Elemental variation in prehistoric *Unionoida* shell: Implications for ceramic provenance

Matthew T. Boulanger, Michael D. Glascock

Abstract

As part of ongoing efforts to refine ceramic-provenance methodology, we examine the universality of freshwater mussel shell chemistry as reported in an earlier study. We find that samples of prehistoric shell from several locations in eastern North America are chemically distinct from the modern sample of shell from Missouri that was previously used to develop a formula for adjusting elemental abundances in shell-tempered pottery. The observed elemental differences may be attributable to the use of prehistoric versus modern shell, or they may relate to watershed-specific geological chemistry. Regardless of the source of these differences, we suggest that future provenance studies involving shell-tempered wares would be well served by complementary analyses of locally derived prehistoric shells to better the effects of shell tempering on ceramic chemistry.

1. Introduction

When present in a ceramic matrix, shell (and other Ca-rich materials such as bone, limestone, and calcite) creates a dilution effect that reduces the detected abundances of all other elements in the specimen (Cogswell et al., 1998; Steponaitis et al., 1996). The effects of Ca-rich tempers are analogous to those introduced by Si-rich tempers such as quartz (Perlman and Asaro, 1971; Sterba et al., 2009) except that unlike Si, Ca can be detected and quantified using neutron activation (NAA). The use of shell as a tempering agent significantly increases the amount of Ca in pottery, and it causes an apparent decrease in other elements present in the pottery. This is because elemental abundances determined by NAA are typically reported in a fixed-sum matrix (e.g., parts per million, weight percent). Thus, most elements are “diluted” by the large proportion of Ca present in the specimen. If a particular element is present in sufficient abundance within the shell, but absent or exceedingly low in the clay to which shell is added, this element will be enhanced in the resultant pottery. Thus, shell tempering has the potential to both dilute and enrich the bulk chemistry of pottery.

Cogswell et al. (1998) reported the results of a study directed at evaluating methods for correcting this well-documented elemental dilution/enrichment effect of shell as a tempering agent in prehistoric ceramics. The goals of their research were to (1) assess whether elemental differences significant to ceramic-provenance research exist among shells of freshwater mussel genera, (2) evaluate potential elemental contributions of freshwater mussel–shell temper to prehistoric pottery, and (3) compare three proposed methods for eliminating or minimizing the dilution/enrichment effects of shell temper so as to more accurately estimate the chemical makeup of the clay. Here, we expand upon this research through an evaluation of whether the mean values reported by Cogswell et al. (1998) are universally precise estimates for freshwater mussel shells used as ceramic temper across a broad swath of eastern North America. The research reported here is part of larger efforts to refine protocol of the analysis of archaeological ceramics at the University of Missouri Research Reactor (Boulanger et al., 2013; Stoner et al., 2013).

2. Background

Five factors are known to influence the elemental composition of mussel shell: Local geology, water temperature, water salinity, species of organism, and the calcite:aragonite ratio of the shell itself (Turekian and Armstrong, 1960; Crisp and Richardson, 1975). As discussed by Peacock et al. (2012), freshwater mussels are filter feeders that tend toward chemical equilibrium within their immediate environment. In the absence of foreign input from contaminants and pollution, stream and lake chemistry is largely dependent on local geology and climate. Particulates within a river system are most likely to derive from the immediate vicinity, and are thus determined by geology within a watershed. Miller (1980) observed that modern marine shell specimens exhibited elemental compositions that were significantly different than those of prehistoric shell specimens from the same localities. She attributed the differences to changes in land-use practices and the introduction of modern pollutants into the water system. Thus, within the context of archaeological and paleobiological studies, time may be considered a sixth factor influencing shell chemistry.

Given that water chemistry is largely a result of local environment, and that mussels exist in equilibrium within the water, it stands to...
reason that the provenance postulate (Weigand et al., 1977) could be applied to shell chemistry (Claassen and Sigmann, 1993; Eerkens et al., 2007; Eerkens et al., 2009; Eerkens et al., 2010; Miller, 1980; Peacock et al., 2010). That is, we expect that freshwater mussel shells from different locations may be chemically distinct insofar as local geology varies chemically (Peacock et al., 2010; Peacock et al., 2012). If local habitat and geology does indeed strongly influence shell chemistry—and present evidence suggests that it does—this may have implications for the bulk analysis of shell-tempered pottery and the use of mathematical adjustments to compositions of shell-tempered ceramic specimens. In short, time-specific, region- or watershed-specific formulae may be necessary rather than a universal formula.

