Direct Determination of the Contents of a Ceramic Bottle from the Moundville Site, Alabama

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Abstract A complete subglobular bottle was excavated from a linear feature at the Moundville site in the Black Warrior Valley of Alabama, dating to A.D. 1200–1500. Absorbed residue from the bottle and soil contained within the vessel were extracted, analyzed, and compared with residue from soil outside of the bottle. The residues suggest that the bottle was buried containing a stew or soup made with meat and a wide range of plants, rather than a tea or ritual beverage, which would have been the expected contents of a bottle based on vessel form. The bottle contents identified through residue analysis indicates that the vessel and its contents were an offering of food for the deceased.

A common approach in organic residue analysis involves the extraction of lipids that are either absorbed within the ceramic matrix of a potsherd, or preserved within visible encrustations on the surfaces of sherds. These extracted lipids are then chemically analyzed. Gas chromatography/mass spectrometry (GC/MS) is one of the preferred methods for this analysis, as it allows for the separation and identification of complex mixtures of compounds which are commonly found in archaeological residues. Once the compounds have been identified, the analyst tries to identify their biological source or sources, keeping in mind that the lipids probably underwent some degree of hydrolysis, oxidation, and/or microbial breakdown while buried. Despite the uncertainties inherent in this process, organic residue analysis is one of only a few methods that demonstrate a direct relationship between a vessel and the resources processed or stored in it. As such, residue analysis is particularly useful in studies of pottery use and food processing, and in discussions of pottery form and function.

Due to this usefulness, residue analysis should be particularly fruitful

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when applied to a vessel whose form is definitively known, such as a complete vessel. Since absorbed residue analysis generally destroys the sampled potsherd, however, this type of analysis is almost never done on whole pots, and rarely even on rim sherds. One study has attempted non-destructive sampling of absorbed residues on whole pots (Gerhardt et al. 1990), but it the study was dependent on pots containing very lipid-rich resources and has not been replicated. The rarity of analysis on whole vessels appears to explain the fact that analysis of soil interior to a whole vessel is seldom performed, even though it has often verbally been suggested as a 'best practice' for residue analysis. If and when analysis of interior soil does take place, it is important to compare the interior soil to a control soil sample from the archaeological site in question to prevent confusion between compounds naturally found in the local soil and compounds originating from archaeological residues.

The Ceramic Bottle: Description, Provenience, and Context

The pottery vessel analyzed for residue analysis was recovered at the Moundville site (1TU500) during excavations by the University of Alabama, Early Moundville Archaeological Project (EMAP) in 2006. Moundville is one of the largest prehistoric sites in the Southeast. It was the central town of a regional polity that occupied the Black Warrior River Valley in west-central Alabama, *ca.* A.D. 1200–1500. The site core, covering about 75 hectares, consists of 29 earthen mounds arrayed around a central plaza, extensive habitation areas, middens, cemeteries, and remnant palisade lines (Knight and Steponaitis 1998:2–6). The pottery vessel examined in this study is a subglobular bottle with a simple base, typical of a form found at Moundville (Steponaitis 1983:67). Moundville subglobular bottles were fired in a reduced oxygen atmosphere, which produced a dark surface color. The bottles are well smoothed or burnished, and often decorated with complex motifs executed in fine incised or engraved lines. However, this particular bottle was undecorated. It is assumed that ceramic bottles in the native Southeast were used for serving or storing liquids, an inference based primarily on attributes of form such as tall vertical necks and restricted orifices (Hally 1986:290). In contrast to the unburnished utility-ware found at Moundville, reduction-fired bottles (and bowls) were fine wares used for serving. They were not used in cooking because re-heating would mar the dark surface finish (Steponaitis 1983:27). Functional inferences about prehistoric Southeastern pottery are mostly limited to observations about form or context as evidence from residue analysis is rarely available. However, a fortuitous find

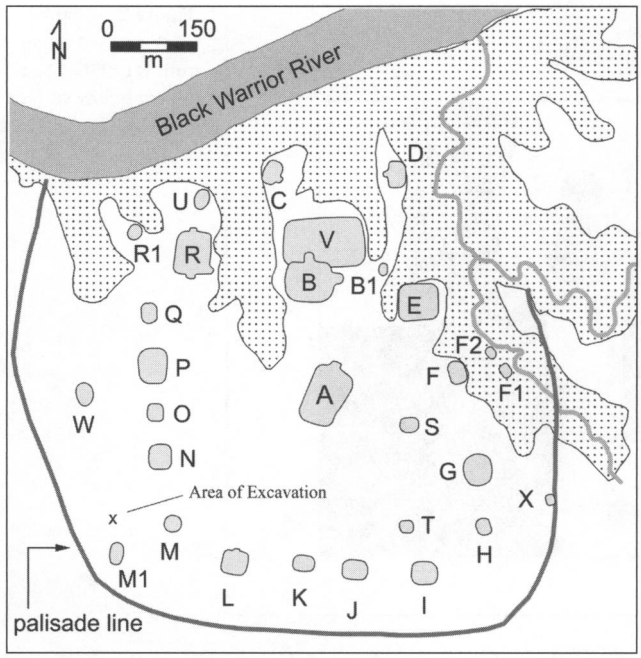

Figure 1. Area of excavation at Moundville.

provided an opportunity for the first residue analysis conducted on Moundville pottery.

