

FOOD AND SOOT: ORGANIC RESIDUES ON OUTER POTTERY SURFACES

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ABSTRACT. Organic residues preserved on the outer surfaces of archaeological pottery are commonly considered to be soot and, not being subject to reservoir effects, as more reliable for radiocarbon (¹⁴C) dating compared to food crusts from the inner surface. However, unlike food crusts, outer surface residues are never analyzed prior to ¹⁴C dating. This study confronts ¹⁴C dates on inner and outer surface residues preserved on prehistoric pottery from Bazel Sluis (Belgium) with the results of stable isotope analysis and thermally assisted hydrolysis and methylation pyrolysis-gas chromatography-mass spectrometry (THM-GC-MS). These analyses clearly show that food residue is also present on the outer pottery surface, causing a possible reservoir effect on ¹⁴C dates. At Bazel, ¹⁴C dates on both the inner and outer surface residues are too old compared to dates obtained on associated animal bone. In addition, the outer surface residues systematically date younger than the inner food crusts, a discrepancy that is also known from other archaeological sites. It is suggested that these age differences are due to the mixed presence of soot and food residue on the exterior vessel wall as opposed to more homogeneous food crusts on the internal surface.

KEYWORDS: prehistoric pottery, radiocarbon dating, organic residue analysis, soot, food crusts.

INTRODUCTION

Organic residues that are preserved on archaeological pottery can yield a lot of information on the dietary habits of past populations. Furthermore, since most of these remains are the results of cooking or related activities, there is a clear chronological association with the period during which the pottery was used and by extension with the occupation of the site. Pottery residue is therefore often sampled for radiocarbon (¹⁴C) dating. There are several ways in which these residues can survive up to the present day, either being absorbed inside a vessel wall or encrusted on the internal and external pottery surfaces.

Most residue analyses have focused on the inside of pottery, where the presence of proteins and lipids indicates a clear association with the processing of animal or plant resources. These types of residues form attractive samples for ¹⁴C dating. However, dates on “food crusts” do not always correspond to dates obtained on other kinds of evidence. This led to discussions about the reliability of accelerator mass spectrometry (AMS) dates on food residues, especially where the processing of aquatic resources is expected (Fischer and Heinemeier 2003; Craig 2004; Hart and Lovis 2007; Boudin et al. 2009, 2010; Philippsen 2013; Roper 2013; Philippsen and Meadows 2014; Roper 2014; Hart and Lovis 2014; Heron and Craig 2015). Residues sticking to the outer pottery surface, on the other hand, are almost never analyzed, not even when they are used for ¹⁴C dating.

Outer Surface Residues

Carbonized material on the outside of pottery is commonly considered to be soot, derived from the combustion of wood. Apart from carbon, soot may be composed of various other products such as organic tars and resins. When resin droplets in the rising smoke come in contact with the cooler ceramic surface, they can solidify, forming a hard and waterproof layer (Skibo 2015).

Most research on soot has been conducted within the context of vessel use and use-alteration traces (Beck et al. 2002; Hally 1983; Skibo 1992, 2013, 2015). Experiments by Hally (1983) and Skibo (1992) point out that temperature is a key variable in the formation and patterning of soot, as it cannot form on surfaces approaching 400°C. Soot is therefore unlikely to be found on

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a vessel's base, where it is in close contact with the fire. It will rather adhere to higher parts of the vessel, in particular when water inside the vessel is cooling down the ceramic surface.

The determination of residue as soot is usually based on visual inspection. A distinction is often made between thick, charred deposits or "food crusts" on the inside and a rather thin layer of black, sometimes glossy coating on the outside of pottery. In some cases, however, traces of food residue are observed on the external surface, mostly near the rim, as a result of cooking contents boiling over or even leaking through pores from the inside out (Andersen and Malmros 1985:85; Koch 1998:117; Evershed 2008:904). Even though food crusts may be present on the outer pottery surface, external residues are never analyzed prior to ^{14}C dating. In fact, with few exceptions (e.g. Oudemans and Boon 1991; Oudemans 2006), hardly any research has been done on the composition of these residues. As is the case with food crusts, ^{14}C dates obtained on outer surface residues often do not correspond with the expected pottery age. Moreover, in many cases these dates also do not agree with those on food crusts coming from the same type of pottery or potsherd. These dating discrepancies are usually explained as the result of a reservoir effect on inner food crusts or of an old wood effect on outer soot (Fischer and Heinemeier 2003; Miyata et al. 2011; Philippsen 2012, 2013; Piezonka et al. 2016).