Cogswell et al. (1998) evaluated three methods for minimizing elemental dilution/enrichment effects of shell when used as a tempering material in ceramic production. Specifically, they analyzed a sample of modern freshwater mussel shells obtained from the Gasconade River, in Mt. Sterling, Missouri. Three genera (Cumberlandia, Lampspilsis, and Fusconia) were present in the sample, and the shells were analyzed both before and after burning in a laboratory furnace. Shells were burned in the furnace to simulate the effects of firing a ceramic vessel or the burning of shell by the potter to facilitate crushing for use as temper. No significant chemical differences resulting from burning were observed among any of the genera, leading the authors to conclude that burning of shell leads only to minor changes in the elemental composition (see also Collins, 2012). The authors also found that elemental compositions of shell did not vary significantly across taxa from the same river (Cogswell et al., 1998:66–71). Significantly, the authors also reported that concentrations of Sr, Na, and Mn in their shell sample were greater than those in the New Ohio Redart Clay (NOR, a commercially available clay used as a check-standard at MURR) and in several specimens of clays from various locations in the Mississippi River Valley. Thus, a novel observation of their study was that the concentrations of these elements in a ceramic body could potentially be influenced by the presence of shell tempering.

In order to correct for elemental dilution/enhancement caused by shell tempering, Cogswell and colleagues advocated the use of a mathematical correction formula first suggested by Steponaitis et al. (1996):

$$e' = \frac{10^6 \times e}{10^6 - 2.5c}$$

where $e'$ is the adjusted concentration of a given element in ppm, $e$ is the measured concentration of an element, and $c$ is the measured concentration of Ca. The value 2.5 is a gravimetric factor compensating for the difference in the mass of Ca in ppm to the mass of calcium carbonate ($\text{CaCO}_3$) in shell. This formula normalizes abundances of all elements to the measured amount of Ca, and thus Ca is removed from the compositional data after applying the correction formula. Because Sr freely substitutes for Ca in shell, it too is removed from the compositional database.

As noted above, Cogswell and colleagues also found that the abundances of Na and Mn in their shell sample were greater than those in samples of commercial art clay and unrefined clays of the sort that may have been used prehistorically. In these instances, shell tempering would lead to an enrichment of Na and Mn, but the analyst is blind to which component of mixture (i.e., the pot sherd) is responsible for the elevated Na and Mn levels: the clay, the temper, or a combination of both. To correct for the added contribution of these two elements to a ceramic matrix, their concentrations are modified as follows:

$$e'' = \frac{e - 1.25 \times e_m}{1 - 1.25 \times e_m}.$$  

This is similar to the Ca-normalization formula presented above, but with the inclusion of the factor $e_m$ which is defined as the average concentration of the particular element in shell. In practice, the shell-correction as historically implemented at MURR assumes concentrations of 1488 ppm for Na and 578 ppm for Mn (mean [average] values determined in the Cogswell et al. study), and adjusts the concentrations of those elements in the ceramic matrix accordingly.

As suggested above, the uncritical use of the chemical data reported by Cogswell and colleagues may present some problems in understanding the chemistry of shell-tempered wares. There is no a priori reason to assume that the chemical composition of shell from central Missouri is identical to, say, that of shell from east Texas, because of differences in geology and water chemistry. Further, there is no a priori reason to assume that the chemistry of modern shells from central Missouri is identical to prehistoric shells from central Missouri. Cogswell and colleagues had no intention of evaluating these aspects of shell chemistry; the goals of their study were to evaluate how best to minimize the dilution effects caused by Ca in a ceramic matrix. Our research is a logical extension of their earlier study. We note that our approach is purposefully pottery-centric, and aims to address only the potential confounding effects of shell temper in pottery; however, we point out that the implications of shell chemistry being influenced by land-use, local geology, and watershed chemistry are far ranging, including provenance studies of shell itself, conservation biology, and landscape ecology.

3. Methods

We are primarily interested in shell-tempered ceramics produced prior to the arrival of Europeans in the Western Hemisphere. Miller (1980) previously demonstrated that modern shell is an inappropriate analog for prehistoric shell because of the introduction of industrial pollution, increased sediment load from deforestation, changes in land use, and agricultural chemical use within a watershed. Therefore, all of the freshwater mussel shells analyzed in this study come from unequivocally prehistoric contexts (Table 1). We also adopt a broad-scale approach to evaluating variation in shell chemistry, and our sample reflects this. In total, 111 specimens of shell from several freshwater mussel genera were obtained from six archaeological sites from the Midwest, the Middle Atlantic, and New England (Table 2, Fig. 1). Because of differences in habitat, we were unable to ensure that all mussel shells from sites were of the same species. All specimens were identified to at least the genus level. We compare our archaeological sample with the previously reported data of Cogswell et al. (1998).

