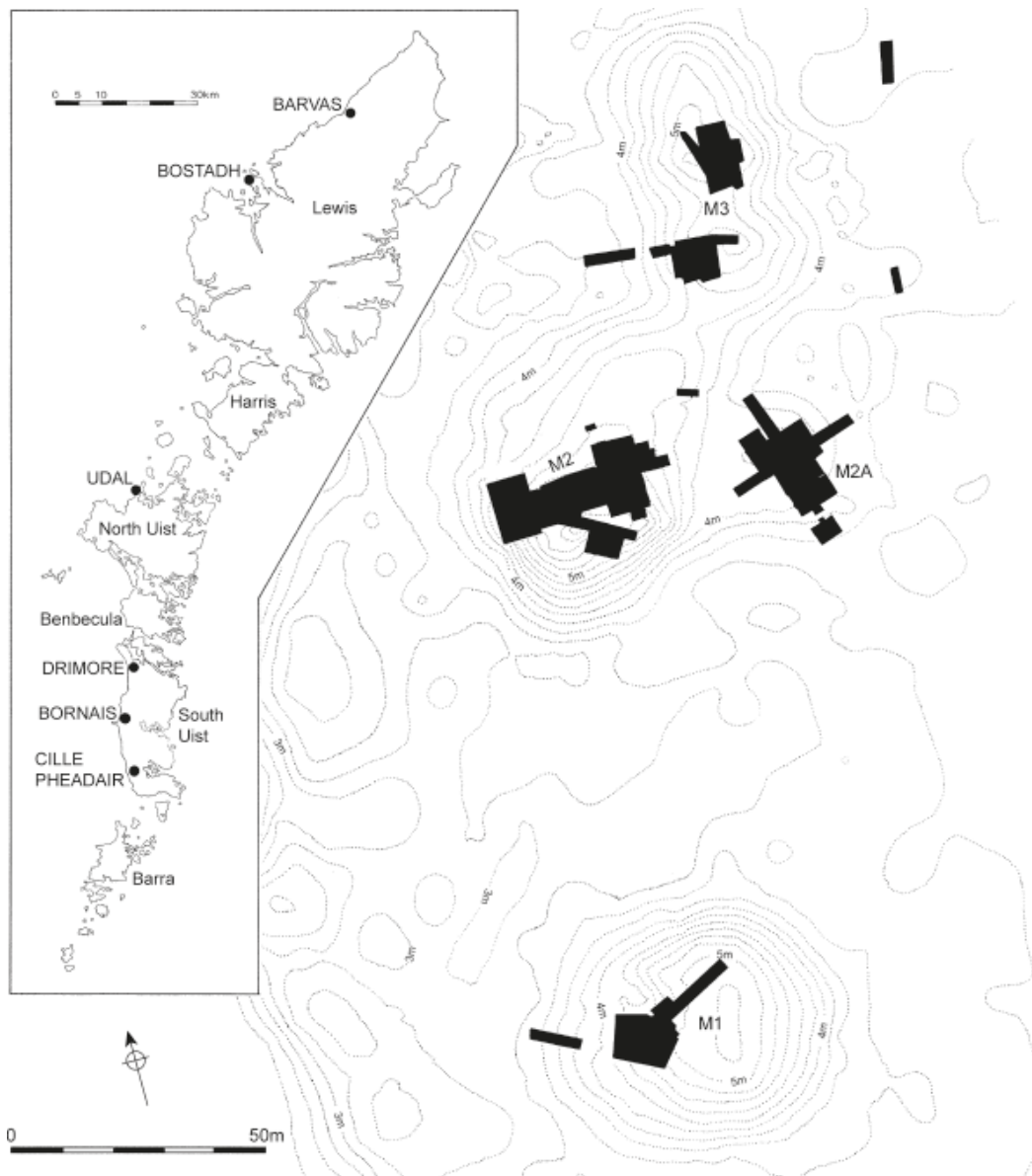## S1- Site location and stratigraphic information of Mound 2

