CHAPTER EIGHT
Organic Residue Analysis and the Decomposition of Fatty Acids in Ancient Potsherds
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Determining the function of prehistoric artifacts has long been an important avenue of archaeological inquiry (for instance Bennett 1943, 1944; Clark 1939; Linton 1944; Smith 1910 or Steward and Setzler 1938). Although archaeology has moved beyond the 'functionalist' theoretical paradigm, so influential in the 1930's through 1950's (Trigger 1989; Willey and Sabloff 1980), where every artifact was understood to confer some adaptive advantage to the people who used it, determining the use of artifacts continues to play an important role in reconstructing prehistoric behavior. In archaeology today, determining the function of an object is rarely an end product. Instead, the function of an artifact is usually used as one data set to help inform on other behavior, such as the organization of technology, the division of labor, gender relations and issues concerning diet, among other topics.

Organic residue analysis reflects one line of investigation that archaeologists have employed to attempt to deduce function of artifacts, especially pots (Charters et al. 1997; Copley et al. 2005; Deal and Silk 1988; Eerkens 2002, 2005; Evershed et al. 1997, 2003; Heron et al. 1991; Malainey 1999c; Morton and Schwarcz 2004; Mottram et al. 1999; Reber and Evershed 2004; Skibo 1992; Stott et al. 1999) which are the subject of this chapter, though pipes (Rafferty 2002), hunting weapons (Craig and Collins 2002; Fullager and Jones 2004; Pearsall et al. 2004; Rots and Williamson 2004; Wadley et al. 2004) and cooking stones (Quigg et al. 2001, Buonasera 2005) have also been examined. There are other approaches to help reconstruct the function of ancient pots, including engineering analyses (Arnold 1985; Bronitsky and Hamer 1986; Brown 1989; Feathers 1989; Juhl 1995; Linton 1944; Rice 1987; Rye 1976; Skibo et al. 1989; Smith 1985), use wear studies (Beck et al. 2002; Halley 1983; Rice 1987; Shiffer 1989; Skibo 1992) and ethnographic analogy (Costin 2000; Hegmon 2000; Henrickson and McDonald 1983), but these methods are not often definitive. They usually provide only hypotheses about the types of foods that may have been cooked or stored in a pot. Organic residue analysis has the potential to be more precise about the foods that were prepared or stored within a pot, hence the intense interest by archaeologists in developing this method over the last decades. Indeed, if the rapidly expanding literature is any measure, the expected future payoffs from this field are high. However, as several of the chapters in this volume attest, residue analysis is still in its infancy and there is much to be learned and fine-tuned, particularly on the methodology of the final interpretation of the biochemical findings.

Organic Residue Analysis

Although a range of organic compounds have been recovered from archaeological potsherds including amino acids, waxes, and cholesterol, fatty acids have been the principal class of compounds targeted for analysis in archaeological studies. This is due in part to their ease of extraction from potsherds and the widespread availability of the instruments needed to detect and quantify their presence. However, the main reason fatty acids have been targeted is undoubtedly the stability of these biomolecules over long periods of time (Christie 1989; Evershed 1993). Relative to DNA, proteins or carbohydrates, lipids (including fatty acids) are relatively resistant to decomposition and degradation.

That fatty acids are often present in ancient sherds, occasionally in very high quantities, has been amply demonstrated by archaeologists and chemists. Fatty acids are particularly prevalent in the interior walls of pots, especially near the neck and rim and occupy small vugs or open spaces within the ceramic fabric. What is less clear is that such residues actually represent the unmodified, or little modified, byproducts of ancient foods cooked or stored in the vessels as several alternatives exist. First, fatty acids are produced by nearly every organism, from bacteria to mammals, and are therefore present in virtually every environment on earth and can simply be native to the clays that people use to make pots. Second, fatty acids could represent post-depositional contamination by, for example, bacteria that are consuming other food residues such as proteins within the sherds, or free fatty acids leaching into sherds from the surrounding soil. Third, the fatty acids that we find may only represent a small fraction of what remains after decomposition due to processes such as oxidation and hydrolysis. Finally, fatty acids may be entirely the product of laboratory contamination.