All specimens were rinsed under water and scrubbed with a plastic-bristle brush to remove adhering soil, sediment, and organic materials. Once cleaned, specimens were rinsed in deionized water and placed under a heat lamp to dry. Cleaned specimens were fired in a laboratory furnace to a temperature exceeding 700 °C for 1 h. Once burned, each specimen was ground to a powder in an agate mortar and pestle. The pulverized specimens were placed into a glass vial and allowed to dry in a warming oven for at least 24 h.

Specimens were analyzed by neutron activation at the University of Missouri Research Reactor (MURR) following standardized protocols (Glascock, 1992; Glascock and Neff, 2003).

4. Results

All shell specimens in our sample show low concentrations of most elements (Table 3). Indeed, concentrations of most elements were

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Archaeological sites from which samples of mussel shell were obtained.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site number</td>
<td>Site name</td>
</tr>
<tr>
<td>28SX17</td>
<td>Beisler</td>
</tr>
<tr>
<td>12HR1</td>
<td>Breeden</td>
</tr>
<tr>
<td>15OH1</td>
<td>Chiggerville Shell Mnd</td>
</tr>
<tr>
<td>15BT6</td>
<td>DeWeese Shell Mnd</td>
</tr>
<tr>
<td>27CH85</td>
<td>Fort Hill</td>
</tr>
<tr>
<td>28WA302</td>
<td>Indian Hollow</td>
</tr>
<tr>
<td>12HR12</td>
<td>Overflow Pond</td>
</tr>
</tbody>
</table>

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determined to be at or below detection limits in most specimens. Concentrations of Na in all of our specimens are notably higher than anticipated based on abundances reported by Cogswell et al. (1998). The mean Na concentration in the Gasconade River sample was 1488 ppm (Cogswell et al., 1998); however, all of our shell samples have mean Na concentrations exceeding this value (Fig. 2). Similarly, Mn concentrations in all but one of our shell samples were below the mean value reported by Cogswell et al. (579 ppm). The shell sample from 28SX17 (Beisler) in New Jersey exhibited a higher mean Mn concentration than any other sample (826 ppm).

Interestingly, three other elements appear to be present in prehistoric shell samples at significant levels: Ba, Ti, and Sr. Ba concentrations in most of our samples are within two standard deviations of those reported by Cogswell et al.; however, the sample from 28SX17 exhibits a Ba concentration nearly double all other samples (210 ± 66 ppm). Concentrations of Ti, at or below detection limits in Cogswell and colleagues’ sample, averaged around 1000 ppm in all of our samples. Abundances of Sr in our sample ranged from a low of 189 ppm (28WA38) to a high of 591 ppm (12HR11). For comparison, the shell sample from mid-Missouri had a mean Sr concentration of 104 ppm.

5. Discussion

Compositional analysis by NAA of a large sample of freshwater mussel shell from multiple locations in the eastern United States has important implications for mathematical models used to correct for the influence of shell tempering in prehistoric ceramics. Most notably, we find that the average values for Mn and Na observed in a sample of modern freshwater shells from Missouri cannot be assumed to accurately represent those in shell obtained elsewhere in eastern North America. These two elements are routinely adjusted by fixed factors, and data reported here indicate that abundances of these elements vary substantially. We also find that concentrations of three other elements—Ba, Sr, and Ti—can differ significantly among mussel–shell samples. Sr values observed in our samples were significantly higher than those reported by Cogswell et al. (1998); however, Sr is routinely removed after application of the Ca-correction. Data presented here underscore the importance of this practice.