Figure S1: Location of the site of Bornais and the 4 mounds excavated. From Sharples *et al.* (2016), Fig.17.1.
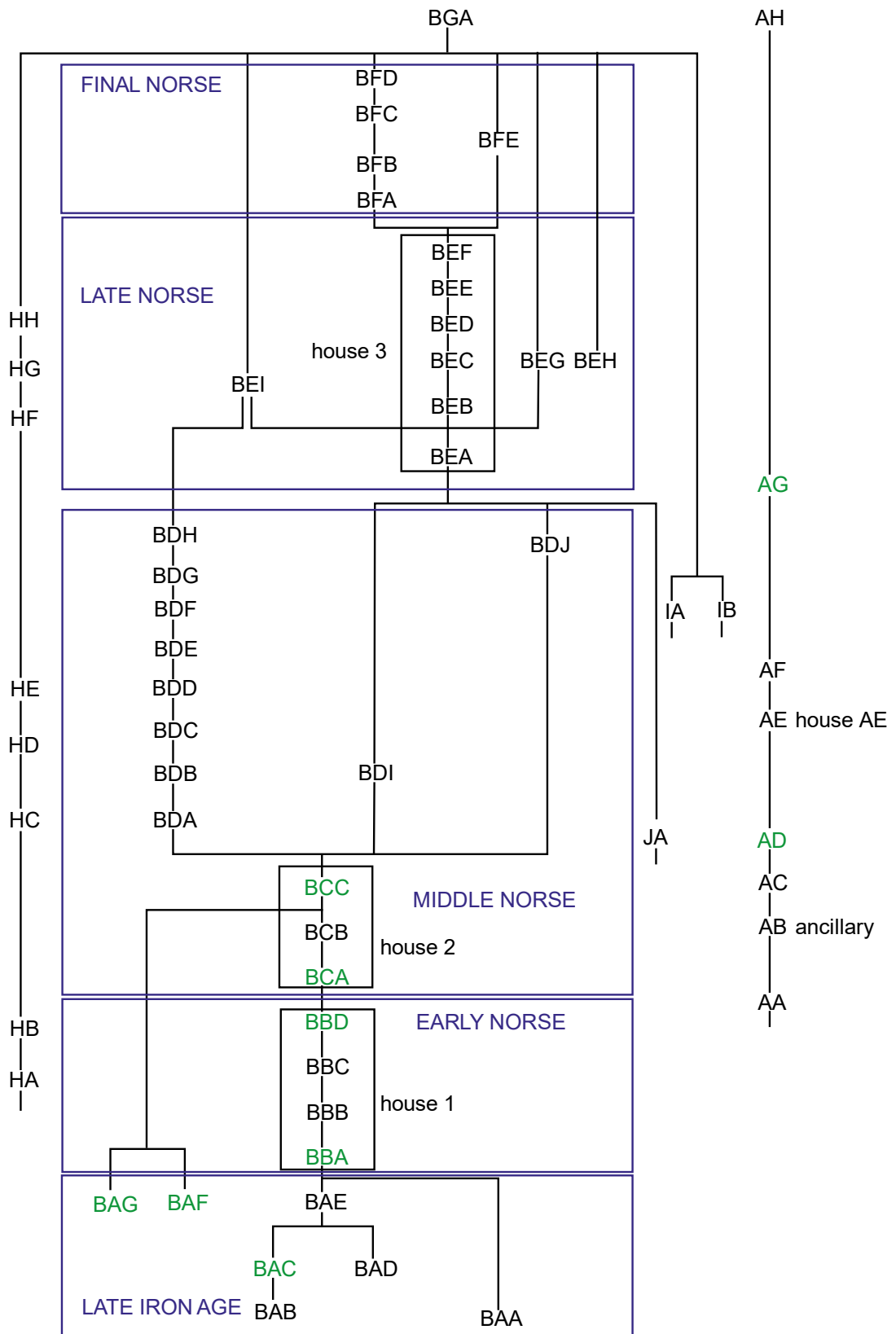
Figure S2: Schematic diagram showing the stratigraphic information for the Mound 2. Green contexts correspond to the ones studied in this paper.

S2- Detailed method for lipid residue analyses

To remove surface contaminants, a small part of the potsherd (~ 2 - 7 g) was cleaned with a modelling drill then sampled using hammer and chisel and ground to fine powder using mortar and pestle. Approximately 1 to 2 g of ground potsherd were weighed into a clean culture tube (I) with stopper and 20 µL of internal standard (IS; n-tetratriacontane) at 1 mg.ml^{-1} was added. The lipids were extracted using a solution of H_2SO_4/MeOH (4% v/v, 5 mL, 70 ºC, 1 h,). The supernatant of culture tube I was then centrifuged (2500 rpm, 10 min) and transferred to a clean culture tube (II) before adding double distilled water (2 mL). N-hexane was added (2 x 3 mL) to culture tube I and the supernatant transferred to culture tube II. Following this, 2 x 2 ml n-hexane was added directly to the H_2SO_4/MeOH solution in culture tube II and whirlimixed to extract the remaining residues, then transferred to the 3.5 mL vials and blown down until a full vial of n-hexane remained. A procedural blank was prepared and analysed alongside every batch of archaeological materials to assess whether contamination was introduced during the protocol. Before analysis, an aliquot of the total lipid extract (TLE; 1/4) was derivatised by the addition of BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide; 20 µL, 70 ºC, 1 h). Excess BSTFA was blown down at 40 ºC under a gentle stream of nitrogen, and an appropriate amount of n-hexane was added, prior to analysis with GC, GC-MS and GC-C-IRMS (Correa-Ascencio and Evershed 2014).

GC analysis of TLEs (Section 2.3.2.1) for quantification was performed on a Hewelett Packard 5890 series II gas chromatograph or an Agilent Technologies 7890A GC. Helium was used as carrier gas at constant flow (2 mL.min^{-1}), and a flame ionisation detector (FID) used to monitor column effluent. Lipids extracts (1 µL) were injected into a non-polar fused silica capillary column (50 m x 0.32 mm i.d., DB1 stationary phase (100 % dimethylpolysiloxane), 0.17 µm film thickness, Agilent technologies). The oven temperature program started with an isothermal hold at 50 ºC for 2 min, then the temperature was increased at 10 ºC.min^{-1} to 300 ºC and held for 10 min (Evershed et $al.$ 1990).