The ceramic bottle was encountered during subsurface sampling of hectare N1700E600, when a 30 × 30 × 60 cm deep shovel test pit (STP) at grid N1705E675 was extended in size to 50 × 50 cm to provide a strata control profile for an adjacent 2 × 2 m excavation unit (Figures 1, 2). The bottle was left in situ. Subsequently, when the 2 × 2 m unit, N1703E675, was excavated down to the subsoil at 55 cm below surface, it became apparent that the bottle was associated with a linear feature (F-100) dug into the subsoil (Figure 3). F-100 originated from a higher stratum, probably the dark midden deposit directly over the subsoil, and it was not visible until the midden was removed. The undecorated bottle is not diagnostic to a specific time phase, and neither the bottle nor F-100 was directly dated. However, the overlying midden deposit from which it likely originated dates to the early Moundville II through Moundville III phases (A.D. 1250–1450).

Following University of Alabama protocol for excavation at Moundville Archaeological Park, we chose not to excavate F-100 because the feature had the linear outline suggesting a burial pit. Thus there was the possibility of encountering human remains, although none were found in the portion of F-100 removed by the STP extension. The portion of F-100 visible in the STP

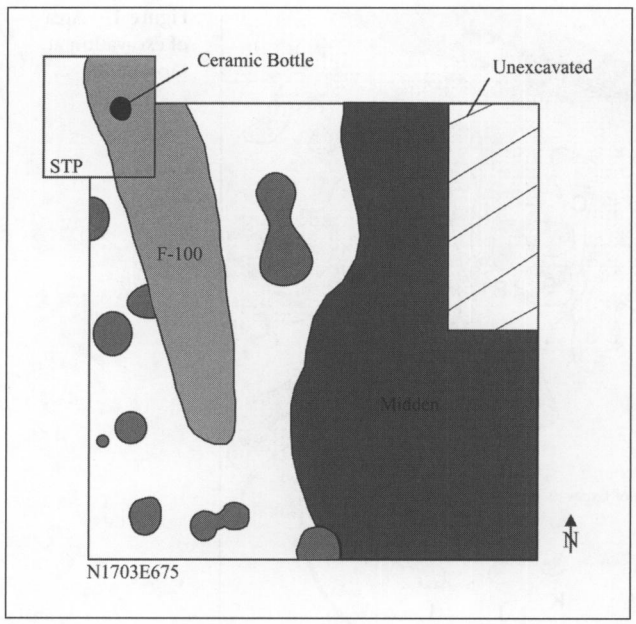

Figure 2. Plan view of 2 × 2 meter unit N1703E675 at 55 cm below surface.

profile revealed a 15-cm deep feature with straight walls and flat bottom. The ceramic bottle rested at the bottom of F-100. F-100 may have been a narrow burial pit or a wide wall trench, but because it was not completely excavated, the feature's function remains unknown.

The exposed bottle, in primary context, was fully uncovered, photographed in situ, and removed. The entire vessel was present, deposited intact in an upright position. However, the weight of the overburden had fractured it, and fragments separated from the rest of the vessel on removal. Approximately one-half of the bottle remained intact, held together by the soil that filled the interior (Figure 3). This intact half of the bottle was lifted directly from the in situ position and placed in a bucket, cushioned by clean bags, and covered with plastic. Once removed from the field, the bottle was sealed in a plastic bag. Because the soil contents covered and protected the interior surface, chances of contamination were minimal, so the vessel was deemed to be an ideal candidate for residue analysis.

Intact subglobular bottles are frequently associated with Moundville burials, placed intact and upright in the grave, most commonly with a single individual (Steponaitis 1983:Appendix A). While most people were not buried with bottles, there is no reason to suspect the bottles were restricted to a particular social rank since bottle sherds are widely distributed in both habitation debris and mound contexts. Instead, spatial distribution and context implies that bottles were valued personal possessions used in dis-

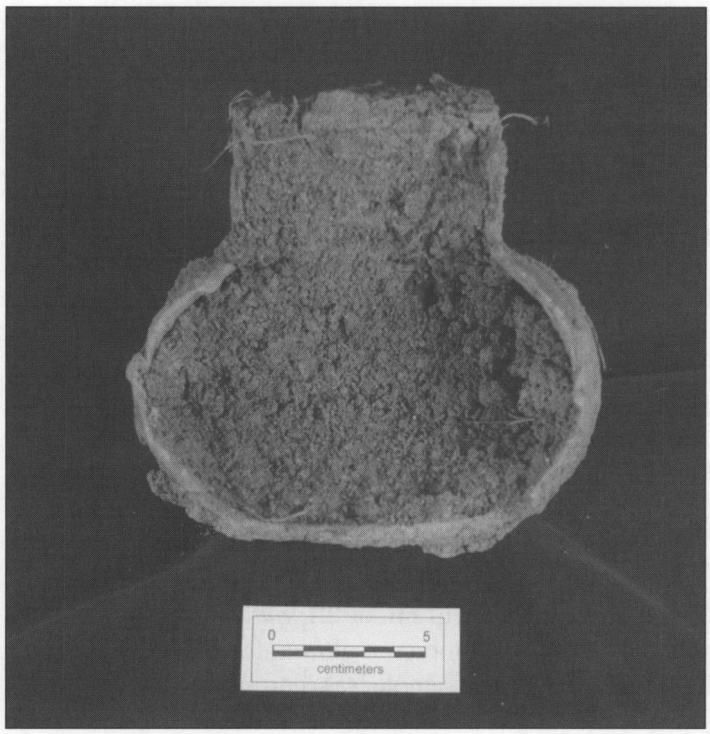

Figure 3. Interior view of the ceramic bottle.

plays involving the consumption of liquids. In contrast to earlier Woodland societies, Mississippian ceramic assemblages, such as those at Moundville, contain small bottle (and cup) forms, often highly decorated, suggesting that the individual-oriented consumption of liquids became a widespread and important social practice. Moreover, bottles were widely exchanged or copied, with distributions that sometimes extend far beyond localized style zones (e.g., Blitz and Lorenz 2006:114–118; Steponaitis 1983:327–341). The value placed on ceramic bottles and their use at Moundville and elsewhere in the Mississippian world highlights a rather obvious lacuna in our understanding of their social implications: we do not know what liquids were served from Mississippian bottles. Residue analysis provided an opportunity to address this question with an example from Moundville.