This study confronts ^{14}C dates on internal and external surface residues preserved on Mesolithic/Neolithic pottery from Bazel Sluis (Belgium) with the results of bulk isotope analysis and thermally assisted hydrolysis and methylation pyrolysis-gas chromatography-mass spectrometry (THM-GC-MS).

MATERIALS AND METHODS

Site and Samples

The prehistoric wetland site of Bazel Sluis is situated in northwestern Belgium, on the left bank of the lower Scheldt River (51°08'09''N, 4°19'23''E; Figure 1). It is located on the top and gentle slope of a former sand ridge, most likely a point bar. Apart from numerous burnt and unburnt animal bones and ecofacts, this site yielded thousands of pottery fragments and lithic artifacts dating from the Middle Mesolithic to the Middle Neolithic (Crombé et al. 2015a). The selected pottery fragments come from the eastern slope of the sand ridge, where the occupation levels have been covered by peat and fluvial sediments (Crombé et al. 2015b), offering favorable preservation conditions for plant material, unburnt animal bone, and organic pottery residues.

Eight sherds with residues on both the internal and external surfaces were selected for analysis and ^{14}C dating. They represent rim, wall, and base fragments from vessels belonging to the same pottery group. Based on decorative elements (rim decoration, knobs, perforations) this pottery could be related to that of the Final Mesolithic-Neolithic Swifterbant culture, known from nearby sites at Doel "Deurganckdok" (Crombé et al. 2008; Crombé 2010). At Doel, the ^{14}C dates on food crusts and on organic material seem to be incompatible, the former clustering in the first half of the 6th millennium BP and the latter around the middle and in the second half of the 6th millennium BP (Boudin et al. 2009, 2010). The older ^{14}C dates probably result from a freshwater reservoir effect on the food crusts, since these sites are located in the Scheldt River valley and cremated bones of freshwater fish were found during the excavations (Boudin 2009:697; Crombé et al. 2008).

For the selected Bazel pottery, indirect ^{14}C dates are available on unburnt animal bone originating from the same stratigraphic layer (Table 1) (Meylemans et al. 2016). Based on these three dates, the pottery is expected to date between 5350 and 5000 BP or 4350 and 3700 cal BC. The calibration method is described in the section below.