Table 2

<table>
<thead>
<tr>
<th>Site</th>
<th>Genera</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>28SX17</td>
<td>Union</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Pleurobema</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Quadrula</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Unionidae sp.</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>c.f. Plethobasus</td>
<td>1</td>
</tr>
<tr>
<td>12HR11</td>
<td>Elliptio</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Pleurobema</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Fusconaia</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Plethobasus</td>
<td>1</td>
</tr>
<tr>
<td>15OH1</td>
<td>Cyprinella</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Elliptio</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Epiphragma</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Fusconaia</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Pleurobema</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Quadrula</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Unident.</td>
<td>1</td>
</tr>
<tr>
<td>15BT6</td>
<td>Elliptio</td>
<td>3</td>
</tr>
<tr>
<td>27CH95</td>
<td>Unio</td>
<td>6</td>
</tr>
<tr>
<td>28WA392</td>
<td>Cyprinella</td>
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</tr>
<tr>
<td></td>
<td>Epiphragma</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Obovaria</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Pleurobema</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Quadrula</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Unionidae sp.</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 1. Archaeological sites from which shell samples were obtained. Location of the Gasconade River sampling locality of Cogswell et al. (1998) is shown.

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Concentrations of both Ba and Ti were significantly different than those reported by Cogswell et al. (1998), and we believe that they, like Na and Mn, may artifically enrich a ceramic body. For example, the concentration of Ba in Nor is 612 ppm, and its average abundance in NIST SRM 679 (Brick Clay) is 432 ppm. If these values can be considered reliable indicators for Ba levels in average clays, any shell with Ba concentrations exceeding these levels will artificially enhance a ceramic body. Similarly, Ti concentrations in our samples were significantly higher than those reported by Cogswell et al. (1998). Our values range from a low of 881 ppm (12HR12) to a high of 1184 ppm (28WA38); whereas, concentrations of Ti in the Cogswell et al. sample were below detection limits. Again, using the values of NOR (6121 ppm) and NIST SRM 679 (5770 ppm) as baseline clay values, the observed concentrations of Ti in our prehistoric freshwater shell samples would likely enhance this element’s presence in shell-tempered wares. Under the assumption that Ti is present in only trace amounts in shell, a ceramic vessel produced using a 50/50 mixture of shell and Nor would have a Ti abundance of 3061 ppm. Tempering the same clay with shell from site 12HR12, with its observed average Ti composition would have a Ti abundance of 3061 ppm. Tempering the same clay with shell from site 28WA38 (3653 ppm).

6. Conclusion

Data presented here for the elemental composition of Unionoida shell from several prehistoric localities in EMn, Sr, Ba, and Ti. The discrepancies between our data and those reported by Cogswell et al. (1998), and the variation observable between samples of shell in our own data, we note that there is uncertainty in precisely what elements may be enriched by the use of freshwater shell temper. These data indicate that attempts to remove the dilution effects of Ca in a ceramic body introduced by shell tempering could be improved through the analysis of local prehistoric shell to determine precisely what elements and in what abundances have been contributed by the temper. We do not question the validity or primacy of the mathematical model used to adjust ceramic compositions to account for dilution/enhancement effects produced by shell temper (Cogswell et al., 1998; Steponaitis et al., 1996). We concur with Cogswell et al. (1998:71) that currently employed mathematical methods are the best available means for reducing the confounding effects of shell temper. However, we do see the data presented here as an evaluation of the universality of the correction formula employed by Cogswell et al. (1998) and by Steponaitis et al. (1996), and we find that it requires geographically specific adjustment. Our data demonstrate that elemental compositions of freshwater mussel shells are more variable than previously assumed and that some elements, previously assumed to be minor constituents in shell, may in fact be artificially enhanced by shell tempering. Average values of Na and Mn obtained from modern shell cannot be used as analogs for prehistoric shells from elsewhere, and other elements (Ba and Ti in our sample) may be affected by shell tempering.