Methods

The sampled sherd was taken from the upper third of the rounded portion of the bottle, as that appeared to be the most likely upper limit of vessel

contents. The sampling location in this project was selected based on two criteria. First, lipids in aqueous solutions tend to float, thus a higher concentration of lipids might be expected towards the upper limit of the vessel contents. Second, it offered the best trade-off between abundant residue and lipids that might have been degraded by possible heating (Charters et al. 1993:216, 219). Although the bottle showed no evidence of fire-clouding or heat, it seemed wiser to sample the jar based partially on the possibility that heating may have taken place. The interior soil sample was taken from soil found directly adjacent to the sampled sherd and in contact with the pottery. The soil control sample was taken from the dark midden layer directly above subsoil in which F-100 was believed to originate, but not from F-100 fill. Unfortunately, no soil sample was taken from F-100 fill, and so the midden soil sample was the closest to the feature fill that could be obtained.

Residues were extracted using the methodology published by Evershed et al. (1990). The sherd was cleaned with a solvent-washed Dremel bit to remove surface impurities and crushed in a solvent-washed mortar and pestle. The internal standard of *n*-tetratriacontane was then added and the sherd was extracted with approximately 10 mL of 2:1 v/v chloroform/methanol per 2 g of powdered sherd. The solution was ultrasonicated for 20 min twice, with a 10 min cooling period. The sample was centrifuged at 2000 rpm for 20 min, the supernatant was pipetted into a solvent-washed vial, and filtered through solvent-washed 220–440 mesh amorphous silica gel. The resulting solvent/residue mixture was evaporated under N_2 gas and mild heat to dryness. An aliquot of this residue was derivatized with approximately 200 mL N,O-bis(trimethylsilyl)fluoroacetamide (BSTFA) +1% trimethylchlorosilane (TMCS) and analyzed in a Fisons 8065 gas chromatograph interfaced to a Trio 1000 mass spectrometer, using a DB-1HT 15 m × .32 mm column with .1µm film thickness and with a column head pressure of 13 psi. The temperature was held at 50°C for 2 min, then ramped at 10°C/min until 350°C, followed by a 10 min hold at that temperature. Total runtime was 42 minutes. Prior to analysis, the GC/MS was tuned with Decafluorotriphenylphosphine (DFTPP) to Environmental Protection Agency (EPA) standards to ensure consistent and precise mass spectrometry. This portion of the analysis is called the total lipid extract (TLE) since it contains all the components in the residue without saponification. The same procedure was followed for the soil samples, except that powdering in a mortar and pestle was not necessary.

The samples were then separated into neutral and fatty acid methyl ester (FAME) fractions for better quantification and analysis of the various compounds in the residues. Sixty percent of the total residues extracted were

transferred to a solvent-washed culture tube, then saponified with 2 mL NaOH/methanol and heated at 75 °C for 1 hour. The saponified residue was then extracted with 3 × 2 mL hexane, which was evaporated under N_2 gas and mild heat. These extractions became the neutral fractions, containing compounds such as alkanes, alkanols, and sterols. These fractions were stored under N_2 gas and refrigeration until analyzed using the same instrument and temperature program as in the TLE.

The remainder of the residues, containing primarily free fatty acids, was acidified to pH 3–4 with 2 M HCl, and extracted with 3 × 2 mL hexane into cleaned culture tubes. These solutions were evaporated and heated at 70–80° C (45 min) with boron trifluoride (BF_3)/methanol, Purified water (2–3 mL) was added after the solutions had cooled. These solutions were extracted with diethyl ether (2 × 3 mL) which was evaporated to dryness. The resulting FAMEs were stored under N_2 and refrigerated until analyzed using the same instrument and column as the TLE, but with a temperature program ramping from 50–150° C at 15°C min^{-1}, followed by 150–250° C at 3° C min^{-1}, and a 10 min hold at 250° C.

Blanks were run in parallel with the samples to control for laboratory contamination. Overall TLE, FAME, and neutral runs were clean except for small amounts of plasticizers; these were subtracted from the archaeological samples using the 'Background Subtract' function of the XCalibur program. Quantification of fatty acids and alkanes was done using the fractionated portions of the residues, which led to some differences between the apparent compositions of residues from TLEs and fractions. This is because free fatty acids and alkanes in the TLE underwent more oxidation and hydrolysis than the compounds in the fractionated portions of the residues, which were generally bound in triacylglycerols and wax esters prior to chemical preparation in the laboratory.