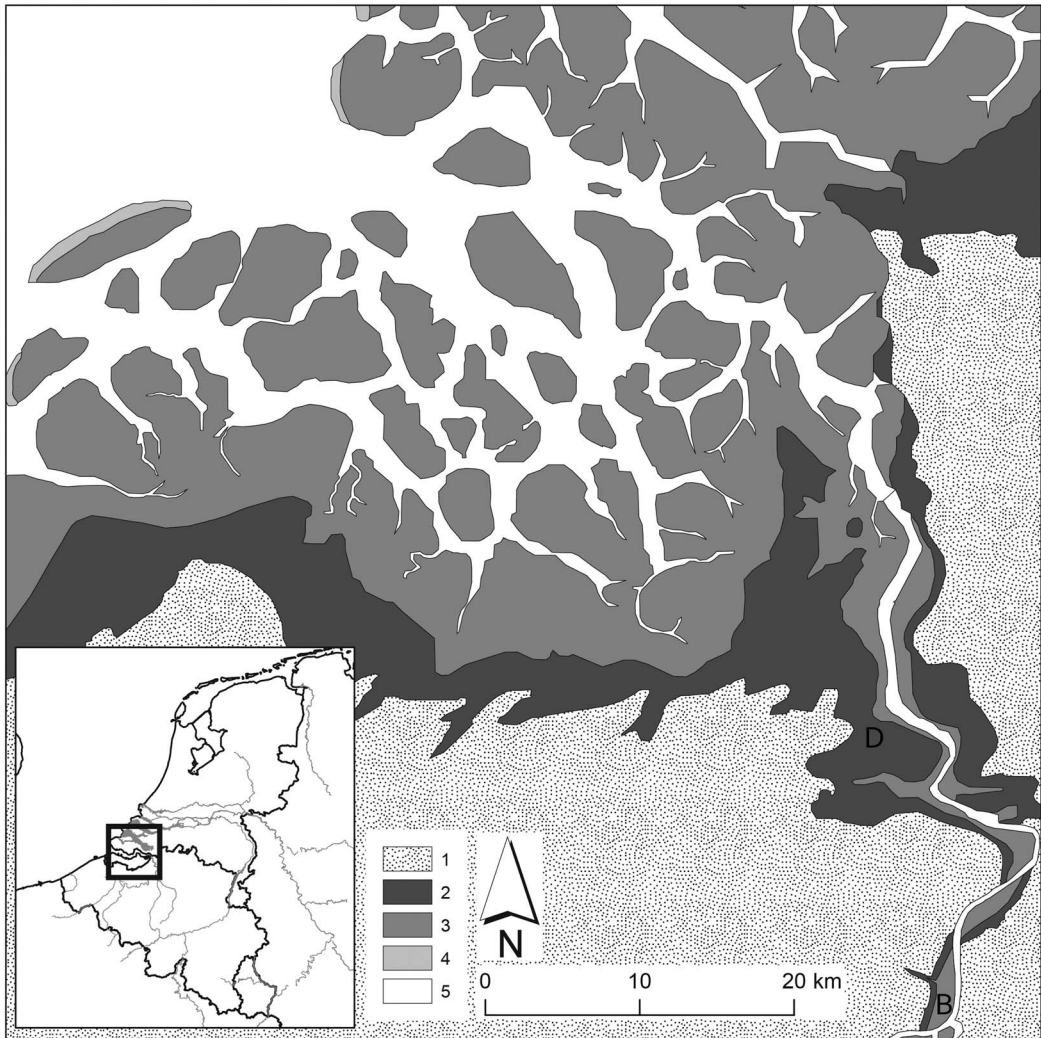


Figure 1 Palaeogeographical map of the Scheldt estuary around 6300 cal BP (modified after Vos and Van Heeringen 1997) with indication of the prehistoric sites mentioned in the text: Bazel Sluis (B) and Doel Deurganckdok (D). Key: 1. Pleistocene coversand area; 2. peatland; 3. tidal area (mudflats and saltmarshes); 4. beaches and dunes; 5. North Sea, tidal inlets and tidal channels.

Table 1 AMS ^{14}C determinations on collagen from animal bones excavated at Bazel Sluis (Meylemans et al. 2016).

Find reference	AMS lab code	Animal species	Dating material	Conventional ^{14}C age BP ($\pm 1\sigma$)	Calibrated age BC ($\pm 2\sigma$)
2/12/16/1	KIA-47410	<i>Ovis ammon f. aries</i>	Upper skull, horned	5320 \pm 45	4318–4004
2/12/86/6	KIA-47412	<i>Cervus elaphus</i>	Metatarsus, pierced	5030 \pm 55	3957–3706
2/3/30/6	KIA-47413	<i>Bos primigenius f. taurus</i>	Metatarsus	5105 \pm 40	3976–3797



Figure 2 Organic residues preserved on the outer (left) and inner (right) surfaces of sherd 2/12/17/6 from Bazel Sluis.

The inner surface residues consist of thick layers of charred crusts, while the outer surfaces are patched with dusty black particles and/or a glossy black film or coating (Figure 2), in line with the descriptions of pottery residues from other archaeological sites. Visually, these residue types seem to be of different origins.

AMS ^{14}C Dating

All residues were pretreated with the acid-alkali-acid (AAA) method. ^{14}C determinations were measured on the AMS at the Royal Institute for Cultural Heritage, Brussels (Lab code RICH-) (Boudin et al. 2016). CO_2 was obtained by sample combustion in the presence of CuO and Ag . Graphitization was performed with H_2 over a Fe catalyst. Targets were prepared at the Royal Institute for Cultural Heritage in Brussels (Belgium) (Van Strydonck et al. 1990–1991). ^{14}C calibrations were performed using OxCal version 4.2 (Bronk Ramsey 2009) and the IntCal13 calibration curve date (Reimer et al. 2013).

Stable Carbon and Nitrogen Isotope Analysis

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analyses were performed in duplicate on a Thermo Flash EA/HT elemental analyzer, coupled to a Thermo Delta V Advantage Isotope Ratio Mass Spectrometer via ConFlo IV interface (Thermo Fischer Scientific, Bremen, Germany). Standards used were IAEA-N1, IAEA-C6, and internally calibrated acetanilide. Analytical precision was 0.25‰ for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ based on multiple measurements of the standard acetanilide.

THM-GC-MS

In total 7 residue samples from both the inside and outside of different pottery fragments have been analyzed using THM-GC-MS. Prior to analysis, 20 μL 2.5wt% tetramethylammonium hydroxide (TMAH) in methanol solution was added to a tiny aliquot of sample (not weighed, but in the order of a few tens of micrograms). This solution also contained 100 $\text{ng}/\mu\text{L}$ heptadecanoic acid (C17:0) as an internal standard. The content of this vial was well-mixed to homogenize, and 2 μL was transferred to the stainless-steel pyrolysis cup (Frontier Lab Eco-cup LF) with auto-Rx glass fiber disc. The cup was pyrolyzed at 480°C in a He atmosphere for 12 s.