GC-MS analysis of TLEs for molecular identification was performed on a Finnigan Trace MS quadrupole instrument coupled to a Trace GC, or on a Thermo Scientific ISQ LT single quadrupole GC-MS coupled to a Trace 1300, with manual or auto-sampling injections. The lipid extracts (1 µL) were introduced into a non-polar fused silica capillary column (50 m x 0.32 mm i.d., DB1 stationary phase, 0.17 µm film thickness, Agilent Technologies). For TLEs analysis the oven temperature program started with an isothermal hold at 50 ºC during 2 min, then the temperature increased at 10 ºC.min^{-1} to 300 ºC and held for 10 min. The MS used electron ionization (EI) mode operating at 70 eV with a GC interface temperature of 300 ºC and a source temperature of 200 ºC. Acquisition used the total ion current (TIC) mode over the range m/z 50-650 Daltons at 8.3 scans.s^{-1} (Evershed et $al.$ 1990). Screening for di-hydroxy fatty acid methyl esters (DHYAs, aquatic biomarkers) used selected ion monitoring

(SIM) mode, monitoring *m/z* 159, 187, 215, 243, 259, 287, 315, 443, 459, 471, 487, 499 and 515 (for -COOMe derivatives instead of -COOTMS as published; Cramp and Evershed 2014).

In order to determine the presence of other aquatic biomarkers (APAAs and isoprenoid acids), TLEs were run on a polar column (60 m x 0.32 mm i.d., VF-23ms stationary phase (polydimethylsiloxane highly substituted with cyanopropyl groups), 0.15 μm film thickness, Agilent Technologies). The temperature program started with an isothermal hold at 70 ºC for 2 min, followed by a ramp at 10 ºC.min^{-1} to 220 ºC, then a ramp at 4 ºC.min^{-1} to 300 ºC and finally an isothermal hold for 10 min. Full scan mode *m/z* 50-650 and SIM mode, screening for the masses *m/z* 105, 262, 290, 318 and 346, were performed for the detection of APAAs (Cramp and Evershed 2014).

The GC-C-IRMS analyses on $C_{16:0}$ and $C_{18:0}$ FAs (for identification of the source of animal fats) was performed on an Agilent Technologies 7890A, coupled via an IsoPrime GC5 combustion interface (CuO and silver reactor, 850 ºC) to an IsoPrime 100 mass spectrometer. The FAME extracts (1 μL) were injected into a non-polar column (50 m x 0.32 mm i.d., DB1 stationary phase, 0.17 μm film thickness, Agilent technologies). The GC oven temperature was held for 2 min at 40 ºC and increased to 300 ºC at 10 ºC.min^{-1} and held for 10 min. The MS used EI at 70 eV and had three Faraday cups collecting for the masses *m/z* 44, 45 and 46. Data were acquired and processed by the IonVantage software (Copley *et al.* 2003).

S3- Results of lipid residue analysis

Table S1: Results of lipid residue analysis of potsherds from the site of Bornais Mound 2, House 2. P corresponds to the Phytanic acid and TMDT to the 4,8,12-trimethyltridecanoic acid. Compounds in brackets corresponds to trace amounts (not clearly identified).

