Buying Local: A Multi-Method Approach to Determining the Provenance of Locally-Made Lead-Glazed Earthenwares.

***Archaeological and Anthropological Sciences* (2022) 14: 136**
DOI: 10.1007/s12520-022-01597-0

Matthew C. Greer[1,2,*] and Brandi L. MacDonald[3]

[1] Carter G. Woodson Institute for African-American and African Studies, University of Virginia, 108 Minor Hall, Charlottesville, VA 22904
[2] Department of Anthropology, Syracuse University, 209 Maxwell Hall, Syracuse, NY 13244
[3] Archaeometry Laboratory, University of Missouri Research Reactor, Columbia, MO 65211
[*] Corresponding Author. Email address: mcg5s@virginia.edu

Orcid: Greer (0000-0002-3977-9707), MacDonald (0000-0003-2887-4351)

Abstract: This article presents the results of a combined neutron activation analysis (NAA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis of 243 locally-made ceramic vessels from the northern Shenandoah Valley region of Virginia (USA). The goal of this study was to determine if the geochemical composition of lead glazes on locally-made coarse earthenwares could be combined with an analysis of these vessels' paste composition to create a robust, multi-method approach for determining the provenance of ceramics made within a single region. Our results show that 57 out of 120 vessels whose glazes we analyzed by LA-ICP-MS had geochemical characteristics that allowed us to determine which town(s) they were likely made in. This is a lower success rate than our NAA study, which suggested the provenance of 90 out of 99 locally-made samples, but we argue that this is due to common knowledge, widespread materials, and itinerate potters circulating throughout the small (25 km) portion of a single region we focused on, and that a larger study should be more successful. Regardless, our research demonstrates that when combined with paste characterization by NAA, the composition of lead glazes can be used to create stronger arguments about the provenance of ceramic pots made within a single region.

Keywords: Ceramic Analysis, Historical Archaeology, Provenance Analysis, NAA, Glaze Composition, LA-ICP-MS

Competing Interests: The authors have no competing interests to declare.

Acknowledgments: We thank Barry Higgins, April Oga, Alexa Kuo, Whitney Goodwin, and Jacques Burlot for their assistance with the analytical runs. We also thank Erica Moses, Kristen Laise, and staff members at Belle Grove. Samples were provided by Lindsay Bloch, Newtown History Center, Belle Grove, Inc., Museum of the Shenandoah Valley, and the Strasburg Museum. Funding for the Belle Grove excavations was provided by the Wilkins Family Foundation, Syracuse University's Roscoe Martin Fund, The National Trust for Historic Preservation's Battlefield Preservation Fund. Funding for the NAA and LA-ICP-MS analysis was provided by the National Science Foundation (NSF-1912776), which was awarded to the MURR Archaeometry Laboratory. The NAA was also funded by Sigma Xi (Grant

G2019100194732789) and Syracuse University's Roscoe Martin Fund. The Carter G. Woodson for African-American and African Studies at the University of Virginia provided funds for writing up our results.

Introduction

Studies of ceramic provenance often focus on the movement of vessels across vast swaths of land and sea, providing important data on large-scale political economies that connected disparate people. But they often do so by downplaying the movement of ceramics across shorter distances within the regions we study, lumping locally-made pots into an under-theorized analytical category that only gets used as a backdrop for narratives about long-distance trade (Druc, 2013). This elides the movement of locally-made pots, which were also part of the political economies we seek to learn about. Intra-regional provenance studies that address local trade and the important ways it structured everyday life are becoming more popular (e.g., Eckert and James, 2011; Monette et al., 2007; Pezzarossi, 2015; Stark et al., 2007), but these often rely on a single analytical technique to determine the provenance of locally-made pots (but see Minc et al., 2016; Stoner, 2016). To produce more robust studies, we need multi-method approaches (Neff, 2012; contra Mommsen, 2004). Using multiple analytical techniques to produce independent lines of evidence creates better results for inter-regional studies (e.g., Beck and Neff, 2007; Druc et al., 2017; Stahl et al., 2008), and are critically important for intra-regional analyses where there is less geochemical variation, making provenance determinations (potentially) less reliable. By combining the results from multiple analytical techniques, we can create stronger arguments about where local pots were made, the trade networks they traveled through, and how these networks shaped life in the past.

This article discusses the results of a combined neutron activation analysis (NAA) of ceramic bodies and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis of lead glazes from 18th- and 19th-century coarse earthenwares made in the northern Shenandoah Valley region of Virginia (USA). Data for this comes from locally-made ceramics from Quarter Site B (QSB) at Belle Grove Plantation. Results of the NAA are published elsewhere (Greer and MacDonald, 2020), but in summary, we determined which town(s) 90 locally-made vessels were likely made in. This article 1) presents the results of the LA-ICP-MS analysis of 189 lead glazes from QSB and four historic pottery workshops in surrounding towns, 2) compares these results to the NAA data, and 3) provides preliminary observations on the future use of glaze composition to determine the provenance of vessels made within a single region.