Analyses were carried out with a Frontier Lab Multi-Shot Pyrolyzer (3030D) in conjunction with an autoshot sampler AS-1020ET (both Frontier Lab, Japan). The interface and the injector of the chromatographic system were kept at 300°C. The analytical column was directly coupled to the pyrolyzer via a custom made split device (split ratio 20), minimizing dead volume and improving the signal. For the chromatographic separations, a TraceGC gas chromatograph (Thermo), hyphenated with a PolarisQ Ion Trap mass spectrometer (Thermo), was used. Separations were accomplished on a SLB-5ms capillary column (Supelco, 20 m × 0.18 mm i.d. × 0.18 µm film thickness) applying the following temperature program: initially the oven temperature was maintained at 35°C for 1 min after pyrolysis. Next, a 10°C/min gradient was applied up to 240°C; finally, the column was heated to a temperature of 315°C at a rate of 6°C/min; this temperature was maintained for 5 min. The carrier gas was helium 6.0 grade at a constant flow of 0.9 mL/min. The MS transfer line temperature was kept at 290°C. Ionization was carried out in the ion volume of the ion trap mass spectrometer under the standard EI positive mode at 70 eV. The mass spectrometer was scanned in the 35–650 atomic mass unit (amu) range, with a cycle time of 0.59 s.

RESULTS AND DISCUSSION

AMS ¹⁴C Dating

The ¹⁴C ages for charred residues on the inner and outer surfaces of the Bazel pottery are given in Table 2. Sample 8 did not contain enough residue on the outside to date.

The outer surface residues systematically date younger than the food crusts. Chi-squared (χ^2) tests indicate a statistically significant difference in most samples for which both residues have been dated. Only samples 4 and 7 pass the test. The extent to which the ¹⁴C dates on food crusts and outer surface residues differ seems to vary quite a lot between samples, with a discrepancy of up to approximately 400 ¹⁴C yr for sample 3.

The ¹⁴C dates from organic residues preserved on pottery from other archaeological sites show similar deviations between inner and outer surface residues (Table 3). In all cases but one—a recently published date on the outer crust of Narva pottery at Veksa 3 (Piezonka et al. 2016)—residues on the outer surfaces yield younger ages. Again there seems to be a considerable variation as to how much these ages differ from those obtained on food crusts. Sample SLAS-1713, a potsherd from the Ertebølle site of Schlamersdorf in northern Germany, probably is not representative here. This sample presents an exceptionally large dating discrepancy that is difficult to explain. According to Philippsen (2013), a freshwater reservoir effect is however likely for the food crusts on the inside of this pottery.

Fischer and Heinemeier (2003) and Miyata et al. (2011) find reason for the dating discrepancies in a (freshwater) reservoir effect on food crusts—in the light of younger ¹⁴C dates on associated organic material—and/or in an old wood effect on the outer surface soot. Miyata et al. (2011), in a recent article about this same dating problem, mention diagenesis as a third possible cause. According to these authors, the less carbonized food crusts on the inner surfaces could be more vulnerable to the influence of humic acids in the soil. However, a harsh AAA treatment prior to AMS ¹⁴C dating, as was done for this study, should remove all humic acids. Piezonka et al. (2016) emphasize that there is currently no direct evidence for a significant freshwater reservoir effect at Veksa 3, but that high $\delta^{15}\text{N}$ values for both inner and outer surface residues on sample VE-2007/118 suggest the use of aquatic resources. Regardless, on this site there seems to be no difference between the ¹⁴C dates on both types of residue.

Table 2 AMS ^{14}C determinations on inner and outer surface residues preserved on pottery fragments from the prehistoric site of Bazel Sluis. When multiple ^{14}C dates from the same sample are combined (prior to calibration) a χ^2 test (Shennan 1988) is performed to establish their internal consistency. If the χ^2 value (T) is higher than the 5% confidence limit of 3.8, the combined ^{14}C dates are not coherent and the test fails. For the χ^2 tests, the uncalibrated ^{14}C dates on both types of residue from each sample were combined using OxCal v. 4.2 (Bronk Ramsey 2009).

