Is there an “Aquatic” Neolithic? New insights from organic residue analysis of early Holocene pottery from European Russia and Siberia

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« Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that way we may fear less »

Marie Sklodowska Curie

Abstract

English abstract

This thesis investigates the function of early Holocene hunter-gatherer ceramic vessels in northern Eurasia. It presents the first systematic application of organic residue analysis (ORA) to Early Neolithic pottery from European Russia and Siberia. During the early Holocene (ca. 9,700 to 5,000 cal BC) pottery was widely produced by hunter-gatherers across Eurasia. One existing theory suggests that the advent of pottery was linked to an intensification of aquatic resource exploitation; the so-called “Aquatic” Neolithic (Gibbs et al. 2017). This theory is supported by recent ORA of early pottery from eastern Asia and northern Europe, where lipid markers derived from aquatic resources were frequently encountered, absorbed in the pots themselves. One area neglected by ORA is the vast territory of what is now Russia where the arrival of pottery marks the start of the Neolithic period, predating agriculture by several thousand years. Despite its importance in defining the Neolithic in this region, little is known about how early pottery was used and what drove its adoption during the early Holocene. Here, ORA was applied to 417 samples, representing 314 ceramic vessels, recovered from three important early Neolithic sites: the East Siberian site of Gorelyi Les, and Rakushechny Yar and Zamostje 2 in the southern and northern part of European Russia respectively. Overall, the results generated by this thesis indicate much greater diversity in the use of early pottery than predicted from the “Aquatic” Neolithic theory. While aquatic products were indeed prevalent at many sites, lipids derived from terrestrial plants and animals were also common and, overall, the initial use of pottery seems to have varied according to the regional context. These results challenge the idea that the widespread adoption of pottery by Holocene Eurasian foragers was driven primarily by the need to process aquatic resources.

Samenvatting in het Nederlands

Dit proefschrift onderzoekt de functie van jager-verzamelaars aardewerk in Noord-Eurazië gedurende het vroeg Holoceen. Het omvat de eerste systematische toepassing van organische residu-analyse (ORA) op vroeg-Neolithisch aardewerk uit Europees Rusland en Siberië. Tijdens het vroeg Holoceen (ca. 9.700 tot 5.000 cal v. Chr.) werd aardewerk geproduceerd door jager-verzamelaars in heel Eurazië. Een bestaande theorie suggereert dat de eerste opkomst van aardewerk verband hield met een intensivering van de exploitatie van aquatische soorten: het zogenaamde "Aquatic Neolithic". Deze theorie wordt ondersteund door recente ORA van vroeg aardewerk uit Oost-Azië en Noord-Europa, waar zogeheten "biomarkers", afkomstig van aquatische bronnen, vaak werden aangetroffen, geabsorbeerd in het aardewerk zelf. Een gebied waar ORA nog niet eerder is toegepast is het uitgestrekte grondgebied van wat nu Rusland is. Hier markeert de komst van aardewerk het begin van het Neolithicum, dat hier duizenden jaren ouder is dan de landbouw. Ondanks het belang van aardewerk bij het definiëren van het Neolithicum in deze regio, is er weinig bekend over de functie, en waarom het in gebruik genomen werd tijdens het vroeg Holoceen. In dit onderzoek werd ORA toegepast op 417 monsters, die 300 aardewerken potten vertegenwoordigen, afkomstig van drie belangrijke vroeg Neolithische vindplaatsen: de Oost-Siberische vindplaats Gorelyi Les, en Rakushechny Yar en Zamostje 2 in respectievelijk het zuidelijke en noordelijke deel van Europees Rusland. Al met al duiden de resultaten van dit proefschrift op een veel grotere diversiteit in het gebruik van vroeg aardewerk dan voorspeld op basis van de "Aquatic Neolithic" theorie. Hoewel aquatische producten inderdaad op veel vindplaatsen prominent aanwezig waren, kwamen lipiden afkomstig van planten en landdieren ook veel voor in het aardewerk. Over het algemeen lijkt het aanvankelijke gebruik van aardewerk te variëren afhankelijk van de regionale context. Deze resultaten betwisten het idee dat de wijdverbreide adoptie van aardewerk door Holocene Euraziatische jager-verzamelaars voornamelijk werd gedreven door de noodzaak om aquatische soorten te verwerken.

Table des matières

ABSTRACT ..... **III**

ENGLISH ABSTRACT III

SAMENVATTING IN HET NEDERLANDS IV

TABLE OF FIGURES ..... **XIII**

TABLE OF TABLES ..... **XIX**

ACKNOWLEDGMENTS ..... **XXI**

AUTHOR'S DECLARATION ..... **XXV**

ABBREVIATIONS ..... **XXVII**

CHAPTER 1 INTRODUCTION **29**

1. RESEARCH CONTEXT: EARLY HUNTER-GATHERER POTTERY 29

2. MAIN RESEARCH QUESTION: DID EXPLOITATION OF AQUATIC RESOURCES DRIVE WIDER ADOPTION OF POTTERY? 31

3. AIMS AND OBJECTIVES 37

4. RESEARCH QUESTIONS AND THESIS ORGANISATION 38

REFERENCES 42

CHAPTER 2 ORGANIC RESIDUE ANALYSIS AND EARLY CERAMIC VESSELS **49**

1. WHAT ARE ORGANIC RESIDUES? 49

2. LIPIDS 51

2.1. Fatty acids 51

2.2. Triacylglycerols (TAGs) 52

2.3. Wax ester 53

2.4. Sterols 53

2.5. The n-alkanes and n-alkanols 54

2.6. Terpenes 55

3. MOLECULAR ANALYSIS 56

3.1. The Biomarker concept 56

3.1.1. Natural degradation markers 56

3.1.2. Anthropogenic transformation markers 56

3.1.3. Contamination markers 57

3.2. Main natural products identified in early Eurasian ceramic vessels 58

3.2.1. Aquatic products 58

3.2.1.1. Biomarkers 58

3.2.1.2. Degradation markers 60

3.2.2. Terrestrial animals fats 63

3.2.2.1. Biomarkers 63

3.2.2.2. Degradation markers 66

3.2.3. Dairy products 68

3.2.3.1. Biomarkers 68

3.2.3.2. Degradation markers 69

3.2.4. Beehive products 70

3.2.4.1. Biomarkers 70

3.2.4.2. Degradation markers 70

3.2.5. Plant products 72

3.2.5.1. Plant oils, plant waxes and cereal 72

3.2.5.2. Resins, wood tars and pitches 78

3.2.7. Bitumen 80

4. ISOTOPIC ANALYSIS 81

4.1. Stable isotopes definition 81

4.2. Isotopic fractionation and signatures ... 82

4.3. Compound-specific stable isotope analysis ... 85

References ... 92

CHAPTER 3 RESOURCE-PROCESSING, EARLY POTTERY AND THE EMERGENCE OF KITOI CULTURE IN CIS BAIKAL: INSIGHTS FROM LIPID RESIDUE ANALYSIS OF AN EARLY NEOLITHIC CERAMIC ASSEMBLAGE FROM THE GORELYI LES HABITATION SITE, EASTERN SIBERIA.....111

Abstract: ... 111

1. Introduction: hunters in transition ... 112

2. "Becoming Neolithic": Kitoi motivations for adoption of pottery ... 114

3. Case-study: Early Neolithic pottery at Gorelyi Les ... 116

3.1. The Early Pottery Layer (VI) ... 117

3.2. The Early Neolithic Pottery Assemblage ... 118

3.3. Subsistence and Site Function ... 119

4. Materials: Sampling Strategy ... 122

5. Methods: Lipid Residue Analysis ... 122

6. Results ... 123

6.1. Survival of Absorbed Lipids and Contamination ... 123

6.2. Molecular Characterization ... 124

6.3. Stable Isotope Analysis ... 127

6.4. Summary of Results ... 130

7. Discussion: early pottery and the émergence of Kitoi culture ... 130

Conclusion and outlook ... 131

References ... 133

CHAPTER 4 FRUITS, FISH AND THE INTRODUCTION OF POTTERY IN THE EASTERN EUROPEAN PLAIN: LIPID RESIDUE ANALYSIS OF CERAMIC VESSELS FROM ZAMOSTJE 2 ...143

ABSTRACT: 143
1. INTRODUCTION: HUNTER-GATHERERS POTTERY AND NEOLITHIZATION OF NORTHERN EURASIA 144
2. THE MULTI-LAYER WATERLOGGED SITE OF ZAMOSTJE 2, CENTRAL RUSSIA (UPPER VOLGA REGION) 146
3. MATERIAL AND METHODS 151
3.1. Sampling strategy 151
3.2. Lipid residue extraction 151
4. ORGANIC RESIDUE ANALYSIS OF EARLY AND MIDDLE NEOLITHIC POTSHERDS 151
4.1. Lipid quantification and characterisation 151
4.2. Stable carbon isotope analysis of individual fatty acid 156
4.3. Bulk isotope analysis of charred surface deposit 157
5. DISCUSSION 159
6. CONCLUSION 161
REFERENCES 162
CHAPTER 5 ON THE BOUNDARY OF THE "HUNTER-GATHERER" AND "AGRICULTURAL" NEOLITHIC: SUBSISTENCE AND CULINARY PRACTICES AT THE SITE OF RAKUSHECHNY YAR IN THE LOWER DON 173
1. INTRODUCTION 174
2. RAKUSHECHNY YAR: SITE AND CONTEXT 176
3. MATERIALS AND METHODS 179
3.1. Lipid residue analysis and bulk stable isotope analysis of pottery 179
3.2. Digital Microscopy and Scanning Electron Microscopy (SEM) 180
3.3. Bulk analysis of bone collagen 181
3.4. ZooMS (Zooarchaeology by Mass Spectrometry) 181
3.5. AMS ^{14}C dating 182
4. RESULTS AND DISCUSSION 182

4.1. *Preservation of animal fats in RY pottery* 182

4.2. *Molecular and isotopic evidence for aquatic resources in pottery* 183

4.3. *Digital Microscopy and Scanning Electron Microscopy* 190

4.4. *Domesticated animals at Rakucheshny Yar?* 191

4.5. *A clear boundary between the aquatic and agricultural Neolithic?* 192

REFERENCES 194

CHAPTER 6 INVESTIGATING THE FORMATION AND DIAGNOSTIC VALUE OF Ω-(O-ALKYLPHENYL)ALKANOIC ACIDS IN ANCIENT POTTERY 205

ABSTRACT: 205

1. INTRODUCTION 205

2. MATERIAL AND METHOD 208

2.1. *Cooking experiments* *208*

2.2. *Lipid analysis* *209*

3. RESULTS AND DISCUSSION 210

3.1. *Under what conditions do APAAs form in archaeological ceramics?* 210

3.1.1. Time and temperature 210

3.1.2. Do APAAs form in absence of ceramic? 211

3.1.3. Evacuated vs aerobic conditions 212

3.2. *What degree of resolution can APAAs offer for product identification?* 213

3.2.1. Distinguish different foodstuffs based on APAA-C_{18} distribution 213

3.2.2. Distinguishing aquatic from terrestrial resources (APAA-C_{20} vs. APAA-C_{18}) 215

4. CONCLUSION 217

REFERENCES 218

CHAPTER 7 IS THERE AN "AQUATIC" NEOLITHIC? CONCLUDING COMMENTS AND FUTURE HORIZONS..... 223

1. DISCUSSION 223
2. DIRECTIONS FOR FUTURE RESEARCH 233
2.1. Sites, contexts and dates 233
2.2. Methodology improvement for lipid analysis 234
2.2.1. Issue of plants detection in ancient pottery 234
2.2.2. Identification of triacylglycerols (TAGs) 235
2.3. Integration of other methods and approaches 236
2.3.1. Microscopic analysis of charred residues associated with pottery 236
2.3.2. Proteomics 237
2.3.3. Experimental archaeology 237
3. FINAL CONCLUSION 238
REFERENCES 239
APPENDICES 247
APPENDIX 1: METHOD AND MATERIALS 247
1. LIPID EXTRACTION 247
1.1. Direct methanolic acid extraction 247
1.2. Solvent extraction and trimethylsilyl (TMS) derivatization 247
2. COLLAGEN EXTRACTION FROM ARCHAEOLOGICAL BONES FOR ISOTOPIC ANALYSIS 247
3. COLLAGEN EXTRACTION AND ANALYSIS FROM ARCHAEOLOGICAL BONES FOR ZOOMS 248
4. INSTRUMENTATION SETTINGS 248
4.1. Gas Chromatography-Mass Spectrometry (GC-MS) 248
4.2. Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) 249
4.3. Bulk isotope analysis - Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS) 250
5. RADIOCARBON DATING FOR RAKUSHECHNY YAR SITE 251

Appendix 2: Stable carbon isotopic of *n*-hexadecanoic ($C_{16:0}$) and *n*-octadecanoic ($C_{18:0}$) acid found in the literature of reference fats from modern products and used to make the figure 2.22 255

Appendix 3: Radiocarbon dates for Gorelyi Les layers (Weber, 1995) calibrated with CALIB Rev 7.0.4 (Reimer et al., 2013). 264

Appendix 4: List of samples from Gorelyi Les selected for lipid analysis (GCMS, GC-C-IRMS) and bulk isotope characteristics of charred deposits (EA-IRMS). 265

Appendix 5: (a) Gorelyi Les site overview from the Belaia River (view from the Southwest) and (b) Excavation campaign season 1994, led by N.A. Savel'ev and A.W. Weber. Photo from A.W. Weber (1997). 271

Appendix 6: Bulk isotope measurement of modern and archaeological collagen bones from Angara region. 272

Appendix 7: Mixing model 276

Appendix 8: Photos of Zamostje 2 site and the surrounding landscapes. Photo from O. Lozovskaya 277

Appendix 9: List of samples from Zamostje 2 selected for lipid analysis (GCMS, GC-c-IRMS) and bulk isotope characteristics of charred deposits and bone collagen (EA-IRMS). 278

Appendix 10: List of samples from Rakushechny Yar selected for lipid analysis (GCMS, GC-c-IRMS) and bulk isotope characteristics of charred deposits (EA-IRMS). 304

Appendix 11: Stable carbon isotopic of *n*-hexadecanoic ($C_{16:0}$) and *n*-octadecanoic ($C_{18:0}$) acid of reference fats from modern animal products. Data are from different studies, with additional new freshwater fish and shellfish, ruminants and terrestrial plants from Rakushechny Yar region or Western Russia. 324

Appendix 12: Bulk isotope measurement of archaeological collagen bones from Rakushechny Yar site 330

Appendix 13: List of samples selected for ZooMS analysis and the results. 331

Appendix 14: scheme showing the different forms and volumes of cooking pottery found at Rakushechny Yar. 332

Appendix 15: photo of Rakushechny Yar site showing the two excavated areas where the sherds analysed were recovered. 332

Appendix 16: Elongated ceramic found at Rakushechny Yar. 333

Appendix 17: Table summarizing the results of the thermal degradation of rapeseed oil and mono- and unsaturated fatty acids C_{18} (A) and various foodstuffs (B) carried out in laboratory and the experimental parameters. 334

Appendix 18: Table summarizing the results of the simulated cooking in replicate pots of various foodstuffs on an open fire and the field experimental parameters. The layer of fats formed from salmon and red deer during the cooking was skimmed and gathered in another pot to then be heated on the open fire. These samples are noted with *... 337

Appendix 19: photos showing (a to d) the field cooking experiments and (e) the burying half of each pottery used in the experiments for 6 months. These experiments were performed at the YEAR Center (University of York). 340

Appendix 20: APAAs-C_{18} A to I isomeric distribution (from A to I) of rapeseed oil subjected to different heating conditions (time, temperature) under either evacuated (line patterns) or air (diamond patterns). 341

Appendix 21: Partial SIM chromatogram of rapeseed oil cooked under open air showing ω-(o-alkylphenyl)alkanoic acids C_{18} isomers (m/z 290 ion) with or without ceramic powder. 342

Appendix 22: APAAs-C_{18} A to I isomeric distribution of pure unsaturated fatty acid (UFA) heated in open glass tube at 270°C during 5 hours with ceramic powder. For each UFA the experiments were duplicated and the APAAs-C_{18} isomeric distribution given here correspond to the average of these two analyses along with the error bars. 343

References 344

Table of figures

Figure 1.1 (a) Map modelling the spread of pottery technology from the two main innovation centres i.e. East Asia and North Africa (Jordan et al., 2016). (b) Graph of the S Curve model showing the early pottery emergence in East Asia among hunter-gatherer communities during the late Pleistocene and the later pottery development and its widespread dispersal across Eurasia during the Holocene (Gibbs and Jordan, 2013). 31

Figure 1.2 Map showing the location of the three sites selected for this PhD project and the areas where organic residue analyses have already been conducted to explore the function of early Holocene pottery (Baltic, Korea and Sakhalin Island) (Gibbs et al., 2017; Oras et al., 2017; Shoda et al., 2017). The pie charts indicate the proportion of ceramic vessels displaying aquatic signals in these previous studies. 33

Figure 1.3 Reconstruction of the temperatures from the Late Pleistocene epoch based on Oxygen isotope level records from the Greenland Ice core (Cummings, 2014). 35

Figure 2.1 Amorphous organic remains which could be preserved and found in archaeological context (Adapted from Regert, 2017). 49

Figure 2.2 Examples of the most abundant fatty acid in nature: Two saturated fatty acids, a) palmitic acid ($C_{16:0}$) and b) stearic acid ($C_{18:0}$) and monounsaturated fatty acid, c) oleic acid ($C_{18:1}$ [n-9]). 52

Figure 2.3 Example of a typical of triacylglycerol, the tripalmitin formed of a glycerol core and three palmitic acids ($C_{16:0}$). 53

Figure 2.4 Example of a wax ester, the triacontanyl palmitate derived from palmitic acid ($C_{16:0}$) and triacontanyl alcohol (*n*-alkanol with 30 carbon atoms). 53

Figure 2.5 Structures of sterols skeleton and its main derivatives found in plant and animal tissues. 54

Figure 2.6 Examples of a) diterpene and b) triterpene structure. 55

Figure 2.7 Diagram summarizing information obtained from biomarkers (Regert, 2017). 57

Figure 2.8 Scheme showing the formation of the isoprenoid compound present in aquatic organisms (after Ackman and Hooper, 1968). The two precursors Zamene and Phytadiene being only present in appreciable amounts in zooplankton, fish and aquatic mammals (Blumer and Thomas, 1965; Ackman and Hooper, 1968). 59

Figure 2.9 Example of dihydroxy fatty acid (DHYAs) formation by oxidation of its analogue monounsaturated fatty acid (modified from Cramp and Evershed, 2014). 61

Figure 2.10 Reaction pathway for the formation of ω-(o-alkylphenyl)alkanoic acids (APAAs) from cis, cis, cis -9, 12, 15-octadecatrienoic acid subjected to prolonged heating (after Hansel et al., 2004). .. 62

Figure 2.11 Carbon number distribution of TAGs of ruminant and non-ruminant adipose fats. The values used to make these charts were found in (Evershed et al., 1997b; Dudd and Evershed, 1998; Dudd, 1999; Drieu, 2017). 64

Figure 2.12 The formation process of mid-chain alkanones and secondary products induced by fatty acid pyrolysis (Raven et al., 1997). 67

Figure 2.13 TAGs distribution profile of fresh milk, degraded milk absorbed in pottery after 90 days under oxic conditions and fresh ruminant adipose fat (after Dudd and Evershed, 1998; Dudd et al., 1998)... 68

Figure 2.14 Diagram showing the different degradation mechanisms of beeswax (from Regert et al., 2001)... 71

Figure 2.15 Miliacin molecule structure. 74

Figure 2.16 The basic structure of alkylresorcinols. 75

Figure 2.17 Plot of $C_{12:0}/C_{14:0}$ fatty acid ratio against $C_{16:0}/C_{18:0}$ ratio for modern food products enabling to separate plant and animal fatty acid origins (from Eerkens, 2005). 76

Figure 2.18 Degradation pathway of abietic acid one of the Pinaceae biomarker (in the green square) leading to the formation of a collection of derivatives arising from natural degradation or anthropogenic activities. Molecules in the red squares are the main tracers used for the identification of pine resins in ancient pots. 80

Figure 2.19 Structure of the main compounds found in bitumen. 81

Figure 2.20 $\delta^{13}C$ values of modern terrestrial C_3 and C_4 plants (Evershed, 2009). 83

Figure 2.21 Overview of carbon and nitrogen isotopic values (bulk) of terrestrial and aquatic food webs (adapted and supplemented from Evershed, 2009; Robson et al., 2016). 85

Figure 2.22 $\delta^{13}C$ values of individual $C_{16:0}$ and $C_{18:0}$ alkanoic acids extracted from authentic reference terrestrial (a) and aquatic (b) fats shown with ellipses. (c) and (d) represent the $\Delta^{13}C$ ($\delta^{13}C_{18:0}$–$\delta^{13}C_{16:0}$) values of the same references, respectively, plotted against their $\delta^{13}C_{16:0}$ values. The terrestrial animals were raised on pure C_3 diets. The isotope values used to make these plots were found in (Dudd, 1999;

Spangenberg and Ogrinc, 2001; Outram et al., 2009; Craig et al., 2011; 2013; Cramp and Evershed, 2014; Horiuchi et al., 2015; Choy et al., 2016; Lucquin et al., 2016a; Pääkkönen et al., 2016). The reference data used to produce this figure are available in appendix 2. 87

Figure 2.23 Diagram showing the routing of dietary fatty acids and carbohydrates in the rumen, adipose tissue and mammary gland of the ruminant animal (Copley et al., 2003). 89

Figure 3.1 Location map of Cis Baikal, Eastern Siberia, showing the core areas of the Early Neolithic Kitoi Culture along the Angara River and in SW Baikal. Habitation sites mentioned in the text are Gorelyi Les located on the Belaia River. Dozens of other Kitoi habitation sites and several small cemeteries are located across the region, predominantly along riverbanks and lake edges (not shown). 113

Figure 3.2 Photo of Gorelyi Les site (view from northwest) along the Belaia River and surrounded by forest and low hills (after Weber, 1997). 117

Figure 3.3 Examples of Early Neolithic pottery types recovered from Layer VI of Gorelyi Les during the 1994-1996 excavations: (a) net-impressed pottery; (b) “Khaita” cord-impressed pottery; (c) sherd of unclassified type. 119

Figure 3.4 A typical total ion current (TIC) chromatogram of lipid residues from the Gorelyi Les pottery (sample: GL 94.00158). This shows the presence of saturated fatty acids (FA), diacids (DC), branched (br), long-chain unsaturated fatty acids, mid- and long-chain alkanes (Alk). Several contaminants are also present (see *), including phthalates. 124

Figure 3.5 Molecular evidence for the processing of aquatic resources of the foodcrust sample GL 94.00557 run on the DB-23 column): (a) a partial summed mass chromatogram (m/z 105) showing the presence of ω-(o-alkylphenyl) alkanoic acids with 16(O), 18(*), 20(#) or 22(+) carbon atoms; (b) chemical structure of APAAs (from Hansel et al., 2004); (c) a partial summed mass chromatogram (m/z 101) revealing the diastereomers of phytanic acid (SRR and RRR). 125

Figure 3.6 Lipid stable isotope characteristics from the all Gorelyi Les samples compared with theoretical mixes of animal fats, plant oils (C_3 types) and fish oils. (a) Scatter plot of $\Delta^{13}C$ ($C_{18:0}$-$C_{16:0}$) against $\delta^{13}C_{16:0}$ of Gorelyi Les samples with the foodcrusts represented by a star. Samples containing aquatic biomarkers are shown by filled markers. The data are compared with the median and ranges (1σ) of bone collagen of archaeological ruminant (R), modern fish (F) and non-ruminant animals (NR) from the Baikal region, after being corrected for the collagen to tissue offset (Fernandes et al. 2015), plotted on the x-axis only (Weber et al., 2002; 2011; Katzenberg et al., 2012; Appendix 6). Density distributions of $\Delta^{13}C$ values obtained by theoretical mixing (Appendix 7) of authentic reference lipids from modern tissues of fish with (b) ruminant, (c) non-ruminant adipose fats and (d) plant were

obtained by using published (Dudd, 1999; Spangenberg et al., 2010; Craig et al., 2012; Choy et al., 2016) and unpublished data and using fatty acid concentration values obtained from the USDA database (https://fdc.nal.usda.gov/). 129

Figure 4.1 Location of Zamostje 2 along the Dubna river. 146

Figure 4.2 Pottery from Zamostje 2: EN sherds with (a, b) long-comb decorations (late stage), (c) covered by incised lines (early stage); (d) Ceramic from EN layer (early stage) with remains of Viburnum (*Viburnum opulus L.*) berries in the crust, (e) MN Pottery with pit ornamentation. 148

Figure 4.3 Plant and faunal remains and artefacts from Zamostje 2: (a) bone hooks from the EN, Final Mesolithic and mixed layers (from left to right), (b) bone net needle from the Upper Mesolithic, (c) floats from the Lower and Upper Mesolithic layer (from top to bottom), (d) tool made from beaver mandible from the Lower Mesolithic layer, (e) elk head figures made from elk antler from the Lower Mesolithic layer, (f) and (g) pine cone and nut remains from the Lower Mesolithic and mixed layer respectively, (h) barbed point from the EN.. 149

Figure 4.4 Summary of archaeological evidence changes in Zamostje 2: dates, pottery cultures, subsistence strategies and environmental conditions. Based on the following references: Lozovski, 1996; Clemente et al., 2002; Ershova, 2013; Gyria et al., 2013; Lozovskaya and Lozovski, 2013, 2016; Lozovski et al., 2013a, 2013b; 2014a; 2014b; Mannermaa, 2013; Radu and Desse-Berset, 2013; Berihuete-Azorin and Lozovskaya, 2014; Leduc and Chaix, 2014, 2018; Mannermaa and Treuillot, 2014; Meadows et al., 2015; Berihuete, 2018; Ershova and Lozovskaya, 2018. 150

Figure 4.5 Total ion current of an acid/methanol extract of the foodcrusts sample from pot LN10642, Zamostje 2. Partial gas chromatogram of lipid showing saturated fatty acids (FA), diacids (DC), branched chain fatty acids (br), long-chain unsaturated fatty acids, sterols and triterpenes whose amyrin derivatives are indicated. 152

Figure 4.6 SIM chromatogram indicating the aquatic biomarkers from sample LN10642 analysed on the DB-23 column. The ω-(o-alkylphenyl) alkanoic acids were identified with ions m/z 105, 262, 290, 318, with the last three ions corresponding to the carbon length C_{16}, C_{18}, and C_{20} respectively. 4,8,12-trimethyltridecanoic acid was monitered with ions m/z 87, 270 and phytanic acid with ions m/z 101, 171, 326. The m/z 101 ion chromatogram shows the diastereomers of phytanic acid (SRR and RRR), which allowed.. 154

Figure 4.7 $\Delta^{13}C$ ($\delta^{13}C_{18:0}$–$\delta^{13}C_{16:0}$) values against $\delta^{13}C_{16:0}$ values obtained from foodcrusts and sherds from (A) EN (n = 100) and (B) MN (n = 70) samples. Crosses indicate modern elk from the Zamostje 2 region. Samples with the full and partial set of aquatic biomarkers are shown by filled circles. 157

Figure 4.8 Plot of $\delta^{15}N$ bulk isotope values against C:N ratio obtained from foodcrusts samples from Early (n = 56) in orange and MN (n = 52) in green showing (A) samples in which amyrin derivatives were detected by filled diamonds, (B) samples with the full set of aquatic biomarkers by filled circles. ... 158

Figure 5.1 Map a) plotting early pottery sites and their associated subsistence economy as well as Rakushechny Yar site and (b) showing the location of Rakushechny Yar on the Porechny Island, in the lower Don River. Note: the data in Fig 5.1a are taken directly from the entire data set of dates associated with the earliest pottery as reported by (Jordan et al. 2016). 177

Figure 5.2 Archaeozoological assemblage distribution of fish and terrestrial animal from Early Neolithic phase of Rakushechny Yar (Sablin 2018).. 179

Figure 5.3 Plot of $\Delta^{13}C$ values against $\delta^{13}C_{16:0}$ values of (a) Rakushechny Yar samples (including Early Neolithic, Late Neolithic and Eneolithic) compared with pottery from (b) Zamostje 2 site and early agricultural sites in (c) Syria and (d) Anatolia. For (a) and (b) plots, the filled circles indicate samples with aquatic signal. For (c) and (d) aquatic derived lipids are not reported but presumed to be absent (Evershed et al. 2008; Nieuwenhuyse et al. 2015; Debono Spiteri et al. 2016). The data generated here are compared with the mean and ranges (2σ) of bone collagen of archaeological non-ruminant (including pig and beaver) and ruminant (red deer) recovered at Rakushechny Yar, plotted on the x-axis only. The collagen $\delta^{13}C$ values were adjusted by -8‰ to correct for the collagen to tissue offset in order to make these values comparable with $\delta^{13}C_{16:0}$ of lipids extracted from pottery (Fernandes et al. 2015).. 183

Figure 5.4 Plot of the $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ *n*-alkanoic acids extracted from (a and b) Rakushechny Yar pottery from Early Neolithic layers and Late and Eneolithic layers and (c) Iron Gates region ceramic vessels (Cramp et al. 2019). Samples with aquatic biomarkers are shown by filled circles. The data are compared with reference ranges for authentic reference lipids from modern tissues from published studies (Dudd 1999; Spangenberg et al. 2006; Outram et al. 2009; Craig et al. 2011; Craig et al. 2012; Craig et al. 2013; Choy et al. 2016; Lucquin et al. 2016; Pääkkönen et al. 2016) and additional new Unio and Viviparus shellfish data from the Low Don River and freshwater fish and ruminants from Russia (95% confidence; Appendix 11). The $\delta^{13}C$ values of the modern references were adjusted for the addition of the effects of post-industrial carbon in order to facilitate the comparison with the archaeological samples (Schmitt et al. 2012; Hellevang and Aagaard 2015; Lucquin, Gibbs, et al. 2016). SEM micrographs showing fragments of sturgeon bony components (d) in foodcrust sample from Rakushechny Yar (Raku-929) and (e) of archaeological sturgeon reference materials. 187

Figure 5.5 (a) $\delta^{15}N$ against C:N ratio and (b) weighted fatty acid $\delta^{13}C$ against C:N ratio obtained from Rakushechny Yar foodcrusts samples of which fatty acids were available. Filled circles indicate samples

with aquatic biomarkers, * represents samples where sturgeon osseous structures were detected by SEM and # samples were cyprinid and sturgeon osseous structures were observed. 189

Figure 6.1 Scheme of the reaction pathway for the formation of ω-(o-alkylphenyl)octadecanoic acid (APAA) through heating of cis, cis, cis-9, 12, 15-octadecatrienoic acid (after Hansel et al. 2004). 208

Figure 6.2 Partial SIM chromatogram (*m/z* 105 ion) of the cooked Viviparus shellfish showing the distribution of the ω-(o-alkylphenyl)alkanoic acids with 18 (letters from A to I corresponding to the isomers) and 20 (*) carbon atoms.. 213

Figure 6.3 Principal component analysis (PCA) scatter plot of the first two principal components (PCs) based on the APAA-C_{18} isomeric distribution derived from different foodstuffs subjected to heating at 270°C for 5 hours.. 214

Figure 6.4 Boxplots of the APAA-C_{18} isomers E+F contribution (%). The E+F isomers contribution was computed over the contribution of APAA-C_{18} isomers C to I. Plots represent median, ranges and quartiles.. 215

Figure 6.5 Boxplots of APAA C_{20}/C_{18} ratio of modern references, heated either in the laboratory or during field experiments after 6 months burial (*), and archaeological samples............................ 217

Figure 7.1 Map showing the locations of the three sites that were selected for research in this PhD and the proportion of pottery displaying aquatic signal obtained from previous research studying the function of early pottery made during the early Holocene from Baltic, Korea and Sakhalin Island (Gibbs et al., 2017; Shoda et al., 2017; Oras et al., 2017) compared with the new data generated during this PhD.. 224

Figure 7.2 The average lipid concentration of the samples analysed in this project. These results are compared with those obtained from pottery found in other regions such as the Mediterranean Basin, Korea, the Baltic region and Sakhalin Island (Debono Spiteri, 2012; Nieuwenhuyse et al., 2015; Gibbs et al., 2017; Oras et al., 2017b; Shoda et al., 2017; Whelton et al., 2018). (n = x) indicate the number of samples analysed for each of this study. 227

Figure 7.3 Boxplots of the C_{20}/C_{18} APAA obtained from the pottery samples analysed for the three case studies of this research. Plots represent median (solid line), mean (dashed line), ranges and quartiles.. 230

Table of tables

Table 1.1 Table summarising the number of vessels, sampled foodcrust and sampled sherds selected from each site for analysis.. 40

Table 3.1 Summary of the artefact and faunal assemblages found at Gorelyi Les site in Layers VII (Late Mesolithic) and VI (Early Neolithic). After: Weber, 1997 (1); Ready, 2008 (2); Kurzybov, 2011 (3); Bazaliiskii, 2003, 2010 (4, 5). 121

Table 4.1 Table summarizing the proportion of plant and aquatic biomarkers detected in the samples according to the period and comparing the proportion of the main plant biomarkers (amyrin and derivatives) and aquatic biomarkers through the different EN stages and MN. 155

Table 4.2 Mann-Whitney U test showing correlation between the bulk $\delta^{15}N$, C:N ratio and molecular characterization. The test revealed a significant difference of $\delta^{15}N$ and C:N ratio between EN and MN samples, samples with or without the full set of aquatic biomarkers and samples with or without Amyrin derivatives. However, there is no correlation between $\delta^{13}C$ values and periods or molecular characterization of samples. 159

Table 6.1 Table summarising the conditions required, and tested here, to form APAAs by heating rapeseed oil. 212

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Author’s declaration

I declare that this thesis is a presentation of original work and I am the sole author. This work has not previously been presented for an award at this, or any other, University. All sources are acknowledged as References. The work carried out as part of this thesis has resulted in the following publications:

Manon Bondetti, Sofia Scott (Chirkova), Alexandre Lucquin, John Meadows, Olga Lozovskaya, Ekaterina Dolbunova, Peter Jordan, Oliver E. Craig (2020). Fruits, fish and the introduction of pottery in the Eastern European plain: Lipid residue analysis of ceramic vessels from Zamostje 2. Quaternary Internonal 541, 104–114*.*

Manon Bondetti, Erin Scott, Blandine Courel, Alexandre Lucquin, Shinya Shoda, Jasmine Lundy, Catalina Labra-Odde, Léa Drieu, Oliver E. Craig. Investigating the formation and diagnostic value of ω-(o-alkylphenyl)alkanoic acids in ancient pottery. *Archaeometry - Submitted*.

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Manon Bondetti

Abbreviations

‰: per mille

%C: % Carbon

%N: % Nitrogen

ACL: average chain length

APAA: ω-(o-alkylphenyl)alkanoic acids

AR: alkylresorcinols

BC: before Christ

BP: before present (by convention, the year 1950 is used as the commencement date)

BSTFA: N,O-Bis(trimethylsilyl)trifluoroacetamide

Cx:y: fatty acid with *x* carbon atoms and *y* unsaturation

Cx: linear alkane with *x* carbon atoms

Ca.: circa

Cal.: calibrated ^{14}C dates on the calendar years

C:N: carbon-nitrogen ratio

CPI: carbon preference index

DAG: diacylglycerol

DHA: dehydroxyabietic acid

DHYAs: dihydroxy fatty acids

DMDS: dimethyl disulfide

EA-IRMS: elemental analyser-isotope ratio mass spectrometry

EN: Early Neolithic

ESI: electrospray ionization

GC-MS: gas chromatography-mass spectrometry

GC-C-IMRS: gas chromatography-combustion-isotopic ratio mass spectrometry

GC-Q-ToF-MS: gas chromatography-quadrupole-time-of-flight mass spectrometry

HCL: hydrochloric acid

HPLC: high performance liquid chromatography

IFAs: isoprenoid fatty acids

Kx: linear alkanone with *x* carbon atoms

L: litre

m/z: mass to charge ratio

MAG: diacylglycerol

MALDI: matrix assisted laser desorption ionisation

MN: Middle Neolithic

µg: microgram

mg: milligram

MS: mass spectrometry

PCA: principal composant analysis

pH: a logarithmic scale for expressing the acidity or alkalinity of solution

PUFAs: polyunsaturated fatty acids

P/S ratio: palmitic/stearic ratio

PTME: pentacyclic triterpene methyl ether

SEM: scanning electron microscopy

SRR: 3S,7R,11R,15-phytanic

RRR: 3S,7R,11R,15-phytanic

RY: Rakushechny Yar

Tx: triacylglycerol with *x* carbon atoms

TAG: Triacylglycerol

TFA: trifluoroacetic acid

TMTD: 4,8,12-trimethyltridecanoic acid

ToF: time of flight

UFA: unsaturated fatty acid

UPLC-HRMS: high-performance liquid chromatography–atmospheric pressure chemical ionization-mass spectrometry

v/v: volume per volume

Wx: wax ester with x carbon atoms

Chapter 1

Introduction

1. Research context: early hunter-gatherer pottery

Pottery is one of the most important technological inventions in human history. Indeed, from its prehistoric origins to its broad spread across the world, it became an essential everyday technology for preparing, serving and storing food in almost every society for several thousands of years. The term "pottery" refers to "portable ceramic vessels" made of clay and intentionally fired to generate a "**durable product**" (Lepère, 2009; Hommel, 2014). Clay displays plastic properties when wet. This characteristic allows the modelling in almost any shape offering a wide range of possibilities to produce different types of containers. Whilst ceramic material can prove, in some way, to be fragile, easily breakable during its use, it also presents a very high resistance to biological, chemical and physical degradation (Pollard and Heron, 2008; Schneider, 2016). These properties have made pottery one of the most common artefacts found in archaeological context. As a prevalent element of the material culture of prehistoric human societies, pottery plays an important role in archaeological research to piece together the human past.

In north-western European and South-western Asia this new technology appears in association with early farming communities who are increasingly sedentary. In fact, the combination of farming, pottery and village has been used to define the Neolithic (Gibbs and Jordan, 2016). However, in other parts of northern Eurasia, including European Russia, Siberia and Northeast Asia it is **the emergence of pottery production within hunter-gatherer societies** that defines **the onset of the Neolithic**. The argument here is that pottery marks a new epoch, and forms part of a wider set of changes, including increasing sedentism and economic intensification (Blockley and Gamble, 2012; Cummings, 2014; Hayden, 2014; Tallavaara et al., 2015; Volokitin and Gribchenko, 2017). The latter is not associated with a transition to farming, but to increasing use of aquatic resources (Gibbs and Jordan, 2016; Gibbs et al., 2017).

The trajectory of the Northern Eurasia Neolithic has slowly spread across the "Old Word" (Gibbs et al., 2017). It first emerged **towards the end of the last Ice Age between 16,000 and 13,000 years cal BC in East Asia**. To date, the oldest pottery found was recovered in **South China**, **Japan** and the **Amur River basin in the Russian Far East** (Habu, 2004; Kudo, 2004; Kuzmin, 2006; 2017; Keally et al., 2007;

Boaretto et al., 2009; Budja, 2009; Hommel, 2012; Wu et al., 2012). At this early stage of pre-Holocene pottery production, the use of such technology remains relatively limited geographically. K. Gibbs and P. Jordan (2013) have characterized this early stage as "**pottery-making experimentation**" (Fig. 1.1b).

By considering AMS dates for early pottery sites and using spatio-temporal modelling, researchers have attempted to reconstruct the early dispersal of ceramic technology. This reveals that the **major increase in pottery production** only occurred around **the onset of the Holocene** (Fig. 1.1b) (Gibbs and Jordan, 2013; Jordan et al., 2016). During this period, greater use of pottery is observed within East Asia which became more deeply integrated into the social life and subsistence activities. Furthermore, during the Early Holocene pottery started to break-out of the East Asia core and a sudden "horizon" of hunter-gatherer pottery use emerged across northern Eurasia participating in its subsequent gradual widespread distribution all over the continent. During the early Holocene it appears that pottery technology also independently emerged among hunter-gatherers living in **North Africa** (Fig. 1.1a). It is likely that this early pottery-making tradition also has diffused across Eurasia, especially western Europe possibly through the Near East alongside farming culture (Gibbs and Jordan, 2013; Jordan et al., 2016).

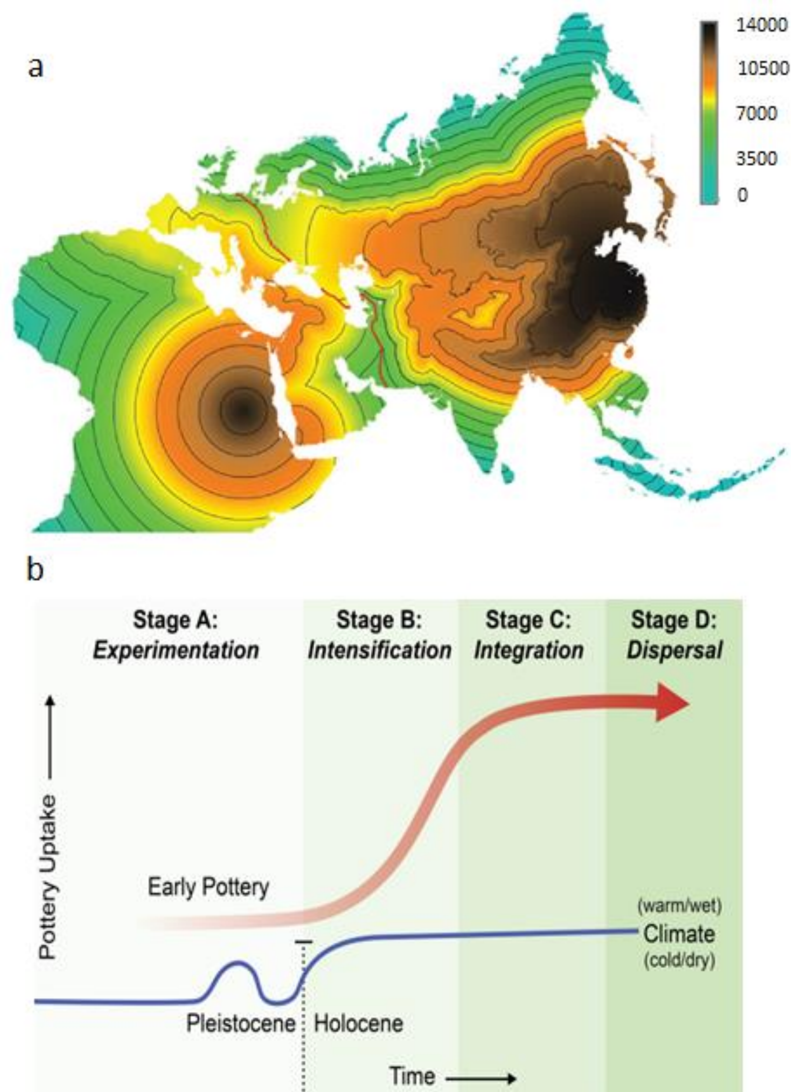

Figure 1.1 (a) Map modelling the spread of pottery technology from the two main innovation centres i.e. East Asia and North Africa (Jordan et al., 2016). (b) Graph of the S Curve model showing the early pottery emergence in East Asia among hunter-gatherer communities during the late Pleistocene and the later pottery development and its widespread dispersal across Eurasia during the Holocene (Gibbs and Jordan, 2013).

2. Main research question: did exploitation of aquatic resources drive wider adoption of pottery?

In the last 5-10 years major effort has been directed at understanding the Late Pleistocene origins of pottery in East Asia by using **chemical** and **isotopic** analysis of **organic residues** preserved on pottery surfaces and within the clay matrix (Craig et al., 2013; Lucquin et al., 2016). This approach enables the determination of pottery contents and provides direct proxies for reconstructing **pottery function**. More recently research has started to analyse the early hunter-gatherer pottery in Korea, Sakhalin island in the Russian Far East and Baltic which seems to first appear during the early Holocene (Fig. 1.2). In all these studies, there appears to be a **close link between early pottery and the processing of**

aquatic resources, despite faunal and botanical evidence for the exploitation of a wide range of foodstuffs (e.g. ruminant and other terrestrial animal, plants) (Lucquin et al., 2016; 2018; Gibbs et al., 2017; Oras et al., 2017; Shoda et al., 2017; Jordan and Gibbs, 2018).

Figure 1.2 Map showing the location of the three sites selected for this PhD project and the areas where organic residue analyses have already been conducted to explore the function of early Holocene pottery (Baltic, Korea and Sakhalin Island) (Gibbs et al., 2017; Oras et al., 2017; Shoda et al., 2017). The pie charts indicate the proportion of ceramic vessels displaying aquatic signals in these previous studies.

Based on these emerging insights, archaeologists have suggested that the relationship between pottery and the processing of aquatic resources may actually be the defining feature of the (eastern) Neolithic. Against this background, a new model coined the **“Aquatic” Neolithic** has been proposed (Gibbs et al., 2017; Oras et al., 2017), in contrast to the **“Agricultural” Neolithic** of western Europe (Evershed et al., 2008a; Nieuwenhuyse et al., 2015; Debono Spiteri et al., 2016). However, despite this early insight, the study of early Holocene pottery function is still in its infancy. Actually, there has been no real research focused on testing this model in the intervening spaces of Eurasia and this needs to be properly investigated by more in-depth analysis at specific sites. Notably, **one area neglected by organic residue analysis** is the vast territory of **Russia**, stretching from the pacific through Siberia and into Europe. This region was clearly the scene of a wider spread of pottery among forager societies across the continent after its break-out of the East Asia core, where pottery was first invented. However, very little is known about how this early pottery was used, and what drove this adoption into this region during the early Holocene. This thesis aims to close this gap in knowledge, and to test whether the oldest pottery at a “transect” of early Holocene pottery sites in Siberia, north European Russia and southern Russia was used to process aquatic resources (or not).

What happened to the environment when pottery production dramatically increased? The **Holocene** is characterised by a sustained climatic stability beginning around 9,500 cal. BC and represents the current geological epoch (Alley et al., 1993; Smith et al., 2011; Cummings, 2014). This epoch, also referred to as the post-glacial period, distinguishes itself from the previous Late Pleistocene glacial period, mainly by warmer conditions that contributed to a profound environmental transformation. During the Last Glacial Maximum (ca. 25,000 to 17,000 cal. BC) (Tallavaara et al., 2015) the landscape all around the world was quite different. The ice sheets were particularly thick and reached their maximum coverage spreading out from the Arctic to northern Eurasia and most of northern North America at *ca.* 22,000 to 19,000 cal. BC (Hoffecker and Elias, 2003). At this time, the earth’s temperatures were overall 20°C below the current averages (Smith et al., 2011; Blockley and Gamble, 2012; Roberts, 2013; Cummings, 2014). Towards 18,000 BP climatic fluctuations, alternating between warm and cold periods (e.g. Bølling-Allerød and Younger Dryas, respectively) occurred (Renssen et al., 2001; Blockley and Gamble, 2012; Roberts, 2013; Cummings, 2014; Hayden, 2014; Volokitin and Gribchenko, 2017). These marked the onset of the final phase of the Late Pleistocene, a transitional phase preceding the climatic stabilization and warming of the Holocene (Fig. 1.3).

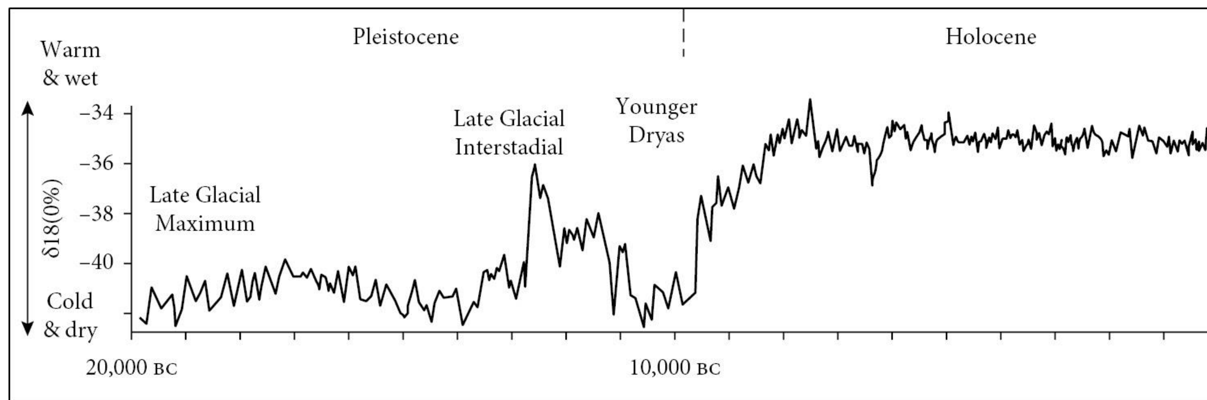

Figure 1.3 Reconstruction of the temperatures from the Late Pleistocene epoch based on Oxygen isotope level records from the Greenland Ice core (Cummings, 2014).

The consequences of global warming were variable according to region, whereas the increase in global sea level, due to the melting of the ice caps, caused the flooding of most coastal areas and the loss of landmass. This greatly affected tropical and subtropical regions with, for instance, the submersion of Sundaland localised in the Malaysian Peninsula. Higher latitudes were also impacted by the flooding, with e.g. the submersion of Doggerland and the Bering Land Bridge (Smith et al., 2011; Roberts, 2013). In contrast, the north, notably northern Eurasia, was marked by extensive deglaciation creating new and huge living areas. Progressively the vegetation in these areas flourished through the development of either tundra, shrub or forests possibly including deciduous woodland (Jochim, 2012; Cummings, 2014). This environmental change had important repercussions for the fauna. Some species went extinct, such as the megafauna (e.g. Woolly Mammoth, Wooly Rhinoceros, Steppe Bison) (MacPhee et al., 2002; Orlova et al., 2004; Blockley and Gamble, 2012; Mann et al., 2013; Roberts, 2013). While on the contrary, the development in vegetation and the opening of new areas, now free of ice, led to the proliferation and penetration into the north of mammals previously absent such as reindeer, deer, wild boar, elk and auroch (Blockley and Gamble, 2012; Jochim, 2012).

In northern Eurasia, these major environmental changes created new opportunities for hunting and gathering for the prehistoric populations. Particularly, the melting of the ice-sheet generated the formation of **numerous chains of meltwater lakes** and the **remodelling of riverine systems** (Kulkova et al., 2001). Due to the increased temperatures and humidity, the **lacustrine ecosystems** were significantly **enriched and diversified**. This mainly led to reduced mobility as sites were occupied for longer periods during the year. Riverbanks and lakesides became foci for such occupations (Jochim, 2012) allowing **economic intensification**, especially **widespread fishing** by early Holocene populations (Chairkina and Kosinskaia, 2009; Haaland, 2009; Jordan and Zvelebil, 2009; McKenzie, 2009; Bērziņš, 2010; Gibbs and Jordan, 2013; Cummings, 2014).

It is often assumed that increased emphasis on aquatic resources exploitation was, at least partly, related to the emergence of pottery technology, or increased production, as these factors seem to coincide in many regions of northern Eurasia and Africa (Haaland 2009; Chairkina and Kosinskaia 2009; McKenzie 2009; Gibbs and Jordan 2013). Ceramic pots possibly offered certain advantages over other perishable container technologies in order to more efficiently exploit, process and store aquatic food. Particularly, it could have played a significant role in the management of the seasonal spikes in the availability of aquatic resources, such as during spawning and migration transient episodes. The production of better preservable products (e.g. oil) could have been essential for surviving the more adverse seasons. On the other hand, as suggested by P. Jordan and M. Zvelebil (2009), settlement of forager population on the shores of lakes and rivers may have also favoured pottery production by giving direct access to the main materials, i.e. water, temper and quaternary clay deposits. On balance, it seems plausible to suggest that the economic diversification that was taking place at the start of the Holocene, including great exploitation of aquatic resources was a major driving force for the wider adoption of pottery.

Alternative explanations, not directly related to broader economic developments, may have also promoted the adoption of pottery technology among ancient populations. In particular, Hayden claimed that the early use of pottery may have been linked to **more social** and **aesthetic reasons**, with pottery being used as a new "**prestige**" object, for ritual displays or for exhibition at elaborate feasting events (Hayden 1995). Clay pots could have served for preparing exotic and high-prestige products, shared out at aggregations, generating social debts, and perhaps leading to seasonal cycles of competitive feasting. Ceramic vessels have probably played a central role in the socio-political strategies within "trans-egalitarian" hunter-gatherer communities (Hayden 2009; Hayden 2012). This may in part linked to intensive exploitation of aquatic resources since early pottery might have been used to prepare costly-to-produce substances, such as valued fish oils prepared through prolonged boiling (Taché and Craig 2015).

On the other hand, pottery innovation **can be regarded as a minor step change in container technology**. The early ceramic vessels might have simply accomplished a range of functions previously occupied by perishable containers such as baskets, pits or other organic containers (e.g. those made from wood, tree bark or animal tissue). In fact, some ethnographic evidence seems to indicate that organic containers (e.g. textile, basket, wooden boxes, skin bags) or other (durable) container and cooking technologies (e.g. pits, stone slabs, stone bowls) were able to perform (almost) the same function as ceramic vessels, i.e., cooking (even wet cooking), serve and store food (Barnett 1939; Leroi-

Gourhan 1945; Driver and Massey 1957; Stahl and Oyuela-Caycedo 2007; Mullen 2013; Admiraal et al. 2019). Therefore, pots may have just replaced these other containers by offering only incremental improvements for storage and cooking. But this change suddenly made the archaeological containers disproportionately visible in the archaeological record.

Although these alternative explanations for pottery innovation by hunter-gatherer communities are conceivable, it is nevertheless difficult to find tangible supporting archaeological evidence. By determining the use of pots through organic residue analysis, we may begin to untangle some of these competing hypotheses. For example, if pottery simply replaced other container technologies then perhaps more variable use patterns would be expected compared, for example, if they were adopted in response to a specific economic need. If it were a prestige technology, then it is conceivable that the use of pottery was atypical of broader economic practices. In addition, prestige and feasting has been suggested as role for hunter-gatherer pottery when recorded at low frequency, compared to other artefacts, as seen when pottery first appears in north-eastern North America (Vinette 1) (Taché and Craig 2015) and Japan (Incipient Jomon) (Craig et al. 2013). This would seem less likely during the Holocene when pottery appears to at much higher frequency on hunter-gatherer sites and therefore linked with a more utilitarian function.

3. Aims and objectives

The principal aim of this thesis is to **test the "Aquatic" Neolithic model** by using **organic residue analysis** to reconstruct **the function of early pottery** at three important archaeological sites in Siberia and the European part of Russia: **Gorelyi Les, Zamostje 2 and Rakushechny Yar** (Fig. 1.2).

To achieve this aim, the thesis had **four objectives**:

1) assess lipid preservation at these three sites as organic residue analysis has never been undertaken before. Although **lipids** overall show **good preservation in archaeological contexts** compared to other biomolecules (e.g. proteins, DNA), mainly due to their hydrophobicity, the resistance of lipids to decay is greatly related to the physico-chemical conditions of the burial environment, (e.g. humidity level, pH, biomass; Evershed, 1993). As a first study concretely exploring the function of ceramic vessels from different regions of Russia through organic residue analysis, it is important to first assess lipid preservation and **test the workability of such a method** in these "new" environmental contexts.

2) extract and analyse lipids from a large selection of potsherds (here over 300 ceramic vessels) to reconstruct patterns of vessel use using a systematic approach for lipid identification by GC-MS, isotopic characterisation of single compounds by GC-C-IRMS and bulk carbon and nitrogen isotope analysis by EA-IRMS.

3) test the established criteria for the identification of aquatic biomarkers in archaeological pottery. Previous studies have relied on the presence of ω-(o-alkylphenyl)alkanoic acids (APAAs) to identify aquatic products in archaeological pottery. Considering the importance of criteria used for aquatic identification to the thesis aim, a further objective was to test the conditions needed to form these molecules and critically examine their diagnostic capabilities.

4) integrate these results from the three sites to build up a preliminary synthesis of early pottery use in this large region and formally test the hypothesis of an "Aquatic" Neolithic. If successful, this opens up the possibility of a larger comparative and contextual study/studies of early Holocene pottery use within and between regions of northern Eurasia which lies the scope of this thesis.

4. Research questions and thesis organisation

The thesis starts with a **review of the methods** (**Chapter 2**), specifically focused on **organic residues associated with early pottery**. The goals of this chapter are to provide a critical review of the origin and principles of the discipline, and to describe the methodology that will be used in the PhD. Furthermore, in this chapter, a summary of the main natural products identifiable in ancient Eurasian pottery, by using this methodology, is provided. This will be used as a foundation for interpreting the molecular and isotopic results generated during the thesis.

The central core of this thesis consists of the three-local case-studies. Each address specific research questions:

- The **Gorelyi Les** case-study examined the function of the oldest pottery found so far **in the western region of Lake Baikal in Siberia** (McKenzie, 2009; Kuzmin, 2014), just outside the east Asia core areas. This site is part of the first early-Holocene dispersal of pottery technology after its break-out from the region where pottery was first invented, in East Asia, during the Late Pleistocene. This is a crucial region, geographically lying the early pottery Eurasian innovation centres and the later pottery development (Gibbs and Jordan, 2013). Gorelyi Les has five successive cultural layers from the Late Mesolithic to the Early Bronze Age. Therefore, it captures the introduction of the pottery in the Early Neolithic phase, including some of the

oldest pottery discovered in the Cis-Baikal region, dated to ca. 7800 cal. Year BP (Veksler, 1989; Weber, 1995; Weber et al., 2002; Ready, 2008; McKenzie, 2009; Kuzmin, 2014). For this study, **44 sherds** (Table 1.1), recovered from the **Early Neolithic Layer**, were accessible to be subjected to organic residue analysis. This assemblage enabled the following questions to be addressed: How was the oldest pottery in the Cis-Baikal region used? What drove the emerging Kitoi Culture to adopt clay pots into their subsistence strategies?

- **Zamostje 2** is located – further to the west – in the forest zone of the Volga-Oka region, ca. 100 km north of Moscow. In the **northern part of European Russia**, it offers unique opportunities to study pottery adoption since it is **one of the most important sites** in the region due to its well-preserved artefacts and ecofacts and an uninterrupted and well-dated stratigraphic sequence. It grapples the aceramic Mesolithic phase, the introduction of pottery technology at the Early Neolithic (ca. 5700–5400 cal BC) and finally the subsequent development of pottery tradition during the Middle Neolithic (Lozovski, 1996; Mazurkevich et al., 2013; Lozovski et al., 2014; Meadows et al., 2015). In this study, organic residue analysis was conducted on **240 samples** representing **166 ceramic vessels**, including ceramics and foodcrusts (Table 1.1), dating from the **Early Neolithic** to the **Middle Neolithic**. The large selection of pottery from different cultural layers and periods gives a rare opportunity to address the following questions: What was the function of the very first ceramic vessels introduced at this site? Did the function change throughout time? Did the adoption of this technology have an impact on the existing economy and social organisations?

- **Rakucheshny Yar** site is located further to the south, and offers another set of opportunities, here defined by a very particular (economic) context due to its geographical location, its material culture and faunal remains. Rakushechny Yar is located in the **Southern fringe of Eastern Europe** (**Russia**), in the Low Don region, in a putative contact zone between early farmers of the Near East and hunter-gatherers of Eastern Europe. Different cultural and economic traits indicate that local communities were embedded in a wide cultural network stretching from the Northern Pontic steppe and North Caspian Sea to the Near East. At this site twenty-three cultural layers were identified from the Early Neolithic to the Eneolithic and Bronze Age period (Mazurkevich and Dolbunova, 2012; Dolbunova, 2016; Dolbunova et al., 2020). As part of this study, lipid analysis was undertaken on **133 samples** including sherds and foodcrusts, corresponding to **104 vessels** (Table 1.1), recovered from **Early Neolithic layers**

and from the **Late Neolithic and Upper Eneolithic layers**. The following questions were raised for this case study: Was pottery on this site acquired through interaction with farming communities or is it a forager innovation? What was the function of early ceramic vessels? Did patterns in pottery use change over time?

Site	Vessels	Foodcrusts	Sherds	Total samples
Gorelyi Les	44	1	43	44
Zamostje 2	166	119	121	240
Rakushechny Yar	104	50	83	133

Table 1.1 Table summarising the number of vessels, sampled foodcrust and sampled sherds selected from each site for analysis.

Overall, these sites have produced a very significant collection of **well-preserved artefacts** and **ecofacts**. This valuable source of information is essential to build a high-quality interpretation of the organic residue results and to better assess the place of pottery technology within hunter-gatherer groups in general. Additionally, strong evidence of aquatic resource exploitation by prehistoric populations inhabiting these three regions have been previously documented through archaeological and zooarchaeological research as well as isotope analysis on human bones (Clemente et al., 2002; Weber et al., 2002; 2011; Katzenberg et al., 2010; Lozovskaya and Lozovski, 2013; Lozovski et al., 2013a; 2013b; Radu and Desse-Berset, 2013; Leduc and Chaix, 2014; 2018; Dolbunova et al., 2020). This provides an excellent context to examine the relationship between pottery technology and the use of aquatic resources and to adequately address the issue of an "Aquatic" Neolithic.

These case-studies were conducted as stand-alone **journal articles** with all now either published, accepted or close to being submitted to journals and are, here, presented by chapter. In these articles, more information on the specific context of each site is provided. This is viewed in the context of the results of the organic residue obtained from pottery in order to give some interpretative conclusions on the role played by pottery technology among these different hunter-gatherer communities living during the early Holocene. Here is reviewed the main details:

Chapter 3 – CIS-BAIKAL, EASTERN SIBERIA: *Resource-Processing, Early Pottery and the Emergence of Kitoi Culture in Cis Baikal: Insights from Lipid Residue Analysis of an Early Neolithic Ceramic Assemblage from the* ***Gorelyi Les*** *Habitation Site, Eastern Siberia*. These research results will be published (currently in press) in *Archaeological Research in Asia* in a special issue under the title of "Middle Holocene

Hunter–Gatherers of Lake Baikal: Integrating Individual Life Histories and High-Resolution Chronologies", and edited by guest editors Andrzej W. Weber, Christopher Ramsey, and Rick Schulting.

Chapter 4 – NORTH EUROPEAN RUSSIA: *Fruits, fish and the introduction of pottery in the Eastern European plain: Lipid residue analysis of ceramic vessels from* ***Zamostje 2***. These results were published in 2020 in a special issue of *Quaternary International* entitled "Stone Age Subsistence Strategies" and edited by guest editor Dr. Berihuete Azorin.

Chapter 5 – SOUTHERN EUROPEAN RUSSIA: *On the boundary of the "hunter-gatherer" and "agricultural" Neolithic: subsistence and culinary practices at the site of* ***Rakushechny Yar*** *in the Lower Don*. These results are intended to be submitted shortly to *Archaeological and Anthropological Sciences*.

While most of the research issues are tackled using established approaches in lipid analysis, however the work on hunter-gatherer pottery has also raised some gaps in organic residue analysis knowledge. One objective was to critically evaluate criteria for identifying aquatic products in pottery, particularly, the interpretation of **ω-(o-alkylphenyl)alkanoic acids** (**APAAs**). These molecules are routinely used to identify aquatic products in pottery (Lucquin et al., 2016; Gibbs et al., 2017; Oras et al., 2017; Shoda et al., 2017; Bondetti et al., 2020), although they can be produced by heating a range of animal and plant products (Matikainen et al., 2003; Hansel et al., 2004; Evershed et al., 2008b). Therefore, additional research was required to determine whether these compounds could be used to discriminate other commodity sources processed in archaeological pottery beyond what is already possible. This was addressed through a series of laboratory and field experiments. These series of experiments were designed to assess the diagnostic value of these compounds and to gain insight into the behaviour of the organic matter subjected to diverse transformations during the use of the pottery.

This experiment study provided significant inputs strengthening the interpretations and inferences that can be drawn from the organic residue analysis results. The results have been compiled in a methodological paper entitled: *Investigating the formation and diagnostic value of ω-(o-alkylphenyl)alkanoic acids in ancient pottery*. This article is in the process of being published in *Archaeometry* and is presented here in **chapter 6**.

Finally, **chapter 7** integrates and summarises all new organic residue data generated during this doctoral project to compare results from the three case studies and puts them into a wider research

context. This exercise also highlights several directions for further research, including both archaeological aspects and potential methodological improvements for the analysis of organic residues associated with archaeological pottery.

Finally, the appendix to this thesis contains: further information about the laboratory protocol used during this work (Appendix 1) as well as tables collecting all the results generated during this PhD (organic residue analysis, bulk collagen isotope, ZooMS, cooking experiments), the reference data used in the articles, and additional illustration and photos of the sites and pottery (Appendix 3 to 22). These appendices correspond to the "Supplementary materials" of the journal articles presented in chapters 3 to 6. Also provided are the data used to realise some of the figures illustrating chapter 2 (Appendix 2).

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Chapter 2

Organic residue analysis and early ceramic vessels

1. What are organic residues?

In archaeology, the term of organic residues refers to a wide range of **amorphous organic** remains found in archaeological context (Heron and Evershed, 1993). "Organic" describes all the material mainly composed of carbon, hydrogen, oxygen and nitrogen encompassing e.g. DNA, carbohydrates, lipids and proteins (Evershed, 1993; Dunne, 2017; Regert, 2017). The word "amorphous" literally means lack of morphology. In other words, these materials cannot be characterised by visual examination, unlike other biological materials such as bones, wood, leather, textiles, seeds and pollen. Thus, organic residues describe all the soft materials without morphologic structures that allow to identify them. This includes natural products such as waxes, animal fats, resin or materials derived from other anthropogenic processes like vegetable tars, wine, beer, oils, etc (Fig. 2.1;Heron and Evershed, 1993; Regert, 2011; 2017).

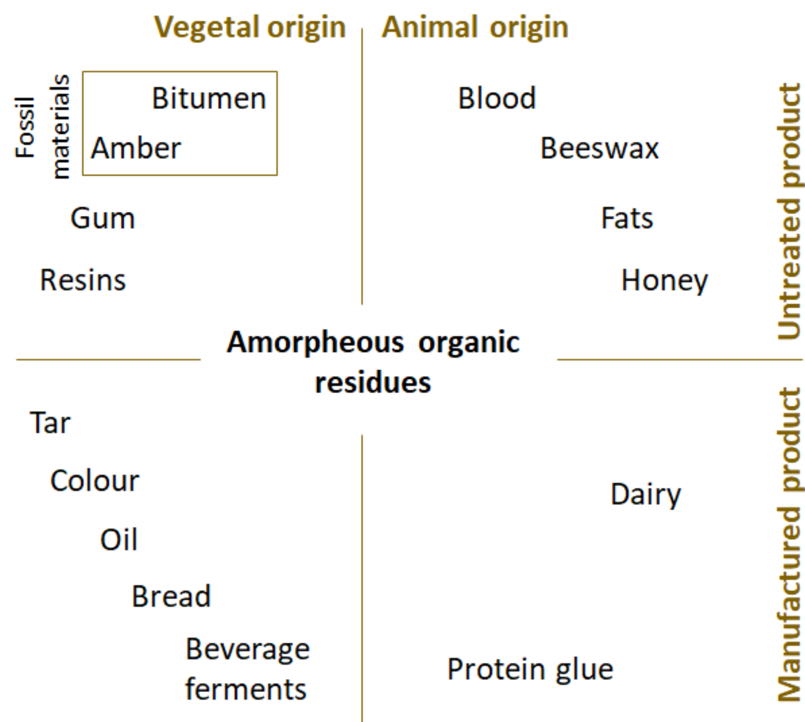

Figure 2.1 Amorphous organic remains which could be preserved and found in archaeological context (Adapted from Regert, 2017).

In archaeological context, amorphous organic residues could be found on different archaeological artefacts (objects and tools), used for many different purposes (Regert and Rolando, 2002; Ribechini, 2009; Solazzo et al., 2016; Courel et al., 2018; Croft et al., 2018). However, in this chapter, only **organic residue associated with ceramic vessels** are discussed. Organic residue analysis is a quite recent field which quickly turned out to be a powerful tool to study the function of pottery. Indeed, the chemical characterisation of organic remains in archaeological vessels has only started to receive attention from the end of the 1980s by the development of a suitable methodology for the analysis and the use of Gas chromatography (GC) and GC-mass spectrometry (GC-MS) (Rottländer and Schlichtherle, 1980; Evershed et al., 1990; 1991; Oudemans and Boon, 1991; Charters et al., 1993b; Oudemans, 2007; Evershed, 2008a)**.** The development of the scientific procedure over the last three decades, particularly with the enhancement of instrumentation performance (e.g. GC-MS), and the combination of innovative applications in this field, such as stable isotope, analysis allowed to fully establish the discipline within archaeological research. Therefore, over the last decade, the number of chemical analysis studies focusing on pottery function significantly increased, with the main aim to better understand the drivers of pottery adoption by ancient populations, and which role this technology played within different societies across the world and over time (Gregg, 2009; Craig et al., 2011; 2013; Debono Spiteri, 2012; Soberl et al., 2014; Horiuchi et al., 2015; Taché and Craig, 2015; Carrer et al., 2016; Heron et al., 2016b; Lucquin et al., 2016a; Gibbs et al., 2017; Shoda et al., 2017; Taché et al., 2017; Admiraal et al., 2019).

In ceramic vessels, these residue remains reflect the original pottery content. Most of the time they follow from cooking activities encompassing either foodstuffs processing or its storage. Nevertheless, organic remains present in potsherds can also arise from specific manufacturing, such as tar and pitch; or reflect specific surface treatment (e.g. resins, bitumen and tars use as sealed agent to waterproof the pottery vessels or use as the adhesive to fix them), or the use of fuels for lamps (Heron and Evershed, 1993; Regert et al., 2003; Copley et al., 2005b; Heron et al., 2013; Regert, 2017). These organic vestiges can take different forms in pottery. The most well-known by archaeologists, because still visible, are the **carbonized surface deposits** covering some of the inner and also sometimes the outer pottery surface. These residues, often called **foodcrusts,** are formed during cooking and could remain adhered on the pottery wall until their discovery. However, they are not always present. The most common form of organic residues is those which have diffused and have been trapped within the pores of the ceramic matrix. These, invisible to the naked eye, are commonly named **absorbed residues** (Heron and Evershed, 1993; Evershed, 2008a) and can survive for thousands of years.

Organic compounds in archaeological contexts comprise a wide range of molecules, including proteins, carbohydrates, lipids, nucleic acids and amino acids. Among these, **lipids** show the best resistance to decay due to their hydrophobic properties and their low chemical reactivity (Evershed, 1993; Dunne, 2017) limiting their post-depositional exchanges with the surrounding sediment (Heron et al., 1991; Oudemans and Boon, 1991; 2007). Furthermore, in ceramic vessels, lipids preservation is enhanced as molecules become entrapped in either organic (foodcrusts) and mineral (ceramic) matrices (Evershed, 1993). Indeed, microencapsulation of a small amount of lipids in foodcrusts seems to occur. Thereby, the carbonized crusts, formed during pottery use, appears to inhibit microbial activity and limit lipids degradation (Oudemans and Boon, 1991; 2007). Likewise, the ceramic fabrics restrict access of microorganisms of absorbed lipids. Furthermore, the biomolecules adsorbed on clay surfaces limit the lipids availability as a substrate for microorganisms. As well, in some archaeological context a preferential decomposition phenomenon, called "sacrificial", of co-deposited biological organic matter happen, in favour of lipids (Eglinton and Logan, 1991; Evershed, 1993). All these elements overall promote the preservation of lipids in ceramics, making them very good candidates to investigate the function of archaeological pottery and therefore will be the subject of our attention in this work.

2. Lipids

Lipids are a category of natural substances that, with carbohydrates, proteins, water and other elements, constitute an essential component of living beings, fulfilling various functions (e.g. energy storage, biological membrane components) (Gurr, 1980; Evershed, 1993; Heron and Evershed, 1993). Biochemists and chemists overall define lipids to be organic matters with high solubility in organic solvents such as chloroform, ethers, alcohols and hexane, separating them from the other organic residue categories (Gurr, 1980; Christie, 1989; Evershed, 1993). As all organic compounds, lipids are mainly composed of carbon, hydrogen and oxygen, arranged around a carbon core either linear, branched or cyclic and substituted with hydrogen, or other atoms (Evershed, 1993). This structure mainly constituted by hydrocarbon moiety gives them their hydrophobic character which reduces their solubility in water (Evershed, 1993). Lipids encompass a variety of molecules presented below.

2.1. Fatty acids

The definition of **fatty acid** is a **straight aliphatic chain**, either saturated or unsaturated (from one to six), ending by a **carboxylic acid group**. Examples of fatty acids are presented in figure 2.2. Fatty acids from natural substances contain usually even numbers of carbon atoms varying most of the time between 14 to 22, although many microorganisms also synthesise odd-chain fatty acids (Gurr, 1980; Christie, 1989). In the shorthand nomenclature, fatty acids are designated by **Cx:y (n-z)** with x and y

indicating the number of carbon and unsaturation on the aliphatic chain respectively, and z the position of the double bond from the terminal methyl (Christie, 1989). Although fatty acids are important constituents of organic matter, they are rarely found free naturally but rather bond to other molecules and form bigger molecules such as **triacylglycerols** and **wax esters** (Drieu, 2017).

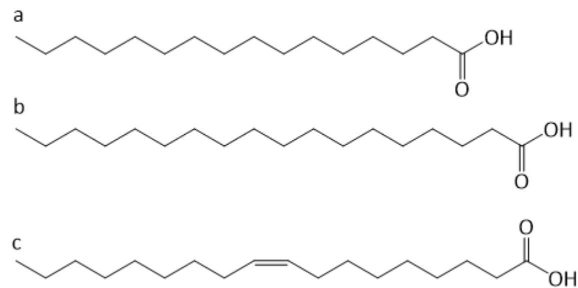

Figure 2.2 Examples of the most abundant fatty acid in nature: Two saturated fatty acids, a) palmitic acid ($C_{16:0}$) and b) stearic acid ($C_{18:0}$) and monounsaturated fatty acid, c) oleic acid ($C_{18:1}$ [n-9]).

2.2. Triacylglycerols (TAGs)

TAGs are the major components produced by plants and animal organisms (Oudemans, 2007). They represent more than 95% of lipids in our diet (Dunne, 2017). They are made up of glycerol moiety whose hydroxyl groups (n = 3) are linked to a fatty acid via an ester bond (Fig. 2.3) (Christie, 1989; Dunne, 2017). The three moiety fatty acids constituting the TAG may be either all the same or different (Killops and Killops, 2004), and their nature (length, double bound number and position) and their position on the glycerol skeleton can be informative about the TAGs original sources, since it arises from various metabolic processes differing according to the organisms (Evershed, 2008b). By convention, the prefix "**sn**", placed before the stem name of the compound, is used to indicate **the position of the fatty acid on the glycerol**. Thereby, sn-2 identifies the central position, whereas sn-1 and-3 correspond to the side positions (Christie, 1989) (Fig. 2.3). TAGs are sensitive to the hydrolysis process, breaking the ester bond (Dudd et al., 1998). These reactions lead to the formation of monoacylglycerol (MAGs) and diacylglycerol (DAGs) by the loss of two and one fatty acyl moieties of the TAGs respectively and produce consequently free fatty acids.

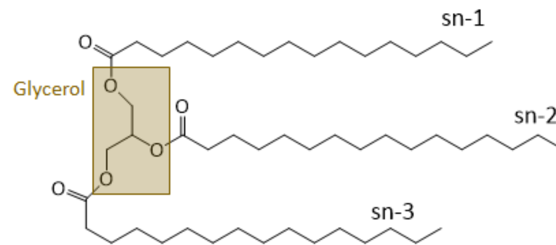

Figure 2.3 Example of a typical of triacylglycerol, the tripalmitin formed of a glycerol core and three palmitic acids ($C_{16:0}$).

2.3. Wax ester

Wax esters are found in animals, plants and microbial tissues. They are constituted of fatty acids and long-chain alcohols linked by an ester bond (R-COO-R') (Fig. 2.4). The aliphatic chain of alcohol and fatty acid is mainly a straight-chain, saturated or monounsaturated, although branched and hydroxyl-chain can also be present (Christie, 1989). Alike TAGs, wax esters can be hydrolysed and thus release free fatty acids and alcohols.

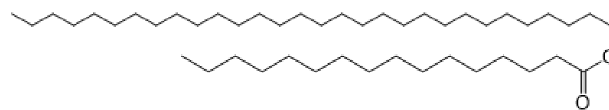

Figure 2.4 Example of a wax ester, the triacontanyl palmitate derived from palmitic acid ($C_{16:0}$) and triacontanyl alcohol (*n*-alkanol with 30 carbon atoms).

2.4. Sterols

Sterols are a molecule family comprising mainly a sterane core with a hydroxyl group on carbon 3 (Fig. 2.5). Different sterols can be distinguished according to the functional group bonded to the sterol skeleton, allowing some origin diagnostics (Evershed et al., 1991b; Oudemans and Boon, 2007). For instance, **cholesterol** and its derivatives are typically animal-derived sterols (including terrestrial and aquatic species) (Evershed et al., 1991b; Evershed, 1993; Heron and Evershed, 1993), although it also occurs in plant tissue but only in trace amounts (Christie, 1989). Sterols coming together under the name of **phytosterols**, such as **stigmasterol**, **β-sitosterol** and **campesterol** (Fig. 2.5), are characteristic of plant commodities (Christie, 1989; Evershed et al., 1991b; Evershed, 1993; Oudemans and Boon, 2007).

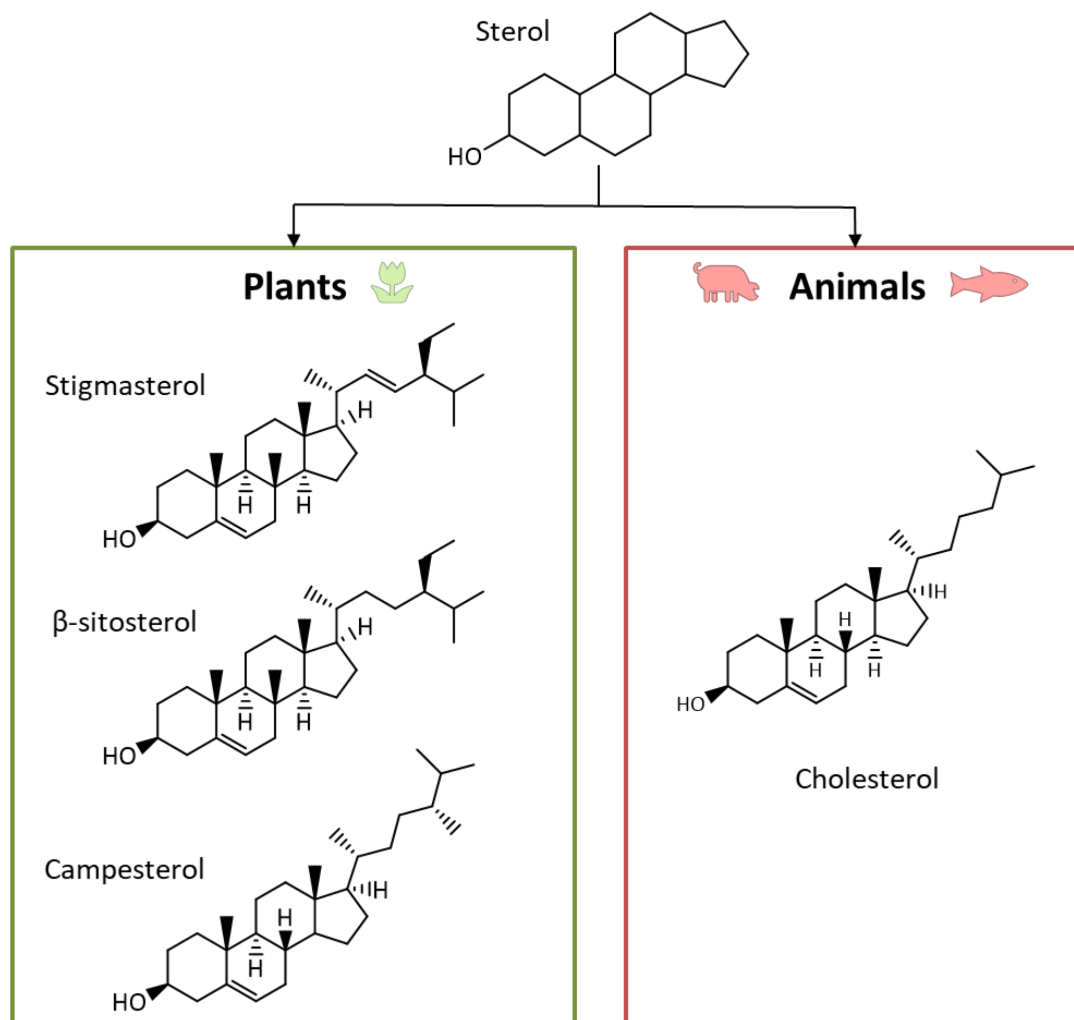

Figure 2.5 Structures of sterols skeleton and its main derivatives found in plant and animal tissues.