By assessing the composition of glazes made in different towns, we identified primary glaze components, lead sources/forms/mixtures, colorants, and trace elements that can be used to determine the provenance of locally-made lead-glazed earthenwares in the Shenandoah Valley. Comparing these results with the NAA data gives us two independent lines of evidence that together strongly suggest enslaved people at Belle Grove acquired most of their earthenwares from the town of Newtown, even though this was not the closest ceramic producing town to the plantation. Archaeologists have used LA-ICP-MS and other analytical techniques like lead isotope analysis to study the compositions of ceramic glazes (e.g., Klesner et al., 2019; Niculescu, 2017; VanValkenburgh et al., 2015) and determine the provenance of glaze components (e.g., Klesner et al., 2021; Schurr et al., 2018; Tite et al., 2016), but these data have not been used to identify where individual pots were made. Our results show that when considering lead-glazed earthenware from a single region, glaze composition can be used in conjunction with NAA data to create stronger arguments about ceramic provenance.

Shenandoah Valley Lead-Glazed Earthenwares

The Shenandoah Valley, located in western Virginia between the Blue Ridge and Allegheny Mountains, was colonized by Britain in the 1730s.Local ceramic production began in the 1760s (Comstock, 1994) (Figure 1). By 1800, potters operated in most major towns in the northern Valley, making vessels used by almost every household in the region. These ceramics fall into two categories: salt-glazed stonewares and lead-glazed coarse earthenwares (often called redwares). This article focuses on the earthenwares, but the NAA study assessed both ceramic types.

[Insert Figure 1]

Valley potters jealously guarded their glaze recipes, as quality glazes were critical to making marketable vessels. H.E. Comstock (1994: 52–60) has compiled sketches of these recipes from the few available written sources. Lead, used as a fluxing agent, was the primary ingredient. Early potters used lead carbonate ($PbCO_3$) but most used red lead (Pb_3O_4) or litharge (PbO) by the early-19th century (Comstock, 1994: 52). No major lead sources have been identified in the northern Shenandoah Valley, leading most potters to acquire lead imported by local merchants (e.g., Comstock, 1994: 451; Park, 2001: 12). Raw clay was added to the glaze as a source of silicon (Si) and as a source of aluminum (Al,) which stabilized the glaze and made it less likely to melt in the kiln (e.g., Comstock, 1994: 53; Molera et al., 2001: 1124).The third component was another source of Si, typically sand, crushed chert, and/or crushed quartz (Comstock, 1994: 53). The final ingredient was "pap," a slurry of flour and water that kept glazes from pooling at vessels' bases before firing (Comstock, 1994: 54). Mixed with water, these ingredients created a clear glaze. Many potters added mineral colorants to produce black, brown, green, red, tan, and yellow glazes. Comstock (1994: 55–60) notes five primary colorants. Manganese (MnO) and iron oxides (Fe_2O_3) both produced black, brown, and tan glazes. Copper oxides (CuO) were fired in oxidized environments to create green glazes and in reduced environments (generally achieved by placing a vessel within a larger, upturned vessel) to create red glazes. Antimony oxide (Sb_2O_5) and Fe_2O_3 both produced yellow glazes. And a combination of Fe_2O_3, CuO, and cobalt oxide (CoO) produced brown and black glazes.

Materials

Because each potter, theoretically, made their own unique glazes, we should be able to identify discrete compositional groups that correspond with individual recipes. And, if we know which towns these recipes are associated with, we should be able to use this to determine the provenance of locally-made earthenwares. To test these assumptions, we analyzed 184 lead-glazed vessels from the northern Shenandoah Valley using LA-ICP-MS (Table 1). Sixty-four vessels were wasters (vessels that broke during production) from four early 19th-century potteries. This included samples from the Peter Lauck (1780-1839) and Anthony Bacher (1862-1889) Potteries in Winchester (39° 10’ 54” N, 78° 9’ 54” W) and the Andrew Pitman (1782-1838) and John Pitman (1794-1820s) Potteries in Newtown (39° 4’ 59” N, 78° 13’ 6” W, now called Stephens City) (Greer and MacDonald, 2020: 141). All coordinates are rounded to the nearest second and indicate the location of Winchester and Newtown (respectively).