Sherd #	Block	Code	C ($\mu g \cdot g^{-1}$)	FAs	DHYAs	APAAs	IFAs	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment (before CSRA dating)
BN-132	BCA	1259/3790	849	C_{14}-C_{18}	-	-	(TMTD), P	-25.8	-31.0	-5.2	Mixture dairy, non-ruminant fats
BN-133	BCA	1280/9448/3/3887	137	C_{14}-C_{18}	C_{18}	-	-	-	-	-	nd
BN-134	BCB	6/8656	190	C_{14}-C_{22}	-	C_{18}, C_{20}, C_{22}	TMTD, P	-	-	-	nd
BN-135	BCB	1089/8654	1444	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	-	(TMTD), P	-26.3	-26.6	-0.2	Mixture ruminant adipose, marine fats
BN-136	BCB/C	1074/2/3529	207	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	-	-26.7	-32.9	-6.2	Mixture dairy, marine fats
BN-137	BCC	182/1/8659	676	C_{14}-C_{22}	-	C_{18}, C_{20}, C_{22}	TMTD, P	-24.9	-28.4	-3.5	Mixture dairy, marine fats
BN-138	BCC	528/2199	19	C_{14}-C_{22}	-	-	-	-	-	-	nd
BN-139	BCC	549/2264	3135	C_{14}-C_{20}	C_{18}, C_{22}	C_{18}	-	-26.6	-29.3	-2.7	Ruminant adipose fats
BN-140	BCC	550/5/2458	216	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, C_{20}, C_{22}	TMTD, P	-22.1	-25.2	-3.1	Marine fats
BN-141	BCC	550/5/2458	28	C_{16}-C_{22}	(C_{18})	-	-	-26.6	-32.5	-5.9	Mixture dairy, non-ruminant fats
BN-142	BCC	557/5/2341	2220	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20})	(TMTD), P	-24.9	-27.9	-3.0	-
BN-143	BCC	557/5/8660	5630	C_{14}-C_{20}	C_{18}	C_{18}	P	-25.8	-27.9	-2.2	Mixture ruminant adipose, marine fats
BN-144	BCC	558/5/8670	2483	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	(TMTD), P	-25.6	-28.9	-3.3	Mixture dairy, marine fats
BN-145	BCC	565/8655	1425	C_{14}-C_{22}	C_{18}	-	P	-27.0	-31.3	-4.3	Mixture dairy, non-ruminant fats
BN-146	BCC	921/2992	1349	C_{14}-C_{22}	C_{18}	C_{18}	P	-25.6	-30.2	-4.6	Mixture dairy, non-ruminant fats
BN-147	BCC	1008/3063	56	C_{16}-C_{22}	(C_{18})	-	-	-	-	-	nd
BN-148	BCC	1008/9452/8657	60	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20}, C_{22})	TMTD, P	-25.3	-29.2	-4.0	Mixture dairy, marine fats
BN-149	BCC	1010/9685/2/3279	3984	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	(TMTD), P	-26.3	-30.4	-4.1	Mixture dairy, marine fats
BN-150	BCC	1010/2/3266	1460	C_{14}-C_{22}	C_{18}, (C_{20}, C_{22})	C_{18}, C_{20}, C_{22}	TMTD, P	-25.2	-29.0	-3.8	Mixture dairy, marine fats
BN-151	BCC	1049/9809/8661	2141	C_{14}-C_{22}	C_{18}, (C_{20}, C_{22})	C_{18}	P	-26.9	-29.6	-2.7	Mixture ruminant, non-ruminant adipose fats
BN-152	BCC	1057/9895/8656	0	-	-	-	-	-	-	-	-
BN-153	BCC	1057/9894/3522	1409	C_{14}-C_{22}	(C_{18})	C_{18}	-	-26.5	-29.8	-3.3	Mixture dairy, non-ruminant fats
BN-154	BCC	1057/9893/3461	1153	C_{14}-C_{20}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20}, C_{22})	TMTD, P	-27.0	-30.1	-3.0	Mixture ruminant adipose, marine fats
BN-155	BCC	1057/9894/3535	4198	C_{14}-C_{22}	-	-	-	-26.5	-28.6	-2.2	Mixture ruminant, non-ruminant adipose fats
BN-156	BCC	1057/9894/8666	276	C_{14}-C_{18}	-	-	-	-25.3	-28.9	-3.6	Mixture dairy, non-ruminant fats
BN-157	BCC	1079/2/8671	11	C_{16}-C_{22}	C_{18}	-	TMTD, P	-	-	-	nd
BN-158	BCC	1220/9991/3662	12	-	(C_{18})	-	-	-	-	-	nd
BN-159	BCC	1220/9991/8664	1178	C_{14}-C_{20}	C_{18}	C_{18}	P	-26.4	-32.0	-5.6	Mixture dairy, non-ruminant fats
BN-160	BCC	1234/9492/8665	4559	C_{14}-C_{22}	C_{18}	C_{18}	(TMTD), P	-26.4	-31.0	-4.6	Mixture dairy, non-ruminant fats
BN-161	BCC	1260/9467/3779	546	C_{14}-C_{18}	(C_{18}, C_{20}, C_{22})	-	-	-25.7	-31.2	-5.5	Mixture dairy, non-ruminant fats
BN-162	BCC	1260/9465/8672	1574	C_{16}, C_{18}	(C_{18})	-	-	-26.7	-29.3	-2.6	Mixture ruminant, non-ruminant adipose fats
BN-163	BCC	2192/11902/10/2192	452	C_{14}-C_{18}	C_{18}	C_{18}	-	-27.3	-31.5	-4.2	Mixture dairy, non-ruminant fats
BN-164	BCC	2225/11943/6230	129	C_{16}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	TMTD, P	-25.8	-31.6	-5.8	Mixture dairy, marine fats

Sherd #	Block	Code	C ($\mu g.g^{-1}$)	FAs	DHYAs	APAAs	IFAs	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment (before CSRA dating)
BN-165	BCC	2231/11968/14/6214	1823	C_{14}-C_{18}	(C_{18})	-	-	-26.3	-30.1	-3.7	Mixture dairy, non-ruminant fats
BN-166	BCC	2258/11287/15/8663	246	C_{16}, C_{18}	C_{18}	C_{18}, C_{20}	TMTD, P	-25.8	-31.7	-5.9	Mixture dairy, marine fats
BN-167	BCC	2264/6314	946	C_{14}-C_{22}	(C_{18}, C_{20}, C_{22})	C_{18}, C_{20}, C_{22}	TMTD, P	-23.5	-26.6	-3.1	Marine fats
BN-168	BCC	2264/14/6312	1105	C_{16}, C_{18}	C_{18}	C_{18}	-	-29.2	-31.5	-2.3	Ruminant adipose fats
BN-169	BCC	2264/14/8667	2	C_{18}, C_{22}	-	-	-	-	-	-	-
BN-170	BCC	2285/11278/19/8662	4231	C_{14}-C_{22}	-	C_{18}, C_{20}, C_{22}	TMTD, P	nd	nd	nd	Marine fats
BN-171	BCC	2297/11318/19/8658	872	C_{14}-C_{22}	C_{18}	C_{18}	P	-26.2	-32.2	-6.0	Mixture dairy, non-ruminant fats
BN-172	BCC	2613/9/6398	834	C_{16}-C_{20}	(C_{18}, C_{20})	C_{18}	P	-26.1	-28.5	-2.4	Mixture ruminant, non-ruminant adipose fats
BN-173	BCC	2637/11398/6500	2376	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, C_{20}, C_{22}	TMTD, P	-26.0	-30.5	-4.5	Mixture dairy, marine fats
BN-174	BCC	2657/11464/16/6523	1176	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	$C_{18}, (C_{20}, C_{22})$	(TMTD), P	-25.9	-28.5	-2.6	Mixture ruminant adipose, marine fats
BN-175	BCC	2673/11489/13/8669	41	C_{16}-C_{22}	$C_{18}, (C_{22})$	C_{18}, C_{20}, C_{22}	(TMTD), P	-25.6	-29.8	-4.2	Mixture dairy, marine fats
BN-176	BCC	2692/12041/7300	924	C_{16}-C_{20}	$C_{18}, (C_{20}, C_{22})$	$C_{18}, (C_{20}, C_{22})$	P	-26.4	-29.0	-2.6	Mixture ruminant adipose, marine fats
BN-177	BCC	2700/12057/6631	497	C_{16}-C_{22}	C_{18}, C_{20}, C_{22}	$C_{18}, (C_{20})$	TMTD, P	-25.1	-30.3	-5.2	Mixture dairy, marine fats
BN-178	BCC	2715/12090/20/6637	280	C_{16}-C_{22}	C_{18}, C_{20}, C_{22}	$C_{18}, C_{20}, (C_{22})$	TMTD, P	-	-	-	-
BN-179	BCC	2731/1204/20/6686	1083	C_{14}-C_{20}	(C_{18})	C_{18}	P	-26.5	-29.8	-3.2	Mixture dairy, non-ruminant fats
BN-180	BCC	545+39/2501	536	C_{16}-C_{20}	(C_{18})	C_{18}, C_{20}, C_{22}	P	-24.4	-28.1	-3.7	Mixture dairy, marine fats