In order to account for these effects, we suggest that future studies involving compositional analyses of shell-tempered pottery be complemented with analyses of prehistoric shell to determine site- or region-specific correction factors for individual elements. This could be accomplished through disaggregation of sherds to obtain temper particles. Cogswell et al. (1998) were unsuccessful in their attempts to disaggregate their test tiles; however, they did not employ methods involving sonication (Elam et al., 1992; Gaines and Handy, 1977). Peacock and Feathers (2009) successfully separated shell temper from Mississippian pottery by crushing sherds laterally and picking out shell fragments from the resultant powder. Disaggregation, either by sonication or manually, is both destructive and labor intensive, but given the possibility of directly isolating shell fragments for analysis, data presented here for the elemental composition of Unionoida shell from several prehistoric localities in EMn, Sr, Ba, and Ti. The discrepancies between our data and those reported by Cogswell et al. (1998), and the variation observable between samples of shell in our own data, we note that there is uncertainty in precisely what elements may be enriched by the use of freshwater shell temper. These data indicate that attempts to remove the dilution effects of Ca in a ceramic body introduced by shell tempering could be improved through the analysis of local prehistoric shell to determine precisely what elements and in what abundances have been contributed by the temper. We do not question the validity or primacy of the mathematical model used to adjust ceramic compositions to account for dilution/enhancement effects produced by shell temper (Cogswell et al., 1998; Steponaitis et al., 1996). We concur with Cogswell et al. (1998:71) that currently employed mathematical methods are the best available means for reducing the confounding effects of shell temper. However, we do see the data presented here as an evaluation of the universality of the correction formula employed by Cogswell et al. (1998) and by Steponaitis et al. (1996), and we find that it requires geographically specific adjustment. Our data demonstrate that elemental compositions of freshwater mussel shells are more variable than previously assumed and that some elements, previously assumed to be minor constituents in shell, may in fact be artificially enhanced by shell tempering. Average values of Na and Mn obtained from modern shell cannot be used as analogs for prehistoric shells from elsewhere, and other elements (Ba and Ti in our sample) may be affected by shell tempering.

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such methods could be beneficial for any ceramic-sourcing study involving shell-tempered wares. Barring the mechanical separation of shell temper from its ceramic matrix, it would be possible to use laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) to analyze only the individual components of a ceramic sherd to characterize clay, temper, or both (Peacock et al., 2007; Stoner and Glascock, 2012). However, exclusive use of LA-ICP-MS for compositional analysis presents its own set of problems, including calibration with the extant NAA database.

If bulk analysis by NAA is the preferred analytical technique, the data presented here suggest that the most-appropriate means of eliminating the Ca-dilution problem in prehistoric shell-tempered pottery is to complement ceramic analyses with analyses of prehistoric mussel shell from within the particular watershed. Given that long-distance transportation of shell for either food or for ceramic production seems unlikely (e.g., Peacock et al., 2012), and that mussel shell can be extremely abundant in archaeological assemblages, this seems to us to be the most effective manner by which to accurately characterize shell being used as temper and to document any potential elemental enhancement/dilution effects introduced by the temper itself. Analysis of archaeological shell may present its own set of problems, including the assumption that bulk chemistry of shell does not significantly fluctuate through time or from degradation. Current evidence supports this assumption. Collins (2012) found minimal variation in major element chemistry of archaeological shell from deposits spanning several centuries. Peacock and Seltzer (2008) observed some variability in the Sr/Ca ratio of shell from two strata at a Vaughn Mound in Mississippi. However, no significant differences were observed in Ba, Mg, or Sn, and differences in mean Sr abundances were ca. 80 ppm.

Finally, despite our narrow focus on the effects of freshwater-mussel–shell chemistry on bulk pottery analyses, we reiterate that these data have broader implications beyond viewing shell as a confounding aspect in archaeometric studies. Chemical analyses of shell temper itself may inform directly on selection and procurement of shell by prehistoric potters in the same way in which chemical analyses of ash and sediment may provide greater understanding of ceramic production (Arnold et al., 2000; Hirshman and Ferguson, 2012). Comparative analyses of prehistoric and modern shells have the potential to inform on conservation biology and ecology (Peacock et al., 2012; Peacock, 2012; Peacock and Seltzer, 2008). And, the observation of varying chemical compositions among shells strengthens the empirical warrant for attempts to establish provenance of shell artifacts themselves (Peacock et al., 2010). Data presented here strengthen the empirical warrant of all such studies.
Acknowledgments

All data used in this study are available as an on-line supplementary material as well as at the web site of the MURR Archaeometry Laboratory: http://archaeometry.missouri.edu. An earlier version of this research was presented in 2011 at the Modern Trends in Activation Analysis conference in College Station, Texas. Richard Burdin (University of Kentucky), George Crothers (Office of State Archaeology/University of Kentucky), Christopher R. Moore (University of Indianapolis), the Kentucky Office of State Archaeology, and Gregory D. Lattanzi (New Jersey State Museum) are thanked for loaning shell samples for analysis. Jonathan Baker (University of Tennessee) visually identified the Fort Hill shell specimens. Evan Peacock (Mississippi State University) identified the mussel shells from Kentucky and Indiana. The MURR Archaeometry Laboratory is supported by a grant from the National Science Foundation (#1110793). We thank R. Lee Lyman, Cheryl Claassen and one anonymous reviewer for providing helpful comments that improved the quality of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jasrep.2014.08.001.

References


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