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AQUATIC RESOURCES IN FOODCRUSTS: IDENTIFICATION AND IMPLICATION

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ABSTRACT. Foodcrusts, the charred surface deposits on pottery vessel surfaces, provide a rich source of data regarding container function. This article reviews recent applications focusing on the detection of aquatic resources (marine and freshwater) in pottery vessels using a range of analytical approaches including bulk isotope measurements of carbon and nitrogen, lipid biomarker analysis, and compound-specific carbon isotope determinations. Such data can help to evaluate the presence of reservoir effects when undertaking radiocarbon dating of foodcrust samples. In particular, molecular and isotopic analysis can aid in the selection of suitable candidates for ^{14}C where it can be demonstrated that aquatic resources are unlikely to contribute to the residue. Prospects for compound-specific ^{14}C analysis of lipids in foodcrusts and ceramic-absorbed residues are also discussed.

INTRODUCTION

Ceramic containers are durable and abundant. The record of pottery manufacture on the planet extends well into the last glacial period and pottery vessels were used widely in Africa and Eurasia from the early Holocene. Ceramic containers have myriad uses but the most common association is with food and drink. The very earliest pottery sherds from Xianrendong Cave, China, have recently been dated to 20,000 cal BP. Scorching and soot marks on their exterior surfaces indicate that they were most likely used for cooking (Wu et al. 2012). The study of early pottery, aiming to identify and to understand the origins and adoption of ceramic containers throughout the world, has been enriched by molecular and isotopic studies of organic residues preserved in association with pottery sherds (Craig et al. 2011, 2013; Taché and Craig 2015). In addition, these same methods are well established in later periods, particularly with the onset of farming (see Evershed 2008; Regert 2011 for reviews).

The term "foodcrust" is a generic and rather unspecific term that has become widely used to describe amorphous charred or burnt deposits adhering to the surface of containers associated with heating organic matter, often considered to be specific episodes of cooking food. Other terms include "carbonized residues" or "chars." The containers are usually ceramic in origin but similar deposits can also be found stone and other vessels (e.g. Namdar et al. 2009). Surface deposits on potsherds may derive from a wide range of functions involving heating of which food preparation is only one. Burnt matter on the interior surfaces of sherds may also derive from other uses such as organic sealants (e.g. Regert et al. 2003) or deposits from burning oil for illumination (Heron et al. 2013). Foodcrusts can occur on the rim and the exterior surface when contents spill, boil over, or even penetrate the permeable ceramic matrix and burn. Such encrustations can usually be distinguished from soot deposited from fuel during the heating of the vessel over a fire.

Foodcrusts have long been targets for ^{14}C dating. The opportunity to date directly organic matter considered to represent the period of use of a pottery vessel is appealing, especially considering the limited options for directly dating ceramic material. However, a number of uncertainties have been highlighted, especially the possibility of reservoir effects, both from freshwater and marine environments (e.g. Fischer and Heinemeier 2003; Philippsen and Meadows 2014).

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APPROACHES TO THE STUDY OF FOODCRUSTS

The primary interests for archaeology are to determine the uses of containers, to identify specific foodstuffs and the way they were prepared and, finally, to directly date the vessel by accelerator mass spectrometry (AMS). Foodstuffs are enormously diverse in their composition of food-derived molecules (lipids, proteins, and carbohydrates) and the culinary choices made during food preparation add to this complexity. For example, Longacre, observing pottery use among the Kalinga in the northern Philippines in the 1970s, noted that pottery vessels were used to cook rice, vegetables, and meat, although in addition he recorded less common food sources in one notable recipe: "The Kalinga seine their rice fields after each harvest and collect a small snail, a long-legged water spider and a large black water beetle with orange flesh. All three are cooked with water in ceramic pots to form a highly popular soup" (Longacre 1995:278). Heating, and subsequent charring of foods, leads to thermal alteration of food constituents. During long-term burial, organic matter is potentially transformed by chemical and microbiological action. Therefore, the composition of archaeological foodcrusts is a complex range of small molecule and macromolecular decomposition products formed by protracted heating and exposure to the burial environment. The extent of these changes to organic residues in foodcrusts is not well understood, but losses of soluble and/or labile constituents are likely together with uptake of mobile organic species from the surrounding burial environment.