2.5. The *n*-alkanes and *n*-alkanols

The alkanes are components characterised by an unsaturated hydrocarbon skeleton, straight-chain or cyclic, without any other functional group. The ***n*-alkanes**, for "normal" alkane, refer to the acyclic alkanes (Christie, 1989). The *n*-alkanes, owning an odd carbon number, are the major constituents of waxes, including plant and insect origin (e.g. beeswax) (Eglinton and Hamilton, 1967; Tulloch, 1971; Charters et al., 1995; Baeten et al., 2013; Roffet-Salque et al., 2015).

The ***n*-alkanols** (or linear alcohols) are molecules composed of an aliphatic chain, owning a hydroxyl group at the end of the carbon-chain. They are found in tissues of living organisms, and mainly bond to other molecules forming, for instance, wax esters, although they also occur in very low amounts in the free state (Christie, 1989).

2.6. Terpenes

This type of compounds is not always encompassed in the lipid definition (Christie, 1989; Killops and Killops, 2004), however it forms one of the widest classes of natural products, exhibiting a great diversity in terms of structure and function, and are extensively found in higher plants (Evershed, 1993; Hill, 1993; Killops and Killops, 2004). Terpenes derive from the polymerization of the isoprene molecule (C5H8) followed by various cyclisations and rearrangements (Connolly and Hill, 1991). They are classified according to the number of carbon atoms present in their skeleton. Thus, mono-, sesqui-, di- and triterpenes, which have respectively 10, 15, 20 and 30 carbon atoms, can be distinguished (Harborne, 1984; Connolly and Hill, 1991). The di- and triterpenes are terpenoids usually found in archaeological context unlike the mono- and sesquiterpenes which are much more volatile (Harborne, 1984). Figure 2.6 shows examples of diterpenoid and triterpenoid structures displaying a great diversity of structures and functions.

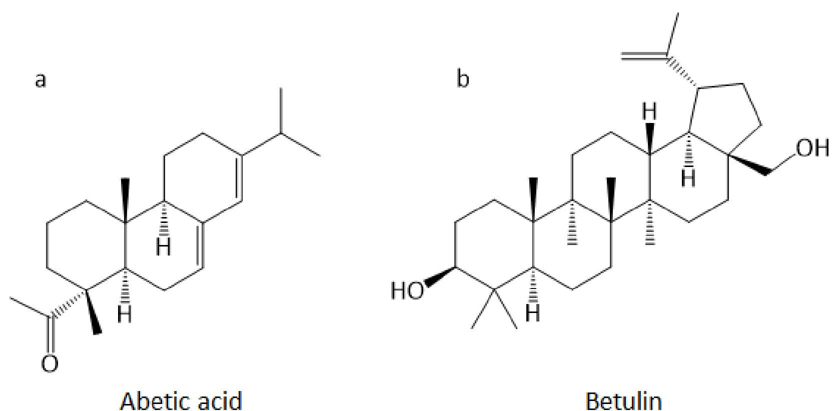

Figure 2.6 Examples of a) diterpene and b) triterpene structure.

By using a set of chemical processes, it is possible to recover and separate lipids and their decay products from the fabric of the pot. It is then possible to characterise them, thanks to modern analytical techniques, and trace back the original substance(s) contained in the pots. This is the **concept of biomarkers**. Such study can provide substantial and various information about culinary and medicinal practices as well as technical, economic and symbolic activities (Regert, 2017) and thereby contributes to learning about the prehistoric ways of living.

3. Molecular analysis

3.1. The Biomarker concept

The use of biomarkers in archaeology is a concept originally borrowed from organic geochemistry and palaeontology to determine the nature of biomolecular constituents in ancient sedimentary deposits (Evershed, 1993; 2008b; Evershed et al., 1999; Regert, 2011). The biomarkers are defined as organic compounds which persist over long timescales and are characterised by a "chemical fingerprint", corresponding to a specific carbon skeleton, that might be used as a tracer to identify their biological source (Philp and Oung, 1988; Evershed et al., 1999; Regert, 2011; Dunne, 2017). In archaeology, biomarkers are compounds occurring in archaeological remains and are used to gain information concerning ancient human activities (Evershed, 2008b). However, while **biomarkers** refer to the **native molecules** directly related to their **natural sources**, archaeological organic residues can also endure some modifications altering their initial chemical composition, caused by different natural processes or **anthropogenic activities**. Therefore, bioarchaeologists have defined distinct molecular marker types: degraded markers, encompassing anthropogenic transformation markers and **natural degradation** markers, and **contamination markers** (Regert, 2011; 2017; Fig. 2.7).

3.1.1. Natural degradation markers

Natural degradation markers are compounds which have been subjected to natural decay leading to molecular structural transformation of the initial biomarkers. These modifications are induced by chemical, biochemical and/or enzymatic processes occurring during the pottery use life; exposure to sunlight and oxygen; or by different microorganism activity and/or water leaching in the burial environment (Evershed et al., 1991b; Regert, 2011; Drieu, 2017). Nevertheless, these molecular markers can be informative about the **natural source** of the residue and provide clues about its **deterioration conditions** over time (Fig. 2.7).

3.1.2. Anthropogenic transformation markers

Anthropogenic transformation markers arise from chemical transformations of biomarkers under anthropogenic actions such as thermal treatment. These markers convey information about **original substances** contained in the pots, but they are also direct witnesses of either particular culinary practices or the manufacturing of products (Evershed et al., 1991b; Regert, 2011; 2017).

3.1.3. Contamination markers

This last category of markers refers to **exogenous compounds** transferred to potsherds during burial or due to post-excavated activities (Evershed et al., 1991b; Regert, 2011; 2017). In the first case ("burial contamination"), some natural substances can migrate from the burial sediment to the archaeological residues (Evershed, 1993; 2008b; Regert, 2011). These molecules may sometimes be hard to recognise as contaminants since they can be similar to those arising from the use of the pots itself. This is why, it is recommended, when possible, to analyse the surrounding sediments from where pottery was excavated, in order to rule out or identify some possible contamination from the soil.

As stated above, some contaminations can also arise from the handling and packaging of the samples after their excavation. A common contaminant, introduced during the manipulation of the artefacts, are human skin lipids, such as squalene and cholesterol. The specific structure of the former, constituted of a large number of double bonds, makes it highly sensitive to degradation (Evershed, 1993). Its preservation over such a span of time is unlikely. Therefore, its detection in archaeological samples is clear evidence of contamination. Although in smaller quantities, cholesterol could also originate from the direct contact of human skin with the potsherds. However, being also a common constituent in the whole animal kingdom, cholesterol is usually regarded as a contaminant when it co-occurs with squalene (Evershed, 1993). Finally, a non-biological contaminant frequently identified is phthalate plasticizer, coming from storing conditions of samples in plastics (Evershed, 1993). If these components are readily recognised, their presence can cause an identification failure of some molecules of interest by completely hiding their signal. To prevent such inconveniences, it is prescribed to use gloves while handling the artefacts and wrap them in aluminium foil before storing them in a plastic bag.

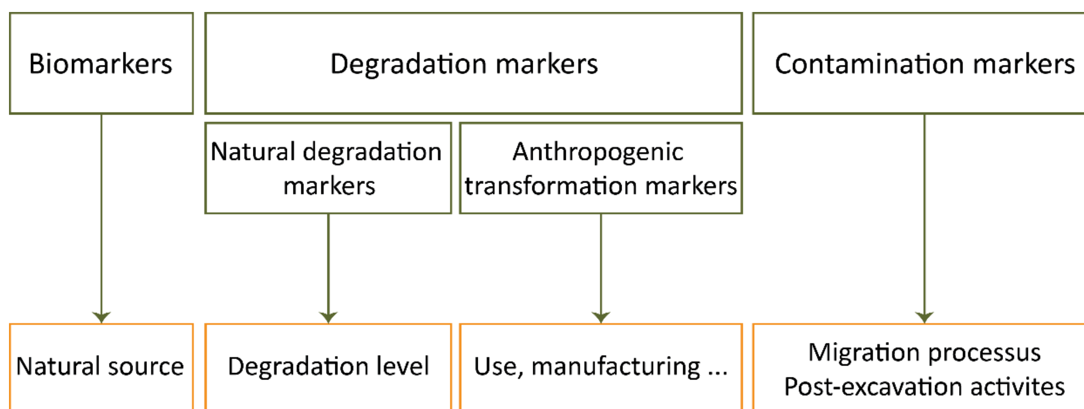

Figure 2.7 Diagram summarizing information obtained from biomarkers (Regert, 2017).

The main analytical instruments/techniques used for the study of lipid from foodcrusts and absorbed residues are the gas chromatography-mass spectrometry (GC-MS), the gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) and the elemental analysis isotope ratio mass spectrometry (EA-IRMS) which provide molecular and isotope data. GC-MS enables to both, quantify the lipid remains to assess the preservation level, and access their chemical compositions allowing to trace back the origin of commodities processed or stored in ancient pottery through the archaeological biomarker concept. Further identification of animal fat origins can be supplied via bulk stable carbon and nitrogen isotope analysis by using EA-IRMS and compound-specific stable carbon isotope compositions with GC-C-IRM of carbonized and absorbed residues. Indeed, isotopic analyses enables to discriminate freshwater, marine animals, herbivore, carnivore terrestrial animal and plant fats (Dufour et al., 1999; Yoneda et al., 2004; Craig et al., 2007; 2013; Yoshida et al., 2013; Cramp and Evershed, 2014) as well as to distinguish fat adipose from non-ruminant and ruminant animal and ruminant dairy products (Dudd and Evershed, 1998; Evershed et al., 1999; Copley et al., 2003; 2005c; Evershed, 2008a).

3.2. Main natural products identified in early Eurasian ceramic vessels

3.2.1. Aquatic products

3.2.1.1. Biomarkers

Aquatic fats and oils are characterized by the presence of saturated fatty acids, dominated by palmitic acid ($C_{16:0}$), **long-chain mono-** and **polyunsaturated fatty acids** (PUFAs) (mainly $C_{16:1}$, $C_{18:1}$, $C_{20:1}$; $C_{22:1}$ and $C_{20:5}$ and $C_{22:6}$), and specific **isoprenoid fatty acids** (IFAs), including 4,8,12-trimethyltridecanoic acid (TMTD), 3,7,11,15-tetramethylhexadecanoic acid (phytanic acid), and 2,6,10,14-tetramethylpentadecanoic acid (pristanic acid) (Ackman and Hooper, 1968; Passi et al., 2002; Evershed, 2007; Gunstone et al., 2007; Evershed et al., 2008b; Hansel and Evershed, 2009; Cramp and Evershed, 2014). PUFAs are the major constituents of aquatic fat sources, but their high chemical and biological degradation sensitivity leads to a very low survival rate in an archaeological context, and are only rarely detected (Evershed et al., 1991b; 2008b; Heron and Evershed, 1993). By contrast, IFAs due to their chemical structure with a high branching level, are more resistant to degradation (Cramp and Evershed, 2014). They are synthesised from the phytol, a constituent of chlorophyll (Fig. 2.8) (Ackman and Hooper, 1968; Cramp and Evershed, 2014). Their presence in aquatic organisms comes from algae and phytoplankton, both containing chlorophyll, that is digested by zooplankton and fish (Avigan and

Blumer, 1968). Nevertheless, these IFAs compounds are not exclusively found in aquatic products since they also occur in terrestrial animals. Indeed, they are formed in the ruminant rumen, through bacterial oxidation and hydrogenation of phytol present in terrestrial plants as well (Gurr, 1980; van den Brink et al., 2004; Wanders et al., 2011). They are, thereby, found in ruminant tissues, milk and processed butterfat (Hansen, 1969; Ackman and Hooper, 1973; Cramp and Evershed, 2014).

A recent study undertaken by Lucquin and co-workers (Lucquin et al., 2016b) has demonstrated that by computing the phytanic diastereomers ratio (3S,7R,11R,15-phytanic (SRR) and 3S,7R,11R,15-phytanic (RRR)) it is possible to distinguish the two phytanic sources. The proportion of SRR-isomer is higher than the RRR-isomer in aquatic animals. Thereby, an SRR% >75.5% (relative abundance) is used as a complementary tool for the identification of aquatic products in archaeological pots. Likewise, the detection of TMTD in archaeological pottery is commonly ascribed to the processing of aquatic products (Evershed et al., 2008b; Cramp and Evershed, 2014), although it is also present in low quantity in ruminant tissues. Indeed, in ruminant tissues, like in aquatic organisms, this compound is formed via the degradation of pristanic acid (Hansen, 1969) (Fig. 2.8). Nevertheless, the TMTD is also produced from other molecular precursors (e.g. Zamene, phytadiene) (Fig. 2.8), only present in appreciable amounts in zooplankton, fish and aquatic mammals (Blumer and Thomas, 1965; Ackman and Hooper, 1968). Thereby, when found in archaeological ceramics, its origin is more likely due to the processing of aquatic products.

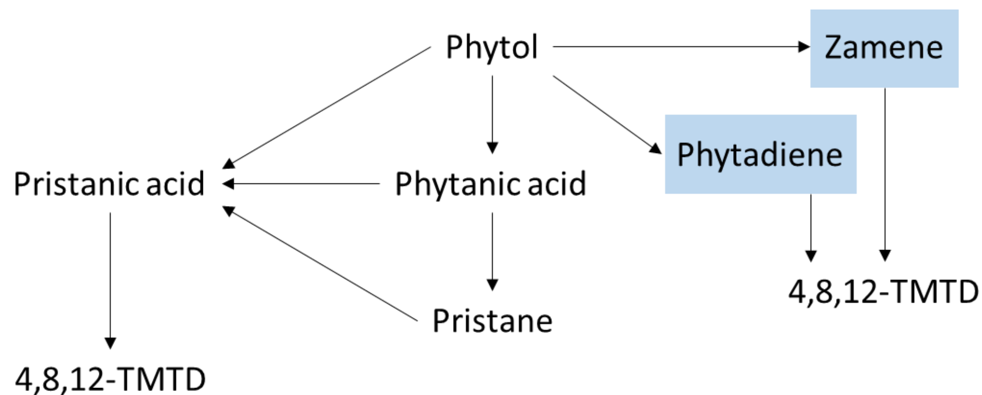

Figure 2.8 Scheme showing the formation of the isoprenoid compound present in aquatic organisms (after Ackman and Hooper, 1968). The two precursors Zamene and Phytadiene being only present in appreciable amounts in zooplankton, fish and aquatic mammals (Blumer and Thomas, 1965; Ackman and Hooper, 1968).

Additionally, it has been proposed (Baeten et al., 2013) to use the simultaneous presence of the two monounsaturated fatty acid $C_{17:1}$ and $C_{19:1}$ as a biomarker for aquatic food sources. Indeed, several studies have shown that the co-occurrence of them were representative of fish products (e.g. carp and

catfish) (Rasoarahona et al., 2004; 2008) and seafood (e.g. limpets, shrimps, cuttlefish, crabs and sponges) (Carballeira and Alicea, 2001; Barnathan et al., 2003; Ando and Nozaki, 2007; Le Bihan et al., 2007; Kawashima et al., 2008; Denis et al., 2009). Yet, these two compounds are almost never identified in archaeological context due to oxidation processes (Evershed et al., 1991b) and were, so far, co-identified only once in pottery from Southampton in England (Baeten et al., 2013).

Finally, **cholesterol**, the main sterol in animal fats (Evershed, 1993), can be used to characterise animal products, encompassing aquatic and terrestrial animal, in pottery (Evershed et al., 1991b; Drokin, 1993; Badiani et al., 1996; Copeman and Parrish, 2004). However, this compound is rarely found in archaeological potsherds (Evershed, 1993; Manzano et al., 2016). The reasons for this can be twofold: (1) sterols are a minor constituent of animal adipose (usually less than 1%) (Heron and Evershed, 1993) and (2) they are quickly degraded when subjected to heating treatment (from 100ºC), catalysed by both clay and free fatty acids (Hammann et al., 2018). This is commonplace in the case of cooking ceramic vessels.

3.2.1.2. Degradation markers

The highly sensitive unsaturated fatty acids undergo oxidation process that leads to the formation of various compounds such as **dicarboxylic acids** (also called diacid) and **hydroxy** and **dihydroxy fatty acids** (DHYAs) (Regert et al., 1998; Copley et al., 2005b; Regert, 2011). These compounds are not always found in archaeological pottery due to their relatively high-water solubility and high chemical reactivity. Moreover, as they can also be synthesised in other products that are rich in unsaturated fatty acids (e.g. plants; See chapter 2, section 3.2.5.1.2) or formed through other pathways (Knappett et al., 2005) they are consequently of limited diagnostic value. Nevertheless, the detection of vicinal dihydroxy fatty acids (DHYAs) in archaeological pottery can add substantially to the interpretative potential of the lipid biomarker evidence. These stable compounds are formed naturally by oxidation of monounsaturated fatty acids (Hansel and Evershed, 2009; Hansel et al., 2011). The co-occurrence of a wide range of dihydroxy fatty acids (from C_{16} to C_{22}) is indicative that aquatic products were contained in the pot. Indeed, monounsaturated fatty acids with numbered carbon ranged from C_{16} to C_{22} do not concurrently occur in terrestrial animal and are rather restricted in the plant world (Brockerhoff et al., 1966; Marai et al., 1969; Hansel and Evershed, 2009). Furthermore, the hydroxyl groups position allows to identify the original position of the double bond in their precursor fatty acids, providing additional information on their possible origin (Fig. 2.9). In fact, some specific DHYAs are ascribed to the processing of plant oil (e.g. Brassicaceae and castor oils, see Plant products part; See chapter 2, section 3.2.5.1.2) in archaeological vessels (Colombini et al., 2005b; Copley et al., 2005b)

while some DHYAs such as 9,10-dihydroxypalmitic (C_{16}), 9,10-dihydroxyarachidic (C_{20}) and 11,12-dihydroxydocosanoic (C_{22}) acid, are more likely originated from aquatic products since their analogue monounsaturated fatty acid are significantly more abundant in aquatic organisms (Drokin, 1993; Dahl et al., 2000; Falk-Petersen et al., 2004; Birkeland et al., 2005).

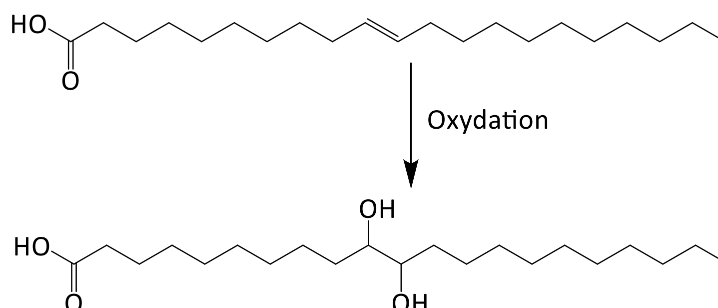

Figure 2.9 Example of dihydroxy fatty acid (DHYAs) formation by oxidation of its analogue monounsaturated fatty acid (modified from Cramp and Evershed, 2014).

In addition, if PUFAs are highly degraded by the ages and therefore poorly identified in archaeological samples they can form stable compounds reflecting anthropogenic activities during the lifetime of the use of pottery vessels. A series of reactions hold to produce **ω-(o-alkylphenyl)alkanoic acids** (APAAs) (Matikainen et al., 2003; Hansel et al., 2004; Cramp and Evershed, 2014) (Fig. 2.10). The successive steps allowing to yield these aromatic isomers only occur when the PUFAs are subjected to a protracted heating. Moreover, the creation of these compounds is highly catalysed by the metal ions present in the ceramic matrix (Schneider, 1989) and the steric properties of the clay matrix promoting the isomerization step (Fig. 2.10) (Evershed et al., 1995; Raven et al., 1997). Not only marine fats contain C_{18} PUFAs, but they also occur in vegetable fats and oils as well as terrestrial adipose fats (Heron and Evershed, 1993; Evershed et al., 2008b). Thus, the detection of APAAs of carbon length C_{18} does not allow to discriminate their origin. However, since PUFAs C_{20} and C_{22} are only present in significant amount in aquatic organisms (Cramp and Evershed, 2014), the presence of APAAs C_{20} and C_{22} make them currently one of the main molecular identification tools for the processing of marine and freshwater material in ancient ceramic vessels (Copley et al., 2004; Hansel et al., 2004; 2011; Hansel and Evershed, 2009; Cramp and Evershed, 2014; Lucquin et al., 2016a; Oras et al., 2017; Shoda et al., 2017).

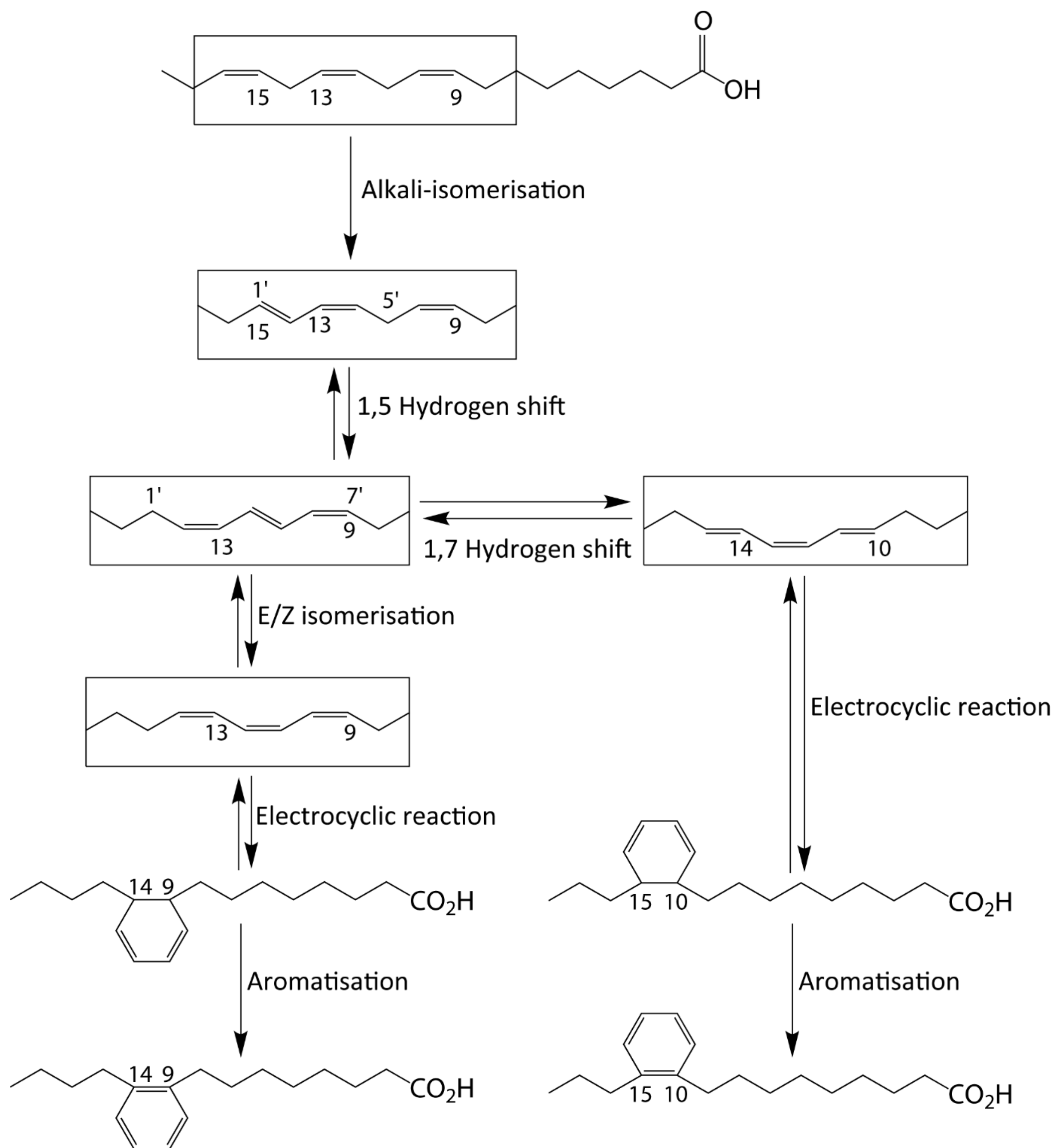

Figure 2.10 Reaction pathway for the formation of ω-(o-alkylphenyl)alkanoic acids (APAAs) from cis, cis, cis -9, 12, 15-octadecatrienoic acid subjected to prolonged heating (after Hansel et al., 2004).

Alteration structures of cholesterol compounds can occur during heating of fats in pottery or burial leading to the formation of a set of cholesterol derivatives (hydroxy-, oxo- and epoxy-) and can be detected in archaeological materials (Evershed, 1993; Regert, 2011).

3.2.2. Terrestrial animals fats

3.2.2.1. Biomarkers

The adipose tissue of animals contains a very high amount of fats. The main components are TAGs, since it constitutes over 80% of the total lipids (Gurr, 1980; Regert, 2011), mostly holding an **even number of carbon atoms** (Regert, 2011). The **distribution profile** of the TAGs in fresh adipose fats can provide information on animal origins by for instance discriminating, non-ruminant and ruminant fats as well as dairy fat product sources (Dudd and Evershed, 1998; Dudd et al., 1999; Kimpe et al., 2002; Mukherjee et al., 2007; Regert, 2011). In fact, ruminant fats display a “smooth” TAGs distribution profile ranging between T_{42} and T_{54} mainly centred on T_{50} or T_{52} without any predominance for one of them (Fig. 2.11) (Evershed et al., 1997b; Dudd and Evershed, 1998; Dudd, 1999). In contrast, non-ruminant adipose fats exhibit a narrower distribution that ranges between T_{46} to T_{54} with a high prevalence for one or two TAG(s) (Evershed et al., 1997b; Dudd and Evershed, 1998; Dudd, 1999).

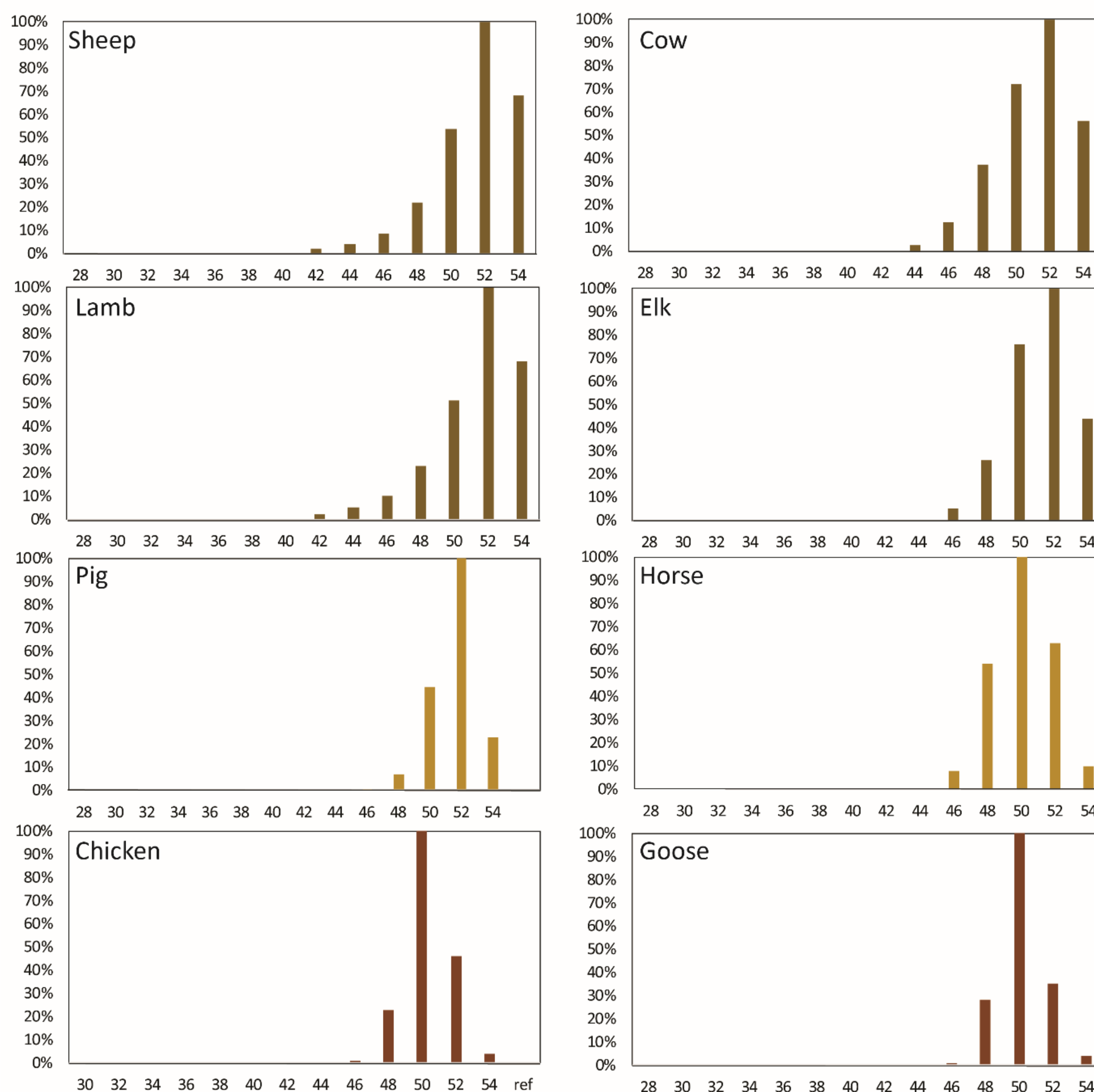

Figure 2.11 Carbon number distribution of TAGs of ruminant and non-ruminant adipose fats. The values used to make these charts were found in (Evershed et al., 1997b; Dudd and Evershed, 1998; Dudd, 1999; Drieu, 2017).

Another molecular criterion to distinguish TAGs' origin have been proposed, that is by looking at their structure (Mirabaud et al., 2007). Indeed, the examination of the fatty acid distribution constituting the glycerol backbone can enable to identify whether TAGs originate from adipose fat and milk products, but also to differentiate sources of animal species (Evershed et al., 2002; Mirabaud et al., 2007; Romanus et al., 2007; Garnier et al., 2009). However, the use of other instrumentations (e.g. NanoESI MS and MS/MS, HPLC) are required since classic GC-MS, usually used for the analysis of lipids from ancient pottery, does not provide such identification (Mirabaud et al., 2007). Nevertheless, because of different degradative reactions including hydrolysis, oxidation, polymerization,

condensation, cyclization or microbial degradation, probably differing depending on burial conditions, (Dudd and Evershed, 1998; Dudd et al., 1998; Evershed et al., 2002; Mukherjee et al., 2007; Evershed, 2008b; Regert, 2011), characterisation of lipid origins by studying TAGs distribution in archaeological context, has to be viewed cautiously. Additionally, the coelution of unsaturated TAGs and their saturated counterpart can hamper an accurate determination of TAGs proportion (Drieu, 2017). Finally, one must bear in mind the possible use of pottery for the preparation of multiple products, which might alter the TAGs distribution.

Monomethyl branched fatty acids with odd carbon chain $C_{15:0}$ and $C_{17:0}$ are also encountered in high amount in ruminant fats adipose and dairy products. They are synthesised by bacterial action in the ruminant gut (Christie, 1981a; Evershed, 1993). Whilst these two compounds are in high amount in ruminant adipose, they are also present in many bacterial membranes and consequently, widely occur in nature (Evershed, 1993; Dudd et al., 1998; Oudemans and Boon, 2007). Thereby their assignation to ruminant adipose fats in archaeological samples must be used cautiously. Additionally, branched fatty acid $C_{17:0}$ is also synthesised in the hindgut of horse by similar microorganisms as found in ruminant guts and thereby also present in equine adipose fats (Mileto et al., 2017). The calculation of the ratio **$C_{17:0}$ (branched chain)/$C_{18:0}$** fatty acid has been proposed in order to differentiate non-ruminant fats, ruminant adipose and dairy products processed in ancient pots (Dudd et al., 1999). It appears that dairy products exhibit a markedly higher $C_{17:0}$ (branched chain)/$C_{18:0}$ ratio than non-ruminant fats. This difference is even more pronounced between dairy fats and ruminant adipose. These two compounds both display similar structures and weights, meaning that they are exposed to comparable diagenetic influences making this ratio quite reliable. However, as just alluded to above, ancient pots can have been used for mixtures of different products, restricting its diagnostic potential.

Alike various **polymethyl branched fatty acids** occur in ruminant adipose tissue, synthesized in the rumen by fermentation of the compounds constituting the consumed plants (Gurr, 1980). Among these, it is found phytanic and pristanic acid and TMDT arising from the digestion process of the phytol (van den Brink et al., 2004; Wanders et al., 2011), a constituent of the chlorophyll (Ackman and Hooper, 1968; Cramp and Evershed, 2014). As stated before, these also occur in aquatic organisms. Although not very specific, it is, however, possible to identify the phytanic acid origin (aquatic or ruminant organism) by computing the phytanic diastereomers ratio (Lucquin et al., 2016b; See chapter 2, section 3.2.1.1).

As stated previously, **cholesterol** can also be detected in pottery that has been used to process or contain terrestrial animal fat (e.g. animal adipose fats or dairy products), although seldom detected in archaeological pots, due to its low amount in animal fat and its fast degradation when exposed to heating treatment (Evershed, 1993 ; Manzano et al., 2016 ; Hammann et al., 2018).

3.2.2.2. Degradation markers

Fatty acids represent another class of biomolecular constituents highly identified in animal adipose fats. They are formed naturally by the hydrolysis of TAGs or arise from anthropogenic activities such as cooking (Evershed et al., 1997b; Regert, 2011; Hammann et al., 2018). The two main free fatty acids found in animal fats are **palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acid** (Dudd and Evershed, 1998; Evershed et al., 2002). In favorable preservation conditions, the $C_{16:0}/C_{18:0}$ ratio (P/S ratio) can be calculated to guide about animal fats origin, since ruminant adipose tend to have a P/S ratio lower than 1 while dairy products and non-ruminant fats display a P/S ratio, usually, higher than 1 (Romanus et al., 2007; Baeten et al., 2013). However, it is noteworthy that the microbial degradation rate, as well as the solubility, is different according to the carbon chain length (Dudd and Evershed, 1998; Evershed et al., 2002; Steele et al., 2010). Fatty acids are all the more prone to the decay processes as its carbon chain is short leading inevitably to modify the P/S ratio. Additionally, the use of the ceramic for the processing of various products cannot be ruled out and can thus also greatly affect this ratio (Heron and Evershed, 1993; Mottram et al., 1999), limiting its diagnostic value. Therefore, the P/S ratio must be used carefully and employed only combined with other evidence.

To a lesser extent, unsaturated fatty acids (mono and polyunsaturated) can also be detected in animal adipose fats (Regert, 2011; Colonese et al., 2017). Notably, **$C_{18:1}$** is frequently found in potsherds (Regert, 2011) and the position of the unsaturation can provide further fat origin identifications. Due to biohydrogenation processes occurring in the rumen, ruminants synthesise a mixture of $C_{18:1}$ isomers with double bond in position 9, 11, 13, 14, 15, and 16 (Evershed et al., 1997b; Mottram et al., 1999; Regert, 2011), while non-ruminant, such as pigs, produce only one isomer with the unsaturation located on the 9th position of the aliphatic chain (Evershed et al., 1997b; Regert, 2011). To characterise these isomers, it is, however, indispensable to derivatize the fatty acid double bonds with dimethyl disulfide (DMDS) (Evershed et al., 1997b; Mottram et al., 1999; Regert, 2011). Although unsaturated fatty acids can be preserved, they are often subjected to different degradation processes, notably oxidation, conducting to create several compounds such as **dicarboxylic acids** (also called diacids), **hydroxy** and **dihydroxy fatty acids** (Regert et al., 1998; Copley et al., 2005b; Hansel et al., 2011; Regert, 2011).

Further lipid markers directly formed from the degradation of TAGs can be produced. The hydrolysis of TAGs, besides releasing free fatty acids, produces **MAGs** and **DAGs**. However, they are often in low amount since the complete hydrolysis of the TAGs occurs rapidly once the first fatty acid has been lost from the glycerol backbone (Dudd et al., 1998; Evershed et al., 2002).

Mid-chain alkanones with an odd-numbered carbon-chain ranging from K_{29} to K_{35} (Evershed et al., 2002; Regert, 2011) are formed by dehydration and ketonic decarboxylation of fatty acyl lipids (free fatty acids and TAGs) followed by a self- or cross-condensation, generated by an intensive heating of animal fats in ceramic vessels (> 300°C) (Fig. 2.12) (Evershed et al., 1995; 2002; Raven et al., 1997; Baeten et al., 2013). Thereby, the detection of these compounds, which have been widely described as epicuticular waxes components of higher plants (See chapter 2, section 3.2.5.1.1), must be interpreted carefully.

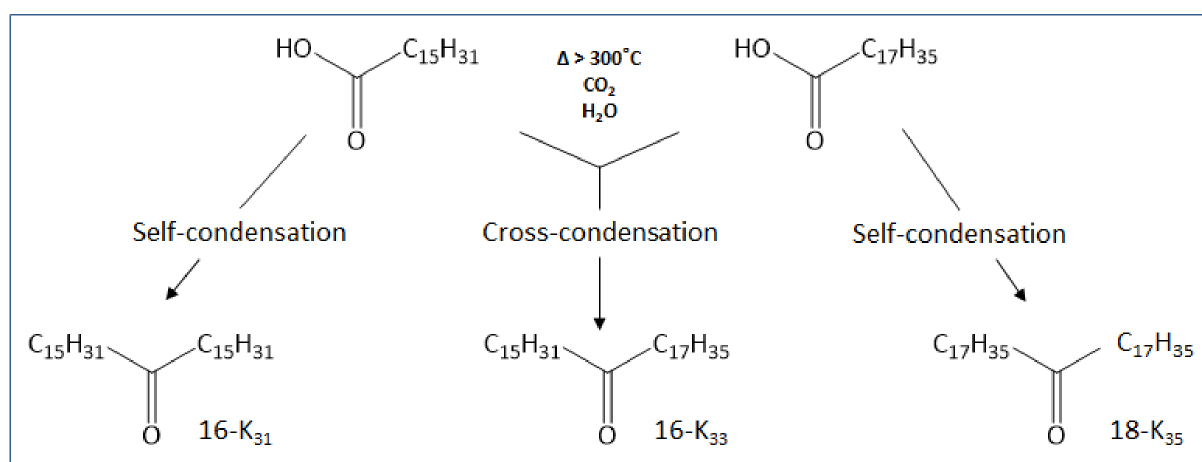

Figure 2.12 The formation process of mid-chain alkanones and secondary products induced by fatty acid pyrolysis (Raven et al., 1997).

Whilst animal adipose is less rich in mono and polyunsaturated fatty acids than aquatic and plant products, their presence in animal fats is likely to be converted into **ω-(o-alkylphenyl)alkanoic acids** (APAAs) when they are subjected to a heating treatment during cooking practices (Hansel et al., 2004; Cramp and Evershed, 2014). Although the unsaturated fatty acid with carbon-chain lengths with more than 20 carbons is part of lipid composition of animal fat adiposes, it however remains minor, whereas those containing 16 and 18 carbons are broadly majority (Morgan et al., 1992; Strazdina et al., 2012; 2015; Cramp and Evershed, 2014; Del Puerto et al., 2017). Thereby, the main compounds arising from the cooking of such commodities are APAAs C_{16} and C_{18}, which are also formed by heating aquatic and plant products (Evershed et al., 2008b; Cramp and Evershed, 2014).

As already described above (See chapter 2, section 3.2.1.2), the natural or anthropogenic degradation of cholesterol leads to the formation of a number of **cholesterol derivatives** (Evershed, 1993; Regert, 2011).

3.2.3. Dairy products

3.2.3.1. Biomarkers

The main components of fresh milk are the triacylglycerols (TAGs) with a number of acyl carbon ranging from **T_{26} to T_{54} holding fatty acids between C_4 and C_{20}** (Evershed, 1993; Dudd and Evershed, 1998; Dudd et al., 1998; Mirabaud et al., 2007). Fresh milk exhibits a **high proportion** of low molecular weight **TAGs ranging from T_{26} to T_{44}** (Dudd et al., 1998) (Fig. 2.13). Under good preservation conditions, this particular TAGs distribution enables to distinguish dairy fats from other sources having TAGs, such as animal fats and plant oils. However, rapid and preferential degradation of the lighter TAGs produces a very similar TAGs distribution as in animal adipose fats (Fig. 2.13) preventing the source identification of these compounds (Dudd and Evershed, 1998; Dudd et al., 1998).

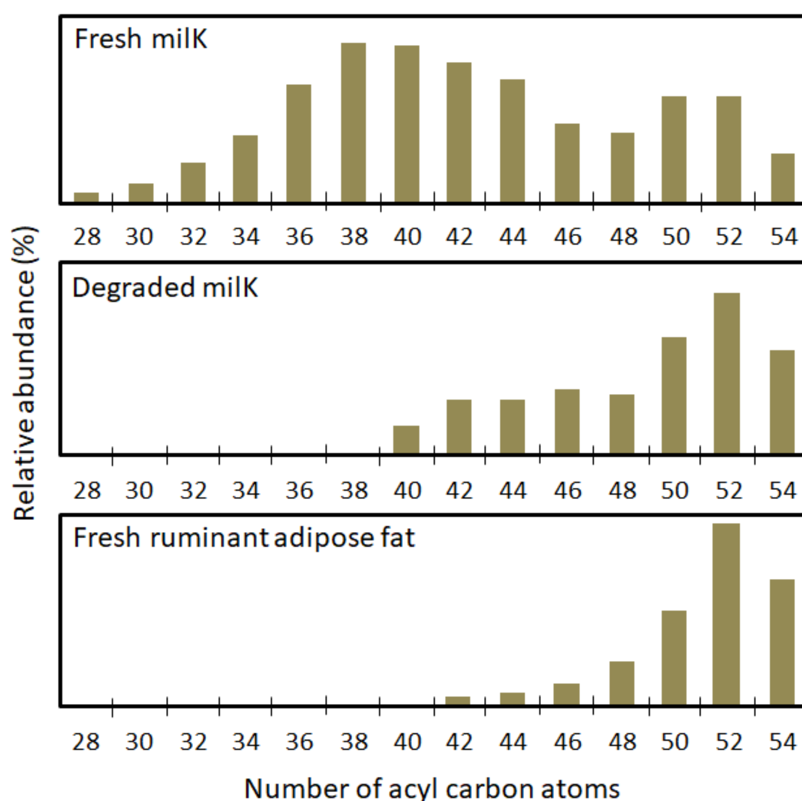

Figure 2.13 TAGs distribution profile of fresh milk, degraded milk absorbed in pottery after 90 days under oxic conditions and fresh ruminant adipose fat (after Dudd and Evershed, 1998; Dudd et al., 1998).

Furthermore, as mentioned previously, the use of other instrumentations (e.g. NanoESI MS and MS/MS or HPLC) allows to precisely determine the fatty acid distribution constituting the glycerol backbone (See chapter 2, section 3.2.2.1), making possible, based on modern references, to specify the origin of dairy products (e.g. cow, goat) (Mirabaud et al., 2007; Romanus et al., 2007; Garnier et al., 2009).

Milk fat, alike ruminant adipose fat, naturally contains **branched-chain fatty acids**, mainly synthesised in the rumen glut by bacterial action (Christie, 1981b; Dudd et al., 1998).

3.2.3.2. Degradation markers

Due to the hydrolysis of TAGs, free monounsaturated and saturated fatty acids are produced in dairy products, predominated by **$C_{14:0}$, $C_{16:0}$ and $C_{18:0}$** (Dudd et al., 1998; Roffet-Salque et al., 2017), producing also, just like animal adipose fats, **MAGs** and **DAGs** (See chapter 2, section 3.2.2.2). Owing to the fact that light TAGs are present in dairy products, **free short-chain fatty acids ($C_{4:0}$ to $C_{12:0}$)** are produced in high abundances in partially degraded milk products and could be used as an indicator of dairy products (Christie, 1989; Dudd et al., 1998; Copley et al., 2003). However, short-chain fatty acids are subjected to a higher degradation process, such as hydrolysis, than their long-chain counterparts, and are much more water-soluble and volatile (Dudd and Evershed, 1998; Evershed et al., 2002; Steele et al., 2010). These properties make them often undetectable in archaeological samples. Additionally, short-chain fatty acid detection could also result from the damaging cleavage of longer free fatty acid due to e.g. thermal or catalytic cracking, or by bacterial action (Shimoyama et al. 1993; Raven et al. 1997). Therefore, their detection in archaeological pottery should be treated with caution.

Besides, degradation experiments of milk undertaken by Dudd and her team have determined the presence of **ergosterol** in degraded milk. This compound, which does not occur in fresh milk, was suggested to result from the degradation process involving yeast and fungi action (Dudd et al., 1998; Isaksson et al., 2010; Weete et al., 2010).

Overall, the lipid profile of dairy products in archaeological contexts tends to be very close to the degraded ruminant profile. Thus, to date, the best method for their detection and to make them distinguishable to adipose fats, is to have recourse to single compound carbon isotopic analysis (See chapter 2, section 4.3).

3.2.4. Beehive products

3.2.4.1. Biomarkers

The main beehive products exploitable are honey and wax. Albeit honey was certainly used by prehistoric people as a rare source of sweetener, it is never found in archaeological context. Indeed, mainly made up of saccharides, this characteristic confers it a high hydrosolubility, which led to their leaching in archaeological context (McGovern et al., 2004; Roffet-Salque et al., 2015). Moreover, they are also quickly attacked by microorganisms (Drieu, 2017). However, beeswax is one of the best-preserved materials over time in ancient pots due to its hydrophobic nature (Roffet-Salque et al., 2015; Regert, 2017). This material is very well characterized by a specific molecular signature which can be used very reliable for its identification in archaeological ceramic vessels.

Fresh beeswax is made up of a complex mixture of aliphatic compounds mainly encompassing a series of **odd-chain alkanes** (C_{25}–C_{33}) with C_{27} as the major compounds; an **even-chain of free fatty acids** (C_{22}-C_{36}) of which lignoceric acid ($C_{24:0}$) prevail; and a **long-chain of palmitate esters** (**C_{40}-C_{52}**) including monoesters, diesters, hydroxymonoesters and hydroxy esters, with a prevalence of the ester containing 46 carbon atoms (Tulloch, 1971; Tulloch and Hoffman, 1972; Heron et al., 1994; Charters et al., 1995; Regert et al., 2001; Garnier et al., 2002; Evershed et al., 2003; Regert, 2009; Baeten et al., 2013; Roffet-Salque et al., 2015).

3.2.4.2. Degradation markers

Even though beeswax is a relatively stable natural product, it can endure several degradation processes. Indeed, chemical and physical mechanisms are involved in beeswax degradation such as sublimation, hydrolysis and oxidation (Fig. 2.14), occurring either by natural processes through time that take place after burial, or anthropogenic transformations such as heating (Heron et al., 1994; Charters et al., 1995; Evershed et al., 1997a; Regert et al., 2001).

First of all, a modification of the *n*-alkane distribution with a loss of the smallest chain *n*-alkanes has been noted, probably due to a sublimation process (Heron et al., 1994; Regert et al., 2001). The more volatile these compounds are, the more easily vaporised during either the heating of beeswax or simply in the case of samples conserved in a dry and warm context during several centuries or millennia. Intense heating of beeswax with direct contact with the open flame can even lead to the total loss of the *n*-alkanes (Heron et al., 1994).

While the profile of wax esters remains overall very stable over time (Evans and Heron 1993; Heron et al. 1994; Charters et al. 1995; Evershed et al. 1997; Regert et al. 1999), hydrolysis processes can occur and produce a slight modification of its profile. As *n*-alkanes, a preferential degradation of the lightest esters appears (mainly C_{40}, C_{42} and C_{44}) (Regert et al., 2001). Furthermore, the partial hydrolysis of these wax-esters generates the formation of a low amount of **even-numbered long-chain alcohols** (C_{26}-C_{34}) often detected in archaeological samples (Charters et al., 1995; Evershed et al., 1997a). Through the same process, **palmitic acid** ($C_{16:0}$), not present in fresh beeswax, can also be formed and detected in archaeological pots (Charters et al., 1995). However, its low melting point (62-64°C) (Regert et al., 2001), may explain its absence in some samples which could have been heated. Its absence could also result from a natural degradation of fatty acids (microbial action and groundwater leaching) (Evershed et al., 2003).

Finally, **phenolic compounds** are also formed during the degradation of the beeswax by both heating and oxidation processes (Regert et al., 2001). These organic matters probably derive from flavonoid compounds present in very low amounts in fresh beeswax (Tomás-Barberán et al., 1993).

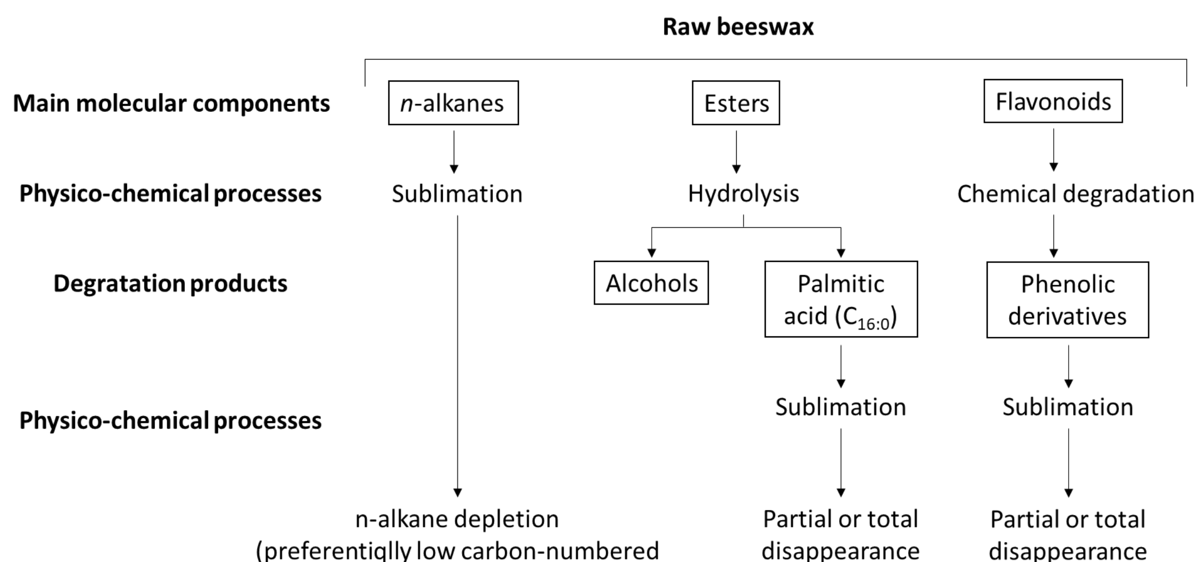

Figure 2.14 Diagram showing the different degradation mechanisms of beeswax (from Regert et al., 2001).

3.2.5. Plant products

3.2.5.1. Plant oils, plant waxes and cereal

3.2.5.1.1. Biomarkers

Plant oils refer to the "fat" constituent of plants. Thus, vegetable oils can be consumed either in the form of seeds or fruits, as it is, or extracted (Drieu, 2017). They are mainly constituted of **TAGs** (Gurr, 1980; Evershed, 1993; Dubois et al., 2007) but, as already mentioned previously, they are very sensitive to different degradation process (Dudd et al., 1998) and therefore not always detectable in archaeological contexts.

The primary function of ***plant waxes*** (also called epicular waxes), covering the leaf and the stem surface (Gülz, 1994; Dunne et al., 2016), is to isolate and protect leaf tissues from the atmosphere (Gülz, 1994; Diefendorf et al., 2011). The identification of such waxes informs about the processing of leafy vegetables in ancient pottery (Evershed et al., 1994). These epicular waxes are made up of a variety of highly complex mixtures of molecules (Kolattukudy, 1970; Gülz, 1994). The main components used for their identification in potsherds are the following:

- **Long-chain *n*-alkanes** with a carbon chain length between C_{21}–C_{37} one or two dominant (Baeten et al., 2013; Bush and McInerney, 2013). Plant waxes display a high **odd-to-even carbon number predominance** (Eglinton and Hamilton, 1963; 1967; Bush and McInerney, 2013). In order to evaluate the *n*-alkanes origin, **the carbon preference index** (**CPI**) can be calculated. This index reflects the predominant degree of *n*-alkanes with odd over even carbon number (between C_{20} and C_{34} alkanes) (Diefendorf et al., 2011; Bush and McInerney, 2013; Wang et al., 2017).

$$CPI = [\sum_{odd} (C_{21}\text{-}C_{33}) + \sum_{odd} (C_{23}\text{-}C_{25})]/[2\sum_{even} (C_{22}\text{-}C_{34})]$$

  Commonly used in geochemistry, it can also be used to evaluate whether *n*-alkanes found in ancient potsherds are originating from the processing of plants (Dunne et al., 2016). Thereby, a **CPI greater than 1** is usually used to indicate plant source.

  The odd *n*-alkane distribution profile can also be informative about the plant types. Indeed, the predominance of *n*-alkanes C_{27} and C_{29} appears to be indicative of woody plants, while C_{31} prevails in graminoids (grasses) (Bush and McInerney, 2013). Alike, enhanced amounts of mid-chain C_{23} and C_{25} *n*-alkanes (Ficken et al., 2000) seems to be characteristic of submerged and

floating-leaved aquatic plants, although some terrestrial plants also exhibit a similar profile, such as Sphagnum mosses (Bush and McInerney, 2013). Thereby, a proxy ratio P_{aq} has been proposed in order to make out submerged and floating macrophyte to the emerged macrophyte and terrestrial plants (Ficken et al., 2000) and can be employed to discriminate plant types in archaeological pots (Dunne et al., 2016).

$$P_{aq} = (C_{23} + C_{25})/ (C_{23} + C_{25} + C_{29} + C_{31})$$

A **P_{aq} < 0.1** points to a **terrestrial plant** input while a P_{aq} that lies **between 0.1–0.4** corresponds to **emergent macrophytes** and **0.4–1.0** to **submerged** or **floating macrophytes** (Ficken et al., 2000)

- **Mid-chain *n*-alkanone** with odd number of carbon and the carbonyl group (C=O) in the middle-position (Evershed et al., 1995; Raven et al., 1997; Baeten et al., 2013) occur naturally in higher plants and bacteria (Evershed et al., 1995; Raven et al., 1997). Specific symmetrical *n*-alkanones have been identified, such as nonacosan-15-one (K_{29}) derivating from Brassica sp. leaf waxes (including cabbage, broccoli, kale, or turnip leaves) (Evershed et al., 1991a; Evershed, 1993; Heron and Evershed, 1993; Baeten et al., 2013), and hentriacontan-16-one (K_{31}) from Allium porrum (leek) (Evershed et al., 1991b; Raven et al., 1997). However, as already mentioned previously *n*-alkanones can also result from intensive heating of animal adipose fats (> 300°C; See chapter 2, section 3.2.2.2) (Evershed et al., 1995; Raven et al., 1997; Baeten et al., 2013). Thereby, such findings in archaeological pottery must be interpreted with caution and need further clues to conclude their plant origin. Notwithstanding, the determination of ketone origin was attempted by Baeten and his co-workers (Baeten et al., 2013) by examining the carbon number distribution. Despite very interesting and promising results, this methodology was, to my knowledge, used just once hitherto and should be more often considered to resolve the ketone origin found in ancient ceramics.

- **Aliphatic long-chain wax esters** with mainly an **even number of carbon** compounds ranging from **W_{30} to W_{56}**. They are commonly composed of *n*-alkanols with carbon numbers ranging between C_{22} and C_{34}, and esterified to various carbon chain lengths of fatty acids from C_{12} to C_{34} (Gülz, 1994; Ribechini et al., 2008; Colombini and Modugno, 2009; Cramp et al., 2011). This particular wide range of fatty acids constituting the wax esters distinguishes it from those found in beeswax (almost entirely composed of $C_{16:0}$).

To date, the identification of ***cereals*** in archaeology pottery is an elusive task due to a lack of species-specific biomarkers. Nevertheless, some molecules can be used to characterise some grain plants. This is the case with the pentacyclic triterpene methyl ether (PTME), called **miliacin** (Fig. 2.15). This terpenoid is used as a tracer of **broomcorn millet** (*P. miliaceum*). It was initially used in sediment analysis to evidence millet cultivation (Bossard et al., 2013), but it has also been recently characterised in ceramic vessels (Heron et al., 2016a). Miliacin is synthesised by a wide range of plants but only occurs in very large amount in broomcorn millet (ca. 99%) compared to the other PTMEs (Bossard et al., 2013; Heron et al., 2016a). Therefore, when miliacin form the exclusive or at least the predominant PTME, it can be related to the processing of broomcorn millet in pots (Bossard et al., 2013).

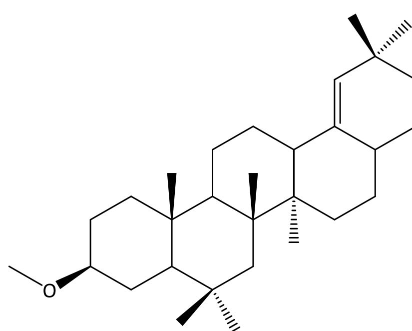

Figure 2.15 Miliacin molecule structure.

Another molecule family characteristic of cereals are **alkylresorcinols** (ARs) (Fig. 2.16). These compounds are molecular evidence of **wheat** and **rye** (Ross et al., 2003). The relative composition of AR homologues can also be informative. Notably, the **$C_{17:0}$/$C_{21:0}$ ratio** can be used to distinguish wheat and rye displaying a significantly different value (ca. 0.1 versus 1.0 respectively) (Chen et al., 2004; Ross, 2012; Colonese et al., 2017). The ARs distribution profile seems also able to discriminate different wheat species (Ziegler et al., 2015). These ARs have been identified in archaeological wooden containers (Colonese et al., 2017), proving their preservation over a long timescale. While these molecules are promising biomarkers, they have however not yet been evidenced in ancient pottery. A recent study (Hammann and Cramp, 2018) has shown that during the cooking of cereal in pottery only a low amount of cereal lipids is transferred into the ceramic matrix. Moreover, the ARs appear to be very sensitive to microbial degradation in anoxic conditions. This combination of circumstances can explain their low recovery in pots found in archaeological contexts.

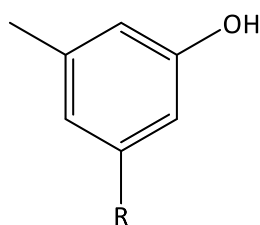

Figure 2.16 The basic structure of alkylresorcinols.

The presence of **phytosterols** (also called plant sterols), such as **stigmasterol**, **campesterol** and **β-sitosterol**, enables the characterisation of plants products in ceramic vessels (Evershed, 1993), although β-sitosterol also occurs in shellfish (Copeman and Parrish, 2004; Steele et al., 2010). Since phytosterols is a ubiquitous constituent of plant kingdoms their detection does not allow further plant species identification. Moreover, although rather resilient to microbial degradation (Hammann and Cramp, 2018), they are not often encountered in archaeological samples, probably due to their low abundance in plant tissue (Heron and Evershed, 1993) and their degradation during the pottery use life. Many other derived phenolic compounds that are only occurring in the plant kingdom, even though rarely found in archaeological contexts, such as **Tocochromanols** (e.g. γ-tocopherol) (Dörmann, 2007; Shoda et al., 2018), can be used to indicate the processing of plant in pots.

3.2.5.1.2. Degradation markers

Fatty acids constitute a large part of ***vegetable oil*** lipids, resulting from the hydrolysis process of the TAGs. The amount of unsaturated fatty acids is higher in plant oils than in terrestrial animal fat adipose which gives them a better fluidity (Heron and Evershed, 1993; Serpico and White, 2000; Romanus et al., 2008; Baeten et al., 2013; Dunne et al., 2016). The unsaturated fatty acid profile of partially degraded plant oils enable to separate some oil types such as oleic (e.g. olive, rapeseed), linoleic (e.g. cotton, soya, grape seed, sesame) and linolenic oils (e.g. linseed) displaying respectively a high amount of $C_{18:1}$, $C_{18:2}$ and $C_{18:3}$ (Dudd et al., 1998; Drieu, 2017). However, unsaturated fatty acids are more predisposed to oxidation processes, occurring both during the vessel use and burial (Heron and Evershed, 1993; Regert et al., 1998; Baeten et al., 2013), restricting their preservation in an archaeological context. Instead, saturated fatty acids less prone to degradation process may be used to discriminate animal fats to plant oils origin in archaeological samples. Indeed, vegetable oils exhibit a much higher proportion of palmitic acid than stearic acid compared to other fat origins (Copley et al., 2005b; Steele et al., 2010). Thereby, a high fatty acid ratio $\mathbf{C_{16:0}/C_{18:0}}$ value, **greater than 4**, indicates a plant origin (Dunne et al., 2016), although values comprise between 2 and 4 are also accepted to determine the processing of plants in pottery when associated with other evidence (Debono Spiteri, 2012; Taché and Craig, 2015). Alike it has been demonstrated that an unusual high abundance of **lauric**

acid ($C_{12:0}$) and **myristic acid** ($C_{14:0}$) along with a low content of palmitic and stearic acid could be indicative of **palm fruits** (Copley et al., 2001), whereas Eerkens (Eerkens, 2005) has also proposed the use of other fatty acid ratios to identify very general categories of foodstuffs. Notably, looking at **$C_{12:0}/C_{14:0}$ ratio against $C_{16:0}/C_{18:0}$** (Eerkens, 2005; Fig. 2.17).

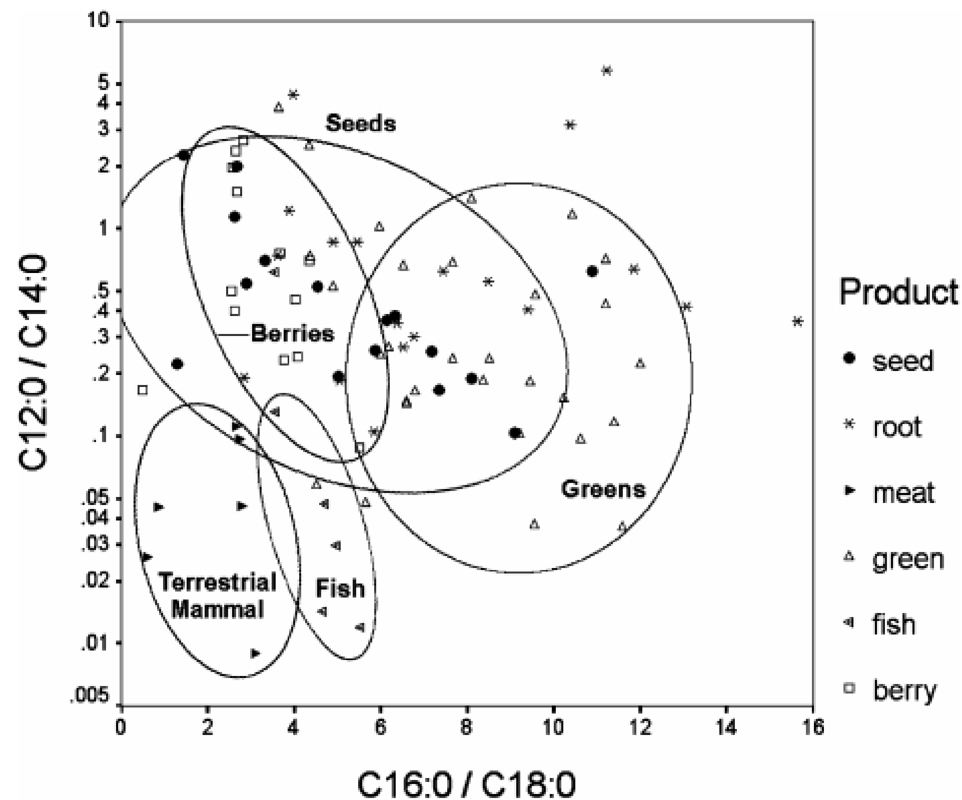

Figure 2.17 Plot of $C_{12:0}/C_{14:0}$ fatty acid ratio against $C_{16:0}/C_{18:0}$ ratio for modern food products enabling to separate plant and animal fatty acid origins (from Eerkens, 2005).

However, as already mentioned before, the preferential degradation and dissolution of the fatty acid according to their carbon-chain length (Dudd and Evershed, 1998; Evershed et al., 2002; Steele et al., 2010) could greatly affect fatty acid ratios, as well as the extraction protocol used to extract them from the pottery fabric (Steele et al., 2010). Additionally, the possibility of foodstuff mixtures in pottery cannot be ruled out, which could modify these ratios, especially as plants have much lower lipid amounts than other products (e.g. terrestrial mammals, aquatic animals) (Debono Spiteri, 2012). Therefore, with the exception of specific context (e.g. dry environments) (Romanus et al., 2008; Dunne et al., 2016) favourable to fatty acids conservation, this approach may be limited, and the identification of botanical oil sources elusive.

As stated above, unsaturated fatty acids are subject to oxidation leading to form various compounds such as **dicarboxylic acids** (also called diacids), hydro**xy** and **dihydroxy fatty acids** (Regert et al., 1998; Copley et al., 2005b; Regert, 2011). Similar to aquatic products (See chapter 2, section 3.2.1.2), some specific mono- and dihydroxy fatty acids formed from monounsaturated fatty acid (Cramp and Evershed, 2014), allow to precisely identify some vegetable oils. In fact, the position of hydroxyl substituents directly relates to the original position of the double bond in the precursor fatty acid leading thereby to the identification of some vegetable oils (Copley et al., 2005b):

- **Castor oil** by the detection of **9,12-dihydroxy-$C_{18:0}$** and/or **12-hydroxy-9-$C_{18:0}$**. Indeed, castor oil is abundant in of 12-hydroxy-$C_{18:1}$ (n-9) which can undergo acid catalysed hydration to produce 9,12-dihydroxy-$C_{18:1}$ acid (Colombini et al., 2005b; Copley et al., 2005b).
- **Oils from *Brassicaceae*** plant species, also called Cruciferae (e.g. radish, turnip, rape, mustard) (and other oil of the Brassicaceae) with the presence of **13,14-dihydroxy-$C_{22:0}$**, **11,12-dihydroxy-$C_{20:0}$** and **15,16-dihydroxy-$C_{24:0}$** formed from $C_{22:1}$ (n-13), $C_{20:1}$ (n-11) and $C_{24:1}$ (n-15) relatively abundant in Brassicaceae plants (Colombini et al., 2005b; Copley et al., 2005b; Romanus et al., 2008)

Similarly to aquatic products, plant oils are rich in mono and polyunsaturated fatty acids (Heron and Evershed, 1993) and their heating during cooking practices cause the formation of **ω-(o-alkylphenyl)alkanoic acids** (APAAs) (Hansel et al., 2004; Cramp and Evershed, 2014). Nevertheless, the majority of unsaturated fatty acids present in vegetable oils are made up of carbon chains of less than 20 carbon atoms. The main APAAs thus formed by vegetable oils are APAAs C_{16} and C_{18}, which are also formed by heating terrestrial and aquatic products (Evershed et al., 2008b; Cramp and Evershed, 2014) and therefore not very specific.

Comparable to beeswax, the wax esters can undergo hydrolysis and thus release free *n*-alkanols and fatty acid counterparts forming the wax esters, that is to say with carbon lengths ranging from C_{22} to C_{34} and C_{12} to C_{34}, respectively (See chapter 2, section 3.2.4.2; Kolattukudy, 1970; Evershed et al., 1994; 1997a; Baeten et al., 2013).

Finally, sterols may undergo structural alteration by different degradation processes. As a result, various **phytosterol derivatives** can be extracted from organic residues of archaeological pottery (Evershed, 1993).

3.2.5.2. Resins, wood tars and pitches

3.2.5.2.1. Biomarkers

Resins, wood tars and pitches are composed of a complex mixture of terpenoid compounds. In archaeological contexts, we generally focus on the di- and triterpenes. Indeed, the mono- and sesquiterpenes constitute the volatile fraction, responsible among other things for resin odour, and are most of the time no longer present in archaeological samples. The di- and triterpenoids are never jointly synthesized in the same resins (Evershed, 1993) and some of them very specific can be useful diagnostic molecular markers. If a number of plant resins can be identified (Serpico, 2000), the two resins that are mainly found in archaeological pottery are birch bark tar and coniferous (*Pinaceae*) resin or pitch (Heron et al., 1994; 2015; Mitkidou et al., 2008; Rageot, 2015). They could have been used for their sealing and adhesive characteristics either to waterproof the ceramic vessels or to repair them respectively (Charters et al., 1993a; Heron and Evershed, 1993; Colombini et al., 2005a; Jerković et al., 2011). However, the presence of such resin in pottery can also reflect other technical activities or culinary practices. Indeed, for the same characteristics mentioned before such materials were also used for caulking boats (Connan and Nissenbaum, 2003) or hafting differents stone and bone tools (Croft et al., 2018). Pottery could have, thus, served to prepare and store resin or any by-product (tar, pitch). The resin could have also been processed in pottery to either exploit its medicine, antiseptic properties (Colombini et al., 2005a) or simply directly or indirectly be part of the food consumption such as with pine needles used either as aromatic herbs to flavour different recipes or for beverages (Cumo, 2015).

Birch bark tar stems from heating treatment of birch bark, and can be characterised by some specific triterpene biomarkers of the **lupane family**, including betulone, **acid betulinic**, **betulin**, **lupeol** and **lupenone**, of which the three latter are majority (Cole et al., 1991; Regert, 1996; 2004; Colombini et al., 2009; Rageot, 2015). These components have not undergone any structural alteration and are found in varying amounts in birch bark tar.

Regarding fresh Pinaceae resin, **diterpene** biomarkers constitute the non-volatile fraction and include among others **pimaric**, **abietic** (Fig. 2.18) and **isopimaric acid** (Regert and Rolando, 2002; Colombini et al., 2005a; Modugno and Ribechini, 2009).

3.2.5.2.2. Degraded biomarkers

During the heating of the **birch bark**, its natural biomarkers endure some molecular transformations forming two characteristic anthropogenic degradation markers. Betulin is partly converted into lupa-2,20 (29) -dien-28-ol and lupeol is mainly converted into **lupa-2,20 (29) -diene** (Regert, 2004). These two constituents are the witness of pyrolytic treatment and inform about manufacturing processes. The **allobetul-2-ene** molecule reflects the birch bark tar natural alteration subjected to post-depositional decay processes and tells about conservation degree of such artefact.

The **natural transformation** of **Pinaceae resin biomarkers**, undergoing oxidation and dehydrogenation process during burial, forms some characteristic molecules such as dehydroabietic acid (DHA) and 7-oxo-DHA (Fig. 2.18) (Modugno and Ribechini, 2009). The **thermal treatment** of Pinaceae **resin** and **woods**, needed to produce tar and pitch, lead to the formation of various compounds (Fig. 2.18), of which the retene is the most frequently found in archaeological pottery samples (Serpico, 2000; Colombini et al., 2005a; Modugno and Ribechini, 2009). Similarly, the **methyl-dehydroabietate** compound is produced by methanolysis process only occurring during intensive heating of Pinaceae wood bark but is absent in heated resin (Modugno and Ribechini, 2009). All these four molecules are the main tracers, usually used for the identification of such resins in ancient pots. However, the detection of dehydroabietic and abietic acids in a wide range of cyanobacteria (Costa et al., 2016), as well as retene in marine-derived sediments (Naihuang et al., 1995), can call into question its use as plant biomarkers or at least their detection in ceramic vessels has to be treated with caution.

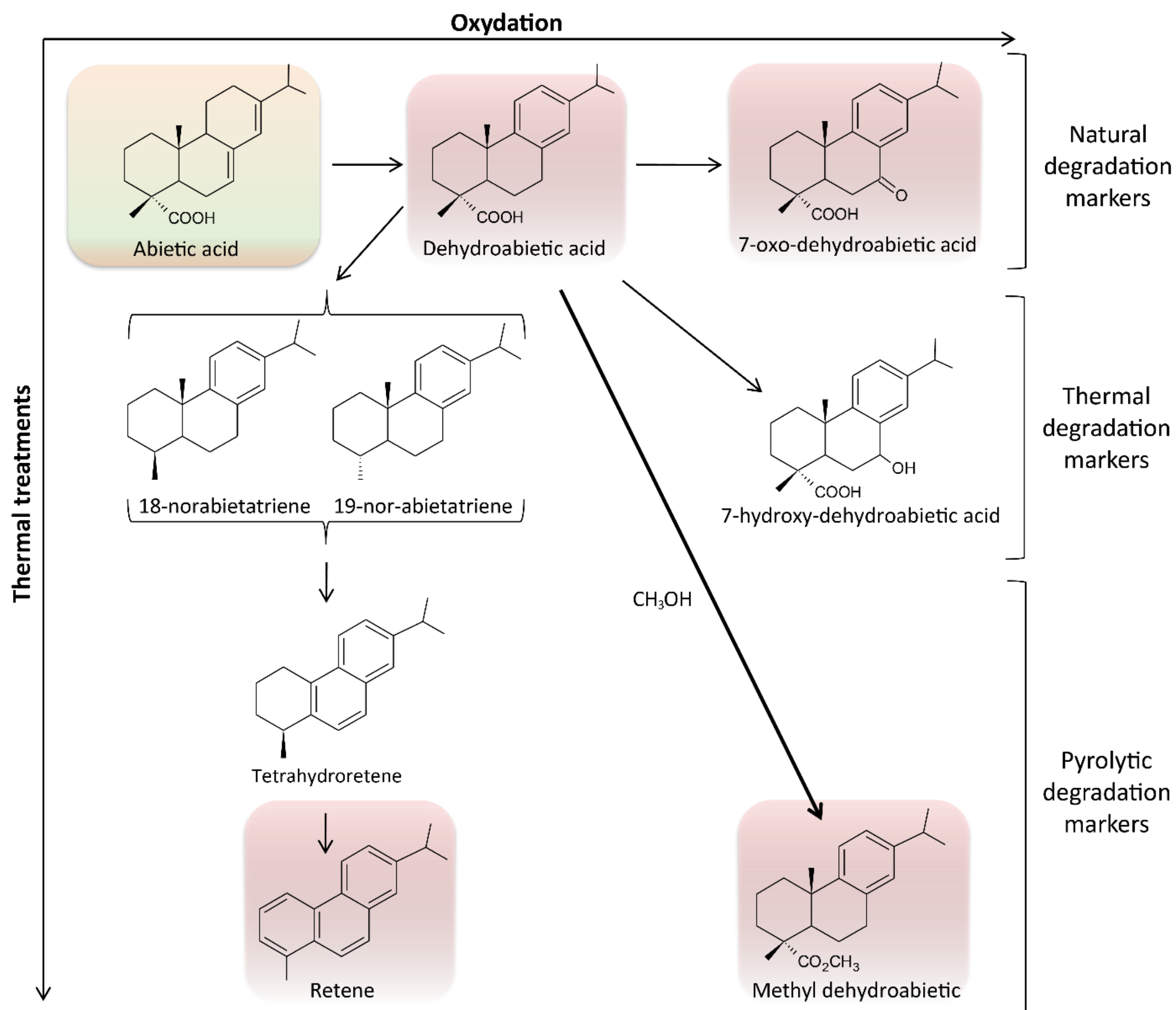

Figure 2.18 Degradation pathway of abietic acid one of the Pinaceae biomarker (in the green square) leading to the formation of a collection of derivatives arising from natural degradation or anthropogenic activities. Molecules in the red squares are the main tracers used for the identification of pine resins in ancient pots.

3.2.7. Bitumen

The formation of bitumen goes far back into geological time. These materials result from the accumulation of organic sediment matter produced from the degradation of terrestrial and marine plants combined with anaerobic and high-temperature conditions (Serpico, 2000). Its detection in pottery is mainly related to technical purposes such as waterproofing or to repair broken pottery (i.e. used as glue) (Knappett et al., 2005; Gregg et al., 2007; Connan et al., 2008; 2013), although it appears to have been also used to decorate some ceramic vessels (Connan et al., 2004). The recovery of thick bituminous crusts in some pottery might also suggests its storage and processing in such artefacts (Connan et al., 2013). The characteristic compounds of bitumen are *n*-alkanes, with odd and even number of carbon (notably pristane (C_{19}), phytane (C_{20}) and polycyclic compounds such as

phytosterols, steranes and terpanes (e.g. hopanes, moretanes) (Fig. 2.19 ; Serpico, 2000; Connan et al., 2004; 2008; 2013; Knappett et al., 2005; Gregg et al., 2007; Roffet-Salque et al., 2017). The *n*-alkane distribution can display different profiles according to the original deposit (Knappett et al., 2005). Similarly, the ratio of certain molecules (especially sterane/terpane) can markedly differ between different bitumen sources and are often used for the identification of origin deposits (Connan et al., 2004; 2008; 2013).

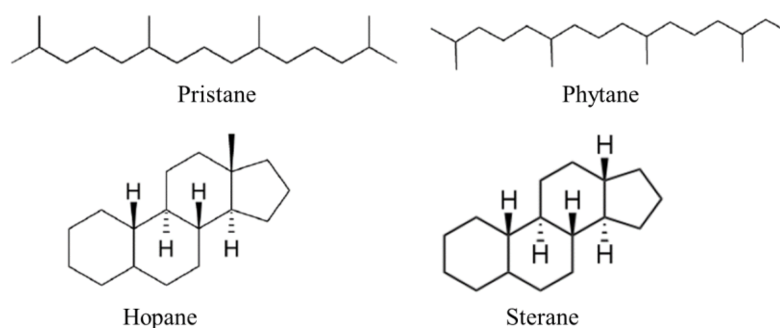

Figure 2.19 Structure of the main compounds found in bitumen.

4. Isotopic analysis

The use of lipid biomarkers absorbed in archaeological ceramic vessels has proved to be a powerful tool to define the nature, origin and transformations of organic residues, notably for the identification of e.g. aquatic resources, beeswax or even some specific resins and tars (Heron et al., 1994; 2015; Mitkidou et al., 2008; Cramp and Evershed, 2014; Roffet-Salque et al., 2015; Rageot, 2015). Nevertheless, sometimes this approach might be limited either in the case of poor preservation of organic matter or when the biomarkers mainly detected are not very specific because of their ubiquity, such as fatty acid and related acyl lipids (e.g. TAGs and its derivatives). Thereby, other approaches, based on **stable carbon and nitrogen isotopes ratios** (^{12}C, ^{13}C, ^{14}N and ^{15}N), have been developed and used as additional criteria for organic residue analysis in ancient pottery (DeNiro and Epstein, 1978; Hastorf and DeNiro, 1985; DeNiro, 1987).

4.1. Stable isotopes definition

Isotopes are **atoms** of the same chemical element exhibiting the same number of protons and electrons but exhibiting **different numbers of neutrons**. This difference in neutrons number results of a chemical element with different masses (Kendall and Doctor, 2003). Two types of isotopes are distinguished, **stable and radioactive**. On geologic timescales, radioactive isotopes are subjected to degradation producing other isotopes. In contrast, stable isotopes, as the name says, are stable over

time and do not form other isotopes (Kendall and Doctor, 2003). The difference of the masses between isotopes of the same element induces different reaction rates, leading to a change in the relative proportion of the isotopes in the reactants compared to the initial substrates (Evershed, 2009; Regert, 2011). This phenomenon is called **isotopic fractionation**. Thereby, the **isotopic ratios** can be measured in order to trace the origin of various natural substances.

By convention, the **isotopic ratios** are defined by the following formula (Deniro and Epstein, 1981; DeNiro, 1987; Evershed, 2009; Regert, 2011):

$$\delta^{E}X = (R_{sample} - R_{standard}) \times 1000/R_{standard}$$

Where the δ value is expressed as a per mille (‰), X is the involved analyte (e.g. C, N), E corresponds to the highest mass number of the two isotopes taken into consideration, and R_x is the ratio of heavy to light isotopes (e.g. $^{13}C/^{12}C$).