Sample nr.	Fragment type	Find reference	Residue location	AMS lab code	Conventional ^{14}C age BP ($\pm 1\sigma$)	Conventional age BC ($\pm 2\sigma$)	χ^2 -Test (pass/fails)
1	Rim	2/12/74/6	Inside	RICH-22460	5974 \pm 45	4983–4730	Fails
			Outside	RICH-22474	5791 \pm 49	4777–4526	T = 7.550 (5% 3.8)
2	Rim	2/12/52/8	Inside	RICH-22461	5814 \pm 44	4778–4551	Fails
			Outside	RICH-22477	5661 \pm 38	4590–4371	T = 6.944 (5% 3.8)
3	Rim	2/12/62/7	Inside	RICH-22462	6040 \pm 36	5034–4840	Fails
			Outside	RICH-22491	5642 \pm 34	4545–4370	T = 64.719 (5% 3.8)
4	Rim	2/12/74/7	Inside	RICH-22466	5865 \pm 37	4831–4617	Pass
			Outside	RICH-22473	5791 \pm 49	4777–4526	T = 1.4 (5% 3.8)
5	Base	2/3	Inside	RICH-22463	5854 \pm 36	4823–4612	Fails
			Outside	RICH-22475	5713 \pm 41	4682–4461	T = 6.662 (5% 3.8)
6	Wall	2/12/74/6	Inside	RICH-22465	5814 \pm 37	4770–4551	Fails
			Outside	RICH-22476	5658 \pm 38	4583–4371	T = 8.645 (5% 3.8)
7	Rim	2/3	Inside	RICH-22464	5902 \pm 36	4848–4695	Pass
			Outside	RICH-22478	5893 \pm 35	4841–4696	T = 0.0 (% 3.8)
8	Wall	2471	Inside	RICH-22459	5672 \pm 38	4612–4374	

Table 3 AMS ¹⁴C determinations on paired organic residue preserved on pottery from archaeological sites in Denmark, Germany, Russia, and Japan.

Site (country)	Find reference	Residue location	AMS lab code	Conventional ¹⁴ C age BP (±1σ)	χ ² -Test (pass/fails)	Reference
Åkonge (DK)	49,5/77,0:26	Inside	AAR-5108	5385 ± 45	Fails	Fischer and Heinemeier (2003)
		Outside	AAR-5109	5195 ± 45	T = 8.912 (5% 3.8)	
Åkonge (DK)	50,0/75,5:18	Inside	AAR-5112	5185 ± 40	Pass	Fischer and Heinemeier (2003)
		Outside	AAR-5113	5070 ± 45	T = 3.6 (5% 3.8)	
Åkonge (DK)	49,5/77,5:10	Inside	AAR-5110	5150 ± 100	Pass	Fischer and Heinemeier (2003)
		Outside	AAR-5111	5140 ± 40	T = 0.0 (5% 3.8)	
Irienaiko (JP)	SGMB-4232a	Inside	PLD-5314	5055 ± 25	Pass	Miyata et al. (2011)
	SGMB-4332b	Outside	PLD-5315	5035 ± 25	T = 0.3 (5% 3.8)	
Irienaiko (JP)	SGMB-4233a	Inside	PLD-5316	5040 ± 25	Pass	Miyata et al. (2011)
	SGMB-4233b	Outside	MTC-06987	4975 ± 35	T = 2.3 (5% 3.8)	
Irienaiko (JP)	SGMB-4236a	Inside	PLD-5319	5065 ± 25	Fails	Miyata et al. (2011)
	SGMB-4236b	Outside	PLD-5320	4980 ± 25	T = 5.780 (5% 3.8)	
Irienaiko (JP)	SGMB-4238a	Inside	PLD-5322	5060 ± 25	Fails	Miyata et al. (2011)
	SGMB-4238b	Outside	PLD-5323	4950 ± 30	T = 7.914 (5% 3.8)	
Irienaiko (JP)	SGMB-4239a	Inside	PLD-5324	5040 ± 30	Pass	Miyata et al. (2011)
	SGMB-4239b	Outside	PLD-5325	4970 ± 30	T = 2.7 (5% 3.8)	
Schlamersdorf (DE)	SLAS-1713	Inside	AAR-11481	6850 ± 120	Fails	Philippson (2012, 2013)
	SLAS-1713	Outside	AAR-11481s	5190 ± 110	T = 104.006 (5% 3.8)	
Veksa 3 (RU)	Ve-2007/118a	Inside	KIA-33926	5425 ± 30	Pass	Piezonka et al. (2016)
	Ve-2007/118b	Outside	KIA-49796	5492 ± 23	T = 3.1 (5% 3.8)	

At Bazel Sluis, not only do the outer surface residues date systematically younger than the food crusts, but both types of residue yield ^{14}C dates that are too old in comparison to dates obtained on associated animal bone. An old wood effect on the outer residues in combination with a (larger) freshwater reservoir effect on the inner residues is a possible explanation for this discrepancy. However, in order to gain insight into the reasons for this age difference we need to look at the biochemical composition of both residue types.