To reconstruct the original composition of foodstuffs from such a highly modified complex mixture presents a daunting analytical challenge. Table 1 summarizes some of the approaches employed to identify the nature and composition of foodcrusts. Lipid analysis is also commonly applied to ceramic-absorbed organic matter (Evershed 2008). Other approaches have been employed to study organic residues absorbed into the ceramic matrix, including proteomics (Solazzo and Erhardt 2007; Solazzo et al. 2008) and DNA sequencing (Hansson and Foley 2008; Foley et al. 2012).

Table 1 Common methods employed to investigate the composition of foodcrusts associated with pottery vessels, the data obtained, and example publications.

Method	Data	Example publication(s)
IRMS	Bulk $\delta^{13}C$, $\delta^{15}N$, C/N ratios	Yoshida et al. (2013)
GC-MS	Lipid biomarkers	Craig et al. (2013)
GC-C-IRMS	Compound-specific $\delta^{13}C$ values	Craig et al. (2013)
Pyrolysis GC-MS, DTMS, FTIR, NMR	Bulk characteristics of main food groups present	Isaksson (1999), Oudemans and Boon (1991), Oudemans et al. (2007a,b), Kubiak-Martens et al. (2015)
Microscopy, SEM	Floral and faunal remains, starch, phytoliths	Saul et al. (2012), Kubiak-Martens et al. (2015)

Most investigations have focused on the measurement of the stable isotope values of carbon and nitrogen in the foodcrust and the extraction and identification of lipid components. The former provides data on the total carbon and nitrogen present in the sample; the latter focuses on the soluble lipid fraction only. Typically, the soluble lipid fraction accounts for as little as 0.01–5.00% by weight of the total foodcrust (Craig et al. 2007:148). Only a few studies have explored the chemical nature of the charred matrix in greater detail. Curie-point pyrolysis GC-MS was employed by Oudemans and Boon (1991) to examine surface deposits adhering to pottery sherds from Uitgeest-Groot Dorregeest (about 0 to AD 300) in the Netherlands. This study detected a broad range of organic moieties including denatured peptides as well as furans, phenols, and benzenes thought to derive

from polysaccharides. Fatty acids, and additional compounds formed from lipids under carbonizing conditions, were also identified. Direct-temperature mass spectrometry (DTMS), Fourier-transform infrared spectroscopy (FTIR), solid-state ^{13}C-NMR, and elementary carbon-hydrogen-nitrogen (CHN) analysis was used to further characterize the foodcrusts (Oudemans et al. 2007a,b). DTMS provides information on a wide range of organic compounds present in the foodcrusts, including lipids, polynuclear aromatic hydrocarbons, and markers for residual proteins and polysaccharides. Multivariate analysis of the DTMS spectra identified five different "chemotypes" or groups of residues with comparable chemical characteristics, although it was difficult to attribute these to a specific source.

Sherriff et al. (1995) used ^{13}C-NMR to compare foodcrusts from the boreal forest of central subarctic Canada with those experimentally charred onto replica ceramics. The presence and character of the main compound classes present in the crust were evaluated together with evidence of thermal alteration, for example, through the presence of polyaromatic hydrocarbons. The experimentally produced foodcrusts showed good preservation of lipids and the presence of denatured proteins. The absence of what was considered to be a diagnostic peak for carbohydrates in the archaeological samples suggested plant-based foods were not cooked or else degraded over time.

Other approaches applied to the study of foodcrusts include the use of microscopic investigation. Fish bones are rare but have been observed embedded in foodcrusts in some studies (e.g. Andersen and Malmros 1985). Some studies have demonstrated the value of combining scanning electron microscopy (SEM) to detect botanical remains and DTMS to evaluate the presence of organic compound classes in foodcrusts on pottery from Early Neolithic (Raemaekers et al. 2013) and Late Neolithic sites (Kubiak-Martens et al. 2015) in the Netherlands. In both studies, fish scales are reported in a small number of the vessels, but it was not possible to identify the species origin. Further developments have been made in the recovery and identification of starch granules (Saul et al. 2012) and phytoliths (Saul et al. 2013) in foodcrusts adhering to late Mesolithic–early Neolithic pottery sherds from northern Europe. In the latter study, phytoliths were isolated from 26 out of 74 foodcrusts recovered from the inside of pots from three sites in Denmark and Germany spanning the transition to agriculture, some of which were morphologically equivalent to phytoliths found only in the seeds of modern garlic mustard [*Alliaria petiolata* (Bieb.) Cavara & Grande].