In the context of studies investigating ancient diet and organic residue analysis of pottery, we are interested in stable isotope ratios of carbon and nitrogen (^{12}C, ^{13}C, ^{14}N and ^{15}N).

4.2. Isotopic fractionation and signatures

Carbon and nitrogen analytes are incorporated into the living organisms through the diet. Their abundance in biological tissues is directly linked to the geological substrate, the food consumed, the biochemical pathways for foodstuff assimilation into biological tissues occurring with more or less important isotopic fractionation, as well as the **position within the trophic chain** (DeNiro, 1987). Thus, isotope composition measurements display strong diagnostic values and enable to define isotopically distinct commodity groups from plants to higher trophic level (DeNiro, 1987).

In the plant tissues, carbon isotope values depend on the photosynthetic pathway for the incorporation of atmospheric CO_2 (Hastorf and DeNiro, 1985; DeNiro, 1987; Evershed, 2009). Three different classes of plants have been defined:

- **C_3**: fix the CO_2 by Calvin-Benson cycle. These plants mainly grow in temperate environments, including amongst others: temperate shrub, trees and some grasses (Evershed, 2009; Regert, 2011).
- **C_4**: uses the Hatch-Slack cycle to incorporate the CO_2 in which the first reaction contains four carbon atoms instead of three as with C_3 plants (Regert, 2011). This category encompasses

herbaceous tropical, arid-adapted grasses (e.g. maize, sugarcane, and sorghum) (Evershed, 2009; Regert, 2011).

- **CAM** (Crassulacean acid metabolism): a hybrid of C_3 and C_4 metabolisms and concerns mostly succulent plants.

These different carbon assimilation mechanisms, commonly called **isotopic fractionation**, lead to product distinct stable isotope ratios between these three classes of plants, enabling their discrimination (Fig. 2.20; Evershed, 2009)

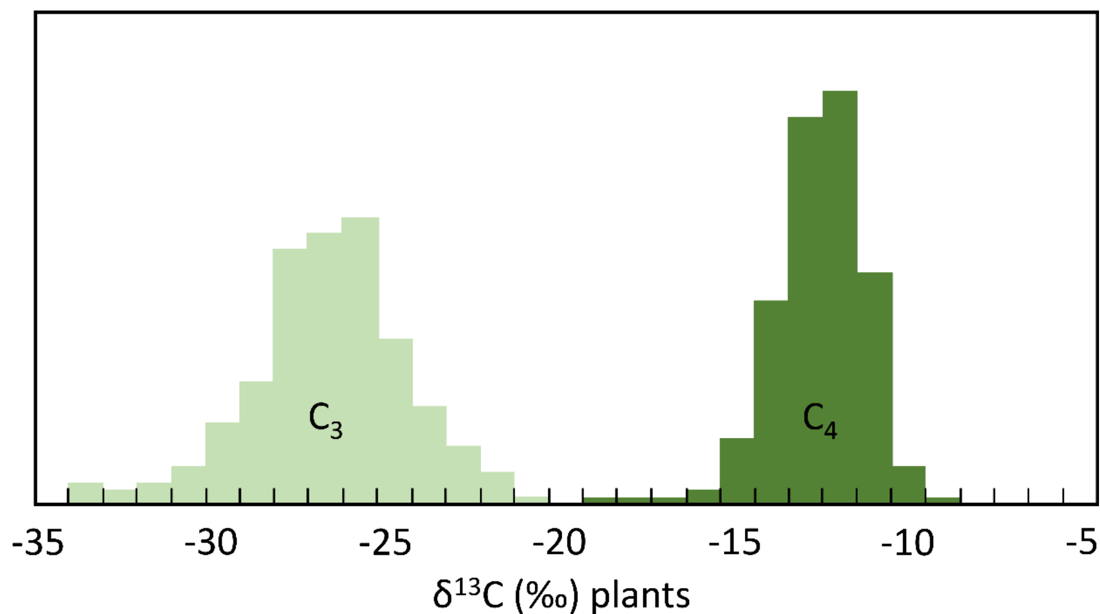

Figure 2.20 $\delta^{13}C$ values of modern terrestrial C_3 and C_4 plants (Evershed, 2009).

The nitrogen isotopes found in plants originate from the nitrate present in the fertile soils (Garten, 1993), and from the atmospheric nitrogen for plants able to fix it (e.g. legumes). As plants do not significantly fractionate nitrogen isotopes, their $\delta^{15}N$ value directly reflects the $\delta^{15}N$ of their source (Delwiche and Steyn, 1970; Handley and Raven, 1992).

In animal tissues, the fractionation of carbon isotopes is very low between the consumer and its diet (ca. 1-2%; DeNiro and Epstein, 1978). Thereby, the $\delta^{13}C$ value of animals reflects the ingested plant values at the start of the food web (Regert, 2011). However, the $\delta^{15}N$ value varies according to the trophic level with an increase of ca. +3% at every step in the food chain (Deniro and Epstein, 1981; DeNiro, 1987; Katzenberg, 2008; Evershed, 2009). Thereby, for instance, $\delta^{15}N$ values of herbivore

tissues are more positive than those of the consumed plants and carnivore tissues again more enriched than herbivores.

Whilst the major source of nitrogen in terrestrial soils is from atmosphere, the main source for aquatic ecosystems is inorganic nitrate. These two sources of stable nitrogen isotope display important differences in stable nitrogen isotope ($^{15}N/^{14}N$) compositions. The inorganic nitrate is enriched in ^{15}N (Sweeney et al., 1978) leading to a trophic level effect, giving fish a higher $\delta^{15}N$ value than terrestrial organisms (Katzenberg, 2008; Evershed, 2009). The isotopic segregation between marine and freshwater organisms can then be done by using the stable carbon isotope (Hobson, 1999; Robson et al., 2016). Although freshwater fish can exhibit a wide range of $\delta^{13}C$ according to their various living environments, it is accepted that they overall display similar values to terrestrial C_3-consuming organisms (Katzenberg, 2008). Indeed, $\delta^{13}C$ of seston[1] tends to gradually increase with the salinity of the water (Gladyshev, 2009) implying higher $\delta^{13}C$ values in marine environments and organisms, than in freshwater ones (Hobson, 1999; Robson et al., 2016; Fig. 2.21).

[1] Seston: also called particulate organic matter (POM), it describes all mineral or organic particles and very small organisms suspended in water.

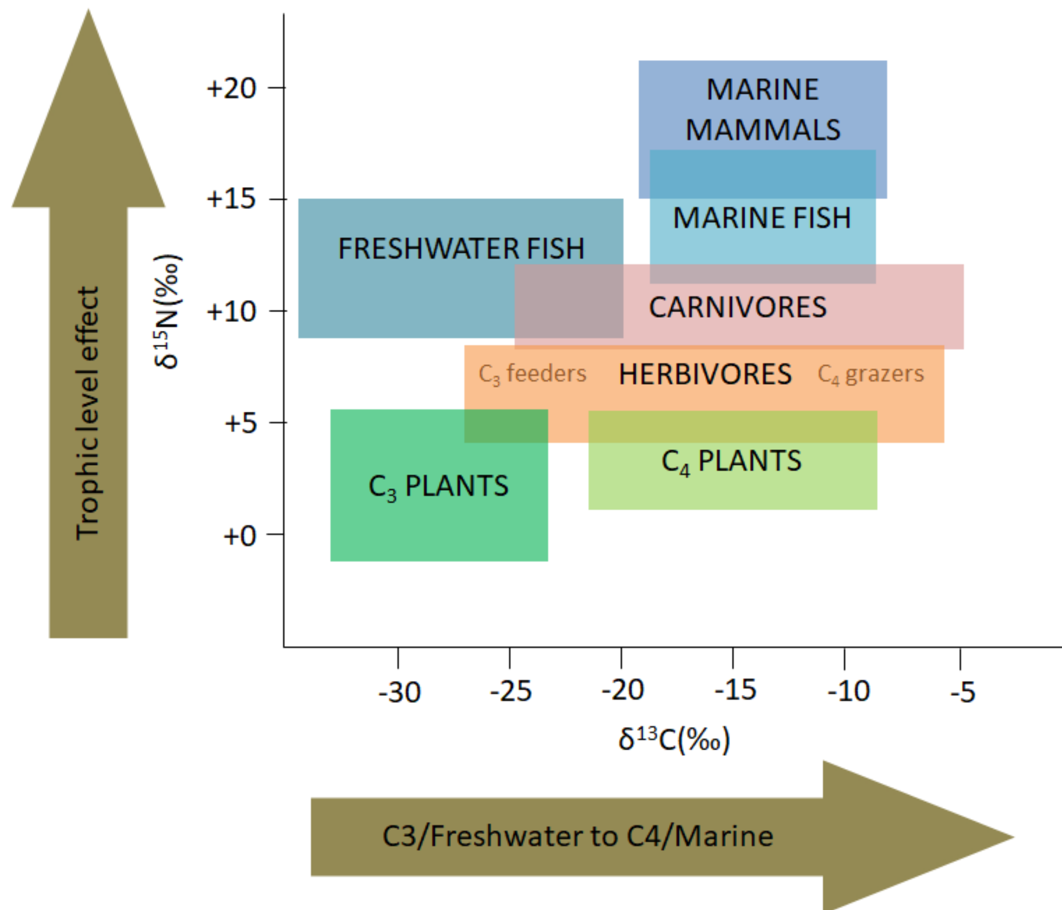

Figure 2.21 Overview of carbon and nitrogen isotopic values (bulk) of terrestrial and aquatic food webs (adapted and supplemented from Evershed, 2009; Robson et al., 2016).

Bulk carbon and nitrogen isotopic analysis have been first employed to study the pottery function (Hastorf and DeNiro, 1985; DeNiro, 1987). Although the method is still used to isotopically characterise charred residues found in archaeological pots, its diagnostic values are limited, and it is mainly carried out to provide an overall overview of foodstuffs preserved and formulate initial assumptions. Indeed, such analyses are commonly undertaken on bone remains for studying ancient diet and provide relatively reliable results but because it only focuses on the protein collagen. In contrast, organic remains preserved in pottery comprise of a more complex mixture of compounds, including lipids, proteins, and polysaccharides. Bulk analysis of such samples gives mean values for all these compounds and thereby involves many uncertainties restricting its utility (Evershed, 2009; Regert, 2011).

4.3. Compound-specific stable isotope analysis

The major advance for the isotopic analysis of organic residues in pottery was the advent of gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) in the 1970s (Matthews and Hayes, 1978). This technique allows to access the $^{13}C/^{12}C$ ratios from individual molecules,

separated beforehand by Gas Chromatography-Mass Spectrometry from the complex mixture and offers a higher specificity since the molecules can be directly related to their isotope values. The first application in archaeology field was undertaken in the 1990s (Evershed et al., 1994; 1997b) giving promising results and was thereafter adopted and used routinely by several teams to study organic residues preserved in ancient ceramic vessels.

Although a number of individual compounds can be isotopically analysed with this technique (e.g. *n*-alkanes, *n*-alkanol, *n*-alkanone, sterols) (Evershed et al., 1994; 1995; 1997a; 2003), the isotopic analysis studies in the context of archaeological potsherds have been mainly focused on molecules, that is palmitic ($C_{16:0}$) and stearic acid ($C_{18:0}$). In fact, these fatty acids present the advantage that they are both ubiquitous in living beings and rather stable over time. They are thus the most commonly compounds observed in archaeological pottery (Evershed, 2009) and will be the main subject of the following discussion.

Thereby, based on modern reference materials, and by plotting the $\delta^{13}C$ values of $C_{16:0}$ against $C_{18:0}$, on a chart, it is possible to discriminate different commodity categories processed in the pots (Fig.2.22. a and b). Ellipses, created through statistical processing, allow to define isotopic value areas for each reference material category (Copley et al., 2003). After having applied a correction for adjusting the data for the post-industrial revolution effects and make them thus comparable with archaeological times (Evershed et al., 1997b; Schmitt et al., 2012; Hellevang and Aagaard, 2015; Lucquin et al., 2016a), these references can be compared to the archaeological samples to characterise organic residues.

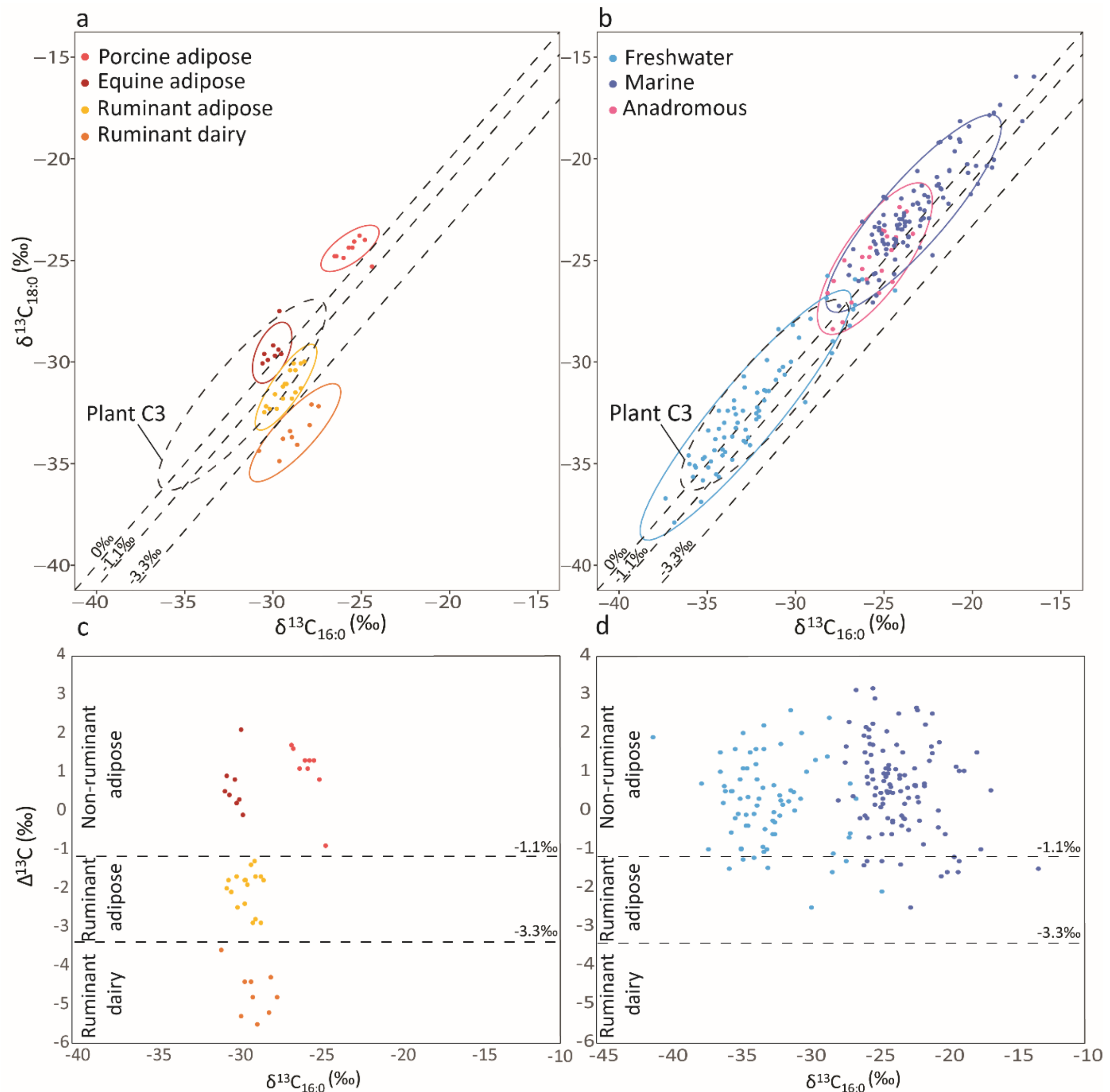

Figure 2.22 δ^{13}C values of individual $C_{16:0}$ and $C_{18:0}$ alkanoic acids extracted from authentic reference terrestrial (a) and aquatic (b) fats shown with ellipses. (c) and (d) represent the Δ^{13}C ($\delta^{13}C_{18:0}$–$\delta^{13}C_{16:0}$) values of the same references, respectively, plotted against their $\delta^{13}C_{16:0}$ values. The terrestrial animals were raised on pure C_3 diets. The isotope values used to make these plots were found in (Dudd, 1999; Spangenberg and Ogrinc, 2001; Outram et al., 2009; Craig et al., 2011; 2013; Cramp and Evershed, 2014; Horiuchi et al., 2015; Choy et al., 2016; Lucquin et al., 2016a; Pääkkönen et al., 2016). The reference data used to produce this figure are available in appendix 2.

One of the main applications of isotope analysis of $C_{16:0}$ and $C_{18:0}$ is to distinguish **ruminant adipose** (e.g. sheep, goats, cattle) from other **terrestrial non-ruminant sources** (e.g. porcine, horses) and it has been the subject of the first studies at the end of 1990s/beginning of 2000s to identify them in ancient pots (Evershed et al., 1997b; 2002; Dudd and Evershed, 1998; Dudd, 1999; Dudd et al., 1999; Mottram et al., 1999; Copley et al., 2003). In fact, whilst ruminants and non-ruminants, both synthesize their

adipose fats via novo synthesis, the incorporation of plant lipids into their tissues slightly differs owing to their specific digestive systems, inducing a clear distinction of the d^{13}C values between them. Indeed, in ruminants the biosynthesis of fatty acids use only the carbon from acetates (derived mainly from dietary carbohydrates) in their feeding, whereas non-ruminants, such as pigs, produce their fatty acids from acetate and glucose from their food (Dudd, 1999; Spangenberg et al., 2006; Regert, 2011). Yet, the glucose is more enriched in ^{13}C than acetate ($\delta^{13}C_{acetate}<\delta^{13}C_{glucose}$) (Dudd, 1999; Spangenberg et al., 2006; Regert, 2011). Therefore, ruminant fats display significant lower carbon isotopic values than non-ruminant fats, allowing distinctions to be drawn between fats from non-ruminant (e.g. porcine) and ruminant (e.g. ovine or bovine) origins (Fig. 2.22c). Furthermore, the range of δ^{13}C values in porcine adipose fats can be slightly greater than for ruminants reflecting a diet usually more diverse for the former (Dudd, 1999). Additionally, among these studies, S.N. Dudd and team (Dudd, 1999; Dudd et al., 1999) have also pointed out that equine adipose fats stand out isotopically. They are less enriched in ^{13}C than the non-ruminant pigs and can be distinguished to ruminant and porcine fat sources. This latter finding is of great interest to the study of pottery function in the Eurasian steppe where these animals were frequently hunted (Mileto et al., 2017). The database was thereafter supplemented to further investigate the processing of horse meat in pots by ancient population (Outram et al., 2009; 2011; 2012).

Another major category of fats, being of considerable importance to grasp the question of the domestication process, are **dairy products**. Ruminant dairy fats were the first subject of research and have revealed a characteristic isotopic signature, separating them from ruminant adipose fats (Dudd and Evershed, 1998; Copley et al., 2003). The short fatty acids ($C_{4:0}$ to $C_{16:0}$) in milk ruminant is mainly formed, in the mammary gland, from acetate of carbohydrates found in the diet (Dudd, 1999). However, mammary glands are unable to synthesize the $C_{18:0}$ fatty acid. Thus, the presence of this latter in milk arises from distinct biochemical pathways (Fig. 2.23). A part of which (60%) derives from bacterial reduction (biohydrogenation), occurring in the rumen, of unsaturated fatty acids ($C_{18:2}$ and $C_{18:3}$) swallowed when feeding. The other part (40%) is obtained via remobilisation of stearic acid found in adipose fats. Thus, the isotopic value of $C_{18:0}$ in milk is similar to fatty acid of the diet, whereas $C_{16:0}$ exhibit values near to carbohydrates. Consequently, the $\delta^{13}C_{18:0}$ of ruminant dairies is substantially more negative than ruminant adipose fats (Dudd and Evershed, 1998; Copley et al., 2003; Spangenberg et al., 2006; Evershed, 2009).

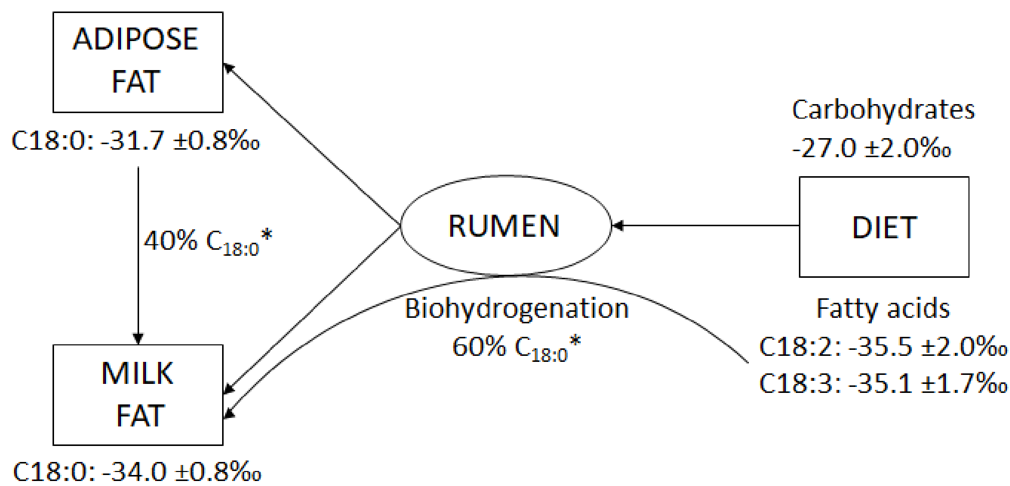

Figure 2.23 Diagram showing the routing of dietary fatty acids and carbohydrates in the rumen, adipose tissue and mammary gland of the ruminant animal (Copley et al., 2003).

The question of horse domestication in Western Eurasian steppe (e.g. Kazakhstan and North-Pontic region) was also raised and were revealed through isotopic analyses measuring hydrogen isotopes, incorporated within animal tissues via plant consumption and water intake (Outram et al., 2009; Mileto et al., 2017). In fact, the deuterium isotopic value is directly linked to the seasonality and rainfall. Thereby, as mares produce milk only during summertime, this latter displays summer environmental isotopic signature whereas adipose fats exhibit average values reflecting the year-round diet.

Regarding aquatic resources, although there is a great variety in the isotopic values range, mainly due to the position in the food web and the diversity of aquatic habitats, $\delta^{13}C$ values of palmitic and stearic fatty acids allow to distinguish species from marine or freshwater ecosystems (Cramp and Evershed, 2014; Roffet-Salque et al., 2017). Indeed, as previously stated, $\delta^{13}C$ gradually rise with the water salinity (Gladyshev, 2009) directly impacting the $\delta^{13}C$ of the whole organisms living in these distinctive habitats. Thereby, marine organisms show more positive $\delta^{13}C$ values easily discernible to freshwater organisms (Hobson, 1999; Robson et al., 2016). There are also species that live in intermediate environments, such as brackish fish, or alternatively in both ecosystems, like anadromous (e.g. salmon, sturgeon) and catadromous (e.g. eel) fish. Anadromous fish live mostly in the marine environment but were born in freshwater environment. Every year they migrate upriver to spawn. This process works vice versa for catadromous fish. Overall, they exhibit, to a certain extent, intermediate isotope values as illustrated in figure 2.22.b. The $\delta^{13}C$ values may vary significantly between individuals of the same category since they are directly correlating with fish age at the time of its catch (Doucett et al., 1999). Indeed, for instance juvenile anadromous fish have not yet migrated to the sea will display more negative $\delta^{13}C$ values, similar to freshwater environment one where they were spawned.

$\Delta^{13}C$, corresponding to the differences of isotopic values between stearic and palmitic acid ($\delta^{13}C_{18:0}$–$\delta^{13}C_{16:0}$), can also be calculated to further discriminate non-ruminant and ruminant adipose fats, and ruminant dairy products. Whilst $\delta^{13}C$ of individual fatty acids are influenced by environmental and food conditions, $\Delta^{13}C$ values, however, gets rid of all these variabilities (Evershed, 2009). The isotopic fractionation of $C_{16:0}$ and $C_{18:0}$ appears to be similar in animal tissues (Drieu, 2017). Thereby, the $\Delta^{13}C$ values remain stable irrespective of the diet, only reflecting the distinct biosynthetic pathways, and thus provides a reliable means of discriminating these fat sources (Copley, 2002; Copley et al., 2005c; Craig et al., 2005a; 2005b; 2012; Šoberl et al., 2008; Evershed, 2009; Salque et al., 2012; Cramp and Evershed, 2014) :

- $\Delta^{13}C$ values **higher than -1.1‰** are associated with **non-ruminant adipose**, encompassing terrestrial non-ruminants, plants and aquatic organisms.
- $\Delta^{13}C$ values **between -1.1‰ and -3.3‰** are consistent with **ruminant adiposes**.
- $\Delta^{13}C$ **lower than -3.3%** indicates **ruminant dairy products**.

Nevertheless, although these values are widely used, it appears that they are not really adapted for animals raised in the Mediterranee region and Africa. Thus, some researchers working on materials from these regions employed $\Delta^{13}C$ values 0.3‰ and -3.1‰ to distinguish non-ruminant/ruminant fats and ruminant fats/ruminant dairy respectively (Debono Spiteri, 2012; Dunne et al., 2012; Nieuwenhuyse et al., 2015; Debono Spiteri et al., 2016). Moreover, these values have been obtained from domesticated animal tissues. Yet, ^{13}C of wild ruminant adipose carcasses tend to be slightly more depleted and displayed a wider range of $\Delta^{13}C$ from -2.7‰ to -4.3‰ (Craig et al., 2012), falling between domesticated ruminant fats and dairy products, which may have interpretative implications.

These results are usually illustrated by using another graphical representation, confronting $\delta^{13}C_{16:0}$ against $\Delta^{13}C$ (Fig. 2.22. C and d). This graph enables to both characterise the commodity sources exempted of environmental/diet influences on the y-axis, while the x-axis gives information about diets, with a low $\delta^{13}C_{16:0}$ corresponding to C_3 diet or freshwater environment while a more positive $\delta^{13}C_{16:0}$ is consistent with C_4 diet or marine organisms (Copley et al., 2003; Craig et al., 2007; Evershed et al., 2008a; Evershed, 2009; Cramp and Evershed, 2014).

Isotopic analysis proved to be a powerful tool to identify the sources of lipids in archaeological pots. It allows, amongst others, to discriminate different terrestrial animal fat sources (ruminant fats and dairy, porcine, equine), as well as marine and freshwater organisms; information that molecular

analysis alone does not provide. Similarly, the isotopic values of ruminant adipose and dairy products are relatively well distinguishable from aquatic resources (Figure 2.22). Nevertheless, the method becomes much more challenging when attempting the distinction of adipose fats of non-ruminant and aquatic. Indeed, the former, such as porcine and equine, fall within isotope values range of marine and freshwater respectively (Fig. 22.2.a and b). Same observations are made when looking at isotopic values of plants. In fact, for instance, the isotopic values of C_3 plants (Spangenberg and Ogrinc, 2001; Horiuchi et al., 2015; Lucquin et al., 2016a) widely overlap the freshwater range, including consequently the equine area, as well as cover part of ruminant adipose fats (Fig. 22.2.a and b).

Furthermore, the isotopic analysis is not efficient for the detection of all the commodities commonly found in potsherds such as resins and beeswax. Some isotopic analyses have been undertaken on hydrocarbons and terpenes encountered in resins, which allowed to distinguish two resin types (Pines and pistacia) (Stern et al., 2008). However, this requires determining bulk carbon, hydrogen and oxygen isotope ratios. Regarding beehive products, $\delta^{13}C$ measures of *n*-alkanols, *n*-alkanes and palmitic acid from modern beeswax have been generated (Evershed et al., 1997a; 2003). Nevertheless, this method of identification has not been extensively used since this product is already well identifiable by its molecular signature. Finally, the hydrogen and carbon isotopic measurements undertaken on bitumen have also been used sometimes to pinpoint the geographical origin of the deposit. However, the molecule ratio calculation turns out to be much more accurate to provide such information (Gregg et al., 2007; Connan et al., 2008; 2013).

This emphasizes the importance to combine isotopic and molecular data, but also stresses to integrate the archaeological contextual information. The identification of specific (bio)markers (e.g. phytosterols, *n*-alkanes, *n*-alkanols characteristic of plants; isoprenoid acids and ω-(o-alkylphenyl)alkanoic acids with more than 18 carbons for aquatic products), is a key point to assign the isotopic results to the original fat source processed in ancient pots. On the other hand, certain archaeological contexts are not conducive to the preservation of organic remains. It has, therefore, to be borne in mind that the failure to detect some specific markers may be the result of their degradation. A detailed study of the archaeological context (e.g. faunal remains, carpology) and the general context (e.g. environment) is fundamental to guide the interpretation of the results and make them as consistent as possible.

In addition, in some instances, isotopic values do not match with any of reference data, but rather exhibit intermediate values and plot between the isotopic areas defined for each commodity group.

This most likely reflects a mixture of various foodstuffs processed in the same pot. To address this issue, statistical computations, simulating different mixing, have been undertaken. Thus, hypothetical mixing lines, between the mean values of each category, have emerged and have been compared with sample values in order to provide information on theoretical foodstuffs combination (Evershed et al., 2002; Copley et al., 2005a; Mukherjee et al., 2007; Evershed, 2008b; Craig et al., 2011; Cramp et al., 2015). Recently, other statistical tools have been set up and applied on organic residues found in pottery using Bayesian model (e.g. Food Reconstruction Using Isotopic Transferred Signals (FRUITS)), in order to determine the proportional contribution of different foodstuffs in a mixture of different food compositions (Fernandes et al., 2018), or to examine how isotope values respond to different mixture (Hendy et al., 2018), supplying interesting results.

Finally, it is important to underscore the importance of the use of appropriate reference values to compare with the archaeological corpus. Indeed, numerous isotopic analyses undertaken on modern materials have allowed to constitute a substantial reference database whether for aquatic products, encompassing freshwater and marine ecosystems, (Dudd, 1999; Outram et al., 2009; Craig et al., 2011; 2013; Debono Spiteri, 2012; Cramp and Evershed, 2014; Horiuchi et al., 2015; Choy et al., 2016; Lucquin et al., 2016a; Pääkkönen et al., 2016), or wild or domestic ruminant and non-ruminant adipose fats and dairy products (Evershed et al., 1997b; 2002; Dudd, 1999; Spangenberg et al., 2006; Gregg et al., 2009; Outram et al., 2009; Craig et al., 2012; Debono Spiteri, 2012; Dunne et al., 2012; Taché and Craig, 2015; Carrer et al., 2016). However as the $\delta^{13}C$ values is affected by a range of environmental variables depending upon climatic influences and the availability of plant types (e.g. C_3, C_4, etc), it is fundamental to compare the archaeological data with references generated from modern materials collected from the same investigated region, or at least displaying a similar environmental context. Otherwise, if such a database is not available it will be necessary to establish reference materials for the region of interest.

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Chapter 3

Resource-Processing, Early Pottery and the Emergence of Kitoi Culture in Cis Baikal: Insights from Lipid Residue Analysis of an Early Neolithic Ceramic Assemblage from the Gorelyi Les Habitation Site, Eastern Siberia

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Abstract: In the early Holocene, Mesolithic hunter-gatherer communities inhabiting the Cis Baikal region of Eastern Siberia were participating in a series of important cultural changes. These included the establishment of large cemeteries in the Angara Valley and on the Southwest shores of Lake Baikal, culminating in the formation of the distinctive Early Neolithic Kitoi cultural pattern ca. 7560 cal BP. Around the same time, the appearance of pottery in a few Kitoi graves and at some contemporary habitation sites marks the formal transition to the Early Neolithic. Little is known about how this early pottery was used, and why it was adopted into the region, though links to the intensification of fishing have occasionally been postulated. In this paper we present lipid-residue analysis of the oldest and relatively well-dated pottery in the Cis-Baikal region, which was recovered from the Gorelyi Les habitation site. Our results indicate that the pots had been used to process a broad spectrum of food resources, including ruminants, fish and plants, and possibly resin and other by-products derived from pine trees. These results suggest that the vessels were being used as general-purpose containers, and

not as specialized vessels for processing aquatic resources. We conclude that there is scope for a much larger-scale investigation of diversity and change in prehistoric pottery use in Cis-Baikal, and that this research would improve current understandings of the diet, health and subsistence strategies of the Kitoi and other prehistoric populations.

Keywords: Holocene hunter-gatherers; early pottery; Early Neolithic; Cis Baikal; Siberia; Kitoi Culture; lipid residue analysis.

1. Introduction: hunters in transition

The Cis Baikal region of Eastern Siberia includes the Angara Valley, the western shores of Lake Baikal, and the Upper Lena River. In the early Holocene, this region was the scene of several major cultural transitions. While there is general continuity in bone and stone tool-making traditions throughout the Mesolithic, the transition from the Early Mesolithic (10,000-8630 cal BP) to the Late Mesolithic (8630-7560 cal BP) is marked by the emergence of mortuary practices, including isolated burials of individuals, and rarely, a few small cemeteries. Evidence from these burials and from faunal evidence recovered from habitation sites suggest that aquatic resources contributingto Late Mesolithic diets (Weber, in prep; Weber et al., in prep).

At the end of the Late Mesolithic, during a period of further climatic warming and the expansion of forest cover, further changes gathered pace (White and Bush, 2010; Weber, in prep). The small mobile groups of the Mesolithic appear to coalesce into larger social units, leading to the rather sudden formation of large cemeteries, especially along the Angara River and in Southwest Baikal (Weber, *In prep*). These complexes contain highly distinctive mortuary traditions, starting with the “Kitoi” (Bazaliiskii, 2010), and have since been subject to comprehensive radiocarbon dating, including corrections for freshwater reservoir effects (Bronk Ramsey et al., 2014; Schulting et al., 2014; 2015; Nomokonova et al., 2015; Weber et al., 2016a; 2016b; Weber et al., in prep). The “classic” Kitoi cemeteries include Shamanka II at the head of the Kultuk Bay, as well as other large burial grounds located at the mouths of the main tributaries of the Angara River, including Kitoi (Kitoi River) and Lokomotiv (Irkut River) or smaller ones such as Ust’ Belaia and Galashikha (Belaia River) (Fig. 3.1).

Figure 3.1 Location map of Cis Baikal, Eastern Siberia, showing the core areas of the Early Neolithic Kitoi Culture along the Angara River and in SW Baikal. Habitation sites mentioned in the text are Gorelyi Les located on the Belaia River. Dozens of other Kitoi habitation sites and several small cemeteries are located across the region, predominantly along riverbanks and lake edges (not shown).

The Kitoi mortuary protocol is defined by copious use of red ochre, and a large number of other diagnostic traits, including distinctive composite fishhooks (Weber, in prep). More generally, analysis of grave goods from Shamanka II indicates that Kitoi populations appear to have acquired several important new technologies, including powerful composite hunting bows, and a range of new fishing implements that supported exploitation of aquatic resources (Weber, in prep). Notable disparities in the richness and quantity of Kitoi grave goods may point to emerging social differentiation (Weber et al., 2002; Weber and Bettinger, 2010), while the deeper continuity in other bone and lithic artefact

types suggests that it was essentially local Mesolithic populations who were central to these developments (Weber, 1995; Saveleev, 2001; McKenzie 2009).

It is around this time that pottery makes its first appearance in Cis-Baikal, with isolated finds in a few Kitoi graves, and at some contemporaneous habitation sites. In Russian archaeology, this marks the formal shift from the aceramic Mesolithic into the pottery-using Early Neolithic (EN) at around 7560 cal BP (Chard, 1974: 63-64 ; McKenzie, 2009; Weber, in prep) This early use of pottery appears to have been relatively limited in scale, and many campsites and Kitoi graves remain essentially aceramic. Very little is known about why pottery was first adopted by the Kitoi Culture, nor what kind of commodities were processed in it (McKenzie, 2009). Much older evidence of pottery, extending back into the Late Glacial, has been reported from archaeological sites further to the east, including Transbaikal, on the middle and lower sections of the Amur River in the Russian Far East, and in Japan (Kuzmin, 2014). Knowledge of pottery may have dispersed into Cis Baikal from these areas, though the precise timing and exact routes remain unclear (Jordan et al., 2016).

Along the Angara River and in Southwest Baikal, two different early pottery styles appear at around the same time in habitation sites: net-impressed wares and cord-impressed “Khaita” wares, while only net-impressed wares have been recovered from Kitoi graves (McKenzie, 2009; Berdnikov and Sokolova, 2014; Weber, in prep). The oldest radiocarbon-dated pottery assemblage from Cis-Baikal was recovered from Layer VI at the Gorelyi Les habitation site, which is situated on the Belaia River that runs into the Angara River (Fig. 3.1). This pottery-bearing cultural horizon yielded a radiocarbon date on charcoal of ca. 7860 cal BP (Veksler, 1989; Kuzmin, 2014), and while the date is derived from a highly-compressed occupation level, its suggests that pottery starts to appear at around the same time that Kitoi Culture was emerging ca. 7560 cal BP (Chard, 1974: 63–-64; McKenzie, 2009; Weber, in prep). The assemblage of early pottery from Gorelyi Les is therefore the oldest on the western side of Lake Baikal, and offers an important opportunity to investigate how early pots were used and also to look at why they may have been adopted into this area by the emerging Kitoi Culture.

2. “Becoming Neolithic”: Kitoi motivations for adoption of pottery

The formation of the Early Neolithic Kitoi cultural pattern can be viewed as a rather sudden socio-economic transition, underpinned by a series of important technological innovations (Weber, in prep). In many ways, the gradual intensification of fishing appears to define the trajectory of the Kitoi Culture, and bioarchaeological analysis of skeletal remains indicates that the contribution of fish to Kitoi diets increased steadily over time (Weber et al., 2016b; Weber et al., in prep). The rich fisheries of the

Angara River, which remain open throughout the winter months, appear to have stimulated the emergence of a range of either new or more morphologically variable fishing devices, including nets and sinkers, new type of harpoons and leisters, as well as composite fish-hooks (Bazaliiskii, 2010; Weber and Bettinger, 2010; Weber et al., in prep). Nephrite wood-working tools would have enabled the building of such mass capture facilities as fish weirs, fences and baskets (Weber et al., 2002; Bazaliiskii 2010; Weber and Bettinger, 2010; Weber et al., 2011, Weber, in prep). Cooperative fish harvests along the main rivers could also have been processed, stored and shared out during leaner months. Perhaps not surprisingly, all the main Kitoi cemeteries are located along the major water courses (Fig. 3.1), and may have reflected regional aggregation sites, where funerary rites and feasting events may have been combined with cooperative fishing activities.

Hunting played an important role in Kitoi groups, and the appearance of powerful composite hunting bows would have greatly improved return rates in hunting local game, including moose, red deer, roe deer and boar (Weber, in prep). In contrast, the extent to which the Kitoi exploited local plant and nut resources is less well understood.

Clay pots offer an effective means for the slow simmering of resources to extract rich lipids and to combine elements into nourishing stews. The intensification of fishing may have encouraged Kitoi adoption of pottery, with clay pots offering a relatively efficient technology for processing large catches and for rendering fish oil. Large numbers of pots can also be produced much more efficiently than baskets (Brown, 1989), especially if net or other textile moulds were used, and the pots then cached at seasonal fish harvesting sites. It is interesting to note that fishing technologies appear to coincide with the appearance of pottery in most other areas of Eastern Siberia as well (McKenzie, 2009:189).

While lean meat can also be stewed, investment in making clay pots can be justified by their use to produce bone grease, which may have enabled groups to extract maximum nutrition from hunted game, especially during leaner seasons (Elston et al., 2011). The process of extracting bone fats involves breaking open the long bones with simple hammer stones and anvils, and then the fragments are slowly heated in water to render the grease (Karr et al., 2015). Using direct heating of clay pots over a fire is less time consuming than using hot stones to maintain the heat and would have freed up time for other activities. Seal fat could also have been rendered in the Kultuk Bay area.

Processing of plant resources in early pottery is less well-studied. Stands of Siberian pine nuts (*Pinus sibirica*) would also have been available to the Kitoi, and can easily be harvested, stored in the cones

and consumed without any need for boiling. More usually, they are dry heated, and nut oil can be rendered by cold pressing. Other local plant resources such as berries, lichen and inner bark (e.g. pine, birch or willow) (Bogdanova, 2016; Shikov et al., 2017; Weber, in prep), which is rich in vitamin A and C and a well-known "starvation food", could also have benefitted from boiling to remove bitter tannins (Lashmanova et al., 2012; Shikov et al., 2017). These plant foods could also have been added to mixed dishes to add flavour or thicken up stews. Finally, pots may also have been used by Kitoi people to produce tree resins, mastics and pitch for the hafting of tools (Connan and Nissenbaum, 2003; Croft et al., 2018) or other waterproof boxes and containers (Heron and Evershed, 1993; Colombini et al., 2005). This process usually involves the slow heating of tree bark in a sealed container (e.g. a pot with a wooden lid); oil can also be thickened into pitch by slow simmering.

Several kinds of social dynamic may also have encouraged pottery adoption, such as the use of pots to create rich and nutritious dishes (involving costly-to-produce oils, fats and lipids) that could be prepared and shared out at collective aggregations, generating social debts, and perhaps leading to seasonal cycles of competitive feasting (Hayden 2009). Kitoi society, which appears to have acquired the technological means to generate abundant fish harvests, also bears signs of emerging status inequalities (Weber et al., 2002; Weber and Bettinger, 2010; Weber, in prep), with feasting events potentially serving as a central socio-political strategy among these trans-egalitarian hunter-gatherer communities (Hayden, 2012). On the other hand, pottery may simply have been attractive in more mundane domestic contexts. It can be left unattended for long periods, generating efficiencies in time-management in hearth-side contexts, and can also be used for producing soft weaning foods (Jordan and Zvelebil, 2009; Hommel, 2012).

3. Case-study: Early Neolithic pottery at Gorelyi Les

The Gorelyi Les habitation site is situated on the Belaia River about 50 kilometers from its confluence with the main Angara River (Fig. 3.1, Appendix 6a and b). The site is located on the first terrace above the river, and is surrounded by forest and forest steppe, low hills and open plains (Fig. 3.2). At the start of the Kitoi Culture around 7560 cal. BP (Weber, in prep), this area would already have been experiencing a slow warming trend since around 8630 cal. BP, combined with increased precipitation, expansion of forest cover, and thicker, longer-lasting snow cover. The forest expansion would have peaked around 7000-6500 cal. BP (Weber, in prep). While the site is distant from the abundant year-round fisheries of the Angara River, the landscapes around Gorelyi Les would have provided diverse game and plant resources, with the river providing transport links and also substantial fishing opportunities.

Figure 3.2 Photo of Gorelyi Les site (view from northwest) along the Belaia River and surrounded by forest and low hills (after Weber, 1997).

The first excavations at Gorelyi Les were undertaken by the Department of Archaeology of Irkutsk State University in the early 1970s (Savel'ev et al., 1974). During three seasons 750 m2 was excavated, generating large archaeological collections (Weber, 1995). Unfortunately, this work has never been fully published. Three further excavation seasons were led jointly by N.A. Savel'ev and A.W. Weber from 1994 to 1996 (Appendix 6b), generating additional archaeological materials (Weber, 1997; Ready, 2008; Kurzybov, 2011), which are the focus of the current paper. In addition, one further excavation season took place in 2002 (Igumnova et al., 2004; McKenzie, 2009).

The stratigraphications and chronology of the site have been discussed in previous publications (Weber, 1995; Weber et al., 2002; Ready, 2008; McKenzie, 2009: 186-187), with consensus that the site was occupied throughout a period of at least three thousand years, with five distinct occupation levels that have almost all been radiocarbon dated (Appendix 3). These phases equate to: Late Mesolithic (Layer VII; ca. 10,240 to 9300 cal. years BP); Early Neolithic (Layer VI; ca. 7950 to 7440 cal. years BP); a Middle/Late Neolithic (Layer Vb, compression of MN and LN materials into one layer; ca. 6320 to 6010 cal. year BP); Late Neolithic (Layer Va; ca. 5890 to 5530 cal. year BP); the Early Bronze Age (Layer IV; undated).

3.1. The Early Pottery Layer (VI)

With a chronological range of ca. 7950 to 7440 cal. years BP , the Early Neolithic Layer VI (Veksler, 1989; Kuzmin 2014) is generally accepted as forming a settlement correlate of the Kitoi (mortuary) tradition (Weber, 1995; McKenzie, 2009: 186–187), which extends from 7560 to 6660 cal BP when

corrected for FRE (Weber, in prep, Weber et al., in prep). While more radiocarbon dates are clearly needed to strengthen the dating of Layer VI, the recovery of a highly-diagnostic composite fishhook of the Kitoi type, plus early finds of net-impressed pottery, which also appears around the same time in several Kitoi graves, further strengthens the argument that Layer VI is indeed broadly contemporaneous with the Kitoi mortuary tradition.

It is also worth clarifying that 16 sherds, probably from a single pot, have been reported as originating in Layer VIIa, which is the Late Mesolithic occupation level dated from 10,240 to 9300 cal. BP (Weber, 1995). If correct, this would make this pottery vastly older than the Early Neolithic assemblage in Layer VI. However, both the dates and the archaeological context remain controversial, as they appear to have been affected by burrowing animals and other post-depositional disturbances. As a result, they are not widely accepted (McKenzie, 2009: 186; Weber, 1995; Weber, 1997).

3.2. The Early Neolithic Pottery Assemblage

Weber (1997) reports that a total of 72 fragments of pottery were recovered from Layer VI during three excavation seasons (1994-1996); these consisted of 49 net-impressed sherds, 19 smooth-walled sherds, and four cord-impressed pieces. This assemblage forms the focus of the current study, and we did not have sampling access to materials recovered during earlier or later excavations. It still remains unclear exactly how many pottery sherds have been recovered from Layer VI at Gorelyi Les, including from the last excavations conducted by Igumvova in 2002.

As with many other (undated) habitation sites across Cis-Baikal, the earliest pottery assemblage at Gorelyi Les layer VI contain two distinctive pottery styles (Weber, 1995, in prep, McKenzie, 2009): Net Impressed 1 pottery, which are mitre-shaped with net-impression, with an everted rim (Fig. 3.3a); Cord-impressed “Khaita” (Fig. 3.3b), which may also have herringbone and other geometric motifs on the upper half of the pots (Savel’ev, 1982; McKenzie, 2009). In addition, a third type of pottery was also recovered from Layer VI, which appears to correlate with neither styles; these are reported as “smooth-walled pottery” with everted rim and no ornamentation (McKenzie, 2009), and have also been referred to elsewhere as ‘plain pottery’ (Weber, 1997). While the chronometric chronology of Gorelyi Les makes it difficult to date precisely the appearance of these pottery styles, we suspect that the Khaita pottery — since sherds recovered from Layer VII display “Khaita” cord-impressions — may relate to the early and more formative stages of the Kitoi cultural pattern and may even predate it. In contrast, the Net-Impressed 1 pottery – and possibly smooth-walled pottery – may correlate more closely with the existence of Kitoi Culture.

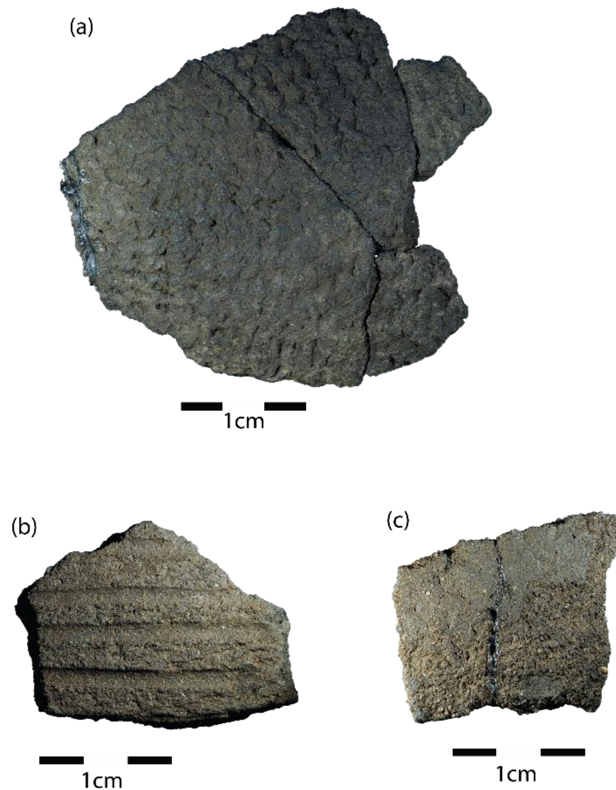

Figure 3.3 Examples of Early Neolithic pottery types recovered from Layer VI of Gorelyi Les during the 1994-1996 excavations: (a) net-impressed pottery; (b) "Khaita" cord-impressed pottery; (c) sherd of unclassified type.

3.3. Subsistence and Site Function

According to the faunal reports and lithic inventories, hunting activities appear to have been central to Gorelyi Les inhabitants' subsistence strategy. Cervidae, including moose (*Alces alces*), red and roe deer (*Cervus elaphu*s and *Capreolus capreolus* respectively), were in the Early Neolithic of this site, with a clear preference for roe deer. Traces of butchery such cut and chop mark mainly on mandible, metatarsal and long bone shafts suggest marrow cracking (Ready, 2008) (Table 3.1). The site also had isolated finds of hare, bovid and bear remains. Plant remains have not been recovered, although this may rather be related to recovery bias as no flotation or wet screening was undertaken (Table 3.1).

Interestingly, even though fish bones (e.g. northern Pike bones, *Esox lucius*) and fishing implements (one composite fishhook shank) were recovered (Weber, 1997; Ready, 2008) – and these perhaps indicate that fish remains and perhaps some active fishing were practised – the overall quantity of fish remains is very low (n = 8), especially in comparison to larger land mammals, though this could also reflect recovery and preservation biases (Ready, 2008). This may also be linked to site function since Ust'-Khaita habitation site located only 2km further upstream from Gorelyi Les, produced a lot of fish bones from chronologically similar Layers (Savel'ev et al. 2001; Kurzybov, 2011).

To summarise, the Early Neolithic Layer VI of the Gorelyi Les habitation site has the oldest relatively reliably dated pottery in Cis-Baikal, and its occupation broadly correlates with the Kitoi mortuary tradition. The site appears to have been either an active hunting camp or a “gearing up” station used for readying hunting expeditions, and for the processing of large game after their return.

Period	Lithic assemblage[1,3,4]	faunal assemablage (NISP)[2]	Pottery assemblage[1, 5]	Other[1]
Layer VI EARLY NEOLITHIC	Total of 1360 lithic artefacts including 65 formal tools. Processing tools: Blades and microblades (n = 41), burins (n = 4), cores and core fragments (n = 12), borers (n = 2), scraper (n=2). Hunting gears: Arrowheads (n = 4), points (n = 6). Fishing tools: **Shank of a composite fishhoo**k (n = 1). Culturally significant artefact for **Kitoi Mortuary tradition**. Identification of the main functions: meat knives, drills, borers, scrapers, chopping (hewing) tools. Large amount and diverse waste of flints suggesting that the flintknapping activity was intensive. Likewise, evidence for local production of tools made with light- and dark-coloured banded grey cherts, red platy chert, quartzite pebbles, argillite, and conglomerates, available on the vicinity of the site. In contrast, tools made with materials such as slate and high-quality chert, also locally available, were manufactured in other areas at Gorelyi Les or in other locations distant from the site.	Total of 10623 faunal remains whose 9507 unidentified. Mammal (n = 1084), artiodactyl (n = 273), cf. cervidae (n=4**), *Capreolus pygargus* (n = 232**), *Cerphus elaphus* (n = 28), *Alces* alces (n = 142), rodentia (n = 2), *Ursus* arctos (n = 4), bison spp. Aut Bos spp. (n = 3). *Esox lucius* (n = 8) Trace of butchery (cut and chop marks, n=168 bones) mainly on mandibles, metatarsals, long bone shafts. Suggests **marrow cracking** and/or possibly tool production. Burt bones. Notably all the fish remains were burnt.	Pottery appears ca. 7870 cal BP (and appears to be broadly contemporaneous with **Kitoi Culture**) 72 fragments: -49 Net-Impressed 1 (**this tradition is also found in Kitoi mortuary contexts)** - 19 smooth-walled - 4 cord-impressed	**Three hearths** found: - 50 cm diameter, cobbleless and dark charcoal stain. - One with distinct pit (ca. 20 cm deep, 50 cm diameter) filled with numerous small bone and charcoal fragments, plus small limestone cobbles on the surface. - One large charcoal stain (1 m diameter) and cobbleless. **A deliberate arrangement of 15 pebbles (3 rows)**: purpose unknown. **An articulated deer limb**.
Layer VII LATE MESOLITHIC	Total of 49 lithic artefacts with only 4 formal tools (blade or microblades).	Total of 417 faunal remains whose 404 unidentified. Mammal (n = 9), Rodentus (n = 4). Burnt bones.	Pottery sherds reported from this level, but chronology and context are controversial	No feature

Table 3.1 Summary of the artefact and faunal assemblages found at Gorelyi Les site in Layers VII (Late Mesolithic) and VI (Early Neolithic). After: Weber, 1997 (1); Ready, 2008 (2); Kurzybov, 2011 (3); Bazaliiskii, 2003, 2010 (4, 5).

4. Materials: Sampling Strategy

We were able to access a total of 44 pottery fragments from the Early Neolithic assemblage from Layer VI at the Gorelyi Les habitation site from the 1994–1996 excavations (Weber, 1997; Kurzybov, 2011). To establish whether the region's two main early pottery types had been used in different ways we had initially aimed to target both the net-impressed 1 and cord-impressed (Khaita) sherds. However, given the limited size of the assemblage, and the small and often non-diagnostic nature of many sherds, we were only able to sample 11 net-impressed sherds (absorbed residues n = 10, foodcrust sample n = 1), and only one cord-impressed sherd (absorbed residues n = 1). The remaining samples (absorbed residues n = 32) were either from the "smooth-walled vessels" or from non-diagnostic sherds that could not be assigned to any particular pottery tradition (for a full list of samples please see Appendix 4).

5. Methods: Lipid Residue Analysis

When pottery is used to cook and store resources lipid residues are frequently absorbed into the ceramic fabric (Evershed, 2008a), or can be burnt onto the vessel surface where they form carbonized food remains (or "foodcrusts") (Evershed, 2008a). In certain archaeological conditions, these organic residues can survive for thousands of years (Evershed, 1993; Dunne, 2017). Methods for recovery and analysis of organic residue have seen major development over the last three decades, and are now routinely deployed to study the function of archaeological pottery (Rottländer and Schlichtherle, 1980; Evershed et al., 1990; 1991; 1994; 1997; Heron et al., 1991; Oudemans and Boon, 1991; Charters et al., 1993; Oudemans, 2007; Evershed, 2008a; 2008b).

Typically, a combination of chemical processes and analytical techniques is employed to recover the lipids and generate insights into vessel use, including GC-C-IRMS (Gas Chromatography - Combustion – Isotope Ratio Mass Spectrometry) to measure stable isotope ratios, and GC-MS (Gas Chromatography-Mass Spectrometry) to analyse the molecular character of the residues and identity lipid biomarkers (Evershed et al., 1990; 1994; 1997; Evershed, 2008a; Correa-Ascencio and Evershed, 2014).

To sample the absorbed residues, several millimetres of the outer sherd surface were mechanically removed using a modelling drill in order to eliminate exogenous residue. We then drilled around 1 g of clay dust from the interior portion of the larger and medium sherds, while the very small sherds

were crushed down into a fine powder. The single foodcrust sample was also crushed. An established one-step acidified methanol protocol was used to extract lipids from these powdered samples (Craig et al., 2013; Papakosta et al., 2015). This involves adding methanol to the powdered samples in the following proportions: potsherd: 1g/4ml; foodcrust: 10-20mg/1ml, plus an internal standard (*n*-tetratriacontane: 10 µg) to verify that extraction is running correctly. The mixtures were then sonicated for 15 minutes and acidified with concentrated sulphuric acid (800 ml and 200 ml, respectively), and finally heated for 4 hours at 70 °C. After the samples were left to cool, then lipids were extracted with *n*-hexane (3 x 2ml) and centrifugation (3000 rpm, 5 minutes), and finally reduced and concentrated under an Argon flow. Finally, an additional internal standard was added (*n*-hexatriacontane: 10 µg) to quantify the yielded lipids.

All the lipid extracts were then analysed with GC-MS and GC-C-IRMS to generate molecular and carbon isotope values for the two most abundant fatty acids, hexadecanoic and octadecanoic acid ($C_{16:0}$ and $C_{18:0}$ respectively). Ten of the extracts were also methylsilylated using BSTFA (N, O-bis (trimethylsilyl) trifluorocetamide) in order to better detect dihydroxy fatty acids and alkanols. The single foodcrust sample was also analysed by Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS) to provide stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope values. Instrument settings were selected following established methodologies (Lucquin et al., 2016a; Shoda et al., 2017; Bondetti et al. 2020) and are also available in the Appendix 1.

6. Results

6.1. Survival of Absorbed Lipids and Contamination

Both the absorbed residues and the single foodcrusts sample exhibited satisfactory levels of lipid preservation (potsherds >5 µg/g; foodcrusts >100 µg/g) (Evershed, 2008a; Lucquin et al., 2018a). The average lipid concentration of 80 µg.g-1 for the absorbed samples was not especially high, although this is broadly similar to levels reported in other recent studies of early Holocene pottery in adjacent regions (Lucquin et al., 2016a; Gibbs et al., 2017; Oras et al., 2017; Shoda et al., 2017). In contrast, the single foodcrusts sample had significantly higher lipid concentration (459 µg.g-1), suggesting that organic matter tends to be well-preserved in this particular burial context.

Many of the samples had high levels of contamination, especially phthalates, which were identified in all the absorbed samples, but not in the food crust sample. This is probably a result of the sherds being stored in plastic. Many had also been labelled with a combination of varnish, correction-fluid and ink,

and some had also been mended with glue. These contaminants often dominated the chromatogram, forming major peaks (Fig. 3.4). In some cases, this can be problematic, as potentially informative biomarkers may sometimes be hidden by contaminant signals.

6.2. Molecular Characterization

Figure 3.4 illustrates typical gas chromatogram of organic residue extracted from pottery samples. The lipid profile of the acid/methanol extracts shows the presence of saturated fatty acids. These range from C_6 to C_{32}, and were mainly dominated by palmitic acid ($C_{16:0}$), unsaturated fatty acids with mainly even numbers of carbons ranging from $C_{14:1}$ to $C_{24:1}$, and branched fatty acids ranging from C_{13} to C_{26} (Fig. 3.4; Appendix 4). In addition, dicarboxylic acids, which ranged from C_6 to C_{26}, were present in almost all samples, plus hydroxy acids, ranging from C_{22} and C_{24}, were detected in some samples. Both tend to indicate the cooking of plant and animal resources as they are typical oxidation products of unsaturated fatty acids, although they can also result from different degradation processes occurring during burial (Regert et al., 1998; Copley et al., 2005; Baeten et al., 2013).

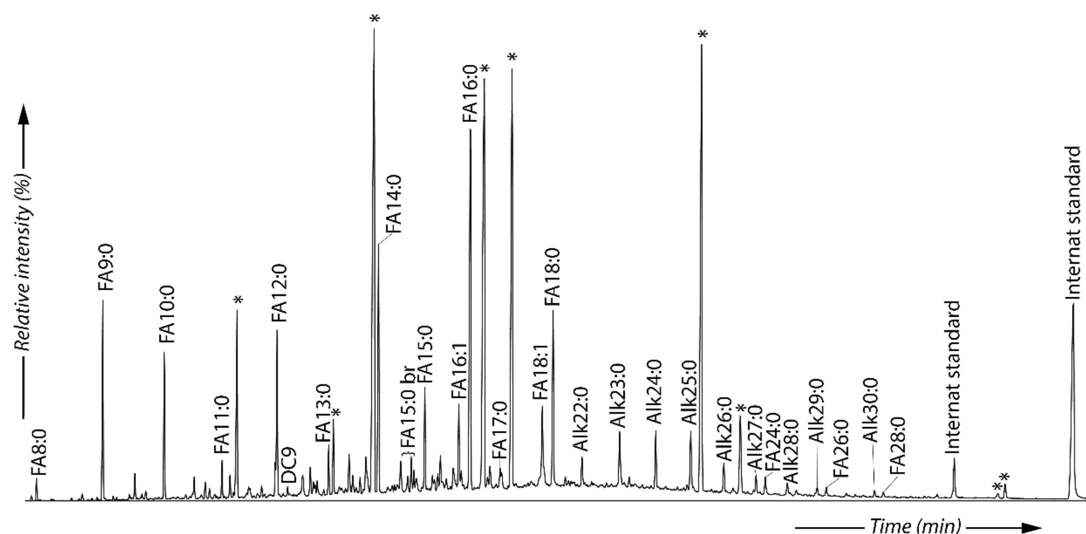

Figure 3.4 A typical total ion current (TIC) chromatogram of lipid residues from the Gorelyi Les pottery (sample: GL 94.00158). This shows the presence of saturated fatty acids (FA), diacids (DC), branched (br), long-chain unsaturated fatty acids, mid- and long-chain alkanes (Alk). Several contaminants are also present (see *), including phthalates.

Eight of the absorbed samples met established criteria for identifying the processing of aquatic resources (Hansel et al., 2004; Cramp and Evershed, 2014; Lucquin et al., 2016b). These samples contained either long chain (⩾C20) ω-(o-alkylphenyl) alkanoic acids (APAAs), along with at least one isoprenoid acid(e.g. 4,8,12-trimethyltridecanoic acid (TMTD), phytanic acid, pristanic acid) or a phytanic's diastereomers ratio (SRR%) above 75.5% (Fig. 3.5; Appendix 4).

The former (APAAs) are formed by the heating of mono and polyunsaturated fatty acids (M/PUFAs) at a temperature of at least 200°C, from 1 hour of heating (Bondetti et al. in prep; See chapter 6). Moreover, M/PUFAs with carbon length superior or equal to 20 are only present in significant concentrations in aquatic animals, and so the detection of APAAs in combination with $\geqslant C_{20}$ is highly consistent with the processing of freshwater and/or marine organisms (Evershed, 2008b; Baeten et al., 2013; Cramp and Evershed, 2014).

Although the isoprenoid TMTD is mainly formed by aquatic organisms, both phytanic and pristanic acid, which are synthesized from phytol, are present in both aquatic and ruminant resources (Ackman and Hooper, 1968; Cramp and Evershed, 2014; Heron and Craig, 2015). However, the co-occurrence of these isoprenoid acids with APAAs ⩾C20 confirms that they are derived from aquatic rather than terrestrial resources. In addition, the ratio of the two natural diastereomers of phytanic acid, 3S,7R,11R,15-phytanic acid (SRR), which is usually predominant in aquatic organisms, and 3R,7R,11R,15-phytanic acid (RRR) can also be calculated. Therefore higher % contributions of SRRs is characteristic of the processing of aquatic resources (Lucquin et al. 2016b).

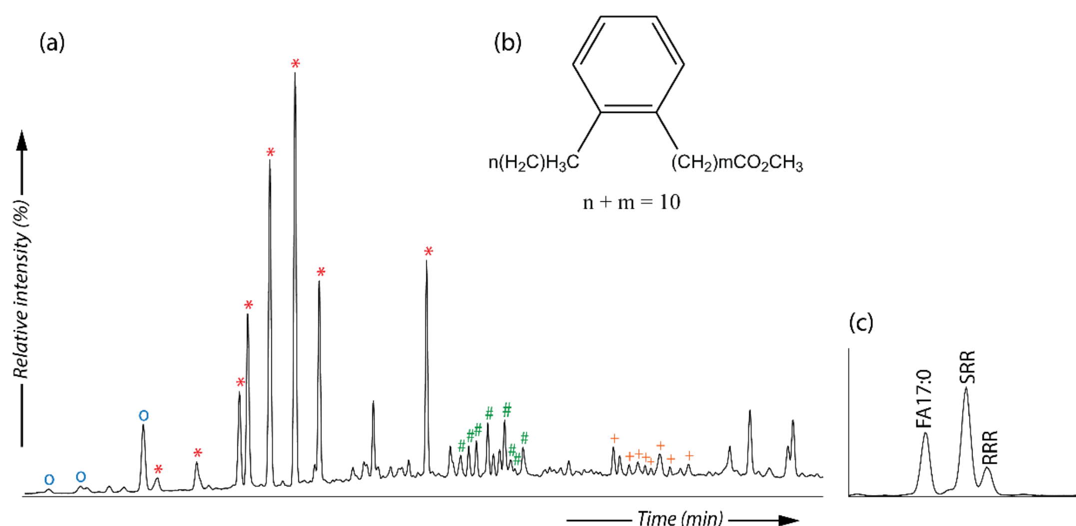

Figure 3.5 Molecular evidence for the processing of aquatic resources of the foodcrust sample GL 94.00557 run on the DB-23 column): (a) a partial summed mass chromatogram (m/z 105) showing the presence of ω-(o-alkylphenyl) alkanoic acids with 16(O), 18(*), 20(#) or 22(+) carbon atoms; (b) chemical structure of APAAs (from Hansel et al., 2004); (c) a partial summed mass chromatogram (m/z 101) revealing the diastereomers of phytanic acid (SRR and RRR).

There was tentative evidence that plant leaves had been processed. Substantial quantities of diverse mid- and long-chain alkanes (C_{14}-C_{33}) were detected in all the samples, except for the single foodcrust samples (Fig. 3.4; Appendix 4). One of the main sources of alkanes is wax covering the leaf and the stem surface of plants (Turunen et al. 1997; Oros et al. 1999, Bush and McInerney, 2013; Horiuchi et

al., 2015). In 26 of the 44 samples these compounds were found in combination with a symmetrical ketone (16-Hentriacontanone). Moreover, in all the methylsilylated samples (n = 10) diverse mid and -long chain *n*-alkanols (C_{12} to C_{28}) were also detected (Appendix 4). Although the combined presence of all these compounds meets the established criteria for identification of plant-derived waxes (Baeten et al., 2013), the *n*-alkane distributions did not show a more typical profile associated with the processing of leafy plants (Diefendorf et al., 2011; Bush and McInerney, 2013; Horiuchi et al., 2015; Dunne et al., 2016). Such profiles commonly display a predominance of alkanes with an odd number of carbon atoms with the prevalence of one or two of them (Eglinton and Hamilton, 1963; 1967; Bush and McInerney, 2013). Furthermore, the 16-hentriacontanone compound could also be generated by the pyrolysis of animal fats alike the non-symmetrical ketones also present in 19 pots (Evershed et al. 1995; Raven et al. 1997; Baeten et al. 2013). Finally, *n*-alkanes and *n*-alkanols are common lipid components of soils (van Bergen et al., 1998), and their presence in the pottery could be related to the burial context. Further analysis of soils from the archaeological site could clarify this issue but remain beyond the scope of the current paper.

In contrast, the samples contained clearer evidence for the use of coniferous tree resources, possibly in relation to firewood, or potentially in the form of food, flavourings or medicine, and perhaps in relation to production of glues and sealants. Use of tree resources is suggested by presence of various diterpenes. A total of 38 samples (86%) yielded totarol, 7α-hydroxy (Appendix 4). This diterpene (totarol) and its various derivatives have been identified in numerous coniferous resin plants, including Cupressaceae (e.g. juniper) (Bendall and Cambie, 1995), and especially, although in low amount, in Pinacea such as spruce (Alwehaibi et al., 2016), which was a major component of the early Holocene forests in the Cis Baikal region (Demske et al., 2005; White and Bush, 2010).

Furthermore, diterpenes such as methyl dehydroabietate (DHA) and 7oxo-dehydroabietate (7-oxo-DHA) were also identified in 35 (80%) of the pottery samples. They are indicative of altered Pinaceae resins and wood (Regert, 2004; Mitkidou et al., 2008; Modugno and Ribechini, 2009; Jerković et al., 2011), although they are also produced by bacteria found in various environments (Costa et al., 2016) and would require analyses of soil from the site to confirm or rule out possible exogenous contamination. These biomarkers may have resulted from smoke from campfires if pine was being used as a fuel (Simoneit et al., 2000; Simoneit, 2002). However, the absence of other smoke indicators such as polyaromatic hydrocarbons (PAHs) makes this unlikely.

A possible scenario is that resources gathered from pine trees were deliberately added to the pots as part of local cooking practices. Pine nuts and the inner bark are important elements in the diet of many Siberian indigenous peoples (Okladnikov, 1950; Okladnikov, 1955; Rushforth, 1987; Shikov et al., 2017). Both are full of nutrients and can easily be harvested and stored for later use. While pine nuts require minimum processing, the bark could have been stewed to remove unpleasant flavours or to remove tannins or added to stews and casseroles as a source of fibre or starch, to add flavour and variety, or to thicken up soups. Finally, pine needles also contain resins and therefore such diterpenoids (Turunen et al., 1997), and may have been added to dishes as they contain abundant vitamin C and are rich in flavour, or the needles may have been used to brew hot tea or medicinal infusions (Cumo, 2015).

These results may also suggest that the pots were used to produce other useful non-food substances, including pine resin or tar, which could have been used for hafting, gluing and sealing various stone tools, bone or organic tools (Croft et al., 2018), or resin could have been used to seal new pots after firing or to repair cracked vessels (e.g. via boring holes, stitching and then sealing) (Charters et al., 1993; Jerković et al., 2011; Colombini et al., 2005). Pine resin may also have been produced for waterproofing and repairing dug-out canoes and to seal birch-bark boats or other household containers (Connan and Nissenbaum, 2003).

6.3. Stable Isotope Analysis

Further insights about pottery use were generated by undertaking single-compounds isotope analysis of the two main fatty acids: palmitic ($C_{16:0}$) and stearic ($C_{18:0}$). Due to the good lipid preservation, all 44 samples were analysed by Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) (Appendix 4). Furthermore, the foodcrust sample was also subjected to bulk isotope analysis to determine its stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope values using Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS).

The results are presented in Figure 3.6a, with $\delta_{13}C_{16:0}$ values plotted against $\Delta^{13}C$ ($\delta^{13}C_{18:0}$- $\delta^{13}C_{16:0}$). $\Delta^{13}C$ values provided a means of distinguishing lipids derived from ruminant adipose, dairy fats and other non-ruminant sources, including other terrestrial and also aquatic sources (Evershed et al., 1999; Craig et al., 2012; 2013a; Colonese et al., 2015; Taché and Craig, 2015; Lucquin et al., 2016a).

In total, 25 samples (57%) had $\Delta^{13}C$ values of < -1.1 which are commonly taken to indicate the presence of ruminant fats (Copley et al., 2003; Šoberl et al., 2008; Craig et al., 2012; Salque et al., 2012). Interestingly, a negative correlation could be observed between the $\delta^{13}C_{16:0}$ and $\Delta^{13}C$ values: samples

with progressively more negative $\Delta^{13}C$ produced fatty acids enriched in ^{13}C. Enrichment in ^{13}C is observed in the tissues of ruminant animals that feed on C_4 plants (Dunne et al. 2016). However, given that C_4 plants are absent in this region (Lam, 1994; Katzenberg et al., 2010), and that ruminants recovered from modern and archaeological contexts exhibit carbon isotope values that are consistent with a diet consisting exclusively of C_3 plants (Fig. 3.6a) (Weber et al., 2002; Katzenberg et al., 2012), it is difficult to explain this pattern properly. Potentially, the negative correlation between $\delta^{13}C_{16:0}$ and $\Delta^{13}C$ values could be a result of resources from different sources being mixed in the pottery during cooking activities.

Interestingly, samples with aquatic biomarkers, usually exhibiting $\Delta^{13}C$ value > -1.1, here mainly plot in the ruminant area ($\Delta^{13}C$ < -1.1) but with relatively enriched $\delta^{13}C_{16:0}$. Likewise, the $\delta^{15}N$ isotopic value generated for the single foodcrust sample clearly point to the processing of aquatic resources ($\delta^{15}N$ = 10.64 ‰) (Weber et al., 2011; Craig et al., 2013; Choy et al., 2016) while its $\Delta^{13}C$ values fall within the range expected for ruminant fats (Fig. 3.6). This suggests a mixture between fish, with a more positive $\delta^{13}C$ value, ie. > -27.2 ‰, and ruminant fats. Collagen of modern fish, notably salmonidae (e.g. lenok and black grayling) found in the rivers of Angara region have carbon isotope values relatively lower compared to terrestrial ($\delta^{13}C_{mean}$ = -19.6 ± 0.8) (Weber et al., 2011), although more archaeological fish would require to be analysed to confirm this trend.

To explore this hypothesis further, we tested how $\Delta^{13}C$ values respond to a range of simulated mixing scenarios where aquatic foods, including freshwater and migratory fish, are mixed either with C_3 plants (e.g. fruits, nuts and grass), non-ruminant or ruminant commodities. The theoretical mixing model presented in figure 3.6 shows that when even a modest amount (ca. >10%) of ruminant fats are mixed with fish oils, the $\Delta^{13}C$ values can shift to below -1‰ (Fig. 3.6b). While, in contrast, when ruminant fats are mixed with plants or non-ruminant fats, these do not have an influence on the $\Delta^{13}C$ when mixed with fish (Fig. 3.6c and d). Therefore, it seems to confirm the assumption for the use of these pots for the treatment of both fish and ruminant resources resulting either in intentional mixing or successive uses of pots.

In total, a further 19 samples (43%) had $\Delta^{13}C$ value consistent with non-ruminant products. As highlighted previously, only few samples (n = 2) with aquatic biomarkers falls within this isotopic value area. Therefore, the pot samples displaying such isotopic signal may instead suggest the processing of terrestrial non-ruminant animal fats. Another eventuality, which cannot be ruled out, is the processing of plants or tree resources in these pots (see above).

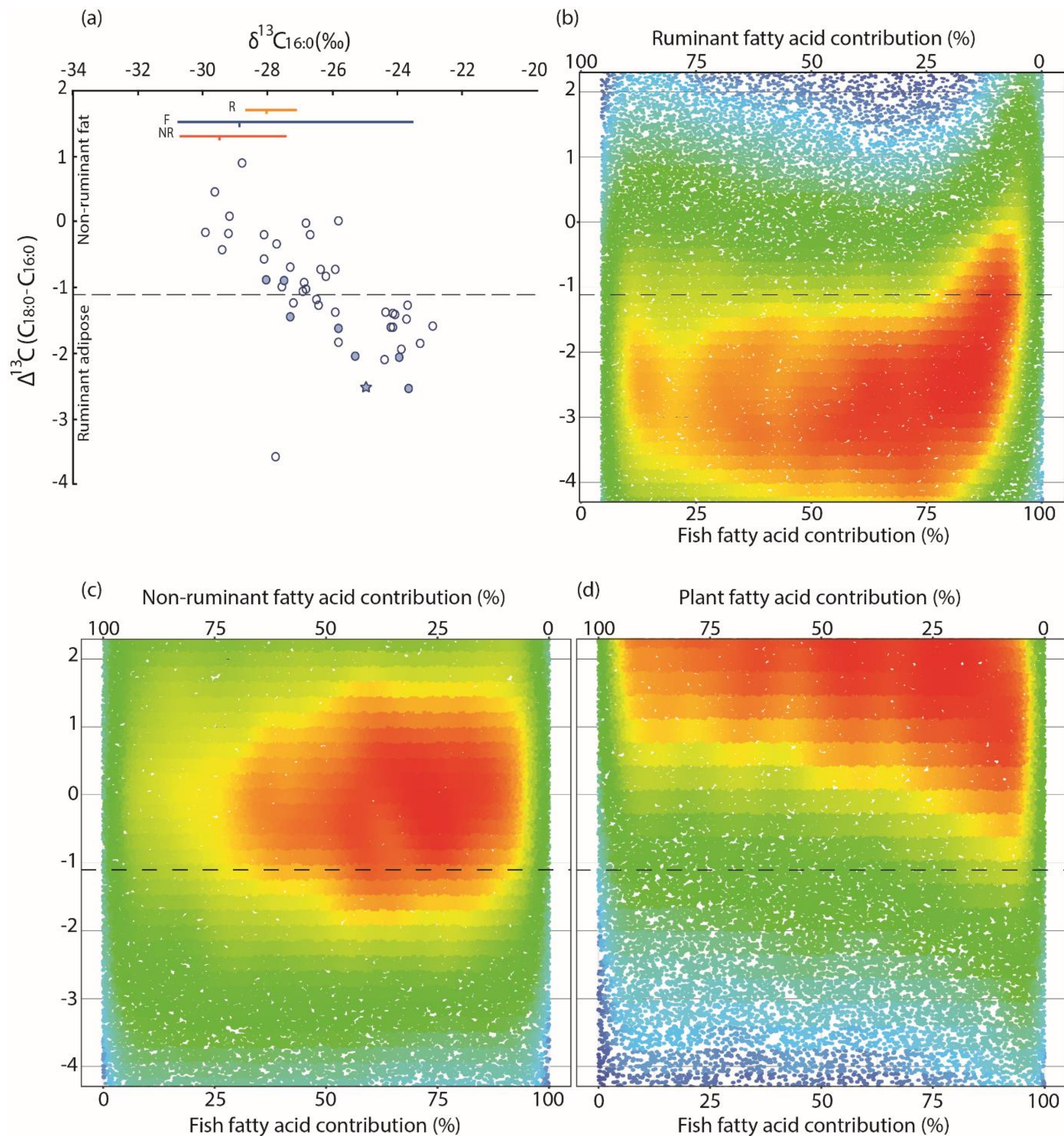

Figure 3.6 Lipid stable isotope characteristics from the all Gorelyi Les samples compared with theoretical mixes of animal fats, plant oils (C_3 types) and fish oils. (a) Scatter plot of $\Delta^{13}C$ ($C_{18:0}$-$C_{16:0}$) against $\delta^{13}C_{16:0}$ of Gorelyi Les samples with the foodcrusts represented by a star. Samples containing aquatic biomarkers are shown by filled markers. The data are compared with the median and ranges (1σ) of bone collagen of archaeological ruminant (R), modern fish (F) and non-ruminant animals (NR) from the Baikal region, after being corrected for the collagen to tissue offset (Fernandes et al. 2015), plotted on the x-axis only (Weber et al., 2002; 2011; Katzenberg et al., 2012; Appendix 6). Density distributions of $\Delta^{13}C$ values obtained by theoretical mixing (Appendix 7) of authentic reference lipids from modern tissues of fish with (b) ruminant, (c) non-ruminant adipose fats and (d) plant were obtained by using published (Dudd, 1999; Spangenberg et al., 2010; Craig et al., 2012; Choy et al., 2016) and unpublished data and using fatty acid concentration values obtained from the USDA database (https://fdc.nal.usda.gov/).

6.4. Summary of Results

Overall, we take these combined results to indicate that: (a) the Early Neolithic pottery had been used to process a wide spectrum of resources, ranging from fish and ruminants, through to pine tree resources possibly including pine needles, inner bark or pine resin; (b) there was some diversity in patterns of pottery use, with approximately half of the pots containing molecular signals consistent with the processing of non-ruminant products (probably a broad array of terrestrial plant and animal products), while the other half had been used to process ruminants, most probably in combination with aquatic resources; however (c), the single sample from a cord-impressed pot, combined with the relatively large number of samples from non-diagnostic sherds, did not enable us to examine systematically whether the two main early pottery types in Cis-Baikal – net-impressed and cord-impressed - had been used in different ways at Gorelyi Les.

7. Discussion: early pottery and the émergence of Kitoi culture

Clearly, Kitoi groups were starting to take up a number of important technological innovations after ca. 7500 cal BP, including adoption of powerful hunting bows and the appearance of a wide array of specialised new fishing equipment (Weber, in prep). From the wider spectrum of hunting, fishing and gathering activities, the cooperative harvesting of river fish appears to have offered the Kitoi the only viable pathway towards economic intensification, especially after the boreal forest started to close in from about 7500-7000 cal BP, with aquatic contribution to Kitoi diet increasing steadily over time (Weber et al., *In prep*, Weber, *In prep*). It is into this dynamic social and ecological setting that early pottery starts to appear in Cis Baikal, and it is logical to postulate some kind of general association between the growing importance of fishing, and the coeval appearance of ceramics (McKenzie, 2009:198).