[Insert Table 1]

The remaining 120 vessels came from Quarter Site B (QSB), a large early-to-mid-19th century quartering site for enslaved Africans at Belle Grove Plantation (39° 1’ 15” N, 78° 18’ 14” W, location of the plantation not QSB, rounded to the nearest second). During this time the plantation owners enslaved between 36 and 102 people at four properties, and we believe that 30-50 people were enslaved at Belle Grove while QSB was inhabited (Greer and MacDonald, 2020: 140). The site was extensively excavated between 2015 and 2019 to study the lives of enslaved people in the Shenandoah Valley (Greer, Forth.). The analyzed ceramics come from four middens and two root cellars. In total, the LA-ICP-MS dataset includes most (85.71%) of the locally-made lead-glazed earthenwares from QSB. Three vessels were not analyzed because the only available specimen was used for the NAA analysis and the remaining 17 were left intact to preserve them for the project's study collection and/or a forthcoming museum display. Five of the QSB vessels had different interior and exterior glazes and we sampled each side separately, bringing the total number of sampled glazes from QSB to 125 and the total for this analysis to 189.

The Lauck and Pitman Potteries were within 20 km of Belle Grove and all three operated while QSB was inhabited, so vessels from these workshops could be present in the QSB collection. The Bacher Pottery postdates QSB, so Bacher vessels should not be at the site. We included these samples as a control group because if glazes only associated with Bacher were identified at QSB, this would indicate that the glaze compositions may not be as diagnostic as hypothesized. Potteries also operated in Strasburg and Woodstock, but lead-glazed earthenware samples from these towns were not available for our study. Glaze recipes not associated with the Lauck, Bacher, or Pitman Potteries may be from these towns or other potteries in Winchester or Newtown.

Paste Characterization by NAA

We prepared and analyzed the 189 ceramic samples at the Missouri University Research Reactor (MURR) using the laboratory's standard procedures (Glascock, 1992; Glascock and Neff, 2003), and preliminary interpretations were reported in (Greer and MacDonald, 2020). While this is the same number of samples as the LA-ICP-MS analysis (see above) it did not include the exact same specimens. Eighty-nine wasters were analyzed by NAA, including all 64 samples used in the LA-ICP-MS analysis and 25 additional samples without lead glazes. Among these are 20 samples from the Strasburg Steam Pottery (1890-1897) in Strasburg (38 ° 15' 18" N, 78 ° 21’ 32” W, coordinates are rounded to the nearest second and indicate the location of Strasburg). One hundred vessels from QSB were sampled, including 66 vessels used in the LA-ICP-MS analysis, one lead-glazed earthenware (SYU085) determined by NAA not to be locally-made (and therefore excluded from the LA-ICP-MS dataset), and 33 salt-glazed stonewares. Six paste groups were identified in the NAA dataset (Greer and MacDonald, 2020: 144–158) (Figure 2, Table 2, Online Resource 1). Each was statistically validated using Mahalanobis distance group membership probabilities (MD-GMP) (Online Resources 2 and 3). We used the first seven principal components for the MD-GMP calculations, which explained 85.4% of the variance within the dataset. The results indicated strong positive group assignments (>20%) for 88% of the samples, validating the identified groups.

[Insert Figure 2 / Table 2]

The NAA results were especially helpful in determining which town vessels did *not* come from, as only Paste Group 1 contains wasters from Winchester, Newtown, and Strasburg. However, the Winchester and Strasburg samples had low membership probabilities, strongly suggesting that Paste Group 1 is associated with Newtown. While this provides important information, it fails to provide definitive evidence about the provenance of 82 of the 99 locally-made vessels from QSB. Furthermore, of the two groups only associated with one town, Paste Group 5 only contains two wasters, making arguments about its association with Strasburg somewhat tenuous. To make stronger arguments about where the QSB vessels were made, we needed additional lines of evidence. For this, we turned to a LA-ICP-MS analysis of lead-glazed earthenwares.

LA-ICP-MS Methods

We conducted the LA-ICP-MS analysis at MURR using the laboratory's standard procedures. Squares of < 1 cm^2 were broken off from each sample using tile nippers, washed in deionized water, air dried, and mounted on thin-section slides. We also mounted samples of standard reference materials from NIST SRM-610, SRM-612, and Corning glasses Brill-B, Brill-C, and Brill-D. The data were acquired using a PerkinElmer SCIEX NexION 300 Quadrupole ICP-MS coupled with a Teledyne Instruments Inc. Analyte Excite HelEx 193 nm laser ablation system. We selected five 40 x 80 µm ablation pass lines on each standard and unknown sample. A 110 µm-wide pre-ablation pass was done on each line to remove surface contamination. The laser moved at a rate of 5 µm/s firing 110 bursts per second at 42.6 % of the maximum power output. We paused the laser for 25 seconds after each ablation while the ICP-MS continued to collect data. We monitored instrument stability and drift by "bracketing" five glaze samples with a set of standards. The ablated sample vapor was transported by He carrier gas to the ICP-MP torch where it was ionized and passed through two detectors that measured the signal intensity in counts per second. The experiment collected data for 59 isotopes: ^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{24}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{35}Cl, ^{39}K, ^{44}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}N, ^{63}Cu, ^{66}Zn, ^{71}Ga, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{115}In, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{197}Au, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, and ^{238}U.