Bulk Isotope Analysis of Foodcrusts

The isotopic ratios of carbon (δ^{13}C) and nitrogen (δ^{15}N) have been applied to foodcrusts in two main themes: (i) to distinguish C_3 and C_4 plant contributions and (ii) to determine the presence of, and to differentiate, marine, terrestrial, and freshwater resources. Studies have been undertaken in many different geographical and chronological contexts (e.g. Hastorf and DeNiro 1985; Morton and Schwarcz 2004; Beehr and Ambrose 2007; Craig et al. 2007; Kunikita et al. 2007, 2013; Miyata et al. 2009; Yoshida et al. 2013; Cassiodoro and Tessone 2014). In paleodietary studies, the stable isotope ratios in human bone collagen are often used to evaluate the contribution of aquatic resources to the diet. Nitrogen isotope ratios vary with tropic level with a stepwise trophic shift of +2–6‰ from plants to herbivores and from herbivores to carnivores. Higher δ^{15}N values are usually encountered in "longer" food chains in aquatic (marine and freshwater) environments. In addition, marine foods are generally enriched in ^{13}C compared to terrestrial foods, while freshwater resources tend to be depleted in ^{13}C. In practice, there is wide variation within each main resource group (e.g. Dufour et al. 1999 for collagens of modern European freshwater fish).

When working with collagen, various criteria can be applied to determine the presence of well-preserved samples using data such as the amino acid profile, the collagen yield, and the atomic

C:N ratio. In the case of foodcrusts of unknown origin, no criteria for establishing the reliability of isotope data can be applied. Also, the isotope ranges for collagen corresponding to different potential foodstuffs, which can often be established in different archaeological settings by measuring identified fauna, cannot be used for interpreting the isotope values measured in foodcrusts. Isotope values, particularly carbon and to a lesser extent nitrogen, vary greatly between different tissues of a single organism, depending largely on the biomolecular composition of those tissues (e.g. Tieszen 1991). Since the biomolecular composition of the foodcrust is unknown and highly variable, it is not appropriate to compare data with collagen values.

Despite these uncertainties, some broad observations can be drawn from the bulk isotope analysis of foodcrusts, especially where large isotopic differences in putative foodstuffs exist. Hastorf and DeNiro (1985) investigated 71 foodcrusts from the central Peruvian uplands (200 BC–AD 1470). In this region, maize is the only C_4 plant. They suggested that C_3 non-legumes and C_3 legumes could be distinguished by $\delta^{15}N$, with the former producing much higher values, and C_4 plants distinguished from these with higher $\delta^{13}C$ values. The crusts on large slipped jars thought to have been used for cooking were apparently dominated by C_3 non-leguminous isotope signals, yet both the C_4 maize and C_3 legumes were well represented in sieved samples from all occupation phases. From the rather uniform pattern of foodcrust isotope data dominated by C_3 non-leguminous plants, the authors used ethnographic evidence to suggest that C_3 legumes were largely eaten raw or toasted and maize was usually toasted or fermented. In a related study, DeNiro and Hastorf (1985) observed that the isotope ratios of prehistoric carbonized plants were similar to those of modern counterparts but that uncarbonized plant remains exhibited significant differences, especially in $\delta^{15}N$ values.