S4- Summary of published Δ determinations in the Hebrides Islands

Table S2: Summary of ΔR values published for the Hebridian Islands

Location	Site	$\Delta R \pm 1\sigma$	Time period	Reference
Outer Hebrides Lewis and Harris	Guinnerso	-130 ± 36	1,460 - 1,630 AD	Ascough *et al.* 2017
	Bostadh	-56 ± 14	893 - 984 AD	Ascough *et al.* 2009
	Garenin	-85 ± 17	887 - 995 AD	Ascough *et al.* 2009
	Traigh na Beirigh	-126 ± 39	4,540 - 4,240 BC	Ascough *et al.* 2017
	Northton	64 ± 41	6,390 - 6,290 BC	Ascough *et al.* 2017
		79 ± 32	6,390 - 6,230 BC	Ascough *et al.* 2007
Outer Hebrides North Uist	Baleshare	-79 ± 17	252 BC - 149 AD	Ascough *et al.* 2004
		68 ± 95	77 BC - 111 AD	Reimer *et al.* 2002
Outer Hebrides South Uist	Hornish point	-79 ± 17	252 BC - 149 AD	Ascough *et al.* 2004
		-184 ± 122	394 BC - 24 AD	Reimer *et al.* 2002
		-146 ± 71		
Inner Hebrides (& Mainland)	Carding Mill Bay	150 ± 28	3,641 - 3,521 BC	Russell *et al.* 2015
		86 ± 67	3,942 - 3,653 BC	Reimer *et al.* 2002
		-44 ± 91	3,965 – 3,714 BC	Reimer *et al.* 2002
	Sand	64 ± 41	6,480 - 6,420 BC	Ascough *et al.* 2017
		64 ± 19	6,480 - 6,420 BC	Ascough *et al.* 2007

S5- Details on CSRA dates

Table S3: Details of CSRA dates on pottery vessels and aquatic biomarker detection