Switching the laser on and off for a pause of 25 seconds between scans formed a series of plateaus representing signal intensity measured by the ICP-MS for each isotope. Each plateau represents a single ablation pass, whereas the baseline between them serves as the sample blank. An Excel-based macro script subtracted the sample blank (the average of 5 baseline replicates both before and after the sample peak) from each replicate. The blank-subtracted replicates for each measured isotope were summed and averaged. Anomalous spikes were identified and eliminated. The averaged signal intensity data for each isotope in counts per second were corrected to a total elemental signal by comparing the signal intensity measured for each element in the sample for the same element measured in the standards. We used isotope Si^{29} as our internal standard. For NIST SRM glasses and Corning glasses we used values published by Pearce et al (1997) and Brill and Rising (1999), respectively, to calculate the *Ky:*

$$Ky = \frac{Standardized\ signal\ for\ Y}{[Y] in\ the\ reference\ material} * [internal\ standard] in\ the\ reference\ material$$

Where *K* is the conversion factor for element *y.* The standard signal was then divided by the *Ky* and the sum of all elements normalized to 100 percent oxide, as proposed by Gratuze *et al.* (2001). The resultant data is presented in Online Resource 4. Online Resource 5 lists the average elemental concentrations and percent deviations of replicates of NIST SRM-610 and SRM-612. The relative standard deviation for most elements in SRM-610 is < 5%.

Postdepositional processes can contaminate lead glazes, impacting the resulting data from surface analyses. In a previous study of imported British refined earthenwares from QSB (Greer et al., 2021) we screened samples for contamination using scanning electron microscopy (SEM) and found no evidence of contamination (see Online Resource 6). This is likely because glazes high in Al (like those on refined earthenwares and the locally-made earthenwares discussed below) are relatively stable (Molera et al., 2001: 1127). As a result, while we did not screen our samples for contamination, we are reasonably confident that our samples are not contaminated.

Glaze Characterization by LA-ICP-MS

To characterize the glazes, we analyzed the data in four ways to identify primary glaze components, lead sources/forms/mixtures used in the glazes, coloring agents, and trace elements. Each analysis is presented below in its own subsection.

Glaze Types

Lead (PbO) and silica (SiO_2) oxides are ubiquitous in the dataset (2.05-62.27 wt% and 25.40-61.44 wt%, respectively), confirming that all 189 samples are lead-glazed. Fourteen samples have low to moderate aluminum oxide (Al_2O_3) (2.25-7.12 wt%), tin oxide (14.2-1008.3 ppm), and alkali oxides (see Table 3), indicating lead-silica glazes (35-65 wt% PbO and 25-55 wt% SiO_2). The remaining samples have additional components and can be divided into eight glaze types. The most common are lead-silica-aluminum glazes (n=102), defined by 30-65 wt% PbO, 25-50% SiO_2, and ~6-20 wt% Al_2O_3 and a lack of elevated concentrations of other glaze components. Thirteen samples are tin-opacified, defined as 0.5-5 wt% SnO_2. Ten of these have PbO, SiO_2, and Al_2O_3 concentrations in the same range as the lead-silica-aluminum glazes, making them lead-tin-silica-aluminum- glazes, while one sample has an Al_2O_3 concentration that corresponds with the lead-silica glazes, making it a lead-silica-aluminum glaze. The final two-tin opacified samples have elevated potassium (K_2O) and calcium oxides (CaO), indicating the presence of alkali fluxes and making these lead-tin-silica-aluminum-alkali glazes. We identified alkali fluxes in 60 other samples, with the most common oxides being K_2O (n=48, 0.5-7 wt%), CaO (n=5, 1-2 wt%), or a mixture of various alkali oxides (n=7, notably 1.51-7.39 wt% K_2O and 0.13-1.82 wt% CaO). Each of these was determined to be its own glaze type, along with a separate group with low Al_2O_3 (<6 wt%). Despite the presence of SnO_2 and alkali oxides, most tin-opacified and alkali-fluxed samples have similar PbO concentrations to the lead-silica and lead-silica-aluminum groups, indicating these glaze components were not substitutes for PbO (Figure 3). Eight alkali-fluxed samples, however, have lower PbO concentrations (< ~20 wt%), suggesting that in these cases alkali elements may have been added as a substitute for PbO.