Interpretive Background

Absorbed lipid residues are interpreted in two major ways. The first uses relative abundances of compounds, particularly fatty acids. Relative abundances of fatty acids and other compounds can be used to determine the overall general origin of the absorbed lipid residue, such as primarily meat or primarily plant (Reber et al. 2004). Fatty acids alone cannot be used to determine the precise contents of a vessel, because this compound type is prone to oxidation and hydrolysis (Evershed 2008; Evershed et al. 1990; Reber and Evershed 2004). The second approach utilizes biomarkers, which are compounds unique to a particular resource or class of resource (Evershed 1993;

Mares 1988). Certain biomarkers for classes of compounds are relatively common, such as cholesterol for meat, phytosterols for plants, or certain terpenoids for resins. Other biomarkers are present in a limited group of potential sources and can be used to identify specific foods in the presence of corroborating archaeological evidence. Examples of this type of biomarkers are theobromine and caffeine, which can be attributed to chocolate (Hall et al. 1990; Hurst et al. 1989; Hurst et al. 2002). Biomarkers unique to a specific foodstuff are rarer, and knowledge of them at present is largely confined to tree resins and substances such as nicotine in tobacco (Beck and Borromeo 1990; Charters et al. 1993; Evans and Heron 1993; Evershed 1993; Gianno et al. 1990; Hocart et al. 1993; Rafferty 2002).

When interpreting a lipid residue, several different classes of compounds are examined. The fatty acid relative abundances, particularly in terms of chain length and saturation, are examined to determine the general overall composition of the residue as described above. Saturation is the number of double bonds present in a carbon chain. Fatty acids are generally written in the form $C_{\text{carbon chain length: N of double bonds}}$. Fatty acids most commonly occur linked to a glycerol backbone in the form of triacylglycerols, which are the most abundant constituents of fats and oils in nature. Free fatty acids, although present in normal lipids, occur in only small amounts and tend to dissolve in water more easily than the glycerol-linked forms (Evershed 1993; Evershed et al. 1992 and many others). In most cases, fatty acids with more unsaturated fatty acids, particularly $C_{16:1}$ and $C_{18:1}$, and more $C_{16:0}$ than $C_{18:0}$, tend to be formed primarily from plant or marine resources. Fatty acids with less unsaturated fatty acids and more $C_{18:0}$ than $C_{16:0}$ tend to be comprised primarily of meat lipids. Odd chain fatty acids often originate in bacterial or fungal lipids. Also, fatty acids with shorter chain lengths tend to wash out of absorbed residues earlier, while more unsaturated fatty acids are more prone to hydrolysis or oxidation. Due these and other issues described at length in other publications (Evershed 2008; Reber and Evershed 2004), this preliminary interpretation of fatty acid composition must be paired with the interpretation of other compound types.

Sterols are one of the compound types most likely to produce general category biomarkers. Cholesterol is a biomarker for the presence of meat resources, while there is a series of plant biomarkers, including sitosterol, campesterol, and stigmasterol that indicate the presence of plant resources. The presence of cholesterol or plant sterols can help support a fatty acid composition interpretation, as well as definitively determining whether plant and meat resources were present in the lipid residue. Unfortunately,

sterols are not as common as fatty acids, and are not always present. When they are present, however, they provide valuable and clear information concerning vessel contents.

Terpenoids are another compound type particularly useful in interpreting residues. They are plant biomarkers; pentacyclic triterpenoids are commonly found in non-pine plant resins and surface waxes (Harborne and Tomas-Barberan 1991; Langenheim 2003:38–40; Mills and White 1977:13, 19–20). Diterpenoids, particularly those with the pimarane and abietane carbon skeletons, are often biomarkers for pine resin.

Alkanols are long-chain alcohols—carbon chain lengths of 12–34 are often found in lipid residues. Alkanols often originate in wax esters, linked to alkanes. As such, alkanols give valuable information concerning the presence of waxes in the lipid residue. Waxes occur in all resource types (Kolattukudy 1976), but even-chain alkanols are particularly prevalent in higher plant waxes (Tulloch 1976). In this paper, alkanols will be notated by the form $OL_{\text{chain length}}$. By carefully examining references on plant waxes, sometimes a plant resource or a range of resources may be identified partially through alkanol composition. For example, very long-chain alkanols (such as OL_{32}) are rare in most plants but relatively common in panicoid grasses (Bianchi et al. 1984; Reber et al. 2004). Panicoid grasses are a large subfamily of about 2000 grasses, including maize and many other grasses from around the world. The presence of this compound indicates that a panicoid grass or panicoid grasses may be present in the residue. Additionally, most (but not all) plant waxes consist of a small number of alkanols esterified with a range of alkanes, or of a range of alkanols with a gradual increase in abundance of chain length to the most abundant alkanol, followed by a gradual decrease in chain length abundances (Tulloch 1976:245). Residues containing a wide range of alkanols, particularly those of very different chain length and not fitting either of these patterns, probably indicate that more than one plant resource is present.

Alkanes are unsaturated carbon chains, usually originally found linked to alkanols in waxes, or to sterols. Alkanes will be described in this paper in the form $AL_{\text{carbon chain length}}$. Like alkanols, they occur in all resource classes. Higher plant alkanes usually have odd carbon chains; highly branched alkanes often indicate microbial or fungal breakdown of the original wax ester. Furthermore, the alkane AL_{29} can be used as a biomarker for higher plant epicuticular wax (Evershed 2008:898). They can also be used to determine whether more than one resource source is present in a lipid similar to the way alkanols are used.