Interestingly, however, our results fail to identify a specialised relationship between processing of aquatic foods and the early use of pottery at the Gorelyi Les site. This contrasts strongly with the more general pattern of early ceramic usage across Eastern Eurasia, which suggests a close and often enduring link between hunter-gatherer pottery and the specialised processing of aquatic resources (Craig et al., 2007; Craig et al., 2013; Lucquin et al., 2016a; Gibbs et al., 2017; Kunikita et al., 2017; Oras et al., 2017; Shoda et al., 2017; Lucquin et al., 2018). While the results from Gorelyi Les are somewhat unexpected, it is worth noting that specialised processing of aquatic foods in the pottery may have emerged later, as has been identified in other regions of boreal-forest Eurasia (e.g. Bondetti et al 2019), and that the current relative dating of the Gorelyi Les pottery may place it earlier in the Kitoi cultural sequence, which is prior to the increased dietary importance of fishing (Weber et al., in prep).

Geographic location and site function may have played a role at Gorelyi Les, which is 50 km from the richest fisheries on the Angara River (Weber, in prep). The faunal and tool-kit evidence suggest that it may have been a more general-purpose site, perhaps serving as a stopping off point as groups moved up and down the Belaia River. Few fish bones have been recovered here, whereas there are abundant ruminant bones, suggesting that it was not a major processing site for aquatic resources. In contrast, excavations of Early Neolithic occupation levels at the Ust' Khaita site located further upstream, generated abundant evidence of fish processing (Savel'ev et al., 2001; Kurzybov, 2011), and pottery may have been used differently here.

Nor is there evidence that the pottery analysed from Gorelyi Les was used for specialised processing of ruminant fats – or served as a kind of "grease station" technology (Elston et al 2011; Karr et al 2015) – despite the fact that the site may have operated as a general hunting camp (Ready, 2008). Clearly, a much wider range of activities was going on at the site, including some fishing and also processing of plant resources, perhaps in relation to the production of resin and mastics for tool production, especially if the site functioned as a "gearing up" camp for hunting expeditions.

Overall, then, the general use of the pottery noted at Gorelyi Les appears to match a broad-based and flexible economic strategy grounded in hunting, fishing and gathering in a boreal forest environment. There are no indications that this pottery was used for ritual activity nor for the serving of exotic or lavish foods in feasting events (Hayden 2009). In managing routine tasks around the hearth, the pots may simply have offered advantages over stone boiling of foods in baskets and boxes, allowing the slow simmering of foods and preparation of nutritious mixed dishes, while freeing up time for performance of other domestic tasks (Weber, in prep). Nevertheless, it is noteworthy that fish and ruminant products were processed in different pots compared to other products, such as non-ruminant animals. It is difficult to speculate on the meaning of this culinary or even technological distinction and further research should be directed toward examining whether the pattern corresponds to distinct pottery forms, technological attributes or decorative motifs.

Conclusion and outlook

The Late Mesolithic communities living in Cis-Baikal in the early Holocene were undergoing major changes. As the Kitoi mortuary traditions started to from around 7560 cal BP, these groups were gradually "becoming Neolithic" through their initial adoption of clay cooking pots. In this study, however limited in the geographic scope, we have identified that, at least at Gorelyi Les, the earliest

and rather small-scale use of this novel technology was highly generalised, with the pots used to prepare a wide range of foods. This mirrors the broad and flexible foraging strategies that existed at the start of the Kitoi cultural pattern. Ironically, the combined impacts of the bow and arrow – along with improved fishing technologies – may have had a far more substantial effect on Kitoi subsistence and social life than the earliest adoption of pottery that actually defines them as "being" Early Neolithic.

Beyond these more specific conclusions, this pilot study has demonstrated that recovery, analysis and interpretation of lipid residues from archaeological pottery assemblages is viable at Cis Baikal archaeological sites. Much more work clearly needs to be done on a wider selection of Kitoi pottery assemblages, and some interesting patterns will likely emerge via analysis of residues in the net-impressed "mortuary" pottery recovered from Kitoi graves, as well as via analysis of pottery use at other contemporary habitation sites. Combined with this, it would be useful to source clays used in pottery manufacture, to test whether pots were being moved around the landscape, or just made and cached at camp sites and other hunting or fishing stations.

In later periods of Cis-Baikal prehistory, the scale of pottery use, and the diversity of styles, undergoes significant expansion (McKenzie, 2009), and may have led to the emergence of more specialised roles for certain vessels. Comparative lipid-residue analysis of these diverse assemblages could generate useful insights into the spatiotemporal variability of food processing and consumption, and would greatly complement the existing bioarchaeological datasets that pertain to the diet, health and mobility of individuals from the Kitoi and Cis Baikal's subsequent Late Neolithic and Early Bronze age mortuary traditions (i.e. the Isakovo, Serovo and Glazkovo).

Mixing Model

The mixing model was performed using R studio (version 3.5.1). Further information is provided in the Appendix 7.

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Chapter 4

Fruits, fish and the introduction of pottery in the Eastern European plain: Lipid residue analysis of ceramic vessels from Zamostje 2

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Author contributions: OEC, **MB** and designed the research. OL undertook the sampling. **MB** and SS undertook the lipid residue analysis. OL, ED and PJ providing contextual information. **MB**, AL and OEC worked on the interpretation of the lipid residue analysis. **MB** and OEC wrote the manuscript with contributions from all authors.

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Abstract: The Neolithization of Northern Eurasia is marked by the emergence of pottery among hunter-gatherer societies. The driving forces behind the adoption of ceramic cooking vessels among non-agricultural societies remain unclear, although previous research, mainly in North East Asia (e.g. Japan, Korea and the Russian Far East), suggests that it was adopted as a specialist technology for processing aquatic resources, linked to the intensification of fishing activities and a move to sedentism. The stratified site of Zamostje 2 in the forest zone of the Volga-Oka region includes both aceramic Mesolithic and two early ceramic horizons dating to Early Neolithic (EN) and Middle Neolithic (MN). This provides a unique opportunity to look at the impacts of the adoption of pottery on the wider economy and determine whether pottery function changes over time. This was achieved through the analysis of lipids from 166 potsherds dating from the earliest phases (mid-6th millennium cal BC) to the MN (5th millennium cal BC). Contrary to our expectations, the pottery from the EN phase was used to process a broad range of foodstuffs including terrestrial resources, such as forest fruits, in addition to freshwater fish. In contrast, pottery from the MN phase was used exclusively for processing aquatic

resources. The results show that in this case, pottery was adopted as a more general-purpose cooking container, at least in the earliest phases of use, and that a specialist function only emerged later.

Keywords: Early pottery, Hunter-Fisher-gatherers, Lipid residue analyses, Early Neolithic (EN), Middle Neolithic (MN), Zamostje 2.

1. Introduction: Hunter-gatherers pottery and Neolithization of Northern Eurasia

Archaeologists now acknowledge two contrasting processes of Neolithization. The classic definition of the Neolithic arose in Western Europe and involved the emergence of farming in the Near East, and the dispersal of a package of innovations including domestic crops and animals, village life and pottery into Northwest Europe. In contrast, archaeologists working in other parts of Eurasia define the onset of the Neolithic by the emergence of pottery cooking containers among hunter-gatherer societies, along with an increase in sedentism, emergence of new subsistence strategies with food storage and fishing intensification, and settlement at strategic locations giving access to a high biomass (Barnett and Hoopes, 1995; Kuzmin, 2006; Keally et al., 2007; Jordan and Zvelebil, 2009; Gibbs, 2015; Jordan et al., 2016). The earliest hunter-gatherer ceramic cooking vessels derive from East Asia. So far, the oldest pottery, securely dated, appears to have been made towards the end of the Late Pleistocene epoch, between 16,000 and 13,000 cal BC in South China, Japan, and the Amur River basin in the Russian Far East (Serizawa, 1979; Habu, 2004; Kudo, 2004; Kuzmin, 2006, 2017; Keally et al., 2007; Boaretto et al., 2009; Jordan and Zvelebil, 2009; Hommel, 2012). Although debated, it is suggested that pottery technology spread westward across Eurasia during the Holocene, eventually influencing several Northern European Mesolithic cultures (van Berg and Cauwe, 1998; Dolukhanov et al., 2005, 2009; Haaland, 2009; Jordan and Zvelebil, 2009; Gronenborn, 2011; Hartz et al., 2012; Jordan et al., 2016). Its adoption may have had a major impact on prehistoric populations’ lifeways as it became an essential everyday technology to cook and store foods. However, the motivations for the emergence, adoption and spread of pottery are still an ongoing debate in archaeology. The main questions are: (1) What was the function of the earliest ceramic vessels and did function change over time? (2) Was the adoption associated with substantial changes in economy, technology, society? (3) Did the adoption coincide with major environmental changes?

The increase of pottery abundance and its spread across large parts of Eurasia appears to occur in the Early Holocene, ca. 9700 to 5000 cal BC, and corresponds with a period of climate amelioration (Alley et al., 1993; Smith et al., 2011; Cummings, 2014). In Eurasia, numerous environmental changes occurred and rich new ecotopes emerged at this time. New vegetation (e.g. tundral, deciduous

woodland) and fauna (e.g. reindeer, deer, wild boar, elk) spread to areas now free of ice (Khotinsky, 1993; Cummings, 2014; Zhilin, 2014) creating new opportunities for hunting and gathering. In the Postglacial landscapes, numerous chains of lakes were also formed and the rise of temperature and humidity that followed considerably enriched and diversified the productivity of the lacustrine ecosystems (Kulkova et al., 2001). In particular, the emergence of pottery appears to correlate with an increasing emphasis on exploitation of aquatic resources, combined with establishment of riverside and lake-edge settlements across large parts of Eastern and Western Siberian (Chairkina and Kosinskaia, 2009; Haaland, 2009; McKenzie, 2009), as well as Eastern Europe and the Baltic Sea Basin (Jordan and Zvelebil, 2009; Pesonen and Leskinen, 2009). These combined developments make it plausible to suggest that early pottery may have been linked to the processing of fish and other aquatic resources, and that ceramic cooking vessels may have offered certain advantages over other perishable container technologies.

Recent research has employed organic residue analysis of early pottery containers to clarify vessel function and explore some of the motivations that may have led to its emergence among hunter-fisher-gatherer societies (Jordan and Zvelebil, 2009). One clear pattern emerging from many of these regional studies is the apparent association between pottery and the processing of aquatic resources, including Northern and North-Eastern Europe (Craig et al., 2007; Isaksson, 2009; Oras et al., 2017), Sakhalin Island in the Russian Far East (Gibbs et al., 2017), Japan (Craig et al., 2013; Lucquin et al., 2016a, 2018), Korea (Shoda et al., 2017) and even in north-eastern North America (Taché and Craig, 2015). Interestingly, the close association between pottery and the processing of aquatic resources is observed even at sites where the faunal, botanical and artefactual evidence indicate exploitation of a much wider range of food resources (Lucquin et al., 2016a, 2018; Shoda et al., 2017; Jordan and Gibbs, 2018).

One area neglected by organic residue analysis is the vast forest zone of the Eastern European Plain. This extends from the Ukraine and western Belarus through European Russia to the Ural Mountains in the East. This region clearly participated in the wider uptake of pottery by local hunter-gatherers, but the driving forces of its adoption are not yet properly understood. Our study analyses the function of pottery from a key Upper Volga site, Zamostje 2. This site is an ideal case-study due to its significant assemblage of well-preserved artefacts and ecofacts and an uninterrupted and well-dated stratigraphic sequence. Crucially, it captures the introduction of the first pottery culture in the Upper Volga Region, Central Russia, and its subsequent development during the MN (Lyalovo Culture). This gives us a rare opportunity to evaluate the economic impact of this technological change but also,

using organic residue analysis, to reconstruct the use of early pottery and therefore to help understanding the motivations behind its adoption.

Our goals were twofold. Firstly, we aimed to determine whether the newly introduced pottery had a specific function, that is to say, was adopted for a specific reason. Secondly, we aimed to examine the evolution of pottery use over time from its emergence until the typological change concurrent with the MN. In this study we test the hypothesis that pottery was introduced within hunter-gatherer societies mainly for the processing of aquatic resources to then become a more general cooking container, as has been demonstrated elsewhere, e.g. Japan (Lucquin et al., 2016a).

2. The multi-layer waterlogged site of Zamostje 2, central Russia (Upper Volga Region)

Zamostje 2 is located ca. 110 km north of Moscow in the Sergiev Posad Region along the Dubna River (Fig. 4.1; Appendix 8). The site was established on the edge of a vast lake basin with numerous river channels and was occupied during the Atlantic period from ca. 6600-4000 cal BC (Radu and Desse-Berset, 2013; Kulkova, 2014; Lozovski et al. 2014b). Two anthropogenic activity peaks are recorded, attributable to five successive cultural layers from the Late (Lower and Upper Layers from ca. 6500 to 5900 cal BC) and Final Mesolithic (from ca. 5900 to 5700 cal BC) to the Early (ca. 5700–5400 cal BC) and MN (ca. 5000-4000 cal BC) (Fig. 3.4) (Lozovski, 1996; Lozovski and Lozovskaya, 2013; Lozovski et al., 2013a, 2013b; 2014b; Mazurkevich et al., 2013; Meadows et al., 2015).

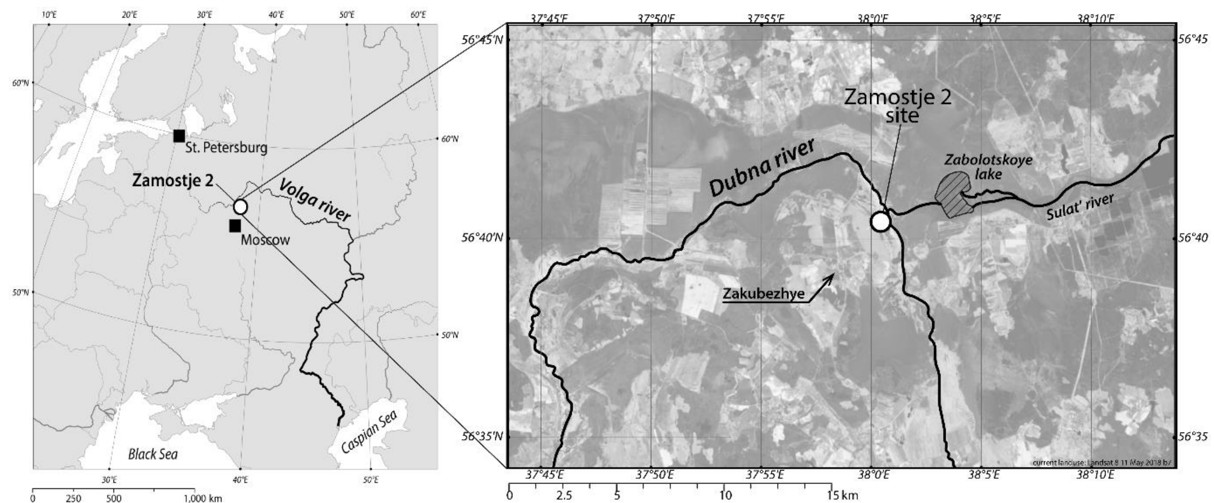

Figure 4.1 Location of Zamostje 2 along the Dubna river.

Pottery constitutes the most important artefact in the Neolithic layers at Zamostje 2. In total, 18,300 sherds have been recovered from the EN layer, far more than similar sized excavations from

contemporary sites in the Eastern European forest zone (Lozovski, 2003; Lozovski et al. 2014a; Mazurkevich et al., 2013; Mazurkevich and Dolbunova, 2015). In total, 26,911 sherds were recovered from the MN layer (Lozovski et al., 2015). The Upper Volga culture (UVC), attributed to the EN (Fig. 4.2; Fig. 4.4), was the first pottery culture in this region and consisted of several ceramic stages (Kostyleva 1986, 1987; 1994; 2003. Dolbunova et al. 2017). The ceramic material associated with the central zone of UVC culture, includes pottery that is either undecorated or decorated by rows of pointed impressions (Early Stage), "false-cord" decoration, incised lines, teethed-stamp impressions (end of Early Stage) (Kostyleva, 1994), short-teethed stamp impressions (Middle Stage) and finally different lengths of comb stamps (Late Stage) (Hartz et al., 2012; Mazurkevich et al., 2013; Lozovski et al. 2014a; Dolbunova et al., 2017). It is not clear whether these styles evolved within the region or developed from external influence(s) (Smirnov 2004; Mazurkevich et al., 2013).

Overall, the Zamostje 2 pottery assemblage is very fragmented, preventing an accurate quantification of the size and capacity of vessels through the different phases. The whole early Neolithic layer is "compressed" within a rather narrow horizon which complicated identification of specific functional/household areas or any specific "cultural" context, as well as identifying particularities of pottery type location. The EN phase comprises a wide range of pottery forms, mainly flat-bottomed cooking vessels and some bowls, most likely due to the extended period of time over which this material was deposited. Within the undecorated pottery, two completely different technological and morphological traditions were distinguished, which might indicate influences from different regions (Mazurkevich et al., 2013). Firstly, pottery which appeared here in the first half of the 6th millennium cal BC (Zaretskaya and Kostyleva, 2008) bears similarities with the pottery of the Middle Volga culture, Late Elshanian culture and Rakushechny Yar culture (Kostyleva, 2003). Later ceramic stage (Late Stage) might reflect influences from the Volga-Kama area.

The MN Phase is defined by the appearance of Lyalovo culture pottery vessels, characterised by pit and pit-comb ornaments across the whole of their exterior surfaces (Fig. 4.2e). This pottery style may appear to originate in the Volga–Oka interfluve (Lozovski et al., 2015; Vybornov et al., 2018). In contrast to the preceding UVC with a high proportion of flat-bottomed ware, Lyalovo complex vessels have roundish and conical bases (Lozovski et al., 2015; Vybornov et al., 2018). Nonetheless, vessels reconstruction, based on similar types of vessels found on other sites in this region, does not indicate a significant form change from Early Neolithic to Lyalovo culture (Gurina and Krainov, 1996; Lozovski, 1996). On other Lyalovo culture sites some vessels were found fulfilled with fish scales (Gurina and Krainov, 1996).

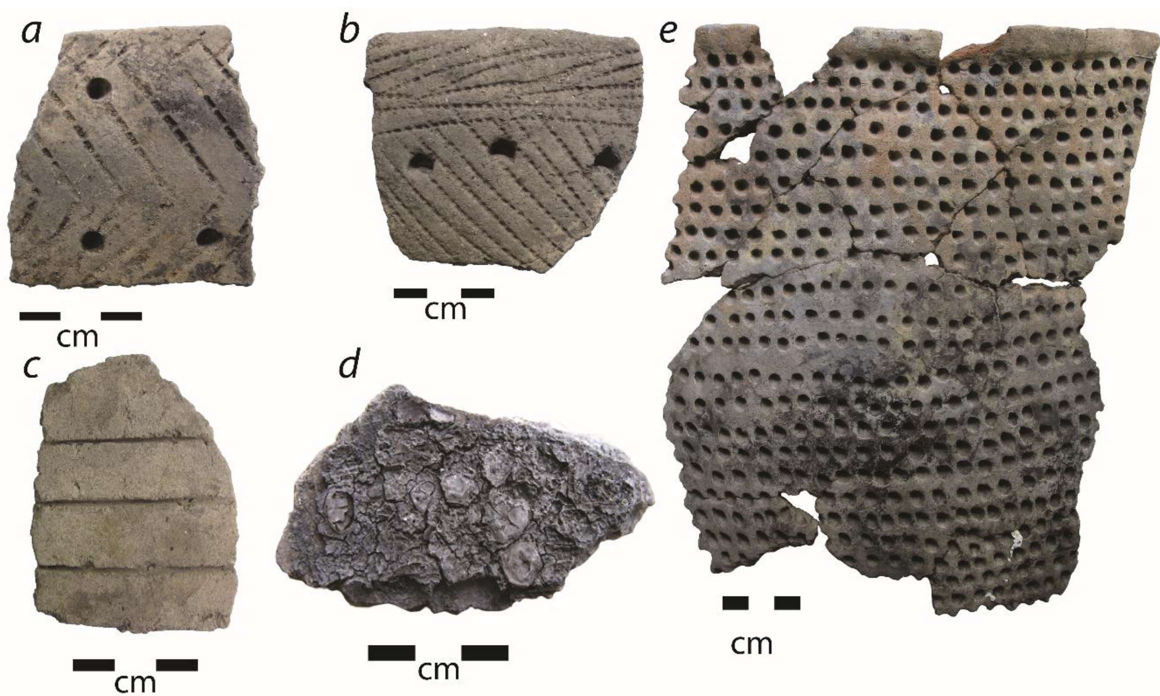

Figure 4.2 Pottery from Zamostje 2: EN sherds with (a, b) long-comb decorations (late stage), (c) covered by incised lines (early stage); (d) Ceramic from EN layer (early stage) with remains of Viburnum (*Viburnum opulus L.*) berries in the crust, (e) MN Pottery with pit ornamentation.

Gathering practices were an important component of the Zamostje 2 inhabitants' lifeways. Up to 51 plant macrofossil taxa have been recovered and identified, including seeds and fruits (Fig. 4.3; Fig. 4.4). Most of the identified plant remains are from edible species or species that conceivably had a medicinal purpose (Berihuete-Azorin and Lozovskaya, 2014; Berihuete, 2018). Of the mammalian fauna, elk (*Alces alces*) and beaver (*Castor fiber*) were preferentially targeted, both easily accessible for hunting at the lake edge environment. Combined, these two species represent 70–90% of the mammal remains from Zamostje 2 (Leduc and Chaix, 2014, 2018). Birds such as waterfowl and forest species (mainly duck, *Anatidae* and capercaillie, *Tetrao urogallus* respectively) were exploited, with a rise of the latter in the Neolithic period, but this does not seem to have been a major economic activity (Mannermaa, 2013; Mannermaa and Treuillot, 2014). However, fishing at Zamostje 2 seems to have been a substantial subsistence activity, with hundreds of thousands of fish bones recovered (Lozovski et al., 2013a; Radu and Desse-Berset, 2013; Leduc and Chaix, 2014, 2018), as well as numerous fishing structures (e.g. fish traps, screens and fences) and fishing related tools (Fig. 4.3) (harpoons, barbed points, hooks, floats, small knots from nets, knives for fish processing) (Clemente et al., 2002; Lozovskaya and Lozovski, 2013; Lozovski et al., 2013b; Radu and Desse-Berset, 2013). From this evidence, two major fishing practices have been suggested. The first, during the earlier occupation of

the site (i.e. Late Mesolithic), involved the use of hand nets from boats on the lake, whilst the second, from the Final Mesolithic, involved the inhabitants of Zamostje 2 fishing on flooded channels or ponds with hooks and harpoons and started to use stationary wooden structures (fish fences and traps) to conduct a more “passive fishing” (Gyria et al., 2013; Lozovski et al., 2013b) (Fig. 4.4). Apart from that, general food procurement, based on hunting, fishing and gathering, seems to have remained stable from the Late Mesolithic to Neolithic, despite the introduction of pottery.

Figure 4.3 Plant and faunal remains and artefacts from Zamostje 2: (a) bone hooks from the EN, Final Mesolithic and mixed layers (from left to right), (b) bone net needle from the Upper Mesolithic, (c) floats from the Lower and Upper Mesolithic layer (from top to bottom), (d) tool made from beaver mandible from the Lower Mesolithic layer, (e) elk head figures made from elk antler from the Lower Mesolithic layer, (f) and (g) pine cone and nut remains from the Lower Mesolithic and mixed layer respectively, (h) barbed point from the EN.

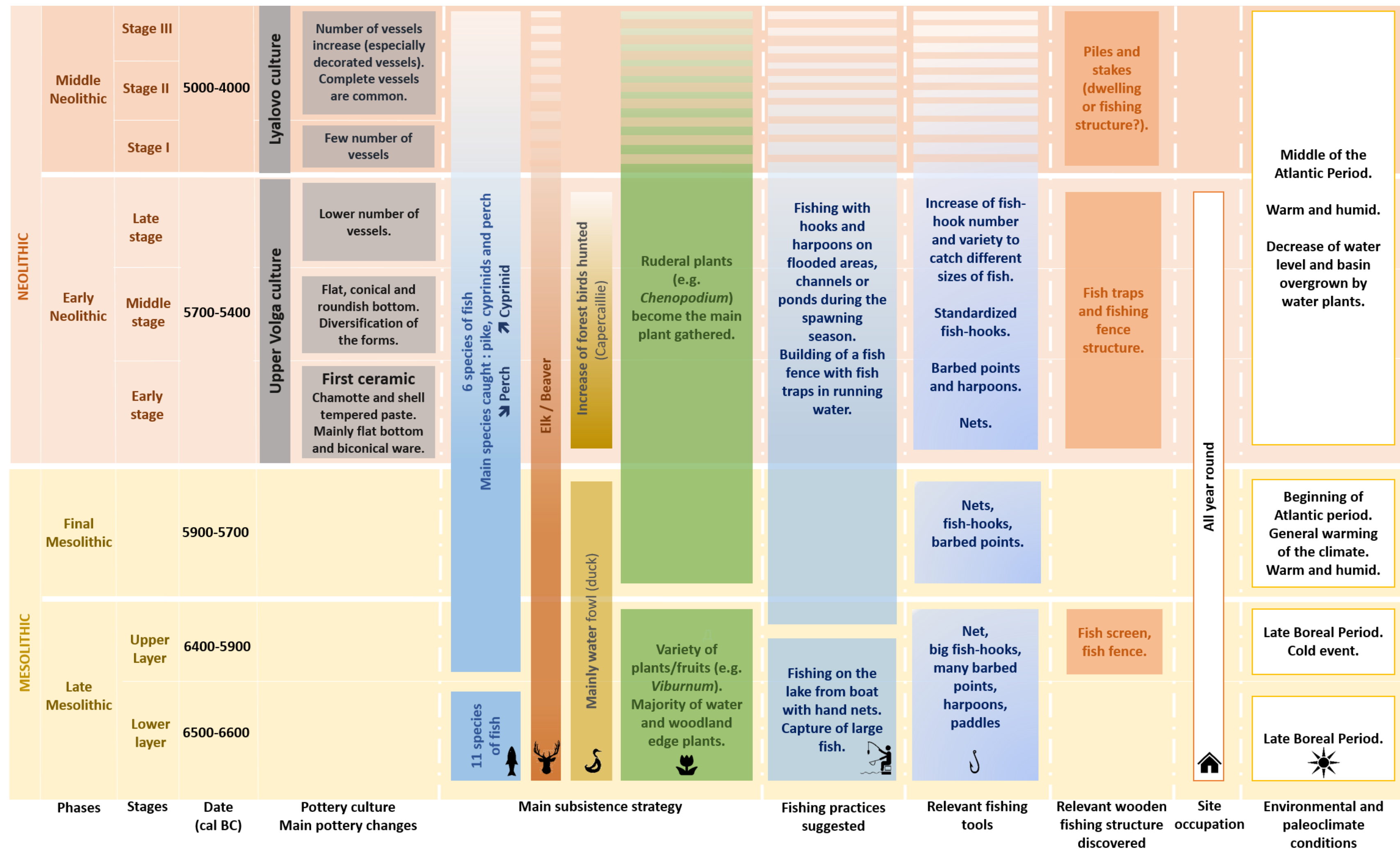

Figure 4.4 Summary of archaeological evidence changes in Zamostje 2: dates, pottery cultures, subsistence strategies and environmental conditions. Based on the following references: Lozovski, 1996; Clemente et al., 2002; Ershova, 2013; Gyria et al., 2013; Lozovskaya and Lozovski, 2013, 2016; Lozovski et al., 2013a, 2013b; 2014a; 2014b; Mannermaa, 2013; Radu and Desse-Berset, 2013; Berihuete-Azorin and Lozovskaya, 2014; Leduc and Chaix, 2014, 2018; Mannermaa and Treuillot, 2014; Meadows et al., 2015; Berihuete, 2018; Ershova and Lozovskaya, 2018.

3. Material and methods

3.1. Sampling strategy

A total of 240 samples were subjected to organic residue analysis, representing no fewer than 166 vessels. Of the pottery studied, 114 (63 from EN; 51 from MN) had charred residues indicating they had been used for cooking. A further 52 vessels (32 from EN; 20 from MN) without foodcrusts were selected. Pot sherds assigned from the Early to Late stage of EN (76 potsherds; 67 foodcrusts) and to the MN (45 potsherds; 52 foodcrusts) (Appendix 9) were chosen in order to examine whether there was a temporal change in pottery use. In addition, lipids of modern plants (Viburnum, *Viburnum opulus L.*), ruminants (elk), wild non-ruminants (beaver) and fish (pike, *Esox lucius*, perch, *Perca fluviatilis*, cyprinids, *Cyprinidae* and bream, *Abramis brama*) from the region were also analysed for comparison with the archaeological samples (Appendix 9).

3.2. Lipid residue extraction

Lipids were extracted and methylated from all samples following a modified one step acidified methanol protocol (Craig et al., 2013; Papakosta et al., 2015). A selection of samples (Appendix 9) was subjected to solvent extraction following published methodologies (Charters et al., 1993; Regert et al., 1998; Stern et al., 2000; Gregg, 2009; Papakosta et al., 2015) in order to facilitate the detection of any triacylglycerols or wax esters. All extracts were analysed by Gas Chromatography-Mass Spectrometry (GC-MS) using different columns and modes to identify characteristic compounds (e.g. aquatic biomarkers). Where the lipid yield was sufficient, the methanolic acid extracts were subsequently analysed by Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) in order to determine the carbon isotope values of the two most abundant fatty acids ($C_{16:0}$ and $C_{18:0}$). Foodcrusts were also analysed by Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS) to determine their stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope values, as described previously (Craig et al., 2007; Lucquin et al., 2016a; Shoda et al., 2017). Further information is available in Appendix 1.

4. Organic residue analysis of early and Middle Neolithic potsherds

4.1. Lipid quantification and characterisation

All the charred surface deposits (EN, n = 67; MN, n = 52) and absorbed residues (EN, n = 76; MN, n = 45) were extracted with the acidified methanol protocol and analysed by GC-MS and GC-C-IRMS to obtain specific compositional information. Additional solvent extraction (n = 27) was carried out where enough materials were present. Over 78% of the samples analysed provided interpretable lipid yields

(potsherds > 5 µg/g; foodcrusts > 100 µg/g) (Evershed, 2008a; Lucquin et al., 2018), confirming the excellent preservation conditions at the Zamostje 2 site.

In general, the lipid profiles obtained (Fig. 4.5; Appendix 9) contained saturated fatty acids, ranging from $C_{10:0}$ to $C_{30:0}$, mainly dominated by $C_{16:0}$. Monounsaturated fatty acid from $C_{14:1}$ to $C_{24:1}$ and branched fatty acids (C_{13}–C_{25}) were also identified. Dicarboxylic acids are present in more than 63% of the samples, mainly C_9 (azelaic acid), although a few samples (n = 8) contained a broader range (C_7–C_{22}). Cholesterol and its derivatives were broadly represented (n = 126 samples) in the samples, confirming that animal resources have been processed in the vessels.

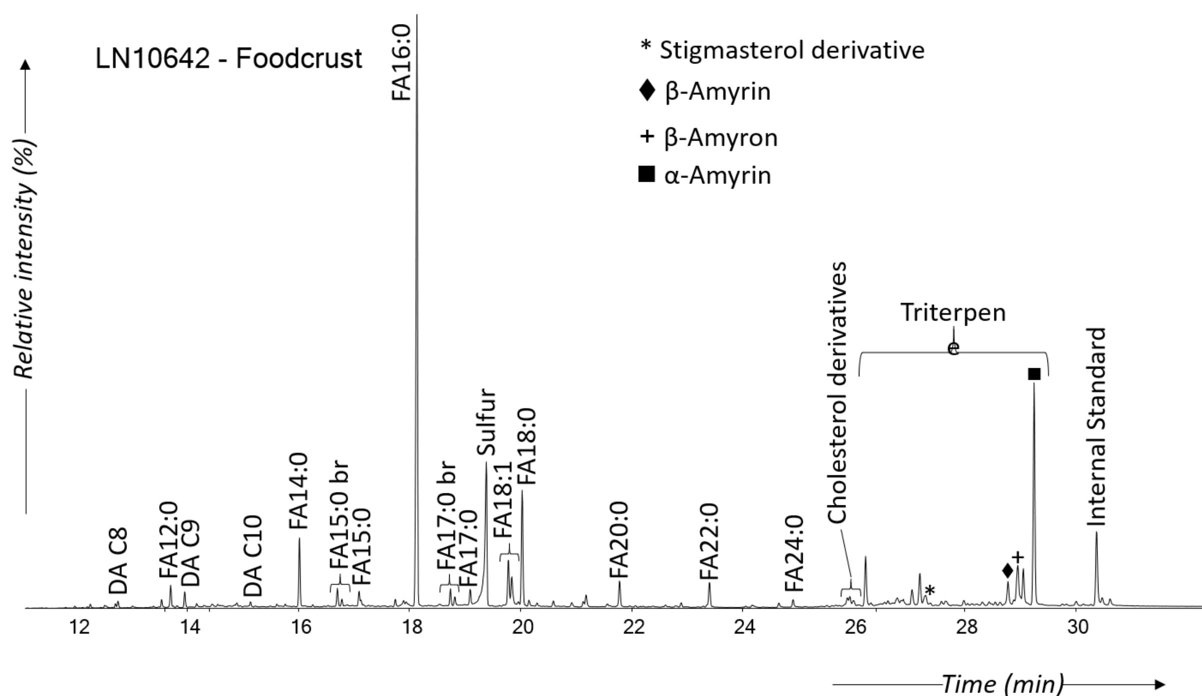

Figure 4.5 Total ion current of an acid/methanol extract of the foodcrusts sample from pot LN10642, Zamostje 2. Partial gas chromatogram of lipid showing saturated fatty acids (FA), diacids (DC), branched chain fatty acids (br), long-chain unsaturated fatty acids, sterols and triterpenes whose amyrin derivatives are indicated.

A range of plant biomarkers such as diterpenes, mainly methyl dehydroabietate and 7-oxo-Dehydroabietate and 7-oxo-Dehydroabietate, which are markers of pine resin (Regert, 2004; Mitkidou et al., 2007; Jerković et al., 2011), terpenoids, plant sterols and their derivatives were identified (n = 140 samples) (Fig. 4.5). Interestingly, α-Amyrin, β-Amyrin, β-Amyrone terpenoids, common among angiosperm triterpenoids (Phillips et al., 2006; Courel, 2016), were identified. In some foodcrusts, these compounds were one of the most dominant peaks (Fig. 4.5), which in some cases may obtain up to 498 µg/g. These compounds are found in a wide range of plants and conceivably present in the

sedimentary environment. However, their unusually high relative abundance (Fig. 4.5) shows that they are most likely endogenous and derived directly from prehistoric plant processing. Such biomarkers could be ascribed to the Viburnum berry, whose remains are macroscopically visible in some of the charred residues (Fig. 4.2d) (Berihuete-Azorín, 2016; Lozovski et al. 2014a). The analysis of modern Viburnum both undertaken here (Appendix 9) and previously published (Powers and Powers, 1940) confirms that amyrin derivatives are present in Viburnum. There is a striking consistency between samples that contain the visible remains of Viburnum berries and amyrin derivatives. Indeed, 100% of samples containing Viburnum berries also contained terpenoid markers and the relative amount of amyrins in the total lipid extracts is significantly higher in the samples with visible Viburnum (mean = 3.6% of total lipid extracted) compared to those without visible Viburnum (mean = 1.9%; Mann-Whitney $U = 82$, $z = 2.3$, $p = 0.02$).

The presence of visible Viburnum has been reported at other UVC sites (Engovatova, 2000) suggesting it was widely exploited during this period. The fruits are rich in minerals and sugars and may have held medicinal properties due to the presence of antioxidants and its astringent and antispasmodic properties (Rop et al., 2010; Kalyoncu et al., 2013; Berihuete, 2018). Whilst they can be consumed raw, cooking removes their naturally sour taste (PFAF). Also, the fresh fruits can be used to obtain red dye (Berihuete, 2018, PFAF).

In addition, biomarkers for aquatic products were identified (Fig. 4.6, Appendix 9) in many of the samples. The co-occurrence of ω-(o-alkylphenyl) alkanoic acids (APAAs) with 18 and 20 carbon atoms and isoprenoid fatty acids (phytanic, pristanic and 4,8,12- trimethyltridecanoic acid (TMTD)) are considered reliable indicators for aquatic processing in archaeological ceramics (Cramp and Evershed, 2014). Indeed, C_{20} APAAs result from thermal transformation of $C_{20:x}$ mono and polyunsaturated fatty acids, only present in appreciable concentrations in freshwater and marine animals (Evershed, 2008b; Baeten et al., 2013; Cramp and Evershed, 2014).

Whilst TMTD is mainly formed in aquatic resources, phytanic and pristanic acids are found in both aquatic and ruminant resources (Ackman and Hooper, 1968; Cramp and Evershed, 2014; Heron and Craig, 2015). To further distinguish the phytanic origin we examined the ratio of its diastereomers (3S,7R,11R,15-phytanic (SRR) and 3R,7R,11R,15-phytanic acid (RRR)) since the SRR-isomer is usually predominant (> 75.5% relative abundance) in aquatic animals (Lucquin et al., 2016b). Therefore, the detection of APAAs C_{18} and C_{20} along with either TMTD or an SRR% above 75.5% was used to confirm

the presence of aquatic products in pots. In total, 68% of the samples analysed satisfied the full molecular criteria for the processing of aquatic products in archaeological pottery.

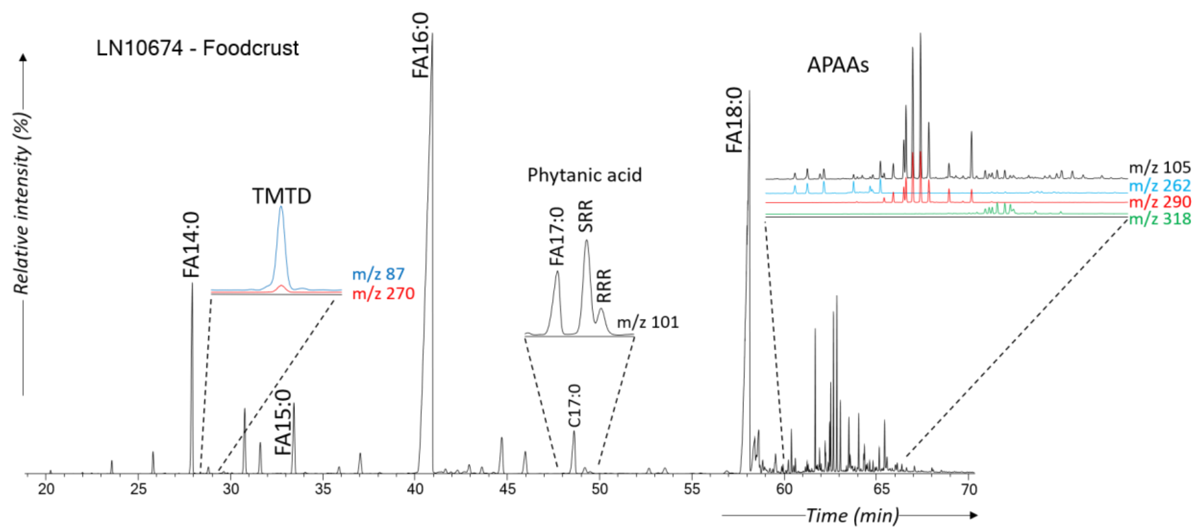

Figure 4.6 SIM chromatogram indicating the aquatic biomarkers from sample LN10642 analysed on the DB-23 column. The ω-(o-alkylphenyl) alkanoic acids were identified with ions m/z 105, 262, 290, 318, with the last three ions corresponding to the carbon length C_{16}, C_{18}, and C_{20} respectively. 4,8,12- trimethyltridecanoic acid was monitered with ions m/z 87, 270 and phytanic acid with ions m/z 101, 171, 326. The m/z 101 ion chromatogram shows the diastereomers of phytanic acid (SRR and RRR), which allowed.

Interestingly, the results indicate an increase in the processing of aquatic resources during the MN. In total, 81% of these samples contained the full set of aquatic biomarkers, compared to only 55% of the EN samples (Table 4.1). An increase in the proportion of samples containing aquatic biomarkers appears to begin at the end of the EN (Table 4.1). The occurrence of plant biomarkers follows an opposite trend, with a higher proportion of EN vessels yielding these compounds compared to the Lyalovo vessels (Table 4.1). The main plant biomarkers, amyrin derivatives, decline gradually through the EN and are absent in the MN pottery.

Period	Stage	Samples analysed	Yielding lipids (%)*	Yielding triterpenes (%)	Yielding amyrin and derivatives (%)	Yielding diterpenes (%)	Yielding plant sterols (%)	Yielding aquatic biomarkers (%)
Early Neolithic	Early stage	52			52			53
	Middle stage	44			47			49
	Late stage	10			30			73
Total		**143**	**82**	**65**	**45**	**32**	**22**	**55**
Middle Neolithic		97	86	23	0	23	12	81

Table 4.1 Table summarizing the proportion of plant and aquatic biomarkers detected in the samples according to the period and comparing the proportion of the main plant biomarkers (amyrin and derivatives) and aquatic biomarkers through the different EN stages and MN.

4.2. Stable carbon isotope analysis of individual fatty acid

To provide more information about the origin of the lipid residues, stable carbon isotope analysis of palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids was undertaken using GC-C-IRMS. Analyses were carried out on all samples yielding sufficient quantities of fatty acids; 170 samples in total, which included 100 EN and 70 MN samples. In Figure 4.7, the $\delta^{13}C$ values of the $C_{16:0}$ acid is plotted against the difference between the carbon isotope values of two main fatty acid ($\Delta^{13}C = C_{18:0}$-$C_{16:0}$). This approach enables us to distinguish ruminant adipose and dairy fats from other non-ruminant sources (Dudd, 1999; Craig et al., 2012, 2013; Cramp et al., 2014; Colonese et al., 2015; Taché and Craig, 2015; Lucquin et al., 2016a). We also include some modern samples from the Zamostje 2 area (Appendix 9). In the majority of cases the observed values are consistent with a non-ruminant source. The large carbon isotope range and negative correlation between $\delta^{13}C_{16:0}$ and $\Delta^{13}C$ is however perplexing, and points to a mixture of different sources, which could include freshwater fish with different isotope values, plants or non-ruminant terrestrial animals, such as beaver, which are abundant in the faunal assemblage. Analysis of the collagen extracted from the bones of pike (n = 10) and cyprinids (n = 10), shows a wide range of $\delta^{13}C$ values (pike between −23.3 and −19.5‰; cyprinids between −27.2 and −22.3‰) (Meadows et al., 2019 In prep). The more positive $\delta^{13}C_{16:0}$ values could have been obtained by the processing of ruminants consuming C_4 plants (Gregg, 2009; Craig et al., 2012). However, the absence of C_4 plants in this region means that ruminant products do not adequately explain the variation; two modern local elk samples are plotted to illustrate this point. There is also no difference in the fatty acid carbon isotope value by period or by presence/absence of aquatic-derived lipids. However, the $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values of EN samples show a greater variability compared to the MN (Mann-Whitney test U = 2846, z = 2.07, p = 0.04; U = 2780, z = 2.28, p = 0.02 respectively), which presumably reflects the wider range of foodstuffs processed in these vessels.

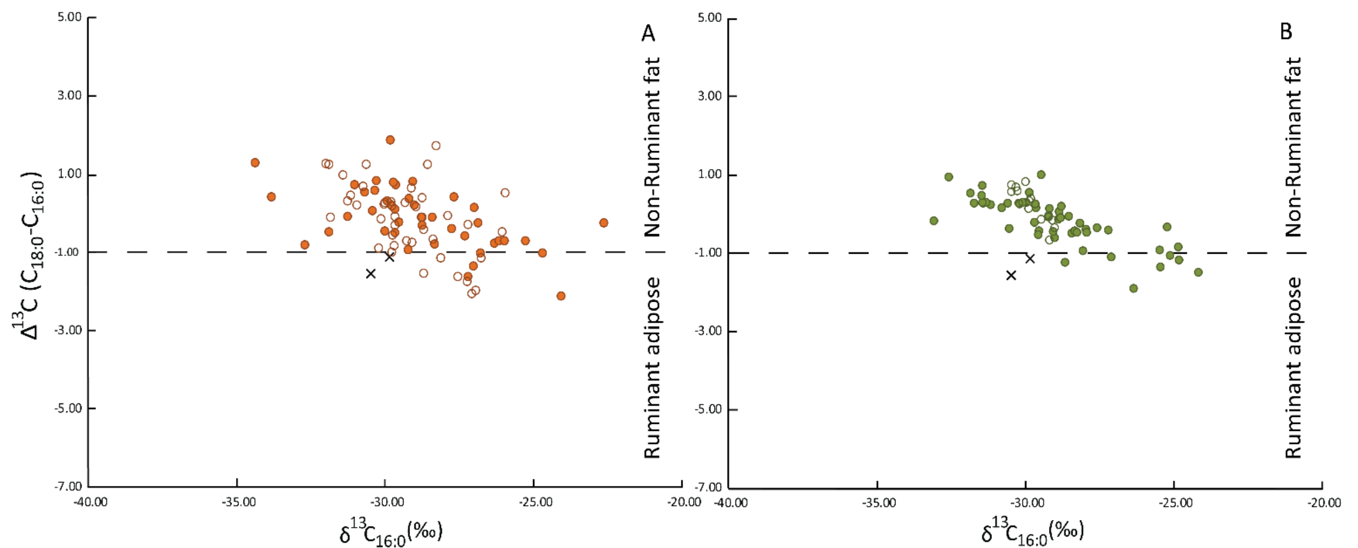

Figure 4.7 $\Delta^{13}C$ ($\delta^{13}C_{18:0}$–$\delta^{13}C_{16:0}$) values against $\delta^{13}C_{16:0}$ values obtained from foodcrusts and sherds from (A) EN (n = 100) and (B) MN (n = 70) samples. Crosses indicate modern elk from the Zamostje 2 region. Samples with the full and partial set of aquatic biomarkers are shown by filled circles.

4.3. Bulk isotope analysis of charred surface deposit

Bulk stable isotope values and the elemental analysis for the charred surface deposits (n = 108) are plotted in Figure 4.8 and reported in Appendix 9. The bulk $\delta^{13}C$ isotope values from Zamostje 2 range from −23.3 to −29.6‰ and are indicative of a range of terrestrial C_3 plants, terrestrial mammals and freshwater fish, but these data are also influenced by the relative degree of preservation of lipids, carbohydrates and proteins making them difficult to interpret (Craig et al., 2007, 2011; 2013; Yoshida et al., 2013; Heron et al., 2016). Conversely, the nitrogen present in the charred products is derived from proteins and therefore the $\delta^{15}N$ values reflect the trophic level of the organisms processed in the vessels. Thus, high $\delta^{15}N$ values, above ca. +7.0–9.0‰, are usually characteristic of aquatic resources (Dufour et al., 1999; Craig et al., 2013; Choy et al., 2016), whereas lower ones are consistent with terrestrial organisms (Yoneda et al., 2004; Craig et al., 2007; Yoshida et al., 2013). The atomic C:N ratio is indicative of the amount of protein versus other macromolecules (carbohydrates and lipids). Generally animal tissues, enriched in protein, will have lower C:N ratios compared to plant tissues, enriched in carbohydrates such as starch and cellulose (Yoneda et al., 2004; Yoshida et al., 2013; Choy et al., 2016; Heron et al., 2016; Lucquin et al., 2016a).

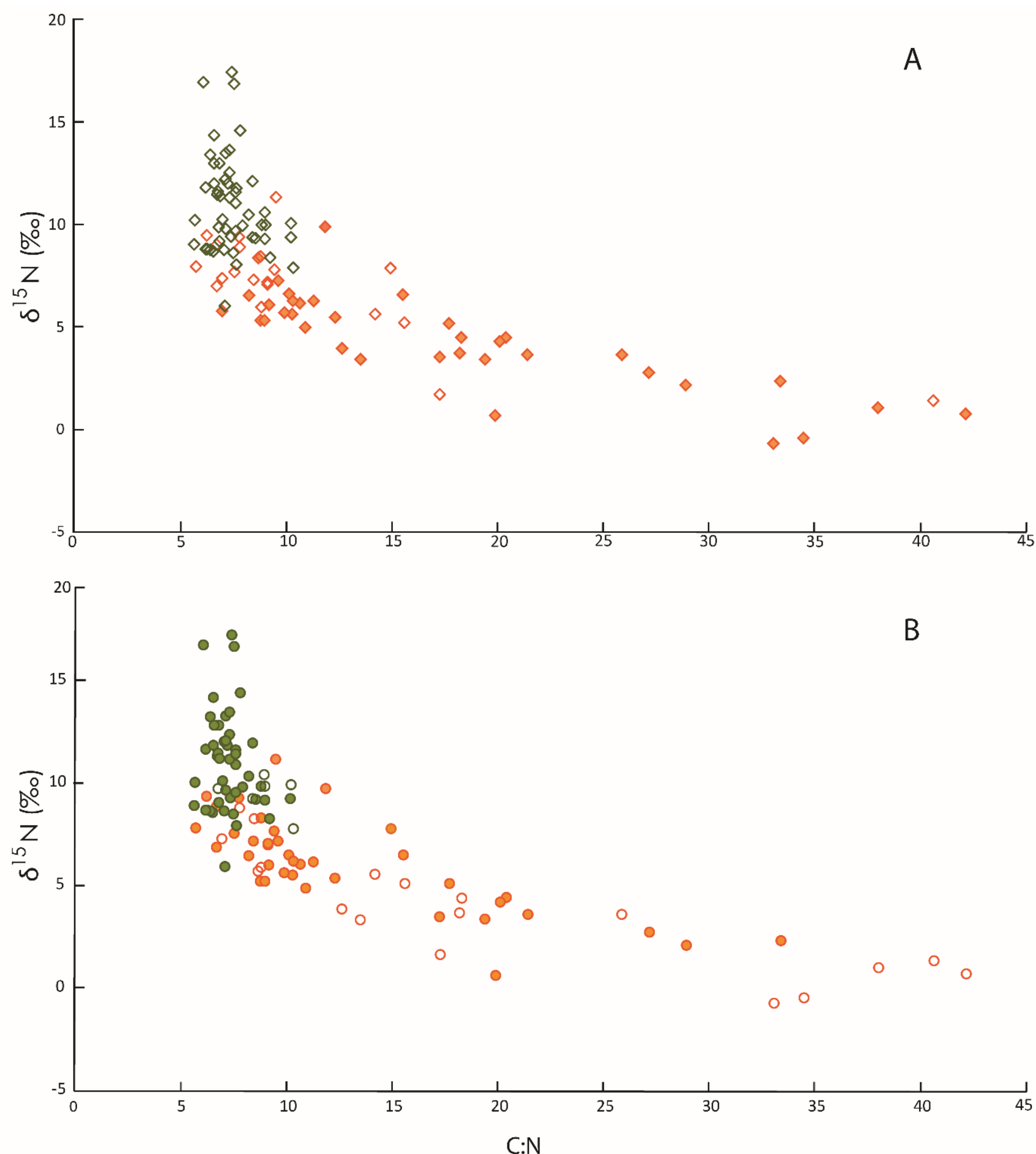

Figure 4.8 Plot of $\delta^{15}N$ bulk isotope values against C:N ratio obtained from foodcrusts samples from Early (n = 56) in orange and MN (n = 52) in green showing (A) samples in which amyrin derivatives were detected by filled diamonds, (B) samples with the full set of aquatic biomarkers by filled circles.

Interestingly, there is a clear correlation between the bulk $\delta^{15}N$, C:N ratio (Table 4.2) and molecular characterization of these samples. Pottery vessels with high C:N ratios tend to have lower $\delta^{15}N$ values, indicating that they are mainly derived from plant products, supported by a greater proportion containing amyrins (Fig. 4.8a). Samples with lower C:N ratios and higher $\delta^{15}N$ values have a greater proportion of aquatic derived lipids (Fig. 4.8b), suggesting they were used for processing fish. Furthermore, there is a clear difference in $\delta^{15}N$ and C:N ratios between EN and MN pottery. The former

has more variable values, indicating that a wider range of foodstuffs were processed, which must include mixtures of aquatic and plant products (and possibly terrestrial animals). The later pots have a greater proportion of aquatic products, consistent with increasing specialisation focused on fish processing. These data contrast with the lipid-specific carbon isotope measurements made on the same samples which show no clear difference between periods (Fig. 4.7). The reason for this is that the bulk isotope measurements reflect greater variation in the contribution of other macronutrients (carbohydrates and proteins) to the potsherds compared to the lipid-specific measurements.

Category	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	C:N ratio
Period (EN vs. MN)	U = 118; z = 8.2; $p<0.01$	U = 1217; z = 1.3; $p = 0.2$	U = 339; z = 6.8; $p<0.01$
Aquatic biomarkers (presence vs. absence)	U = 457; z = 3.9; $p<0.01$	U = 949; z = 0.1; $p = 0.9$	U = 397; z = 4.3; $p<0.01$
Amryin derivatives (presence vs. absence)	U = 156; z = 7.4; $p<0.01$	U =1126; z = 1.0; $p = 0.3$	U = 198; z = 7.1; $p<0.01$

Table 4.2 Mann-Whitney U test showing correlation between the bulk $\delta^{15}N$, C:N ratio and molecular characterization. The test revealed a significant difference of $\delta^{15}N$ and C:N ratio between EN and MN samples, samples with or without the full set of aquatic biomarkers and samples with or without Amyrin derivatives. However, there is no correlation between $\delta^{13}C$ values and periods or molecular characterization of samples.

5. Discussion

The main aim of our study was to examine the function of pottery recovered from Zamostje 2 following its introduction, during the early Neolithic period (ca. 5700-5400 cal BC), and its subsequent development in the MN (Lyalovo period, after 5000 cal BC). Based on expectation from previous studies of pottery use by Eurasian hunter-gatherers (Craig et al., 2007, 2013; Taché and Craig, 2015; Lucquin et al., 2016a; Gibbs et al., 2017; Oras et al., 2017; Shoda et al., 2017), we hypothesized that the first pottery in this region would have been used for processing aquatic resources. The organic residue analyses we undertook refute these assumptions. All the evidence shows that pottery at Zamostje 2 initially was used to process a wide range of foodstuffs, certainly including aquatic and terrestrial plants products and possibly also terrestrial animals. It is only in the MN that a different pattern emerges, with almost all the samples analysed showing a clear aquatic molecular and isotopic signature, pointing to specialisation in the use of pottery at this time.

The new evidence we have generated from the use of pottery contrasts with faunal analyses so far undertaken on the Zamostje 2 assemblage. These data show that fishing was a significant economic activity even before the introduction of pottery, during the Mesolithic period (ca. 6500-5700 cal BC), and that the importance of this activity did not fundamentally change throughout the EN period. Research on the MN faunal assemblage is not complete, but the quantity of fish bone compared to terrestrial species remains similarly high (Radu and Desse-Berset, 2013). Locally, the paleoenvironmental records show dense forest cover during EN with greater afforestation of the lake shores, and a change to a marshier landscape during the MN (Ershova and Lozovskaya, 2018). More broadly, the introduction of pottery is not associated with significant change in climate and occurs several centuries after the warming events marking the Holocene Thermal Maximum, ca. 6000–2000 cal BC (Heikkilä and Seppä, 2010). In summary, resources available in the Neolithic inhabitants of Zamostje 2 were readily available to the Mesolithic hunter-gatherers that preceded them. How then do we explain the appearance of pottery at Zamostje 2 and its changing use in the MN?

One hypothesis is that the pottery use reflects a change in culinary practices rather than any major shift in the economic strategy. Indeed, there is evidence that fish were prepared and consumed without being cooked or extensively processed during the aceramic Mesolithic phases. Human and dog coprolites at the site frequently contained fish bone, suggesting that fish was eaten whole (Engovatova and Hrustalyov, 1996; Lozovski et al., 2013a; Radu and Desse-Berset, 2013). The eggs of parasitic worms (*Diphylobothrium latum*) have also been interpreted to suggest that fish had not been subjected to prolonged heat treatment (Engovatova and Hrustalyov, 1996; Lozovski et al., 2013a). In this scenario, the routine practice of cooking fish in pottery only occurred in the Middle Neolithic, but certainly fish were regularly consumed in other ways well before.

If one accepts this scenario, two interpretations of this shift occurring in the MN can be proposed. It could be, firstly, related to a "simple" change in culinary practices brought by the new population, which also introduced a new pottery tradition. On the other hand, it can reflect new economic strategies, such as changes in the scale of exploitation or changes in the seasonal occupation of the site. Analysis of the fish bones, recovered from the EN and MN layers, shows that fishing mainly occurred during the spring and summer (Lozovski et al., 2013a; Radu and Desse-Berset, 2013). As the residue data we have generated show that new type of pottery containers found from the end of 6th millennia-5th millennia (later EN/Lyalovo culture) were used almost exclusively for fish processing, we suggest that the site became a more specialised seasonal fishing station at this point. Indeed, processing fish in pottery to make storable products (e.g. fermenting or rendering to make oils) may

have been needed to deal with the seasonal surplus, although further analysis of terrestrial fauna and artefactual remains from the MN layers, which are lacking at the moment, is needed to confirm or refute this hypothesis. In contrast, during the Mesolithic and EN, Zamostje 2 appears to have been occupied all year round (Lozovski et al., 2013a), which would be more in keeping with a broader range of products identified in the EN pottery, such as Viburnum fruits that ripen in autumn (Berihuete, 2018).

Finally, the lack of a major shift in subsistence strategies associated with the introduction of pottery suggests it was incorporated into existing cultural and economic practices rather than having a major transformative effect. Pottery may have simply fulfilled a range of functional niches previously occupied by perishable containers, such as baskets, pits or other organic containers, such as those made from wood, tree bark or animal tissue. Ethnographic evidence shows that foodstuffs can be easily heated in such artefacts, negating a specific need for pottery (Driver and Massey, 1957; Leroi-Gourhan, 1973). This "software" to "hardware" transition, although conspicuous by its visibility in the archaeological record, may have therefore had far less actual impact on hunter-gatherer lives than supposed, perhaps only resulting in marginal gains in terms of cooking performance and durability that out-weighed the production costs.

It is interesting to note, however, that at Zamostje 2, where the conditions are highly conducive to the preservation of wood and bark at least, relatively few containers have been found in the Mesolithic layers (Lozovski, 1996; Lozovski and Ramseyer, 1998; Lozovskaya and Lozovski, 2016), and none are directly analogous in form to the ceramic vessels that emerge. Similarly, container finds from the Mesolithic wetlands sites excavated across the region are extremely rare (Burov, 1989; Koltsov, 1989; Oshibkina, 2006). While other forms of container that might not have survived can be proposed, alternative explanations evoking non-functional attributes of pottery (e.g. Hayden, 1998) are perhaps needed to explain its adoption in some regions of Eastern Europe (Mazurkevich and Dolbunova, 2015).

6. Conclusion

The new data generated from analysis of the Zamostje 2 pottery assemblage do not support our hypothesis that the introduction of pottery in Holocene Eurasian hunter-gatherer societies was driven by a specialist need to process aquatic resources. The zooarchaeological and artefactual data show that fishing was already well established before the arrival of pottery and remained important well after the onset of Holocene Thermal Maximum climate optimum. Interestingly, the first pottery of the Early Neolithic was used to process a variety of foodstuffs, including fruit and other terrestrial

resources. A shift towards specialisation in the ceramic use, focused on fish processing only appears ca 700 years later, in the Middle Neolithic. Therefore, at Zamostje there appears to be very little in the way of revolutionary change associated with the first pottery and the onset of the Neolithization. It is also striking that the new technology was adopted with minimal change in other aspects of the economy and society. It appears that pottery was simply adopted as a multi-functional cooking container. Surprisingly, there is little evidence of perishable containers in the Mesolithic deposits at Zamostje, despite the excellent potential for preservation, suggesting that pottery did not simply replace non-ceramic analogues. The use of pottery for processing and combining foods through sustained heating may instead have been linked to social motivations, e.g. preparing dishes for elaborate feasting (Hayden, 1998), or aesthetic reasons that are not directly related to a wider economic shift, as has been suggested for other prehistoric foragers (Saul et al., 2013). Clearly, further work will be needed across the Eastern European Plain to confirm whether the patterns of early pottery use noted at Zamostje are exceptional or perhaps part of a wider trend which involves pottery being adopted as a new way of cooking and combining a diverse array of foodstuffs.

Statistical Analysis

Statistical tests were performed using Past (version 3.21).

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Chapter 5

On the boundary of the “hunter-gatherer” and “agricultural” Neolithic: subsistence and culinary practices at the site of Rakushechny Yar in the Lower Don

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Author contributions: OEC, **MB** and ED designed the research. MB and ED undertook the sampling. **MB** undertook the lipid residue and bone collagen analysis. LGC undertook the SEM and other microscopy analysis. KMcG undertook the ZooMS analysis. JM led on the dating and chronology. PJ, VT, AT and AM providing contextual information. **MB**, AL and OEC worked on the interpretation of the lipid residue analysis. MB and OEC wrote the manuscript with contributions from all authors.

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Abstract: Pottery emergence in Europe derives from two distinct traditions, hunter-gatherers in the north-east of the continent during the early 6th millennium BC and early agricultural communities of the south-east a millennium earlier. However, some of the earliest hunter-gatherer pottery in Europe dating to the early 6th millennium BC is found along the north coast of the Black Sea, providing the potential for contact with ceramic using agriculturalists and pastoralists already established Anatolia. In this key region, it is much less clear whether the Neolithic productive economy was adopted along with Neolithic technological and cultural traits. Here we investigated the function of pottery from Rakushechny Yar site, located in the Southern fringe of Eastern Europe (Russia), in this putative contact zone between these two economic “worlds”. In this study, organic residue analysis was conducted on 133 samples from the Early Neolithic phase (ca. mid-6th mill BC) and Late Neolithic/Eneolithic period (ca. 5th mill BC) along with microscopic and SEM analysis of associated foodcrusts. The results show a very high specialisation in pottery use associated with fishing activities. Many of the vessels have

molecular and isotopic characteristics that could be associated with the processing of migratory fish, such as sturgeon. This was confirmed by sturgeon bony structures embedded in the charred surface deposits. There was no evidence of dairy products in any of the vessels examined. Further analysis of some of the mammalian bone using ZooMS failed to demonstrate that domesticated animals were present in the Early Neolithic. We conclude that pottery was adopted in the Lower Don but not in connection with a pastoral economy.

Keywords: pottery, hunter-gatherer, farmers, Early Neolithic, Late Neolithic, Eneolithic, lipid residue analysis, ZooMS, Scanning Electron Microscopy (SEM), Rakushechny Yar, Russia.

1. Introduction

The transition to the Neolithic characterises a period marked by numerous and profound technical and social changes. This term, drawn from the Western European archaeological community, is frequently used to refer to the economic transition from foraging to farming, the establishment of permanent settlements and the introduction of a package of innovations including pottery (Dixon 1928; Childe 1951; Hommel 2014; Kuzmin 2013). Archaeologists working in eastern Asia and northern Eurasia however derive a different meaning. Here the Neolithic denotes the emergence of pottery production among hunter-gatherer communities. It is often argued this technological change is associated with increased sedentism and the intensified exploitation of wild resources, especially of aquatic resources (Kuzmin 2013), although it seems likely that these other elements were already practiced by some aceramic Holocene hunter-gatherers (e.g. Bondetti et al. 2020; Oras et al. 2017; Bērziņš 2010).

In Europe, prehistoric pottery was used by both hunter-gatherers and early agriculture communities. Pottery was produced by hunter-gatherers in the north-east of the continent, during the early 6th millennium BC (Kriiska et al. 2017; Piezonka 2011) and by early agricultural communities of the south-east, at least, by the end of the 7th Millennium (Fig. 5.1a; Krauß et al. 2018). These traditions are thought to have followed trajectories that are often assumed to be quite separate, i.e. by hunter-gatherers living immediately east of the Ural mountains to the Baltic, and by farming communities from the Near East to Southeastern Europe, around the Black Sea and the Caucasus (Davison et al. 2009; Fuller et al. 2015; Jordan et al. 2016; Dolukhanov et al. 2009; Dolukhanov et al. 2009). It is now clear that European hunter-gatherers had different needs for pottery compared to early farming communities. Widespread organic residue analysis has found that hunter-gatherer pottery is frequently associated with aquatic resources (Craig et al. 2011; Craig et al. 2013; Lucquin et al. 2016; Gibbs et al. 2017; Oras et al. 2017; Shoda et al. 2017; Lucquin et al. 2018; Craig et al. 2007) whilst these

products are rarely found within the pots produced by early farmers (Evershed et al. 2008; Nieuwenhuyse et al. 2015; Debono Spiteri et al. 2016). In this model, ceramic using foragers and early farmers may be regarded as two independent worlds (Fig. 5.1a).

Here we investigate the use of pottery at the site of Rakushechny Yar (RY) located on one such boundary in the Southwestern Pontic–Caspian steppe (Fig. 5.1a and b). During the 6th millennium BC, the region was embedded in a wide cultural network that stretched from the Northern Pontic steppe and North Caspian Sea to the Near East, potentially encompassing both hunter-gatherers of the Eastern European forest zone and early farming communities to the south. Neolithic obsidian in Southern Ukraine is derived from deposits located in Armenia and Central Anatolia (Biagi et al. 2014). Similarly, Early Neolithic pottery at RY shares some stylistic attributes with Near Eastern pottery produced by farmers (Vandiver 1987; Le Mière and Picon 1998; Nishiaki and Le Mière 2005; Budja 2009; Dolbunova 2016). The method of production also appears to have been quite different to that subsequently practiced by hunter-gatherers of the forest zone of Eastern Europe (Mazurkevich et al. 2008; Mazurkevich and Dolbunova 2012; Mazurkevich and Dolbunova 2015).

Other evidence for potential interaction with the early farmers at RY includes the presence of wattle-and-daub architecture (Layer 11) and a female figurine (layer 10) (Belanovskaya 1995; Tsybryi et al. 2017) similar to the many found in Anatolia (Cauvin 2000; Budja 2005; Budja 2009). Nevertheless, it is much less clear whether the Neolithic productive economy was adopted along with Neolithic technological and cultural traits in this region. At RY, it has been suggested that domesticated animals (Cattle, *Bos taurus*, sheep, *Ovis aries*, pig, *Sus domestica*, Fig. 5.2) were present in the faunal assemblage which otherwise consists of wild taxa (Vybornov et al. 2015). Of these sheep are most pertinent to the discussion. Wild sheep are absent in this region (Bobrinskoy et al. 1944), so their presence during the early occupation of the site would provide clear evidence of a pastoral economy.

The main aim of this paper is therefore to investigate pottery use at RY; particularly to establish whether domesticated animals and plants were initially associated with pottery production at this site. Organic residue analysis was used to investigate vessel contents and compared with other examples of prehistoric hunter-gatherers and farmers. In particular, evidence for dairy residues in the RY vessels would provide a strong line of evidence, considering that this practice was widespread in Anatolia during the 6th millennium and earlier (Evershed et al. 2008). Secondly, we used molecular methods and AMS dating of mammalian bone to confirm or refute the presence of domesticated species during the early phases of the site.

2. Rakushechny Yar: site and context

RY, one of the oldest Early Neolithic sites in the Eastern Europe, is located on the northwest part of the Porechny Island (Fig. 5.1b). The site was established on the shoreline of an ancient dammed lake (Dolbunova et al. 2019). The first stage of occupation at RY by Early Neolithic communities was initially dated to the 7th millennium BC (Tsybryi et al. 2017) but this has been more recently revised, based on new AMS dates, to the middle of the 6th millennium BC (Dolbunova et al. 2019; Appendix 1, section 6). It was then occupied, possibly seasonally, until the Eneolithic and Bronze Age period dated to the 5th-4th millennium BC (Mazurkevich and Dolbunova 2012; Dolbunova 2016; Dolbunova et al. 2019). Twenty-three cultural layers were identified, each of them clearly separated by sterile interlayers allowing fine chronological reconstruction. The cultural layers from 23 to 11 are attributed to the Early Neolithic phases.

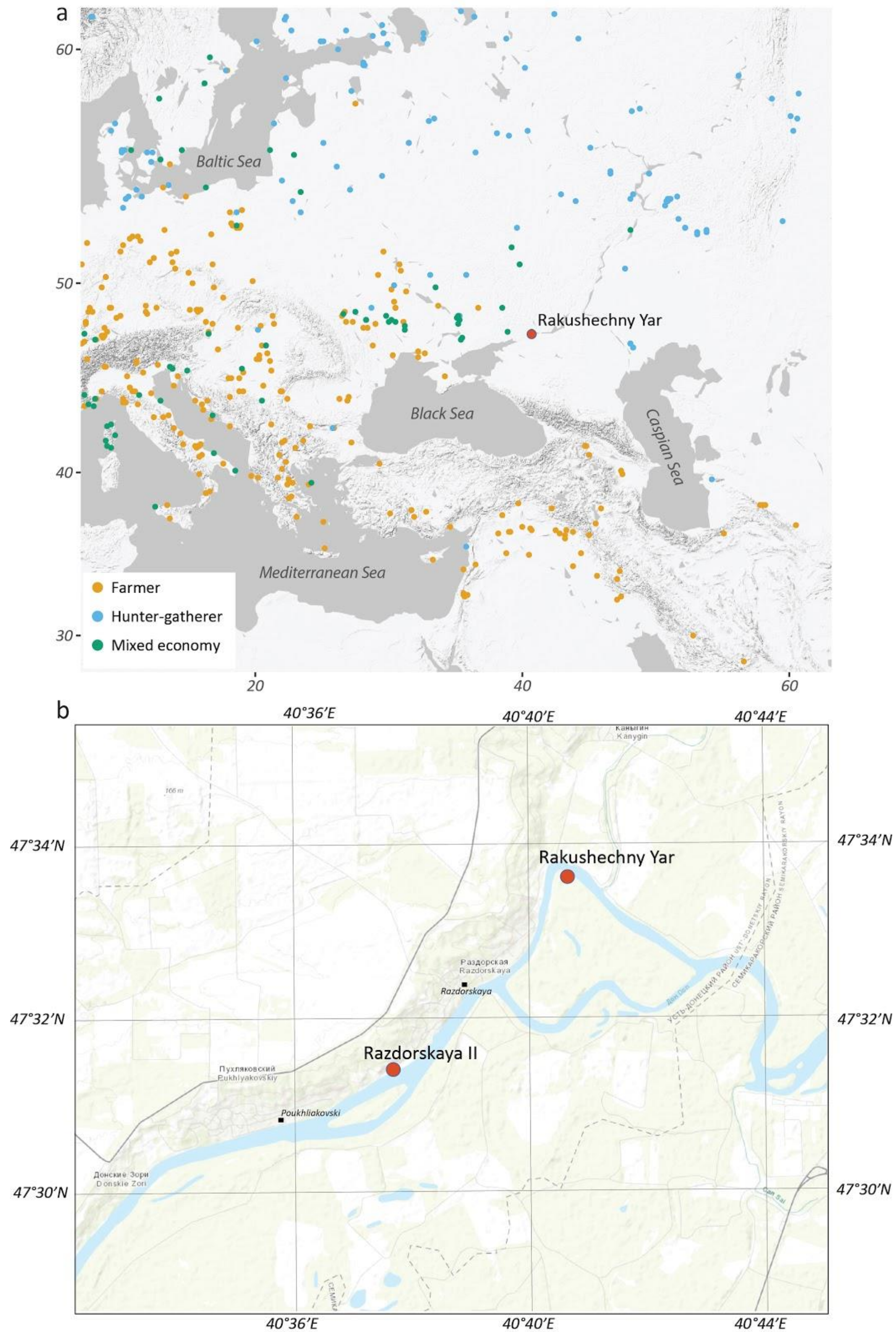

Figure 5.1 Map a) plotting early pottery sites and their associated subsistence economy as well as Rakushechny Yar site and (b) showing the location of Rakushechny Yar on the Porechny Island, in the lower Don River. Note: the data in Fig 5.1a are taken directly from the entire data set of dates associated with the earliest pottery as reported by (Jordan et al. 2016).

Ceramics vessels, at RY, recovered from the earliest cultural layers, show a significant variation in terms of form, volume and technology. Thirteen different vessel forms attributed to the Early Neolithic layers were identified constituting what we can consider a complete repertoire of "kitchenware", encompassing plates, cooking pots, bowls, all with different volumes, from tiny vessels (<0.5 L) to much larger containers (15-20 L; Appendix 14). Pottery making therefore seems to be highly developed from the outset consistent with models for adoption rather than independent innovation. The ceramic vessels are mainly symmetrical and have flat bottoms and are largely undecorated (91%). Nevertheless, pointed bottomed pottery was also found and some of the pottery was covered with red and/or yellow ochre (Mazurkevich and Dolbunova 2015). Four different "chaînes opératoires" were reconstructed as well as the use of various local clay sources and paste recipes reflecting the adaptation of a wide range of techniques for pottery production (Mazurkevich and Dolbunova 2012; Mazurkevich and Dolbunova 2015; Dolbunova 2016).

The well-preserved faunal assemblage reveals a subsistence economy mainly based on hunting and fishing. Wild mammals, such as red and roe deer (*Cervus elaphus*, *Capreolus capreolus*), and riverine resources including both freshwater (e.g. *Cyprinidae*, Wels catfish, *Silurus glanis*, etc) and anadromous (e.g. sturgeon, *Acipenser spp*) fish, and shellfish (e.g. *Unio* and *Viviparus diluvianus*) (Belanovskaya 1995; Zabilska-Kunek 2019), provided the majority of resources (Fig. 5.2). The faunal assemblage consists predominantly of kitchen waste accumulated in cultural layers. Red deer were butchered on the site, as testified by finds from edible and inedible parts of the body (phalanges, including hooves, antlers fragments and teeth). Nevertheless, the location of the site and the amount of fish bones and shell remains as well as the very specific lithic and bone tool assemblage emphasizes the importance of fishing activities at RY. As discussed, putative finds of domesticated animals have been reported in the lower layers (e.g. sheep, cattle, pig) (Sablin 2018; Dolbunova et al. 2019) but these represent only ca. 11% of the mammalian assemblage (Fig. 5.2) otherwise dominated by wild cervids. Although the cattle and pig bones are assigned on morphological grounds to domesticated species, further DNA analysis is needed to confirm given the presence of wild cattle and pigs in the region. Overall, the subsistence economy at RY remains broadly similar throughout the site's occupation.

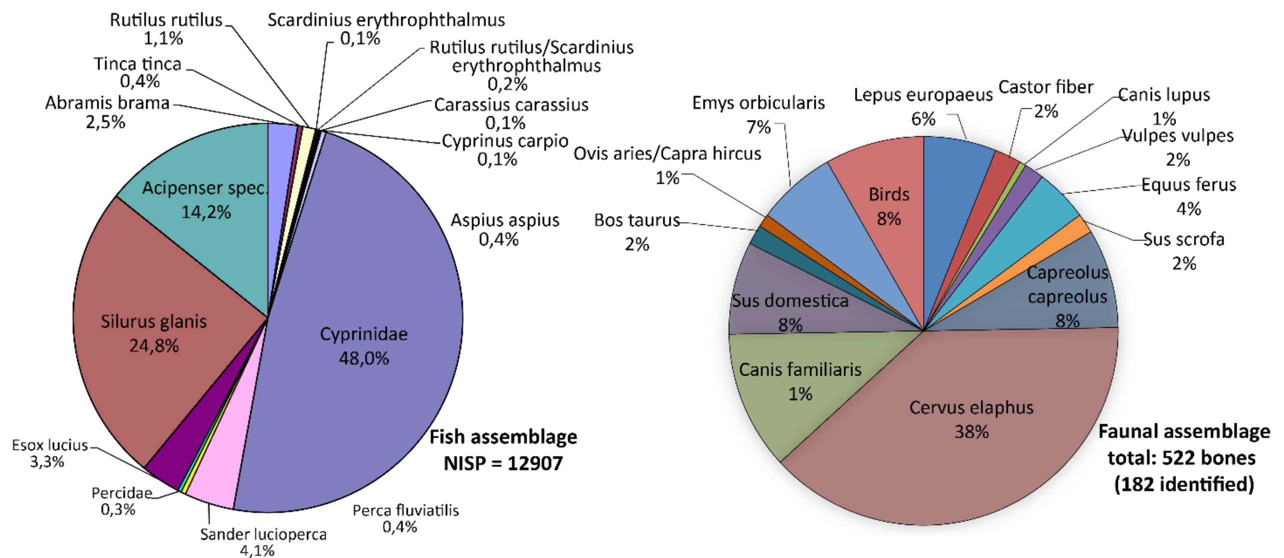

Figure 5.2 Archaeozoological assemblage distribution of fish and terrestrial animal from Early Neolithic phase of Rakushechny Yar (Sablin 2018).

3. Materials and Methods

3.1. Lipid residue analysis and bulk stable isotope analysis of pottery

One hundred thirty-three samples were selected for organic residue analysis, representing 104 vessels, including 83 sherds and 50 charred residues. Ninety-five of these vessels (74 sherds; 46 foodcrusts) are ascribed to Early Neolithic phase (coming from eighteen different layers from 11 to 23 and vivip 3 to 1; Appendix 10). Layers 17 to 15 are dated to between ca. 5,600 to 5,500 cal BC and the other Early Neolithic layers are probably similar in date, or even slightly more recent (Dolbunova et al. 2019; Appendix 1, section 6). A further nine pottery vessels (9 sherds; 4 foodcrusts) recovered from the Late Neolithic and Upper Eneolithic layers (3 to 4) were analysed (Belanovskaya 1995; Dolbunova et al. 2019) (Appendix 10). This assemblage was excavated from two different areas on the site (excavation 1/4 and 2-3; Appendix 15). In addition, lipids of modern edible endemic fruits and plants from RY's vicinity (e.g. bulrush, *Typha*, wild thyme, *Thymus*, silverberry, *Elaeagnu*s, wild rose berry, *Rosa*, wild pear, *Pyrus*, wild apple, *Malus*), shellfish *(Viviparus*, *Unio*) from the Low Don River, fish (Zander, *Sander lucioperca*, Wels catfish) and modern wild ruminants (Red deer) from Russia were analysed for comparison with the archaeological ceramic samples (Appendix 11). Lipids were extracted from soil from some of the cultural layers of the site to control any potential environmental contamination (Appendix 10).

Lipids extracts were obtained for all the samples using a modified one-step acidified methanol methodology (Craig et al. 2013; Papakosta et al. 2015). To enable the detection of any triacylglycerols or wax esters, a selection of pottery or foodcrusts samples was subjected to solvent extraction following published protocols (Charters et al. 1993; Regert et al. 1998; Stern et al. 2000; Gregg 2009; Papakosta et al. 2015). Lipid extracts were analysed using Gas Chromatography-Mass Spectrometry (GC-MS) with different columns and modes. For the methanolic acid extracts yielding sufficient amount of lipid, the carbon isotope values of palmitic acid ($C_{16:0}$) and stearic acid ($C_{18:0}$) were obtained using Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS). Elemental Analysis-Isotope Ratio Mass Spectrometry analysis (EA-IRMS) was also performed on charred residue samples for the determination of their stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope values, as detailed in previous publications (Craig et al. 2007; Lucquin et al. 2016; Shoda et al. 2017). Further information on the extraction methodologies employed here and the instrument condition are provided in the Appendix 1.

3.2. Digital Microscopy and Scanning Electron Microscopy (SEM)

Digital and scanning electron microscopy of the charred food crusts was conducted to complement the lipid analysis. The approach has been used to determine the presence of plant products in foodcrusts adhered to prehistoric pottery from the Netherlands (Raemaekers et al. 2013). Seven of the 49 charred foodcrusts were selected for microscopic analysis; these were chosen among the samples available due to their good preservation and thicker macrostructure which provided a larger mass of material and allowed a thorough investigation of their composition. Initial observation of these under low-powered microscopy was carried out using a Leica MZ APO binocular microscope at magnifications of between 8x to 50x. In order to study the microstructure and physical attributes of the residues, images were created using a VHX-5000 Keyence digital microscope at magnifications from 20x to 200x. From these, food fragments that presented visible inclusions (such as putative animal or plant tissues) were selected for further study under SEM. For SEM observation, samples were cleaned from adhered materials such as clay residue and sediments with a brush and sputter coated with ca. 1 micron of gold when necessary for image quality purposes. These were then examined using a Hitachi S-3700N Scanning Electron Microscope housed at the Scientific Research Department of the British Museum. The two main aims of these analyses were to identify specific types of particles visible in the foodcrusts, such as plant and animal tissues, in order to elucidate the ingredients used; and the exploration of the foodcrusts' microstructures in order to distinguish potential processing and cooking techniques which might have led to the accumulation of these residues.