[Insert Table 3 / Figure 3]

Except for the lead-silica group, our samples have unusually high Al_2O_3 concentrations (6.45-24.49 wt%). By comparison, lead glazes on imported British refined earthenwares from QSB have Al_2O_3 concentrations ranging from 3.72-10.03 wt% (Greer et al., 2021), which is below the Al_2O_3 concentration in 61.37% (n=116) of the locally-made glazes. Adding clay to glaze recipes, as was common in the Valley (see above), increases Al_2O_3 concentrations in glazes but even this cannot fully explain the abnormally elevated Al_2O_3. Al contamination from the ceramic paste could explain this, although the lack of Al contamination in the QSB refined earthenwares analyzed by SEM make Al contamination in other samples from QSB unlikely (Greer et al., 2021: 4–6). However, as noted earlier, Valley potters often used crushed chert as the major source of Si in their glazes. Cherts that form in marine environments can have elevated Al (e.g., Abrajevitch, 2020: 9), and bedrocks in the Valley consist of formerly submerged limestones and shales, suggesting that local cherts may have elevated Al (Greer and MacDonald, 2020: 142). Potters using high Al-cherts in their glazes could help explain the elevated Al_2O_3 concentrations, although a mineralogical study of the glazes is needed to test this hypothesis.

Lead Sources/Forms/Mixtures

With PbO being ubiquitous in the dataset, we performed a principal component analysis (PCA) to identify possible lead sources, forms, and/or mixtures, using trace elements that correlate positively with Pb as variables: arsenic (As), bismuth (Bi), Co, indium (In), manganese (Mn), molybdenum (Mo), and silver (Ag). Here, lead sources refer to the provenance of the lead used in the glazes, lead forms refer to different mineralogical forms (lead carbonate, red lead, litharge, etc.), and lead mixtures refers to lead mixed with other metals, possibly from extracting lead from scavenged pewter. We discuss these together because while our PCA can identify discrete groupings, our dataset cannot determine if these groups are the result of potters getting their lead from different sources, using different forms of lead, or some potters using scavenged lead. In short, the groups identified using these trace elements reveal information about the lead component of different glazes, although additional spectrographic and isotopic analysis will be needed to determine what exactly these groups represent. We identified five lead groups in the dataset shown in Figure 4. Each was validated using MD-GMP. For this we used the first four principal components, which explain 89.6% of the variance in the dataset (Table 4, Online Resources 7 and 8). Lead Groups A and C separate from Lead Groups B, D, and E on Figure 4's X-axis, while Lead Groups A, B, and E separate from Lead Groups C and D on the Y-axis. Lead Group E clusters with Lead Group B in Figure 4, but the MD-GMP shows that this is a separate group. Finally, 18 samples could not be assigned to a group.

[Insert Figure 4 and Table 4]

Colorants

Four colorants were identified in the LA-ICP-MS data, MnO, Fe_2O_3, stibnite (Sb_2S_3), and CoO (Table 5). When assessing colorants, we used a threshold of ~1.0-2.0 wt% for most oxides except Fe_2O_3, (>~2.5 wt%), CoO (> 40 ppm), and chromium (Cr_2O_3, >300 ppm). MnO is the most common colorant (n=42) and was identified in both relatively high (0.5561–4.883 wt%) and low (0.1474–0.4861 wt%) concentrations. While the low MnO group has MnO concentrations that are under our established threshold, these samples have significantly more MnO than other samples, leading us to include them as a separate group. The high MnO samples are black (n=14), brown (n=13), and tan (n=2), and the low MnO glazes are black (n=1), brown (n=7), and tan (n=3), along with three glazes of indeterminate color. Fe_2O_3 is the second most common colorant (n=23) (2.52–6.26 wt%) and is present in brown (n=1), tan (n=21), and red (n=1) glazes. One sample combined Fe_2O_3 (5.48 wt%) with Sb_2S_3 (3.47 wt%) to produce a red glaze. Forty-five samples contained both Fe_2O_3 (2.49–19.40 wt%) and MnO, with the latter present in both high (0.5155-5.34 wt%) and low (0.1434-0.4984 wt%) concentrations. The high MnO samples include black (n=15) and brown (n=14) glazes and two samples whose color could not be determined due to extensive burning. The low MnO samples include black (n=2), brown (n=11), and tan (n=1) glazes. CoO (42.44–211.86 ppm) was the third most common colorant (n=13) and was combined with MnO (0.7485–3.932 wt%) to produce brown (n=9) and green (n=1) glazes, and with both MnO and Fe_2O_3 (1.05–1.98 wt% and 2.59–14.41 wt%, respectively) to produce brown glazes (n=3). Two samples were identified as outliers in the dataset and the remaining 63 samples lacked colorants, indicating clear glazes. Forty-nine of the glazes without colorants appear colored, including brown (n=22), green (n=6), red (n=14), tan (n=1), or yellow (n=6). Further observation of these samples under low-level magnification (60-100x) show the presence of a colored slip underlying the glaze. LA-ICP-MS and/or SEM analysis of the underlying slips is needed to determine the colorants used in these samples.