Sample	Phase	Layer	BRAMS #	mCO₂ (µg)	Age ± 1σ (BP)	σ range	Comments
BN89-C$_{16:0}$	LIA 2	BAC	1549.1.1	199	1396 ± 29	••	
BN89-C$_{18:0}$	LIA 2	BAC	1549.1.2	312	1336 ± 27		No aquatic biomarkers
BN89-C$_{16:0}$	LIA 2	BAC	1549.2.1	230	1404 ± 30	••	
BN89-C$_{18:0}$	LIA 2	BAC	1549.2.2	373	1322 ± 29		
BN74-C$_{16:0}$	LIA 2	BAC	1551.1.1	388	1394 ± 27	••	
BN74-C$_{18:0}$	LIA 2	BAC	1551.1.2	534	1369 ± 26		APAAs
BN74-C$_{16:0}$	LIA 2	BAC	1551.2.1	379	1299 ± 29	•	
BN74-C$_{18:0}$	LIA 2	BAC	1551.2.2	448	1273 ± 29		
BN77-C$_{16:0}$	LIA 2	BAF	1605.1.1	234	1364 ± 29	•	No aquatic biomarkers
BN77-C$_{18:0}$	LIA 2	BAF	1605.1.2	293	1375 ± 28		
BN87-C$_{16:0}$	LIA 2	BAF	1604.1.1	175	1292 ± 29	•	APAAs
BN87-C$_{18:0}$	LIA 2	BAF	1604.1.2	246	1315 ± 28		
BN88-C$_{16:0}$	LIA 2	BAG	1548.1.1	216	1720 ± 28	•	
BN88-C$_{18:0}$	LIA 2	BAG	1548.1.2	141	1729 ± 30		APAAs, DHYAs
BN88-C$_{16:0}$	LIA 2	BAG	1548.2.1	228	1726 ± 30	•	
BN88-C$_{18:0}$	LIA 2	BAG	1548.2.2	165	1728 ± 32		
BN35-C$_{16:0}$	EN	BBD	1552.1.1	112	1389 ± 33	X	
BN35-C$_{18:0}$	EN	BBD	1552.1.2	142	1255 ± 30		APAAs, DHYAs
BN35-C$_{16:0}$	EN	BBD	1552.2.1	136	1151 ± 33	•	
BN35-C$_{18:0}$	EN	BBD	1552.2.2	125	1161 ± 34		
BN91-C$_{16:0}$	EN	BBD	1603.1.1	207	1372 ± 29	-	APAAs, DHYAs - No internal control
BN91-C$_{18:0}$	EN	BBD	1603.1.2	*79*	-		
BN101-C$_{16:0}$	EN	BBD	1550.1.1	110	1033 ± 27	X	No aquatic biomarkers
BN101-C$_{18:0}$	EN	BBD	1550.1.2	105	1420 ± 31		
BN101-C$_{16:0}$	EN	BBD	1550.2.1	110	1469 ± 33	-	No internal control
BN101-C$_{18:0}$	EN	BBD	1550.2.2	*70*	-		Small size, exclude
BN105-C$_{16:0}$	EN	BBD	1547.1.1	164	1288 ± 30	•	
BN105-C$_{18:0}$	EN	BBD	1547.1.2	128	1247 ± 31		No aquatic biomarkers
BN105-C$_{16:0}$	EN	BBD	1547.2.1	120	1370 ± 34	••	
BN105-C$_{18:0}$	EN	BBD	1547.2.2	117	1280 ± 34		
BN110-C$_{16:0}$	EN	BBA	1608.1.1	184	1360 ± 29	••	APAAs
BN110-C$_{18:0}$	EN	BBA	1608.1.2	153	1288 ± 30		
BN115-C$_{16:0}$	MN	BCA	1609.1.1	219	989 ± 28	•	No aquatic biomarkers
BN115-C$_{18:0}$	MN	BCA	1609.1.2	214	984 ± 29		
BN142-C$_{16:0}$C$_{18:0}$	MN	BCC	2069.1.1	238	1007 ± 29	-	DHYAs - No internal control
BN149-C$_{16:0}$C$_{18:0}$	MN	BCC	2064.1.1	145	1768 ± 34	-	DHYAs - No internal control
BN160-C$_{16:0}$	MN	BCC	2066.1.1	-	1230 ± 29	•	No aquatic biomarkers
BN160-C$_{18:0}$	MN	BCC	2066.1.2	216	1165 ± 31		
BN165-C$_{16:0}$	MN	BCC	2063.1.1	311	1080 ± 29	•	No aquatic biomarkers
BN165-C$_{18:0}$	MN	BCC	2063.1.2	285	1040 ± 29		
BN167-C$_{16:0}$C$_{18:0}$	MN	BCC	2068.1.1	225	1295 ± 31	-	APAAs, TMTD - No internal control
BN168-C$_{16:0}$	MN	BCC	2061.1.1	123	1211 ± 34	X	No aquatic biomarkers
BN168-C$_{18:0}$	MN	BCC	2061.1.2	253	1062 ± 34		
BN173-C$_{16:0}$C$_{18:0}$	MN	BCC	2067.1.1	167	1234 ± 32	-	APAAs, DHYAs, TMTD - No internal control
BN174-C$_{16:0}$	MN	BCC	2062.1.1	219	1152 ± 31	••	APAAs
BN174-C$_{18:0}$	MN	BCC	2062.1.2	296	1065 ± 33		
BN38-C$_{16:0}$	MN	AD	1606.1.1	121	871 ± 31	-	No aquatic biomarkers - No internal control
BN36-C$_{16:0}$	LN	AG	1607.1.1	201	767 ± 29	••	APAAs, DHYAs
BN36-C$_{18:0}$	LN	AG	1607.1.2	115	816 ± 31		

S6- Quantification of marine derived-C using FRUITS (v2.1)

Table S4: Determination of the percentage marine products in pottery vessels CSRA dated using FRUITS.