Selected fragments of foodcrust were analysed using SEM for specific observation of the matrix/microstructure. During this, up to five images of the matrix of each fragment were captured, at 10-16 mm working distance and at 50x magnification, to cover the whole surface. Then, the visible particles were captured one by one for further identification. Identification of any tissues was carried out in comparison with modern and archaeological reference materials as well as available published data.

3.3. Bulk analysis of bone collagen

Stable isotopic analysis of bone collagen was undertaken from a range of fauna from the site to provide a broad reference with which to interpret the lipid data. Archaeological bones of red deer (n = 2), pig (n = 2), beaver (n = 1), zander (n = 4) and Wels catfish (n = 1) from RY were selected (Appendix 12) to serve as an archaeological isotopic reference. Bone collagen was extracted using a standard procedure (Longin 1971; Brown et al. 1988; Richards et al. 1998; Jørkov et al. 2007) and isotopically analysed by EA-IRMS akin to the foodcrusts samples. Further information about the methodology is provided in the Appendix 1.

3.4. ZooMS (Zooarchaeology by Mass Spectrometry)

To confirm the presence of domesticated species, sixteen bone samples from different layers at RY were subjected to collagen peptide mass fingerprinting, also known as ZooMS. Two of the bones had been morphologically identified as sheep, while the others could only be assigned to the family Bovidae or unidentified (Appendix 13). Frequently used in archaeology and palaeontology, ZooMS was developed by Buckley et al. (2009) as a technique to identify collagen-based remains (i.e. bone, antler, leather) and is particularly useful for fragmented or worked remains where morphological indicators have been modified or removed. It involves peptide mass fingerprinting of Type I collagen using Matrix Assisted Laser Desorption/Ionisation Time of Flight Mass Spectrometry (MALDI-ToF-MS). Extracted collagen peptides from a specimen are compared to known peptide markers in order to identify the source of the raw material, usually to the genus level. ZooMS was performed following a slightly modified method to that outlined in Buckley et al. (2009), with the extracted collagen peptides analyzed on a Bruker ultraflex III MALDI-ToF-MS. Sample spectra were analyzed using mMass software (www.mmass.org, Strohalm et al. 2008) and compared to a database of known m/z markers (Buckley et al. 2009; Buckley et al. 2010; Kirby et al. 2013; Buckley and Collins 2011). More information about the protocol and instrument conditions are available in the Appendix 1.

3.5. AMS ^{14}C dating

The ceramic assemblage discussed in this paper can be dated by stratigraphic association with mammal bones interpreted as food waste, which are being dated by Accelerator Mass Spectrometry (AMS) following routine protocols. Bone identifications have been tested by ZooMS, as described above, and collagen from the dated bones analysed by EA-IRMS, providing additional isotopic reference data. A summary of relevant methods and results, and a re-evaluation of legacy ^{14}C data from Rakushechny Yar, is given in Appendix 1 (Section 5).

4. Results and discussion

4.1. Preservation of animal fats in RY pottery

The preservation of lipids in association with pottery from RY was excellent with 95% of the samples yielding amounts of lipids above the accepted threshold of interpretation (i.e. >5 µg/g for potsherd or >100 µg/g for foodcrusts) (Evershed 2008a; Lucquin et al. 2018). Overall, the lipid profiles are characterized by a complex mixture of aliphatic compounds, encompassing saturated fatty acids ranging from $C_{6:0}$ to $C_{30:0}$, monounsaturated fatty acid (C_{14}-C_{24}), branched fatty acids (C_{12}-C_{19}) and dicarboxylic acids (C_5-C_{15}). Cholesterol and its derivatives were also detected in over one-third of the samples. Overall, the lipid evidence points overwhelmingly to the presence of animal fats in the majority of pots from RY, which could include both aquatic and terrestrial animal sources.

Only one sample (151) displayed a different molecular and isotopic signal, with diterpenes typical of *Pinaceae* resin (dehydroabietic acid and derivatives) along with traces of retene characteristic of thermal treatment (Appendix 10; Colombini et al. 2005; Modugno and Ribechini 2009). Interestingly, this vessel had a very specific elongated form, similar to “oil lamps” recovered from hunter-gatherer Baltic contexts (Heron et al. 2013; Appendix 16). Whilst these compounds can arise from environmental contamination (Naihuang et al. 1995; Costa et al. 2016), the absence of such markers in the sediments collected at RY does not favour this interpretation. Furthermore, the stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope analysis carried out on the charred residue adhering to this ceramic gives values expected from carbonised plant tissues, i.e a relatively low $\delta^{15}N$ (6.4‰), low nitrogen amount (0.1%) and a relatively high atomic C:N ratio (31.7) (Yoshida et al. 2013; Heron et al. 2016). Pinaceae resin may have had various functions in prehistory, as an adhesive, disinfectant or as a waterproofing agent. However, from its form, the vessel could have been used for burning conifer resin for its odoriferous properties, i.e. as an incense (Lucquin et al. 2007) or conceivably as an insect

repellent. Interestingly, no aquatic derived lipids were detected in this sample which contrasts with the western Baltic examples that were mainly used for the burning of aquatic oils (Heron et al. 2013).

4.2. Molecular and isotopic evidence for aquatic resources in pottery

The stable carbon isotope values of the two most abundant unsaturated fatty acids ($C_{16:0}$ and $C_{18:0}$) were measured for 125 samples in order to provide further information regarding contents. The $\Delta^{13}C$ ($\delta^{13}C_{18:0}$-$\delta^{13}C_{16:0}$) value has been widely used to discriminate ruminant adipose and dairy fats from other non-ruminant sources (Dudd, 1999; Craig et al., 2012; 2013; Cramp et al., 2014; Colonese et al., 2015; Taché and Craig, 2015; Lucquin et al., 2016a). These values are plotted against $\delta^{13}C_{16:0}$ in figure 5.5a. At RY, 85% of the samples have non-ruminant lipid isotope signatures. Considering the faunal assemblage at RY, non-ruminant sources could include aquatic or non-ruminant terrestrial animals, such as pigs or beaver (*Castor fiber*).

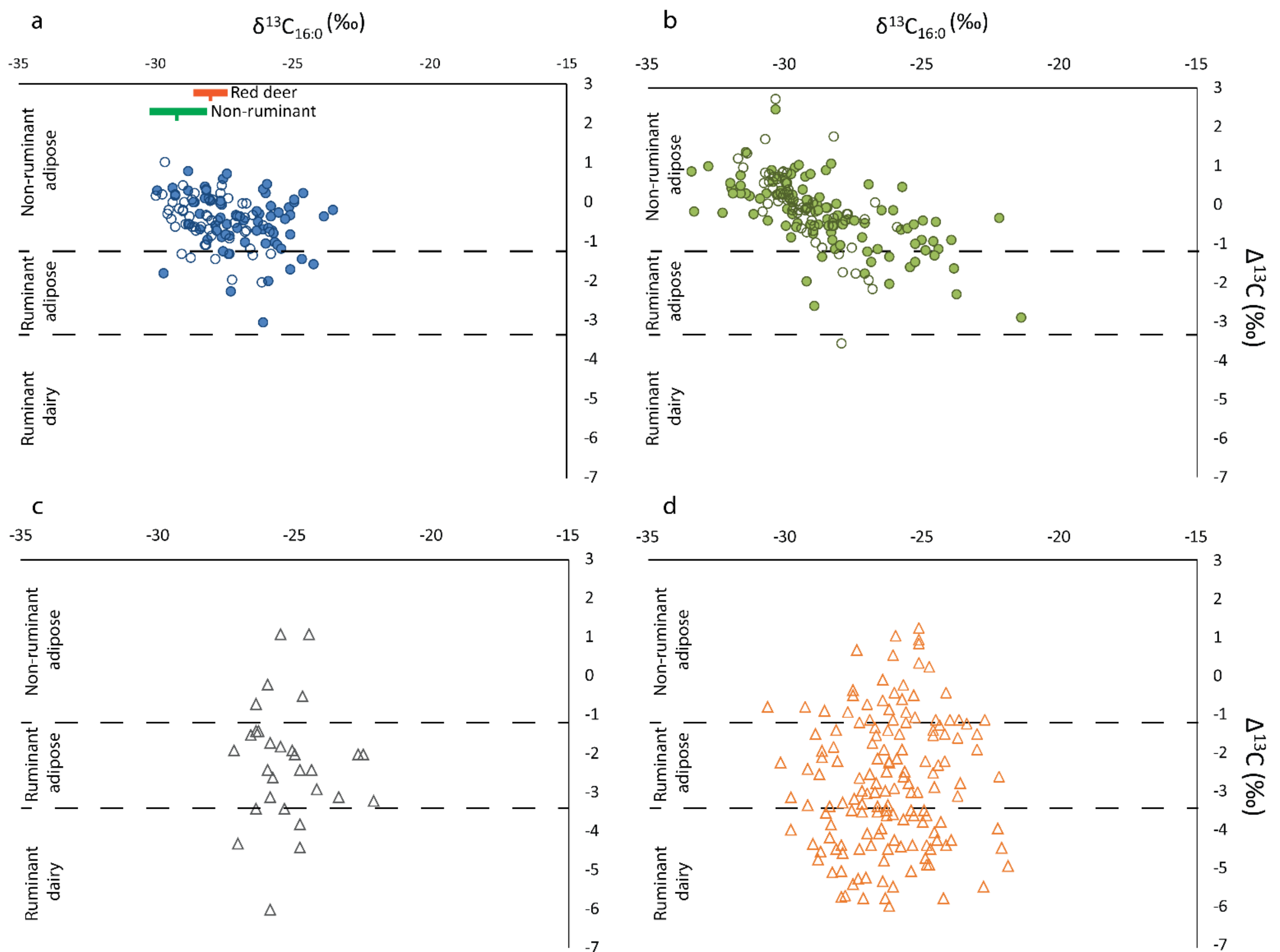

Figure 5.3 Plot of $\Delta^{13}C$ values against $\delta^{13}C_{16:0}$ values of (a) Rakushechny Yar samples (including Early Neolithic, Late Neolithic and Eneolithic) compared with pottery from (b) Zamostje 2 site and early agricultural sites in (c) Syria and (d) Anatolia. For (a) and (b) plots, the filled circles indicate samples with aquatic signal. For (c) and (d) aquatic derived lipids are not reported

but presumed to be absent (Evershed et al. 2008; Nieuwenhuyse et al. 2015; Debono Spiteri et al. 2016). The data generated here are compared with the mean and ranges (2σ) of bone collagen of archaeological non-ruminant (including pig and beaver) and ruminant (red deer) recovered at Rakushechny Yar, plotted on the x-axis only. The collagen $\delta^{13}C$ values were adjusted by -8‰ to correct for the collagen to tissue offset in order to make these values comparable with $\delta^{13}C_{16:0}$ of lipids extracted from pottery (Fernandes et al. 2015).

A total of 69 samples, corresponding to 55% of all vessel assemblage, contained diagnostic compounds for aquatic foods, either including *ω*-(*o*-alkylphenyl)alkanoic acids (APAAs) containing 20 or more carbon atoms alongside at least one isoprenoid acids (either 4,8,12-trimethyltridecanoic acid, phytanic or pristanic acid) (Evershed, 2008; Hansel and Evershed, 2009; Cramp and Evershed, 2014) or a contribution of SRR-isomer of phytanic acid >75%. The former arises from the heating (from 1 hour of heating at a temperature ≥ 200°C) of their precursor long-chain unsaturated fatty acids, which occur only in an appreciable amount in freshwater and marine animals (Hansel et al., 2004; Evershed et al., 2008b) and constitute, therefore, a direct/important marker for the cooking of aquatic source fats in pots. Furthermore, whilst phytanic acid occurs both in the tissues of aquatic and ruminant animals, the ratio of the phytanic diastereomers (3S,7R,11R,15-phytanic acid (SRR), and 3R,7R,11R,15-phytanic acid (RRR)) provides an additional tool to distinguish these sources (Lucquin et al., 2016b). A greater contribution of SRR-isomers (i.e. >75%) is usually ascribed to aquatic species (Lucquin et al., 2016b). A further 20 samples contained C_{18} APAAs and at least one isoprenoid or an SRR% between 65.6% and 75.5% (Appendix 10), indicating that aquatic resources were most likely processed in these vessels as well (Evershed et al., 2008b; Heron et al., 2015; Lucquin et al., 2016a), although definitive evidence is lacking.

The other samples, falling in the non-ruminant isotopic value area, without aquatic biomarkers might either result from the degradation of these specific molecules or could also reflect the processing of non-ruminant terrestrial mammals. These samples tend to have fatty acids more depleted in ^{13}C ($\delta^{13}C_{16:0}$ = -28.0 ± 1.1‰; $\delta^{13}C_{18:0}$ = -28.5 ± 1.0‰) than samples with aquatic biomarkers ($\delta^{13}C_{16:0}$ = -26.3 ± 3.5‰; $\delta^{13}C_{18:0}$ = -26.8 ± 3.6‰; Mann-Whitney test: U = 1017; z = 4.85; $p < 0.01$ for $\delta^{13}C_{16:0}$ and U = 982; z = 5.02; $p < 0.01$ for $\delta^{13}C_{18:0}$) in keeping with measurements made on collagen from beaver and pigs from the site (Fig. 5.3a and b and 4a, Appendix 12) after a collagen to lipid offset has been applied by -8‰ (Fernandes et al., 2015). Nevertheless, in the absence of further diagnostic lipid the contribution of terrestrial non-ruminants to this overall signature cannot be clearly resolved.

The $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values of fatty acid potsherds are plotted in Figure 5.3a and b. These have a wide range of $\delta^{13}C$ isotopic values varying between -23.5 to -31.5‰. Whilst some samples have fatty acid $\delta^{13}C$ values corresponding to the reported range for modern authentic freshwater fish oils (Fig 3a), the majority have more positive $\delta^{13}C$ values outside this range. These are more consistent with values expected from anadromous or marine fish (Outram et al., 2009; Craig et al., 2011; 2013; Choy et al., 2016; Lucquin et al., 2016a; Pääkkönen et al., 2016). Given the site's location, some distance from the Sea of Azov and Black Sea (ca. 100 and 500 km from RY site, respectively), the residues in the pottery are more parsimoniously attributed to anadromous fish, such as sturgeon, than marine species. Anadromous fish spend most of their lives in the sea and ocean and migrate into riverine habitats to spawn (Zydlewski and Wilkie, 2012). Therefore adult anadromous fish, having fed mainly in the marine environment, maintain a relatively enriched $\delta^{13}C$ signature even when caught up-river (McCarthy and Waldron, 2000). Sturgeon are the third most represented species in the fish bone assemblage (Zabilska-Kunek, 2019). Conversely, pots with relatively depleted in ^{13}C are more in keeping with freshwater fish such as cyprinids and Wels catfish, constituting the major part of the fish remains in RY (Zabilska-Kunek, 2019), or even juvenile sturgeon which would still provide a more freshwater signal (Doucett et al., 1999).

To test these assumptions, we examined $\delta^{13}C$ collagen values of fish present in the assemblages and reported in the literature. A correction of -7‰ was applied to the collagen values to allow comparison with lipid values (Fernandes et al., 2015). The mean adjusted carbon isotopic value obtained from non-migratory freshwater fish recovered at RY (catfish and zander) is -28.5‰ (± 3‰; n = 5; Appendix 12). This is consistent with the more depleted values obtained from pottery and foodcrusts samples at RY (Appendix 10). There was insufficient collagen in the sturgeon bones from RY for analysis but collagen isotope data from sturgeon bones from the Danube Gorges or Central Balkan sites show generally more positive $\delta^{13}C$ values after applying the lipid to collagen correction ($\bar{x}$ = -26.6 ± 1.2‰; n = 4; Borić et al., 2004; Jovanović et al., 2019) than freshwater species, although their ranges overlap.

The homogeneity of the residues at RY is intriguing given the typologically diverse pottery assemblage, which ranges from very small vessels (< 0.5 L) to the large containers (15-20 L) with a wide range of thicknesses. There was no statistical difference between the frequency of aquatic biomarkers when the data are disaggregated according to different volume categories and there was no correlation with vessel wall thickness.

The results potentially show a decrease in the processing of aquatic resources during the later periods (Late Neolithic and Eneolithic). In total, 38% (n = 5) of these samples contained the full set of aquatic biomarkers, compared with the Early Neolithic samples (56%). Furthermore, the fatty acids from these vessels tend to exhibit more negative $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values (-28.1 ± 1.1‰ and -28.7 ± 1.2‰ respectively) compared to the Early Neolithic y ($\delta^{13}C_{16:0}$ = -26.3 ± 3.5 ‰; $\delta^{13}C_{18:0}$ = -26.8 ± 3.6 ‰; T-test t = 2.17, p = 0.03; t = 2.4, p = 0.02 respectively). Whether this change in vessel use and a lesser reliance on aquatic products is attributable to the establishment of agriculture during these periods needs to be assessed by increasing the sample size and more archaeozoological evidence of the later layers.

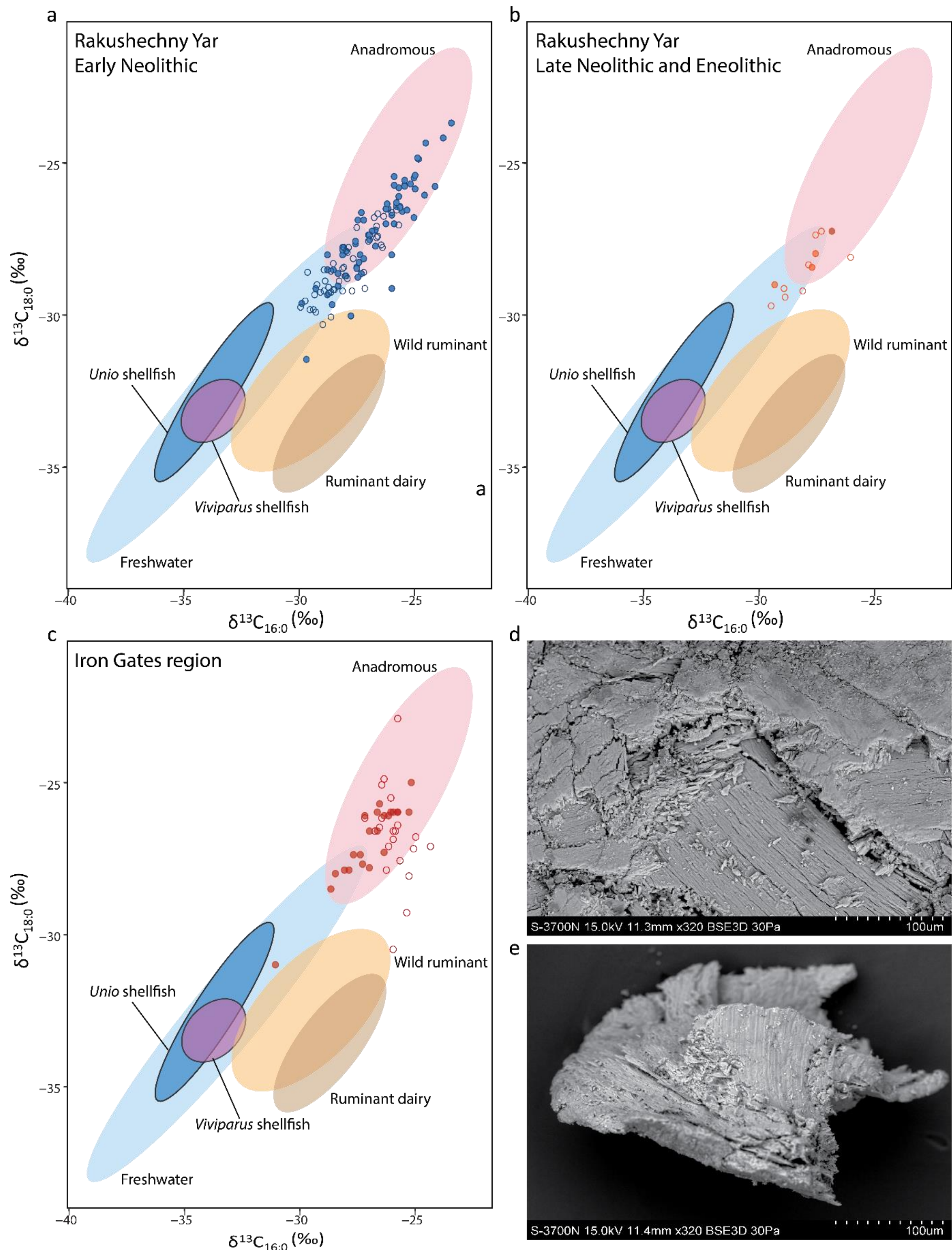

Figure 5.4 Plot of the $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ *n*-alkanoic acids extracted from (a and b) Rakushechny Yar pottery from Early Neolithic layers and Late and Eneolithic layers and (c) Iron Gates region ceramic vessels (Cramp et al. 2019). Samples with aquatic biomarkers are shown by filled circles. The data are compared with reference ranges for authentic reference lipids from modern tissues from published studies (Dudd 1999; Spangenberg et al. 2006; Outram et al. 2009; Craig et al. 2011; Craig et al. 2012; Craig et al. 2013; Choy et al. 2016; Lucquin et al. 2016; Pääkkönen et al. 2016) and additional new

Unio and Viviparus shellfish data from the Low Don River and freshwater fish and ruminants from Russia (95% confidence; Appendix 11). The $\delta^{13}C$ values of the modern references were adjusted for the addition of the effects of post-industrial carbon in order to facilitate the comparison with the archaeological samples (Schmitt et al. 2012; Hellevang and Aagaard 2015; Lucquin, Gibbs, et al. 2016). SEM micrographs showing fragments of sturgeon bony components (d) in foodcrust sample from Rakushechny Yar (Raku-929) and (e) of archaeological sturgeon reference materials.

Additionally, the bulk stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope values of foodcrusts adhering to the ceramic vessels were measured. Figure 5.4a shows the $\delta^{15}N$ values of foodcrusts plotted against the C:N ratios. Six samples have a relatively higher C:N ratios (i.e. > 20) along with $\delta^{15}N$ values above +10‰, which is consistent with fish oil (Dufour et al., 1999; Craig et al., 2013; Heron et al., 2013; Choy et al., 2016). Interestingly, these samples and the pottery sherds they were associated with, have $\delta^{13}C$ relatively enriched and previously ascribed to anadromous fish fats ($\delta^{13}C_{16:0}$ = -25.7 ± 0.9‰ and $\delta^{13}C_{18:0}$ = -26.1 ± 1.1‰) with over 85% of them having aquatic biomarkers (Fig. 5.4b). In addition, many of the foodcrusts had a microscopically observable thin and oily microstructure also consistent with high-temperature processing and oil extraction.

The rendering of fish to produce storable oils would have helped deal with the seasonal surplus of migratory sturgeon, available only during the late spring (Kovalchuk et al., 2018). Sturgeon, which can reach several hundred kilograms, likely constituted an important and valued source of food for prehistoric communities. Indeed, their flesh and roe are rich in fat and protein (Badiani et al., 1996; Ovissipour and Rasco, 2011). Rendered oils could be stored and consumed during the colder seasons when resources were scarcer but also could be accumulated and exchanged, with potential implications for social organisation and the creation of ownership and inequality. Other traditional non-culinary uses of fish products include collagen extraction for making glue and tanning of skins to make leather, all of which would have been valuable commodities (Jackinsky-Sethi, 2014). The lack of use-wear traces on the vessels suggests that they were not used for the daily household activities but most likely for specialist activity during short-lived seasonal periods, although comparative experimental material would be needed to test this hypothesis.

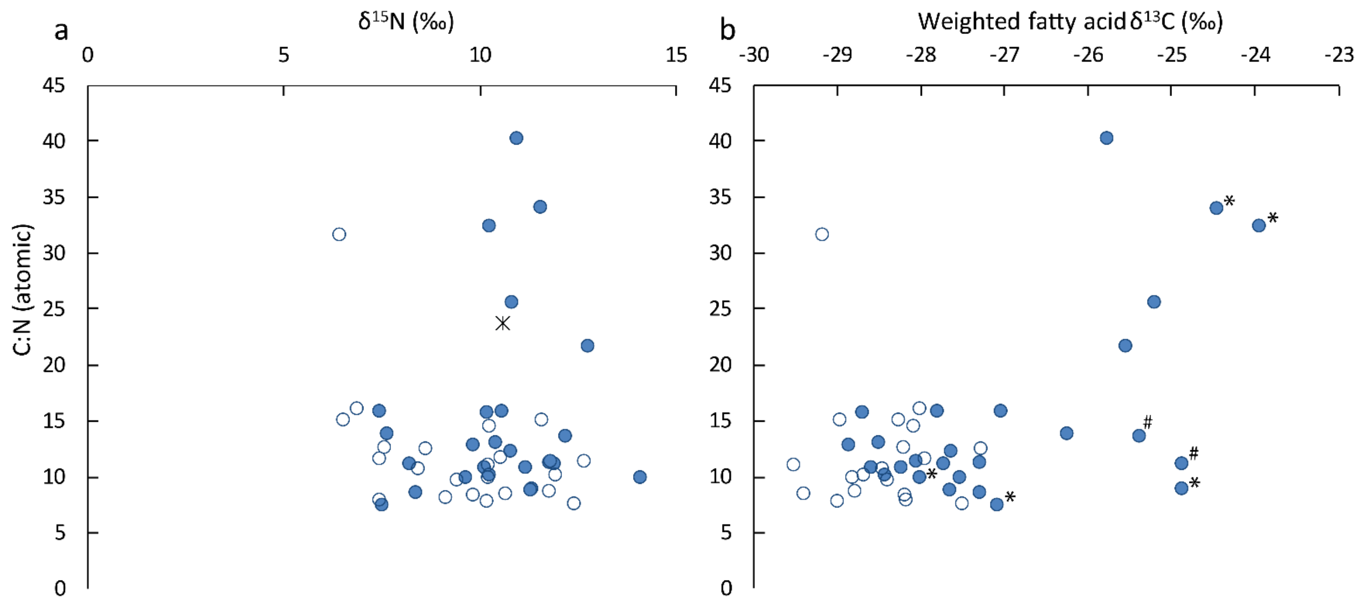

Figure 5.5 (a) $\delta^{15}N$ against C:N ratio and (b) weighted fatty acid $\delta^{13}C$ against C:N ratio obtained from Rakushechny Yar foodcrusts samples of which fatty acids were available. Filled circles indicate samples with aquatic biomarkers, * represents samples where sturgeon osseous structures were detected by SEM and # samples were cyprinid and sturgeon osseous structures were observed.

The faunal remains at RY also point to an extensive processing of shellfish, namely *Viviparus dilluvianus* and *Unio* (Dolbunova et al., 2019). These two shell species were widely used for different technological purposes (e.g. pavement for platform construction, as scraper tools and ochre containers) but potentially they were also consumed in large quantities. Given that an efficient way to extract molluscs meat from their shell is by boiling (Miracle, 2002; Milner, 2009), it is worth considering whether ceramic containers were used to facilitate this task, as has been suggested for Jōmon pottery in Japan (Ikawa-Smith, 1976). However, the isotope values obtained from modern shellfish (*Unio* and *Viviparus dilluvianus*) harvested in the Don River nearby RY and corrected for the Suess effect, rules out this hypothesis as they have fatty acids more depleted in ^{13}C compared to those from the vessels (Fig. 5.3). Instead, alternative methods may have been used for processing prior to consumption. Indeed, the discovery of a pit filled with shell remains at RY might suggest it was used as an oven for this purpose (Aldeias et al., 2019; Dolbunova et al., 2019).

Similarly, ruminant animals make a significant contribution to the mammalian faunal assemblage but less than 15% of the ceramic samples have fatty acids with ruminant stable carbon isotope signature ($\Delta^{13}C$ values <-1; Fig. 5.5a). Over half of these samples contain aquatic biomarkers. A likely explanation is that ruminant carcass fats and fish oils were mixed in these pots. Bondetti et al. (*In prep*) and others (Cramp et al., 2019) have shown that low $\Delta^{13}C$ values are theoretically observed when fish oils are

mixed with even a modest (ca. >10%) amount of ruminant fats due to differences in the fatty acid concentrations between these products. Furthermore, some of these samples exhibit more enriched $\delta^{13}C$ values than archaeological wild ruminants found at RY also indicating that they were mixed with anadromous fish (Fig. 5.5a; Appendix 10). Overall, therefore ruminant carcass fats seem to be only a minor addition to culinary practices involving cooking pots at RY.

4.3. Digital Microscopy and Scanning Electron Microscopy

Foodcrusts analysed using Scanning Electron Microscopy (SEM) presented a thin and compacted microstructure formed by vitrified shiny layers of charred matter. Embedded in this microstructure, particles whose preservation status varied from uncharred to charred were clearly seen, representing the remains of the ingredients used in the cooking or processing activities carried out in the vessels.

All seven of the analysed foodcrusts were seen to contain small fragments of sturgeon bony structures. In most cases, these were found to be derived from dermal scutes as they presented a laminated microstructure typical of this type of bony tissue. In addition, potential fragments of sturgeon fin spine bones or round based scales have been identified in a single foodcrust, from sample 926. Fragments of sturgeon bones appeared embedded in the foodcrusts' microstructures and their preservation differed from completely charred to non-charred. These were seen to measure between ca. 50 µm and 1000 µm in size and presented a clear laminated microstructure formed by a grid of parallel tubes forming horizontal bony layers as seen from modern and archaeological sturgeon reference materials (Hilton et al., 2011; Thieren et al., 2015) (Fig. 5.3d and e). Positive identification of these remains as fragments of sturgeon bone structures was possible through the comparison with reference sturgeon bones, in particular lateral scutes and fin fragment. Reference materials were provided by Museum of London Archaeology (MOLA).

In addition to the remains of sturgeon bony structures, foodcrusts from samples 915 and 921 were seen to contain remains of partially preserved soft-edged (cycloid) fish scales. Based on the observation of typical morphological traits (Esmaeili et al., 2007), these are believed to belong to members of the cyprinid family (e.g. common bream, *Abramis brama*, carp, *Cyprinus carpio*, asp, *Aspius aspius* or tench, *Tinca tinca*) widely present in the archaeological fish bone assemblage at the site (Zabilska-Kunek, 2019). In contrast to cyprinids, the other types of fish recovered from the archaeological record at Rakucheshny Yar such as Wels catfish and sturgeon have scale-less bodies. In the case of Wels catfish, their bodies are covered in slime-like substance which is invisible in the archaeological record.

In contrast with the high proportion of fish, microscopic analysis of the selected samples has shown no clear evidence of any other animal ingredients being used. Potential plant tissues were identified in three of the seven foodcrust analysed. Although not well enough preserved to allow identification to type or genus level, these have similar appearances to some of the tissues contained in the epidermis of grasses, such as the aleurone layer's cells containing what it looks like aleurone protein. This can be specifically seen in samples 920, 926 and 927.

4.4. Domesticated animals at Rakucheshny Yar?

Against expectations, we found no evidence of dairy products in the Neolithic pottery from RY (Fig. 5.5a). All the $\Delta^{13}C$ values are above the range for modern dairy reference fats (-3.3‰; Fig. 5.5a). Other clear molecular indicators of dairy, such as lower molecular weight triacylglycerols, were also absent. Twenty-six samples exhibited short-chain fatty acids ($C_{6:0}$ to $C_{12:0}$; Appendix 10) characteristic of milk fats (Christie, 1989; Dudd et al., 1998; Copley et al., 2003), although these most likely reflect the degradation of longer free fatty acids through thermal or catalytic cracking, or by bacterial action (Shimoyama et al., 1993; Raven et al., 1997). The absence of dairy contrasts sharply with the results of residue analysis of pottery from agricultural Early Neolithic sites in southwest Asia, which contained a high proportion of ruminant dairy and fat products (Evershed et al., 2008a; Nieuwenhuyse et al., 2015; Debono Spiteri et al., 2016; Fig. 5.5c and d).

Our data cannot rule out the presence of domesticated ruminant carcass fats in the pottery but, as noted above, these only made a minor contribution and are most likely derived from wild ruminants, particular cervids, that dominate the mammalian bone assemblage (Belanovskaya, 1995; Dolbunova et al., 2019). The pattern of pottery use at RY instead resembles other hunter-gatherer examples, such as Zamostje 2 in the Upper Volga (Fig 5.5b) and the Estonian Narva culture (Oras et al., 2017), which was more focused on the processing of aquatic resources notably fish. Interestingly, pots from the site's later phases, such as the Late Neolithic/Eneolithic period (layer 3, 4, 5) exhibit a potential change in pottery use, although fish is still present.

Given the absence of any clear evidence for domesticated animals in the pottery from RY, it was important to establish whether any Early Neolithic domesticated species were present in the faunal assemblage. Among the faunal assemblage, the identification of sheep remains is the most pertinent evidence of pastoral practices. As mentioned previously, wild sheep are totally absent in the Low Don region (Bobrinskoy et al. 1944). Therefore, their presence at RY is a strong indication of the import of sheep, most likely from the Near East where they have been reared since the 8th millennium BC (Harris

et al., 1996; Clutton-Brock, 1999; Evershed et al., 2008a). Of the sixteen samples of bones subjected to ZooMS analysis, only one of them, found in the upper layer (upper vivip layer 1) could be assigned to sheep (Table 5.1 and Appendix 13). This sample failed to produce an AMS date but is derived from layers with other bones that were directly dated to the 3rd millennium BC, so it could not be reliably assigned to the Early Neolithic. Notably, the two samples, from the Early Neolithic layers (15a and 17) and directly dated to the 6th millennium BC were initially morphologically identified as sheep. However, ZooMS revealed these were from deer (likely red deer based on the faunal assemblage), clearly distinguishable from sheep with the peptide Col1AT40 displaying a mass of 1550.8 instead of 1580.8 for the latter (Buckley et al., 2009).

Consequently, there is no secure identification of any domesticated animals during the Early Neolithic at RY and, based on our current knowledge, RY should be considered as an entirely forager site. It should be noted however that only a relatively small area along the shoreline at RY has so far been excavated (ca, 90 m^2) with little evidence for habitation structures. It is possible that these deposits represent a specialised fishing station and that domesticated animals were instead kept closer to the settlement, although this would be surprising given their absence amongst the other mammalian remains so far recovered.

4.5. A clear boundary between the aquatic and agricultural Neolithic?

The organic residue analysis undertaken on 95 vessels from the Early Neolithic layers at RY clearly shows a very strong association with fishing activities, particularly the processing of migratory fish, such as sturgeon. While some typological and stylistic details can be attributable to Early Neolithic agricultural settlements to the South and East (Fig 5.1), there is no evidence that the agricultural or pastoral economy was adopted at this site, as has been supposed. So, it seems that pottery was adopted in the Lower Don but not in connection with a pastoral economy.

Instead, in light of these findings several alternative hypotheses can now be proposed. Firstly, that knowledge of pottery production was gained through contact with farming communities but incorporated into an entirely fisher-hunter-gatherer economy. Secondly, that early farmers moved to this region but abandoned food production in favour or intensive aquatic resource exploitation and adapted their use of pottery accordingly. Thirdly, that pottery production at RY was either innovated locally or acquired from other foragers, perhaps to the north and east, and bore only a coincidental relationship to pots produced by contemporary farmers. Each of these hypotheses demands further investigation, particularly more precise ^{14}C dating and comparative typological assessment, on a regional and super-regional scale.

In particular, the acculturation of famers into a foraging lifeway is gaining increasing traction through studies of this nature and should no longer be considered as anomalous. In the Iron Gates Gorge and in Southern Scandinavia, Early Neolithic agricultural communities clearly turned their pot craft towards the processing of aquatic foods (Craig et al., 2011; Cramp et al., 2019). Many of these sites were previously occupied in the Mesolithic and are situated along rivers, lakes and coasts with high aquatic productivity, particularly in seasonal aquatic foods.

It has been argued that agriculture, pastoralism and intensive fishing require similar technological adaptations, including pottery, in anticipation of a predictable resource, and led to similar outcomes in terms of reducing mobility and demographic change (Oras et al., 2017). The evidence from RY fits well with this model, given the seasonal nature of sturgeon exploitation. Careful advanced preparation would be needed to efficiently exploit this resource, including provision for processing and storage, prompting the need for pottery production. Ethnographic studies on native communities of coastal British Columbia show that different sizes of containers were used for the rendering oil from anadromous fish (Kuhnlein et al. 1982). This may also be the case for RY where a diverse range of pottery containers were used to process aquatic products to maximize returns from this seasonal resource and perhaps facilitate its long-term storage.

Interestingly however, at site of Razdorskaja 2, ca. 6 km downstream from RY on the right bank of the Don river there is no evidence of pottery production, despite several small ceramic figurines (Tsybrij et al., 2008; 2017), yet here too fishing constituted the main economic activity. The occupation of Razdorskaja 2 appears to have been partially contemporary to RY (Tsybriy et al., 2016; Tsybrij et al., 2017), although the chronology of these two sites needs to be better clarified. If shown to be contemporary, the absence of pottery at Razdorskaja 2 is intriguing and clarification of the nature of the fishing economy between these sites might provide critical insight into the drivers for pottery production in this region.

Finally, we found no evidence that the boundary between the aquatic and agricultural Neolithic was permeable, at least in terms of economic exchange. Perhaps the most likely hypothesis is that these semi-sedentary communities held very different world views, which translated into separate notions regarding pottery production and usage. Investigations of pottery use and detailed archaeozoological investigations at other points of potential contact along the forager/farmer border are needed to confirm whether this pattern is sustained inter-regionally. Intriguing, widespread analysis of 5th

millennium BC forager pottery from the Baltic points to some exchange between forager and farmers, at least in the western extreme prior to the wholescale adoption of farming (Courel et al., 2020).

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Chapter 6

Investigating the formation and diagnostic value of ω-(o-alkylphenyl)alkanoic acids in ancient pottery

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Authors contributions: OEC, **MB** and AL designed the research. MB and ES undertook the laboratory experiments. **MB** and BC undertook the field experiments. **MB** and ES undertook the lipid residue analysis for the experiments. **MB**, AL, BC, JL, CLO and LD undertook lipid analysis of raw foodstuffs. SS undertook lipid analysis of the archaeological Japanese samples (Joto). **MB**, AL and OEC worked on the interpretation of the lipid residue analysis. **MB** and OEC wrote the manuscript with contributions from all authors.

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Abstract: Long chain ω-(o-alkylphenyl)alkanoic acids (APAAs) derived from the heating of unsaturated fatty acids have been widely used for the identification of aquatic products in archaeological ceramic vessels. To date little attention has been paid to the diagnostic potential of shorter chain ($<C_{20}$) APAAs, despite their frequent occurrence. Here, a range of laboratory and field experiments were undertaken to investigate whether APAAs could be used to further differentiate different commodities. The results of this study provide new insights regarding conditions for the formation of APAAs and enable us to propose novel criteria to distinguish different natural products.

Keywords: Organic residue analysis, lipid, Archeological pottery vessels, ω-(o-alkylphenyl)alkanoic acids, Heating experiments, Experimental archaeology.

1. Introduction

For the last three decades, lipid residue analysis has been used to study the techno-function of ancient ceramic vessels. Based on the biomarkers concept, it is possible to trace lipids extracted from pots to

specific commodities exploited in the past thereby providing valuable insights into human activities, technology and economies (Heron and Evershed, 1993; Evershed, 2008; Regert, 2017). The identification of specific lipid markers (biomarkers) using gas chromatography-mass spectrometry (GC-MS) has been used to track a range of commodities in ancient pottery, such as aquatic (Copley et al. 2004; Lucquin et al., 2016b; Gibbs et al., 2017; Shoda et al., 2017; Admiraal et al., 2019; Bondetti et al., 2020) and beehive products (Roffet-Salque et al., 2015; Shoda et al., 2018), edible plants (Dunne et al. 2016; Heron et al., 2016; Bondetti et al., 2020) and various types of resins, wood tars and pitches (Heron et al., 1994; Mitkidou et al., 2008; Heron et al. 2015; Rageot, 2015).

Lately, a great deal of attention has been paid to the detection of ω-(o-alkylphenyl)alkanoic acids (APAAs). These compounds do not occur naturally, but are formed during protracted heating of mono- and polyunsaturated fatty acids (MUFAs, PUFAs) present in animal and plant tissues (Matikainen et al., 2003; Hansel et al., 2004; Evershed et al., 2008; Cramp and Evershed, 2014). Due to their high stability over time, these compounds have been identified in vessels from a wide range of archaeological contexts (Copley et al., 2004; Lucquin et al., 2016b; Gibbs et al., 2017; Shoda et al., 2017; Bondetti et al., 2020). One application has been to overcome the challenge of identifying aquatic products in pottery. Aquatic products are rich in PUFAs that readily degrade in the burial environment and therefore rarely encountered. As APAAs are produced from these liable precursor molecules, their presence along with other biomarkers such as isoprenoid fatty acids (IFAs; e.g. 4,8,12-TMTD, phytanic and pristanic acids; Ackman and Hooper, 1968; Copley et al., 2004; Hansel et al., 2004; Cramp and Evershed, 2014; Lucquin et al., 2016a) and long chain dihydroxy fatty acids (Hansel and Evershed, 2009; Cramp et al., 2019) have brought to light a range of examples of aquatic resource processing in the archaeological record.

More specifically, the presence of long chain APAAs ($\geq C_{20}$) provides the most convincing evidence for the cooking of aquatic commodities, since they are formed from their long-chain MUFA and PUFA precursors (especially n-3 fatty acids $C_{20:5}$ and $C_{22:6}$) which are only present in significant amount in aquatic organisms, such as freshwater and marine animals (Cramp and Evershed, 2014). For example, the detection of APAAs has shown that Early Woodland hunter-gatherer pottery in North America was used for processing aquatic resources, hitherto contested (Taché et al., 2019). Similarly, APAAs have been identified in some of the earliest pottery in the world, revealing the motivations for pottery innovation (Craig et al., 2013).

While the use of APAAs to identify aquatic products in pottery represents a significant advance in organic residue analysis, APAAs with a shorter chain length homologue (i.e. $<C_{20}$) are readily generated through heating non-aquatic products, especially tissues rich in unsaturated fatty acids (UFAs). These include a wide range of foodstuffs including aquatic and vegetable fats and oils as well as terrestrial adipose fats (Heron and Evershed, 1993; Evershed et al., 2008). Therefore, the detection of APAAs with 16 and 18 carbon atoms (i.e. ω-(o-alkylphenyl)hexadecanoic acid and ω-(o-alkylphenyl)octadecanoic acid) is currently of limited diagnostic value, despite the fact that these compounds are frequently recovered from archaeological pots.

The synthesis of APAAs involves a number of different reactions encompassing mainly alkali isomerization and aromatization steps (Fig. 6.1 Matikainen et al., 2003; Hansel et al. 2004; Evershed et al., 2008). Crucially, during this process, various double bond rearrangements occur, resulting in the formation of several isomers. Controlled heating experiments undertaken by Evershed and co-workers (Evershed et al., 2008), have shown that the distribution of APAAs isomers with 18 carbon atoms (APAA-C_{18}) differed according to the number of unsaturation in the fatty acid from which it was derived. Similarly, the difference in the APAA-C_{18} isomeric distribution in thermally degraded rapeseed oil, cod liver oil and horse adipose fat was interpreted as a direct consequence of the relative amounts of precursor $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ fatty acids present in these products. Furthermore, (Shoda et al., 2018) noted the dominance of two APAA-C_{18} isomers in pottery where starchy plants, such as nuts and cereals, were processed. Based on this research, here we investigate the value of APAA-C_{18} as a diagnostic tool to identify commodities processed in ancient pottery through a series of experiments involving heating different fats and oils.

In addition, these experiments provide the opportunity to improve our knowledge about the conditions required for the formation of APAAs in archaeological ceramics. Previous studies (Matikainen et al., 2003; Hansel et al., 2004; Evershed et al., 2008) involving different natural commodities (rapeseed oil, horse adipose fat and cod liver oil) have shown that APAAs are formed when UFAs are subjected to protracted heating (≥17 hours at temperatures above 270°C), although a shorter cooking time and lower temperatures has so far not been really assessed. Yet, understanding the minimum time and temperature needed to form these compounds is often important for archaeological interpretation. Secondly, previous studies have shown that APAAs are only formed in the presence of fired clay, containing the metal ions (Redmount and Morgenstein, 1996; Mallory-Greenough et al., 1998) required for the prior alkali isomerization step. And thirdly, anaerobic conditions are regarded as necessary to produce APAAs, promoting the cyclization process. To evaluate

these assumptions, thermal degradation experiments were first undertaken, where rapeseed oil was heated for different lengths of time (1, 5, 10 and 17h), at different temperatures (100, 150, 200, 250°C), both with or without adding ceramic powder and with or without the presence of oxygen (Table 6.1).

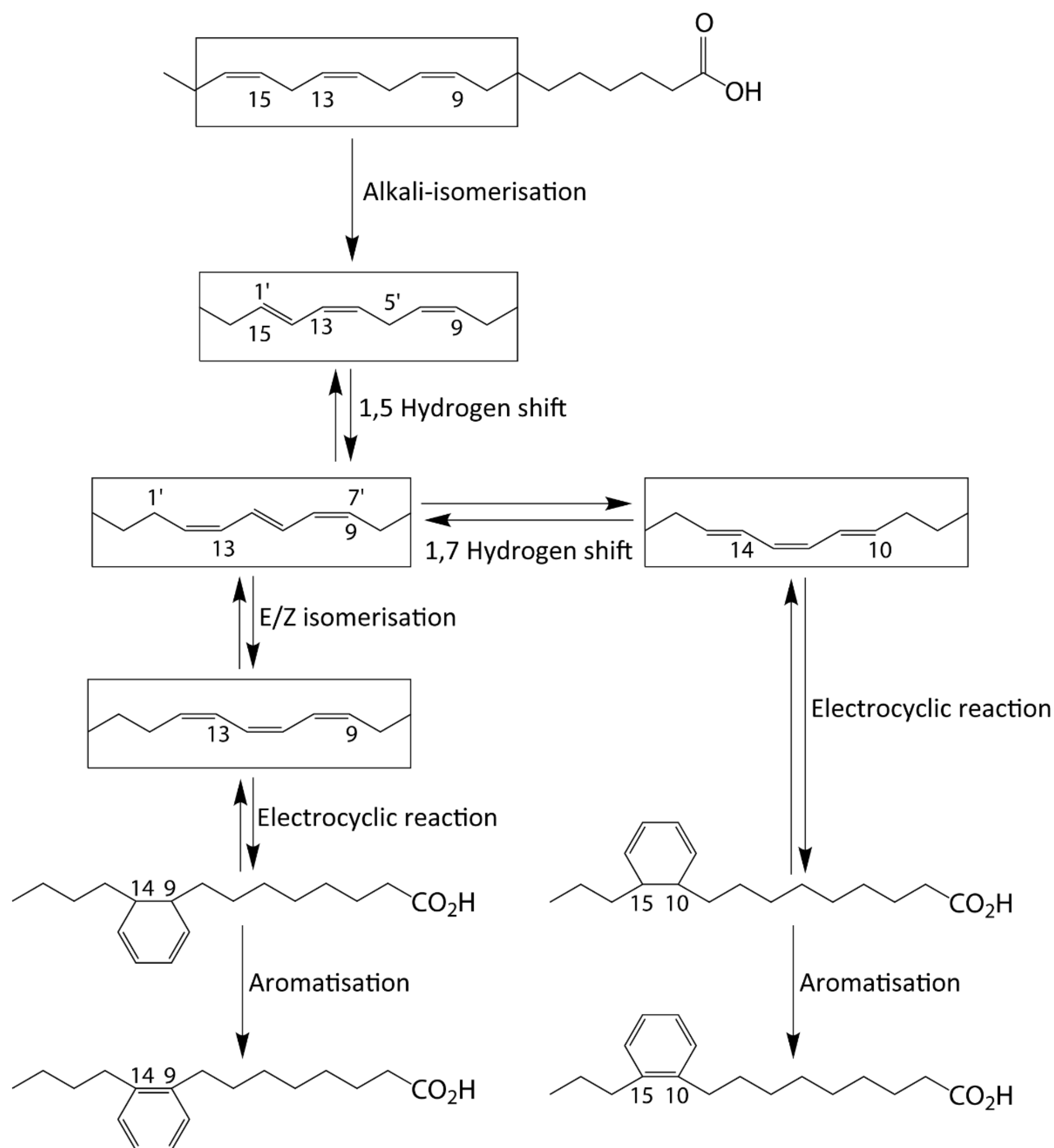

Figure 6.1 Scheme of the reaction pathway for the formation of ω-(o-alkylphenyl)octadecanoic acid (APAA) through heating of cis, cis, cis-9, 12, 15-octadecatrienoic acid (after Hansel et al. 2004).

2. Material and Method

2.1. Cooking experiments

For all the experiments, wheel-thrown replica pottery was used, made with "Standard Red" clay, chosen for its relatively high amount of metal ions (Al_2O_3- 22.78, Fe_2O_3- 7.37, CaO- 0.57, Mg0- 0.86, K_2O- 1.6, Na_2O- 0.1) known to catalyse the isomerization reaction involved in the APAAs formation (Fig.

6.1) (Raven et al., 1997; Evershed et al., 2008). No temper was added to the matrix, preventing any organic exogenous contamination in the clay matrix, and the pots were fired at 700°C, by an experimental potter (Mr. Graham Taylor, Experimental Archaeologist and Ancient Pottery Technology Specialist, Rothbury, UK). The pottery powder used for the laboratory experiments was obtained by crushing one of these replica vessels with a mortar and pestle.

For the first series of laboratory experiments ca. 65 mg of rapeseed oil (Commercial Organic, cold-pressed, extra virgin rapeseed oil, origin United Kingdom) was heated in glass ampoules. These were left open or sealed under nitrogen and heated for 1, 5, 10 or 17 hours at temperature of 100, 150, 200, 250, or 270°C (Table 6.1). For each of these parameters, the experiments were carried out in duplicates either with or without the addition of ceramic powder. Analogous to the first experiment, 20 mg of pure fatty acids ($C_{18:0}$, $C_{18:1}$, $C_{18:2}$ and $C_{18:3}$) were also heated in open glass tubes with or without powdered ceramic for 5 hours at 270 °C. Finally, a selection of foodstuffs, encompassing meats, fish and edible plants (vegetables, fruits, nuts and cereals) along with ceramic powder were subjected to similar heating experiments involving 5 hours of heating at 270°C. All the heating parameters for each laboratory experiment are collected and available in Appendix 15A and B.

Experiments were also conducted in the field (YEAR centre, University of York) aiming at simulating cooking conditions on an open fire. Portions of red deer meat, salmon flesh and chestnut flour were individually placed into replica pots, submerged in water and heated on an open fire (Appendix 18). A thermocouple was used to measure the temperature on the outside of the vessels for each pot. The pots were left to boil for 1 hour and regularly refilled with water. Subsequently, each pot was emptied and reused for another 1 hour in the same manner. This action was repeated five times for the chestnut flour and 15 times for the meat and fish. Each commodity was boiled in three pottery replicates along with one blank, which consisted of boiling water in pottery. All pots were split into two parts, one was directly analysed and the other was buried for six months (from May to November 2018) at YEAR centre (Lat. 53.95; Long. -1.09; pH_{soil} = 7.16) before to be analysed. Photos illustrating cooking experiences are given appendix 19.

2.2. Lipid analysis

For the cooking experiments performed in replicate pots, ca. 1g of pottery powder was drilled following cleaning of the vessel surface with a modelling drill to remove any exogenous contamination. Any carbonized surface deposits (foodcrusts) that were formed during cooking, were detached from the surface of the pot using a sterile scalpel and were finely crushed. An aliquot of *ca.* 20 mg of

foodcrusts was weighed out for the analysis. For the experiments undertaken in the laboratory, all of the carbonised remains formed during the heating were used for the analysis. In addition, each unheated foodstuff used in the experiments was also extracted in order to confirm the absence of APAAs in the raw commodities.

Subsequently, lipid extraction was performed following the established acidified methanol protocols (Craig et al., 2013; Papakosta et al., 2015). Briefly, the samples were placed into glass vials in which methanol was added (4 mL and 1 mL for potsherds and foodcrusts samples respectively) along with an internal standard (*n*-tetratriacontane: 10 µg). The mixture was then ultrasonicated for 15 min before acidification with concentrated sulphuric acid (800 µl and 200 µl, respectively) and heated for 4 hours at 70 °C. After cooling, the lipids were extracted with *n*-hexane (3 x 2 mL). Finally, a second internal standard was added (*n*-hexatriacontane: 10 µg) and the samples were directly analysed by Gas Chromatography-Mass Spectrometry (GC-MS).

An Agilent 7890A series chromatograph coupled to an Agilent 5975C Inert XL mass selective detector with a quadrupole mass analyser (Agilent technologies, Cheadle, Cheshire, UK) was used to analyse the samples. A splitless injector was employed and held at 300°C. The GC column was directly connected to the ion source of the mass spectrometer. The ionisation energy of the MS was 70 eV and spectra were obtained by scanning between m/z 50 and 800. All the samples were run on a DB23 (50%-Cyanopropyl)-methylpolysiloxane column (60 m x 250 µm x 0.25 µm; J&W Scientific, Folsom, CA, USA) in selected ion monitoring mode (SIM) and using a temperature program setup to better detect and resolve the three isoprenoid fatty acids (phytanic and pristanic acids and 4,8,12-TMTD) and the ω-(o-alkylphenyl) alkanoic acids (Shoda et al. 2017). The temperature was set at 50°C for 2 min and increased at a rate of 10 °C/min until 100 °C. The temperature was then raised by 4 °C/min to 140 °C, then by 0.5 °C/min to 160 °C and finally by 20 °C /min to 250 °C, where the temperature was maintained for 10 min. Helium was used as carrier gas at a flow rate of 1.5 mL/min.

3. Results and discussion

3.1. Under what conditions do APAAs form in archaeological ceramics?

3.1.1. Time and temperature

This first set of experiments demonstrates that the production of the APAAs requires less intensive heating conditions than previously stipulated. Whilst experiments confirm their occurrence in the rapeseed oil heated for 17 hours, we found that APAAs are readily formed after just one hour of

heating at 270°C. The experiments also indicate that heating at 200°C is sufficient to generate APAAs (Table 6.1). The experiments suggest that APAAs are more likely to form when the UFA precursors are in direct contact with the pottery wall, where temperatures in excess of 200°C are easily achieved even when the vessels are used to heat (boil) liquid contents. This point is verified by experiments conducted on the open fire, where the external ceramic surface frequently reached temperatures greater than 300°C. Here, appreciable amounts of APAAs were formed in all the experiments (deer, salmon and chestnut flour) following five or 15 hours of simulated cooking (Appendix 18). Interestingly, the relative abundance of APAAs is higher following burial, especially for cooked salmon where APAAs were only clearly visible after burial. This is probably due to the relative loss of other more soluble compounds.

Importantly, the APAA-C_{18} isomeric distribution is not significantly altered by the temperature (Kruskal-Wallis; Chi^2 = 0.49; p = 0.78) or the length of heating (Kruskal-Wallis; Chi^2 = 0.05; p = 1) (Appendix 18); Overall, heating conditions do not seem to influence the APAAs formation process allowing for further investigation of the diagnostic value of APAA-C_{18} isomeric distribution in archaeological context.

3.1.2. Do APAAs form in absence of ceramic?

This study also shows that APAAs are produced in either the presence or absence, of ceramic powder (Table 6.1; Appendix 18). This could suggest that, instead of the prior alkali isomerisation, the APAAs were formed here via the allylic radical intermediates mechanism, an alternative pathway described by (Matikainen et al., 2003). However, it is worth noting that these experiments were undertaken in glass tubes, where metal ions are also present, as part of the silicate glass composition (Norman et al., 1998), and therefore could have contributed to the isomerization process. However, due to the amorphous structure of such material, metal ions are likely to be less accessible than in low fired and powered ceramic, partially crystalline (Rice, 1987). This may explain the lower conversion of UFAs to APAAs observed during our experiments carried out without pottery powder (Appendix 21). Overall the experiments show that the pottery matrix assists the formation rate of such compounds (Evershed et al., 2008). Nevertheless, APAAs can also be produced by heating the UFA precursors in other kind of containers providing a minimal amount of metal ions, such as stone bowls or griddle stones (Admiraal et al., 2019). They have also been identified in charred food remains that have no clear association with a mineral artefact (Heron et al., 2016). Overall, this suggests that the steric properties, as previously proposed by (Evershed et al., 2008), and/or the chemical composition of the cooking container influence, to a certain extent, the reaction but that other mechanisms could also be important requiring further inquiry.

3.1.3. Evacuated vs aerobic conditions

Finally, these experiments also demonstrate that APAAs can be produced under fully aerobic conditions contrary to previous reports (Table 6.1; Evershed et al., 2008), and therefore formation does not require the UFA precursors to be trapped in the ceramic matrix. Nevertheless, differences in the isomeric distribution of APAA-C_{18} are noted between the experiments in evacuated and fully aerobic conditions perhaps affecting the formation process. Whilst in both cases the thermal degradation has induced the formation of isomers A to I, the rapeseed oil heated in the open tubes produced greater relative amount of E and F isomers (Appendix 20). In contrast, the rapeseed oil heated in anaerobic condition exhibits a higher prevalence for the G isomer. Interestingly, the distribution of the APAA-C_{18} isomers obtained by heating salmon, chestnut flour and red deer undertaken in the field experiments are not significantly different to those carried out in the laboratory in open tubes (Kruskal-Wallis test: chestnut flour, $Chi^2 = 1.22$; $p = 1$; salmone; $Chi^2 = 0.93$; $p = 0.99$; red deer; $Chi^2 = 0.19$; $p = 0.91$); either before, or after, burial. These findings suggest that the formation of APAAs during cooking is more likely to occur under aerobic conditions, and the isomeric distribution remains stable over time.

Products	Time (h)	Temperature (°C)	Sealed	Pottery powder present	Formation of APAAs
Rapeseed oil	1	270	✓	✓	✓
Rapeseed oil	5	270	✓	✓	✓
Rapeseed oil	10	270	✓	✓	✓
Rapeseed oil	17	270	✓	✓	✓
Rapeseed oil	5	250	×	✓	✓
Rapeseed oil	5	200	×	✓	✓
Rapeseed oil	5	150	×	✓	×
Rapeseed oil	5	200	×	✓	×
Rapeseed oil	5	270	×	×	✓

Table 6.1 Table summarising the conditions required, and tested here, to form APAAs by heating rapeseed oil.

3.2. What degree of resolution can APAAs offer for product identification?

3.2.1. Distinguish different foodstuffs based on APAA-C_{18} distribution

Different foodstuffs were heated in order to assess whether analysis of APAA-C_{18} could provide further diagnostic information. A wide range of foodstuffs was selected, including meat, fish and edible plants (vegetables, fruits, cereals and nuts) either raw, or in the form of oil (Appendix 17B). These commodities were all subjected to the same experiments involving identical heating conditions (5h, 270°C, presence of ceramic powder and using open-air conditions; Appendix 17B). For all the samples the whole set of APAA-C_{18} isomers (n = 9, from A to I; Fig. 6.2) were produced. The contribution of each isomer was then computed by the integration of the *m/z* 290 ion (Appendix 17B). Variability in the distribution of APAAs isomers in carbonised residues resulting from the experiments were investigated using principal components analysis (PCA).

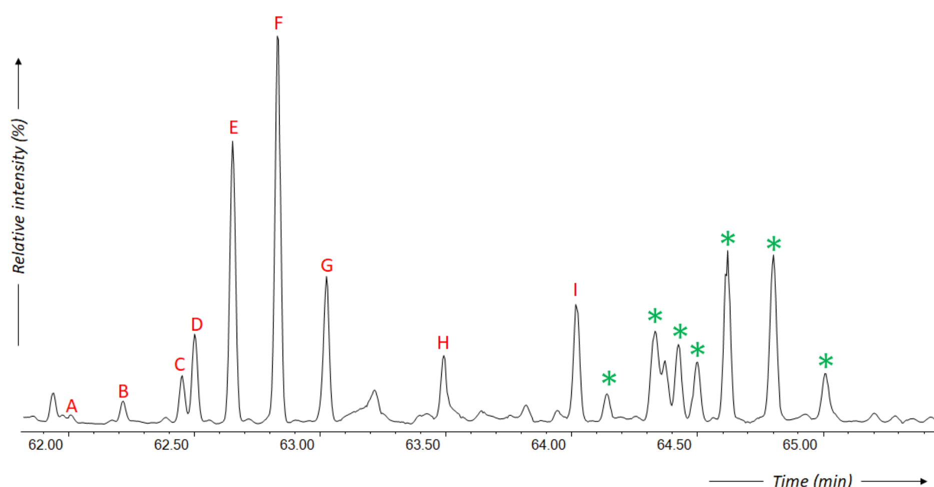

Figure 6.2 Partial SIM chromatogram (*m/z* 105 ion) of the cooked Viviparus shellfish showing the distribution of the ω-(o-alkylphenyl)alkanoic acids with 18 (letters from A to I corresponding to the isomers) and 20 (*) carbon atoms.

By plotting the first two principal components (Fig 6.3), representing 57.2% and 32.8% respectively of the total variance in the dataset, one group of foodstuffs (n = 9) tends to stand out from all others (n = 30). Interestingly, this group contains only plant products, more specifically cereals and nuts including barley, wheat, sesame, rice (oil and grain), pistachio, almond, walnut and broomcorn millet, and corresponds to a relatively greater contribution of E and F isomers in these products. Indeed, the isomers E and F have large positive loadings on component 1 (0.68) and component 2 (0.67) respectively. Therefore, we suggest that the contribution of these two isomers of APAA-C_{18} compared to C to I, since the A and B isomers are not always visible in archaeological samples, could offer a novel index to identify cereals and nuts processing in ancient pottery. When summed, the E+F contribution

produced from cereals and nuts (n = 15; x̄ = 65%) was significantly higher than those originating from either animal products (n = 15; x̄ = 56%; T-test: t = 4.3; $p < 0.01$), and fruits and vegetables (n = 9; x̄ = 55%, T-test: t = 3.5; $p < 0.01$), as shown in Figure 4.

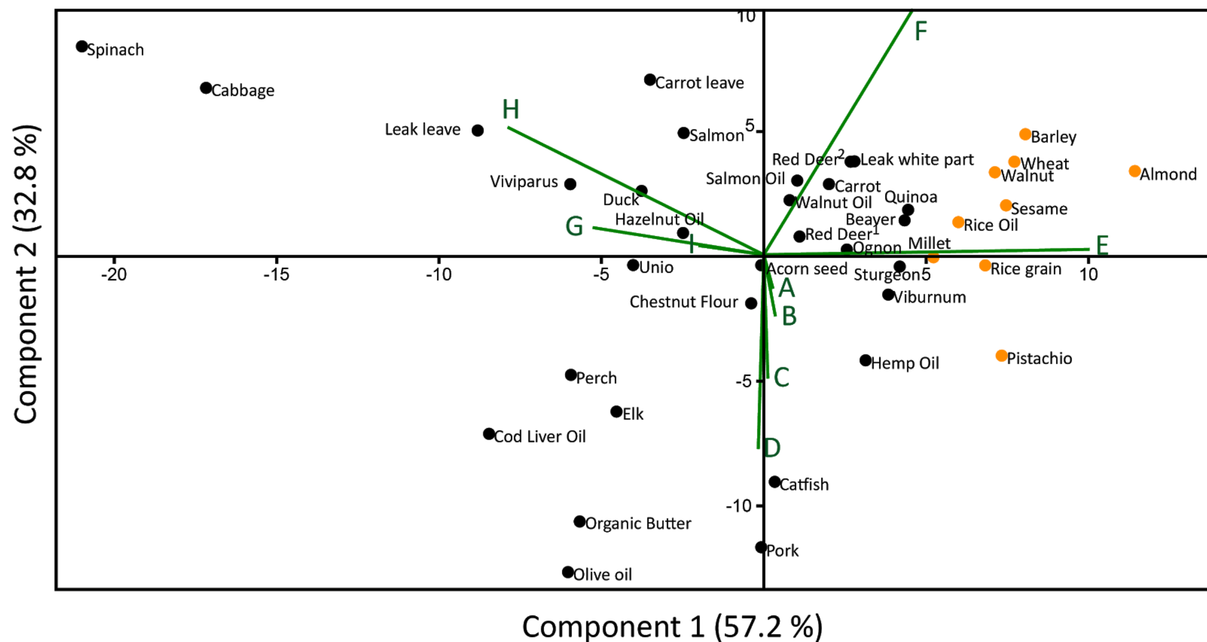

Figure 6.3 Principal component analysis (PCA) scatter plot of the first two principal components (PCs) based on the APAA-C_{18} isomeric distribution derived from different foodstuffs subjected to heating at 270°C for 5 hours.

To explore the application of this index in an archaeological context, the APAA-C_{18} isomers distribution was determined in pots from two sites; Zamostje 2 is a riverine hunter-gatherer site located in Russia whereas Joto is an early agricultural site (Yayoi period) in Japan. These sites were chosen due to their strong association of pottery with the processing of fish and plant products, respectively. Organic residue analysis carried out on potsherds (n = 46) excavated from the Middle Neolithic period (5th millennium BC) at Zamostje 2 have shown that ceramic vessels were highly used for processing aquatic resources (Bondetti et al., 2020). At the early agricultural site (1st and 2nd centuries) of Joto, SEM has previously identified the charred remnants of rice pericarp tissue in two surface deposits at the site (Shoda et al., 2011) and neither contained APAA-C_{20}. As shown in Figure 6.4, the contribution of the E+F isomer of APAA-C_{18} clearly separates the pots from these two sites in accordance with the commodities apparently cooked in it. The vessels from Zamostje 2 display a mean E+F contribution of 51.1% (±6.2) against 63.3% (±0.98) for Joto pottery matching with the results obtained during the experiments.

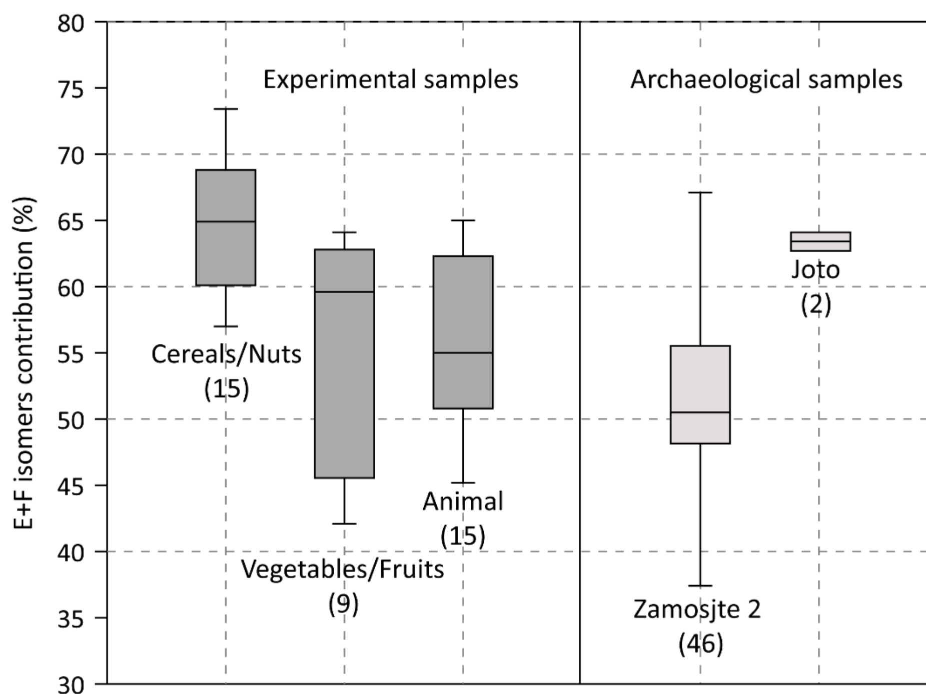

Figure 6.4 Boxplots of the APAA-C_{18} isomers E+F contribution (%). The E+F isomers contribution was computed over the contribution of APAA-C_{18} isomers C to I. Plots represent median, ranges and quartiles.

The analysis of unsaturated fatty acids $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ both undertaken here on pure compounds (Appendix 17A and 22) and previously published (Evershed et al., 2008) shows that the APAA-C_{18} isomeric distribution is dependent on the relative abundance of UFAs-C_{18} in the initial foodstuffs. However, the isomeric distribution observed in the foodstuffs after heating showed no clear correlation with their fatty acid content, indicating that a more complex series of reactions was involved in APAAs formation. Previous thermal degradation of γ-$C_{18:3}$ and α-$C_{18:3}$ (Evershed et al., 2008), heated under the same conditions, resulted in a significantly different isomeric distribution and bears this assumption. Therefore, it may not be possible to predict the APAA-C_{18} distribution based on a product's original UFAs content, necessitating empirical investigations as described above.

3.2.2. Distinguishing aquatic from terrestrial resources (APAA-C_{20} vs. APAA-C_{18})

As expected for aquatic products where UFAs-C_{20} are particularly abundant (Passi et al., 2002; Wirth et al., 2002; Cramp and Evershed, 2014), APAAs containing 20 carbon atoms (i.e. ω-(o-alkylphenyl)ecosainoic acid, APAA-C_{20}) were recovered (Fig. 6.2). As stated previously, APAA-C_{20} are important criteria to highlight the processing of aquatic products in ancient pottery (Hansel et al., 2004; Cramp and Evershed, 2014). However, these compounds are not exclusively produced by processing of aquatic products. The thermal degradation of other animal products, such as elk, beaver, pork and red deer fats also yielded APAA-C_{20}. Likewise, trace amounts of APAA-C_{20} were detected in some of the

heated plant samples (e.g. broomcorn millet, quinoas, rice, sesame, and acorn; Appendix 15B). In all cases, they are derived from trace amounts of C_{20} UFA precursors present in these foodstuffs.

Consequently, the reliability of using APAA-C_{20} as biomarkers of aquatic resources may be questionable, especially when other aquatic derived compounds (e.g. isoprenoid fatty acids, APAA-C_{22}) are absent. This would appear to be a major limitation of the approach considering that APAA-C_{22} are observed much less frequently than the C_{20} homologous. Nevertheless, our results also show that the relative abundance of APAA-C_{20} (obtained by the integration of the *m/z* 318 ion) in aquatic products is much greater than those observed in other foodstuffs. For example, the ratio of APAA-C_{20} to APAA-C_{18} (APAA C_{20}/C_{18}) of aquatic animals (n = 9; $\bar{x}$ = 0.21 ± 0.03) is significantly higher than both terrestrial plants (n = 5; $\bar{x}$ = 0.02 ± 0.00; Mann-Whitney test: U = 0; z = 2.93, $p < 0.01$) and terrestrial animals (n = 5; $\bar{x}$ = 0.04 ± 0.00; T-test: t = 2.41; z = 2.93; $p = 0.03$). This ratio therefore provides a useful criterion to separate aquatic commodities from the other foodstuffs (Figure 6.5). The APAA C_{20}/C_{18} ratio observed in the different foodstuffs is strongly correlated with the relative abundances of precursor UFA-C_{18} and C_{20} (Spearman; R = 0 .84; $p < 0.01$).

For future applications the APAA C_{20}/C_{18} ratio of >0.06 could provide a useful criterion for distinguishing aquatic sources from terrestrial products. Preferential degradation processes differentially acting on the two homologous potentially could compromise the utility of this approach, for example due to differences in solubility. However, in the burial experiments conducted here on pots used to cook salmon, the APAA C_{20}/C_{18} ratio was still greater than 0.6 (n = 3; $\bar{x}$ = 0.10 ± 0.00) following 6 months burial (Fig. 6.5).

Interestingly, this criterion appears to be useful for archaeological pottery. Indeed, the APAA C_{20}/C_{18} ratio obtained from Middle Neolithic pottery at Zamostje 2 (n = 43; $\bar{x}$ = 0.12 ± 0.00;), which were mostly used to process freshwater resources (Bondetti et al., 2020), fall in the range of modern aquatic data (Fig. 6.5).

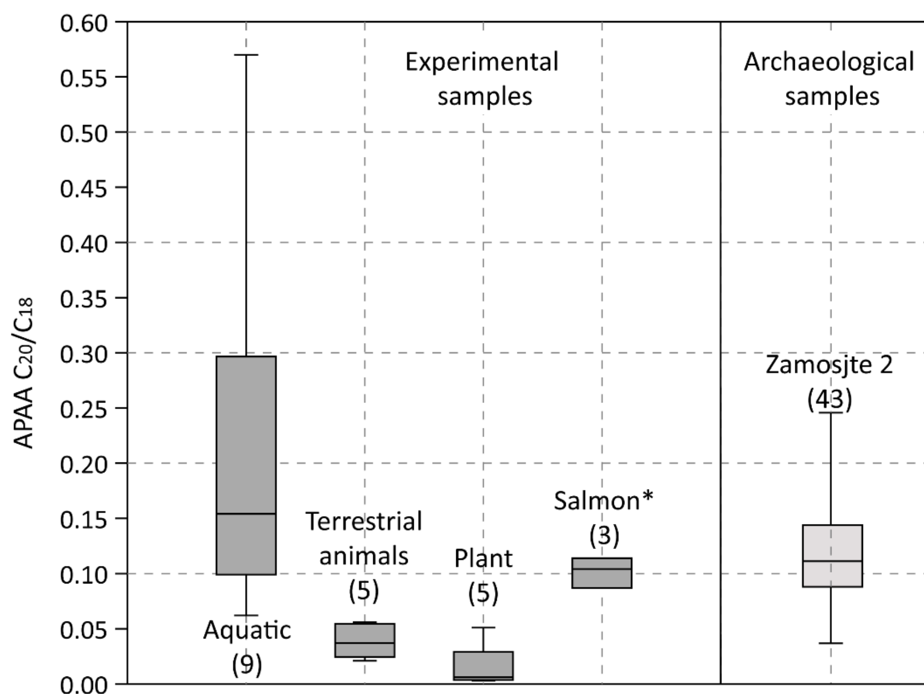

Figure 6.5 Boxplots of APAA C_{20}/C_{18} ratio of modern references, heated either in the laboratory or during field experiments after 6 months burial (*), and archaeological samples.

4. Conclusion

The thermal degradation of a wide range of commodities brought new insights with regard to the interpretative degree of APAAs in ancient ceramic vessels. Indeed, the APAA-C_{18} isomers distribution profile could offer novel diagnostic biomarkers to identify the processing of specific plants in archaeological pottery, such as cereals and nuts. Finally, these experiments have shown that APAA-C_{20} do not exclusively occur during the cooking of aquatic products, since they have been yielded from the heating of meats as well as some plants. However, the APAA C_{20}/C_{18} ratio can be used to determine whether the APAA-C_{20} arose from the processing of aquatic or terrestrial products and should be used as a complementary molecular tool to identify aquatic processing in ancient pottery.

Furthermore, our experiments, described above, have shown that APAAs were formed either in laboratory experiments or during real-cooking context and have demonstrated that:

- APAAs form relatively rapidly ca. 1 hour of heating.
- Heating at 200°C is sufficient for APAA formation.
- APAAs form under aerobic conditions and are readily formed by simulated cooking on an open fire.

- The presence of pottery is not a prerequisite for their formation, even though it greatly enhances their synthesis due to the accessibility of the metal ions present in the matrix allowing alkali isomerization.

This study shows that the production of APAAs requires much less intensive cooking conditions than previously thought, which probably explains why these compounds are commonly encountered in archaeological pottery. This has important implications for the interpretation of the mode of cooking as it implies that they could theoretically form during a single cooking event rather than from many hours of protracted heating and extensive re-use of a vessel.

Statistical Analysis

Statistical tests were performed using PAST3 software package (version 3.25 for Windows).

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Chapter 7

Is there an "Aquatic" Neolithic? Concluding comments and future horizons

1. Discussion

Pottery technology first emerged among **Late Pleistocene hunter-gatherer communities** between 16,000 and 13,000 year cal BC in South China, Japan and the Amur River basin in the Russian Far East (Habu, 2004; Kudo, 2004; Kuzmin, 2006; 2017; Keally et al., 2007; Boaretto et al., 2009; Budja, 2009; Hommel, 2012; Wu et al., 2012). At this early stage, pottery production and use remain relatively limited geographically. By the **early Holocene** (ca. 9,700 to 5,000 cal BC) greater use of pottery is observed within East Asia and this technology started to diffuse out of the East Asia core to progressively appear across much of **northern Eurasia**.

The principal aim of this thesis was **to examine whether the exploitation of aquatic resources drove this wider Holocene appearance** by investigating the **function of early pottery** emerging within hunter-gatherer communities in northern Eurasia**.**

The advent of pottery represents a clear archaeological horizon in the prehistoric sequence of this region and is often used to define a period known as the **Neolithic**, contrasting with Western European definitions. One theory that has recently emerged is that the advent of pottery, or its increased production, was linked to an intensification of aquatic resource exploitation (Chairkina and Kosinskaia, 2009; McKenzie, 2009; Gibbs and Jordan, 2013; Oras et al., 2017b); the so-called **"Aquatic" Neolithic**. This theory is supported by recent organic residue analysis of Late Glacial and early Holocene pottery from eastern Asia and northern Europe (Craig et al., 2013; Lucquin et al., 2016a; Gibbs et al., 2017; Oras et al., 2017b; Shoda et al., 2017), where lipid markers derived from aquatic resources were frequently encountered directly in the pots themselves.

This PhD project aimed at testing this "Aquatic" Neolithic model and tackled this research question by undertaking the first systematic application of **organic residue analysis** to Early Neolithic pottery recovered from three important archaeological sites in Siberia and the European part of Russia: **Gorelyi Les, Zamostje 2 and Rakushechny Yar** (Fig. 7.1).

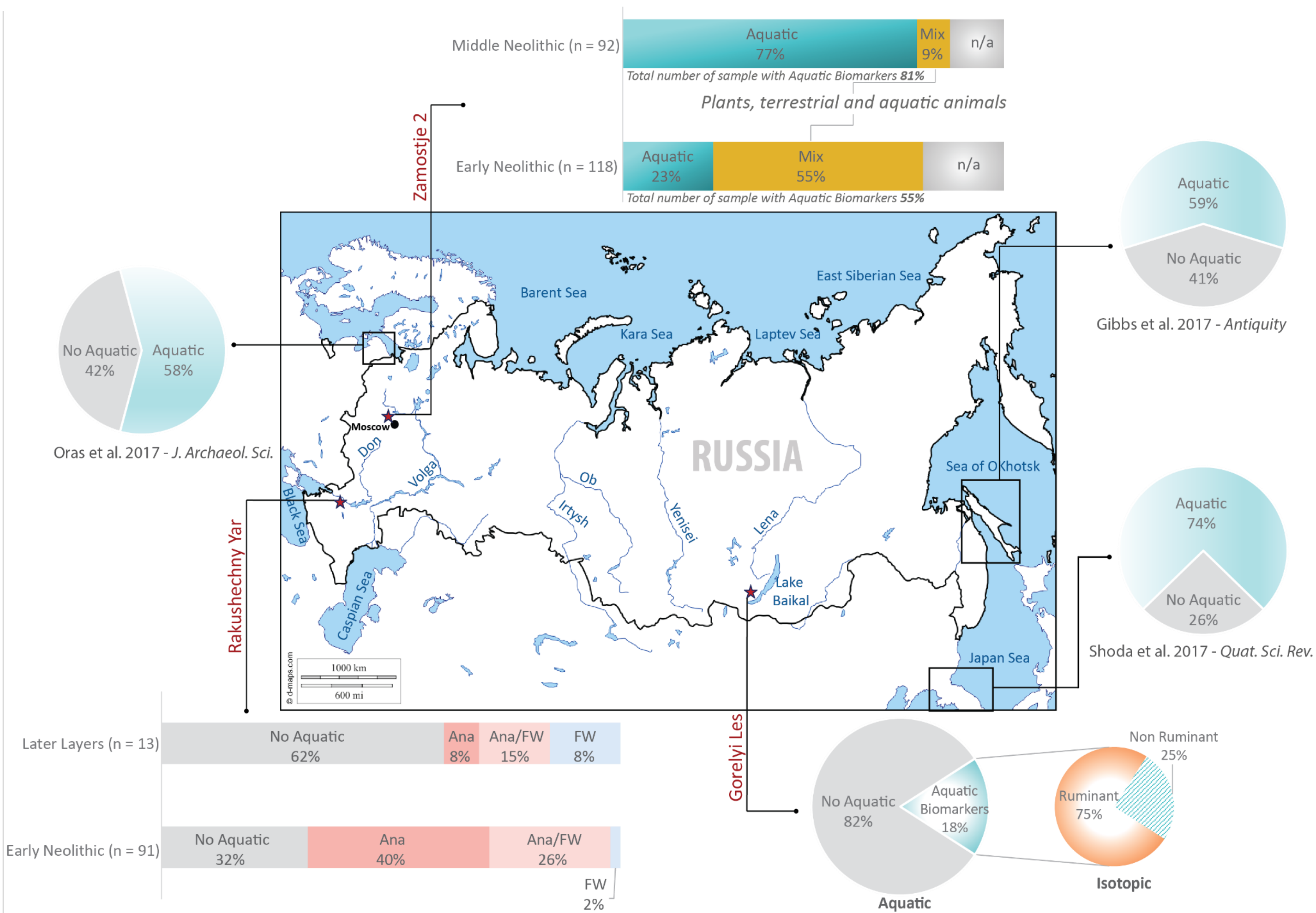

Figure 7.1 Map showing the locations of the three sites selected for this PhD project. This map also includes the percentage of pottery displaying an aquatic signal reported in previous research studying the function of early Holocene pottery in the Baltic region, Korea and on Sakhalin Island (Gibbs et al., 2017; Shoda et al., 2017; Oras et al., 2017b) and is compared with the new data generated during this PhD project.

