Sourcing Shell and Shell-Tampered Artifacts Using Laser Ablation | 2009-02

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Executive Summary

This project involved developing a new method for using the chemical content of freshwater mussel shell as a means of sourcing prehistoric, shell-tempered pottery and shell artifacts to their places of origin. By extension, this means that prehistoric trade and exchange networks can be mapped out. The method is based upon the fact that freshwater mussels take up chemicals from the waterways they inhabit. Because each waterway is chemically different to some extent, and because mussels incorporate the chemicals into their shells, it is theoretically possible to identify where shell artifacts or shell-tempered pottery was made by chemically analyzing the shell. It was proposed to do this using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry, a non-destructive method that uses a laser beam to remove a very small amount of material for chemical analysis. The non-destructive nature of the method means that it can be applied to sensitive artifacts such as burial accompaniments or museum specimens.

The first step in developing this method was to begin construction of a freshwater shell chemical database against which the chemical content of shell artifacts could be compared. Because of modern pollutants, archaeological shells representing food waste were obtained from a number of sites and chemically analyzed via LA-ICP-MS. The results show that shells from different waterways form distinct chemical groups, validating the theory and providing the first set of background data for applying the method at a regional scale.

Introduction

Traditional methods for sourcing archaeological materials, such as X-ray Diffraction and X-ray Fluorescence, Particle-Induced X-ray Emission, and Neutron Activation Analysis all have some technical limitations or complicating factors such as accounting for the diluting effects of temper (Neff 1995; Larson et al. 2005:100). Where ceramics are concerned, another problem is that clay sources may be homogenized or thoroughly mixed over large areas, making precise sourcing difficult (e.g., Neff 2008; Steponaitis et al. 1996). Although these limitations may be addressed by focusing on surface slips or pigments rather than clay matrices (e.g., Neff 2003; Sall et al. 2005; Speakman 2005; Vaughn et al. 2005), the development of new methods and techniques for sourcing artifacts is desirable.

Aquatic mollusks intake chemicals in general proportion to what is in the environment (e.g., Lee and Wilson 1969), providing a theoretical base for employing shell in sourcing studies. This has been done for salt-water species (Claassen 1998:212-218), but prior to this NCPTT-funded study it had not been done with freshwater mussel shell. Because of modern pollutants and other changes in aquatic ecosystems, modern shells serve poorly in establishing comparative baseline data (Claassen and Sigmann 1993; Clayton et al. 2001; Das and Jana 2003; Jacomini et al. 2003; Markich et al. 2002; Miller 1980). However, enormous amounts of freshwater shell have been excavated from archaeological sites, and although shell artifacts and shell-tempered ceramics could easily have been imported, unmodified valves incorporated into site matrices usually represent the remains of food obtained from waterways near the sites of deposition (Peacock 2000, 2002). Thus, the material necessary for establishing baseline elemental data already exists in archaeological collection, data that would be especially pertinent to sourcing shell-tempered ceramics.

Methods/Materials

The method employed in this study was Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry, a method increasingly being employed in archaeometric work because of its high precision (ppm) and the fact that it is essentially non-destructive (Resano et al. 2009; Speakman and Neff 2005). Data were obtained from over a hundred specimens from six sites in three major drainages. These include site 15CL58, a Middle Archaic shell midden on the Ohio River in Kentucky, site 22SU531, a Mississippian site on the Sunflower River in Sunflower County, Mississippi, and four sites (22LO527, 22LO530, 22OK520, and 22OK578) in the Tombigbee
River drainage of east Mississippi. The Tombigbee sites are particularly interesting in that they allow a detailed look into the precision of the LA-ICP-MS shell sourcing method. Two of the sites, 22LO527 and 22LO530, are very near to one another on the main stem of the central Tombigbee River and thus should be chemically very similar. The other two sites are on lower-order tributary streams. Site 22OK520 is located on Line Creek, a tributary of Tibbee Creek, itself a tributary of the Tombigbee River. Site 22OK578 is located near Hollis Creek, a tributary of the Noxubee River, a major Tombigbee tributary. If analysis shows these individual feeder streams to be chemically distinguishable, then it would suggest that the method is potentially even more precise than clay sourcing.

