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Cautionary tales on the identification of caffeinated beverages in North America

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ABSTRACT

In recent years several studies have attempted to understand the use of caffeinated beverages in North America before the coming of Europeans using absorbed residues. These studies have focused on the two key plant sources of caffeine in North America: *Theobroma cacao* (cacao) and *Ilex vomitoria* (yaupon holly). The authors initiated a study to explore the possibility that one or both plants were used at the Mississippian period (900–1600 CE) center of Etowah in northern Georgia. In the process, a series of problems with methodologies in use were revealed. Key among those were limitations on the methods used to identify ancient caffeinated beverage residues, distinguish them from modern contamination, and differentiate residues made by each plant. In this paper we explore what our data from the Etowah site reveal about methodologies currently in use and make suggestions for future studies of residues created by caffeinated beverages in North America.

1. Introduction

Scholars have been studying absorbed residues for many years looking for evidence of ancient food-related cultural practices (Barnhard and Eerkens, 2007; Evershed et al., 1990, 1992; 2003). This is especially the case in the archaeological search for evidence of subsistence changes associated with the origins of agriculture, seasonal variation, or environmental shifts (for example Copley, 2003; Dudd et al., 1999; Reber and Evershed, 2004). Absorbed residues also are an important tool for identifying the use of non-food residues such as resins and tar (Stern et al., 2003; Urem-Kotsou et al., 2002), plant and bees waxes (Evershed et al., 1991, 2003), palm kernel oil (Copley et al., 2001), and petroleum bitumen (Connan et al., 2004), to name a few. Similar studies have focused on fermented beverages (Correa-Ascencio et al., 2014; McGovern et al., 2013) and caffeinated beverages made from cacao (Cyphers et al., 2013; Hall et al., 1990; Hurst et al., 2002; Powis et al., 2002, 2008, 2011) and yaupon holly (Crown et al., 2012).

The cacao and yaupon holly studies explore beverages that often were consumed by elites or in ritual contexts. As such, they offer a means for finding the remains of ritual beverages and allowing us to explore issues relating to medicine traditions, ritual practices, and elite culture. They also open the door for exploration of how practices and traditions moved across cultural boundaries, how and why they were adopted and potentially changed, and how they contributed to ongoing processes of culture making.

While the exploration of caffeinated beverages through absorbed residues has a long history in Central America (see Powis et al., 2002 for a review), similar studies in North American have only recently been conducted. These began with a presentation of data suggesting that cacao was present in the North American Southwest at Chaco Canyon (Crown and Hurst, 2009), and have grown into arguments for the use of caffeinated beverages from Utah to Ohio in both Ancestral Pueblo and Mississippian contexts. The list of sources has doubled to include the Black Drink (yaupon holly or *Ilex vomitoria*), a ritual tea made by native people of the southeastern US in the historic period (Hudson, 2004). There are some fascinating issues at stake that touch on the movement of ritual practices and elite traditions from Central America to complex Native American societies, as well as the transfer of plants and practices from Mississippian societies in the American South to Ancestral Pueblo people in the Southwest.

As attempts to use absorbed residue analyses to identify cacao-

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and yaupon-related beverages have become more common, it has become clear that this growing field is hampered by a set of problems relating to recognizing contamination and methodological approaches that affect results. As McGovern and Hall (2015) indicate, this is a problem that affects organic residue studies in archaeology more generally. While in some respects these problems already have been considered in the history of absorbed residue studies, some also are unique challenges facing caffeinated beverage studies in the Americas. In this paper we discuss our own encounters with these challenges during our recent attempt to identify ancient residues from caffeinated beverages consumed during the Mississippian period (900–1600 CE) at the archaeological site known as Etowah (9Br1).

2. Cacao and yaupon studies in the Americas

Absorbed residue studies conducted on samples from the American Southwest and Southeast were patterned after work done in Mesoamerica that focused on the identification of cacao residues. Most of those studies collected samples by removing the exterior surfaces of a pottery fragment and pulverizing the remainder (burr-and-grind method) and then used mass spectrometry to identify theobromine, caffeine, and theophylline (Hurst et al., 1989; see also Powis et al., 2002). The first study to attempt to find evidence for cacao north of Mexico was conducted by Crown and Hurst (2009). In this study, pottery sherds were analyzed from recently recovered excavations at Pueblo Bonito in Chaco Canyon, New Mexico. The samples were collected by abrading the surface of pottery sherds and then grinding a 10 g sample of the remainder. The samples were analyzed using mass spectrometry and the presence of a single xanthine, theobromine, was used to detect cacao residues.