Russia has a rich record of Holocene forager pottery use, many of which are important for tracking the dispersal of this technology across Eurasia. Despite this, this region has so far been neglected by organic residue analysis. Little is known about how early pottery was used and what drove its adoption into this region during the early Holocene or how it compares, in terms of use, with other forager pottery in other regions of Eurasia. This thesis aims to fill this gap in knowledge, and to test whether the oldest examples of pottery from key sites, dating to the early Holocene, in Siberia, northern European Russia and southern Russia was actually used to process aquatic resources.

To achieve this aim, the thesis had four **objectives**:

1) To assess lipid preservation

Hydrophobic properties of lipids, as well as their absorption into the mineral matrix (ceramic) or their encapsulation in the organic matrix (charred residues) greatly enhance their survival potential on archaeological time scales (Evershed, 1993). However, some environments can turn out to be rather unfavourable to the preservation of lipids. For example, in regions around the Mediterranean, such as the western Mediterranean, Greece or Syria, the percentages of samples providing interpretable lipid yields extracted from pottery are relatively low, not exceeding 27% (Fig. 7.2.a) (Nieuwenhuyse et al., 2015; Debono Spiteri et al., 2016; Whelton et al., 2018). Climatic conditions in the Mediterranean regions, displaying seasonal variations alternating between abundant rainfall and periods of hot drought, probably play a crucial role in lipids decay and appear to be not very appropriate for the survival of lipid residues (Aillaud, 2002; Gregg et al., 2009; Debono Spiteri, 2012; Drieu, 2017). On the other hand, the calcareous nature of Mediterranean soils, which are overall not very acidic, also tends to be not propitious to the preservation of organic matter (Debono Spiteri, 2012; Drieu, 2017). Microbial activity is optimal under such pH conditions (DeLaune et al., 1981; Moucawi et al., 1981) and fatty acids present as soluble salts are more easily leached out (Evershed et al., 1997; Drieu, 2017).

Lipids are, however, more likely to survive in waterlogged and desiccated environments (Regert et al., 1998; Copley et al., 2005) and pottery recovered from northern latitudes show much better preservation. This is notably the case in Russian Far East (Sakhalin island), Korea and Baltic where pottery analysed displayed significantly higher lipid-preservation rates with respectively 71%, 84% and 88% of the samples yielded sufficient lipids, respectively (> 5 µg/g for ceramic; > 100 µg/g for foodcrusts; Fig. 7.2.a). Despite this general observation and a high potential for lipid preservation in the sites studied in this project, all located in waterlogged environments, the degree of lipid preservation needed to be tested. Many other factors, such as soil moisture level, pH, microbial activity

leading to various physico-chemical processes have a significant impact on their preservation degree (Evershed, 1993). This is clearly dependent on the burial environment characteristics and therefore particular to each site. Preservation conditions for lipids associated with archaeological pottery are consequently difficult to predict, especially in new environmental contexts never yet investigated.

Therefore, one of the first challenges of this PhD project was clearly to assess the lipid preservation and test the workability of organic residue analysis methods. The percentage lipid recovery in Russia is excellent since over 90% of all sample assemblage studied in this project provided sufficient lipids (Fig. 7.2.a). Taken individually, the three sites also provide very satisfactory results. They all exceed the percentage of lipid recovery reported in published research studying early hunter-gatherer pottery from northern Eurasia (e.i. Baltic, Sakhalin Island and Korea) (Gibbs et al., 2017; Oras et al., 2017b; Shoda et al., 2017).

In terms of lipid concentration, the results follow the same line. While the single foodcrust sample from Gorelyi Les does not exhibit a particularly high lipid concentration, it remains broadly similar to levels reported in the other comparable studies using the same extraction procedure (Fig. 7.2.b). It suggests that organic matter in this burial environment tends to be preserved, although a greater number of charred residue samples would be needed to confirm this. On the other hand, the average lipid concentrations for foodcrust samples recovered in Rakushechny Yar and Zamostje 2 provided very high amounts of lipids per sample, demonstrating exceptional preservation of organic matter in both contexts (Fig. 7.2.b). Similarly, ceramic samples show excellent preservation of the absorbed lipids.

Interestingly, while Zamostje 2 foodcrusts showed higher lipid concentrations than the other two sites, this seems to be the opposite for ceramic samples. As the environment and climatic conditions at these three sites appear to be highly conducive to the preservation of the organic matter, the reason behind this discrepancy is most likely related to a different use of ceramic vessels (e.g. type of products processed, how many times pots were used). For example, it appears that Rakushechny Yar pottery was highly specialised in treatment of sturgeon, very rich in fat. In addition, the results of the lipid analysis indicate that these pots were most likely used to produce and/or store fish oil. This likely contributed to a better and greater penetration of fats into the ceramic matrix, leading to a higher lipid concentration in these sherds.

a)

Mediterranean region

Syria (n=287) 14%

Greece (n=856) 25%

Western Mediterranean (n=363) 27%

Norhern Eurasia

Baltic (n=100) 88%

Korea (n=131) 84%

Sakhalin island (n=41) 71%

Russia (n=418) 92%

100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%

Zamostje 2 (n=241) Rakushechny Yar (n=133) Gorelyi Les (n=44)

Significant amount of lipid (> 5 µg/g for ceramic; > 100 µg/g for foodcrusts)

b)

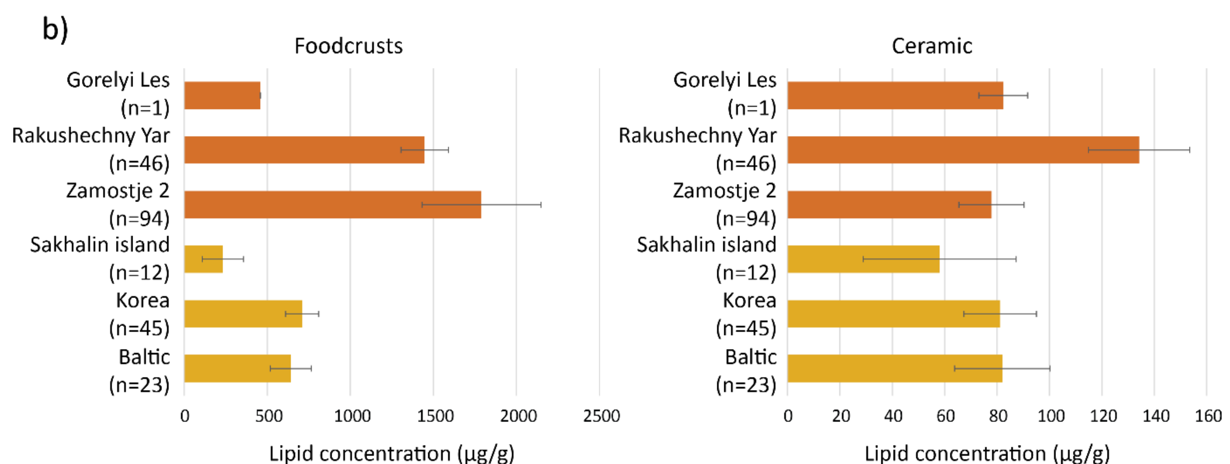

Figure 7.2 The average lipid concentration of the samples analysed in this project. These results are compared with those obtained from pottery found in other regions such as the Mediterranean Basin, Korea, the Baltic region and Sakhalin Island (Debono Spiteri, 2012; Nieuwenhuyse et al., 2015; Gibbs et al., 2017; Oras et al., 2017b; Shoda et al., 2017; Whelton et al., 2018). (n = x) indicate the number of samples analysed for each of this study.

Overall, it is reasonable to conclude that although lipid preservation shows some variation according to the sites studied here, organic residue analysis is a viable method to tackle questions concerning comparative pottery function.

2) To extract and analyse lipids from a large selection of potsherds (over 300 ceramic vessels) from three key early pottery sites to reconstruct patterns of vessel use using a systematic approach for lipid identification by GC-MS, isotopic characterisation of single compounds by GC-C-IRMS and bulk carbon and nitrogen isotope analysis by EA-IRMS. This objective was guided by two central questions. What was the function of the first pottery adopted by these three different forager communities in Russia used for? Is there any evidence that the function of pottery changed over time?

The first question can be addressed at each site under investigation as access to the earliest ceramic layers (ca. early and mid-6th millennium BC) was available. The analysis of organic residues from the **Gorelyi Les**, showed that earliest ceramic vessels were used to process a wide spectrum of resources. There was some diversity in patterns of pottery use. Approximately half of the pottery vessels have molecular signals consistent with non-ruminant products which may include a broad array of terrestrial or aquatic animals but also plants, including the by-products derived from pine trees such as needles, inner bark or resin. The other half had been used to process ruminants, most probably in combination with aquatic resources, either intentionally or during successive use of the pots; here 75% of samples meeting the molecular criteria for the identification of aquatic resources (n = 8) also display ruminant fat isotopic signals (Fig. 7.1). Evidence therefore suggests that **Early Neolithic pottery from Gorelyi Les does not support the "Aquatic" Neolithic hypothesis, and that it was adopted as a cooking vessel for more general use**.

Interestingly, a **similar pattern** of pottery use seems to emerge for **Zamostje 2**. Once again, organic residue analysis results generated here indicate that the "Aquatic" hypothesis was not supported, and that the newly introduced **pottery was initially used to process a wide spectrum of foodstuffs**. This includes terrestrial plant resources, such as fruits (e.i. *Viburnum* berries) along with aquatic products and probably also terrestrial animals (Fig. 7.1).

In contrast, at **Rakushechny Yar site**, we found a very **high specialisation in pottery use associated with fishing activities, particularly with** migratory fish, such as sturgeon (Fig. 7.1). In fact, this is the only site of this study that does support unambiguously the "Aquatic" hypothesis. Overall then, although aquatic resources were identified in all phases at all sites investigated, the **initial use of**

pottery seems to have **varied by site and regional context** meaning that no single answer to this question emerges.

In order to examine any temporal change in pottery use, vessels from Zamostje 2 and Rakushechny Yar assigned to different cultural layers were also selected and analysed (later samples from Gorelyi Les were not available). At **Zamostje 2** a completely different pattern of pottery emerged from the **Middle Neolithic phase** (ca. 5000-4000 cal BC). It shows an unambiguous **shift towards a specialist function**, focusing on aquatic commodities (Fig. 7.1). Less pronounced than at Zamostje 2 but still visible, pottery at **Rakushechny Yar** seems to slightly change during the later period of site occupancy (Late and Eneolithic; ca. 5th millennium cal. BC). Interestingly here, in contrast to Zamostje 2 case, a trend seems to emerge showing **lesser reliance on aquatic products** as well as a lesser focus on migratory fish processing (Fig. 7.1). It seems therefore that **no single trajectory**, e.g. from specialised to a more general use, or vice versa, is evident for the sites investigated here. Nevertheless, temporal trends in the use of pottery are evident but difficult to disentangle from wider potential changes in the subsistence base.

3) To test the established criteria for the identification of aquatic biomarkers in archaeological pottery.

For the **identification of aquatic products** in archaeological pottery, many previous studies have relied on the presence of **ω-(o-alkylphenyl)alkanoic acids** (APAA). Since criteria used for aquatic identification represent significant input into the aim of the thesis, it was also important to investigate the conditions under which these molecules are formed and to make a detailed examination of their diagnostic potential. Therefore, concurrently with the archaeological case studies, a series of laboratory and field cooking experiments were performed to reinforce the interpretations and conclusions that can be gained from these organic residue analysis results.

This experimental study, presented in chapter 6, has provided interesting and important results which in particular helped to **refine the formation conditions** of these molecules (e.g. time, temperature, aerobic vs. anaerobic conditions). These findings have important implications for the interpretation of the cooking process. On the other hand, this work has led to the setting of new criteria. First for the **identification of different food** treatments (e.g. animal fat, cereal/fruit/non-leafy vegetable, leafy vegetable) in archaeological pottery, through the **isomeric distribution of APAAs-C_{18}**. Secondly to **determine the real origin of APAAs-C_{20}** previously identified as an aquatic marker. Indeed, experiments have shown that the latter molecules are not exclusively formed by the transformation

of aquatic products but can also arise from the thermal degradation of animal products (e.g. elk, beaver, pork and deer fat) as well as from certain plants (e.g. broomcorn millet, quinoas, rice, sesame and acorn).

However, this work has identified a complementary molecular tool to determine the origin of APAA-C_{20} identified in ancient pottery, i.e. the **APAA C_{20}/C_{18} ratio**. A value of 0.06 appears to be a reliable threshold for distinguishing aquatic sources from terrestrial products. This additional criterion strengthens our ability to identify aquatic products in archaeological pottery. Interestingly, the APAA C_{20}/C_{18} ratio obtained from samples recovered from the three case studies generally display values higher than this threshold (Fig. 7.3). These same pots are all found in close association with aquatic resources and meet other molecular and isotopic criteria for the identification of aquatic products (Hansel et al., 2004; Evershed et al., 2008; Cramp and Evershed, 2014; Lucquin et al., 2016b). This therefore confirms their use for the treatment of aquatic resources beyond doubt providing a solid methodological basis to properly address the issue of the "Aquatic" Neolithic.

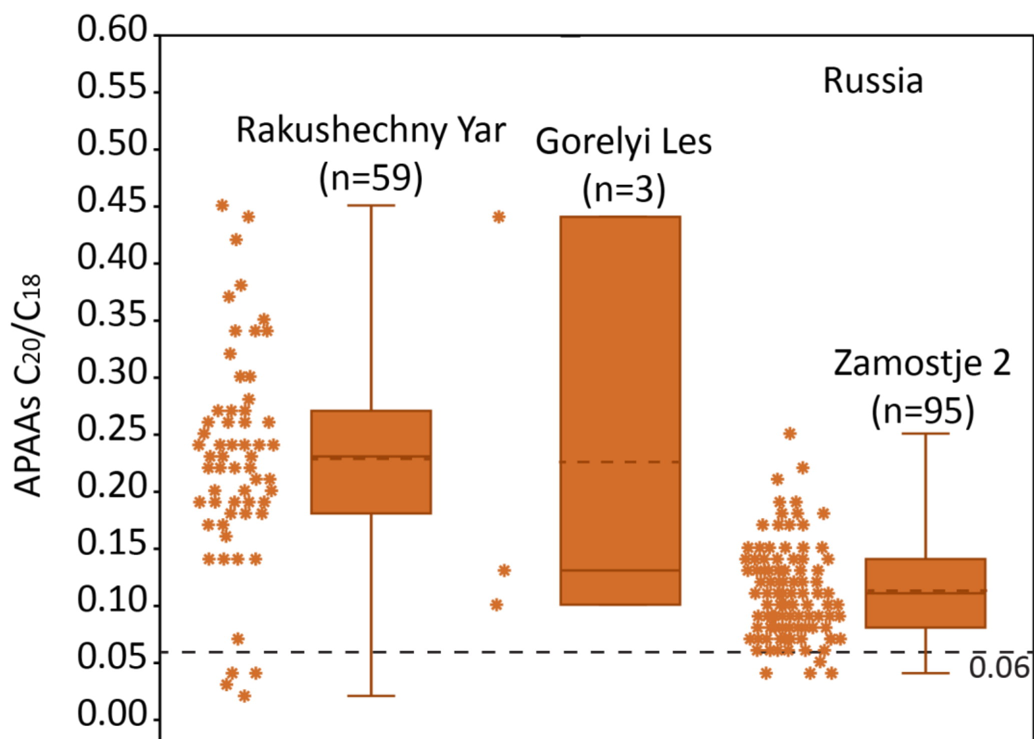

Figure 7.3 Boxplots of the C_{20}/C_{18} APAA obtained from the pottery samples analysed for the three case studies of this research. Plots represent median (solid line), mean (dashed line), ranges and quartiles.

4) To integrate these results from the three sites to build up a preliminary synthesis of early pottery use in this large region and formally test the hypothesis of an aquatic Neolithic.

This research forms an important contribution to the wider debate of pottery adoption among north Eurasian hunter-gatherer societies during the early Neolithic. While previous studies in northern Eurasia have pointed to a recurrent relationship between early ceramic technology and fishing activities, and used these preliminary results to suggest a general "Aquatic" model for this vast region, this research has started to formally test this idea at three key sites. The emerging results generate contrasting views. This indicates that adoption of pottery by Eurasian hunter-gatherer communities was not necessarily driven by the singular need to process aquatic foods. In fact, **pottery** appears to have been used in many cases as **a more general cooking technology**. Even at sites like Gorelyi Les and Zamostje 2, where fishing appears to have been substantial economic activity, other resources were also being cooked in the pots. Only the results from Rakushechny Yar confirm the "Aquatic" model, which is most likely related to the site's function since the fauna remains and the very specialized toolkit seems to suggest that the site was in fact a seasonal fishing station. The other results indicate that pottery use had a far more variable and complex pattern of use that was initially predicted, and that a singular "Aquatic" model does not fit all sites studied. Thus, **adoption of this new kind of container** technology appears to have been **driven by contingent local mechanisms**, and **not by singular factor**.

Overall, the reason behind the adoption of pottery within Eurasian foragers societies seem to have been highly diverse, and not a single driving force, such as increasing exploitation of aquatic resources. Perhaps this is not all that surprising, as it now seems unlikely that any single explanation would have led to the emergence of pottery given that hunter-gatherer communities had rich and diverse cultural, social and economic identities and constraints. Instead, as already stressed by P. Hommel (2014) and J. Habu et al. (2017) the advent and dispersal of pottery more likely result from a series of multifactorial circumstances and requirements. This likely combines economic, practical (benefit and cost) and ideological judgements, peculiar to each hunter-gatherer group rather than as just a response determined by shifts in the economy oriented towards fishing activities.

While diverse regional and temporal trends in hunter-gatherer pottery were observed, it is not clear that pottery simply reflected the local subsistence practices. As discussed above, specialised pottery uses strongly orientated towards the exploitation of riverine fish were observed at Rakushechny Yar and the later Middle Neolithic phases at Zamostje 2. The hypothesis that pottery was a general container with a range of utilitarian uses, perhaps as a replacement of pre-existing perishable

containers, would therefore also seem unlikely. It seems that the ways and means of producing pottery was learnt from adjacent hunter-gatherer groups but the vessels themselves were put to a range of functions, sometimes specialised, within these different economic and cultural settings. Whether these functions were entirely utilitarian or had some ritualistic aspects associated with feasting (as postulated by Hayden, 1995), is harder to determine. However, this would seem unlikely given the large number of pots typically found at early pottery sites of the steppe/forest during the Holocene and that they derive from a wide range of depositional contexts (Dolukhanov et al., 2009; Mazurkevich et al., 2013; Lozovski et al., 2014; Mazurkevich and Dolbunova, 2015; Dolbunova, 2016). The exception might be Gorelyi Les where pottery use was much more limited (McKenzie, 2009), but here use specialisation was not evident.

Implications for future research

General postulates are essential for defining research questions and directions. Here the "Aquatic" Neolithic model has been the building block of this PhD project and has formed a concrete hypothesis to test. However, this research also highlights how important it is that future research conducts more contextualised studies by both increasing the number of samples by sites and to integrate analysis results more systematically and rigorously with the broader sets of contextual data. The latter are valuable sources of information and are essential for building a high-quality interpretation of the organic residue results that are generated. This would allow us to grasp the drivers more accurately behind pottery uptake. Indeed, the broad geographic scale study, as undertaken by e.g. (Oras et al., 2017b), are important to generate a general picture of pottery function. However, such studies undeniably do suffer from small sample size by site and a poor contextualisation of each site. This probably leads to misinterpretation of the real role played by this technology within different groups and, the lack of accurate or robust chronologies, disguises potential temporal changes. Therefore, this thesis emphasises the **need to design and undertake much more local and contextual research**, as the entire process of origins and dispersals is probably far more complex and variable than we ever appreciated.

More generally, this research also demonstrated the **need to conduct a diachronic** analysis of pottery function because it is clear from these results that pottery function can evolve over time, even at the same site, and where general subsistence stays the same. Furthermore, it undoubtedly contributes to a better appreciation of the function and role of pottery by further highlighting certain trends in the use of pottery. The case of Zamostje 2 is the perfect example to illustrate this point. In fact, at this site, the initial observation of the Early Neolithic vessels could have led us to conclude a specialisation in

pottery use associated with fishing activities. Indeed, the proportion of pottery with aquatic biomarkers is relatively high (55%) and similar to those observed in other studies such as in Baltic and Korea with 52% and 65% of samples having such markers, respectively. Yet, it is only when these results are confronted with those generated for the Middle Neolithic pottery that the real specialisation of pottery focusing on aquatic food clearly emerges. Likewise, as already discussed in chapter 2, this case study stresses the **importance to combine molecular and isotopic data**. Although the number of Early Neolithic vessels with aquatic biomarkers is important, the addition of isotopic data (especially bulk isotope analysis in this case) have confirmed both the use of this pottery as a more general-purpose cooking vessels, to process a wide range of foodstuffs, and the specialisation of Middle Neolithic pots.

2. Directions for future research

The results of this doctoral research provided very interesting insights into the function of early Holocene hunter-gatherers pottery. It already challenges many assumptions about the relationship between humans and pottery technology. Nonetheless, the study of (Holocene) hunter-gatherer pottery is still in its nascent phase. Further work is required to continue to improve our knowledge about the active role of pottery technology among these populations. Some suggestions for the direction of future research are given below.

2.1. Sites, contexts and dates

This work focuses on the organic residue analysis of pottery from three sites. The aim was to analyse a wide range of pottery from each site to provide a more accurate understanding of functions, integrating a deeper contextualisation. Whilst the strategy brought conclusive results and a new vision about the function of early Holocene hunter-gather pottery, it, however, represents only three sites distributed over a very large geographical scale. This obviously limits a proper comparison and only gives us a small glimpse of pottery function in each of these regions. More studies of this type must be conducted in adjacent sites within each of these regions, but also within other regions, to complement the knowledge presented in this doctoral thesis, and tackle the research question adequately. Providing an assessment of pottery function from different site types (e.g. inland, along rivers), located in the same landscape, would be worthwhile to determine whether the patterns observed in each of these case studies reflect either a specialised regional function of the ceramics, or rather a specific use related to site location and/or function.

In addition, closer examination and **refinement of pottery dispersal and chronology** is clearly needed, both in Western Russia and Eastern Siberia. Here an essential requirement is to establish a more robust

spatio-temporal chronologies in these regions. Many of the dates for the arrival of pottery are based on pottery total organic carbon dates and many of these are radiometric dates (Tsybrij et al., 2017). Considering the additional confounding factor of freshwater reservoir effects, the dates for the arrival of pottery, currently accepted by many scholars, are undoubtedly to be too old thereby preventing a sensible, informed discussion on how pottery dispersed and how manufacture and use changed through time.

Combined lipid studies, technological studies and radiocarbon dating of pottery would greatly help to trace the exchange networks of this technology. By combining these approaches, it would be interesting to explore whether pottery technology spread and was adopted as a single innovation or in combinations with other cultural traits. In other words, whether hunter-gatherers adapted pottery technology to meet their own economic and cultural requirements or whether they used pots in the same way and for the same reasons as the communities where this technology came from. In the future, this hopefully will be possible thanks to a large-scale new AMS dating program (INDUCE project) which will incorporate the results of this research to investigate use, manufacture, and the dispersal of hunter-gatherer ceramics at a finer scale.

2.2. Methodology improvement for lipid analysis

In order to increase the reliability, fidelity and scope of organic residue analysis to investigate ancient pottery function, the research has highlighted potential improvements to the lipid analysis method. The following methods are proposed to help improve the detection and identification of food sources in pottery.

2.2.1. Issue of plants detection in ancient pottery

Plants, either wild or cultivated, hold a significant place in the human diet as a supplier of important nutrients and calories, including essential fatty acids and proteins. Plants also provide several essential vitamins that humans are unable to produce (e.g. vitamin C, B), as well as amino acids vital for humans to synthesise proteins. Moreover, plants are the primary dietary source of carbohydrates and minerals (McKevith, 2004; Cumo, 2015). Therefore, they must have been an important part of the prehistoric diet. This is especially true during the milder climate of the Holocene which significantly increased the access and range of wild plants (Jochim, 2012; Cummings, 2014) and may have been fundamental to the eventual adoption of cereal agriculture. Ceramic containers could have been easily used to cook and/or store plant resources. However, as highlighted in chapter 2, the **detection of edible plants** processed in ancient pottery is **relatively elusive through lipid analysis**.

Besides the **lack of robust biomarkers** for plant-based food products, one of the main reasons for the underrepresentation of plants in archaeological pottery is their **low lipid contribution**. Indeed, the content of lipids in plants is overall ten times lower than in animal fats (Hammann and Cramp, 2018). Therefore, most of the time **plant lipids are imperceptible** with the classical GC-MS methods used in organic residue analysis for studying pottery function.

One way for improving plant lipid detection is to **use new and more sensitive methods** such as GC-Q-ToF-MS (gas chromatography-quadrupole-time-of-flight mass spectrometry) or UPLC-HRMS (high-performance liquid chromatography–atmospheric pressure chemical ionization-mass spectrometry), enabling both the detection of plant biomarkers (e.g. plant sterols, alkylresorcinols) and the elution of the polar fraction of plants even in low quantity (Hammann and Cramp, 2018; Manzano et al., 2019). Although these techniques cannot provide a complete screening of all the compounds present in the extract, they offer much greater sensitivity for specific targets. When combined with archaeological evidence to guide our research, they offer a chance to reveal plant lipid biomarkers in archaeological pottery.

2.2.2. Identification of triacylglycerols (TAGs)

As mentioned in chapter 2, **TAGs** are the **main components produced by plants and animal organisms** (Oudemans, 2007). TAGs distributions can provide insight on the initial substances, for instance to discriminate non-ruminant and ruminant fats as well as dairy fat product sources (Dudd and Evershed, 1998; Dudd et al., 1999; Kimpe et al., 2002; Mukherjee et al., 2008; Regert, 2011). The exploration of TAGs structures can provide valuable information on their natural origins, which including improved **taxonomic resolution** for the identification animals (Mirabaud et al., 2007) and plants (Garnier et al., 2009; Ogrinc et al., 2012; Shevchenko et al., 2017). However, their limited preservation in archaeological contexts, due to rapid hydrolysis (Dudd et al., 1998), is restrictive. The standard set of organic residue analysis methods used in this project (GC-MS methods) do not provide such information. The detection of TAGs in pottery is currently of limited diagnostic value. Nevertheless, alternative methods, relatively easily achievable, can be applied, in order to increase the informative power of TAGs analysis. The use of soft ionization techniques (e.g. Efficiency of Nano-Electrospray Ionization [NanoESI] or Matrix-Assisted Laser Desorption Ionisation [MALDI] in tandem/coupled with Mass spectrometry [MS] or MS/MS are of great benefit. Together, these techniques enable to both **increase the detection threshold of TAGs and provide detailed structural information on individual TAGs**, such as unsaturations and oxidations but also the fatty acid distribution framing the glycerol

core of TAGs (notably thanks to MS/MS) (Mirabaud et al., 2007; Colombini et al., 2012; Oras et al., 2017a).

2.3. Integration of other methods and approaches

There is also much scope for improving our knowledge about pottery function by using other complementary forms of biomolecular (e.g. protein) or microscopic analysis and archaeological experiments, which should be integrated, as far as possible, with the "classic" lipid analysis methodology.

2.3.1. Microscopic analysis of charred residues associated with pottery

Although organic residues found in archaeological context refers to **amorphous** organic remains, (literally meaning that they cannot be identified by simple visual observation [See Chapter 2.1]), the **anatomical study of micro fragments of intact organic tissue** preserved in charred food fragments can provide valuable information. This type of analysis requires the use of **microscopic methods** such as scanning electron microscopy (SEM). Among others, this technique has shown positive results for the **detection of plant remains** in foodcrusts, even allowing **identification at the species level** (Hansson and Isaksson, 1994; Oudemans and Kubiak-Martens, 2013; Raemaekers et al., 2013; Kubiak-Martens et al., 2015; González Carretero et al., 2017). For this reason, it is of great interest for studying the processing of plants in pottery. Whilst SEM analysis is currently mainly used to reveal and identify plant remains, it also enables to detect the processing of other kinds of commodities such as fish products, by the detection of fish scales or bones (Oudemans and Kubiak-Martens, 2013). Similarly, to plant tissues, based on the specific morphological aspect of such remains, species can be determined. This is demonstrated by the examination of foodcrusts from Rakushechny Yar pottery by SEM (See chapter 5, section 4.3). This technique has enabled the confirmation of fish processing in pots, more specifically of sturgeon, and thus confirmed the results of lipid residue analysis. Furthermore, the physical appearance of foodcrusts (e.g. smooth, granulated, shiny) can also inform, or at least give insight, about any **specific processing and cooking practices** (González Carretero et al., 2017). This has also been shown in the case study of Rakushechny Yar, where the glossy appearance of the foodcrusts seems to indicate high-temperature processing, which we interpret as a result of fish oil extraction. These observations, once again, have confirmed lipid analysis results.

Therefore, lipid analysis combined with the microscopic exploration of foodcrusts appears to be an effective complementary approach to investigate the broad range of commodities which may have been originally prepared in ceramic vessels. Although recent studies have started to use this approach

for studying pottery function (Oudemans and Kubiak-Martens, 2013; Raemaekers et al., 2013; Kubiak-Martens et al., 2015), such studies are often conducted in isolation and would benefit from more systematic integration with lipid analysis.

2.3.2. Proteomics

As with lipids, **proteins** are a category of natural substances that constitute an essential component of living organisms. Although this organic substance is less resistant to decay when compared to lipids (Evershed, 1993), when found in archaeological context, proteins can be very informative. In fact, proteins can provide much greater **taxonomic** (i.e. species), and **tissue specific** identification, compared with previous biomolecular approaches (Colonese et al., 2017; Hendy et al., 2018). Whilst investigations on dietary protein preservation and degradation processes in burial environments, as well as on their survival during food processing (especially in the case of prolonged heating) are lacking, the few application cases of proteomics to pottery has already given very promising results (Solazzo et al., 2008; Shevchenko et al., 2017; Hendy et al., 2018). This approach has enabled the taxonomic assignment of different plant products including grass and grain, as well as various animal sources (e.g. aquatic animals, meat and dairy products) prepared or stored in ancient ceramic vessels. Furthermore, recent proteomic analysis (Hendy et al., 2018) undertaken on pottery from the early agricultural site of Çatalhöyük, located in central Anatolia, has demonstrated that food proteins can survive for at least 8,000 years. Therefore, although the application of the method is still in its infancy, proteomics gives us a glimpse of all its potential for the study of archaeological pottery function.

2.3.3. Experimental archaeology

Experimental archaeology offers an alternative approach to **examine the manufacture, the function and the use of archaeological artefacts** through **experimentation**. It relies on controlled experiment and observation to develop or test archaeological hypotheses or theories (Pétrequin, 2008). Regarding the functional study of archaeological pottery through the analysis of organic residues, experimental archaeology provides an approach 1) to assess the mechanisms of interaction between lipids and the ceramic matrix; 2) to gain insight into the behaviour of the organic matter subjected to diverse transformations during the manufacture and/or use of the pottery; 3) but also to better grasp the degradation processes after the abandonment of these artefacts (Drieu, 2017; Admiraal et al., 2020). All this contributes greatly to increasing the interpretative potential that can be made from organic residue analysis of archaeological pottery. This is, therefore, highly beneficial for a better understanding of the use of archaeological pottery, whether for studying culinary or technological

practices as well as pottery manufacturing processes (e.g. pottery surface treatment for making it waterproof). Of course, such experiments can also prove to have certain pitfalls when molecular criteria deriving from them are applied to archaeological materials strictly without understanding the empirical basis, as illustrated in the functional study of wooden pottery in the Great Lakes region of North America. The use of these pots for the treatment of aquatic resources has been greatly underestimated until very recently (Malainey et al., 1999; Skibo et al., 2016; Taché et al., 2019). Moreover, it is impossible to really re-create the full diversity of pottery use, due to such a complex series of micro-processes, cooking, ceramic types (e.g. porosity, clay matrix), vessel shapes, heat sources, re-use, the food product themselves. The range of reactions in the burial environment, specific to each ground, is also difficult to reproduce. All this makes direct comparison with experimental analogues difficult. Nevertheless, when the empirical evidence is rigorously treated, archaeological experiments can clearly help and improve the interpretation that can be made from the organic residue analysis. Clearly, further experiments are essential to complement the more “direct” forms of residue analysis.

Undoubtedly, future research must adopt an interdisciplinary approach, using various complementary analytical techniques and methods to collect as much information as possible from pottery artefacts.

3. Final conclusion

While each case study has its own set of conclusions, the overarching results generated here have overall revealed that pottery was used for processing a wide range of foodstuffs including terrestrial plants and animals, and aquatic products. The initial use of pottery seems to have varied by site and regional context. These results challenge the idea that the widespread adoption of pottery by Holocene Eurasian foragers was driven solely by the need to process aquatic resources. It concludes that the local adoption of pottery by Eurasian hunter-gatherers was more complex and variable than anticipated, opening up many new research questions that will require further investigation. Although this PhD project already forms an important contribution to early hunter-gatherer pottery research, clearly, more work has still to be done to properly understand pottery's role within local hunter-gatherer communities and answer the why early Holocene foragers across Eurasia all started to adopt this technology. Clearly, the motivation appears to have localised and variable, which is something that had hitherto not been properly appreciated. Future work needs to look in more local and contextual details at these processes.

Beyond these more specific conclusions, this research underlines the relevance of organic residue analysis methods combined with in-depth contextualised studies at specific sites for investigating the function of early pottery and better grasps the larger trajectory of hunter-gatherer pottery adoption. This study has also demonstrated that recovery, analysis and interpretation of lipid residues from archaeological pottery assemblages is viable in such environmental contexts. It opens out the possibility of a larger comparative and contextual study/studies of early Holocene pottery use within and between regions of northern Eurasia. Combined with an interdisciplinary approach, using a variety of complementary analytical techniques, essential to increase the scope of information that can be gleaned from organic residue analysis, it outlines an avenue for future research.

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Appendices

Appendix 1: Method and Materials

1. Lipid extraction

Each sherd was firstly mechanically cleaned using a modelling drill to remove few outer millimetres of the surface and then finely crushed. When available, carbonised deposits adhered on the surface, were collected using a sterile scalpel and grounded alike ceramic samples.

1.1. Direct methanolic acid extraction

All the pottery and foodcrusts samples were subjected to the acidified methanol extraction following the established protocol (O. E. Craig et al. 2013; Papakosta et al. 2015) as well as sediments from the site. Powdered samples of ceramic and sediment (*ca.* 1 g) and foodcrusts (*ca.* 10-20 mg) were homogenised with methanol (4 mL and 1 mL, respectively) and sonicated in a water bath for 15 min. Then, concentrated sulfuric acid was added (200 µL and 800 µL, respectively) in the vial and samples were placed in heated block for 4 hours at 70°C. Lipids were subsequently extracted by centrifugation (3000 rpm, 5 min) with *n*-hexane (3 x 2 ml), after which the samples were concentrated under a stream of nitrogen and finally directly analysed by Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS).

1.2. Solvent extraction and trimethylsilyl (TMS) derivatization

A selection of sample was subjected to the solvent extraction based on published methodologies (Charters et al. 1993; Regert et al. 1998; Stern et al. 2000; Michael W. Gregg 2009; Papakosta et al. 2015). Briefly, the powdered samples were weighed (potsherd: 1 g; foodcrusts: 10-20 mg) and mixed with a mixture of dichloromethane-methanol (potsherd: 4 mL; foodcrusts: 2 ml; 2:1 v/v). Samples were ultrasonicated (3 × 15 min) to promote the extraction and next centrifuged (3000 rpm, 10 min) to facilitate the separation of the phases. In order to analyse samples by GC-MS, the total lipid extract (TLE) was derivatized using BSTFA (N, O-bis (trimethylsilyl) trifluorocetamide) (100 µl), during 1 hour at 70 ° C, then evaporated and rediluted in *n*-hexane before to be analysed by GC-MS.

2. Collagen extraction from archaeological bones for isotopic analysis

Bones were extracted using the standard procedure (Longin 1971; T. A. Brown et al. 1988; Richards et al. 1998; Jørkov, Heinemeier, and Lynnerup 2007). Each sample was mechanically cleaned, weighed

out (200-800 mg), immersed in HCl solution (0,6 M) and placed in the fridge, at 4 °C, until the demineralization was completed. Samples were rinsed with ultra-pure water (3 times). A dilute HCl solution (Ph = 3) was added and the tubes were placed in the heat block set at 80 °C for 48h and then cooled when gelatinisation was completed. The samples were firstly filtered using polyethylene Ezee Filters (9 mL, pore size 60–90 µm; Elkay Laboratories Ltd.) to remove the large unwanted particulate matter from the dissolved collagen following by an ultrafiltration using of Amicon filter 30 kDa (Ultra-4 centrifugal filter units; Millipore, Burlington, MA, USA) centrifugal filter to restrict contamination and eliminate molecule larger than 30 KDa. The samples were then frozen at -20C for 48 hours prior to freeze-drying them in a condensing chamber held at -55°C for around 24h. The collagen was then analysed by Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS).

3. Collagen extraction and analysis from archaeological bones for ZooMS

ZooMS was performed similar to that outlined in Buckley et al. (2009). For each specimen, 10-30 mg of bone was sampled and immersed in 0.6 M HCl, then placed in a fridge at 4°C to demineralize. Once demineralized, the samples were rinsed three times with 50mM ammonium bicarbonate (AmBic, pH 8.0). A final 100 µl of AmBic was added and the samples were gelatinized at 65°C for one hour. Following gelatinization, 50 µl of the supernatant was transferred to a new 1.5 ml eppendorf and 0.4 µg of trypsin was added (the remaining 50 µl and residual bone material were stored at -20°C for possible later use). The samples were digested for approximately 18 hours at 37°C, and then acidified to 0.1% TFA to stop the trypsin. Samples were zip tipped using 100 µl C_{18} tips (Millipore) following the manufacturer's recommendations, and collagen peptides eluted in 50 µl of a solution of 50% acetonitrile / 0.1% TFA (v/v). 1 µl of sample was spotted in triplicate on a Bruker ground steel MALDI plate, along with 1 µl of α-Cyano-4-hydroxycinnamic acid matrix and allowed to air dry. Calibration standards were also included. The plate was run on a Bruker ultraflex III MALDI ToF MS in reflector mode with 1000 acquisitions per spot. Spectra were collected over a mass range from *m/z* 800–4000. Resultant spectra were averaged and analyzed using mMass software (www.mmass.org, Strohalm et al. 2008) and compared against a database of published *m/z* markers (Buckley et al. 2009; Buckley et al. 2010, Buckley and Collins 2011 ; Kirby et al. 2013).

4. Instrumentation settings

4.1. Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS analyses were conducted using an Agilent 7890A series chromatography coupled to an Agilent 5975C Inert XL mass selective detector with a quadrupole mass analyser (Agilent technologies, Cheadle, Chershire, UK). Splitless injector was used and held at 300°C. The GC column was directly

introduced in the ion source of the mass spectrometer. The ionisation and fragmentation were accomplished by electron impact (70 eV) and the mass filter was set to scan between m/z 50 and 800. All the samples were screened in scan mode by using a DB-5 (5%-phenyl)-methylpolysiloxane column (30m, 250 µm, 0.25 µm; J&W Scientific, Folsom, CA, USA). The temperature program was set at 50°C for 2 min, followed by a temperature increase at a rate of 10 °C/min, until 325°C where it was held for 15 min. Helium was used as carrier gas at a constant flow 3 mL/min.

All the acid extracts were also analysed on DB23 (50%-Cyanopropyl)- methylpolysiloxane column (60 m, 250 µm, 0.25 µm; J & Scientific, Folsom, CA, USA) in simulation (SIM) mode. The temperature program was 50°C for 2 min, which increased at a rate of 10°C/min until 100°C, came after by an increase to 140 °C at a tate of 4 °C/min, then a raised 0.5°C/min to 160°C and finally by 20°C /min until it reached 250°C where the temperature was kept for 10 min. The rate flow of the carrier gas (helium) was set at 1.5 mL/min. This SIM method enabled to better detect isoprenoid fatty acids (pristanic and phytanic acid and 4,8,12-trimethyltridecanoic acid (TMTD)) and ω-(o-alkylphenyl) alkanoic acids (APAAs) associated with aquatic resources (Cramp and Evershed 2014) by characteristing four specific ion groups (Shoda et al. 2017; Admiraal et al. 2018). Moreover, this method enables to resolve and quantify the two natural phytanic acid diastereomers (Lucquin, Colonese, et al. 2016) giving further argument about its origin.

4.2. Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS)

Instruments and instrument conditions for GC-C-MS followed existing procedures (Oliver E. Craig et al. 2012; Lucquin et al. 2018). The equipment used for measuring stable carbon isotope values of the major compounds is a Delta V Advantage isotope ratio mass spectrometer (Thermo Fisher, Bremen, Germany) linked to a Trace Ultra gas chromatograph (Thermo Fisher) with a GC Isolink II interface to oxidise all the carbon species to CO_2. The instrument was equipped with a DB-5MS ultra-inert fused-silica column (60 m × 0.25 mm × 0.25 µm; J&W Scientific). For each sample one µL was injected in splitless mode. The carrier gas used was ultra-high-purity-grade helium with a flow rate of 2 mL/min. A parallel acquisition of the molecular data was realised by deriving a small part of the flow to an ISQ mass spectrometer (Thermo Fisher). The temperature program was 50°C for 0.5 min, coming after by a temperature rise at a rate of 25°C/min until 175°C, then raised 8°C/min to 325°C where it was held for 20 min.

Eluted products were ionized in the mass spectrometer by electron impact, and ion intensities of m/z 44, 45, and 46 were recorded by automatic calculation of the $^{13}C/^{12}C$ ratio of each peak in the extracts.

The repeatedly measuring of standard reference gas (CO2), for which the isotopic composition is known, allowed the computation carried out with IonOS (Isoprime, Cheadle, UK). The values were reported in per mille (‰) comparative to an international standard, Vienna Pee Dee Belemnite (VPDB).

Standards of *n*-alkanoic acid ester of known isotopic composition (Indiana standard F8-3) were used in order to determine the accuracy and precision of the instrument. The mean ± S.D. values of these were −29.95 ± 0.04‰ and −23.22 ± 0.04‰ (Rakushechny Yar), –30.15 ± 0.04‰ and −23.38 ± 0.05‰ (Gorelyi Les) for the methyl ester of $C_{16:0}$ and and $C_{18:0}$ respectively. For Zamostje 2 this standard was used to ascertain the accuracy (<0.3‰) and precision (<0.5‰) for each instrument. Reported mean value vs. VPDB -29.90 ± 0.03‰ and -23.24 ± 0.01‰ for the methyl ester of $C_{16:0}$ and $C_{18:0}$ respectively. All the samples were analysed in duplicate and the standard deviation (S.D.) computed (mean of S.D. for Rakushechny Yar: 0.06‰ and 0.08‰, Zamostje 2: 0.2‰ and 0.2‰; Gorelyi Les: 0.11‰ and 0.08‰ for $C_{16:0}$ and $C_{18:0}$ respectively). For each batch, a standard mixture of $C_{16:0}$ and $C_{18:1}$ fatty acids of known isotopic composition were measured under identical conditions in order to correct the sample values taking account for the methylation of the carboxyl group, which occurred during the methanolic acid extraction (O. E. Craig et al. 2013a; Lucquin, Gibbs, et al. 2016). The $\delta^{13}C$ values of the modern samples were adjusted for the addition of the effects of post-industrial carbon for comparison with the archaeological samples from the Holocene period (Schmitt et al. 2012; Hellevang and Aagaard 2015; Lucquin, Gibbs, et al. 2016).

4.3. Bulk isotope analysis - Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS)

Charred residues, finely crushed, and archaeological animal collagen were weighed in duplicate (between 0.9-1.1 mg) into tin capsules and then subjected to Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS). The bulk stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotope value were measured using protocols reported elsewhere (O. E. Craig et al. 2007; Lucquin, Gibbs, et al. 2016; Shoda et al. 2017). Instrument precision on the repeated measurements was ±0.2‰ (s.e.m.), $\delta^{13}C$, $\delta^{15}N$ = $[(R_{sample}/R_{standard}-1)]$ 1,000, where R = $^{13}C/^{12}C$ and $^{15}N/^{14}N$. The measurements of international standard reference materials (IAEA 600, IAEA N2, IA Cane) was performed in each run in order to determine the accuracy. Values are given in per mill (‰) relative to the standards, Vienna Pee Dee Belemnite for $\delta^{13}C$ and air N_2 for $\delta^{15}N$, respectively. All the sample which yielded less than 1% of Nitrogen were omitted (Lucquin, Gibbs, et al. 2016; Shoda et al. 2017; Lucquin et al. 2018).

5. Radiocarbon dating for Rakushechny Yar site

Twenty AMS ^{14}C dates on single mammal bone fragments, obtained in the course of a larger ongoing dating programme funded by the INDUCE project, are listed in Table A (below). Thirteen of these results (from samples dated at the Leibniz-Labor, Christian-Albrechts University, Kiel, laboratory code KIA-) were published by Dolbunova, et al. (2019) before the bones were identified by ZooMS at BioArCh, University of York, following methods described in the main text. In some cases, the ZooMS identification given here supersedes the original morphometric identification.

Seven more dates relevant to the chronology of the pottery assemblage analysed for this paper are published here for the first time. These samples were dated at the Scottish Universities Environmental Research Centre, East Kilbride (SUERC-) or the Isotope Climatology and Environmental Research Centre, Hungarian, Debrecen (DeA-). Both laboratories apply published methods (Dunbar, et al., 2016, Major, et al., 2019a, Major, et al., 2019b, Molnár, et al., 2013) for collagen extraction, combustion, graphitisation and AMS measurement, whose efficacy is confirmed by long-term reproducibility of results on internal and international bone standards. Samples yielding <1% collagen by weight are rejected, as are collagen extracts with atomic C/N ratios outside the range 2.9—3.5. Conventional ^{14}C ages were converted to calendar dates using OxCal v.4 (Bronk Ramsey, 2009) and the IntCal13 calibration data (Reimer, et al., 2013).

The new results suggest that the earliest pottery excavated in 2016-18 is no earlier than c.5600 cal BC (Figure A, below). Although many bones from the upper Early Neolithic layers contained no collagen and could not be dated, the few results from the stratigraphically latest early Neolithic layers – "trench" layers 5 and 6 – suggest that the Early Neolithic phase was brief. Two much more recent samples from the uppermost layers (SUERC-86126; SUERC-88042) must be later intrusions or indicate that the Early Neolithic deposits were truncated. Thus, Early Neolithic pottery from the recent excavations may all date to a narrow range in the mid-6th millennium (Figure A).

Legacy ^{14}C dates (Tsybryi, et al., 2017, figure 3 and table 1) on samples from Early Neolithic layers appear to span a much wider range (c.7000-5000 cal BC; Figure A). Most of these results are probably misleading, however, due to freshwater reservoir effects. Although the dated food-crusts have not been analysed directly, it may be assumed that they contained a similar range of ingredients to those analysed for this paper, in which aquatic ingredients feature prominently. The ^{14}C ages of all 10 carbonised food-crusts on sherds from Belanovskaya's layers 15 to 20 fall between those of bulk fish-bones (SPb-1185, 8020±120 BP) and unidentified mammal bones (DeA-20972, 6462±33 BP; SPb-731,

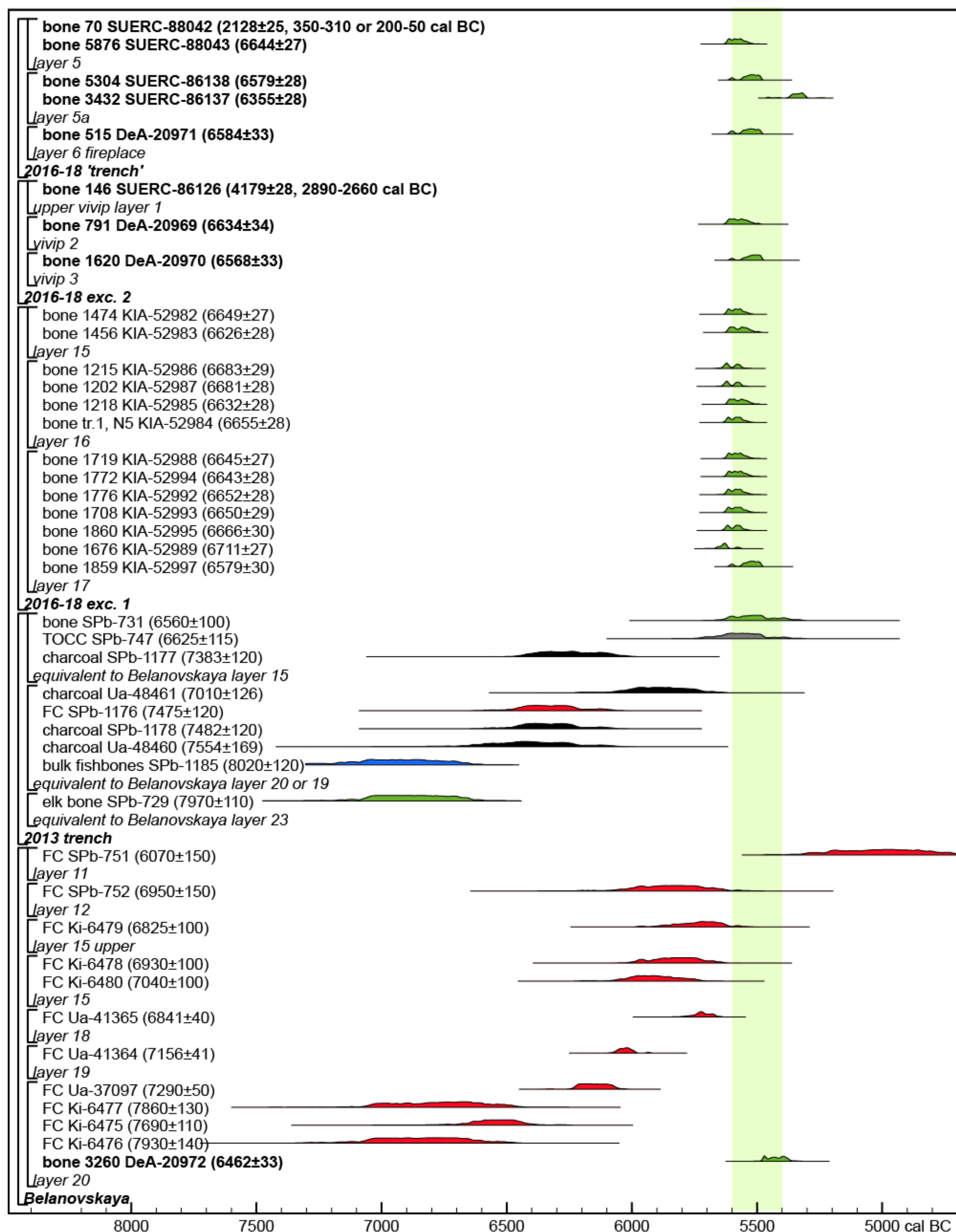
6560±100 BP) attributed to the same layers. One of the legacy food-crust ^{14}C ages (SPb-751, 6050±100 BP, from layer 11) is apparently later than the mammal bones from deeper layers, which may imply that the Early Neolithic phase at Rakushechny Yar lasted rather longer than indicated by the dates from the new excavations. Thus, the sherds from the Belanovskaya excavations analysed for this paper from layers 11—13 may date to the second half of the 6th millennium. Sherds from Belanovskaya layers 14—16, 19—21 and 23 can be dated to the middle of the 6th millennium.

Legacy ^{14}C dates on bulk charcoal and an elk bone from layer 15 and below appear to be much earlier than the oldest dates from the recent excavations (Figure A). Inconsistencies between the charcoal dates from layers 19-20, and between charcoal and animal bone dates in layer 15, suggest that much of the charcoal sampled may have been redeposited (or had a high intrinsic age), a suggestion reinforced by the new AMS date on a bone from layer 20 (DeA-20972, 6462±33 BP, 5490—5360 cal BC). The layer 23 elk bone (SPb-729, 7970±110 BP, 7180—6590 cal BC) is so much earlier than any other dated bone that its association with pottery use is questionable, particularly as there are mid-late 7th millennium ^{14}C dates at the aceramic site Razdorskaya II, on the opposite bank of the Don (Tsybryi, et al., 2017). Thus, the entire Early Neolithic assemblage appears to date to the mid-later 6th millennium cal BC. Legacy ^{14}C dates from the Late Neolithic and Eneolithic levels (Tsybryi, et al., 2017) are difficult to interpret, but may place these phases in the 5th millennium.

Table A. AMS ^{14}C dates on single mammal bone fragments, Rakushechny Yar. Results of samples dated in Glasgow (SUERC-) and Debrecen (DeA-) are previously unpublished; only morphometric identifications are available. ZooMS identifications (*) of samples dated in Kiel (KIA-) supersede morphometric identifications of these samples (Dolbunova, et al., 2019).

Bone ID	Localisation	Identification	Laboratory code	^{14}C age (BP)
70	2013 trench layer 5 upper	large mammal longbone midshaft	SUERC-88042	2128±25
5876	2018 trench layer 5	horse tooth	SUERC-88043	6644±27
5151	2018 trench layer 6 fireplace	bone, not determined	DeA-20971	6584±33
146	2016 exc.2 upper vivip layer 1	deer incisor	SUERC-86126	4179±28
791	2016 exc.2 vivip 2	large mammal longbone midshaft	DeA-20969	6634±34
1620	2016 exc.2 vivip 3	medium mammal longbone midshaft	DeA-20970	6568±33
326	1966 layer 20 square M8	bone, not determined	DeA-20972	6462±33
1525	2016 exc.1 layer 15a upper part, square A7	*red deer phalanx 1	KIA-52981	6590±28
1474	2016 exc.1 layer 15a lower part	*red deer radius	KIA-52982	6649±27
1456	2016 exc.1 layer 15a lower part	*red deer flat bone	KIA-52983	6626±28
N5	2016 exc.1 layer 16 Unio shell #1	*red deer long bone	KIA-52984	6655±28
1218	2016 exc.1 layer 16 Unio shell #1	*red deer long bone	KIA-52985	6632±28
1215	2016 exc.1 layer 16 Unio shell #1	*red deer rib	KIA-52986	6683±29
1202	2016 exc.1 layer 16 Unio shell #1	*pig scapula	KIA-52987	6681±28
1719	2016 exc.1 layer 17 lower part	*red deer rib	KIA-52988	6645±27
1676	2016 exc.1 layer 17 lower part	*red deer rib	KIA-52989	6711±27
1776	2016 exc.1 layer 17 Unio 6	*red deer splinter	KIA-52992	6652±28
1708	2016 exc.1 layer 17 Unio 6	*red deer pelvis	KIA-52993	6650±29
1772	2016 exc.1 layer 17 Unio 6	*red deer splinter	KIA-52994	6643±28
1860	2016 exc.1 layer 17 Unio shell #2	*pig long bone	KIA-52995	6666±30

Figure A. Calibrated radiocarbon results on Early Neolithic samples from Rakushechny Yar. Previously unpublished dates are labelled with bold text. The green band corresponds to 5600-5400 cal BC, a range which would accommodate all new dates on mammal bones (green) (Table A). Legacy ^{14}C dates from adjacent trenches (Tsybryi, et al., 2017) for charred food crust (red) and total organic carbon content (grey) of pottery, and fish bone (blue) have been calibrated without accounting for potential freshwater reservoir effects. Bulk charcoal samples (black) may incorporate wood-age offsets and residual (redeposited) fragments. Within each excavation area, samples are grouped stratigraphically (earlier, deeper layers below later layers).



Appendix 2: Stable carbon isotopic of *n*-hexadecanoic ($C_{16:0}$) and *n*-octadecanoic ($C_{18:0}$) acid found in the literature of reference fats from modern products and used to make the figure 2.22.

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Plant					
Olive	Slovenia	-32.95	-31.85	1.1	Spangenberg and Ogrinc 2001
Olive	Slovenia	-29.82	-29.72	0.1	Spangenberg and Ogrinc 2001
Olive	Slovenia	-30.62	-30.72	-0.1	Spangenberg and Ogrinc 2001
Olive	Slovenia	-31.32	-30.72	0.6	Spangenberg and Ogrinc 2001
Olive	Slovenia	-30.92	-31.32	-0.4	Spangenberg and Ogrinc 2001
Olive	Croatia	-31.42	-30.92	0.5	Spangenberg and Ogrinc 2001
Olive	Croatia	-30.32	-30.52	-0.2	Spangenberg and Ogrinc 2001
Olive	Croatia	-29.02	-29.92	-0.9	Spangenberg and Ogrinc 2001
Olive	Croatia	-31.92	-31.22	0.7	Spangenberg and Ogrinc 2001
Olive	Croatia	-30.92	-29.62	1.3	Spangenberg and Ogrinc 2001
Japanese stone oak	Japan	-37.97	-36.07	1.9	Horiuchi et al. 2015
Sunflower	Slovenia	-31.92	-31.12	0.8	Spangenberg and Ogrinc 2001
Sunflower	Slovenia	-30.72	-29.52	1.2	Spangenberg and Ogrinc 2001
Soybean	-	-32.32	-32.42	-0.1	Spangenberg and Ogrinc 2001
Sesame	-	-28.02	-27.82	0.2	Spangenberg and Ogrinc 2001
acorn	Japan	-35.08	-35.95	-0.87	Lucquin et al 2016
acorn	Japan	-33.12	-34.63	-1.51	Lucquin et al 2016
acorn	Japan	-34.01	-34.45	-0.44	Lucquin et al 2016
acorn	Japan	-32.12	-34.02	-1.9	Lucquin et al 2016
White oak	Japan	-35.07	-33.77	1.3	Horiuchi et al. 2015
acorn	Japan	-32.69	-33.64	-0.95	Lucquin et al 2016
Chestnut	Japan	-35.47	-33.07	2.4	Horiuchi et al. 2015
Walnut	Japan	-31.87	-31.77	0.1	Horiuchi et al. 2015
Pumpkin	Slovenia	-29.62	-31.12	-1.5	Spangenberg and Ogrinc 2001
Anadromous					
Salmon	Japan	-27.32	-28.03	-0.71	Craig et al. 2013
Salmon	Japan	-24.48	-26.05	-1.57	Craig et al. 2013
Salmon	Japan	-25.27	-26.59	-1.32	Craig et al. 2013
Trout	Japan	-25.95	-25.93	0.02	Craig et al. 2013

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Trout	Japan	-26.8	-27.04	-0.24	Craig et al. 2013
Trout	Japan	-25.09	-25.5	-0.41	Craig et al. 2013
Trout	Japan	-24.08	-22.37	1.71	Lucquin et al 2016
Salmon	Japan	-25.78	-24.34	1.44	Lucquin et al 2016
Trout	Japan	-23.32	-23.7	-0.38	Lucquin et al 2016
Salmon	Japan	-27.86	-28.37	-0.51	Lucquin et al 2016
Salmon	Japan	-24.82	-23.81	1.01	Lucquin et al 2016
Salmon	Japan	-23.68	-22.6	1.08	Lucquin et al 2016
Salmon	Japan	-25.83	-24.82	1.01	Lucquin et al 2016
Marine salmon	United kingdom	-24.55	-24.5	0.05	Lucquin et al 2016
Marine salmon	United kingdom	-24.35	-24.23	0.12	Lucquin et al 2016
salmon	Finland	-24.97	-23.57	1.4	Pääkkönen et al. 2016
salmon	Finland	-24.27	-23.87	0.4	Pääkkönen et al. 2016
Coho salmon	Alaska	-28.2	-26.6	1.6	Choy et al 2016
Coho salmon	Alaska	-27.8	-26	1.8	Choy et al 2016
Coho salmon	Alaska	-27.2	-25	2.2	Choy et al 2016
Chum salmon	Alaska	-26.2	-25.4	0.8	Choy et al 2016
Chum salmon	Alaska	-26.2	-24.8	1.4	Choy et al 2016
Chum salmon	Alaska	-25.1	-23.5	1.6	Choy et al 2016
Freshwater					
Pike	Denmark	-34.96	-35.16	-0.2	Craig et al. 2011
Tench	Denmark	-27.86	-28.96	-1.1	Craig et al. 2011
Tench	Denmark	-24.36	-26.46	-2.1	Craig et al. 2011
Tench	Denmark	-37.36	-36.66	0.7	Craig et al. 2011
Amur minnow	Japan	-26.69	-27.39	-0.7	Craig et al. 2013
Topmouth gudgeon	Japan	-26.21	-25.9	0.31	Craig et al. 2013
Perch	United kingdom	-35.71	-35.08	0.63	Cramp et al. 2014
Perch	United kingdom	-35.23	-35.8	-0.57	Cramp et al. 2014
Perch	United kingdom	-34.76	-34.85	-0.09	Cramp et al. 2014
Perch	United kingdom	-34.5	-35.51	-1.01	Cramp et al. 2014
Perch	United kingdom	-34.5	-35.47	-0.97	Cramp et al. 2014
Perch	United kingdom	-34.35	-35.62	-1.27	Cramp et al. 2014
Perch	United kingdom	-34.04	-33.69	0.35	Cramp et al. 2014
Perch	United kingdom	-33.56	-33.64	-0.08	Cramp et al. 2014

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Perch	United kingdom	-33.35	-33.22	0.13	Cramp et al. 2014
Perch	United kingdom	-32.93	-33.86	-0.93	Cramp et al. 2014
Perch	United kingdom	-32.57	-34.05	-1.48	Cramp et al. 2014
Perch	United kingdom	-32.21	-32.81	-0.6	Cramp et al. 2014
Roach	United kingdom	-34.14	-34.25	-0.11	Cramp et al. 2014
Roach	United kingdom	-33.56	-34.77	-1.21	Cramp et al. 2014
Roach	United kingdom	-32.84	-33.91	-1.07	Cramp et al. 2014
Roach	United kingdom	-32.67	-33.66	-0.99	Cramp et al. 2014
Roach	United kingdom	-32.82	-33.29	-0.47	Cramp et al. 2014
Roach	United kingdom	-32.23	-32.49	-0.26	Cramp et al. 2014
freshwater fish	Kazakhstan	-32.15	-32.19	-0.04	Outram et al. 2009
freshwater fish	Kazakhstan	-32.15	-31.49	0.66	Outram et al. 2009
freshwater fish	Kazakhstan	-31.75	-31.87	-0.12	Outram et al. 2009
freshwater fish	Kazakhstan	-31.66	-31.4	0.26	Outram et al. 2009
freshwater fish	Kazakhstan	-31.53	-31.38	0.15	Outram et al. 2009
freshwater fish	Kazakhstan	-31.62	-29.89	1.73	Outram et al. 2009
freshwater fish	Kazakhstan	-31.1	-30.86	0.24	Outram et al. 2009
freshwater fish	Kazakhstan	-30.92	-30.39	0.53	Outram et al. 2009
freshwater fish	Kazakhstan	-30.71	-30.22	0.49	Outram et al. 2009
freshwater fish	Kazakhstan	-30.61	-30.6	0.01	Outram et al. 2009
Carp	United kingdom	-30.16	-28.16	2	Lucquin et al 2016
Pike	United kingdom	-28.16	-25.76	2.4	Lucquin et al 2016
Perch	United kingdom	-30.96	-28.36	2.6	Lucquin et al 2016
Bleak	Finland	-26.62	-25.92	0.7	Pääkkönen et al. 2016
Bleak	Finland	-33.85	-32.35	1.5	Pääkkönen et al. 2016
Bleak	Finland	-34.15	-34.55	-0.4	Pääkkönen et al. 2016
Bleak	Finland	-35.65	-35.15	0.5	Pääkkönen et al. 2016
Bleak	Finland	-36.05	-34.55	1.5	Pääkkönen et al. 2016
Burbot	Finland	-34.35	-32.35	2	Pääkkönen et al. 2016
Ide	Finland	-33.45	-31.85	1.6	Pääkkönen et al. 2016
Ide	Finland	-32.85	-31.25	1.6	Pääkkönen et al. 2016
Northern pike	Finland	-33.25	-32.95	0.3	Pääkkönen et al. 2016
Northern pike	Finland	-33.45	-32.25	1.2	Pääkkönen et al. 2016
Northern pike	Finland	-31.75	-31.35	0.4	Pääkkönen et al. 2016

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Perch	Finland	-34.35	-33.25	1.1	Pääkkönen et al. 2016
Perch	Finland	-35.15	-34.65	0.5	Pääkkönen et al. 2016
Perch	Finland	-33.35	-32.55	0.8	Pääkkönen et al. 2016
Perch	Finland	-34.95	-33.35	1.6	Pääkkönen et al. 2016
Perch	Finland	-32.95	-32.35	0.6	Pääkkönen et al. 2016
Perch	Finland	-32.05	-32.35	-0.3	Pääkkönen et al. 2016
Perch	Finland	-32.05	-32.65	-0.6	Pääkkönen et al. 2016
Perch	Finland	-35.35	-36.85	-1.5	Pääkkönen et al. 2016
Perch	Finland	-35.25	-34.75	0.5	Pääkkönen et al. 2016
Pikeperch	Finland	-34.55	-33.75	0.8	Pääkkönen et al. 2016
Pikeperch	Finland	-30.25	-29.95	0.3	Pääkkönen et al. 2016
Roach	Finland	-29.45	-31.95	-2.5	Pääkkönen et al. 2016
Roach	Finland	-34.05	-32.95	1.1	Pääkkönen et al. 2016
Vendace	Finland	-27.95	-29.55	-1.6	Pääkkönen et al. 2016
Vendace	Finland	-29.15	-27.85	1.3	Pääkkönen et al. 2016
Vendace	Finland	-36.85	-37.85	-1	Pääkkönen et al. 2016
Vendace	Finland	-28.25	-26.85	1.4	Pääkkönen et al. 2016
Arctic grayling	Alaska	-40.9	-39	1.9	Choy et al 2016
Burbot	Alaska	-26.9	-28.2	-1.3	Choy et al 2016
Burbot	Alaska	-29.8	-28.8	1	Choy et al 2016
Northern pike	Alaska	-32.9	-30.7	2.2	Choy et al 2016
Northern pike	Alaska	-35.8	-35.6	0.2	Choy et al 2016
Northern pike	Alaska	-36	-35	1	Choy et al 2016
Sheefish	Alaska	-34	-34.4	-0.4	Choy et al 2016
Bering cisco	Alaska	-34.6	-34.3	0.3	Choy et al 2016
Marine					
Atlantic cod	Denmark	-22.95	-22.45	0.5	Craig et al. 2011
Atlantic cod	Denmark	-22.95	-24.35	-1.4	Craig et al. 2011
Atlantic cod	Denmark	-22.25	-24.75	-2.5	Craig et al. 2011
Spotted seal	Denmark	-20.25	-20.25	0	Craig et al. 2011
Spotted seal	Denmark	-13.05	-14.55	-1.5	Craig et al. 2011
Harbour seal	Germany	-18.85	-20.45	-1.6	Craig et al. 2011
European flounder	Denmark	-18.75	-20.05	-1.3	Craig et al. 2011
Plaice	Denmark	-20.05	-21.75	-1.7	Craig et al. 2011

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Plaice	Denmark	-19.15	-20.35	-1.2	Craig et al. 2011
Eelpout	Denmark	-19.65	-21.25	-1.6	Craig et al. 2011
Eelpout	Denmark	-17.15	-18.15	-1	Craig et al. 2011
Sea bream	Japan	-22.44	-22.11	0.33	Craig et al. 2013
Sea bream	Japan	-22.7	-22.53	0.17	Craig et al. 2013
Rockfish	Japan	-23.72	-23.1	0.62	Craig et al. 2013
Flathead mullet	Japan	-21.94	-21.31	0.63	Craig et al. 2013
Croaker	Japan	-21.79	-21.43	0.36	Craig et al. 2013
Atlantic herring	United kingdom	-27.5	-27.24	0.26	Cramp et al. 2014
Atlantic herring	United kingdom	-26.96	-25.71	1.25	Cramp et al. 2014
Atlantic herring	United kingdom	-26.92	-25.25	1.67	Cramp et al. 2014
Atlantic herring	United kingdom	-26.39	-26.02	0.37	Cramp et al. 2014
Bivalves	United kingdom	-25.62	-27.04	-1.42	Cramp et al. 2014
Bivalves	United kingdom	-24.83	-24.68	0.15	Cramp et al. 2014
Bivalves	United kingdom	-24.39	-23.93	0.46	Cramp et al. 2014
Bivalves	United kingdom	-23.93	-23.46	0.47	Cramp et al. 2014
Bivalves	United kingdom	-25.11	-23.67	1.44	Cramp et al. 2014
Bivalves	United kingdom	-25.23	-23.5	1.73	Cramp et al. 2014
Bivalves	United kingdom	-25.66	-23.71	1.95	Cramp et al. 2014
Bivalves	United kingdom	-25.49	-23.33	2.16	Cramp et al. 2014
Bivalves	United kingdom	-25.24	-23.14	2.1	Cramp et al. 2014
Bivalves	United kingdom	-25.02	-22.77	2.25	Cramp et al. 2014
Bivalves	United kingdom	-26.19	-23.08	3.11	Cramp et al. 2014
Bivalves	United kingdom	-25.02	-21.86	3.16	Cramp et al. 2014
Marine mammal	United kingdom	-23.98	-23.47	0.51	Cramp et al. 2014
Marine mammal	United kingdom	-25.45	-24.2	1.25	Cramp et al. 2014
Marine mammal	United kingdom	-25.54	-25.67	-0.13	Cramp et al. 2014
Marine fish	United kingdom	-25.41	-24.54	0.87	Cramp et al. 2014
Marine fish	United kingdom	-25.35	-24.66	0.69	Cramp et al. 2014
Marine fish	United kingdom	-24.29	-24.12	0.17	Cramp et al. 2014
Marine fish	United kingdom	-24.19	-23.43	0.76	Cramp et al. 2014
Marine fish	United kingdom	-24.22	-23.25	0.97	Cramp et al. 2014
Marine fish	United kingdom	-24.08	-23.21	0.87	Cramp et al. 2014
Marine fish	United kingdom	-23.79	-23.12	0.67	Cramp et al. 2014

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Marine fish	United kingdom	-23.93	-22.96	0.97	Cramp et al. 2014
Marine fish	United kingdom	-23.86	-22.8	1.06	Cramp et al. 2014
Marine fish	United kingdom	-23.86	-22.68	1.18	Cramp et al. 2014
Marine fish	United kingdom	-24.29	-22.75	1.54	Cramp et al. 2014
Marine fish	United kingdom	-24	-21.95	2.05	Cramp et al. 2014
Marine fish	United kingdom	-23.04	-22.21	0.83	Cramp et al. 2014
Marine fish	United kingdom	-23.08	-22.16	0.92	Cramp et al. 2014
Marine fish	United kingdom	-22.72	-22.94	-0.22	Cramp et al. 2014
Marine fish	United kingdom	-22.75	-22.94	-0.19	Cramp et al. 2014
Marine fish	United kingdom	-22.88	-23	-0.12	Cramp et al. 2014
Marine fish	United kingdom	-22.83	-21.32	1.51	Cramp et al. 2014
Marine fish	United kingdom	-21.63	-21.89	-0.26	Cramp et al. 2014
Gastropods	United kingdom	-22.43	-22.93	-0.5	Cramp et al. 2014
Gastropods	United kingdom	-22.46	-21.86	0.6	Cramp et al. 2014
Gastropods	United kingdom	-23.1	-20.6	2.5	Cramp et al. 2014
Gastropods	United kingdom	-21.71	-21.5	0.21	Cramp et al. 2014
Gastropods	United kingdom	-21.99	-21.33	0.66	Cramp et al. 2014
Gastropods	United kingdom	-21.88	-21.23	0.65	Cramp et al. 2014
Gastropods	United kingdom	-21.97	-20.88	1.09	Cramp et al. 2014
Gastropods	United kingdom	-20.23	-20.67	-0.44	Cramp et al. 2014
Gastropods	United kingdom	-20.94	-19.65	1.29	Cramp et al. 2014
Gastropods	United kingdom	-21.85	-19.19	2.66	Cramp et al. 2014
Gastropods	United kingdom	-21.77	-19.18	2.59	Cramp et al. 2014
Gastropods	United kingdom	-21.2	-18.97	2.23	Cramp et al. 2014
Gastropods	United kingdom	-20.73	-19.06	1.67	Cramp et al. 2014
Gastropods	United kingdom	-20.67	-19.18	1.49	Cramp et al. 2014
Gastropods	United kingdom	-20.67	-18.17	2.5	Cramp et al. 2014
Gastropods	United kingdom	-18.98	-17.85	1.13	Cramp et al. 2014
Gastropods	United kingdom	-18.77	-17.75	1.02	Cramp et al. 2014
Gastropods	United kingdom	-18.39	-17.36	1.03	Cramp et al. 2014
Crustaceans	United kingdom	-23.79	-23.3	0.49	Cramp et al. 2014
Crustaceans	United kingdom	-23.32	-22.24	1.08	Cramp et al. 2014
Crustaceans	United kingdom	-22.68	-21.77	0.91	Cramp et al. 2014
Crustaceans	United kingdom	-21.32	-22.19	-0.87	Cramp et al. 2014

Crustaceans	United kingdom	-21.25	-20.62	0.63	Cramp et al. 2014
Crustaceans	United kingdom	-21.25	-20.55	0.7	Cramp et al. 2014
Crustaceans	United kingdom	-20.16	-18.39	1.77	Cramp et al. 2014
Crustaceans	United kingdom	-17.47	-15.97	1.5	Cramp et al. 2014
Crustaceans	United kingdom	-16.49	-15.97	0.52	Cramp et al. 2014
Atlantic cod	United kingdom	-25.42	-26.72	-1.3	Dudd 1999
Haddock	United kingdom	-26.72	-24.42	2.3	Dudd 1999
Plaice	United kingdom	-24.62	-24.02	0.6	Dudd 1999
Atlantic cod	United kingdom	-24.83	-24.43	0.4	Lucquin et al 2016
Oyster	United kingdom	-24.33	-24.93	-0.6	Lucquin et al 2016
European flounder	Denmark	-19.15	-20.35	-1.2	Lucquin et al 2016
Atlantic mackerel	United kingdom	-25.43	-25.63	-0.2	Lucquin et al 2016
Short fin pilot whale	Japan	-22.91	-23.29	-0.38	Lucquin et al 2016
Seashell (Babylonia)	Japan	-23.56	-23.09	0.47	Lucquin et al 2016
Seashell (Ruditapes)	Japan	-25.03	-23.99	1.04	Lucquin et al 2016
Pilot Whale	Japan	-23.57	-23.82	-0.25	Lucquin et al 2016
Saltwater clam	Japan	-25.57	-24.07	1.5	Horiuchi et al. 2015
Horned turban	Japan	-23.27	-21.57	1.7	Horiuchi et al. 2015
Squid	Japan	-24.77	-24.17	0.6	Horiuchi et al. 2015
Finless porpoise	Japan	-19.77	-20.37	-0.6	Horiuchi et al. 2015
Whale	Japan	-25.27	-23.37	1.9	Horiuchi et al. 2015
Sea lion	Japan	-24.87	-21.97	2.9	Horiuchi et al. 2015
Jack mackerel	Japan	-24.27	-23.97	0.3	Horiuchi et al. 2015
Jack mackerel	Japan	-24.37	-25.67	-1.3	Horiuchi et al. 2015
Jack mackerel	Japan	-24.07	-22.97	1.1	Horiuchi et al. 2015
Yellow tail	Japan	-24.97	-24.17	0.8	Horiuchi et al. 2015
Yellow tail	Japan	-25.27	-25.97	-0.7	Horiuchi et al. 2015
Yellow tail	Japan	-24.97	-23.27	1.7	Horiuchi et al. 2015
Yellow tail	Japan	-25.07	-24.07	1	Horiuchi et al. 2015
Grey seal	Finland	-24.39	-24.29	0.1	Pääkkönen et al. 2016
Grey seal	Finland	-25.89	-26.09	-0.2	Pääkkönen et al. 2016
Grey seal	Finland	-23.57	-23.87	-0.3	Pääkkönen et al. 2016
Grey seal	Finland	-23.89	-24.09	-0.2	Pääkkönen et al. 2016
Grey seal	Finland	-23.66	-24.26	-0.6	Pääkkönen et al. 2016

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Domestic equine adipose					
Horse	United kingdom	-29.69	-29.39	0.3	Dudd 1999
Horse	United kingdom	-30.59	-30.09	0.5	Dudd 1999
Horse	United kingdom	-30.49	-29.59	0.9	Dudd 1999
Horse	United kingdom	-29.99	-29.19	0.8	Dudd 1999
Horse	United kingdom	-30.29	-29.89	0.4	Dudd 1999
Horse	United kingdom	-29.49	-29.59	-0.1	Dudd 1999
Horse	United kingdom	-29.59	-27.49	2.1	Dudd 1999
Horse	United kingdom	-29.89	-29.69	0.2	Dudd 1999
Pig	United kingdom	-24.79	-23.99	0.8	Dudd 1999
Pig	United kingdom	-26.39	-24.79	1.6	Dudd 1999
Pig	United kingdom	-26.49	-24.79	1.7	Dudd 1999
Pig	United kingdom	-25.49	-24.39	1.1	Dudd 1999
Pig	United kingdom	-25.99	-24.89	1.1	Dudd 1999
Pig	United kingdom	-25.09	-23.79	1.3	Dudd 1999
Pig	United kingdom	-25.69	-24.39	1.3	Dudd 1999
Pig	United kingdom	-25.39	-24.09	1.3	Dudd 1999
Pig	United kingdom	-24.39	-25.29	-0.9	Dudd 1999
Domestic ruminant adipose					
Sheep	United kingdom	-29.39	-31.19	-1.8	Dudd 1999
Sheep	United kingdom	-28.39	-30.09	-1.7	Dudd 1999
Sheep	United kingdom	-28.69	-30.39	-1.7	Dudd 1999
Sheep	United kingdom	-29.19	-31.09	-1.9	Dudd 1999
Sheep	United kingdom	-29.29	-31.09	-1.8	Dudd 1999
Sheep	United kingdom	-28.39	-31.29	-2.9	Dudd 1999
Sheep	United kingdom	-28.79	-30.09	-1.3	Dudd 1999
Sheep	United kingdom	-28.19	-29.99	-1.8	Dudd 1999
Sheep	United kingdom	-30.39	-32.19	-1.8	Dudd 1999
Sheep	United kingdom	-30.19	-32.29	-2.1	Dudd 1999
Sheep	United kingdom	-30.49	-32.49	-2	Dudd 1999
Sheep	United kingdom	-29.39	-31.79	-2.4	Dudd 1999
Sheep	United kingdom	-28.99	-30.39	-1.4	Dudd 1999
Cow	United kingdom	-28.89	-31.79	-2.9	Dudd 1999
Cow	United kingdom	-29.79	-32.29	-2.5	Dudd 1999

Species	Provenance	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C^{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	references
Cow	United kingdom	-28.69	-31.49	-2.8	Dudd 1999
Cow	United kingdom	-29.89	-31.59	-1.7	Dudd 1999
Domestic ruminant milk					
Cow	United kingdom	-30.79	-34.39	-3.6	Dudd 1999
Cow	United kingdom	-27.79	-32.09	-4.3	Dudd 1999
Sheep	United kingdom	-29.39	-33.79	-4.4	Dudd 1999
Sheep	United kingdom	-28.99	-33.39	-4.4	Dudd 1999
Cow	United kingdom	-27.39	-32.19	-4.8	Dudd 1999
Cow	United kingdom	-28.89	-33.69	-4.8	Dudd 1999
Cow	United kingdom	-29.59	-34.89	-5.3	Dudd 1999
Cow	United kingdom	-27.89	-33.09	-5.2	Dudd 1999
Cow	United kingdom	-28.59	-34.09	-5.5	Dudd 1999

The carbon isotope values given in this table have been adjusted for the addition of post-depositional carbon required to compare them with archaelogical samples (Schmitt et al. 2012; Hellevang and Aagaard 2015; Lucquin et al. 2016).