Data and Discussion

The contents of the absorbed residue and interior soil sample residue overall seem to indicate that the pot was buried with contents intact and that it contained a soup or stew made of a mixture of resources including meat and plants. The fact that the pot was buried with contents intact is indicated both by the large amount of residue in the interior soil and by the unusually high bacterial and fungal load present in the residue. The control soil sample contained very few lipids as shown in Tables 1, 2, and 3. Those present were not strikingly similar to the archaeological absorbed residue, also shown in Tables 1, 2, and 3, and comprised largely of a sequence of alkanes fairly typical of normal soil lipids (Eckmeier and Wiesenberg 2009; van Bergen et al. 1997). The interior soil, on the other hand, contained a large amount of residue that was similar to the residue absorbed by the sherd (see Tables 1, 2, and 3). It may be argued that the absorbed pottery residue simply washed from the pottery matrix into the interior vessel soil, and that the presence of abundant residue in the interior soil sample does not necessarily indicate that the contents of the pot were buried with the vessel. This explanation seems unlikely. Analysis of soil found adjacent to potsherds at the Dean Hall site in South Carolina indicates that while residue often does wash from pottery matrix to adjacent soil, the soil residue generally consists of large amounts of free alkanols and alkanes with very small amounts of triacylglycerols and relatively few free fatty acids (Reber 2009:12–16). The total lipid residue extracted from the interior soil in this vessel, however, contained large amounts of triacylglycerols and fatty acids, and relatively small amounts of free alkanols and alkanes, as shown in Table 1. It looked chemically very similar to the lipids in the absorbed residue. This suggests that intact lipids were present inside the bottle in the form of contents at burial.

The high bacterial load is demonstrated by the large amount of branched alkanols and the presence of trace amounts of ergosterol, a biomarker for fungus, in the neutral fractions of both the absorbed residue and interior soil residue (Table 2).

The presence of a mixture of meat and plant resources is indicated most clearly by a complex sequence of sterols present in the both the absorbed pottery residue and the interior soil sample, shown in Table 2. This series includes cholesterol, sitosterol, campesterol, and stigmasterol. More ambiguously, cycloartenol was also present in this sequence of sterols; cycloartenol is found in both fungi and higher plants (Gunstone et al. 1994:17; Weete 1976:395, 398, 404). Since other compounds in the residues originate from both fungi and higher plants, it is impossible to determine the original source of the cycloartenol.

Table 1. Percentage of total lipid extract fraction for each compound in the absorbed residue, interior soil, and control soil sample.

Compound	Absorbed Residue	Interior Soil	Control Soil
Sitosterol	4	7	
Stigmasterol	1	2	
Campesterol		6	
Cholesterol	2	1	
$C_{8:0}$	1		
$C_{9:0}$	1	1	
$C_{10:0}$	1		
$C_{11:0}$	1		
$C_{12:0}$	1		
$C_{14:0}$	7		
$C_{15:0}$	2		
$C_{16:0}$	10	4	3
$C_{17:0}$	2		
$C_{18:1}$	3	1	
$C_{18:0}$	6	3	3
$C_{24:0}$	1	1	
$C_{26:0}$	1	1	
$C_{32:0}$	1		
C_{17}br	3	1	
OL_{9}		1	
OL_{11}	1		
OL_{12}		1	
OL_{13}		1	
OL_{14}	1	1	
OL_{18}	3		
OL_{20}	1		
OL_{22}	1	1	
OL_{24}	1	2	
OL_{26}	1	2	
OL_{28}	2		
OL_{30}	1	2	
OL_{32}	2	5	
OL_{16}br	2		
AL_{14}		1	
AL_{15}		3	
AL_{16}		4	
AL_{26}	1		
AL_{27}		1	
AL_{29}	1	1	
AL_{31}	1	3	
AL_{32}	2	3	4
AL_{35}		1	
AL_{36}		3	13
AL_{37}			
AL_{38}			
AL_{40}			
AL_{14}br		1	
MAG 14	2	1	
MAG 16	4	1	8
MAG 18	4	2	69
MAG 26	4		
DAG 21.94		1	
DAG 22.31		1	
DAG 22.47	3	2	
DAG 22.72	1	1	
DAG 22.96		1	
DAG 23.27	1	1	
DAG 23.45	7	4	
DAG 24.20	1	1	
DAG 24.37	2	1	
DAG 25.09	1		
TAG 28.91	Trace	2	
TAG 29.56	Trace	2	
TAG 30.83		1	
Unidentified 10.96		4	

Note: Compounds are grouped by lipid type, and then by chain length. Monoacylglycerols are written MAG, diacylglycerols are written DAG, and triacylglycerols are written TAG. Since the precise molecular formula of diacylglycerols and triacylglycerols were difficult to ascertain using mass spectrometry, these compounds are listed by elution time, which should approximate with chain length, with the shorter chains eluting earlier than the longer chains. Note particularly the similarities between the absorbed pottery residue and interior soil residue and the differences with the control soil sample.

Table 2. Percentage of neutral lipid fraction for each compound in the absorbed residue, interior soil, and control soil sample.

Compound	Absorbed Residue	Interior Soil	Control Soil
Sitosterol	6	9	
Germanicol		9	
Stigmasterol	1		
Campesterol		4	
Cholesterol	2	3	
Ergosterol	Trace	1	
Unidentified triterpenoid	Trace	1	
OL_{9}	1		
OL_{12}	1		1
OL_{13}	1		
OL_{14}	2	1	
OL_{15}	2	Trace	
OL_{16}	3	1	
OL_{17}	1	1	
OL_{18}	5	1	
OL_{20}	2	1	
OL_{22}	2	2	1
OL_{23}	1	1	
OL_{24}	2	3	
OL_{25}	1		
OL_{26}		4	
OL_{28}	3	4	
OL_{30}	1	2	
OL_{32}	2	7	
OL_{34}	1		
OL_{36}	1		
di-OL_{18}		1	
OL_{15}br	4	1	
OL_{16}br	3	1	
OL_{17}br	3	Trace	
OL_{18}br	3	Trace	
OL_{20}br	1		
AL_{16}	2		
AL_{18}	1		
AL_{20}	1		
AL_{21}	1		
AL_{22}	2		
AL_{23}	1		3
AL_{24}	2	1	
AL_{25}	3	4	
AL_{26}	3	4	14
AL_{27}	5	6	16
AL_{29}	3	4	12
AL_{30}	2	4	9
AL_{31}	2	4	7
AL_{32}	5		7
AL_{33}	1	3	4
AL_{35}	1	1	
AL_{36}	2	2	5
AL_{37}	1		1
AL_{38}			2
AL_{40}			1
AL_{27}br			1
AL_{28}br			1

Note: Compounds are grouped by lipid type, and then by chain length.