[Insert Table 5]

Trace Elements

We assessed trace elements in the glazes to determine any groupings these might reveal. This analysis indicated that antimony (Sb), barium (Ba), copper (Cu), phosphorus (P), Sn, titanium (Ti), and zinc (Zn) were the most useful trace elements for our purposes. Several of these elements were included in our discussions of major glaze components (Sn), colorants (Sb) or lead sources/forms/mixtures (Cu). Elevated concentrations of Sn were important in our earlier analysis, so we excluded tin-opacified samples from any groups defined by high Sn concentrations. We also removed the one sample with stibnite (Sb_2S_3) from this analysis, from any groups with high Sb concentrations. Cu concentrations did not play a large role in the PC loadings scores for our lead analysis (see Online Resource 8), so including it here should not be replicating the lead groupings we identified earlier. By assessing the distribution of trace elements in the glazes, we identified 12 groups containing a total of 92 samples. These groups and their trace element concentrations are presented in Table 6. Five groups are relatively small (n=<3). Of the larger groups, one is defined by elevated barium (Ba) (n=15), one by elevated copper (Cu) (n=5), and one by elevated zinc (Zn) (n=4). We also identified three groups defined in part by elevated antimony (Sb), two partially defined by elevated Sn, and one by elevated Sb and Sn. Several of the trace elements are colorants (Cu, Ti, Sb, and Zn), but none are present in high enough concentrations to affect the color of these glazes.

[Insert Table 6]

Discussion

Using the data presented above, we can use the geochemical composition of lead glazes to determine the provenance of earthenwares made in the Shenandoah Valley, especially when we pair these with the NAA results (Table 7). We identified nine groups in our analysis of primary glaze components. The most common, lead-silica-aluminum glazes, were present among wasters from every pottery and in QSB samples from every paste group. Because they are so widespread, they do not provide any insight into provenance. Alkali-fluxed samples were present at the Andrew and John Pitman (Newtown) and Lauck (Winchester) Potteries, and in Paste Groups 1-4 (Newtown, Strasburg, and/or Winchester) from QSB. This suggests that even though historic records do not indicate the use of alkali fluxes (e.g., Comstock, 1994), they were relatively common in the Valley. As a result, these cannot be used to determine provenance, nor were different alkali oxides used in different towns. Tin-opacified glazes were only identified among the John Pitman wasters and QSB samples from Paste Group 1 (Newtown). This strongly suggests that the use of tin-opacifiers was limited to Newtown, and possibly to John Pitman's workshop. Finally, low Al_2O_3 glazes were identified among the Lauck and Bacher wasters (Winchester), and QSB samples from Paste Group 2 (Newtown or Winchester), suggesting these glazes are associated with Winchester.

[Insert Table 7]

The five identified Lead Groups also show promise for determining the provenance of Valley ceramics. Lead Group A contains wasters from the Andrew Pitman, John Pitman, and Lauck Potteries, and QSB samples from Paste Groups 1-5, while Lead Group B contains wasters from the Andrew Pitman, John Pitman, Lauck, and Bacher Potteries, and QSB samples from every paste group except Paste Group 5. As a result, the distributions of Lead Groups A and B are too widespread to be used to make provenance determinations. Lead Group C contains wasters from the Andrew and John Pitman Potteries, both in Newtown, and QSB samples from Paste Group 1 which is associated with Newtown, giving Lead Group C an association with Newtown. Lead Group D contains no wasters, but all of its NAA samples belong to Paste Group 1, suggesting an association with Newtown. Finally, Lead Group E contains wasters from all four Newtown and Winchester potteries, and QSB samples from Paste Groups 2 and 3, which are associated with both Newtown and Winchester. This gives Lead Group E an association with Newtown and Winchester, but not Strasburg.