Appendix 3: Radiocarbon dates for Gorelyi Les layers (Weber, 1995) calibrated with CALIB Rev 7.0.4 (Reimer et al., 2013).

Layer	Period	Date and Lab No.	Dated material	C14 age BP	Calibrated year BP (1σ)	Other notes
IV	Early Bronze Age			*Undated*		
Va	Late Neolithic	GIN-4366	Bone	4880±180	5886-5530	
Vb	Middle/Late Neolithic	Ri-0052	m.d.	5430±120	6317-6009	Heavily compacted into one layer
VI	Early Neolithic	Ri-0050a	m.d.	6695±150	7674-7435	
VI	Early Neolithic	Ri-0050	Charcoal	6995±150	7950-7687	
VII	Late Mesolithic	KRiL-0234	m.d.	8850±300	10,242-9542	
VII	Late Mesolithic	Ri-0051	Charcoal	8440±125	9540-9298	

Appendix 4: List of samples from Gorelyi Les selected for lipid analysis (GCMS, GC-C-IRMS) and bulk isotope characteristics of charred deposits (EA-IRMS).

Laboratory code	Type	Lipid conc. (µg g-1)	Pottery type	Major compound detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
GL 9400557	Foodcrust	458.52	Net-impressed	SFA ($C_{12:0-32:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{8-15, 22, 24-26}$), br, terp1, APAA ($C_{16, 18, 20, 22}$), tmtd, phy, pri	92.7	-25.0	-27.5	-2.5	33.5	-21.4	4.6	10.6	8.6
GL 1 94.00046	Ceramic	38.31	Net-impressed	SFA ($C_{10:0-32:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{9, 22-26}$), Alk (C_{16-30}), Alkone (16-K_{31}, 16-K_{33}), br, terp[2], APAA ($C_{16, 18, 20, 22}$), tmtd (tr), pri (tr)		-27.4	-28.6	-1.2					
GL 94.00049	Ceramic	77.87	n/a	SFA ($C_{6:0-32:0}$), UFA ($C_{14:1, 15:1, 16:1, 18:1, 22:1}$), DC ($C_{6, 9-11, 22-26}$), Alk ($C_{14, 16, 18, 20, 22-31}$), Alkone (14-$K_{29}$, 16-$K_{33}$, 18-$K_{33}$), br, terp[1,2], chol, tmtd (tr), pri (tr)		-26.0	-27.8	-1.8					
GL 94.00111	Ceramic*	134.55	n/a	SFA ($C_{6:0-30:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{6, 7, 9-12}$), Alk (C_{16-29}), Alkone (16-K_{31}), Alkol ($C_{16, 18, 20, 22, 24, 26, 28}$), br, 9-10diHFA ($C_{18}$), 2-HFA ($C_{22, 24}$), terp[2], chol, APAA ($C_{18}$) (tr), tmtd (tr), pri (tr), phy	91.7	-24.1	-26.2	-2.1					
GL 94.00158	Ceramic	176.84	Net-impressed	SFA ($C_{9:0-32:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC ($C_{7-14, 16-18}$), Alk ($C_{29, 31, 33}$), br, terp[1], APAA ($C_{16, 18, 20}$), phy	n/a	-25.5	-27.5	-2.1					
GL 94.00159	Ceramic	166.51	n/a	SFA ($C_{8:0-30:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$), DC ($C_{7, 9-13}$), Alk ($C_{22-24}$), br, APAA ($C1_{6, 18, 20}$), tmtd, pri, phy	91.7	-23.9	-26.4	-2.5					
GL 94.00166	Ceramic	35.94	n/a	SFA ($C_{11:0-28:0}$), UFA ($C_{16:1, 22:1}$), DC ($C_{9, 11}$), Alk (C_{16-27}), br, tmtd, phy	74.8	-29.5	-29.9	-0.4					

Laboratory code	Type	Lipid conc. (µg g-1)	Pottery type	Major compound detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
GL 94.00277	Ceramic	40.38	Net-impressed	SFA ($C_{8:0-28:0}$), DC ($C_{9,10}$), Alk ($C_{14, 16, 18-27, 29, 31}$), br, terp[2], tmtd		-28.2	-28.4	-0.2					
GL 94.00278	Ceramic	34.26	Net-impressed	SFA ($C_{10:0-28:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{9, 11}$), Alk (C_{16-30}), Alkone (16-K_{31}, 14-K_{29}, 16-K_{33}), br, terp[1,2], tmtd, pri (tr)		-27.4	-28.1	-0.7					
GL 94.00002	Ceramic	13.75	Net-impressed	SFA ($C_{10:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{9,11}$), Alk ($C_{18, 19, 22-24, 26, 28-30}$), Alkone (16-$K_{31}$, 16-$K_{33}$), br, terp[1,2], tmtd, pri (tr)		-29.3	-29.2	0.1					
GL 95.00010	Ceramic	21.38	Cord-impressed (Khaita)	SFA ($C_{11:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1}$), Alk ($C_{16, 18, 22-26, 31}$), Alkone (16-K_{31}), br, terp[1,2], tmtd		-29.7	-29.3	0.5					
GL 95.00115	Ceramic	36.68	n/a	SFA ($C_{8:0-30:0}$), UFA ($C1_{6:1, 18:1, 22:1}$), DC ($C_{9,11}$), Alk ($C_{22-24, 26-29}$), Alkone (16-K_{31}, 14-K_{29}, 16-K_{33}), 2-HFA ($C_{22, 24}$), br, terp[2], tmtd, phy	84.4	-27.4	-28.9	-1.5					
GL 95.00121	Ceramic	66.49	n/a	SFA ($C_{10:0-28:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{9, 11, 13, 22}$), Alk ($C_{22-24, 26, 27}$), Alkone (16-K_{31}, 14-K_{31}), br, terp[1,2], tmtd, pri		-24.4	-26.0	-1.6					
GL 95.00162	Ceramic	31.52	n/a	SFA ($C_{10:0-28:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{9}) (tr), Alk (C_{16-29}), br, terp[2], tmtd (tr), pri		-27.0	-27.0	0.0					
GL 95.00177	Ceramic	51.39	Net-impressed	SFA ($C_{8:0-32:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$), DC ($C_{9, 11, 14, 15, 22-24, 26}$), Alk ($C_{29, 31, 33}$), Alkone (16-$K_{31}$, 10-$K_{29}$, 16-$K_{33}$), br, terp[2], APAA ($C_{18}$) (tr), tmtd (?), phy	n/a	-24.6	-26.7	-2.1					
GL 95.00180	Ceramic	171.37	n/a	SFA ($C_{8:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1, 24:1}$), DC ($C_{9, 11, 22-24, 26}$), Alkone (16-$K_{31}$, 16-$K_{33}$), br, terp[1,2], pri (tr)		-27.0	-28.0	-1.0					

Laboratory code	Type	Lipid conc. (µg g-1)	Pottery type	Major compound detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
GL 95.00257	Ceramic	42.62	n/a	SFA ($C_{9:0-28:0}$), UFA ($C_{18:1}$), DC (C_9), Alk ($C_{20, 22-24}$), Alkone (16-K_{31}), 2-HFA ($C_{22, 24}$), br, terp[2], tmtd (tr), pri (tr)	81.9	-28.2	-29.0	-0.9					
GL 95.00280	Ceramic	29.52	n/a	SFA ($C_{10:0-24:0}$), UFA ($C_{15:1, 16:1, 18:1, 22:1}$), DC ($C_9$), Alk ($C_{16, 18, 22-24}$), Alkone (16-$K_{31}$) (tr), br, terp[1,2],tmtd (tr), pri (tr), phy		-27.1	-28.1	-1.1					
GL 95.00328	Ceramic	30.38	Net-impressed	SFA ($C_{11:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1}$), Alk ($C_{16-18, 20-29, 31}$), br, terp[1], pri (tr)		-26.5	-27.3	-0.7					
GL 95.00291	Ceramic *	138.94	n/a	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{6, 9, 11}$), Alk ($C_{16, 18, 22-24}$), Alkone (16-K_{31}), Alkol ($C_{12-16, 18, 20-24}$), br, terp[1,2], pri		-26.6	-27.8	-1.2					
GL 95.00292	Ceramic	48.09	n/a	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_9), Alk ($C_{16-18, 20, 22-24, 26, 27}$), br, terp[1,2], tmtd		-29.3	-29.5	-0.2					
GL 95.00307	Ceramic *	81.18	n/a	SFA ($C_{7:0-28:0}$), UFA ($C_{14:1, 15:1, 18:1, 22:1}$), DC ($C_{6, 9, 11}$), Alk ($C_{22-24, 26, 27}$), Alkone (16-$K_{31}$), Alkol ($C_{12, 14, 15, 18, 20- 22}$), br, terp[1,2], tmtd (tr), pri		-24.3	-25.7	-1.4					
GL 95.00311	Ceramic *	72.60	n/a	SFA ($C_{9:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{9, 11, 22, 24}$), Alk ($C_{22-24, 26-29}$), Alkone (16-K_{31}, 14-K_{29}), Alkol ($C_{14-22, 24}$), br, terp[1,2], tmtd (?), pri		-23.1	-24.7	-1.6					
GL 95.00312	Ceramic *	120.21	n/a	SFA ($C_{7:0-30:0}$), UFA ($C_{16:1, 22:1}$), DC ($C_{7, 9, 11, 22, 24}$), Alk ($C_{14, 22-24, 26-30}$), Alkone (16-K_{31}), Alkol ($C_{12, 14-18, 20-24}$), br, terp[1,2], tmtd (tr), pri		-23.9	-25.2	-1.3					

Laboratory code	Type	Lipid conc. (µg g-1)	Pottery type	Major compound detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
GL 95.00314	Ceramic *	105.91	n/a	SFA ($C_{9:0-28:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{6, 9, 11, 22, 24}$), Alk ($C_{16, 22-24, 26-29}$), Alkone (16-K_{31}, 14-K_{29}), Alkol ($C_{12, 14, 16-24}$), br, terp[1], tmtd, pri		-24.6	-26.0	-1.4					
GL 95.00315	Ceramic	53.06	n/a	SFA ($C_{8:0-32:0}$), UFA ($C_{14:1, 15:1, 16:1, 18:1, 22:1}$), DC ($C_{9, 13, 22-24}$), Alk ($C_{22-33}$), Alkone (16-$K_{31}$, 14-$K_{29}$, 16-$K_{33}$), br, terp[1,2], tmtd, pri		-26.0	-26.0	0.0					
GL 95.00559	Ceramic	24.07	Net-impressed (?)	SFA ($C_{10:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{9}), Alk (C_{16-25}), br, terp[2], tmtd (?), pri		-27.9	-28.2	-0.3					
GL 95.00317	Ceramic *	129.99	n/a	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1, 18:1}$), Alk (C_{21-30}), Alkone (16-K_{31}, 14-K_{29}), Alkol ($C_{12, 14, 16-23}$), br, terp[1,2],tmtd (tr), pri (tr)		-26.8	-27.0	-0.2					
GL 95.00318	Ceramic	19.44	Net-impressed	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), Alk (C_{18-28}), 2-HFA (C_{24}), br, terp[1,2], tmtd, pri (?)		-26.1	-27.5	-1.4					
GL 95.00319	Ceramic	49.15	n/a	SFA ($C_{11:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{8-11}), Alk ($C_{16, 18-24}$), br, terp[1,2], APAA ($C_{16, 18, 20}$) (tr), tmtd, pri, phy	89.4	-26.0	-27.6	-1.6					
GL 95.00341	Ceramic	39.49	n/a	SFA ($C_{9:0-28:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{9, 10-12}$), Alk (C_{22-25}), br, terp[1,2], tmtd (tr), pri (tr)		-27.7	-28.7	-1.0					
GL 95.00344	Ceramic *	223.05	n/a	SFA ($C_{9:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{9}), Alk ($C_{22-24, 26-29}$), Alkone (16-K_{31}, 14-K_{29}), Alkol ($C_{12, 14-24, 26}$), 9-10diHFA (C_{18}), br, terp[1,2], tmtd (tr), pri		-26.1	-26.8	-0.7					

Laboratory code	Type	Lipid conc. (µg g-1)	Pottery type	Major compound detected	SRR %	δ13C16:0 (‰)	δ13C18:0 (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ13 C (‰)	%N	δ15N (‰)	C:N
GL 95.00598	Ceramic	188.97	n/a	SFA ($C_{9:0-20:0}$), DC (C_{96}), Alk (C_{17-28}), br, $terp^{1,2}$		-28.9	-28.0	0.9					
GL 95.00564	Ceramic	20.90	n/a	SFA ($C_{10:0-24:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C9), Alk ($C_{16,\ 18,\ 20-29}$), br, $terp_{1,2}$, tmtd, pri (tr)		-28.2	-28.8	-0.6					
GL 95.00595	Ceramic *	143.32	n/a	SFA ($C_{8:0-32:0}$), UFA ($C_{14:1,\ 15:1,\ 16:1,\ 18:1,\ 22:1}$), DC ($C_{9,\ 11}$), Alk ($C_{16,\ 22-30}$), Alkone (16-$K_{31}$, 14-$K_{29}$, 16-$K_{33}$), Alkol ($C_{12-26}$), 9-10diHFA ($C_{18}$), br, $terp^{1,2}$, tmtd, pri, phy	97.2	-24.3	-25.7	-1.4					
GL 95.00600	Ceramic *	269.74	n/a	SFA ($C_{9:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{9-14,\ 16,\ 22,\ 23}$), Alk ($C_{18,\ 22-30}$), Alkone (16-K_{31}, 14-K_{29}, 16-K_{33}), Alkol ($C_{14-20,\ 22}$), br, $terp^{1,2}$, APAA ($C_{16,\ 18,\ 20,\ 22}$), tmtd (tr), pri (tr), phy	50.0	-27.9	-31.5	-3.6					
GL 95.00601	Ceramic	93.99	n/a	SFA ($C_{9:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{9,\ 11,\ 24}$), Alk ($C_{16,\ 18,\ 20,\ 21-28}$), Alkone (16-K_{31}, 14-K_{29}, 16-K_{33}), br, $terp^{1,2}$, tmtd (?), pri		-24.1	-26.0	-1.9					
GL 95.00602	Ceramic	99.74	n/a	SFA ($C_{9:0-30:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 22:1}$), DC ($C_{9,\ 11,\ 22,\ 24}$), Alk ($C_{16,\ 18,\ 20,\ 22-29}$), Alkone (16-$K_{31}$, 14-$K_{29}$, 16-$K_{33}$), br, $terp^{1,2}$, pri (tr)		-23.5	-25.4	-1.9					
GL 95.00611	Ceramic	23.72	Net-impressed	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_9) (tr), Alk (C_{20-29}), Alkone (16-K_{31}), br, $terp^{1,2}$, pri (tr)		-26.4	-27.2	-0.8					
GL 95.00625	Ceramic	94.87	n/a	SFA ($C_{9:0-32:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{6,\ 9,11,\ 22-24}$), Alk ($C_{14,\ 16,\ 18,\ 22-31}$), Alkone (16-K_{31}, 14-K_{29}), br, $terp^{1,2}$,pri		-24.4	-26.0	-1.6					

Laboratory code	Type	Lipid conc. (µg g-1)	Pottery type	Major compound detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
GL 95.00634	Ceramic	73.95	n/a	SFA ($C_{9:0-28:0}$), UFA ($C_{18:1}$) (tr), DC (C_9) (tr), Alk ($C_{20-24,\ 26-29,\ 31}$), br, terp[2], tmtd (tr)		-30.0	-30.2	-0.2					
GL 95.00823	Ceramic	114.47	n/a	SFA ($C_{8:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{9,\ 11,\ 22}$), Alk ($C_{16,\ 18,\ 22-24,\ 26-29}$), Alkone (16-$K_{31}$, 14-$K_{29}$), br, terp[1,2], tmtd (?), pri		-23.9	-25.4	-1.5					
GL 95.00644	Ceramic	46.47	n/a	SFA ($C_{9:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C9), Alk (C_{16-28}), Alkone (16-K_{31}), br, terp[1,2], tmtd (tr), pri (tr)		-26.6	-27.9	-1.3					
GL 95.00847	Ceramic	65.32	n/a	SFA ($C_{8:0-20:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{6,\ 7,\ 9}$), Alk ($C_{16-18,\ 20,\ 22-24}$), 2-HFA (C_{24}), br, terp[1,2], tmtd, phy	92.9	-27.6	-28.5	-0.9					

Sherds and foodcrusts were extracted by acid-methanol extraction. Acid extracted lipids were trimethylsilylated in a selection of sherds*. ($C_{n:x}$) - carboxilic acids with carbon length n and number of unsaturations x, SFA – saturated fatty acid, UFA – unsaturated fatty acids, DC - α,ω-dicarboxylic acids, Alk – alkane, Alkol – alkanol, Alkone – alkanone, HFA- hydroxyfatty acid, diHFA- dihydroxy fatty acid, APAA - ω-(o-alkylphenyl) alkanoic acids, br -branched chain acids dominated by *iso* and *anteiso* C_{15} and C_{17}, tmtd - 4,8,12-trimethyltridecanoic acid, pri – pristanic acid, phy – phytanic acid with the percentage contribution of SRR diastereomer in total phytanic acid, chol - cholesterol or derivatives, phyol - phytosterol or derivatives, terp[1] – abietane mainly dehydroabietic acid, terp[2] – totarol, 7α-hydroxy (also called Podocarpa-8,11,13-triene-7β,13-diol, 14-isopropyl-).

Appendix 5: (a) Gorelyi Les site overview from the Belaia River (view from the Southwest) and (b) Excavation campaign season 1994, led by N.A. Savel'ev and A.W. Weber. Photo from A.W. Weber (1997).

a

b

Appendix 6: Bulk isotope measurement of modern and archaeological collagen bones from Angara region.

Common name	Taxa	Period	Collagen yielded (%)	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$ Calibrated* (‰)	Reference
Fish							
Arctic grayling	Thymallus arcticus	Modern	10.7	-16.4	12.9	-21.6	Katzenberg et al., 2012; Weber et al., 2011
Arctic grayling	Thymallus arcticus	Modern	13.3	-16.4	12	-21.6	Katzenberg et al., 2012; Weber et al., 2011
Burbot	Lota lota	Modern	2.8	-23.6	12.4	-28.8	Katzenberg et al., 2012; Weber et al., 2011
Burbot	Lota lota	Modern	15	-21.7	10.6	-26.9	Katzenberg et al., 2012; Weber et al., 2011
Burbot	Lota lota	Modern	11.5	-19.7	13.6	-24.9	Katzenberg et al., 2012; Weber et al., 2011
Freshwater perch	Perca fluviatilis	Modern	6.6	-25.6	11.4	-30.8	Katzenberg et al., 2012; Weber et al., 2011
Freshwater perch	Perca fluviatilis	Modern	14.3	-24.9	11.5	-30.1	Katzenberg et al., 2012; Weber et al., 2011
Freshwater perch	Perca fluviatilis	Modern	7.9	-25.4	11.8	-30.6	Katzenberg et al., 2012; Weber et al., 2011
Lenok	Brachymys tax lenok	Modern	7.6	-15.6	13.7	-20.8	Katzenberg et al., 2012; Weber et al., 2011
Northern pike	Esox lucius	Modern	4.2	-19.2	18.5	-24.4	Katzenberg et al., 2012; Weber et al., 2011

Common name	Taxa	Period	Collagen yielded (%)	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$ Calibrated* (‰)	Reference
Northern pike	Esox lucius	Modern	5	-20.2	20.6	-25.4	Katzenberg et al., 2012; Weber et al., 2011
Northern pike	Esox lucius	Modern	15.2	-22	9.8	-27.2	Katzenberg et al., 2012; Weber et al., 2011
Omul	Coregonus a. m.	Modern	11.8	-21.8	10.7	-27.0	Katzenberg et al., 2012; Weber et al., 2011
Omul	Coregonus a. m.	Modern	15.3	-24	11.6	-29.2	Katzenberg et al., 2012; Weber et al., 2011
Prussian carp	Carassius auratus	Modern	0.5	-24.1	7.8	-29.3	Katzenberg et al., 2012; Weber et al., 2011
Siberian roach	Rutilus rutilus l.	Modern	16.5	-16.4	12	-21.6	Katzenberg et al., 2012; Weber et al., 2011
Siberian roach	Rutilus rutilus l.	Modern	14.9	-25.2	8.4	-30.4	Katzenberg et al., 2012; Weber et al., 2011
Siberian roach	Rutilus rutilus l.	Modern	9.3	-25.8	8.9	-31.0	Katzenberg et al., 2012; Weber et al., 2011
Siberian roach	Rutilus rutilus l.	Modern	9.9	-24.1	7.7	-29.3	Katzenberg et al., 2012; Weber et al., 2011
Siberian roach	Rutilus rutilus l.	Modern	11.6	-24.5	7.5	-29.7	Katzenberg et al., 2012; Weber et al., 2011
Siberian roach	Rutilus rutilus l.	Modern	9.6	-26.6	7.8	-31.8	Katzenberg et al., 2012; Weber et al., 2011

Common name	Taxa	Period	Collagen yielded (%)	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$ Calibrated* (‰)	Reference
Wild ruminant							
Red deer	Cervus elaphus	Archaeological	65.9	-19.1	5.1	-27.1	Weber et al. 2002; Weber et al., 2011
Red deer	Cervus elaphus	Archaeological	20.1	-18.7	4.9	-26.7	Weber et al. 2002; Weber et al., 2011
Red deer	Cervus elaphus	Archaeological	11.4	-20.2	3.1	-28.2	Weber et al. 2002; Weber et al., 2011
Roe deer	Capreolus capreolus	Archaeological	11	-21.1	4.6	-29.1	Weber et al. 2002; Weber et al., 2011
Roe deer	Capreolus capreolus	Archaeological	19.1	-20.3	6	-28.3	Weber et al. 2002; Weber et al., 2011
Roe deer	Capreolus capreolus	Archaeological	26	-20.1	6.3	-28.1	Weber et al. 2002; Weber et al., 2011
Roe deer	Capreolus capreolus	Archaeological	13.6	-19.9	5.2	-27.9	Weber et al. 2002; Weber et al., 2011
Roe deer	Capreolus capreolus	Archaeological	9.8	-20.6	5.2	-28.6	Weber et al. 2002; Weber et al., 2011
Wild non-ruminant							
Badger	Meles meles	Modern	12.7	-20.1	7.7	-26.3	Katzenberg et al., 2012; Weber et al., 2011
Badger	Meles meles	Modern	16.5	-20.7	4.9	-26.9	Katzenberg et al., 2012; Weber et al., 2011
Bear	Ursus sp.	Modern	15.7	-19.7	4.9	-25.9	Katzenberg et al., 2012; Weber et al., 2011
Fox	Canidae family	Modern	16.3	-23.2	9.2	-29.4	Katzenberg et al., 2012; Weber et al., 2011
Fox	Canidae family	Modern	25.8	-21.6	13.9	-27.8	Katzenberg et al., 2012; Weber et al., 2011
Ground squirrel	Citelius parryi	Modern	15.1	-23.2	2.4	-29.4	Katzenberg et al., 2012; Weber et al., 2011

Common name	Taxa	Period	Collagen yielded (%)	δ13C	δ15N	δ13C Calibrated* (‰)	Reference
Ground squirrel	Citelius parryi	Modern	16.5	-23.5	11	-29.7	Katzenberg et al., 2012; Weber et al., 2011
Ground squirrel	Citelius parryi	Modern	15.9	-23.1	9.8	-29.3	Katzenberg et al., 2012; Weber et al., 2011
Ground squirrel	Citelius parryi	Modern	4.6	-22.2	9.9	-28.4	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	11.3	-23.8	6.9	-30.0	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	12.4	-23.7	6.6	-29.9	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	13.1	-24.7	3.7	-30.9	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	11.8	-24.4	2.2	-30.6	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	11	-24.2	1.7	-30.4	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	8.3	-25	4	-31.2	Katzenberg et al., 2012; Weber et al., 2011
Hare	Lepus timidus	Modern	11.1	-23.7	2.6	-29.9	Katzenberg et al., 2012; Weber et al., 2011

*To facilitate comparison with lipid residue extracted from pottery all the samples were adjusted by -7‰ for fish -8‰ for terrestrial animal to correct for the collagen to tissue offset (Fernandes et al. 2015). The $\delta^{13}C$ values of all the modern bones were then adjusted for the addition of the effects of post-industrial carbon (Schmitt et al. 2012; Hellevang and Aagaard 2015; Lucquin et al. 2016).

Appendix 7: Mixing model

The following table summarised the values used for the mixing model. To investigate the impact of mixing of different foodstuffs on Δ13C values, the δ13C16:0 values were defined using the published (Dudd 1999; Spangenberg et al. 2010; Craig et al. 2012; Choy et al. 2016. Pääkkönen et al. 2016) and unpublished data. Possible $\delta^{13}C_{16:0}$ values for ruminant, non-ruminant, fish and plant were randomly selected (n = 100,000). Next corresponding values for $\delta^{13}C_{18:0}$ were determined using a random process that takes into account uncertainties in regression slope and intercept. Concentration values (n = 100,000) for $C_{16:0}$ and $C_{18:0}$ in each food product were also selected using from the data obtained from the USDA database. Finally, $\Delta^{13}C$ ($\delta^{13}C_{18:0}$ − $\delta^{13}C_{16:0}$) values were calculated by drawing (100,000 iterations) from the randomized isotope values, accounting for the amount of fatty acid in each foodstuff.

Category	$\delta^{13}C_{16:0}$ average calibrated (‰)	stdev	Intercept	stdev	Slope	stdev	$C_{16:0}$ relative concentration average (%)	stdev	$C_{18:0}$ relative concentration average (%)	stdev
Ruminant	-29.0	2.5	-3.13	1.99	0.97	0.07	19.0	0.03	18.0	0.05
Non-ruminant	-29.4	2.2	0.63	2.57	1.01	0.09	18.0	0.05	6.0	0.03
salmonidae and brackish fish	-25.5	2.0	-0.69	2.33	0.95	0.09	14.0	0.03	3.0	0.00
Plant	-31.2	3.0	-0.75	5.04	0.95	0.16	16.0	0.05	1.0	0.01

Appendix 8: Photos of Zamostje 2 site and the surrounding landscapes. Photo from O. Lozovskaya.

Appendix 9: List of samples from Zamostje 2 selected for lipid analysis (GCMS, GC-c-IRMS) and bulk isotope characteristics of charred deposits and bone collagen (EA-IRMS).

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-117	Ceramic[1,3]	EN	es	175.7	SFA ($C_{12:0-24:0}$), UFA ($C_{15:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-11}$), Alk ($C_{27}$) br, chol, abie, amy (tr), terp, APAA (C_{16-20}), tmtd, phy	79.4	-35.01	-33.5	1.55					
	Foodcrust[1]	EN	es	518.2	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{7-11}), br, chol, abie, amy, terp, APAA (C_{16-20}), phy	84.5				40.4	-27.1	4.0	9.9	11.9
ZAM2-118	Ceramic[1, 4]	EN	ms	90.6	SFA ($C_{12:0-26:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{13}$), br, chol, abie, APAA (C_{16-18}), tmtd (tr), phy	28.8	-28.90	-29.4	-0.54					
ZAM2-119	Ceramic[1]	EN	es	148.8	SFA ($C_{12:0-24:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-13,\ 15}$), br, chol, Phyol, amy, terp, APAA (C_{16-20}), tmtd, phy	86.8	-26.19	-27.5	-1.35					
	Foodcrust[1]	EN	es	728.0	SFA ($C_{14:0-22:0}$), UFA ($C_{18:1}$), DC (C_{9-12}), br, amy (tr), APAA (C_{16-20}), tmtd, phy	89.4				36.2	-24.1	4.8	5.3	8.9

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-120	Ceramic[1]	EN	es	74.2	SFA ($C_{12:0-28:0}$), UFA ($C_{14:1-16:1, 18:1, 22:1, 22:2}$), DC ($C_{9-13}$), br, chol, abie, APAA (C_{16-18}), tmtd (tr), phy (tr)	tr	-29.37	-30.0	-0.61					
ZAM2-121	Ceramic[1]	EN	ls	39.3	SFA ($C_{12:0-24:0}$), UFA ($C_{18:1}$), DC (C_{9-11}), br, chol, phyol, APAA (C_{16-20}), tmtd, phy	64.0	-27.17	-28.0	-0.83					
	Foodcrust[1]	EN	ls	59.4	SFA ($C_{14:0-24:0}$), UFA ($C_{18:1}$) (tr), DC (C_{9-11}), br, APAA (C_{16-20}), phy	tr				33.1	-25.2	6.7	8.0	5.8
ZAM2-122	Ceramic[1]	EN	es	8.2	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{9-11}), br, terp, tmtd (tr)		-31.38	-30.1	1.33					
ZAM2-123	Ceramic[1]	EN	ls	53.6	SFA ($C_{12:0-26:0}$), UFA ($C_{14:1, 18:1, 20:1, 22:1}$), DC ($C_{9}$), br, chol, phyol, APAA (C_{16-20}), tmtd, phy	62.4	-28.39	-28.8	-0.41					
ZAM2-124	Ceramic[1]	EN	ls	136.6	SFA ($C_{11:0-24:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC (C_{9}), br, chol, phyol, terp, APAA (C_{16-20}), tmtd, phy	61.2	-29.95	-30.5	-0.55					
ZAM2-125	Ceramic[1]	EN	ls	0.6	SFA ($C_{16:0}$, $C_{18:0}$), br, chol									
	Foodcrust[1]	EN	ls	15.5	SFA ($C_{12:0-18:0}$), br, chol									
ZAM2-126	Ceramic[1]	EN	ms	5.6	SFA ($C_{12:0-28:0}$), br	tr	-30.69	-29.9	0.80					
ZAM2-127	Ceramic[1]	EN	ls	150.5	SFA ($C_{12:0-24:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1, 22:2}$), DC ($C_{9, 11}$), br, chol, abie, APAA (C_{16-18}) (tr), tmtd (tr), phy (tr)	83.9	-25.78	-26.4	-0.64					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-128	Ceramic[1]	EN	ls	0.5	SFA ($C_{14:0-18:0}$), br									
	Foodcrust[1]	EN	ls	19.4	SFA ($C_{14:0-18:0}$), UFA ($C_{18:1}$) (tr), DC (C_9) (tr), br									
ZAM2-129	Ceramic[1]	EN	ms	69.7	SFA ($C_{12:0-30:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-13}$), br, chol, abie, APAA (C_{16-20}), tmtd, phy	42.6	-28.47	-27.6	0.87					
ZAM2-130	Ceramic[1]	EN	ms	286.6	SFA ($C_{12:0-30:0}$), UFA ($C_{14:1-15:1,\ 18:1,\ 22:1}$), DC ($C_{9-11,\ 13}$), br, chol,, phyol, amy, terp, APAA (C_{16-18}) (tr), tmtd, phy (tr)	tr	-29.48	-29.4	0.03					
ZAM2-131	Ceramic[1,3]	EN	es	175.4	SFA ($C_{16:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{9-12}), Alk (C_{27}), Gly (1-C_{16}, 2-C_{16}, 1,2-C_{16}, 1,3-C_{16}, 2-C_{18}), br, chol, APAA (C_{16-18}) (tr), phy (tr)	n/a	-25.89	-26.5	-0.59					
	Foodcrust[1]	EN	es	13266.7	SFA ($C_{8:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{6-12}$), Alkone (16-$K_{31}$, 16-$K_{33}$), br, chol, terp (tr), APAA (C_{16-18}) (tr), phy (tr)	tr								
ZAM2-132	Ceramic[1]	EN	es	69.8	SFA ($C_{10:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_9), br, abie, APAA (C_{16-18}) (tr), tmtd, pri (tr)	tr	-28.19	-28.6	-0.36					
ZAM2-133	Ceramic[1]	EN	ms	18.2	SFA ($C_{11:0-20:0}$), br		-30.44	-30.0	0.41					
ZAM2-134	Ceramic[1]	EN	ms	0.1	SFA ($C_{16:0}$, $C_{18:0}$) (tr)									

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-134	Foodcrust[1]	EN	ms	6.1	SFA ($C_{12:0-18:0}$), br									
ZAM2-135	Ceramic[1,3]	EN	es	82.4	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ C22:1}$), DC ($C_{9,\ 11}$), Alk ($C_{17,\ 18,\ 25,\ 27-30}$), Alkol ($C_{14,\ 16,\ 18}$), Alkone (16-$K_{31}$, 14-$K_{29}$, 18-$K_{35}$, 16K-$_{33}$), br, APAA ($C_{18-20}$), tmtd (tr), phy	81.8								
ZAM2-163	Foodcrust[1,3]	EN	es	118.1	SFA ($C_{11:0-26:0}$), UFA ($C_{18:1}$), DC ($C_{9,\ 13}$), Alk ($C_{27,\ 28,\ 30}$), Alkol ($C_{14-16,\ 18,\ 26}$), br, chol, amy (tr)		-30.34	-27.6	2.72	20.9	-25.5	1.8	3.4	13.6
	Ceramic[1]	EN	es	5.5	SFA ($C_{12:0-18:0}$), APAA (C_{18}), phy (?)									
ZAM2-164	Foodcrust[1]	EN	es	2519.6	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-12}), br, chol, amy, terp, APAA (C_{16-20}), pri (tr), ph	86.7	-28.28	-27.2	1.06	39.0	-25.5	2.3	3.4	19.4
	Ceramic[1]	EN	es	1.1	SFA ($C_{14:0-18:0}$), UFA ($C_{18:1}$) (tr), br									
ZAM2-165	Foodcrust[1]	EN	es	854.2	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-11}), br, chol, amy, terp, APAA (C_{18-20}) (tr), phy	81.4	-29.32	-28.9	0.38	39.4	-26.9	2.2	4.5	20.4
	Ceramic[1]	EN	es	0.8	SFA ($C_{14:0-18:0}$)									
ZAM2-166	Foodcrust[1]	EN	es	150.7	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_{9}), br, chol (tr), amy (tr), terp (tr), APAA (C_{16-20}), phy	87.1				44.8	-26.1	2.9	5.2	17.8
	Ceramic[1]	EN	es	0.4	SFA ($C_{14:0-18:0}$), br									

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-167	Foodcrust[1,3]	EN	es	2370.9	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-12}), Alk ($C_{27,\ 29,\ 31}$), Alkol ($C_{18,\ 24}$), br, amy, terp, APAA (C_{18}) , phy (tr)	tr	-29.04	-30.1	-1.03	36.0	-26.4	1.6	3.7	25.9
	Ceramic[1]	EN	es	2.8	SFA ($C_{12:0-26:0}$), UFA ($C_{18:1}$) (tr), DC (C_{9}), APAA (C_{18}), pri (tr)									
ZAM2-168	Foodcrust[1]	EN	es	652.0	SFA ($C_{14:0-18:0}$), UFA ($C_{1-:1,\ 18:1,\ 22:1}$), DC (C_{7-12}), br, chol, APAA (C_{16-20}), phy (tr)	86.9				30.3	-26.4	4.6	7.7	7.6
ZAM2-169	Foodcrust[1]	EN	es	46.2	SFA ($C_{14:0-28:0}$), br, amy, terp					25.1	-26.4	1.7	1.7	17.3
	Ceramic[1]	EN	es	11.2	SFA ($C_{14:0-18:0}$)									
ZAM2-170	Foodcrust[1]	EN	es	736.8	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-12}), Alk ($C_{18,\ 25-29}$), br, terp, APAA (C_{16-20}), tmtd (tr), phy	72.4	-25.53	-26.1	-0.61	32.5	-23.2	4.4	7.3	8.5
	Ceramic[1,3]	EN	es	11.5	SFA ($C_{12:0-26:0}$), UFA ($C_{18:1}$), DC (C_{9}), Alkol ($C_{14,\ 18,\ 20}$), Gly (1-C_{16}, 1-C_{18}), terp, APAA (C_{16-20}), tmtd, pri (tr), phy	69.6								
ZAM2-171	Foodcrust[1]	EN	es	16924.6	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-12}), br, chol (tr), amy, APAA (C_{16-20}), tmtd, phy	90.0				17.7	-27.7	2.0	5.6	10.4
	Ceramic[1]	EN	es	4.9	SFA ($C_{14:0-20:0}$), br, APAA (C_{16-20}), tmtd (tr), pri (tr), phy	85.0								

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-172	Foodcrust[1]	EN	es	2273.8	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-11}), br, chol, phyol, amy, terp, APAA (C_{16-20}), tmtd (tr), phy	92.1				51.5	-26.0	1.8	2.4	33.4
ZAM2-172	Ceramic[1]	EN	es	13.5	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$) (tr), br, APAA (C_{16-18}), tmtd, pri (tr), phy (tr)	tr								
ZAM2-173	Foodcrust[1]	EN	es	8966.0	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-10}), Alkol ($C_{14,\ 18}$),br, chol, phyol, amy, terp, APAA (C_{16-20}) (tr), tmtd, pri (tr), phy		-30.20	-29.5	0.71	49.2	-26.0	2.0	2.2	28.9
	Foodcrust[1]	EN	es	10.0	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1-18:1}$), DC (C_{9-12}), Alk (C_{22-29}), Gly (1-C_{16}, 1-C_{18}), br, chol, abie, amy, APAA (C_{16-20}) (tr), tmtd	50.7								
ZAM2-174	Foodcrust[1]	EN	es	1507.3	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 24:1}$), DC ($C_{9-12}$), chol, amy, APAA ($C_{16-20}$) (tr), phy	n/a	-26.47	-26.6	-0.14					
ZAM2-175	Foodcrust[1]	EN	es	37.9	SFA ($C_{14:0-18:0}$), UFA ($C_{18:1}$), br, APAA (C_{16-20}) (tr), phy (tr)	tr				53.6	-26.0	4.4	5.6	14.3
	Ceramic[1]	EN	es	3.8	SFA ($C_{12:0-26:0}$), UFA ($C_{18:1}$), DC (C_9), br, chol, APAA (C_{18}) (tr), tmtd (tr), pri (tr), phy	86.0								

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-176	Foodcrust[1]	EN	ms	656.5	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-13}), Alkol ($C_{12-16,\ 18}$), br, chol, amy, terp, APAA (C_{18}) (tr)		-27.87	-29.6	-1.73	17.0	-24.7	1.6	3.9	12.7
	Ceramic[1, 3]	EN	ms	8.3	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-11}), Alk (C_{23-29}), Gly (1-C_{16}), br, chol, abie, amy		-26.93	-28.9	-1.95					
ZAM2-177	Foodcrust[1]	EN	ls	4888.6	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-11}), br, chol, amy, terp, APAA (C_{16-20}), tmtd, phy	84.2	-29.82	-29.7	0.16	47.5	-26.3	21.3	5.0	11.0
	Ceramic[1]	EN	ls	5.4	SFA ($C_{12:0-24:0}$), UFA ($C_{18:1}$), br, abie (tr), APAA (C_{18}) (tr)		-28.62	-29.7	-1.12					
ZAM2-178	Foodcrust[1, 3]	EN	ls	380.8	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), Alk (C_{23-C27}), br, phyol, amy, terp, APAA (C_{18})		-30.76	-30.2	0.54	47.5	-25.9	3.0	4.5	18.3
ZAM2-179	Foodcrust[1, 3]	EN	ms	1497.7	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-11}), Gly (1-C_{16}), br, terp, APAA (C_{16-18}), tmtd, phy		-29.36	-29.4	-0.08					
	Ceramic[1,3]	EN	ms	95.8	SFA ($C_{7:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-11}), Gly (1-C_{16}), br, chol, terp, tmtd (tr)		-28.40	-28.9	-0.54					
ZAM2-180	Foodcrust[1]	EN	ms	1169.9	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 24:1}$), DC (C_{9-11}), br, chol, amy, APAA (C_{16-20}), tmtd, phy	79.7				47.6	-26.4	6.1	5.3	9.1

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-181	Foodcrust[1]	EN	ms	3738.8	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-12}), Alkol (C_{24}), Gly (1-C_{16}), br, chol, amy, terp, APAA (C_{16-20}), tmtd (tr), pri, phy (tr)	tr	-33.39	-32.5	0.86	42.7	-28.7	4.4	6.3	11.4
	Ceramic[1, 3]	EN	ms	4.9	SFA ($C_{12:0-18:0}$), UFA ($C_{18:1}$) (tr), br, APAA (C_{18}) (tr), tmtd (tr)		-29.95	-29.4	0.55					
ZAM2-182	Foodcrust[1]	EN	ms	2027.5	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-12}), br, chol, amy, terp, APAA (C_{16-20}), tmtd, phy	81.3	-31.12	-31.4	-0.23	43.1	-27.1	5.4	6.1	9.3
ZAM2-183	Foodcrust[1]	EN	ms	4300.6	SFA ($C_{14:0-22:0}$), UFA ($C_{16:1,\ 18:1}$), DC ($C_{9,\ 11,\ 12}$), br, chol, amy, terp, APAA (C_{16-20}), tmtd, phy	82.9	-26.94	-26.4	0.52	52.6	-26.5	5.0	5.5	12.4
	Ceramic[1]	EN	ms	10.9	SFA ($C_{14:0-18:0}$), UFA ($C_{18:1}$), DC (C_{9}), br, abie, APAA (C_{18-20}), tmtd, pri (tr), phy (tr)	tr	-28.89	-29.0	-0.08					
ZAM2-184	Foodcrust[1]	EN	ms	691.5	SFA ($C_{14:0-24:0}$), UFA ($C_{18:1}$), DC ($C_{9-11,\ 18}$), br, abie (tr), terp, APAA (C_{16-20}), tmtd (tr)					37.4	-27.5	4.9	8.5	8.9
ZAM2-185	Foodcrust[1]	EN	ms	837.4	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 24:1}$), DC (C_{9-11}), br, chol, amy, APAA (C_{16-20}), tmtd (tr), phy	82.7	-28.94	-29.5	-0.54	41.8	-25.8	5.0	7.3	9.7
	Ceramic[1]	EN	ms	12.1	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9}), br, amy (tr), pri		-26.42	-25.6	0.81					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-186	Ceramic[1]	EN	es	1.8	SFA ($C_{12:0-18:0}$), UFA ($C_{18:1}$) (tr), DC (C_9), br									
	Foodcrust[1]	EN	es	46.6	SFA ($C_{12:0-26:0}$), UFA ($C_{18:1}$) (tr), br, APAA (C_{18}) (tr)					49.1	-25.8	1.4	1.4	40.6
ZAM2-187	Foodcrust[1]	EN	ms	115.1	SFA ($C_{12:0-28:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9,\ 13}$), br, chol (tr), abie, APAA (C_{16-18}) (tr), tmtd		-27.56	-28.7	-1.12					
ZAM2-188	Foodcrust[1]	EN	ms	434.6	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-12}), br, chol, terp, APAA (C_{18}) (tr)					9.2	-27.0	1.4	8.9	7.9
	Ceramic[1]	EN	ms	337.9	SFA ($C_{6:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{6-15}$), br, chol, terp, APAA (C_{18}) (tr), tmtd, pri (tr), phy (tr)	tr	-31.52	-30.6	0.95					
ZAM2-189	Foodcrust[1]	EN	ms	274.7	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{7-15}$), br, chol, amy (tr), terp, APAA (C_{16-18}), tmtd (tr), phy (?)									
	Ceramic[1, 3]	EN	ms	104.3	SFA ($C_{16:0-20:0}$), UFA ($C_{18:1}$), Alkol ($C_{14,\ 16,\ 18}$), br, amy, APAA (C_{16-20}), phy	76.8	-27.69	-27.9	-0.25	44.7	-25.0	6.0	5.8	8.7
ZAM2-190	Foodcrust[1]	EN	ms	4385.8	SFA ($C_{14:0-22:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{9-11}), br, amy, terp, APAA (C_{16-20}), tmtd					47.0	-26.5	2.7	4.3	20.2
	Ceramic[1]	EN	ms	9.5	SFA ($C_{9:0-18:0}$), UFA ($C_{18:1}$), DC (C_9), br		-29.23	-29.4	-0.16					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-191	Foodcrust[1]	EN	es	1730.5	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{9-12, 16-20}$), br, chol (tr), amy, APAA (C_{16-20}), tmtd, phy	53.9	-32.74	-33.5	-0.78	45.6	-27.4	3.4	6.6	15.6
	Ceramic[1]	EN	es	0.7	SFA ($C_{14:0-20:0}$), br									
ZAM2-192	Foodcrust[1]	EN	ms	782.1	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_{9-11}), br, terp, APAA (C_{16-20}), phy (tr)	tr	-30.25	-30.2	0.09	-31.4	-25.6	1.5	0.8	42.2
	Ceramic[1, 3]	EN	ms	18.7	SFA ($C_{12:0-26:0}$), UFA ($C_{18:1}$), DC (C_9), Alk (C_{24-28}), Alkol ($C_{14, 16, 18}$), Gly (1-C_{16}), br, phyol, APAA (C_{16-20}), tmtd (tr)									
ZAM2-193	Foodcrust[1]	EN	es	1178.4	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{9-11}), br, chol, amy, APAA (C_{16-20}), tmtd, phy	77.8				48.8	-23.5	5.6	6.6	10.2
	Ceramic[1]	EN	es	4.2	SFA ($C_{12:0-22:0}$), UFA ($C_{18:1, 22:1}$), br, APAA (C_{18})									
ZAM2-194	Foodcrust[1, 3]	EN	ms	334.5	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_9), Alk (C_{29}), Alkol ($C_{16, 18, 26}$), br, chol (tr), amy, terp, APAA (C_{16-20}) (tr), phy	89.4	-28.79	-29.3	-0.50	49.0	-26.1	2.7	3.7	21.5
	Ceramic[1]	EN	ms	9.5	SFA ($C_{12:0-22:0}$), UFA ($C_{16:1, 18:1}$), amy									

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-195	Foodcrust[1]	EN	ms	716.3	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1, 18:1, 24:1}$), DC (C_{9-12}), br, chol, amy, APAA (C_{16-20}), phy, pri, phy	92.1				46.0	-23.3	5.4	5.7	10.0
	Ceramic[1]	EN	ms	6.1	SFA ($C_{14:0-22:0}$), UFA ($C_{18:1}$), DC (C_9), br, amy (tr), APAA (C_{16-20}), phy	74.3								
ZAM2-196	Foodcrust[1]	EN	es	542.5	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_9) (tr), chol, APAA (C_{16-18}), phy (tr)	tr	-26.72	-26.7	0.07	52.2	-27.1	3.9	5.2	15.7
	Ceramic[1]	EN	es	0.4	SFA ($C_{14:0-20:0}$), br		-28.24	-28.8	-0.56					
ZAM2-197	Foodcrust[1]	EN	es	2163.6	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{9-11}), br, chol, abie, amy, terp, APAA (C_{18})					41.3	-26.7	2.6	3.7	18.3
	Ceramic[1]	EN	es	14.3	SFA ($C_{12:0-18:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{9-11}), br, chol, amy (tr)									
ZAM2-198	Foodcrust[1]	EN	es	2872.0	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_9), br, chol, phyol, amy, terp, APAA (C_{16-20}), tmtd (tr), phy	89.1				44.8	-26.6	3.0	3.6	17.3
	Ceramic[1]	EN	es	4.2	SFA ($C_{14:0-22:0}$), UFA ($C_{18:1, 22:1}$), br									
ZAM2-199	Foodcrust[1]	EN	es	664.1	SFA ($C_{14:0-18:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{11}), br, chol, APAA (C_{16-20})		-23.93	-24.9	-0.93					
	Ceramic[1]	EN	es	7.1	SFA ($C_{14:0-18:0}$), UFA ($C_{18:1}$) (tr), DC (C_{9-12}), br, chol, APAA (C_{16-20}), tmtd, pri, phy	84.4	-26.53	-27.9	-1.39	34.1	-23.3	5.7	7.4	7.0

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-200	Foodcrust[1, 4]	EN	es	445.5	SFA ($C_{12:0-18:0}$), UFA ($C_{18:1}$) (tr), DC ($C_{9-12, 18, 20, 22}$), br, amy, terp, APAA (C_{18}), phy (tr)	tr	-30.79	-31.0	-0.19	46.2	-25.9	1.6	-0.4	34.5
ZAM2-201	Foodcrust[1]	EN	es	24380.9	SFA ($C_{14:0-22:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$), DC ($C_{7-12, 16, 18, 20, 22}$), br, APAA ($C_{16-20}$), tmtd, pri, phy	84.9				47.1	-29.2	5.7	11.4	9.6
	Ceramic[1, 3]	EN	es	827.9	SFA ($C_{6:0-26:0}$), UFA ($C_{7:1-11:1, 15:1, 17:1, 18:1, 22:1}$), DC ($C_{8-11, 16, 18, 20, 22}$), chol, terp, APAA ($C_{16-18}$) (tr)		-29.89	-29.1	0.81					
ZAM2-202	Foodcrust[1]	EN	es	2880.9	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$), DC ($C_{9-12}$), br, chol, amy, APAA ($C_{16-20}$), tmtd, pri, phy	82.1	-28.45	-28.8	-0.38	44.5	-26.9	4.8	6.2	10.7
	Ceramic[1]	EN	es	8.8	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{9-10}), br, chol (tr), amy (tr), APAA (C_{16-20}), tmtd tr), phy	73.1	-28.52	-28.5	0.06					
ZAM2-203	Foodcrust[1]	EN	es	295.9	SFA ($C_{14:0-24:0}$), DC (C_{9}), br, amy, APAA (C_{16-20}), phy	69.6	-28.30	-29.0	-0.71	49.3	-25.8	2.9	0.7	19.9
	Ceramic[1, 3]	EN	es	5.5	SFA ($C_{14:0-20:0}$), UFA ($C_{18:1, 22:1}$) (tr), DC (C_{9-10}) (tr), Alk (C_{25-29}), Alkol ($C_{12, 14, 16, 18}$), br, APAA (C_{18}), tmtd (tr)									
ZAM2-204	Foodcrust ext[1]	EN	ms	186.6	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$) (tr), DC (C_{9-11}) (tr), br, chol, amy (tr), terp, APAA (C_{16-20})		-29.52	-29.7	-0.22	44.9	-25.5	6.1	8.4	8.6

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-204	Foodcrust int[1]	EN	ms	324.2	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_{9-12}), br, chol, amy (tr), APAA (C_{16-20}), phy	77.6				38.7	-27.2	6.7	9.0	6.8
ZAM2-204	Ceramic[1, 3]	EN	ms	169.6	SFA ($C_{10:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{7-13}$), Gly (1-$C_{16}$,1,2-$C_{16}$, 1,3-$C_{16}$), br, chol, APAA ($C_{16-20}$), tmtd, phy	76.3								
ZAM2-205	Foodcrust[1]	EN	es	116.0	SFA ($C_{14:0-26:0}$), br, amy, terp, APAA (C_{16-20})		-30.08	-29.3	0.82	50.5	-27.1	1.6	1.1	38.0
ZAM2-205	Ceramic[1]	EN	es	5.9	SFA ($C_{12:0-28:0}$), DC (C_9), br									
ZAM2-206	Foodcrust[1, 3]	EN	ms	8059.2	SFA ($C_{14:0-22:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-12}$), Gly (1-$C_{16}$,1,2-$C_{16}$, 1,3-$C_{16}$), br, chol, APAA ($C_{16-20}$), tmtd, pri, phy	79.3	-28.13	-28.1	0.03	40.5	-27.4	7.5	9.5	6.3
ZAM2-207	Ceramic[1]	EN	es	18.5	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-12}), br, chol, APAA (C_{18}), tmtd (tr)		-28.85	-29.8	-0.99	49.7	-26.7	2.6	2.8	22.4
	Foodcrust[1]	EN	es	727.0	SFA ($C_{14:0-22:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), br, amy, APAA (C_{18})									
ZAM2-208	Foodcrust[1]	EN	es	567.9	SFA ($C_{9:0-26:0}$), UFA ($C_{18:1}$), DC ($C_{7-18,\ 20,\ 22}$), br, terp, APAA (C_{16-20}), tmtd, phy	74.9	-29.62	-28.7	0.96	46.4	-25.9	6.9	9.4	7.8
ZAM2-209	Foodcrust[1]	EN	es	3225.0	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC ($C_{9-12,\ 18,\ 20,\ 22}$), br, amy, APAA (C_{16-18}), phy (tr)	tr	-27.77	-28.2	-0.41	49.4	-26.4	1.7	-0.7	33.1
ZAM2-210	Foodcrust[1, 3]	EN	es	599.2	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC ($C_{9-13,\ 18,\ 20,\ 22}$), Alkol (C_{18}), br, amy, APAA (C_{16-20}), phy	79.3	-28.96	-29.7	-0.74	32.1	-25.8	4.5	6.6	8.3

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-210	Ceramic[1]	EN	es	15.2	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC ($C_{7-9, 11}$), br		-29.69	-29.8	-0.10					
ZAM2-50683	Foodcrust[1,3]	EN	n/a	n/a	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), br, chol, amy, terp, APAA (C_{16-20}), tmtd (tr), phy	76.1	-27.70	-28.1	-0.40	53.5	-25.0	6.0	6.3	10.4
ZAM2-50684	Foodcrust[2]	EN	n/a	n/a	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), br, amy, APAA (C_{16-20}), tmtd, phy	72.7	-29.16	-29.1	0.11	56.5	-25.5	2.4	2.8	27.2
ZAM2-50685	Foodcrust[1]	EN	n/a	n/a	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1}$), DC (C_9), br, chol, APAA (C_{18}) (tr), tmtd (tr), phy (tr)	tr	-27.71	-28.0	-0.26	45.2	-25.0	6.0	6.0	8.9
ZAM2-50686	Foodcrust[1,3]	EN	n/a	n/a	SFA ($C_{14:0-30:0}$), UFA ($C_{18:1}$), DC (C_9), Alk ($C_{18, 20, 22}$), br, chol, terp, APAA (C_{16-20}), tmtd, phy	82.6	-25.42	-27.0	-1.61	36.9	-24.0	2.9	7.9	15.0
ZAM2-50687	Foodcrust[1,3]	EN	n/a	n/a	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_9), Alk (C_{20}), br, chol, terp, APAA (C_{16-20}), phy	55.4	-31.39	-30.1	1.34	50.1	-28.3	6.3	7.1	9.2
ZAM2-50688	Foodcrust[1]	EN	n/a	n/a	SFA ($C_{14:0-30:0}$), UFA ($C_{18:1}$), DC (C_9), br, chol, APAA (C_{16-20}), tmtd, phy	71.1	-28.92	-31.5	-2.60	48	-25.2	8.2	7.0	6.8
ZAM2-50689	Foodcrust[2]	EN	n/a	n/a	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), br, chol, APAA (C_{18}) (tr), phy	70.9	-28.96	-28.9	0.05	47.8	-25.1	6.1	7.2	9.2
ZAM2-50690	Foodcrust[2]	EN	n/a	n/a	SFA ($C_{14:0-30:0}$), UFA ($C_{18:1}$), br, APAA (C_{18-20}), tmtd (tr), phy	77.6	-30.47	-29.6	0.87	50.9	-26.6	6.3	7.8	9.5

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-10-72	Foodcrust[1]	MN	III	1213.7	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 17:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{9-18}$), br, abie (tr), APAA ($C_{16-20}$), tmtd, pri (tr), phy	82.0	-31.29	-31.1	0.23	24.7	-27.7	4.6	8.8	6.3
ZAM2-10-75	Ceramic[1]	MN	II	7.7	SFA ($C_{12:0-20:0}$), UFA ($C_{16:1,\ 18:1}$), br, abie (tr), APAA (C_{18}) (tr)		-29.89	-29.6	0.33					
	Foodcrust[1]	MN	II	1552.8	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 17:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{12,\ 13}$), br, chol, terp, APAA (C_{16-20}), tmtd, pri, phy	91.1	-24.85	-26.0	-1.18	45.4	-24.7	7.8	11.5	6.8
ZAM2-G8	Foodcrust[1]	MN	n/a	1384.7	SFA ($C_{12:0-28:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-11}$), br, chol, abie, terp, APAA (C_{16-20}),pri (tr), phy	70.5	-28.28	-28.8	-0.49	23.4	-25.6	3.8	8.8	7.1
ZAM2-G9	Foodcrust[1,4]	MN	n/a	187.2	SFA ($C_{12:0-28:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1}$), br, abie, APAA ($C_{18}$) (tr)					48.0	-27.6	6.1	10.6	9.0
ZAM2-G10	Foodcrust[1]	MN	n/a	496.9	SFA ($C_{12:0-32:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{14}$), br, abie, APAA ($C_{16-18}$), pri (tr)					52.0	-27.6	6.4	9.4	8.5
ZAM2-4636	Foodcrust int[1]	MN	n/a	4079.8	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), br, APAA (C_{16-20}), tmtd, phy	86.2	-23.84	-25.5	-1.63	43.6	-25.2	5.9	9.4	8.6
	Foodcrust ext[1]	MN	n/a	523.5	SFA ($C_{14:0-22:0}$), UFA ($C_{16:1,\ 18:1}$), br, abie, APAA (C_{16-20}), tmtd (tr), pri (tr), phy	84.6	-24.54	-25.8	-1.30	47.3	-23.8	8.4	8.7	6.6
ZAM2-4642-x	Foodcrust[1]	MN	n/a	4054.1	SFA ($C_{13:0-28:0}$), UFA ($C_{16:1-18:1,\ 20:1}$), br, chol, abie, APAA (C_{16-22}), tmtd, phy (tr)	tr	-28.48	-28.6	-0.10	50	-26.4	9.0	8.8	6.5

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-4654-25	Foodcrust[1]	MN	n/a	1744.2	SFA ($C_{14:0-34:0}$), UFA ($C_{16:1-18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{10-12}$), br, chol, terp, APAA (C_{16-20}), tmtd, pri (tr), phy	90.7	-24.96	-25.4	-0.42	45.5	-23.5	9.2	10.2	5.8
ZAM2-4655-1	Foodcrust[1]	MN	n/a	942.7	SFA ($C_{14:0-32:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{11}), br, terp, APAA (C_{16-20}), tmtd (tr), pri (tr), phy	87.6	-26.98	-28.2	-1.20	44.3	-24.8	7.5	11.6	6.9
ZAM2-4655-2	Foodcrust[1]	MN	n/a	873.4	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1-18:1}$), br, chol, terp, APAA (C_{16-20}), tmtd, pri (tr), phy	88.2	-25.22	-26.7	-1.47	35.6	-24.9	6.6	11.8	6.3
ZAM2-6221-543	Foodcrust[1]	MN	n/a	415.8	SFA ($C_{14:0-28:0}$), UFA ($C_{18:1}$), br, chol, abie, APAA (C_{16-20}), tmtd (tr), pri (?), phy	84.7				44.9	-25.5	6.8	11.1	7.7
ZAM2-4659-607	Foodcrust[1]	MN	n/a	95.5	SFA ($C_{15:0-30:0}$), UFA ($C_{18:1,\ 22:1}$), br, APAA (C_{16-20}), pri (tr), phy	81.8				46.3	-25.9	6.8	14.6	7.9
ZAM2-4659-604	Foodcrust[1]	MN	n/a	661.6	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), DC ($C_{11,\ 12}$), br, chol, APAA (C_{16-20}), tmtd, phy	79.0	-27.88	-28.3	-0.44	34.3	-25.8	5.6	12.3	7.2
ZAM2-4659-635	Foodcrust[1]	MN	n/a	877.1	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), br, chol, abie, APAA (C_{16-20}), tmtd, pri (tr), phy	89.7	-28.98	-29.7	-0.68	41.3	-26.2	7.2	12.0	6.7
ZAM2-4659-639	Foodcrust[1]	MN	n/a	233.1	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), br, chol, APAA (C_{16-20}), tmtd (tr), pri (tr), phy	86.1				41.5	-26.2	5.8	10.5	8.3
ZAM2-6221-421	Foodcrust[1]	MN	n/a	823.4	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1-18:1,\ 20:1}$), br, chol, phyol, abie, APAA (C_{16-20}), tmtd, pri (tr), phy	83.8	-33.30	-33.5	-0.20	47.8	-26.4	9.1	17.0	6.2

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-6221-488	Foodcrust[1]	MN	n/a	660.7	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), br, chol, APAA (C_{16-20}), tmtd, pri (tr), phy	85.5	-31.58	-30.8	0.76	40	-27.5	6.3	11.4	7.4
ZAM2-6221-536	Foodcrust[1]	MN	n/a	93.1	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), br, APAA (C_{16-20}), pri (?)					48.5	-28.5	6.2	10.0	9.1
ZAM2-6221-592	Foodcrust[1]	MN	n/a	455.7	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{12}), br, chol, abie, terp, APAA (C_{16-20}), tmtd, pri (tr), phy	89.3	-27.46	-27.9	-0.41	42.1	-25.9	6.9	10.3	7.1
ZAM2-6357-343	Foodcrust[1]	MN	n/a	1612.8	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), br, amy, terp, APAA (C_{16-20}), tmtd, phy	tr	-29.75	-29.0	0.77	39.1	-25.1	1.9	0.6	24.0
ZAM2-14-28	Foodcrust[1]	MN	n/a	139.4	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1}$), br, APAA (C_{16-20}), pri (tr), phy	73.5				47.9	-25.9	7.3	16.9	7.6
ZAM2-14-31	Foodcrust[1]	MN	n/a	789.3	SFA ($C_{14:0-32:0}$), UFA ($C_{16:1-18:1,\ 20:1,\ 22:1,\ 24:1}$), br, chol, abie, APAA (C_{16-20}), tmts (?), pri (tr), phy	85.0	-29.70	-30.0	-0.26	47	-26.5	5.3	9.4	10.3
ZAM2-355	Ceramic[1]	MN	III	119.8	SFA ($C_{10:0-30:0}$), UFA ($C_{18:1}$), DC (C_{9-11}), Alk ($C_{16-19,\ 22,\ 23,\ 25}$), br, chol, abie, tmtd, phy	74.1	-29.18	-29.9	-0.72					
ZAM2-356	Ceramic[1]	MN	III	175.5	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-11}$), Alk ($C_{18}$), br, chol, APAA ($C_{16-20}$), tmtd, phy	78.1	-32.00	-31.4	0.55					
ZAM2-358	Ceramic[1]	MN	II	10.7	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1}$), br, tmtd, pri, phy	13.9	-30.04	-29.2	0.83					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-359	Ceramic[1]	MN	II	17.8	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1}$), Alk (C_{17}), br, APAA (C_{16-22}), tmtd, pri, phy	58.6	-30.66	-30.4	0.27					
ZAM2-360	Ceramic[1]	MN	III	38.3	SFA ($C_{14:0-22:0}$), UFA ($C_{18:1}$) (tr), DC (C_{11}), br, chol, APAA (C_{16-20}), tmtd, phy	59.6	-29.66	-29.5	0.13					
ZAM2-361	Ceramic[1]	MN	III	251.5	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1-18:1, 20:1}$), DC (C_{8-11}), br, chol, APAA (C_{16-20}), tmtd, phy	78.9	-25.22	-26.2	-1.03					
ZAM2-363	Ceramic[1]	MN	III	62.2	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{9-15}), br, chol, APAA (C_{16-20}), tmtd, phy	52.7	-27.85	-28.4	-0.53					
ZAM2-365	Ceramic[1]	MN	II	24.7	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{11}), br, chol, APAA (C_{16-20}), tmtd, pri, phy	40.4	-28.85	-29.0	-0.17					
ZAM2-366	Ceramic[1]	MN	n/a	6.6	SFA ($C_{14:0-20:0}$), br, tmtd (tr), pri (tr), phy	16.9	-29.06	-29.3	-0.20					
ZAM2-368	Ceramic[1]	MN	II?	63.6	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC (C_{9-15}), br, chol, APAA (C_{16-20}), tmtd, phy	65.4	-31.55	-31.3	0.28					
ZAM2-369	Ceramic[1]	MN	III	80.1	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{9-13}), br, chol, APAA (C_{16-20}), tmtd, phy	68.6	-29.55	-30.0	-0.49					
ZAM2-370	Ceramic[1]	MN	III?	9.6	SFA ($C_{14:0-20:0}$), br, tmtd, pri (tr), phy	11.1	-30.54	-30.0	0.59					
ZAM2-371	Ceramic[1]	MN	III	5.0	SFA ($C_{15:0-20:0}$), UFA ($C_{18:1}$) (tr), br, abie (tr), tmtd tr), pri (tr), phy	11.2	-29.92	-29.8	0.11					
ZAM2-372	Ceramic[1]	MN	III	19.9	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1, 18:1}$) (tr), br, abie (tr), APAA (C_{16-20}), tmtd, pri (tr), phy	25.6	-29.21	-29.3	-0.11					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-373	Ceramic[1, 4]	MN	III?	111.2	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_{11-15}), 9,10-diHFAC$_{18}$ (tr), br, chol, APAA (C_{16-22}), tmtd, phy	79.3	-30.63	-31.0	-0.41					
ZAM2-374	Ceramic[1, 4]	MN	II	91.9	SFA ($C_{13:0-24:0}$), UFA ($C_{18:1,\ 20:1}$), DC (C_{11}), 9,10-diHFAC$_{18}$ (tr), br, APAA (C_{16-22}), tmtd, phy	79.2	-29.57	-30.1	-0.58					
ZAM2-375	Ceramic[1]	MN	II	9.2	SFA ($C_{14:0-24:0}$), UFA ($C_{18:1,\ 22:1}$) (tr), br, chol (tr), tmtd, pri, phy	40.2	-28.99	-29.4	-0.41					
ZAM2-376	Ceramic[1]	MN	II	18.2	FA ($C_{14:0-26:0}$), UFA ($C_{18:1}$) (tr), DC (C_{11}), br, chol, abie tr), APAA (C_{16-18}) (tr), tmtd, phy	43.7	-29.20	-29.3	-0.08					
ZAM2-378	Ceramic[1]	MN	III	25.8	SFA ($C_{14:0-24:0}$), UFA ($C_{18:1}$) (tr), DC (C_{11-15}), br, chol (tr), APAA (C_{16-20}), tmtd, phy	80.2	-31.43	-31.1	0.29					
ZAM2-379	Ceramic[1]	MN	III	11.0	SFA ($C_{14:0-20:0}$), UFA ($C_{18:1}$) (tr), br, APAA (C_{16-18}) (tr), tmtd, pri, phy	7.1	-30.27	-30.0	0.26					
ZAM2-331	Ceramic[1]	MN	II	21.4	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1}$), br, abie (tr), APAA (C_{16-20}), tmtd (tr), phy	5.9	-30.23	-30.0	0.24					
	Foodcrust[1]	MN	II	84.3	SFA ($C_{16:0-24:0}$), br, APAA (C_{16-20}), pri (tr), phy	35.5				39.5	-25.9	6.17	9.4	7.4
ZAM2-332	Ceramic[1, 4]	MN	II	31.9	SFA ($C_{13:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{10-14}), br, chol (tr), APAA (C_{16-22}), tmtd, pri, phy	62.9	-30.89	-30.7	0.14					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-332	Foodcrust[1]	MN	II	973.6	SFA ($C_{13:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$) (tr), DC (C_{10-14}), br, chol, APAA (C_{16-20}), tmtd, pri, phy	76.4	-31.58	-31.3	0.29	27.6	-27.8	4.37	9.8	7.2
ZAM2-333	Ceramic[1]	MN	II	1.5	SFA ($C_{10:0-24:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), DC ($C_{9,\ 8}$), br, chol, APAA (C_{16-20}), tmtd, pri, phy	29.6								
	Foodcrust[1]	MN	II	199.1	SFA ($C_{15:0-30:0}$), UFA ($C_{18:1}$) (tr), br, APAA (C_{16-20}), tmtd (tr), pri, phy	79.3				40.4	-26.5	7.23	13.4	6.5
ZAM2-335	Ceramic[1]	MN	II	10.5	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1,22:1}$), DC (C_{9}) (tr), Alk (C_{17}), br, APAA (C_{16-18}), tmtd, pri (tr), phy	4.2	-29.85	-29.5	0.39					
	Foodcrust[1]	MN	II	47.4	SFA ($C_{16:0-30:0}$), br, APAA (C_{16-20}), pri (tr), phy	17.1				26.4	-26.8	4.55	13.0	6.9
ZAM2-336	Ceramic[1]	MN	II	160.0	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{8-14}$), br, chol, APAA ($C_{16-20}$), tmtd, phy	0.0	-28.61	-29.9	-1.34					
	Foodcrust[1]	MN	II	485.0	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{12}), br, chol, APAA (C_{16-20}), tmtd (tr), pri (tr), phy	85.5	-27.97	-29.0	-1.03	31.3	-25.1	6.45	9.1	5.7
ZAM2-337	Ceramic[1]	MN	III	38.6	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), DC ($C_{9,\ 11}$) (tr), br, APAA (C_{18}), tmtd, phy	6.0	-30.33	-29.7	0.60					
	Foodcrust[1]	MN	III	67.7	SFA ($C_{16:0-30:0}$), UFA ($C_{18:1}$) (tr), br, APAA (C_{16-20}), tmtd (tr), phy	30.1				35	-24.5	5.91	14.4	6.6
ZAM2-338	Ceramic[1]	MN	III?	24.4	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), DC (C_{9-13}), br, chol, terp, APAA (C_{16-20}), pri, phy	54.4	-31.86	-31.6	0.28					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-338	Foodcrust[1]	MN	III?	449.4	SFA ($C_{14:0-30:0}$), UFA ($C_{18:1,\ 20:1}$), br, chol, abie, APAA (C_{16-22}), tmtd, pri (tr), phy	72.2	-31.60	-31.1	0.48	39.6	-27.2	5.99	11.6	7.7
ZAM2-339	Ceramic[1]	MN	III	6.2	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), DC (C_{9-12}), br, chol, APAA (C_{16-20}), tmtd, pri, phy	17.4								
	Foodcrust[1]	MN	III	54.8	SFA ($C_{16:0-28:0}$), br, chol, APAA (C_{16-20}), pri (tr), phy	57.8				37.7	-27.0	5.94	12.0	7.3
ZAM2-340	Ceramic[1]	MN	III	3.7	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), br, APAA (C_{16-18}), tmtd (tr), pri, phy	8.4								
	Foodcrust[1,4]	MN	III	122.0	SFA ($C_{15:0-30:0}$), APAA (C_{16-22}), tmtd (tr), phy	39.2				37.1	-26.8	5.05	9.3	9.1
ZAM2-341	Ceramic[1]	MN	II	439.6	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1-18:1}$), DC ($C_{10,\ 11}$), chol, APAA (C_{16-22}), tmtd, phy	0.0	-28.75	-28.6	0.18					
	Foodcrust[1]	MN	II	1667.6	SFA ($C_{13:0-26:0}$), UFA ($C_{16:1-18:1,\ 20:1}$), DC (C_{9-12}), chol, terp, APAA (C_{16-22}), tmtd, pri, phy	77.2	-27.08	-27.6	-0.47	27.8	-25.6	4.47	6.0	7.2
ZAM2-343	Ceramic[1]	MN	II?	14.0	SFA ($C_{11:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{8-13}), chol, APAA (C_{16-20}), tmtd, phy	64.8	-26.18	-28.2	-2.06					
	Foodcrust[1]	MN	II?	445.1	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{10-13}), chol, APAA (C_{16-20}), tmtd (tr), pri, phy	81.9	-24.58	-25.5	-0.94	31	-25.6	4.85	13.7	7.4
ZAM2-344	Ceramic[1]	MN	n/a	190.1	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-14}$), chol, terp (tr), APAA (C_{16-22}), tmtd, phy	0.0	-32.77	-31.8	1.00					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-344	Foodcrust[1]	MN	n/a	339.7	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), chol (tr), APAA (C_{16-22}), tmtd, pri, phy	68.0	-29.69	-29.4	0.24	31.4	-26.0	4.85	8.6	7.6
ZAM2-348	Ceramic[1]	MN	II	42.1	SFA ($C_{13:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{10-15}), terp, APAA (C_{16-22}), tmtd, phy	42.3	-29.89	-29.4	0.54					
	Foodcrust[1,4]	MN	II	1245.7	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC ($C_{11,\ 12}$), 9,10-diHFAC$_{18}$ (tr), chol, APAA (C_{16-22}), tmtd, pri, phy	73.2	-28.77	-28.9	-0.13	30.7	-26.1	5.77	8.8	6.3
ZAM2-349	Ceramic[1]	MN	III	45.6	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{11-12}) (tr), APAA (C_{16-18}), tmtd (tr), phy	9.2	-30.00	-29.7	0.29					
	Foodcrust[1]	MN	III	160.0	SFA ($C_{15:0-30:0}$), UFA ($C_{18:1,\ 20:1}$) (tr), chol, APAA (C_{16-22}), tmtd (tr), pri (tr), phy	78.1				35.4	-25.8	6.07	11.4	6.9
ZAM2-350	Ceramic[1]	MN	III	14.4	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{11}), APAA (C_{16-18}) (tr), tmtd, phy	24.9	-30.55	-29.8	0.77					
ZAM2-350	Foodcrust[1]	MN	III	133.6	SFA ($C_{15:0-28:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), chol, APAA (C_{16-20}), tmtd, pri, phy	80.1				32.6	-29.0	4.71	10.0	8.0
ZAM2-351	Ceramic[1]	MN	II	26.6	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{8-12}), APAA (C_{16-20}), tmtd (tr), pri, phy	59.8	-28.07	-28.4	-0.28					
	Foodcrust[1]	MN	II	210.2	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), APAA (C_{16-20}), pri (tr), phy	68.6				25.2	-25.7	3.56	9.7	7.7
ZAM2-352	Ceramic[1]	MN	n/a	28.0	SFA ($C_{12:0-24:0}$), UFA ($C_{18:1,\ 20:1,\ 22:1}$), DC (C_9) (tr), APAA (C_{16-20}), tmtd, pri (tr), phy	28.2	-30.15	-29.9	0.29					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-352	Foodcrust[1]	MN	n/a	14.7	SFA ($C_{16:0-24:0}$), br, APAA (C_{16-20}),pri (?), phy	48.4				16.2	-25.9	4.79	13.0	6.7
ZAM2-353	Ceramic[1]	MN	III?	50.3	SFA ($C_{13:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{9-15}), br, chol, APAA (C_{16-20}), tmtd, phy	76.1	-29.04	-29.5	-0.50					
	Foodcrust[1]	MN	III?	1945.3	SFA ($C_{13:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1}$), DC (C_{9-15}), br, chol, terp, APAA (C_{16-20}), tmtd, phy	86.9	-28.19	-28.7	-0.53	43.3	-27.0	6.40	8.1	7.7
ZAM2-354	Ceramic[1]	MN	II?	3.8	SFA ($C_{13:0-30:0}$), UFA ($C_{18:1}$), br, APAA (C_{18}), phy	3.9								
	Foodcrust[1]	MN	II?	21.1	SFA ($C_{16:0-26:0}$), br, APAA (C_{16-20}), phy	29.6				37.6	-28.1	5.07	12.2	8.5
ZAM2-290	Ceramic[1]	EN	ms	81.8	SFA ($C_{13:0-30:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1}$), DC (C_{9-11}), br, chol (tr), abie, APAA (C_{16-20}), tmtd, pri, phy	68.6	-28.26	-29.2	-0.90					
ZAM2-291	Ceramic[1, 4]	EN	ms	70.8	SFA ($C_{10:0-32:0}$), UFA ($C_{15:1-18:1,\ 20:1,\ 24:1}$), DC ($C_{8-11}$), br, chol, APAA ($C_{16-20}$) (?), tmtd		-26.79	-28.9	-2.16					
ZAM2-292	Ceramic[1]	EN	es	33.3	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-12}), Alk (C_{17}), br, APAA (C_{16-20}), tmtd, pri, phy	86.2	-24.41	-25.6	-1.15					
ZAM2-293	Ceramic[1]	EN	ms	13.4	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), Alk ($C_{17,\ 18}$), br, abie (tr), tmtd, pri, phy	33.0	-29.81	-29.7	0.14					
ZAM2-294	Ceramic[1]	EN	ms	3.6	SFA ($C_{15:0-28:0}$), UFA ($C_{18:1}$) (tr), br, tmtd (tr), pri, phy (tr)	tr								
ZAM2-295	Ceramic[1, 4]	EN	ms	11.5	SFA ($C_{16:0}$, $C_{18:0}$), tmtd (tr), pri (tr), phy (tr)	tr	-29.84	-29.6	0.25					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-296	Ceramic[1]	EN	ms	55.6	SFA ($C_{12:0-20:0}$), UFA ($C_{18:1}$), DC (C_{11}), Alk ($C_{16, 17}$), br, abie (tr), APAA (C_{16-20}) (tr), tmtd, pri, phy	72.7	-23.71	-26.0	-2.32					
ZAM2-300	Ceramic[1, 4]	EN	ms	84.2	SFA ($C_{13:0-26:0}$), UFA ($C_{16:1, 18:1}$), Alk (C_{17}), br, chol, phyol (tr), abie (tr), APAA (C_{16-20}), tmtd, pri, phy	82.9	-26.63	-27.8	-1.15					
ZAM2-303	Ceramic[1]	EN	ms	7.9	SFA ($C_{16:0}$, $C_{18:0}$), UFA ($C_{18:1, 22:1}$), tmtd (tr), pri (tr), phy (tr)	tr	-30.04	-29.8	0.24					
ZAM2-304	Ceramic[1]	EN	ls	209.4	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC (C_{9-15}), br, chol, tmtd, phy	n/a	-29.05	-28.3	0.79					
ZAM2-305	Ceramic[1]	EN	ls	4.8	SFA ($C_{14:0-30:0}$), UFA ($C_{18:1, 22:1}$), br, tmtd, pri, phy	36.3	-29.69	-29.8	-0.13					
ZAM2-306	Ceramic[1]	EN	ls	609.0	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1-18:1, 20:1, 22:1}$), DC ($C_{9-17}$), br, chol, amy, terp, APAA (C_{16-20}), tmtd, phy (tr	tr	-27.07	-28.9	-1.79					
ZAM2-307	Ceramic[1]	EN	ls	12.2	SFA ($C_{14:0-28:0}$), UFA ($C_{18:1, 22:1}$), br, APAA (C_{18}) (tr), tmtd, pri (tr), phy	19.1	-30.09	-29.9	0.18					
ZAM2-309	Ceramic[1]	EN	ms	8.8	SFA ($C_{14:0-30:0}$), UFA ($C_{15:1, 16:1, 18:1, 20:1, 22:1}$), DC ($C_{11}$), br, abie, APAA ($C_{16-18}$), tmtd, pri, phy	33.1	-27.43	-29.2	-1.78					
ZAM2-311	Ceramic[1]	EN	ms	28.3	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1, 18:1}$), br, chol, abie (tr), terp (tr), APAA (C_{16-20}), tmtd, pri, phy	71.5	-30.41	-29.8	0.57					

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-312	Ceramic[1]	EN	es	29.5	SFA ($C_{14:0-28:0}$), UFA ($C_{17:1, 18:1, 20:1, 22:1}$), DC ($C_{11}$), br, chol, abie (tr), APAA (C_{16-18}), tmtd, pri, phy	66.5	-27.07	-27.5	-0.38					
ZAM2-313	Ceramic[1]	EN	es	14.5	SFA ($C_{13:0-30:0}$), UFA ($C_{15:1, 16:1, 18:1, 22:1}$), DC ($C_{11}$), br, chol, abie, APAA (C_{16-18}) (tr), tmtd, phy	37.2	-28.04	-29.3	-1.27					
ZAM2-315	Ceramic[1]	EN	I.1 (type with chamotte)	132.5	SFA ($C_{14:0-30:0}$), UFA ($C_{15:1, 18:1, 22:1}$), DC (C_{9-11}), br, chol, abie, APAA (C_{16-18}), tmtd, phy	84.4	-26.86	-28.4	-1.49					
ZAM2-317	Ceramic[1]	EN	I.1 (type with chamotte)	315.0	SFA ($C_{12:0-32:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC ($C_{9-13, 15}$), br, chol, terp, APAA (C_{16-20}), tmtd, pri, phy	85.8	-22.19	-22.6	-0.36					
ZAM2-318	Ceramic[1]	EN	I.1 (type with chamotte)	63.4	SFA ($C_{14:0-28:0}$), UFA ($C_{15:1, 16:1, 18:1, 20:1, 22:1}$), DC ($C_{16, 18, 29, 22}$), br, abie, terp, APAA (C_{16-20}), tmtd, pri, phy	69.5	-29.69	-29.6	0.06					
ZAM2-kia51172-J001	Ceramic[1]	EN	ms	376.1	SFA ($C_{12:0-28:0}$), UFA ($C_{15:1-18:1}$), DC (C_{9-15}), chol, APAA (C_{16-18}), tmtd, phy	63.7								

Sample	Type	Phase	Stage	Lipid conc. (ug/g)	Compounds detected	SRR %	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
ZAM2-kia51172-J001	Foodcrust[2,3]	EN	ms	n/a	SFA ($C_{12:0-27:0}$), UFA ($C_{18:1, 20:1, 22:1}$), DC ($C_{9, 11, 12}$), br, chol, terp, APAA (C_{16-18}), tmtd (?), phy (tr)	tr	-25.74	-25.3	0.46					
ZAM2-kia51173-J002	Foodcrust[2,3]	EN	n/a	n/a	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1, 24:1}$), br, chol, terp, APAA (C_{18}) (tr)		-28.22	-26.5	1.74					
VirbModern-01	Virbunum (Opilus L.) berry[1]	Modern			SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1, 18:2, 20:1}$), phyol, terp, amy		-34.1	-34.3	-0.27					
ZMOD42	Elk[1]	Modern					-30.5	-32.03	-1.53					
ZMOD52	Elk[1]	Modern					-29.83	-30.96	-1.13					
ZMOD51	Beaver[1]	Modern					-30.79	-30.98	-0.19					
ZMOD16	Pike[1]	Modern					-31.61	-30.98	0.63					
ZMOD28	Perch[1]	Modern					-32.43	-32.33	0.10					
ZMOD30	Cyprinids[1]	Modern					-29.15	-29.64	-0.49					
ZMOD34	Cyprinids[1]	Modern					-31.64	-30.07	1.57					
ZMOD6	Bream[1]	Modern					-31.04	-28.63	2.41					

Sherds, internal **(**int) and external **(**ext) foodcrusts were extracted by acid-methanol extraction[1], solvent extraction and methylated[2], solvent extraction and trimethylsilylated[3]. Acid extracted lipids were trimethylsilylated in a selection of sherds[4]. ($C_{n:x}$) - carboxilic acids with carbon length n and number of unsaturations x, SFA – saturated fatty acid, UFA – unsaturated fatty acids, DC - α,ω-dicarboxylic acids, Alk – alkane, Alkol – alkanol, Alkone – alkanone, diHFA- dihydroxy fatty acid, gly – glycerol, APAA - ω-(o-alkylphenyl) alkanoic acids, br -branched chain acids dominated by *iso* and *anteiso* C_{15} and C_{17}, tmtd - 4,8,12-trimethyltridecanoic acid, pri – pristanic acid, phy – phytanic acid with the percentage contribution of SRR diastereomer in total phytanic acid, chol - cholesterol or derivatives, phyol - phytosterol or derivatives, abie – dehydroabietic acid, terp – indicate the presence of one or several terpenes, amy- α- and β- amyrin or derivatives. Samples from EN – Early Neolithic (es –, ms –, ls –, early stage, middle stage, late stage respectively) and MN – Middle Neolithic.