The same approach was applied to foodcrusts on prehistoric ceramics from Ontario, Canada (Morton et al. 1988; Morton and Schwarcz 2004). The aim was to detect shifts in dietary composition, in particular focusing on the introduction of maize into the diet. These data were re-evaluated comprehensively by Hart et al. (2007), who conducted stable carbon isotope assays on three sets of experimental cooking residues, evaluating isotope fractionation, the relative contributions of different food components, and the contribution of total carbon to the deposits. They also modeled two-part food mixes with green maize (kernels) and maize flour. They suggest that systematic under representation of maize can result from the analysis depending on the composition of the residue, and that some prior knowledge of C_3 plant and animal contents is necessary to interpret stable carbon isotope values. They questioned the independent use of stable carbon isotope analysis of charred cooking residues as a viable technique for extracting paleodietary information.

In a subsequent study, Hart et al. (2012) observed an increase in $\delta^{13}C$ in ^{14}C-dated foodcrusts from pottery vessels from two of three regions studied. These data, where possible, were supported by maize phytolith recovery from the foodcrusts. The increase in $\delta^{13}C$ was considered to correspond to an increase in the maize carbon contribution to the deposits, although it was not possible to specify whether the increased contribution resulted from higher proportions of maize being cooked in a given pot and/or changes in the form of maize being cooked, such as maize meal or flour as opposed to whole kernels.

There is a growing literature on experimental approaches to studying foodcrusts, notably undertaking cooking episodes in replica vessels with authentic foodstuffs. These can be helpful in understanding the formation of foodcrusts and for identifying isotopic and elemental changes during their formation from different food sources (e.g. Sherriff et al. 1995:103). In general, these experiments have tended to show reasonable consistency between the isotopic and elemental composition of a wide range of foods prior to, and after, charring (e.g. DeNiro and Hastorf 1985; Hastorf and DeNiro

1985; Sherriff et al. 1995; Philippsen 2013a). In contrast, Boudin et al. (2010) detected marked changes in atomic C/N ratios when a range of foodstuffs was heated in industrial ceramics until charred, although the changes in isotope ratios were not as dramatic. Yoshida et al. (2013) report experiments on a wider range of foodstuffs comparing stable isotope ratios on the food before and after cooking in unglazed ceramics over an open fire. However, in this case, the atomic C/N ratios of the foodcrusts were not significantly altered and the authors suggest that starchy foods, such as acorn and horse chestnut, could be distinguished from low starch foods by their high C/N ratios (>30).

However, directly comparing bulk isotope values of experimental foodcrusts and archaeological samples may be problematic. Both will have been subject to a degree of thermal alteration, but long-term burial of archaeological samples may impact further on the composition and stable isotope ratios of the residue. Within an organism, lipids are depleted in ^{13}C relative to proteins and carbohydrates (DeNiro and Epstein 1977). Therefore, the loss of more labile and soluble components, notably amino acids and sugars, compared to the more robust and hydrophobic carbon skeletons in lipids, will alter $\delta^{13}C$ values as these components are more enriched in ^{13}C than the lipid fraction (Craig et al. 2007).

Aquatic Resources in Foodcrusts

In a study of pottery used by hunter-gatherers and early farmers in northern Europe, Craig et al. (2007) suggested that bulk isotope measurements of foodcrusts broadly discriminate between marine, freshwater, and terrestrial resources. The data were complemented by the presence of biomarkers consistent with aquatic lipids as well as compound-specific carbon isotope measurements of individual fatty acids extracted from the crusts. The amount of nitrogen present in the deposits ranged from 1% to 10% by weight. The authors acknowledged that the addition of non-proteinaceous nitrogen-containing compounds or the bacterial reworking of nitrogen in the deposits during burial could have altered the $\delta^{15}N$ values, although the extent to which such changes have occurred is unclear without further protein and amino acid analysis. The atomic C/N ratios were also variable from 2.9 to 49.9. Whether the variation in these values is related to the vessel contents, due to changes during the heating of the contents, or subsequent postdepositional alteration is not known. There was no significant correlation between the C/N ratios and either $\delta^{15}N$ or $\delta^{13}C$ values.

Lipid Biomarkers in Foodcrusts

Over the last 10 years, there has been increasing interest in the detection of aquatic resources in pottery vessels, and this has sparked new research into the recognition of lipid biomarkers, identified by gas chromatography-mass spectrometry (GC-MS), arising from the alteration of components found in fresh tissues. Considerable progress has been made in the determining the presence (see Cramp and Evershed 2014 for a comprehensive review) and absence (Cramp et al. 2014) of marine resources in pottery vessels using lipid biomarker and single-compound carbon isotope determinations. In contrast, the processing of freshwater resources in pots has received less attention (see, however, Craig et al. 2007; Hart et al. 2013).