We identified four colorants in the dataset. Two, MnO and Fe_2O_3, were found in wasters from all four potteries and in QSB samples from every paste group except Paste Group 5. There are also no geographically discrete clusters based on the concentration of MnO or the combination of MnO and Fe_2O_3, indicating that these colorants cannot be used to determine the provenance of locally-made vessels. We identified CoO in 12 wasters from the Lauck and

Bacher Potteries and one waster from the John Pitman Pottery. While the Pitman sample prevents us from suggesting a strong association between CoO and Winchester, the Pitman sample was also colored with Fe_2O_3 and MnO while most (83.33%) of the Winchester samples use MnO but not Fe_2O_3. This suggests that the MnO-CoO combination may be unique to Winchester. Furthermore, the Pitman sample (SYU020) has more Fe_2O_3 than the other MnO-CoO-Fe_2O_3 glazes (12.41 wt% versus 2.59–4.10 wt%), suggesting that we can distinguish between Newtown and Winchester samples. Finally, one sample from the Andrew Pitman Pottery used stibnite (Sb_2S_3), which was not found in any other sample, tentatively suggesting that antimony-colored vessels are associated with Newtown.

Of the 12 groups we identified based on trace element concentration, seven were either widespread (high Ba and high Cu) or contained too few samples (n=<5) to adequately assess their distribution. Four groups are defined by elevated Sb. These were identified in wasters from the Andrew and John Pitman Potteries, 11 QSB samples from Paste Group 1, one from Paste Group 2, and two from Paste Group 4 (Strasburg or Winchester). The preponderance of QSB samples from Paste Group 1 suggests that high Sb glazes are associated with Newtown. However, the two samples from Paste Group 4 suggest that high Sb glazes were also made in Strasburg, preventing us from associating these glazes with Newtown, although we can argue that high Sb glazes are not associated with Winchester. Three groups are defined by elevated Sn. These include five wasters from the Andrew and John Pitman Potteries, one from the Lauck Pottery, and QSB samples from Paste Groups 1 and 2. As with the high Sb glazes, most high Sn glazes are from Newtown but the one Lauck sample prevents us from making this association, although we can argue that low Sn glazes are not associated with Strasburg.

Newtown Over Strasburg

We have demonstrated elsewhere (Greer and MacDonald, 2020: 138–139) that enslaved people predominantly acquired locally-made ceramics in the towns where they were made. Therefore, the relatively large percentage of QSB samples from Paste Groups associated solely with Newtown (44.44%) or with Newtown or Winchester (24.24%), and the relatively low percentage of vessels from Paste Groups associated with Strasburg (21.21%) indicate that before the late 1830s people enslaved at Belle Grove routinely bought locally-made ceramics from Newtown even though Strasburg was closer to QSB (8 km versus 11 km) (Greer and MacDonald, 2020: 158–161). (A shift from Newtown to Strasburg seems to have occurred in the 1840s.) The LA-ICP-MS dataset provides independent verification of this preference for buying ceramics in Newtown. Of the QSB vessels whose provenance could be determined by their glaze composition, 13 are associated with Newtown and four with Winchester. An additional 20 are associated with either Newtown or Winchester and 20 with either Newtown or Strasburg, although 78.26% (n=18) of these belong to Paste Group 1, suggesting that they are from Newtown (15 were not analyzed by NAA). With the preponderance of NAA and LA-ICP-MS data pointing to enslaved people from Belle Grove acquiring locally-made ceramics in Newtown, we should ask why they chose to travel the extra 3 km to do so instead of going to Strasburg.

In 1810, Strasburg was a sizable town with 75 households while Newtown was slightly larger at 89 households (US Bureau of the Census, 1810a, 1810b). Newtown had more active potteries (n=3) than Strasburg (n=1), but this alone cannot explain why enslaved people routinely traveled to Newtown. The answer, however, might lie in the number of people enslaved in these towns. Five households in Strasburg enslaved 35 people, while in Newtown 28 households (including Andrew and John Pitman's), enslaved 78 people. Market towns like Newtown and Strasburg were important places for enslaved people to gather and form bonds that transcended the boundaries of individual plantations (Heath, 2004: 28; Hill Edwards, 2021: 28). A survey of 12 merchants ledgers from the Shenandoah Valley (Greer, Forth.) suggests that enslaved people preferred going to larger towns and cities to buy commodities, likely because there were more enslaved people to socialize with. Therefore, women and men enslaved at Belle Grove may have traveled to Newtown to buy ceramics because more enslaved people were in this town than Strasburg.[1] Making arguments about where enslaved people preferred to buy ceramics only using NAA or LA-ICP-MS data might be tenuous, as it relies on our ability to accurately determine the provenance of vessels made within 20 km of one another. However, combining these two lines of evidence allows us to make a stronger argument about which market towns enslaved women and men frequented, and to propose a rationale for these choices that stands on a more robust empirical foundation.