Appendix 10: List of samples from Rakushechny Yar selected for lipid analysis (GCMS, GC-c-IRMS) and bulk isotope characteristics of charred deposits (EA-IRMS).

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-86	Foodcrust int	EN	20	1375.8	SFA ($C_{9:0-24:0}$), UFA ($C_{15:1, 16:1, 18:1, 20:1, 22:1}$), DC ($C_{9-13}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	n/a				24.8	-25.4	3.7	9.1	8.1
Raku-87	Foodcrust int	EN	20	1894.0	SFA ($C_{14:0-24:0}$), UFA ($C_{15:1-18:1, 20:1, 22:1, 24:1}$), DC ($C_{11-13}$), br, terp, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri		-29.4	-29.8	-0.4	8.1	-26.2	0.8	10.2	11.0
Raku-88	Foodcrust int*	EN	20	4733.3	SFA ($C_{12:0-24:0}$), UFA ($C_{14:1-16:1, 18:1, 22:1}$), DC ($C_{9-13}$), br, terp, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri		-28.9	-28.5	0.4	13.5	-26.4	1.6	10.2	9.9
Raku-89	Foodcrust int*	EN	14	1812.2	SFA ($C_{12:0-20:0}$), UFA ($C_{15:1, 16:1, 18:1, 20:1, 22:1}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-28.6	-29.7	-1.1	25.9	-25.2	2.3	9.8	12.9
Raku-90	Ceramic	EN	14	275.6	SFA ($C_{11:0-26:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1}$), DC ($C_{8-16}$), br, Alk ($C_{15, 16, 18, 20}$), terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	32.5	-25.5	-25.6	-0.1					
	Foodcrust int	EN	14	1461.9	SFA ($C_{14:0-24:0}$), UFA ($C_{14:1, 16:1, 18:1, 22:1, 24:1}$), DC ($C_{13}$) (tr), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-27.5	-28.5	-0.9	10.6	-25.7	0.8	10.5	15.9

Sample	Type	Phase	Layers	Lipid conc. (μg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-91	Foodcrust int	EN	14	2864.6	SFA ($C_{14:0-24:0}$), UFA ($C_{14:1-16:1\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol (tr), tmtd, phy, pri	tr	-28.1	-28.7	-0.7	6.8	-25.2	0.7	11.1	10.9
Raku-92	Ceramic	EN	14-15	42.4	SFA ($C_{9:0-26:0}$), UFA ($C_{14:1,\ 16:1,\ 18:1,\ 22:1}$), Alk ($C_{15-18,\ 20,\ 22-24,\ 26-28}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri									
	Foodcrust int*	EN	14-15	1510.0	SFA ($C_{12:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{9-11,\ 13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	63.2	-28.8	-28.5	0.3	27.2	-28.5	2.2	10.1	15.8
Raku-93	Ceramic	EN	14-15	379.6	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{7-16}), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	52.5	-24.6	-26.1	-1.5					
	Foodcrust int	EN	14-15	870.0	SFA ($C_{14:0-26:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), Alk ($C_{14-20}$), Alkone (16-$K_{31}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	tr	-27.9	-28.8	-0.9	22.9	-25.8	2.1	7.5	12.7
Raku-94	Foodcrust int	EN	14-15	885.7	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 24:1}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.8	-29.2	-1.5					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-95	Ceramic	EN	14	53.5	SFA ($C_{12:0-24:0}$), UFA ($C_{14:1,\ 16:1,\ 18:1,\ 22:1}$), Alk ($C_{15-17,\ 19,\ 20}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-29.3	-29.1	0.2					
	Foodcrust int	EN	14	1339.5	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.3	-29.0	-0.7	26.9	-26.8	2.8	10.1	10.8
Raku-96	Ceramic*	EN	12	38.8	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{11,\ 12}$), Alk ($C_{17,\ 18,\ 20-24}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	59.8	-27.6	-27.6	0.0					
	Foodcrust int	EN	12	10.8	SFA ($C_{14:0-26:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 18:2,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.3	-28.1	-0.9	19.8	-25.3	2.4	14.1	10.0
Raku-97	Ceramic	EN	12	115.8	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{9,\ 11}$), Alk ($C_{15,\ 16,\ 18-24}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	58.0	-28.8	-28.0	0.8					
	Foodcrust int	EN	12	2457.7	SFA ($C_{14:0-26:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.4	-28.2	-0.8	10.3	-23.8	1.1	10.8	12.2
Raku-98	Foodcrust int	EN	12	1557.7	SFA ($C_{14:0-30:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	tr	-28.1	-27.8	0.3	18.4	-25.5	1.4	11.5	15.1

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-99	Ceramic*	EN	12	118.8	SFA ($C_{8:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9}), Alk($C_{15-24,\ 28,\ 29}$), br, terp, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	tr	-27.9	-27.8	0.1					
	Foodcrust int	EN	12	2052.1	SFA ($C_{12:0-24:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-29.0	-29.2	-0.2	16.6	-25.7	2.5	10.1	7.9
Raku-100	Foodcrust int	EN	11	3223.1	SFA ($C_{13:0-24:0}$), UFA ($C_{14-16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.5	-28.3	0.2	8.7	-25.7	1.0	8.4	10.7
Raku-101	Foodcrust int	EN	11	2369.0	SFA ($C_{12:0-24:0}$), UFA ($C_{14:1-18:1,\ 20:1,\ 22,\ 24:1}$), DC ($C_{11,\ 13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.5	-28.5	0.0	20.2	-25.8	1.8	10.4	13.1
Raku-102	Foodcrust int	EN	11	1590.0	SFA ($C_{13:0-26:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.7	-29.1	-0.4	17.2	-26.2	2.2	11.7	8.7
Raku-103	Foodcrust int	EN	11	929.5	SFA ($C_{14:0-26:0}$), UFA ($C_{15:1,\ 16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{11-14}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	tr	-27.5	-26.9	0.6	25.7	-24.7	2.5	11.7	11.3
Raku-104	Foodcrust int	EN	11	2538.2	SFA ($C_{14:0-24:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 24:1}$), DC ($C_{13}$) (tr), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.3	-28.9	-0.6	9.7	-24.5	1.1	9.4	9.7

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-105	Foodcrust int	EN	11	1969.8	SFA ($C_{12:0-26:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1, 24:1}$), br, terp, APAA ($C_{16, 18, 20}$), chol (tr), tmtd, phy, pri	29.7	-28.6	-29.2	-0.6	10.7	-26.1	1.2	11.9	10.2
Raku-106	Ceramic	EN	11	70.1	SFA ($C_{10:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), Alk ($C_{15-24, 26, 27}$),br, terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.3	-29.3	0.0					
	Foodcrust int*	EN	11	1858.9	SFA ($C_{14:0-20:0}$), UFA ($C_{14:1, 16:1, 18:1, 22:1}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-27.3	-28.6	-1.3	21.4	-25.1	3.1	11.3	8.9
Raku-107	Foodcrust int*	EN	11	1523.2	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1, 24:1}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-28.1	-28.4	-0.4	13.3	-27.0	2.1	7.4	7.9
Raku-108	Ceramic int	EN	11	32.4	SFA ($C_{11:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_9), Alk ($C_{17-18, 22-24}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.7	-29.5	0.2					
	Foodcrust int	EN	11	1374.6	SFA ($C_{12:0-26:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C_{11, 13}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-28.4	-28.6	-0.3	12.4	-26.9	1.4	10.2	10.1
Raku-109	Foodcrust int	EN	11	1257.1	SFA ($C_{12:0-26:0}$), UFA ($C_{14:1-18:1, 20:1, 22:1, 24:1}$), DC ($C_{11, 13}$), br, terp, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	tr	-28.2	-27.8	0.4	23.5	-25.3	2.3	11.8	11.4
Raku-110	Foodcrust int	EN	11	1498.3	SFA ($C_{13:0-26:0}$), UFA ($C_{14:1-18:1, 18:2, 20:1, 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-28.7	-30.1	-1.4	7.1	-27.8	0.5	6.5	15.1

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-111	Foodcrust int	EN	11	2242.4	SFA ($C_{14:0-28:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C_{13}$), br, terp, APAA ($C_{16, 18, 20}$), chol (tr), tmtd, phy, pri		-28.1	-28.5	-0.3	11.1	-25.5	1.5	9.8	8.4
Raku-112	Ceramic*	EN	11	73.3	SFA ($C_{16:0-24:0}$), UFA ($C_{16:1, 18:1, 22:1}$), Alk ($C_{22-24, 26-29}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.9	-29.6	0.3					
Raku-113	Foodcrust int	EN	11	1256.5	SFA ($C_{11:0-24:0}$), UFA ($C_{14-16:1, 18:1, 20:1, 22:1}$), DC ($C_{7-12}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri					28.0	-26.2	2.8	10.5	11.8
Raku-114	Ceramic	EN	11	26.2	SFA ($C_{11:0-28:0}$), UFA ($C_{16:1, 18:1}$), DC (C_9), Alk (C_{20-30}), br, terp*, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.9	-29.8	0.2					
Raku-114	Foodcrust int*	EN	11	1306.5	SFA ($C_{14:0-24:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1, 24:1}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.3	-29.9	-0.6	9.7	-30.3	0.7	6.8	16.1
Raku-115	Foodcrust int*	EN	11	1830.6	SFA ($C_{12:0-19:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 20:1, 22:1, 24:1}$), DC ($C_{9-13}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.0	-30.3	-1.3	15.0	-25.6	2.1	10.6	8.5
Raku-116	Foodcrust int	EN	11	743.2	SFA ($C_{8:0-25:0}$), UFA ($C_{14:1-16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C_{6-13}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri					20.8	-23.6	2.1	12.6	11.4

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-151	Ceramic*	EN	11	108.2	SFA ($C_{8:0-23:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), Alk (C_{20-30}), br, terp, HAP, tmtd, phy, pri (tr)	tr	-28.5	-29.2						
	Foodcrust int	EN	11	931.6	SFA ($C_{9:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-13}), Alk (C_{20-38}), br, terp*, tmtd (tr), phy	tr	-29.1	-29.3		2.3	-27.7	0.1	6.4	31.7
Raku-152	Ceramic*	EN	11	173.7	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{7,\ 9-14}$), Alk ($C_{15-17,\ 22-24,\ 27-30}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	47.9	-27.5	-28.7	-1.2					
Raku-153	Ceramic	EN	20	286.1	SFA ($C_{6:0-26:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{6,\ 7,\ 9-12}$), Alk ($C_{15-18,\ 22-24}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), chol (tr), tmtd, phy, pri	57.8	-25.7	-26.4	-0.7					
Raku-154	Ceramic	EN	23	41.3	SFA ($C_{12:0-28:0}$), UFA ($C_{15:1-16:1,\ 18:1,\ 22:1}$), DC ($C_{11-13}$), Alk ($C_{16,\ 20,\ 22-24}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.0	-28.7	-0.7					
Raku-155	Ceramic	EN	19	622.8	SFA ($C_{8:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{8,\ 9,\ 11,\ 18}$), Alk ($C_{14-24}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), chol (tr), tmtd, phy, pri	tr	-26.6	-27.4	-0.7					
Raku-156	Ceramic*	EN	19	684.6	SFA ($C_{14:0-26:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{11,\ 13}$), Alk ($C_{22,\ 24}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.9	-28.9	0.0					

Sample	Type	Phase	Layers	Lipid conc. (μg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-157	Ceramic	EN	14	105.9	SFA ($C_{11:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-15}$), Alk (C16, 22-24), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	45.5	-26.7	-27.7	-1.0					
Raku-158	Ceramic	EN	14	80.6	SFA ($C_{11:0-24:0}$), UFA ($C_{14:1-16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-15}$), Alk ($C_{18,\ 22,\ 23}$), br, terp, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	62.9	-26.2	-26.5	-0.3					
Raku-159	Ceramic	EN	16	264.6	SFA ($C_{6:0-28:0}$), UFA ($C_{14:1-16:1,\ 20:1,\ 22:1}$), DC ($C_{9-14}$), Alk (C15-33), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	68.8	-25.7	-26.1	-0.4					
Raku-258	Ceramic	EN	(17-19?)	18.2	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC ($C_{11,\ 13}$), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	58.2	-26.7	-27.2	-0.5					
Raku-259	Ceramic	EN	(17-19?)	83.9	SFA ($C_{10:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{8-15}$), Alk ($C_{27,\ 29}$), Alkone (10-$K_{29}$), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	50.3	-26.6	-26.7	-0.1					
Raku-260	Ceramic	EN	(17-19?)	42.5	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-15}), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	56.9	-25.6	-26.6	-1.0					
Raku-261	Ceramic	EN	pit 2 (11-14?)	65.6	SFA ($C_{11:0-26:0}$), UFA ($C_{18:1,\ 20:1}$), DC (C_{9-16}), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	31.2	-23.5	-23.7	-0.2					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-262	Ceramic	EN	pit 2 (11-14?)	19.1	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1}$), DC (C_{11-15}), br, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	23.6	-25.8	-26.6	-0.8					
Raku-263	Ceramic	EN	vivip 3	65.3	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC (C_{11}), br, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	54.6	-26.9	-27.3	-0.4					
Raku-264	Ceramic*	EN	20	1.1	SFA ($C_{14:0-24:0}$), UFA ($C_{18:1, 22:1}$), Alk (C19-25), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	tr	-27.2	-29.1	-2.0					
Raku-265	Ceramic	EN	20	16.4	SFA ($C_{12:0-24:0}$), UFA ($C_{18:1, 22:1}$), DC (C_9) (tr), Alk (C18-24), br, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	tr	-28.0	-27.9	0.1					
Raku-266	Ceramic	EN	13	92.0	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{9-13}), Alk (C15-24), br, terp, HAP (tr), APAA ($C_{16, 18, 20}$), tmtd, phy, pri	57.0	-26.3	-26.5	-0.2					
Raku-267	Ceramic	EN	20	34.2	SFA ($C_{13:0-24:0}$), UFA ($C_{18:1, 22:1}$), DC (C_{11}), Alk ($C_{16-24, 26, 27}$), br, terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	71.0	-27.0	-27.4	-0.4					
Raku-268	Ceramic	EN	21	1.7	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{13}), Alk (C_{20-24}), br, terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-28.6	-29.3	-0.6					
Raku-269	Ceramic*	EN	20	620.4	SFA ($C_{12:0-29:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC ($C_{9, 11}$), Alk (C_{16-33}), br, terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-29.2	-29.0	0.2					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-270	Ceramic	EN	20	111.6	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-15}$), Alk ($C_{16-29}$), br, terp, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	38.6	-25.0	-25.9	-0.8					
Raku-271	Ceramic*	EN	20	52.6	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{11}) (tr), Alk (C17-33), br, terp, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.0	-27.9	0.1					
Raku-272	Ceramic*	EN	20	113.9	SFA ($C_{11:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_9), Alk (C_{16-27}), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.1	-27.6	-0.5					
Raku-273	Ceramic	EN	21	364.6	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{11}), Alk (C_{17-33}), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	27.3	-26.4	-27.8	-1.4					
Raku-274	Ceramic*	EN	21	37.6	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), Alk (C_{17-31}), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-28.7	-29.3	-0.6					
Raku-275	Ceramic	EN	20	66.2	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{9-16}), Alk (C_{16-29}), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	53.0	-25.5	-25.7	-0.3					
Raku-276	Ceramic	EN	19	79.6	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), DC (C_{9-16}), Alk ($C_{17,\ 18,\ 20-32}$), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	59.2	-26.0	-26.7	-0.7					

Sample	Type	Phase	Layers	Lipid conc. (μg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-277	Ceramic*	EN	19	33.6	SFA ($C_{12:0-24:0}$), Alk (C17-29), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri		-28.6	-28.6	0.1					
Raku-278	Ceramic	EN	15a	240.3	SFA ($C_{8:0-28:0}$), UFA ($C_{16:1, 18:1}$), DC (C_9), Alk (C_{15-25}), br, terp*, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	50.6	-25.7	-25.8	-0.1					
Raku-279	Ceramic	EN	13a	98.1	SFA ($C_{13:0-26:0}$), UFA ($C_{18:1, 20:1, 22:1, 24:1}$), DC ($C_{11-15}$), Alk ($C_{17-24}$), br, terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	33.0	-26.8	-26.8	0.0					
Raku-280	Ceramic	EN	15a	119.7	SFA ($C_{11:0-24:0}$), DC (C_{8-16}), Alk (C_{15-33}), br, terp, HAP, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	54.0	-25.9	-25.7	0.2					
Raku-281	Ceramic	EN	14-15	13.3	SFA ($C_{13:0-24:0}$), UFA ($C_{22:1}$), Alk (C_{17-25}), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	tr	-27.5	-27.1	0.4					
Raku-282	Ceramic	EN	13	22.5	SFA ($C_{12:0-25:0}$), UFA ($C_{18:1, 22:1}$), Alk ($C_{17-24, 26}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	17.4	-26.7	-27.1	-0.4					
Raku-283	Ceramic	EN	10	109.5	SFA ($C_{13:0-32:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC (C_{10-15}), Alk (C_{17-31}), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	26.1	-27.0	-27.4	-0.3					
Raku-284	Ceramic	EN	11	16.6	SFA ($C_{14:0-26:0}$), UFA ($C_{18:1, 22:1}$), Alk ($C_{17-24, 26}$), br, terp, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	41.3	-28.1	-29.2	-1.1					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-286	Ceramic	EN	11	125.6	SFA ($C_{14:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{11}$), Alk ($C_{22-25}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	75.3	-26.0	-26.6	-0.6					
Raku-287	Ceramic	EN	11	110.2	SFA ($C_{8:0-26:0}$), UFA ($C_{18:1}$) (tr), DC (C_{9-11}), Alk (C_{16-29}), br, terp*, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.5	-28.4	-0.9					
Raku-288	Ceramic	EN	12	40.5	SFA ($C_{14:0-28:0}$), UFA ($C_{16:1,\ 18:1}$), DC (C_{11}), Alk (C_{17-28}), Alkone (16-K_{31}), br, terp*, HAP (tr), APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	68.9								
Raku-289	Ceramic*	EN	14	57.8	SFA ($C_{14:0-26:0}$), UFA ($C_{15,\ 16:1,\ 18:1,\ 22:1}$), Alk ($C_{17-33}$), br, terp, HAP (tr), APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.2	-28.6	-1.3					
Raku-913	Ceramic	EN	Gray sand	61.0	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{7-15}), HAP, 9-10diHFA (C_{18}), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	44.6	-27.0	-27.6	-0.6					
	Foodcrust ext	EN	Gray sand	306.9	SFA ($C_{11:0-30:0}$), UFA ($C_{18:1,\ 22:1}$) (tr), DC (C_{7-13}), br, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	48.2	-27.4	-26.6	0.7	43.2	-26.1	3.2	7.4	15.8
Raku-914	Ceramic	EN	vivip 2	65.3	SFA ($C_{11:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{8-13}), 9-10diHFA (C_{18}), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	29.5	-27.4	-28.0	-0.7					
	Foodcrust int	EN	vivip 2	n/a	pas d'extraction mais bulk/ not enough sample for extraction					25.0	-25.7	1.2	10.6	23.7

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	$\delta^{13}C$ (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-915	Ceramic	EN	17-19	109.4	SFA ($C_{11:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{8-12}$), Alk ($C_{14-17}$), Alkone (16-$K_{31}$), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol (tr), tmtd, phy, pri	42.3	-25.9	-26.4	-0.6					
	Foodcrust int	EN	17-19	85.7	SFA ($C_{14:0-24:0}$), UFA ($C_{16:1,\ 18:1}$) (tr), DC (C_{9-12}), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	tr	-24.9	-24.8	0.1	23.1	-27.2	2.4	8.2	11.2
Raku-916	Ceramic	EN	vivip 2	400.1	SFA ($C_{12:0-22:0}$), UFA ($C_{18:1,\ 22:1}$), DC (C_{9-11}), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	75.7	-27.8	-30.0	-2.3					
	Foodcrust int	EN	vivip 2	514.5	SFA ($C_{10:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{7-13}), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	80.3	-27.2	-26.9	0.3	26.9	-28.4	4.2	7.5	7.5
Raku-917	Ceramic	EN	vivip 2	713.8	SFA ($C_{9:0-26:0}$), UFA ($C_{18:1,\ 22:1}$), DC (C_{9-13}), br, terp, APAA ($C_{16,\ 18,\ 20}$), Alkone (16-K_{31}), tmtd, phy, pri		-26.1	-29.1	-3.1					
	Foodcrust int	EN	vivip 2	519.7	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{8-15}), br, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	78.8	-26.0	-28.0	-2.0	22.7	-27.8	3.1	8.3	8.6
Raku-918	Ceramic	EN	17-19	11.4	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{8-12}$), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-26.5	-27.7	-1.2					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-919	Ceramic	EN	17-19	214.0	SFA ($C_{9:0-22:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{6-13}), Alk ($C_{11-12, 14-17}$), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	45.5	-25.8	-26.3	-0.5					
	Foodcrust int	EN	17-19	233.8	SFA ($C_{11:0-30:0}$), UFA ($C_{16:1, 18:1, 22:1}$), DC (C_{7-13}), Alkone (16-K_{31}), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	48.2	-26.2	-26.3	-0.1	22.7	-26.9	1.9	7.6	13.9
	Foodcrust ext	EN	17-19	945.6	SFA ($C_{7:0-30:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C_{5-13}$), Alk ($C_{11, 14, 15, 17}$), br, HAP, APAA ($C_{16, 18, 20}$), chol (tr), tmtd, phy, pri	48.4	-25.1	-25.5	-0.4	37.0	-26.5	1.7	10.8	25.7
Raku-920	Ceramic	EN	17-19	224.7	SFA ($C_{9:0-24:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C7_{-12}$), Alkone (16-$K_{31}$), br, HAP, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	41.4	-25.0	-25.4	-0.3					
	Foodcrust int	EN	17-19	239.6	SFA ($C_{9:0-28:0}$), UFA ($C_{16:1, 18:1, 18:2, 20:1, 22:1, 24:1}$), DC ($C_{7-14}$), Alk ($C_{12-17-33}$), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	53.0	-24.9	-24.9	0.0	27.9	-25.6	3.6	11.3	9.0

Sample	Type	Phase	Layers	Lipid conc. (μg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
Raku-921	Ceramic	EN	21/23	596.2	SFA ($C_{8:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 18:2,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{6-12}$), Alk ($C_{16,\ 17}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, phyol, tmtd, phy, pri	58.7	-26.3	-27.0	-0.7					
	Foodcrust int	EN	21/23	1826.6	SFA ($C_{8:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{5-14}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	56.0	-25.2	-25.7	-0.4	28.7	-27.1	2.5	12.2	13.6
	Foodcrust ext	EN	21/23	1562.2	SFA ($C_{10:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{6-12}), Alk (C15, 16, 17), br, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	58.9	-25.5	-25.8	-0.3	41.7	-26.0	2.3	12.7	21.7
Raku-922	Ceramic	EN	17-19	297.0	SFA ($C_{11:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{7-13}), Alk ($C_{14,\ 15,\ 16,\ 17}$), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol (tr), tmtd, phy, pri	56.6	-27.6	-27.6	-0.1					
	Foodcrust int	EN	17-19	77.8	SFA ($C_{10:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{6-13}), br, APAA ($C_{16,\ 18,\ 20}$), chol (tr), tmtd, phy, pri		-28.0	-27.9	0.0	16.2	-30.2	1.6	7.4	11.6
Raku-923	Ceramic	EN	21/23	91.2	SFA ($C_{10:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{7-13}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, phyol, tmtd, phy, pri	60.6	-26.7	-27.5	-0.8					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-924	Ceramic	EN	vivip 2	49.6	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C_{8-15}$), br, APAA ($C_{16, 18, 20}$), chol (tr), tmtd, phy, pri	29.7	-26.4	-26.7	-0.3					
	Foodcrust int	EN	vivip 2	453.9	SFA ($C_{9:0-30:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$), DC ($C_{7-13}$), br, APAA ($C_{16, 18, 20}$), tmtd, phy, pri	37.6	-25.9	-25.5	0.5	37.7	-26.2	1.1	10.9	40.2
Raku-925	Ceramic	EN	21/23	167.2	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1, 18:1, 20:1, 24:1}$), br, HAP, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	49.6	-24.2	-25.8	-1.6					
Raku-926	Ceramic	EN	vivip 2	65.5	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1, 24:1}$), DC ($C_{9, 11-15}$), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	49.2	-25.9	-27.0	-1.1					
	Foodcrust ext	EN	vivip 2	3701.5	SFA ($C_{8:0-28:0}$), UFA ($C_{16:1, 18:1, 20:1}$), DC (C_{6-13}), Alk (C_{17}), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	50.0	-23.8	-24.2	-0.4	34.4	-25.5	1.2	10.2	32.4
Raku-927	Ceramic	EN	Gray sand uder viv	12.5	SFA ($C_{11:0-28:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$) (tr), DC ($C_{8-14}$), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	58.5	-28.1	-28.0	0.1					
	Foodcrust int	EN	Gray sand uder viv	1741.4	SFA ($C_{9:0-26:0}$), UFA ($C_{16:1, 18:1, 20:1, 22:1}$), DC ($C_{6-14}$), br, APAA ($C_{16, 18, 20}$), chol, tmtd, phy, pri	62.3	-28.1	-27.9	0.3	37.1	-28.4	4.3	9.6	10.0

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-928	Ceramic	EN	vivip 1	63.4	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-12}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	tr	-25.1	-26.8	-1.7					
Raku-929	Ceramic	EN	vivip 1	72.2	SFA ($C_{10:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{7-15}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	24.8	-25.7	-26.5	-0.8					
	Foodcrust ext	EN	vivip 1	541.4	SFA ($C_{10:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 24:1}$), DC ($C_{7-15}$), Alk ($C_{17}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	27.4	-24.6	-24.3	0.2	41.5	-25.5	1.4	11.5	34.1
Raku-930	Ceramic	EN	vivip 1	3.2	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{8-14}), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	50.5	-28.8	-29.3	-0.6					
Raku-931	Ceramic	EN	vivip 1	8.4	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_9) (tr), Alk ($C_{23,\ 27,\ 29}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, phyol, tmtd, phy, pri		-29.6	-28.6	1.0					
Raku-932	Ceramic	EN	15-16	8.7	SFA ($C_{13:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{9-13}), Alk ($C_{29,\ 27}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, phyol, tmtd, phy, pri	42.0	-25.7	-27.1	-1.3					
Raku-334	Ceramic	EN	vivip 1	27.6	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{8-15}), 9-10diHFA (C_{18}), br, HAP, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri		-27.7	-28.2	-0.5					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-933	Ceramic	EN	15-16	13.0	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-13}$), Alk ($C_{27}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	51.9	-25.4	-26.6	-1.2					
Raku-935	Ceramic	EN	17-19	40.3	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1,\ 22:1}$), DC ($C_{9-15,\ 18}$), Alk ($C_{29}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-27.2	-28.2	-0.9					
Raku-936	Ceramic	LN/EL	4-5	144.3	SFA ($C_{10:0-26:0}$), UFA ($C_{18:1,\ 22:1}$), DC (C_{7-16}), br, terp, APAA ($C_{16,\ 18,\ 20}$), tmtd, phy, pri	59.2	-29.7	-31.5	-1.8					
	Foodcrust int	LN/EL	4-5	187.5	SFA ($C_{10:0-30:0}$), UFA ($C_{14:1,\ 16:1,\ 18:1,\ 18:2,\ 20:1,\ 22:1}$), DC ($C_{8-13}$), Alk ($C_{33}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-27.9	-28.4	-0.5	6.9	-29.8	0.6	7.3	14.5
Raku-937	Ceramic	LN/EL	4-5	14.4	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{13}), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-29.5	-29.7	-0.2					
Raku-938	Ceramic	LN/EL	4-5	12.2	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{13}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-28.9	-29.1	-0.2					
Raku-939	Ceramic	LN/EL	4-5	14.0	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 18:2,\ 20:1,\ 22:1}$), DC ($C_{9,\ 11-13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, copr, tmtd, phy, pri		-26.1	-28.1	-2.0					
Raku-940	Ceramic	LN/EL	4-5	13.4	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9,\ 11,\ 13}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-28.9	-29.4	-0.6					

Sample	Type	Phase	Layers	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	δ^{15}N (‰)	C:N
Raku-941	Ceramic	LN/EL	4-5	35.7	SFA ($C_{10:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9,\ 11,\ 13}$), br, HAP, APAA ($C_{16,\ 18,\ 20}$), chol, copr, tmtd, phy, pri	tr	-27.7	-28.4	-0.7					
	Foodcrust int	LN/EL	4-5	135.3	SFA ($C_{12:0-30:0}$), UFA ($C_{16:1,\ 18:1,\ 18:2,\ 22:1}$), DC ($C_{8-10}$), Alk ($C_{29,\ 34}$), br, terp, APAA ($C_{16,\ 18,\ 20}$), chol, phyol, copr, tmtd, phy, pri		-27.3	-27.2	0.1	5.3	-21.4	0.5	8.6	12.6
	Foodcrust ext	LN/EL	4-5	267.7	SFA ($C_{9:0-32:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1}$), DC (C_{6-16}), Alk ($C_{27,\ 29,\ 33}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, copr, tmtd, phy, pri		-27.6	-28.0	-0.4	13.5	-26.8	1.4	11.9	11.2
Raku-942	Ceramic	LN/EL	3?	654.3	SFA ($C_{11:0-24:0}$), UFA ($C_{16:1,\ 18:1,\ 22:1,\ 24:1}$), DC ($C_{9-17}$), Alk ($C_{17}$), br, APAA ($C_{16,\ 18,\ 20}$), copr, tmtd, phy, pri	46.7	-29.3	-29.0	0.4					
	Foodcrust ext	LN/EL	3?	199.9	SFA ($C_{12:0-32:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-13}$), Alk ($C_{33}$), br, terp, HAP, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-27.6	-27.4	0.2	17.3	-25.4	2.7	12.4	7.6
Raku-943	Ceramic	LN/EL	4-5	55.4	SFA ($C_{12:0-28:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-15}$), Alk ($C_{27,\ 29}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri	65.2	-26.9	-27.3	-0.4					
Raku-944	Ceramic	LN/EL	4?	15.7	SFA ($C_{12:0-26:0}$), UFA ($C_{16:1,\ 18:1,\ 20:1,\ 22:1}$), DC ($C_{9-11,\ 13}$), br, APAA ($C_{16,\ 18,\ 20}$), chol, tmtd, phy, pri		-28.1	-29.2	-1.1					

Sample	Type	Area site	Lipid conc. (µg g-1)	Major compounds detected	SRR (%)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	Δ13C ($C_{18:0}$-$C_{16:0}$)	%C	δ^{13} C (‰)	%N	$\delta^{15}N$ (‰)	C:N
SedMB 01	Sediment (clay)	Excavation 3 area	10.3	SFA ($C_{12:0-30:0}$), UFA ($C_{18:1}$), DC ($C_{16, 18-22}$), br, Alk ($C_{25, 27, 29, 31}$), phyol									
SedMB 02	Sediment	Excavation 3 area	0.7	SFA ($C_{16:0-28:0}$), UFA ($C_{18:1}$), DC ($C_{16, 18-22}$), Alk (C_{27}) (tr)									
SedMB 03	Sediment	Excavation 3 area	15.8	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1, 18:1}$), DC (C_{18-25}), br, Alk ($C_{27, 29}$), Triterp, phyol									
SedMB 04	Sediment (ash)	Excavation 3 area	29.1	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{16, 18, 20, 22}$), br, Alk ($C_{27, 29}$), phyol									
SedMB 05	Sediment	Excavation 1/4 area	0.3	SFA ($C_{16:0-28:0}$), UFA ($C_{18:1, 22:1}$)									
SedMB 06	Sediment	Excavation 1/4 area	37.6	SFA ($C_{14:0-30:0}$), UFA ($C_{16:1, 18:1}$), DC ($C_{19, 30}$), br, Alk ($C_{27, 29}$), Triterp, phyol									
SedMB 07	Sediment	Excavation 1/4 area	2.4	SFA ($C_{14:0-30:0}$), UFA ($_{18:1}$) (tr), br, Alk ($C_{23-25, 27, 29}$)									
SedMB 08	Sediment	Excavation 1/4 area	0.8	SFA ($C_{15:0-30:0}$), br									

Sherds, internal (int) and external (ext) foodcrusts were all analysed by acid-methanol extraction and a selection of samples by solvent extraction and trimethylsilylated [2] - carboxilic acids (Cn:x) with carbon length n and number of unsaturations x, SFA – saturated fatty acid, UFA – unsaturated fatty acids, DC - α,ω-dicarboxylic acids, Alk – alkane, Alkone – alkanone, PAH – polyaromatic hydrocarbons, APAA - ω-(o-alkylphenyl) alkanoic acids, br -branched chain acids dominated by *iso* and *anteiso* C_{15} and C_{17}, tmtd - 4,8,12-trimethyltridecanoic acid, pri – pristanic acid, phy – phytanic acid with the percentage contribution of SRR diastereomer in total phytanic acid, chol - cholesterol or derivatives, phyol - phytosterol or derivatives, Copr – coprostanol, abie –, terp – terpenes (mainly methyl-dehydroabietic acid and 7-oxo- dehydroabietic acid), Triterp – triterpenes, samples from EN – Early Neolithic and LN/EL – Late Neolithic/Eneolithic

Appendix 11: Stable carbon isotopic of *n*-hexadecanoic ($C_{16:0}$) and *n*-octadecanoic ($C_{18:0}$) acid of reference fats from modern animal products. Data are from different studies, with additional new freshwater fish and shellfish, ruminants and terrestrial plants from Rakushechny Yar region or Western Russia.

Common name	Provenience	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	Reference
Freshwater fish					
Pike	Denmark	-34.8	-35.0	-0.2	Craig et al. 2011
Tench	Denmark	-27.7	-28.8	-1.1	Craig et al. 2011
Tench	Denmark	-24.2	-26.3	-2.1	Craig et al. 2011
Tench	Denmark	-37.2	-36.5	0.7	Craig et al. 2011
Freshwater fish	Kazakhstan	-32.1	-32.2	0.0	Outram et al. 2009
Freshwater fish	Kazakhstan	-32.1	-31.5	0.7	Outram et al. 2009
Freshwater fish	Kazakhstan	-31.8	-31.9	-0.1	Outram et al. 2009
Freshwater fish	Kazakhstan	-31.7	-31.4	0.3	Outram et al. 2009
Freshwater fish	Kazakhstan	-31.5	-31.4	0.1	Outram et al. 2009
Freshwater fish	Kazakhstan	-31.6	-29.9	1.7	Outram et al. 2009
Freshwater fish	Kazakhstan	-31.1	-30.9	0.2	Outram et al. 2009
Freshwater fish	Kazakhstan	-30.9	-30.4	0.5	Outram et al. 2009
Freshwater fish	Kazakhstan	-30.7	-30.2	0.5	Outram et al. 2009
Freshwater fish	Kazakhstan	-30.6	-30.6	0.0	Outram et al. 2009
Bleak	Finland	-26.6	-25.9	0.7	Pääkkönen et al. 2016
Bleak	Finland	-33.8	-32.3	1.5	Pääkkönen et al. 2016
Bleak	Finland	-34.1	-34.5	-0.4	Pääkkönen et al. 2016
Bleak	Finland	-35.6	-35.1	0.5	Pääkkönen et al. 2016
Bleak	Finland	-36.0	-34.5	1.5	Pääkkönen et al. 2016
Burbot	Finland	-34.3	-32.3	2.0	Pääkkönen et al. 2016

Common name	Provenience	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	Reference
Ide	Finland	-33.4	-31.8	1.6	Pääkkönen et al. 2016
Ide	Finland	-32.8	-31.2	1.6	Pääkkönen et al. 2016
Northern pike	Finland	-33.2	-32.9	0.3	Pääkkönen et al. 2016
Northern pike	Finland	-33.4	-32.2	1.2	Pääkkönen et al. 2016
Northern pike	Finland	-31.7	-31.3	0.4	Pääkkönen et al. 2016
Perch	Finland	-34.3	-33.2	1.1	Pääkkönen et al. 2016
Perch	Finland	-35.1	-34.6	0.5	Pääkkönen et al. 2016
Perch	Finland	-33.3	-32.5	0.8	Pääkkönen et al. 2016
Perch	Finland	-34.9	-33.3	1.6	Pääkkönen et al. 2016
Perch	Finland	-32.9	-32.3	0.6	Pääkkönen et al. 2016
Perch	Finland	-32.0	-32.3	-0.3	Pääkkönen et al. 2016
Perch	Finland	-32.0	-32.6	-0.6	Pääkkönen et al. 2016
Perch	Finland	-35.3	-36.8	-1.5	Pääkkönen et al. 2016
Perch	Finland	-35.2	-34.7	0.5	Pääkkönen et al. 2016
Pikeperch	Finland	-34.5	-33.7	0.8	Pääkkönen et al. 2016
Pikeperch	Finland	-30.2	-29.9	0.3	Pääkkönen et al. 2016
Roach	Finland	-29.4	-31.9	-2.5	Pääkkönen et al. 2016
Roach	Finland	-34.0	-32.9	1.1	Pääkkönen et al. 2016
Arctic grayling	Alaska	-40.9	-39.0	1.9	Choy et al 2016
Burbot	Alaska	-26.9	-28.2	-1.3	Choy et al 2016
Burbot	Alaska	-29.8	-28.8	1.0	Choy et al 2016
Northern pike	Alaska	-32.9	-30.7	2.2	Choy et al 2016
Northern pike	Alaska	-35.8	-35.6	0.2	Choy et al 2016
Northern pike	Alaska	-36.0	-35.0	1.0	Choy et al 2016
Sheefish	Alaska	-34.0	-34.4	-0.4	Choy et al 2016
Bering cisco	Alaska	-34.6	-34.3	0.3	Choy et al 2016
pike	Russia - Middle Don	-36.4	-35.5	1.0	

Common name	Provenience	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	Reference
roach	Russia - Middle Don	-36.3	-34.7	1.7	
crucian	Russia - Middle Don	-35.0	-34.2	0.8	
perch	Russia - Low Don	-32.1	-29.9	2.2	
Ide	Russia - Syktyvkar	-29.3	-29.0	0.3	
Cisco	Russia - Syktyvkar	-35.5	-35.5	0.0	
Grayling	Russia - Syktyvkar	-34.4	-34.1	0.3	
Pike	Russia - Syktyvkar	-35.0	-34.4	0.6	
Catfish	Russia-Low Don	-27.7	-27.8	-0.1	
Freshwater shell					
Unio	Russia-Low Don	-32.6	-31.8	0.7	
Unio	Russia-Low Don	-34.2	-33.5	0.8	
Unio	Russia-Low Don	-34.2	-33.1	1.1	
Unio	Russia-Low Don	-31.6	-31.2	0.4	
Unio	Russia-Low Don	-34.2	-33.0	1.2	
Unio	Russia-Low Don	-35.2	-34.1	1.1	
Unio	Russia-Low Don	-33.8	-32.2	1.5	
Unio	Russia-Low Don	-32.2	-30.2	2.0	
Unio	Russia-Low Don	-33.8	-32.8	1.0	
Unio	Russia-Low Don	-33.0	-31.2	1.9	
Viviparus	Russia-Low Don	-34.3	-33.3	1.0	
Viviparus	Russia-Low Don	-34.0	-33.9	0.1	
Viviparus	Russia-Low Don	-34.5	-33.1	1.4	

Common name	Provenience	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	Reference
Viviparus	Russia-Low Don	-33.7	-32.9	0.8	
Viviparus	Russia-Low Don	-33.4	-33.1	0.3	
Viviparus	Russia-Low Don	-32.8	-33.2	-0.4	
Viviparus	Russia-Low Don	-34.0	-32.7	1.3	
Viviparus	Russia-Low Don	-33.5	-33.2	0.3	
Viviparus	Russia-Low Don	-34.0	-33.7	0.3	
Viviparus	Russia-Low Don	-33.0	-32.5	0.5	
Migratory fish					
Salmon	Japan	-27.3	-28.0	-0.7	Craig et al. 2013
Salmon	Japan	-24.5	-26.1	-1.6	Craig et al. 2013
Salmon	Japan	-25.3	-26.6	-1.3	Craig et al. 2013
Trout	Japan	-26.0	-25.9	0.0	Craig et al. 2013
Trout	Japan	-26.8	-27.0	-0.2	Craig et al. 2013
Trout	Japan	-25.1	-25.5	-0.4	Craig et al. 2013
Trout	Japan	-24.1	-22.4	1.7	Lucquin et al 2016
Salmon	Japan	-25.8	-24.3	1.4	Lucquin et al 2016
Trout	Japan	-23.3	-23.7	-0.4	Lucquin et al 2016
Salmon	Japan	-27.9	-28.4	-0.5	Lucquin et al 2016
Cherry Salmon	Japan	-24.8	-23.8	1.0	Lucquin et al 2016
Coast Salmon	Japan	-23.7	-22.6	1.1	Lucquin et al 2016
Salmon	Japan	-25.8	-24.8	1.0	Lucquin et al 2016
Salmon	Finland	-25.0	-23.6	1.4	Pääkkönen et al. 2016
Salmon	Finland	-24.3	-23.9	0.4	Pääkkönen et al. 2016
Coho salmon	Alaska	-28.2	-26.6	1.6	Choy et al 2016
Coho salmon	Alaska	-27.8	-26.0	1.8	Choy et al 2016
Coho salmon	Alaska	-27.2	-25.0	2.2	Choy et al 2016
Chum salmon	Alaska	-26.2	-25.4	0.8	Choy et al 2016
Chum salmon	Alaska	-26.2	-24.8	1.4	Choy et al 2016

Common name	Provenience	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	Reference
Chum salmon	Alaska	-25.1	-23.5	1.6	Choy et al 2016
Sturgeon	Russia-Volga	-26.0	-26.2	-0.2	
Wild ruminant					
Red deer	Poland	-27.7	-31.5	-3.8	Craig et al. 2012
Red deer	Poland	-27.4	-31.1	-3.7	Craig et al. 2012
Red deer	Poland	-28.4	-32.6	-4.2	Craig et al. 2012
Red deer	Poland	-30.0	-33.7	-3.7	Craig et al. 2012
Red deer	Poland	-29.1	-32.7	-3.6	Craig et al. 2012
Red deer	Poland	-28.8	-33.0	-4.2	Craig et al. 2012
Red deer	Poland	-30.4	-33.0	-2.6	Craig et al. 2012
Red deer	Poland	-29.5	-33.1	-3.6	Craig et al. 2012
Red deer	Poland	-28.9	-32.3	-3.4	Craig et al. 2012
Red deer	Poland	-29.4	-33.0	-3.6	Craig et al. 2012
Red deer	Poland	-31.0	-33.1	-2.2	Spangenberg et al. 2006
Moose	Alaska	-30.8	-31.9	-1.1	Choy et al 2016
Roe deer	Russia - Middle Don	-31.1	-32.4	-1.3	
deer	Russia - Middle Don	-28.7	-32.0	-3.3	
Reindeer	Russia - Syktyvkar	-23.8	-24.9	-1.1	
elk	Russia - Upper Volga	-30.5	-32.0	-1.5	
elk	Russia - Upper Volga	-29.8	-31.0	-1.1	
Elk	Russia - Syktyvkar	-33.2	-34.8	-1.6	
Plants					
Bulrush	Russia - Low Don	-31.79	-33.1	-1.31	
Wild thym	Russia - Low Don	-38.51	-34.79	3.72	
Sylverberry	Russia - Low Don	-31.93	-31.94	-0.01	
Wild rose berry	Russia - Low Don	-28.98	-29.66	-0.68	
Dog rose berry	Russia - Low Don	-32.12	-32.69	-0.57	
Wild pear	Russia - Low Don	-33.53	-32.35	1.18	

Common name	Provenience	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ ($C_{18:0}$- $C_{16:0}$)	Reference
Wild apple	Russia - Low Don	-32.7	-30.1	2.6	
Ruminant dairy					
Cow	United Kingdom	-30.8	-34.4	-3.6	Dudd 1999
Cow	United Kingdom	-27.8	-32.1	-4.3	Dudd 1999
Sheep	United Kingdom	-29.4	-33.8	-4.4	Dudd 1999
Sheep	United Kingdom	-29	-33.4	-4.4	Dudd 1999
Cow	United Kingdom	-27.4	-32.2	-4.8	Dudd 1999
Cow	United Kingdom	-28.9	-33.7	-4.8	Dudd 1999
Cow	United Kingdom	-29.6	-34.9	-5.3	Dudd 1999
Cow	United Kingdom	-27.9	-33.1	-5.2	Dudd 1999
Cow	United Kingdom	-28.6	-34.1	-5.5	Dudd 1999
Cow	United Kingdom	-28.1	-34	-5.9	Dudd 1999

The $\delta^{13}C$ values of the modern references were adjusted for the addition of the effects of post-industrial carbon in order to facilitate the comparison with the archaeological samples (Schmitt et al. 2012; Hellevang and Aagaard 2015; Lucquin, Gibbs, et al. 2016).

Appendix 12: Bulk isotope measurement of archaeological collagen bones from Rakushechny Yar site.

Commone name	Collagen yielded (%)	%C	$\delta^{13}C$ (Collagen)	sdt	%N	$\delta^{15}N$ (collagen)	sdt	C:N
Freshwater fish								
Zander	3.2	37.4	-24.1	0.0	13.6	12.3	0.0	3.2
Zander	2.2	38.6	-16.5	0.3	13.9	12.9	0.0	3.2
Zander	5.8	42.2	-21.7	0.1	15.0	10.4	0.1	3.3
Zander	5.5	43.0	-21.0	0.0	15.8	11.9	0.2	3.2
Wel catfish	4.5	41.9	-24.0	0.1	14.4	11.2	0.2	3.4
Wild ruminant								
Red deer	14.3	41.6	-20.2	0.0	15.1	6.2	0.1	3.2
Red deer	13.2	42.5	-19.8	0.0	15.5	6.0	0.0	3.2
Non Ruminant								
Pig	8.4	44.2	-20.9	0.0	16.1	7.9	0.1	3.2
Pig	11.6	41.2	-20.8	0.0	15.1	8.4	0.0	3.2
Beaver	14.3	41.6	-20.2	0.0	15.1	6.2	0.1	3.2

Appendix 13: List of samples selected for ZooMS analysis and the results.

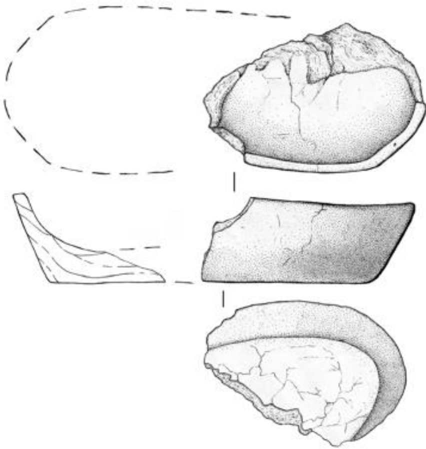
Sample ID	Zooarchaeological identification	Layer	P1	A1	A2	B	C	P2	D	E	F1	F2	G1	G2	ZooMS identification
Raku-0005	large mammal	pit	1105.6	-	-	1453.7	-	-	2131.1	2820.4	-	-	-	-	Pig[2]
Raku-0006	Sheep	15a	1105.6	1180.6	1196.6	1427.7	**1550.8**	1648.8	2131.1	-	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0010	large mammal	15a	1105.6	1180.6	1196.6	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0011	n/a	16	1105.6	-	-	1427.7	1550.8	1648.8	2131.1		2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0012	n/a	16	1105.6	1180.6		1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0013	medium mammal	16	1105.6	-	-	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0014	medium mammal	16	-	-	-	1453.7	-	-	2131.1	2820.4	2883.4	-	3017.5	3033.5	Pig[2]
Raku-0015	large mammal	17	1105.6	1180.6	1196.6	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0016	large mammal	17	1105.6	-	-	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0017	n/a	17	1105.6	-	-	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0018	Sheep	17	1105.6	-	-	1427.7	**1550.8**	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0019	large mammal	17	1105.6	-	-	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0021	large mammal	17	1105.6	-	-	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Red deer[1]
Raku-0023	medium mammal	17	1105.6	1180.6	1196.6	1427.7	1550.8	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	-	Red deer[1]
Raku-0024	large mammal	17	1105.6	-	-	1427.7	1550.8	1648.8	2131.1	-	2883.4	2899.4	-	-	Red deer[1]
Raku-0063	n/a	upper vivip layer 1	1106	1181	1196.6	1427.7	**1580.8**	1648.8	2131.1	2792.3	2883.4	2899.4	3017.5	3033.5	Sheep[2]

1 - ZooMS currently cannot distinguish between red deer (Cervus elaphus), fallow deer (Dama dama), and Eurpoean elk (Alces alces), however based on site context the most likely species is red deer. 2 - includes both domestic and wild species

Appendix 14: scheme showing the different forms and volumes of cooking pottery found at Rakushechny Yar.

Appendix 15: photo of Rakushechny Yar site showing the two excavated areas where the sherds analysed were recovered.

Appendix 16: Elongated ceramic found at Rakushechny Yar.



Appendix 17: Table summarizing the results of the thermal degradation of rapeseed oil and mono- and unsaturated fatty acids C_{18} (A) and various foodstuffs (B) carried out in laboratory and the experimental parameters.

Laboratory experiments

A

Product	Cooking time (h)	Cooking temperature(°C)	Sealed	Pottery amount (mg)	Approximate product amount (mg)	APAAs-C_{18} formed	APAAs-C_{20} formed	APAAs-C_{18} distribution									APAA-C_{20}/APAA-C_{18}	UFA-C_{20}/UFA-C_{18}	APAAs- C_{18} formed without pottery powder
								A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)			
Rape seed oil	1	270	yes	100	65	yes	no	0.4	1.1	2.2	5.1	13.1	17.8	30.1	16.4	13.9	-	-	yes
Rape seed oil	5	270	yes	100	65	yes	no	0.4	1.1	2.5	5.1	14.6	18.2	27.1	16.9	14.1	-	-	yes
Rape seed oil	10	270	yes	100	65	yes	no	0.4	1.1	2.8	5.3	17.0	18.5	25.7	15.7	13.5	-	-	yes
Rape seed oil	17	270	yes	100	65	yes	no	0.4	1.1	2.8	5.1	16.2	18.6	26.5	16.2	13.2	-	-	yes
Rape seed oil	1	270	no	100	65	yes	no	0.7	1.7	3.9	5.2	20.7	27.7	19.5	12.8	7.9			yes
Rape seed oil	5	270	no	100	65	yes	no	1.2	2.8	4.4	8.4	22.2	25.6	16.5	10.5	8.4	-	-	yes
Rape seed oil	5	250	no	100	65	yes	no	0.8	2.4	3.5	6.3	26.0	31.3	12.8	10.1	6.9	-	-	yes
Rape seed oil	5	200	no	100	65	yes	no	0.0	0.9	3.2	5.1	34.6	37.4	10.2	5.1	3.5	-	-	yes
Rape seed oil	5	150	no	100	65	no	no	-	-	-	-	-	-	-	-	-	-	-	no
Rape seed oil	5	100	no	100	65	no	no	-	-	-	-	-	-	-	-	-	-	-	no
C18:0	5	270	no	100	65	no	no	-	-	-	-	-	-	-	-	-	-	-	no
C18:0	5	270	no	100	65	no	no	-	-	-	-	-	-	-	-	-	-	-	no
C18:1	5	270	no	100	20	yes	no	2.3	7.1	14.2	21.6	22.0	14.1	8.5	4.9	5.3	-	-	yes
C18:1	5	270	no	100	20	yes	no	2.9	7.8	14.2	20.9	21.9	13.7	9.2	4.2	5.2	-	-	yes
C18:2	5	270	no	100	20	yes	no	0.5	1.3	2.3	6.5	34.8	37.7	9.0	3.6	4.3	-	-	yes
C18:2	5	270	no	100	20	yes	no	0.6	1.2	2.3	6.1	35.2	38.4	8.7	3.5	4.0	-	-	yes
α-C18:3	5	270	no	100	20	yes	no	0.2	0.6	0.7	2.3	9.9	25.9	25.6	23.6	11.2	-	-	yes
α-C18:3	5	270	no	100	20	yes	no	0.0	0.0	1.2	2.6	8.4	27.6	23.3	27.6	9.2	-	-	yes

B

Product	Cooking time (h)	Cooking temperature(°C)	Sealed	Pottery amount (mg)	Approximate product amount (mg)	APAAs-C_{18} formed	APAAs-C_{20} formed	APAAs-C_{18} distribution									APAA-C_{20}/APAA-C_{18}	UFA-C_{20}/UFA-C_{18}	Presence of APAAs in raw foodstuff
								A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)			
Terrestrial animal																			
Red Deer[1]	5	270	no	65	> 65	yes	yes	1.4	3.7	5.2	9.3	27.8	31.4	12.1	9.3	0.0	0.053	0.033	no
Organic Butter	5	270	no	65	> 65	yes	no	1.8	4.8	8.5	13.9	22.6	20.8	11.2	7.5	8.8	0.000	0.005	no
Elk	5	270	no	65	> 65	yes	yes	2.4	4.7	7.4	11.5	22.6	24.6	10.2	8.5	8.1	0.028	0.275	no
Red Deer[2]	5	270	no	65	> 65	yes	yes	1.0	2.1	3.3	6.9	28.9	33.1	10.7	8.1	6.0	0.056	0.037	no
Beaver-6	5	270	no	65	> 65	yes	yes	1.8	3.7	4.1	7.2	29.6	31.8	8.7	6.4	6.7	0.021	0.032	no
Pork	5	270	no	65	> 65	yes	yes	2.9	5.6	12.6	12.6	25.1	22.7	8.1	4.3	6.1	0.037	0.265	no
Aquatic animal																			
Cod Liver Oil	5	270	no	65	65	yes	yes	0.0	0.0	3.5	16.9	22.4	22.8	17.1	9.5	7.8	0.271	0.910	no
Salmon Fat	5	270	no	65	> 65	yes	yes	0.0	0.0	4.4	6.1	26.5	31.3	9.6	13.6	8.4	0.128	0.156	no
Salmon Oil	5	270	no	65	65	yes	yes	0.0	1.4	3.9	7.4	28.3	31.9	11.9	8.7	6.5	0.062	0.201	no
Duck	5	270	no	65	> 65	yes	yes	1.3	2.8	4.1	7.2	24.4	30.1	11.1	12.2	6.8	0.136	6.661	no
Catfish	5	270	no	65	> 65	yes	yes	2.5	5.2	6.4	12.7	29.3	21.5	8.6	7.7	6.1	0.212	0.397	no
Sturgeon	5	270	no	65	> 65	yes	yes	1.8	3.7	5.1	8.4	29.4	30.8	8.9	5.8	6.3	0.070	0.156	no
Unio Shellfish	5	270	no	65	> 65	yes	yes	1.5	2.9	5.0	8.5	24.2	28.1	12.8	10.1	6.9	0.154	1.689	no
Viviparus Shellfish	5	270	no	65	> 65	yes	yes	1.4	2.8	3.6	6.6	23.2	29.2	12.7	13.0	7.5	0.570	3.454	no
Perch	5	270	no	65	> 65	yes	yes	2.0	4.4	6.2	10.0	23.1	23.9	12.3	9.9	8.2	0.322	4.945	no
Terrestrial plant																			
Chestnut Flour	5	270	no	65	65	yes	no	3.2	4.9	5.3	8.1	25.6	28.3	10.5	6.8	7.4	0.000	0.000	no
Hazelnut Oil	5	270	no	65	65	yes	no	1.1	2.7	4.1	7.6	25.7	29.1	13.6	9.2	6.8	0.000	0.004	no
Hemp Oil	5	270	no	65	65	yes	no	1.6	3.9	6.1	11.0	28.8	28.1	9.4	5.1	6.1	0.000	0.001	no
Rice Bran Oil	5	270	no	65	65	yes	no	1.2	2.9	3.8	8.1	31.1	32.5	9.6	5.2	5.7	0.000	0.006	no
Walnut Oil	5	270	no	65	65	yes	no	1.3	2.5	3.0	7.1	28.1	30.9	12.9	7.7	6.6	0.000	0.002	no
Leek leave	5	270	no	65	300	yes	no	0.8	2.1	2.8	5.7	20.7	30.2	14.1	14.3	9.2	0.000	0.000	no
Leek white part	5	270	no	65	300	yes	no	1.0	2.4	3.2	6.5	28.8	33.1	10.8	7.5	6.8	0.000	0.000	no
Onion	5	270	no	65	300	yes	no	1.2	2.6	4.0	8.5	28.6	30.6	10.7	6.1	7.5	0.000	0.019	no
Cabbage	5	270	no	65	300	yes	no	0.9	2.4	2.4	4.1	15.0	28.6	18.1	19.0	9.5	0.000	0.007	no

Product	Cooking time (h)	Cooking temperature(°C)	Sealed	Pottery amount (mg)	Approximate product amount (mg)	APAAs-C_{18} formed	APAAs-C_{20} formed	APAAs-C_{18} distribution									APAA-C_{20}/APAA-C_{18}	UFA-C_{20}/UFA-C_{18}	Presence of APAAs in raw foodstuff
								A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)			
Almond	5	270	no	65	300	yes	no	1.5	3.1	3.7	6.4	34.9	35.2	6.1	4.0	5.2	0.000	0.000	no
Walnut	5	270	no	65	300	yes	no	1.6	3.0	3.5	6.3	31.6	34.0	8.2	5.4	6.5	0.000	0.000	no
Wheat	5	270	no	65	300	yes	no	1.5	2.9	3.5	6.1	31.9	34.6	8.1	5.1	6.4	0.000	0.000	no
Barley	5	270	no	65	300	yes	no	1.3	2.6	3.0	5.6	32.3	35.3	7.9	5.5	6.4	0.000	0.007	no
Carrot leave	5	270	no	65	300	yes	no	0.8	2.5	2.3	4.5	24.3	33.3	12.4	12.4	7.5	0.000	0.000	no
Carrot	5	270	no	65	300	yes	no	1.3	3.3	3.3	6.5	28.1	32.1	10.9	7.4	7.1	0.000	0.000	no
Olive oil	5	270	no	65	65	yes	no	3.4	6.4	9.0	14.0	22.1	19.3	12.9	6.2	6.7	0.000	0.007	no
Pistachio	5	270	no	65	300	yes	no	1.7	4.2	6.7	10.8	31.6	29.5	6.3	4.0	5.2	0.000	0.005	no
Viburnum	5	270	no	65	300	yes	no	1.9	3.8	5.2	8.9	29.3	29.7	8.8	5.6	6.9	0.000	0.030	no
Spinach	5	270	no	65	300	yes	no	0.8	2.4	3.5	3.4	11.8	29.0	16.4	23.5	9.3	0.000	0.006	no
Millet seed	5	270	no	65	300	yes	yes	1.5	3.0	7.1	7.1	29.9	31.5	8.6	5.1	6.4	0.051	0.007	no
Quinoa seed	5	270	no	65	300	yes	yes	1.4	3.0	6.2	6.2	29.3	32.5	8.6	6.4	6.3	0.007	0.014	no
Rice grain	5	270	no	65	300	yes	yes	2.0	3.9	4.9	8.2	31.4	31.4	7.9	4.6	5.8	0.004	0.007	no
Sesame seed	5	270	no	65	300	yes	yes	1.7	3.4	4.1	7.0	31.6	33.4	7.9	4.7	6.2	0.003	0.000	no
Acorn seed	5	270	no	65	300	yes	yes	1.7	3.6	4.5	8.1	26.6	29.2	10.9	7.5	7.9	0.006	0.009	no

Appendix 18: Table summarizing the results of the simulated cooking in replicate pots of various foodstuffs on an open fire and the field experimental parameters. The layer of fats formed from salmon and red deer during the cooking was skimmed and gathered in another pot to then be heated on the open fire. These samples are noted with *.

Real-cooking experiments																
						APAAs-C_{18} distribution									APAA-C_{20}/APAA-C_{18}
Sample No	Cooking time (h)	Foodstuff cooked	Type of samples	APAAs-C_{18} formed	APAAs-C_{20} formed	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)	
Before burial															
EDA1-cer	15	Red deer	Ceramic	yes	?	-	-	-	-	-	-	-	-	-	-
EDA1-fc-int	15	Red deer	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EDA1-fc-ext	15	Red deer	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EDB1-cer	15	Red deer	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EDB1-fc-int	15	Red deer	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EDB1-fc-ext	15	Red deer	Foodcrusts	yes	?	0.0	3.2	10.2	10.3	23.3	24.5	10.6	10.4	7.6	-
EDC1-cer	15	Red deer	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EDC1-fc-01	15	Red deer	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EDC1-fc-02	15	Red deer	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EFA1-cer	15	Salmon	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EFA1-fc	15	Salmon	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EFB1-cer	15	Salmon	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EFB1-fc	15	Salmon	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EFC1-cer	15	Salmon	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EFC1-fc-01	15	Salmon	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EFC1-fc-02	15	Salmon	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EFC1-fc-03	15	Salmon	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
ECA2-cer	5	Chestnut flour	Ceramic	yes	?	1.1	2.3	3.8	7.8	26.4	28.2	14.6	8.2	7.6	-
ECA2-fc-int	5	Chestnut flour	Foodcrusts	yes	?	0.9	2.7	3.6	7.8	28.3	30.8	11.0	7.7	7.1	-
ECA2-fc-ext	5	Chestnut flour	Foodcrusts	yes	?	1.0	1.9	3.8	5.4	33.7	37.4	7.3	4.9	4.5	-
ECB2-cer	5	Chestnut flour	Ceramic	yes	?	1.1	2.2	4.3	9.4	28.3	29.3	12.3	6.9	6.3	-

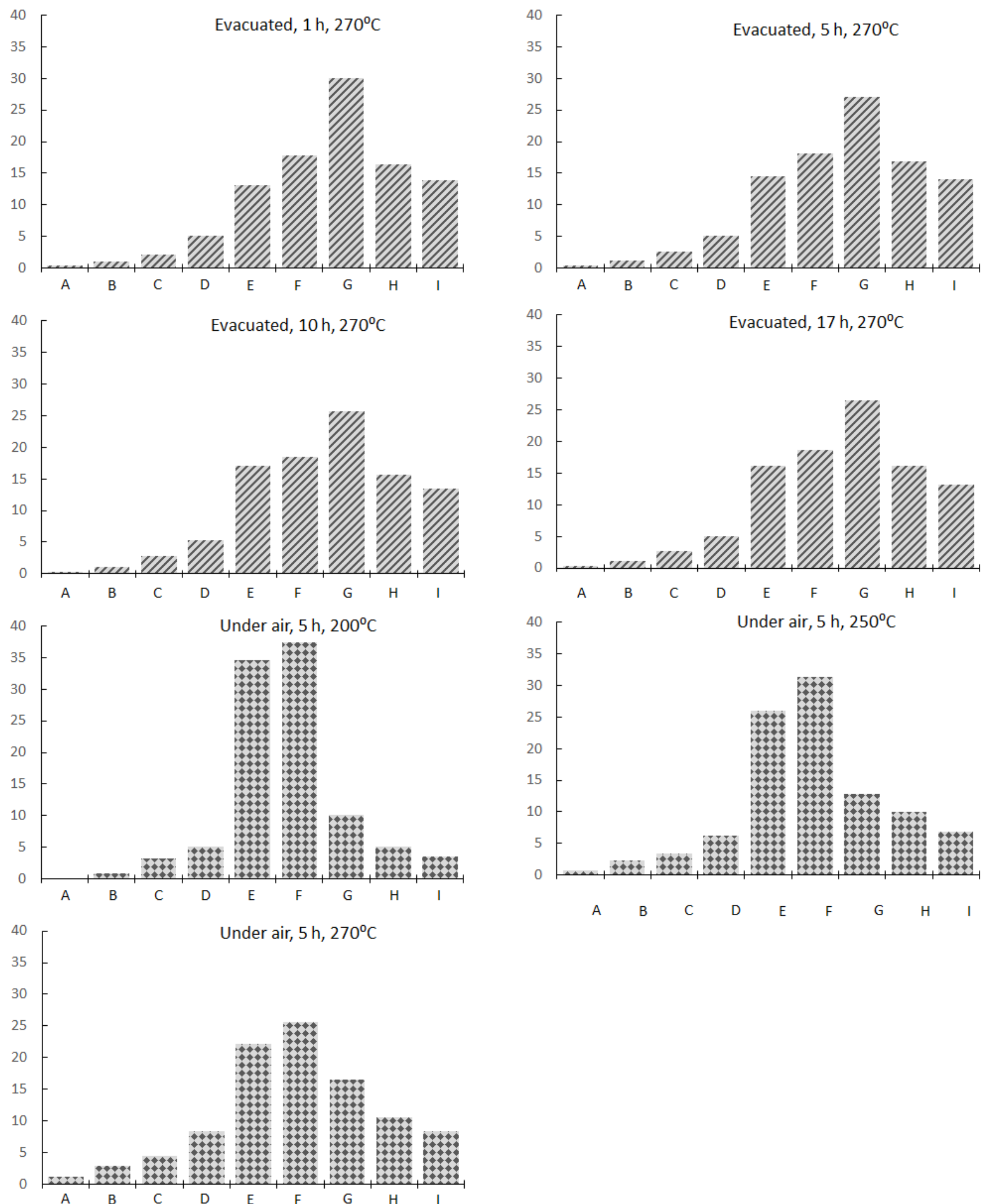
Sample No	Cooking time (h)	Foodstuff cooked	Type of samples	APAAs-C_{18} formed	APAAs-C_{20} formed	APAAs-C_{18} distribution									APAA-C_{20}/APAA-C_{18}
						A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)	
ECB2-fc-int	5	Chestnut flour	Foodcrusts	yes	?	0.9	2.3	3.4	7.3	29.6	32.7	10.6	7.0	6.1	-
ECC2-cer	5	Chestnut flour	Ceramic	yes	?	0.9	2.1	3.4	7.9	26.3	29.3	15.3	7.7	7.1	-
ECC2-fc-int	5	Chestnut flour	Foodcrusts	yes	?	0.8	2.0	3.2	6.4	29.1	33.0	10.7	7.9	7.0	-
ECC2-fc-ext	5	Chestnut flour	Foodcrusts	yes	?	1.0	2.2	3.5	7.0	33.5	35.0	8.1	4.7	5.0	-
EFFA1-cer	15	Salmon*	Ceramic	no	no	-	-	-	-	-	-	-	-	-	-
EFFA1-fc-ext-01	15	Salmon*	Foodcrusts	no	no	-	-	-	-	-	-	-	-	-	-
EFFA1-fc-ext-02	15	Salmon*	Foodcrusts	no	no	-	-	-	-	-	-	-	-	-	-
EFDC1-cer	15	Red deer*	Ceramic	yes	?	-	-	-	-	-	-	-	-	-	-
EFDC1-fc-int-01	15	Red deer*	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
EFDC1-fc-int-02	15	Red deer*	Foodcrusts	?	no	-	-	-	-	-	-	-	-	-	-
Exp1-Blk-cer	15	Blank	Ceramic	?	no	-	-	-	-	-	-	-	-	-	-
After burial (6 months)															
EDA1-cer-bur	15	Red deer	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EDB1-cer-bur	15	Red deer	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EDB1-fc-bur-int	15	Red deer	Foodcrusts	yes	no	-	-	-	-	-	-	-	-	-	-
EDC1-cer-bur	15	Red deer	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EDC1-fc-bur-int	15	Red deer	Foodcrusts	no	no	-	-	-	-	-	-	-	-	-	-
EFA1-cer-bur	15	Salmon	Ceramic	yes	?	0.8	1.3	3.8	4.4	21.3	25.4	12.4	25.6	5.1	-
EFB1-cer-bur	15	Salmon	Ceramic	yes	yes	0.3	1.3	3.1	5.7	20.8	24.6	15.5	22.6	6.1	0.11
EFC1-cer-bur	15	Salmon	Ceramic	yes	yes	1.1	2.8	4.6	8.0	26.8	29.1	11.2	11.0	5.4	0.09
ECA2-cer-bur	5	Chestnut flour	Ceramic	yes	no	1.1	0.0	3.6	8.8	25.6	29.7	17.7	6.7	6.8	-
ECA2-fc-bur-int	5	Chestnut flour	Foodcrusts	yes	no	0.7	2.0	2.4	5.8	31.3	35.5	10.1	6.6	5.7	-
ECB2-cer-bur	5	Chestnut flour	Ceramic	yes	no	0.0	0.0	2.5	6.6	30.0	30.1	12.0	12.5	6.3	-
ECB2-fc-bur-int	5	Chestnut flour	Foodcrusts	yes	no	1.2	2.7	3.8	7.3	27.7	31.3	11.7	7.5	6.9	-
ECC2-cer-bur	5	Chestnut flour	Ceramic	yes	no	1.2	2.6	4.2	8.7	27.0	28.2	13.5	6.5	8.0	-
ECC2-fc-bur-int	5	Chestnut flour	Foodcrusts	yes	?	1.0	2.6	3.5	7.6	29.0	32.0	11.0	6.8	6.4	-
ECC2-fc-bur-ext	5	Chestnut flour	Foodcrusts	yes	no	0.9	2.3	3.0	7.1	33.5	35.8	8.2	4.1	4.9	-
Exp1-Blk-cer-bur	15	Chestnut flour	Ceramic	no	no	-	-	-	-	-	-	-	-	-	-

Sample No	Cooking time (h)	Foodstuff cooked	Type of samples	APAAs-C_{18} formed	APAAs-C_{20} formed	APAAs-C_{18} distribution									APAA-C_{20}/APAA-C_{18}
						A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)	
EFFA1-cer-bur	15	Salmon*	Ceramic	yes	yes	0.0	1.4	3.5	7.3	29.5	34.9	9.8	9.8	3.8	0.10
EFDC1-cer-bur	15	Red deer*	Ceramic	yes	no	-	-	-	-	-	-	-	-	-	-
EFDC1-fc-int-bur	15	Red deer*	Ceramic	no	no	-	-	-	-	-	-	-	-	-	-

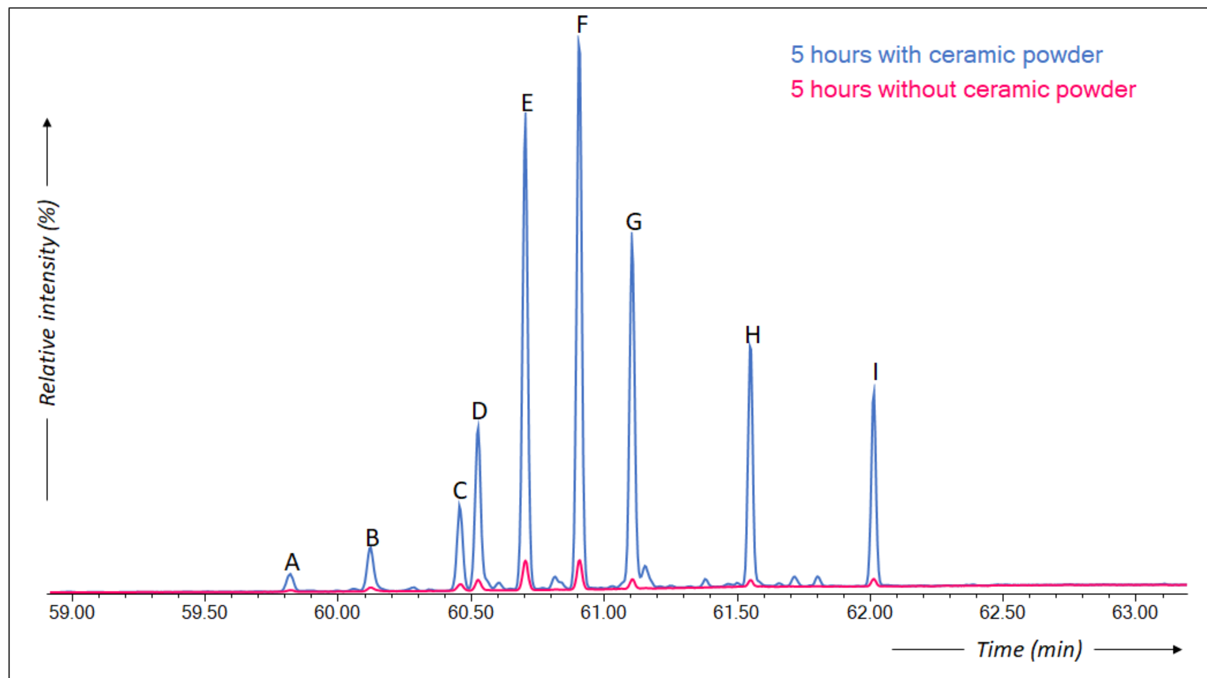
NB. In some samples APAAs, although present, were at very low abundance. In this case the isomeric distribution of APAAs-C18 could not be obtained.

Appendix 19: photos showing (a to d) the field cooking experiments and (e) the burying half of each pottery used in the experiments for 6 months. These experiments were performed at the YEAR Center (University of York).

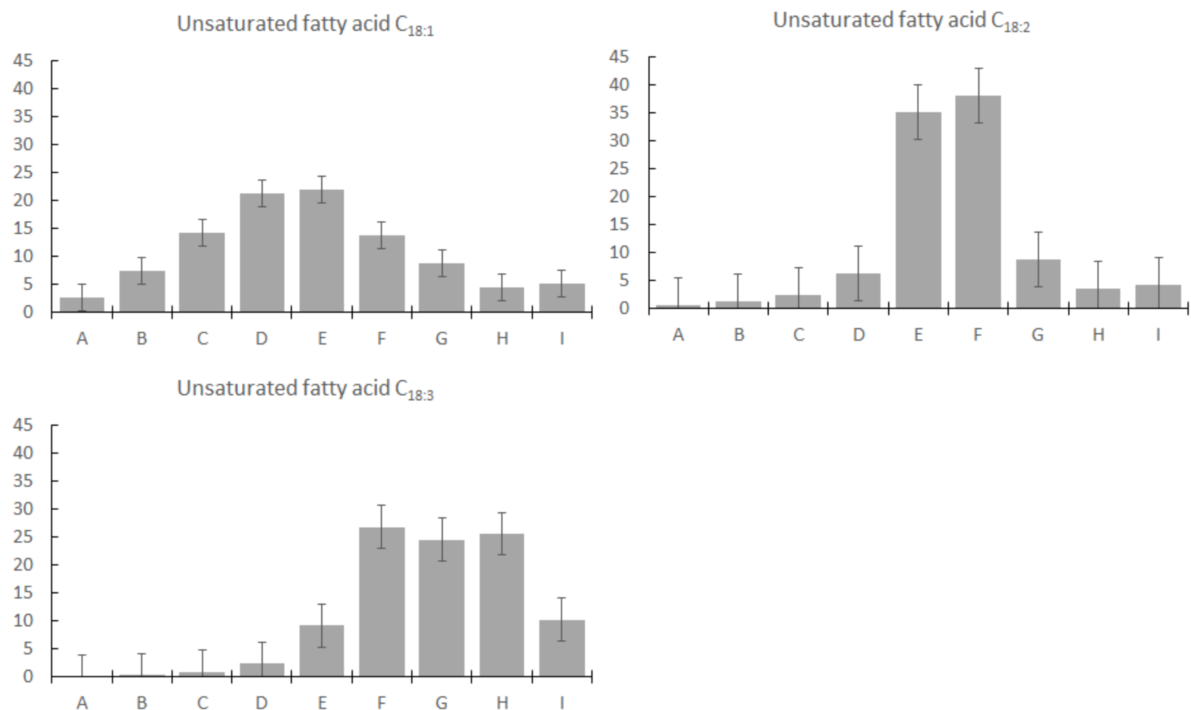
Appendix 20: APAAs-C_{18} A to I isomeric distribution (from A to I) of rapeseed oil subjected to different heating conditions (time, temperature) under either evacuated (line patterns) or air (diamond patterns).



Appendix 21: Partial SIM chromatogram of rapeseed oil cooked under open air showing ω-(o-alkylphenyl)alkanoic acids C_{18} isomers (m/z 290 ion) with or without ceramic powder.



Appendix 22: APAAs-C_{18} A to I isomeric distribution of pure unsaturated fatty acid (UFA) heated in open glass tube at 270°C during 5 hours with ceramic powder. For each UFA the experiments were duplicated and the APAAs-C_{18} isomeric distribution given here correspond to the average of these two analyses along with the error bars.



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