| Target/ Consumer	Source/Food	Mean	sd	2.5pc	median	97.5pc
BN89	ruminant adipose	0.646	0.1001	0.4117	0.6601	0.8014
	marine	0.354	0.1001	0.1986	0.3399	0.5884
BN74	ruminant adipose	0.6361	0.09734	0.4126	0.6486	0.7901
	marine	0.3639	0.09734	0.21	0.3514	0.5875
BN174	ruminant adipose	0.537	0.1158	0.2521	0.5545	0.7138
	marine	0.463	0.1158	0.2862	0.4455	0.7491
BN160	milk	0.7067	0.09375	0.5054	0.7157	0.8641
	marine	0.2933	0.09375	0.136	0.2843	0.4951
BN165	milk	0.6372	0.1027	0.389	0.6489	0.7997
	marine	0.3628	0.1027	0.2004	0.3511	0.6111
BN77	ruminant adipose	0.6823	0.09332	0.4724	0.6928	0.8323
	marine	0.3177	0.09332	0.1678	0.3072	0.5276
BN88	ruminant adipose	0.2925	0.1237	0.03621	0.3041	0.505
	marine	0.7075	0.1237	0.4951	0.696	0.9638
BN110	ruminant adipose	0.3656	0.1253	0.08533	0.3807	0.5757
	marine	0.6344	0.1253	0.4243	0.6193	0.9148
BN87	milk	0.6823	0.08895	0.4844	0.6914	0.8288
	marine	0.3177	0.08895	0.1713	0.3086	0.5156
BN35	milk	0.6692	0.1059	0.4316	0.681	0.8465
	marine	0.3308	0.1059	0.1536	0.319	0.5685
BN105	milk	0.7343	0.094	0.5228	0.7439	0.8934
	marine	0.2657	0.094	0.1067	0.2561	0.4774
BN115	milk	0.4731	0.1099	0.2199	0.4864	0.6534
	marine	0.5269	0.1099	0.3468	0.5136	0.7803
BN36	milk	0.4835	0.1136	0.2177	0.4982	0.6682
	marine	0.5165	0.1136	0.3323	0.5018	0.7824
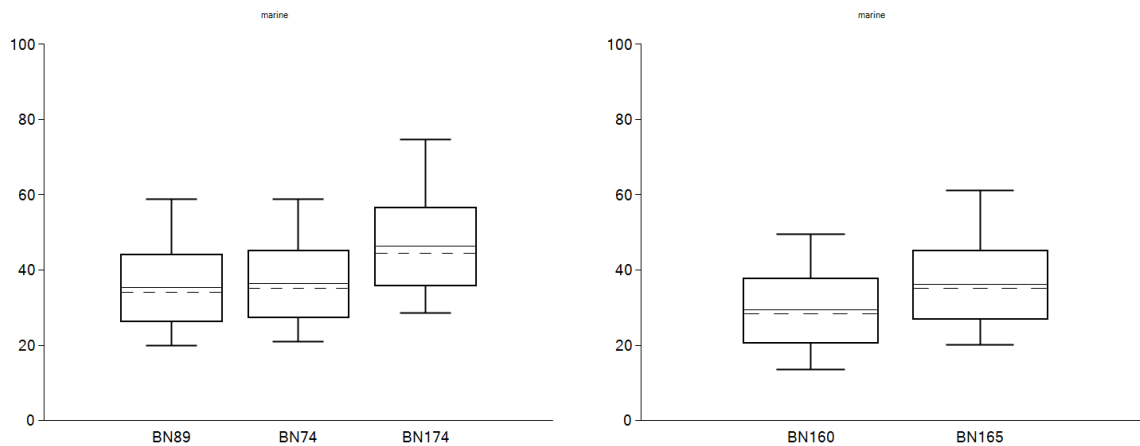
Figure S3: Box and whisker plot for the marine contribution in potsherds dominated by (a) ruminant adipose fats and (b) dairy fats for the potsherds CSRA dated and corrected in the main paper (from FRUITS v2.1).
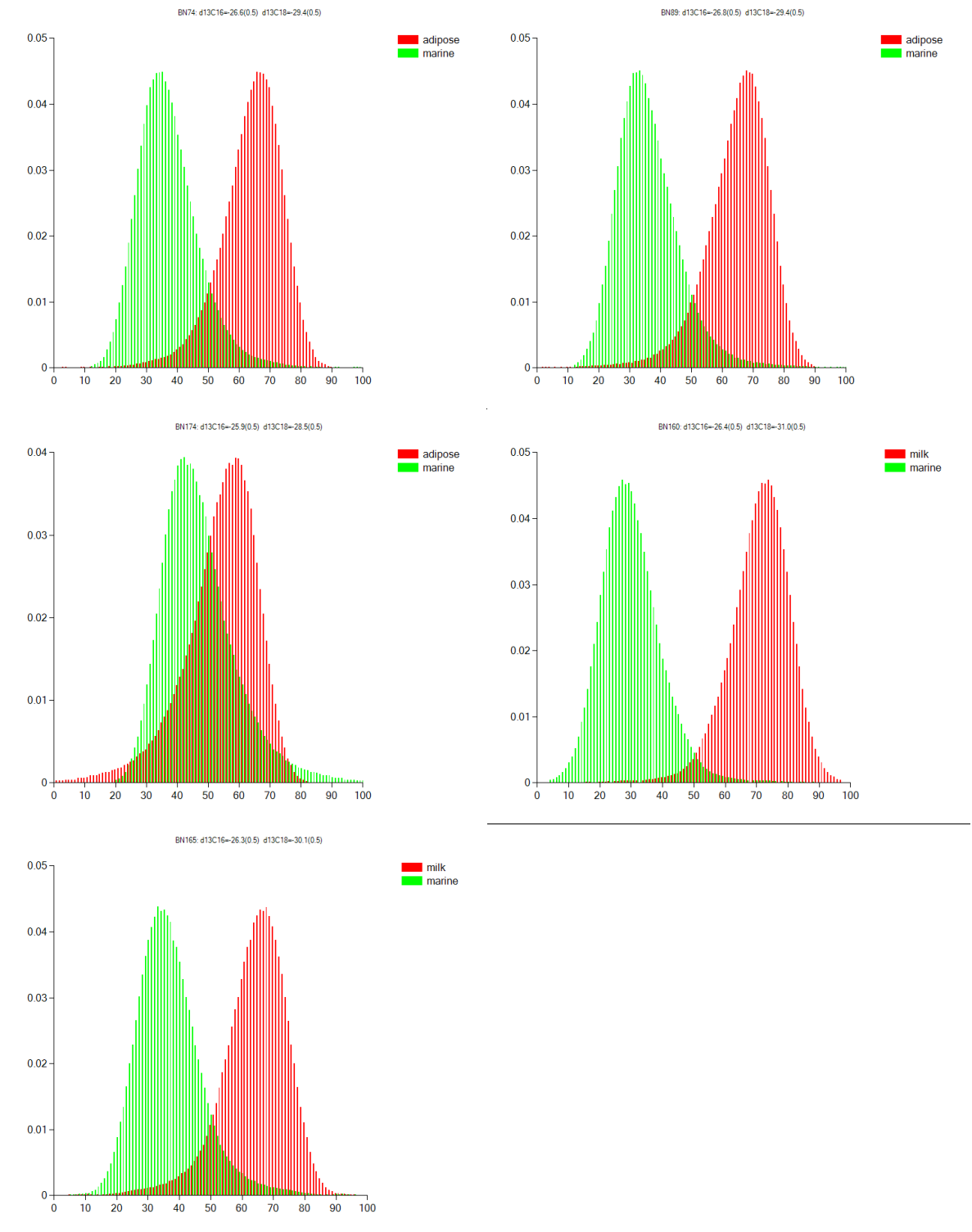
Figure S4: Probability distribution for the proportion of marine (green) and terrestrial (red) resources for the potsherds CSRA dated and corrected in the main paper (from FRUITS v2.1)