Stable Carbon and Nitrogen Isotope Analysis

The $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ values, and atomic C:N determined for charred residues on the inner and outer surfaces of the Bazel pottery are given in Table 4 and plotted in Figure 3. Samples 1 and 8 did not contain enough residue on the outside to analyze.

The isotopic values of inner and outer surface residues cluster within the same range, between approximately -26.5 and -28.5% $\delta^{13}\text{C}$ and between approximately $+6$ and $+10\%$ $\delta^{15}\text{N}$. The only exceptions are the inner residues of sample 2 in nitrogen values and of sample 1 in carbon values. Unfortunately, for the latter sample we do not have comparative data for the external surface. Sample 3 presents the biggest difference in carbon values between the inner and outer surface residues.

Looking at these carbon and nitrogen values, it could well be that aquatic resources have been processed inside these vessels. Craig et al. (2007) defined a bulk isotopic theory to distinguish aquatic products in charred food residue, according to which relatively light $\delta^{13}\text{C}$ values ($<-25\%$) and $\delta^{15}\text{N}$ values between $+6$ and $+10\%$ indicate that freshwater fish is a likely component of these residues, and probably the major component for samples with high $\delta^{15}\text{N}$ values ($+8$ to $+10\%$). At Bazel, both burnt and unburnt freshwater fish bones were collected during the excavation, but it is not clear which of these remains are related to the same occupation phase as the pottery fragments discussed in this article. However, the presence of burnt fish bones and the

Table 4 $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ values and atomic C:N ratios determined for charred residues on the inner and outer surfaces of the Bazel pottery. The right-most column presents the analysis numbers for residues analyzed with THM-GC-MS at the Royal Institute for Cultural Heritage (Brussels, Belgium).

Sample nr	Residue location	$\delta^{13}\text{C}$ (%)	$\delta^{15}\text{N}$ (%)	Atomic C:N	%N	%C	THM-GC-MS analysis nr
1	Inside	-30.5	6.2	25.58	0.10	2.09	
2	Inside	-27.8	11.0	9.01	1.89	14.60	
	Outside	-27.7	8.7	14.77	2.64	33.37	
3	Inside	-28.2	9.3	8.90	1.14	8.68	
	Outside	-26.9	9.0	11.58	4.59	45.60	P217.088
4	Inside	-28.1	7.6	8.49	8.28	60.26	P224.036
	Outside	-28.2	6.6	20.42	0.38	6.57	P224.010
5	Inside	-27.9	7.1	12.25	4.79	50.31	P224.038
	Outside	-27.4	7.2	18.55	0.95	15.09	
6	Inside	-27.9	7.7	7.86	8.26	55.63	P224.035
	Outside	-27.9	8.2	22.33	0.53	10.09	
7	Inside	-27.8	8.5	11.47	2.56	25.14	
	Outside	-27.9	8.6	19.45	1.63	27.10	P224.011
8	Inside	-27.7	7.7	6.7	10.92	62.70	P224.037

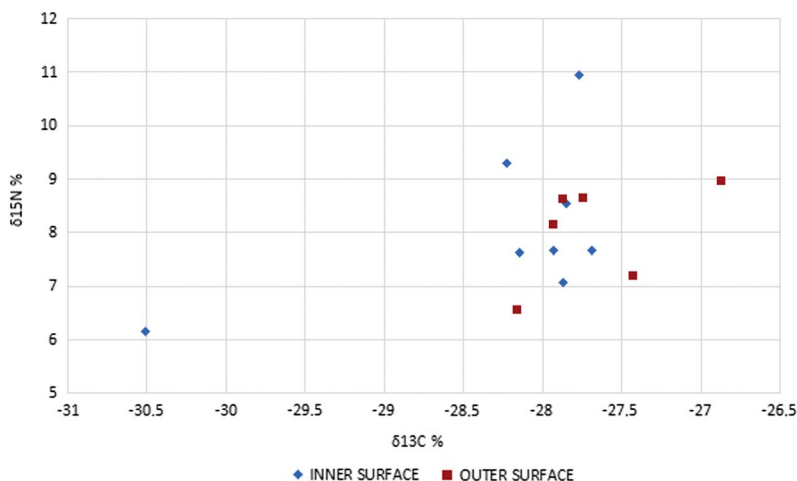


Figure 3 Plot of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values determined for charred residues on the inner and outer surfaces of the Bazel pottery. The analytical precision is 0.25% for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

location of this site near the Scheldt River, in combination with ^{14}C dates on food crusts that are too old, can be considered as indicators for the processing of freshwater fish.