Shells of various species were obtained from each site. Samples were cleaned with deionized, demineralized water. Specimens were then cut with a diamond-bladed band saw. About two-thirds of the posterior portion of the shell was removed; this is cut in half lengthwise, with the bottom half being retained as a chemical voucher specimen. A 1 cm-wide slice was then removed from the top half for chemical analysis (see figures in interim report; also on CDs sent under separate cover). If samples broke or if there was some problem with the test, additional slices were removed as necessary. The saw was cleaned with deionized, demineralized water between samples.

Individual slices of shell were mounted in clay with a cut side facing up. The laser track was set in a raster pattern over this surface. A pre-ablation pass was made to remove any adhering surface materials. An ideal sample consisted of 20 valves of at least 10 different species, to account for inter-species variation in chemical uptake (see data tables on CDs sent under separate cover). Shells of different sizes were used to average out differences in chemical uptake related to faster shell growth in younger individuals. The laser was set to run over seasonal growth rings, as there can be seasonal variation in chemical uptake by mollusks. A total of 46 elements was scanned for, including Li 7, Na 23, Mg 24, Al 27, K 39, Ca 44, Sc 45, Ti 47, V 51, Mn 55, Fe 56, Co 59, Ni 60, Cu 65, Zn 66, As 75, Rb 85, Sr 88, Y, Zr 90, Nb 93, Sn 120, Sb 121, Cs 133, Ba 138, La 139, Ce 140, Pr 141, Nd 142, Sm 152, Eu 153, Gd 158, Tb 159, Dy 164, Ho 165, Er 166, Tm 169, Yb 174, Lu 175, Hf 180, Ta, 181, Pb 208, Th 232, U 238, and Si.

Results and Discussion

Using all of the data in correspondence analysis produces an ordination diagram showing good discrimination of the Tombigbee River drainage sites (Figure 1). Correspondence analysis positions assemblages in multidimensional space based on similarity. In this case, each specimen is an “assemblage” of chemical data representing levels of 45 elements (silicon was removed due to an aberrant reading that was skewing the results) Axes are drawn through the resulting cloud of points in such a way as to account for as much variation as possible. In this case, Axis 1 separates most of the main-stem Tombigbee River shells (shown in red) from the shells derived from the tributary streams. Those streams separate out along Axis 2, the second major axis. It is noteworthy that such separation is possible, given that all of the Tombigbee drainage sites yielding shell lie with a 30 km-radius circle.
Sourcing studies traditionally have not used correspondence analysis, instead employing bivariate plots with confidence ellipses denoting group membership derived from the bivariate means. This approach works well with the shell data gathered thus far. For example, the three main river drainages separate quite well in a bivariate plot of Cr vs Ba (Figure 2). Clear separation of the Tombigbee and Ohio River shells is seen in a plot of Na vs. Cr (Figure 3), a separation that is visible in many other elements as well. A comparison of Na vs. Ca shows good, though not total, separation between the main-stem Tombigbee sites and the tributary streams (Figure 4).
Figure 2. Bivariate plot of Cr vs. Ba showing separation of three major drainages. Ellipses represent 90% confidence intervals.
Figure 3. Bivariate plot of Na vs. Cr showing separation of Ohio and Tombigbee river drainages. Ellipses represent 90% confidence intervals.
Figure 4. Bivariate plot of Na vs. Ca showing separation of main-stem Tombigbee River site shells from tributary stream shells. Ellipses represent 90% confidence intervals.

Conclusion

Based on the initial results, it appears that chemical characterization of archaeological shells via LA-ICP-MS should allow relatively precise sourcing of shell-tempered ceramics and shell artifacts. The data presented herein have not been modified beyond calibration to standards. There are a number of ways in which group delineation can be enhanced. For example, within a drainage it would be appropriate to apply detrending in correspondence analysis. In bivariate analysis, elemental ratios can be compared, bringing four elements instead of two into consideration. Using ratio data also helps compensate for analytical noise and temporal fluctuations in chemical loads. Additionally, principal components can be extracted from the data and compared. These are all techniques that have been employed in clay and obsidian sourcing, and they should work well with the shell data. Such techniques will be employed as the NCPTT-project-generated data are worked into publications.

While the results of this project clearly indicate that the theory is sound and that the methods are appropriate, it must be said that the analysis took longer than anticipated, so that a smaller number of collections was analyzed than originally hoped. This is due primarily to the extremely conservative approach taken in this initial project, for example, shooting each shell specimen three times and averaged the results. Despite this limitation, the data produced are sound and are now available to other researchers. Newer “time of flight” laser ablation units can be employed that will cut the analysis time at least in half, and other procedural modifications can be made as research progresses.
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