References

Ascough, P., Cook, G. and Dugmore, A. 2005. Methodological approaches to determining the marine radiocarbon reservoir effect. *Progress in Physical Geography* 29 (4): 532-547

Ascough, P. L., Dugmore, A. J., Cook, G. T., Higney, E., Barber, J. and Scott, E. M. 2004. Holocene variations in the Scottish marine radiocarbon reservoir effect. *Radiocarbon* 46 (2): 611-620

Ascough, P. L., Cook, G. T., Church, M. J., Dugmore, A. J., Arge, S. V. and McGovern, T. H. 2006. Variability in North Atlantic marine radiocarbon reservoir effects at c. AD 1000. *The Holocene* 16 (1): 131-136

Ascough, P. L., Cook, G. T., Dugmore, A. J. and Scott, E. M. 2007. The North Atlantic marine reservoir effect in the Early Holocene: Implications for defining and understanding MRE values. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 259 (1): 438-447

Ascough, P. L., Cook, G. T. and Dugmore, A. J. 2009. North Atlantic marine 14C reservoir effects: implications for late-Holocene chronological studies. *Quaternary Geochronology* 4 (3): 171-180

Ascough, P. L., Church, M. J. and Cook, G. T. 2017. Marine radiocarbon reservoir effects for the Mesolithic and Medieval periods in the Western Isles of Scotland. *Radiocarbon* 59 (1): 17-31

Casanova, E., Knowles, T. D. J., Williams, C., Crump, M. P. and Evershed, R. P. 2017. Use of a 700 MHz NMR microcryoprobe for the identification and quantification of exogenous carbon in compounds purified by preparative capillary gas chromatography for radiocarbon determinations. *Analytical Chemistry* 89 (13): 7090-7098

Casanova, E., Knowles, T. D. J., Williams, C., Crump, M. P. and Evershed, R. P. 2018. Practical considerations in high precision compound-specific radiocarbon dating: Eliminating the effects of solvent and sample cross-contamination on accuracy and precision. *Analytical Chemistry* 90 (18): 11025-11032

Casanova, E., Knowles, T. D. J., Bayliss, A., Dunne, J., Barański, M. Z., Denaire, A., Lefranc, P., di Lernia, S., Roffet-Salque, M., Smyth, J., Barclay, A. J., Gillard, T., Claßen, E., Coles, B. J., Illet, M., Jeunesse, C., Krueger, M., Marciniak, A., Minnitt, S., Rotunno, R., van de Velde, P., van Wijk, I., Cotton, J., Daykin, A. and Evershed R. P.. In press. Accurate compound-specific ^{14}C dating of archaeological pottery vessels. *Nature.*

Copley, M. S., Berstan, R., Dudd, S. N., Docherty, G., Mukherjee, A. J., Straker, V., Payne, S. and Evershed, R. P. 2003. Direct chemical evidence for widespread dairying in prehistoric Britain. *Proceedings of the National Academy of Sciences* 100 (4): 1524-1529

Correa-Ascencio, M. and Evershed, R. P. 2014. High throughput screening of organic residues in archaeological potsherds using direct acidified methanol extraction. *Analytical Methods* 6 (5): 1330-1340

Cramp, L. J. E. and Evershed, R. P. 2014. Reconstructing aquatic resource exploitation in human prehistory using lipid biomarkers and stable isotope. In *Treatise on Geochemistry: Archaeology and Anthropology Amsterdam*: Elsevier Oxford 12: 319-339

Evershed, R. P., Heron, C. and Goad, L. J. 1990. Analysis of organic residues of archaeological origin by high-temperature gas chromatography and gas chromatography-mass spectrometry. *Analyst* 115 (10): 1339-1342

Reimer, P. J., McCormac, F. G., Moore, J., McCormick, F. and Murray, E. V. 2002. Marine radiocarbon reservoir corrections for the mid to late Holocene in the eastern subpolar North Atlantic. *The Holocene* 12 (2): 129-135

Russell, N., Cook, G. T., Ascough, P. L. and Dugmore, A. J. 2010. Spatial variation in the marine radiocarbon reservoir effect throughout the Scottish post-Roman to late Medieval period: North Sea values (500-1350 BP). *Radiocarbon* 52 (3): 1166-1181

Russell, N., Cook, G. T., Ascough, P. L. and Scott, E. M. 2015. A period of calm in Scottish seas: A comprehensive study of ΔR values for the northern British Isles coast and the consequent implications for archaeology and oceanography. *Quaternary Geochronology* 30: 34-41

Sharples, N., Ingrem, C., Marshall, P., Mulville, J., Powell, A. and Reed, K. 2016. "The Viking occupation of the Herbides: evidence from the excavations at Bornais, South Uist". In *Maritime societies of the Viking and medieval world* (James Barrett and Sara-Jane Gibbon) Chapter 17, pp. 247-268, Monograph 37, Maney, Leeds.