The detection of marine lipids in archaeological organic residues has been reviewed by Cramp and Evershed (2014). Aquatic lipids are characterized by the abundance of long-chain unsaturated fatty acids with 1-6 carbon-carbon double bonds. However, the ease by which these oxidize compromises their role as effective marker compounds, especially those with more than one double bond. A high abundance of isoprenoid fatty acids, especially 4,8,12-trimethyltridecanoic acid (4,8,12-TMTD), 3,7,11,15-tetramethylhexadecanoic acid (phytanic acid), and 2,6,10,14-tetramethylpentadecanoic acid (pristanic acid), arising from the degradation of phytol in aquatic environments is also found in

the tissues of aquatic organisms (Ackman and Hooper 1970). That noted, phytanic acid is also found in the tissues of ruminant animals.

The detection of products of thermal alteration of unsaturated fatty acids has also contributed to the identification of aquatic resources in residues. The presence of C16-C22 ω-(*o*-alkylphenyl)alkanoic acids was first suggested by Hansel et al. (2004). They demonstrated the presence of these thermally induced alkali isomerization products of unsaturated fatty acids in pottery vessels from a 10th century AD coastal site in Brazil. Subsequent experimental work (Evershed et al. 2008) demonstrated that ω-(*o*-alkylphenyl)alkanoic acids are produced through prolonged heating of tri-, di-, and/or monounsaturated fatty acids at 270°C or above, but they are not formed from saturated fatty acids. They proposed that in order to confirm the presence of marine lipids in pottery vessels, ω-(*o*-alkylphenyl)alkanoic acids of carbon length C18, C20, and C22 should be present together with at least one of the three isoprenoid fatty acids. Another group of lipid biomarkers are dihydroxyfatty acids. Hansel and Evershed (2009; see also Hansel et al. 2011) have demonstrated that the positions of the hydroxyl groups identify the position of the double bond in the precursor fatty acid, and these data have been used to confirm the presence of marine resources in archaeological contexts (e.g. Heron et al. 2010). It should be noted that these biomarkers are shared by aquatic organisms from marine, brackish, and freshwater environments; therefore, discriminating a more specific source is problematic since the same precursor molecules and/or the same sequence of alteration (e.g. thermal, oxidative) are likely to produce the same distribution of marker compounds regardless of which environment they derive from.

Compound-specific carbon isotope determinations, obtained by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS), further help to identify aquatic resources (Olsson and Isaksson 2008; Craig et al. 2011, 2013; Heron et al. 2013; Cramp and Evershed 2014; Taché and Craig 2015). This approach determines the carbon isotope value of single biomarkers, usually $C_{16:0}$ and $C_{18:0}$, in the extracts following chromatographic separation. These data are compared with modern reference fats and oils, although determining the carbon isotope values of $C_{16:0}$ and $C_{18:0}$ fatty acids extracted from animal bones of archaeological date has been proposed (Colonese et al. 2015). Compound-specific data have been extremely useful in detecting a wide range of carbon isotope values associated with lipid extracts from pottery, but challenges remain. For example, the wide variation in carbon isotope values in aquatic systems can lead to potential overlap in tissues derived from freshwater, brackish, and marine ecosystems. Furthermore, many organisms display ecological plasticity moving between and subsisting in different aquatic environments during their lifecycle. This is not an issue for species such as salmon, as they do not feed when they migrate from the sea into freshwater. However, some organisms, such as eel, may move between marine, brackish, and freshwater environments. Finally, the possibility that pottery vessels were used to process mixtures of resources from aquatic environments as well as a wide range of terrestrial animals and plants can present further complexity in interpreting signals. Nevertheless, the combination of lipid biomarker and compound-specific data is a powerful approach for determining the contents of pottery vessels.