If we apply Craig's bulk isotopic theory on the Bazel pottery, freshwater fish is likely to be present in all residues, including those from the external surfaces. Regardless of the presence of aquatic resources, the clustering of isotopic values from both types of residue indicates that they at least have some similar components.

Finally, it is noted that the outer surface residues systematically have higher C:N ratios than the inner food crusts. This has also been noticed by Miyata et al. (2011) for the Jomon pottery from the Irienaiko site in Japan and by Philippsen (2012) for residues that had formed on copies of prehistoric vessels during cooking experiments. Based on the isotopic ratios and the C:N values, the latter author suspected a possible presence of food residue in the outer crusts, as a result of food boiling over. Philippsen (2012:125) considered the higher C:N ratios for the outer crusts as an indication that not only food residue but also soot was present on the exterior.

THM-GC-MS

To determine their biochemical composition, 4 samples of inner surface residue and 3 samples of outer surface residue have been analyzed using THM-GC-MS (Table 4). For both types of residue similar chromatograms were obtained (Figure 4), stressing the results of the bulk stable isotope analyses, i.e. that many of the same organic compounds can be found on the inside and outside of the Bazel pottery.

Both pottery surfaces show clear indicators for the presence of food residue. Many fatty acids—mainly palmitic (C16:0) and stearic (C18:0)—are measured, with oleic acid (C18:1) as the most common unsaturated fatty acid. It is noted that the ratio between palmitic (P) and stearic (S) acids is more variable within the outer surface residues (P:S 0.47–1.2) as compared to the inner surface residues (P:S 0.52–0.57). With the exception of the outer crust on sample 3, all residues seem to contain cholesterol-related compounds. In addition, all residues show at least some

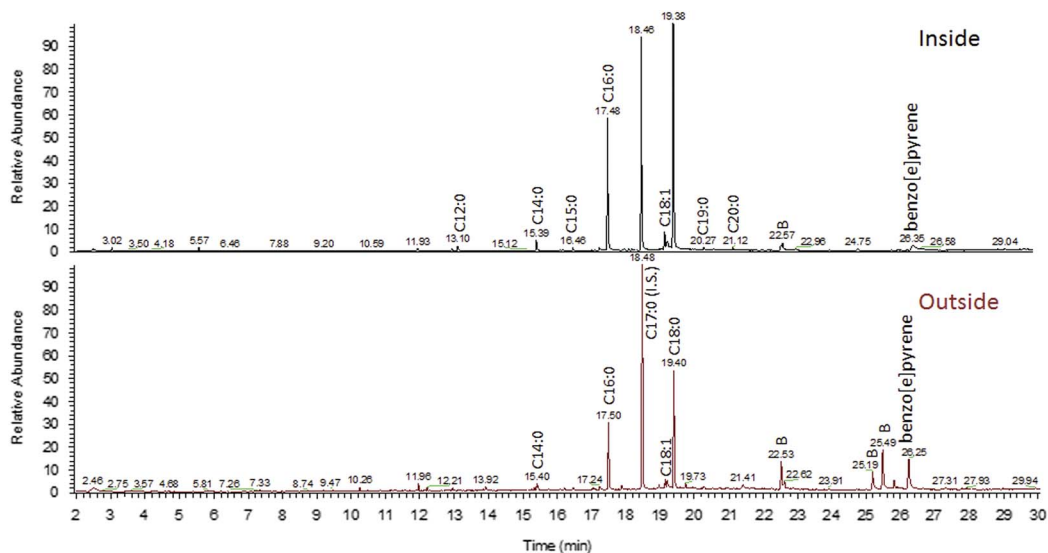


Figure 4 Gas chromatograms (THM-GC-MS) of the inner and outer surface residues of sample 4 from Bazel Sluis. “B” stands for compounds also present in blank samples. “Cx:y” indicates a fatty acid with (*x*-axis) the number of carbon atoms and (*y*-axis) the number of unsaturated bonds. A solution containing C17:0 as an internal standard was added to each sample.

protein fragments. On the inside of sample 5 and the outside of sample 7 palmitone, the ketone of palmitic acid, is detected. Although some of these compounds may derive from plant material, several elements point toward the presence of animal fats and the processing of animal resources inside this pottery. It is not yet clear whether these are related to aquatic or terrestrial animal species.