The particular abundance of epicuticular plant waxes in this residue is indicated by the presence of abundant AL_{29} and the presence of large amounts of even-chain alkanols. Unusual pentacyclic triterpenoids common in plants, both identified (such as germanicol) and unidentified, were also present in the archaeological residues. Despite the distinctive and unusual components in the residues, the most specific definite interpretation that can be reached is a mixture of meat and higher plant components.

Some hypotheses can be constructed concerning the origin of the plant components, however, and could be tested in future. The potential presence of grains from panicoid grass is indicated by the relatively large amount of OL_{32} (Table 2). It is possible that the germanicol and unknown pentacyclic triterpenoids mentioned above originated in a unique epicuticular leaf wax;

Table 3. Percentage of FAME fraction for each compound in the absorbed residue, interior soil, and control soil sample.

Compound	Absorbed Residue	Interior Soil	Control Soil
$C_{14:0}$	3	3	
$C_{16:0}$	34	54	41
$C_{17:0}$	6		
$C_{18:0}$	38	18	59
$C_{20:1}$	7		
$C_{20:0}$	3	2	
$C_{22:0}$	1		
$C_{24:0}$	1		
$C_{26:0}$	1		
di-$C_{18:0}$		4	
di-$C_{20:0}$	3	2	
$C_{16:1}$br		1	
C_{16}br	3	6	
C_{18}br	2		

Note: Compounds are grouped by lipid type, and then by chain length.

alternatively, the compounds may have originated in several different plant resources, all included in the stew or soup.

The ability to analyze a soil sample from the interior of the vessel allows some unexpectedly useful interpretations. For example, without the soil sample, it would not have been possible to determine that the vessel was buried full of contents; just that the absorbed residue was unusually complex and well preserved with a heavy microbial and fungal load. Furthermore, the interior soil sample raised some interesting issues of residue preservation. By looking at the presence of triacylglycerols, the chain lengths of fatty acids and alkanols as well as the presence of branched and unbranched alkanols (Tables 1, 2 and 3), it appears that the residue from the soil sample actually had less microbial and fungal breakdown than the residue within the bottle. The reason for this is unclear; perhaps further archaeological and experimental studies will clarify the mechanisms involved. The larger incidence of short-chain alkanols and alkanes in the absorbed residue suggests that the absorbed residue was better protected from environmental degradation, such as water washing residues out of the pot. Likewise, given that unsaturated fatty acids were present in the absorbed residue but not the

soil sample, the absorbed residue seemed to be better protected from oxidation and hydrolysis than the interior soil residue.

Conclusions

This analysis demonstrates the usefulness of residue analysis in directly determining that, at least in this case, a complete bottle was buried containing a mixed stew of meat and vegetables, rather than the expected liquid offering. The residue analysis therefore confirms that in the Moundville context, at least in this case, complete pottery bottles placed with the dead held food. The wider implication of this finding is that the whole bottles were offerings, possibly from a dedicatory ritual that provided food for the deceased.

The bottle form is not generally associated with stews or soups, as the tall neck and constricted rim appear to be optimal for storage or drinking, rather than food serving. For this reason, bottles have generally been associated with teas or drinks. When the bottle was discovered, we speculated that it contained Black Drink (a tea made from *Ilex vomitoria*, a native North American source of caffeine), or another ritually important drink. This hypothesis, however, relies purely on interpretation of vessel form, which is necessarily a function of archaeological thought. Until the advent of residue analysis, it was not possible to directly determine the contents of a vessel. In this case, residue analysis of the Moundville bottle suggests that a bottle can hold foodstuffs—specifically soup or stew. This discovery does not disagree with the usual interpretation of vessel form. Since the pot was buried with its contents, presumably as an offering, the bottle was not meant as a serving vessel, which would have required a wider aperture and shorter neck, but as an offering which was not meant to be served, at least in the normal, physical sense. A practical vessel form for food serving was therefore unnecessary.

In this study, residue analysis allowed both a direct determination of the contents of an archaeological vessel and, more unusually, an interpretation of its use as an offering vessel. This confirms what has previously been an informal inference about the widespread practice of placing pottery vessels as grave offerings: the vessels continued to serve their primary function as food containers for the dead. More residue analysis of complete pottery vessels might reveal the variation and patterning of offerings, both of foodstuffs and drinks, as well as a better understanding of the relationship between vessel form and offering function. For the present, it is not known whether a specific vessel type or decoration was used for stew offerings vs. other types of postulated offerings, such as Black Drink. Were bottles used for all types of offerings? Did particular types of decoration

indicate the vessel contents? Only further residue analysis at this and other sites can answer these questions.