Relatively few studies have compared lipids extracted from foodcrusts with residues absorbed into the ceramic matrix from the same sherd or vessel (Oudemans and Boon 2007). Although not a study associated with detection of aquatic resources, Mukherjee et al. (2008) examined "surface residues" (i.e. visible deposits adhering to the surface of the potsherd) and absorbed residues from the same sherd. Surface deposits were present on 27 of the potsherds and 18 (67%) were found to contain significant concentrations of lipid. In many cases, higher lipid concentrations were obtained from the surface deposits than the absorbed residues from the same potsherd, although the lipid distributions and $\delta^{13}C$ values obtained on single fatty acids were not always equivalent (Mukherjee et al.

2008:Figure 4). The authors suggested that this is likely to be due to the absorbed lipid extract representing an average lipid distribution reflecting several uses of the vessel over its lifetime, while the surface deposit is most likely to derive from the last vessel use. In addition, lipids extracted from the surface deposits tended to be more highly degraded than their associated absorbed residue, reflecting the different diagenetic influences acting on them during burial with absorbed lipids afforded greater protection from alteration by the inorganic ceramic matrix of the potsherd.

The relationship between bulk carbon isotope measurements in the foodcrust and compound-specific carbon isotope measurements on fatty acids extracted from the foodcrust or the ceramic-absorbed residue from the same vessel has not been evaluated systematically. Although the data set published in Craig et al. (2013) is small, both bulk and single-compound carbon isotope measurements were performed on a sample of 14 foodcrusts from Incipient Jōmon sites in Japan. The bulk carbon isotope values (mean –24.8 ± 1.8‰) are very similar to the mean carbon isotope ratio (–24.6 ± 1.0‰) of the two most abundant fatty acids ($C_{16:0}$ and $C_{18:0}$) extracted from the foodcrusts and measured by GC-C-IRMS. The correlation coefficient, *r*, between these two data sets gives a value of 0.51, which shows a reasonable correlation. The similarity between the bulk carbon and compound-specific isotope values suggests that insoluble lipid, presumably polymerized, is contributing significantly to the bulk carbon isotope signal.

In another published data set (Craig et al. 2011), foodcrusts and pottery sherds from both Ertebølle and Funnel Beaker vessels from a number of sites including the underwater site at Neustadt (LA 156) in northern Germany were analyzed. The foodcrusts (n = 24) have a mean bulk $\delta^{13}C$ value of –23.7 ± 3.0‰. The mean value, again obtained by taking the mean of the $C_{16:0}$ and $C_{18:0}$ carbon isotope values for the lipid-extracted foodcrusts and pottery sherds from the samples from which the foodcrusts were taken is –26.4 ± 4.7‰. In this case, the $\delta^{13}C$ values obtained on the individual fatty acids are depleted compared to the bulk carbon isotope data by an average of –2.7‰. The correlation coefficient, *r*, between these two data sets is 0.86, a higher correlation than in the example above. This suggests that the bulk carbon isotope value has a clear relationship with the carbon isotope values of the principal lipid molecules either associated with the "foodcrust" or with the lipid absorbed in the sherd adjacent to where the crust formed on the pot. These data suggest that while carbon from other food sources, such as proteins and carbohydrates, is likely to be present, there is a clear relationship between the bulk carbon isotope value and the compound-specific values. More work is needed to explore this relationship further.

DATING FOODCRUSTS

The direct ^{14}C dating of pottery vessels and sherds, for example through isolating specific fractions removed from the ceramic (e.g. lipids, temper, humics), has been addressed in a number of papers (e.g. Hedges et al. 1992; Bonsall et al. 2002) and a wide range of applications has appeared including the direct dating of charcoal or other plant matter embedded in the ceramic matrix as well as foodcrusts (e.g. Fischer and Heinemeier 2003), dating organic temper (Yoshida et al. 2004), dating visible resinous linings on pottery surfaces (e.g. Lampert et al. 2003), and dating the low-temperature desorbed organic fraction of potsherds (e.g. Messili et al. 2013). As noted earlier, the direct dating of pottery vessels is an attractive proposition not least to examine the origins, adoption, and use of ceramics in specific regions and contexts (e.g. Hartz et al. 2012; Nomokonova et al. 2013).