In all residues one or several polycyclic aromatic hydrocarbons (PAHs) are detected. It concerns benzo[e]pyrene or benzo[k]fluoranthene¹, possibly in combination with indeno[1,2,3-cd]pyrene for the outer crust of sample 3. These PAHs derive from the incomplete combustion of organic compounds, probably animal fats or fuel (wood?). A study by Oudemans and Boon (1991) also revealed the presence of PAHs in residues on the outside of pottery, using Py-GC-MS, which was interpreted as being indicative for smoke condensates or “soot” from cooking over wood fires (Oudemans 2006:38). In order to test this premise, a reference sample of modern soot was analyzed by using the same technique. This led to the detection of several markers (in the form of PAHs) for soot mentioned in the literature (Wei et al. 2011). However, inside the pottery residues from Bazel only one of these markers, benzo[e]pyrene or benzo[k]fluoranthene, was detected. It is possible that the analyzed samples were too small to detect more PAHs, or maybe other techniques, such as Raman spectroscopy (Coccatto et al. 2015), would be more successful in identifying soot. It seems unlikely that soot is totally absent from the ceramic surface, especially on the outside of the vessels.

It is clear from the analyses that food remains are not only present on the inner pottery surface but also on the outer pottery surface. Most of these remains are located near the rim, but they also seem to occur on wall and even base fragments. During cooking inside these vessels,

¹The mass spectra of both compounds are very similar and their retention times are relatively close to each other. Without a reference standard of one of these compounds, it was unfortunately not possible to make this distinction.

foodstuff probably boiled over, or organic compounds migrated through the vessel wall and burnt on the exterior (Evershed 2008). The possible presence of food residue on the outside of archaeological pottery is an important factor to take into account when sampling material for ^{14}C dating, as it may be subject to the same dating problems as inner food crusts, i.e. a reservoir effect.

However, if only food remains were present on either side of the vessel then there would not be a divergence between their ^{14}C dates. We suggest that this discrepancy results from the mixed presence of food residue and soot on the external pottery surfaces, as opposed to a more homogeneous composition of food residues encrusted on the inside of this pottery. Because the (freshwater) reservoir effect is probably much larger than a possible old wood effect, sampling a mixture of soot and food crusts may lead to younger dates on the external pottery surfaces. Because the residues on the external surfaces are mixed, variations in the age differences of the residues between different pottery fragments could be related to sampling location and quantity, affecting the relative proportions of food and soot present within the dated residue. For example, on the external surface of sample 7 it is theoretically possible that mostly food residue was preserved or sampled, resulting in little or no age difference between the inside and outside. Sample 3, by contrast, presents the largest discrepancy, possibly indicating that the residue sampled on the external surface mostly consisted of soot.

CONCLUSION

This study demonstrates the presence of food residue on the external surfaces of pottery from Bazel Sluis. Using THM-GC-MS it was possible to detect many fatty acids, cholesterol-related compounds and protein fragments, proving that the outer surface crust does not entirely consist of soot. This means that outer surface residues might also be subject to a reservoir age. Chemical analyses (e.g. THM-GC-MS) should be conducted prior to ^{14}C dating to determine the composition of these residues.

THM-GC-MS has also led to the detection of benzo[e]pyrene/benzo[k]fluoranthene, a possible soot marker. However, not enough markers (PAHs) were detected to prove soot, although its presence can at least be presumed for the outer pottery surfaces. Other techniques, such as Raman spectroscopy, might be better suited to identify soot.

^{14}C dates on outer surface residues at Bazel and also on other sites are often younger than those obtained on inner food crusts, but still are not compatible with dates obtained on associated plant and/or bone samples. We suggest that (1) these food crusts are subject to a reservoir effect and (2) the younger dates on the outer surface residues are due to a mixed presence of soot and food residue. Because the reservoir effect is larger than a possible old wood effect on soot, the mixture of both types of residue on the outside leads to younger dates than those obtained on more homogeneous food crusts sampled from the internal pottery surface.

ACKNOWLEDGMENTS

This research is a collaboration between the department of Archaeology of Ghent University and the Royal Institute for Cultural Heritage. The authors wish to thank the Flanders Heritage Agency for providing the sampled material. Part of this research was funded by the “Special Research Fund” (BOF) of Ghent University, in the context of the research project “Agropastoral Neolithic Ways of Life in the Sandy Lowland of Belgium.”

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