A vessel buried whole, but crushed by the weight of sediment following deposition would be an excellent candidate for this type of residue analysis. For the purposes of absorbed residue analysis, it is only necessary that the complete vessel was buried whole. In fact, as has been written elsewhere, residue analysis is peculiarly appropriate for examinations of pottery form and function. The contents of resources processed in a pottery vessel can be determined from a single sherd weighing 2 g or more. Although such an analysis would not be able to be as precise in terms of vessel form and function that from a whole vessel, this type of analysis can be used to distinguish cooking vessels from serving vessels (Charters et al. 1993; Charters et al. 1997), to approximately identify the temperatures to which a sherd has been subjected (Evershed et al. 1995; Hansel et al. 2004), to identify particular contents and constituents of a vessel (Dudd and Evershed 1998; Evershed et al. 1999; Gerhardt et al. 1990; Needham and Evans 1987; Serpico and White 1996), and to identify practices such as resin-sealing of pottery and steatite vessels (Hart et al. 2008; Reber and Hart 2008). As a sidenote, if an excavator is interested in submitting sherds for absorbed lipid residue analysis, the sherd should ideally not be washed, and should not be stored in plastic. That said, the technique is powerful enough that this special treatment is not completely necessary, and that very good results have been obtained from sherds that have been washed and stored in plastic for several years. If the excavator is fortunate enough to have a vessel buried whole, then the interior soil sample should be taken from a point adjacent to the pot wall at a location where the vessel contents were present. The control soil sample should be taken from the same context as the vessel in question, but not directly touching the exterior surface of the pot.

As a secondary benefit, this study demonstrates that in a few cases, destructive analysis of a potsherd may be unnecessary for residue analysis; soil samples found inside whole (or semi-intact) vessels may give valuable information concerning vessel contents. It is important to note, however, that this practice would be much less helpful in sampling vessels that were not buried with contents intact.

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References Cited

Beck, C. W. and G. Borromeo
1990 Ancient Pine Pitch: Technological Perspectives from a Hellenistic Shipwreck. In *Organic Contents of Ancient Vessels: Materials Analysis and Archaeological Investigations*, edited by W. R. Biers and P. E. McGovern, pp. 51–58. MASCA Research Papers in Science and Archaeology. vol. 7. The University Museum of Archaeology and Anthropology, University of Pennsylvania, Philadelphia.

Bianchi, G., P. Avato, and F. Salamini
1984 Surface Waxes from Grain, Leaves, and Husks of Maize (Zea mays L.). *Cereal Chemistry* 61(1):45–47.

Blitz, J H., and K. G. Lorenz
2006 *The Chattahoochee Chiefdoms*. The University of Alabama Press, Tuscaloosa.

Charters, S., R. P. Evershed, L. J. Goad, A. Leyden, P. W. Blinkhorn, and V. Denham
1993 Quantification and Distribution of Lipid in Archaeological Ceramics: Implications for Sampling Potsherds for Organic Residue Analysis and the Classification of Vessel Use. *Archaeometry* 35(2):211–223.

Charters, S., R. P. Evershed, A. Quye, P. W. Blinkhorn, and V. Reeves
1997 Simulation Experiments for Determining the Use of Ancient Pottery Vessels: the Behavior of Epicuticular Leaf Wax during Boiling of a Leafy Vegetable. Journal of Archaeological Science 24(1):1–7.

Dudd, S. N. and R. P. Evershed
1998 Direct Demonstration of Milk as an Element of Archaeological Economies. *Science* 282:1478–1481.

Eckmeier, E. and G. L. B. Wiesenberg
2009 Short-chain n-alkanes (C16-20) in Ancient Soil are Useful Molecular Markers for Prehistoric Biomass Burning. *Journal of Archaeological Science* 36(7):1590–1596.

Evans, K. and C. Heron
1993 Glue, Disinfectant and Chewing Gum: Natural Products Chemistry in Archaeology. *Chemistry and Industry* 12:446–449.

Evershed, R. P.
1993 Biomolecular Archaeology and Lipids. *World Archaeology* 25(1):74–93.
2008 Organic Residue Analysis in Archaeology: the Archaeological Biomarker Revolution. *Archaeometry*50: 895–924.

Evershed, R. P., S. N. Dudd, S. Charters, H. R. Mottram, A. W. Stott, A. Raven, P. F. van Bergen, and H. A. Bland
1999 Lipids as Carriers of Anthropogenic Signals from Prehistory. *Philosophical Transactions of the Research of the Royal Society of London Series B-Biological Sciences* 354:19–31.