The direct dating of foodcrusts has been widely applied. Several studies have noted that "foodcrust" ^{14}C ages may be subject to reservoir effects, both marine and freshwater, producing older than expected ^{14}C ages either in comparison with dates obtained on terrestrial material embedded in the crusts, associated charcoal, and/or on pottery typological grounds (e.g. Fischer and Heine-

meier 2003; Philippsen and Meadows 2014). One study (Miyata et al. 2011) highlighted older dates (~90 ^{14}C yr) for foodcrusts adhering to the interior surface of a pot compared with exterior soot marks from the same vessel and concluded that the difference was due to a freshwater reservoir effect or diagenesis. The outcomes of such investigations have been subject to debate in the literature as to whether or not foodcrust dates are affected by reservoir effects (e.g. Hart and Lovis 2007; Hartz et al. 2012; Hartz and Piezonka 2013; Kuzmin 2013; Roper 2013, 2014; Hart and Lovis 2014). In few cases, however, has this been supported by lipid biomarker evidence. Hart et al. (2013) have cautioned against the over-reliance on bulk carbon and/or nitrogen isotope data alone as a proxy for a freshwater reservoir effect. Using pottery and other data from the Finger Lakes region of the northeastern USA, the authors argued against a freshwater reservoir effect impacting on the ^{14}C dates obtained on foodcrusts. In this case, lipid analysis of the foodcrusts indicated that the biomarkers associated with aquatic resources were not present.

As part of a wider investigation of freshwater reservoir effects in northern Germany and Denmark, Philippsen (2013b) has reviewed dates obtained on foodcrusts from several countries in northern Europe and the southeastern Baltic (see also Philippsen and Heinemeier 2013). Some dates obtained on the base-soluble fraction of foodcrusts from the Ertebølle site at Kayhude in northern Germany, which gave older ^{14}C dates than the total crust, perhaps indicate contamination from the burial environment. Philippsen and Meadows (2014) have highlighted the clear differences in coastal and inland foodcrust dates and bulk isotope measurements obtained on Ertebølle pottery from northern Germany. A more cautionary note has been sounded by Boudin et al. (2009, 2010) in their investigation of Late Mesolithic wetland sites in NW Belgium. They contend that δ^{13}C and δ^{15}N values (Boudin et al. 2009) and the presence or absence of lipid biomarkers (Boudin et al. 2010) are unlikely to detect consistently the presence of aquatic resources in foodcrusts, and so these approaches have only a limited role in screening samples for ^{14}C dating liable to inaccuracies resulting from the presence of marine or freshwater carbon.

Foodcrusts were included in a systematic dating program for the early Neolithic causewayed enclosures of southern Britain, combining new and existing ^{14}C dates and applying a series of Bayesian chronological models (Bayliss et al. 2011). Around 15% of the foodcrust dates were judged to be inaccurate on archaeological grounds and there were some large offsets between replicate pairs of foodcrust dates from the same sherd. No compositional data were included to investigate the underlying causes of this variation. Molecular and isotopic analysis of ceramic-absorbed and surface residues from early Neolithic sites in southern Britain (e.g. Copley et al. 2005) have provided no evidence of the processing of aquatic resources in pottery vessels, so the issues highlighted in this study are unlikely to be the result of an aquatic reservoir effect. Bayliss et al. (2011) note that some of the foodcrust dates were measured in different ^{14}C laboratories with different sample pretreatment protocols. Prior to dating, foodcrusts are most commonly subjected to acid-alkali-acid (AAA) pretreatment to remove carbonates and humic and fulvic acids. The impact of sample pretreatment on the composition of foodcrusts has not been evaluated in detail (see, however, Philippsen and Meadows 2014:2-2) and many studies of foodcrusts have not subjected samples to pretreatment prior to bulk isotope analysis (e.g. Craig et al. 2011, 2013). A recent study compared the effects of different sample pretreatments on the stable isotope analysis of charred plant remains (Vaiglova et al. 2014). This documented clear changes in δ^{15}N values as a result of pretreatment. Fourier-transform infrared spectroscopy proved to be successful in identifying the presence of contaminants (such as carbonates, nitrates, and humics), which could be removed prior to analysis using less aggressive pretreatment protocols.