These results were followed by a study published by Washburn et al. (2011) that looked for cacao residues on pottery from Ancestral Pueblo and Hohokam vessels from Arizona and New Mexico. In this study, whole vessels were sampled by pipetting 25–30 ml of de-ionized water onto their sides and bases and left for 5 min. Using HPLC mass spectrometry the authors looked for not only theobromine but also theophylline and caffeine. For the first time, a North American species of yaupon holly (*Ilex vomitoria*) was recognized as another potential source of ancient caffeine residues. Citing Edwards and Bennett (2005), they assumed that yaupon did not contain theophylline and that yaupon and cacao had different ratios of caffeine to theobromine. Using these distinctions Washburn et al. (2011) made a case for the identification of vessels containing cacao in both Ancestral Pueblo (900–1350 CE) and Hohokam sites (1050–1450 CE).

In a subsequent study, Washburn et al. (2012) attempted to validate the effectiveness of their wash sampling approach by conducting experiments with modern pottery vessels spiked with liquids containing theobromine, caffeine, and theophylline. They confirmed that their technique did allow them to identify the xanthines of interest. They also discovered that the method appeared to preferentially detect caffeine and select against the detection of theobromine. It also appeared to be ineffective in detecting theophylline.

These studies were followed shortly by the publication of a study of pottery vessels from the Cahokia site and surroundings located near St. Louis, Missouri (Crown et al., 2012). Cahokia is the largest and one of the earliest Mississippian period sites in the Midwest, and was a very important place in the 12th century. The authors sampled fragmentary vessels using the burr-and-grind method employed by Crown and Hurst (2009). Using mass spectrometry they looked for the presence of theobromine and caffeine, but not theophylline. Crown et al. (2012) added ursolic acid as an additional biomarker present in yaupon but not in cacao. They acknowledged that a second species of holly (*Ilex cassine*) was present in the American South that could have been another source of caffeinated beverages. Using the presence of ursolic acid and the ratio of caffeine to theobromine, Crown et al. (2012) argued the residues encountered in their samples were most likely the result of the consumption of beverages containing *Ilex vomitoria*.

In 2014 Washburn and colleagues published a paper that followed up on Crown's identification of yaupon at Cahokia and took cacao and yaupon residue studies in a new direction (Washburn et al., 2014). In this study the authors specifically addressed key factors that may complicate the analysis of ancient residues. The first of these is the potential for the concentrations of xanthines in ancient residues to change with time. They acknowledged for the first time that caffeine, theobromine, and theophylline are broken down by bacteria in the soil, thereby changing their concentrations over time. As a test of the potential impact of these processes, Washburn et al. (2014) measured concentrations of an additional xanthine called paraxanthine. Paraxanthine is one byproduct of the bacterial degradation of caffeine. Finding no paraxanthine in their analyses, Washburn et al. (2014) argued that bacterial degradation did not significantly affect the ancient residues they measured.

They also addressed the issue of potential contamination from airborne sources. To do this they collected samples of dust found on surfaces in six different institutions and vessels whose age or geographic origins precluded the presence of cacao or yaupon residues. Their analyses confirmed that airborne contamination was a source of caffeine, theobromine, and theophylline. However, the concentrations of these xanthines in the contamination samples were lower than those found in archaeological samples. Through statistical means, they derived threshold levels for each xanthine. Only those vessels with concentrations above these thresholds were considered to contain the remains of actual ancient residues. Once the authors were able to exclude vessels whose results were presumed to be impacted by contamination, they used the presence of theophylline as well as the ratio of caffeine to theobromine to sort positive results into those resulting from cacao and those from yaupon. Ultimately they argued that cacao was widely used throughout the American Southwest and Southeast.

Most recently, Crown et al. (2015) published a study that examined 177 pottery fragments from 18 sites in the American Southwest and northwestern Mexico. Their focus was on the identification of cacao and yaupon, acknowledging that the latter may be a source of caffeinated beverages in the regions of interest. Samples were collected using the same burr-and-grind methods employed by Crown in previous studies. Most of the samples were taken directly out of the field or from collections that had not been washed and analyzed, thus reducing exposure to airborne contamination. The samples collected from artifacts stored in museums appear to have produced little evidence of modern contamination, suggesting that their sampling technique does limit the impact of airborne contamination. The authors acknowledge the many reasons why the concentrations of specific compounds found in ancient residues might differ from those measured for cacao and yaupon. They argue their methods account for those factors, but offer no specific discussion of bacterial consumption of xanthines or approaches to accounting for that consumption. Ultimately, the authors assign residues to cacao or yaupon based on the presence of theophylline and based on ratios of theobromine to caffeine.

3. Etowah site residue study

In 2013 we initiated a study to explore the possibility that cacao