Eversheed, R. P., C. Heron, S. Charters, and L. J. Goad
1992 The Survival of Food Residues: New Methods of Analysis, Interpretation and Application. *Proceedings of the British Academy*77:187–208.
Eversheed, R. P., C. Heron, and L. J. Goad
1990 Analysis of Organic Residues of Archaeological Origin by High-Temperature Gas Chromatography and Gas Chromatography-Mass Spectrometry. *Analyst* 115:1339–1342.
Eversheed, R. P., A. W. Stott, A. Raven, S. N. Dudd, S. Charters, and A. Leyden
1995 Formation of Long-Chain Ketones in Ancient Pottery Vessels by Pyrolysis of Acyl Lipids. *Tetrahedron Letters* 36(48):8875–8878.
Gerhardt, K. O., S. Searles, and W. R. Biers
1990 Corinthian Figure Vases: Non-destructive Extraction and Gas Chromatography-Mass Spectrometry. In *Organic Contents of Ancient Vessels: Materials Analysis and Archaeological investigations*, edited by W. R. Biers and P. E. McGovern, pp. 41–50. MASCA Research Papers in Science and Archaeology. vol. 7. The University Museum of Archaeology and Anthropology, University of Pennsylvania, Philadelphia.
Gianno, R., D. Erhardt, D. W. von Endt, W. Hopwood and M. T. Baker
1990 Archaeological Resins from Shipwrecks Off the Coasts of Saipan and Thailand. In *Organic Contents of Ancient Vessels: Materials Analysis and Archaeological Investigations*, edited by W. Biers and P. McGovern, pp. 59–67. MASCA Research Papers in Science and Archaeology. vol. 7. University of Pennsylvania, Philadelphia.
Gunstone, F. D., J. L. Harwood, and F. B. Padley (editors)
1994 *The Lipid Handbook*. Chapman and Hall, London.
Hall, G. C., S. Tarka, Jr., W. J. Hurst, D. Stuart, and R. Adams
1990 Cacao Residues in Ancient Maya Vessels from Rio Azul, Guatemala. *American Antiquity* 55(1):138–143.
Hally, D.J.
1986 The Identification of Vessel Function: A Case Study from Northwest Georgia. *American Antiquity* 51(2): 267–295.
Hansel, F. A., M. S. Copley, L. A. S. Madureira, and R. P. Evershed
2004 Thermally Produced ω-(o-alkylphenyl)alkanoic Acids Provide Evidence for the Processing of Marine Products in Archaeological Pottery Vessels. *Tetrahedron Letters* 45(14):2999–3002.
Harborne, J. B. and F. A. Tomas-Barberan (editors)
1991 Ecological Chemistry and Biochemistry of Plant Terpenoids. *Proceedings of the Phytochemical Society of Europe* Vol. 31. Clarendon Press, Oxford.
Hart, J. P., E. A. Reber, R. G. Thompson, and R. Lusteck
2008 Taking Variation Seriously: Testing the Steatite Mast-Processing Hypothesis with Microbotanical Data from the Hunter's Home Site, New York. *American Antiquity* 73(4):729–741.
Hocart, C. H., B. Fankhauser, and D. W. Buckle
1993 Chemical Archaeology of Kava, a Potent Brew. *Rapid Communications in Mass Spectrometry* 7:219–224.
Hurst, W. J., R. Martin, Jr., S. Tarka, Jr., and G. C. Hall
1989 Authentication of Cocoa in Maya Vessels Using High-Performance Liquid Chromatographic Techniques. *Journal of Chromatography* 466:279–289.

Hurst, W. J., S. M. Tarka, Jr., T. G. Powis, F. Vandez, Jr., and T. R. Hester
2002 Cacao Usage by the Earliest Maya Civilization. *Nature* 418:289.
Knight, V. J., Jr., and V. P. Steponaitis
1998 A New History of Moundville. In *Archaeology of the Moundville Chiefdom*, edited by Vernon James Knight, Jr. and Vincas P. Steponaitis, pp. 1–25. Smithsonian Institution Press, Washington and London.
Kolattukudy, P. E. (editor)
1976 *The Chemistry and Biochemistral of Natural Waxes*. Elsevier Press, Amsterdam.
Langenheim, J. H.
2003 *Plant Resins: Chemistry, Evolution, Ecology, and Ethnobotany*. Timber Press, Portland.
Mares, P.
1988 High Temperature Capillary Gas Liquid Chromatography of Triacylglycerols and Other Intact Lipids. *Progress in Lipid Research* 27:107–133.
Mills, John S. and Raymond White
1977 Natural Resins of Art and Archaeology Their Sources, Chemistry, and Identification. *Studies in Conservation* 22(1): 12–31.
Needham, S. and J. Evans
1987 Honey and Dripping: Neolithic Food Residues from Runnymede Bridge. *Oxford Journal of Archaeology* 6(1):21–28.
Rafferty, S. M.
2002 Identification of Nicotine by Gas Chromatography/Mass Spectroscopy Analysis of Smoking Pipe Residue. *Journal of Archaeological Science* 29(8): 897–907.
Reber, E. A.
2009 *Colonoware Residues from the Dean Hall Site*. UNCW Anthropological Papers Vol. 8. University of North Carolina at Wilmington, Wilmington.
Reber, E. A., S. N. Dudd, N. J. Van der Merwe, and R. P. Evershed
2004 Direct Detection of Maize Processing in Archaeological Pottery through Compound-Specific Stable Isotope Analysis of n-dotriacontanol in Absorbed Organic Residues. *Antiquity* 78(301):682–691.
Reber, E. A. and R. P. Evershed
2004 Identification of Maize in Absorbed Organic Residues: a Cautionary Tale. *Journal of Archaeological Science* 31(4):399–410.
Reber, E. A. and J. P. Hart
2008 Pine Resins and Pottery Sealing: Analysis of Absorbed and Visible Pottery Residues from Central New York State. *Archaeometry* 50:999–1017.
Serpico, M. and R. White
1996 A Report on the Analysis of the Contents of a Cache of Jars from the Tomb of Djer. In *Aspects of Early Egypt*, edited by J. Spencer, pp. 128–138. British Museum Press, London.
Steponaitis, V. P.
1983 *Ceramics, Chronology, and Community Patterns: An Archaeological Study at Moundville*. Academic Press, New York.

Tulloch, A.P.
1976 Chemistry of Waxes of Higher Plants. In *Chemistry and Biochemistry of Natural Waxes*, edited by P.E. Kolattukudy, pp. 236–287. Elsevier Press, Amsterdam.

van Bergen, P. F., I. D. Bull, P. R. Poulton, and R. P. Evershed
1997 Organic Geochemical Studies of Soils from the Rothamsted Classical Experiments—I. Total lipid Extracts, Solvent Insoluble Residues and Humic Acids from Broadbalk Wilderness. *Organic Geochemistry* 26(1–2):117–135.

Weete, John D.
1976 Algal and Fungal Waxes. In *Chemistry and Biochemistry of Natural Waxes*, edited by P.E. Kolattukudy, pp. 350–418. Elsevier Press, Amsterdam.