In addition to AMS determinations on bulk foodcrust samples, there is interest in the isolation

and analysis of specific molecules from these materials. Compound-specific radiocarbon analysis (CSRA) of lipid molecules has been applied in sedimentary studies since 1996 (Eglinton et al. 1996; Ohkouchi et al. 2003; Yamane et al. 2014). The challenges of resolving the heterogeneous composition of organic inputs from unknown sources are well known. Consequently, there has been greater focus on isolating discrete biomarkers and determining their ^{14}C content. Research has focused, for example, on lipids synthesized by marine algae (e.g. alkenones) and compounds derived from the epicuticular wax of terrestrial plants (e.g. *n*-alkanes or *n*-fatty acids). Preparative gas chromatography (PGC) is the most widely used method for trapping marker compounds for dating. The principal challenge is the purification of adequate quantities of individual compounds without the introduction of contaminants (Mollenhauer and Rethemeyer 2009). The potential for contamination during PGC has also been explored (Rethemeyer et al. 2013).

Compound-specific ^{14}C analysis can be applied to archaeological enquiries, for example, in dating individual amino acids in bone collagen separated using HPLC (e.g. Nalawade-Chavan et al. 2014). The most ubiquitous lipid-extractable molecules in foodcrusts and pottery sherds are usually fatty acids, notably hexadecanoic ($C_{16:0}$) and octadecanoic ($C_{18:0}$). Applications of CSRA to pottery residues are limited to the work of Stott et al. (2001, 2003) and Berstan et al. (2008), who dated $C_{16:0}$ and $C_{18:0}$ fatty acids absorbed in Early Neolithic pottery associated with the Sweet Track, a preserved timber trackway in southwest Britain dated by dendrochronology. The six ^{14}C determinations for the fatty acids were consistent with each other and with the dendrochronological age of the Sweet Track. Around 120 GC runs were performed to collect sufficient quantities of the fatty acids (as methyl esters) extracted from ceramic-absorbed lipid residues for dating (>200 μg). Advances in PGC, reduction in sample size requirements, and applications to organic geochemistry are likely to renew interest in CSRA in archaeology. Selecting samples for archaeological dating will need to be closely integrated with lipid biomarker analysis and compound-specific carbon isotope measurements.

CONCLUSIONS

The last 10 years has seen considerable progress in the detection of aquatic resources in pottery vessels (Cramp and Evershed 2014). Molecular-based approaches and single-compound carbon isotope determinations lead the way as the most widely used and informative methodology applied to determine the contents of pottery vessels. Bulk carbon and nitrogen isotope analysis has a role to play in evaluating pottery use. Craig et al. (2007:137) describe bulk isotope analysis of foodcrusts as a "very blunt analytical tool." Bulk isotope determinations applied in isolation are likely to be difficult to interpret apart from suggesting general differences between foodcrusts associated with different vessel forms (e.g. Sherriff et al. 1995). However, when combined with GC-MS and GC-C-IRMS, bulk isotope analysis is a useful step in assessing the variation in $\delta^{13}C$ in large samples, which can be compared with single-compound carbon isotope analysis of fatty acids extracted from foodcrusts or from the vessel matrix. Furthermore, $\delta^{15}N$ values can indicate the trophic level of food resources. Further evaluation of the relationship between bulk and compound-specific carbon isotope values is highly desirable. Further characterization of the nature of the biopolymers preserving the soluble fraction is also needed. For example, the relationship of bulk $\delta^{15}N$ to proteins, amino acids, or other nitrogen-containing constituents has yet to be investigated. The presence of carbohydrates, such as starch, has been inferred from pyrolysis-GC-MS and ^{13}C-NMR in particular, but no studies have evaluated the chemical evidence of carbohydrates to complement the recovery of starch granules from foodcrusts. Finally, direct ^{14}C dating of foodcrusts remains an important objective. Combining CSRA with lipid biomarker and lipid isotope data obtained on the biomarkers can offer exciting new approaches to the direct dating of pottery vessels.

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