We can probably rule out several of these possibilities. The first possibility, native contamination, is unlikely. The exposure of fatty acids to high temperatures, which promotes oxidation, leads to decomposition. Fatty acids are quite stable in temperatures below 200°C, but rapidly oxidize between 200-250°C (De Souza et al. 2004; Frankel 1980, 1987, 2005; Santos et al. 2002), with polyunsaturated and monounsaturated fats degrading at slightly lower temperatures than saturated fats. This is much lower than the minimum temperature required to fire a pot, 500-800°C. Thus, any native fatty acids in a clay are extremely unlikely to survive firing. As well, it is higher than the temperature achieved in most pre-industrial ceramic cooking methods. Thus, we can be fairly confident that pots start out clean of fatty acid s and that the act of cooking will not degrade them. Indeed, experiments by Johnson et al. (1988) suggest that firing of clay tiles to 400-600°C in both oxidizing and non-oxidizing environments essentially removes all hydrocarbons and fatty acids, though some carbon remains in the form of inorganic compounds and pure carbon (such as coal).

Similarly, the fourth possibility, that fatty acids are merely the product of laboratory contamination, is also dismissible. Most laboratories run blanks and other controls to evaluate the influence of such contamination. Low levels of fatty acid contamination are in most cases unavoidable due to their ubiquity in the environment. However, archaeological sherds often contain concentrations of fatty acids that are a level of magnitude or greater than the blanks, indicating that most are native to the sherds themselves. In any case, these are the sherds that archaeologists should be including in their interpretations.

As well, it has been demonstrated that sherds buried in archaeological sediments are not contaminated by the influx of fatty acids from nearby soils. Tests examining the fatty acid profiles of sherds and the immediately surrounding soil show that the two are quite different (Deal and Silk 1988; Heron et al. 1991). This is likely due to the fact that fatty acids, like all lipids, are water insoluble which would also help keep water out of the walls of pots infused with lipids or coated with residues or carbonized remains. Many ethnographic studies suggest people either coat cooking pots with, or simply soak them in, lipid-rich products (Arnold 1985, 140). These activities help to prevent water from the interior from leaking through the pot. As well, experimental studies suggest that water rich in organic matter penetrates the walls of porous pots and deposit residues there (Skibo 1992, 151), presumably as the water evaporates leaving behind organic materials. Such residues are not removed by washing. These findings suggest that the residues in the interior walls most likely represent the application of such lipid-rich mixtures, or the primarily remains of the first several uses of a pot. After a pot has become infused with organic residues, water no longer leaks through and there is little room for the accumulation of additional residues.

I am unaware of studies examining the potential role of bacteria in contributing to the pool of fatty acids recovered from archaeological sherds. Bacteria produce the same types of fatty acids as most plants and animals, especially the more common saturated and monounsaturated fats typically found in potsherds. This is a concern that needs to be addressed by future research beyond the scope of this chapter. Instead, I will here examine the final possibility mentioned above, that is, the potential effects of decomposition of fatty acids in ancient sherds. Specifically, I aim to examine how differential decomposition between organic compounds affects our interpretation of fatty acid profiles.

Decomposition: Food Sciences Perspective

While fatty acids are relatively resistant to decomposition when compared to many other biomolecules, they still degrade when exposed to oxygen and water, processes that will be accelerated by higher temperatures.[1] The processes of decomposition have been of much interest to food scientists. Many of the foul tastes and smells associated with spoiled food are the byproducts of fatty acid degradation. As long-chained compounds break down, they form short-chained and often volatile (airborne) aromatic ones. Evolution has predisposed humans to recognize these compounds as foul, representing foods to be avoided, because various toxic-compound-producing bacteria live on rancid foods. These processes, then, have attracted much research by food chemists to understand what exactly happens when foods, and the fatty acids within them, decompose.

Research in the food sciences has demonstrated that fatty acid decomposition is an extremely complex process that can produce a diverse range of organic compounds depending on environment (Frankel 2005; Fritsch and Deatherage 1956; Hudlicky 1990). For example, saturated fatty acids can oxidize to produce several shorter derivative compounds, each of which may further decompose into other unstable and short-lived compounds, which may again decompose into yet other compounds. Indeed, the decomposition process for many isolated fatty acids is still not completely understood by food scientists, much less for whole foods.

[1] In fact, a prominent food chemist at the University of California, Davis expressed amazement when I told him that I was studying fatty acids over 500 years old. He was surprised that any fatty acids could survive that long.