Common Knowledge, Widespread Materials, and Itinerant Potters

Based on our results, the composition of lead glazes can be used to determine the provenance of locally-made earthenwares in the northern Shenandoah Valley, allowing us to pinpoint individual towns where vessels were made. However, the results were not as successful as we had hoped, as we could only determine the provenance of 47.5% of the QSB vessels (n=57), and most of these (n=40) could not be associated with a single town. By comparison, 52.52% of the locally-made NAA samples from QSB could be associated with a single town and we were able to make provenance determinations for 90.90% of the samples. Unfortunately, the

---

[1] More people were enslaved in Frederick County (where Newtown was located) than Shenandoah County (where Strasburg was located). This raises the possibility that more people were enslaved within a few kilometers of Newtown than Strasburg, increasing the number of enslaved women and men that gathered and socialized in Newtown. However, we do not currently have accurate data on where, exactly, within the two counties these people were enslaved, so this remains speculation for now.

historical realities of pottery production in an area as small as the northern Valley make the high number of undiagnostic glazes unavoidable.

When mixing raw materials to produce their glazes, Valley potters drew from lessons they learned during apprenticeships and/or knowledge they acquired while working as journeymen in the workshops of various master potters. Most of these master potters were trained in Hagerstown, Maryland, or by artisans who had learned their craft in Hagerstown (Comstock, 1994). As a result, most Valley potters shared a common knowledge base which the LA-ICP-MS data suggest included how to incorporate alkali oxides into their glazes, and how to produce black, brown, and tan glazes using MnO and/or Fe_2O_3. This forced us to focus our analysis on ways of making glazes that were, by definition, uncommon, like low-Al_2O_3, tin-opacified, and Sb_2S_3 and CoO-colored glazes. Because of this, many identified groups could not be used to determine provenance.

Similarly, clays were widespread throughout the Valley, allowing paste composition to easily differentiate between Newtown, Strasburg, and Winchester. Some glaze components, however, are not distributed as widely, limiting potters' choices about which ingredients to use in their glazes. As a case in point, we are not aware of any sources of lead in the northern Valley, and archival records show potters buying large quantities of lead from local merchants (Comstock, 1994: 451; Park, 2001: 12), suggesting that they relied on lead imported into the region. Looking at the Newtown potteries, the same four lead groups are present at the Andrew Pitman and John Pitman Potteries (Lead Groups A, B, C, and E), although Lead Group A accounts for 83.33% of the Andrew Pitman samples while Lead Group B accounts for 66.66% of the John Pitman samples. If our lead groups are indicative of different sources of lead imported into the Valley, it would seem that the Pitmans predominantly used different lead sources (Lead

Groups A and B), possibly because they purchased lead from different merchants. However, the presence of Lead Groups A and B at the Lack and Bacher Potteries and in QSB samples from Paste Groups 4 and 5 would indicate that potters in Strasburg and Winchester also bought from these merchants, or from other selling lead from similar sources. Therefore, it should come as no surprise that 74.07% of our samples (n=140) appear to be from two widespread lead groups, preventing us from using them to make provenance determinations.

While common knowledge and widespread materials indicate how communities of practice and trade networks shape our ability to use lead glazes to determine provenance, we also need to address the movement of individual artisans throughout the region. So far, we have focused on the master potters associated with each workshop. But they did not work in isolation, instead employing apprentices and journeymen who moved from workshop to workshop building the skillsets and financial means to become more established potters. While working for master potters, journeymen made and sold their own vessels using materials available to them at the workshop (Comstock, 1994). The vessels they made could have easily broken during production, gotten tossed into waster piles alongside vessels made by/for their employers, and sampled as part of our research without us knowing who made the vessel in question. In other words, a vessel could be made by a journeyman potter in John Pitman's workshop using a clay source and lead group predominantly associated with Newtown (Paste Group 1 and Lead Group C) but using the technique of adding CoO to the glaze that the journeyman learned while apprenticing at the Lauck Pottery in Winchester. This makes the somewhat fuzzy boundaries of the CoO-colored glazes or the presence of three samples associated with Strasburg or Winchester among the low Sb or Sn glazes, not outliers to be cursed at or explained away but potential traces (sensu Joyce, 2006; Trouillot, 1995) of journeymen potters' itinerate movements throughout the Valley.

These issues do not mean that we should not use LA-ICP-MS analysis of lead glazes to determine where ceramics were made. Instead, we argue that large sample sizes are needed when working in a small region to increase the number of uncommon samples we can identify and that studies of glaze composition should be paired with studies of paste composition to provide multiple lines of evidence to determine when glazes made by journeymen potters are blurring what might otherwise be geographically discrete clusters of glaze compositions. Part of the limitations of this study may be due to the small study area we focused on. If we had worked at a scale where discrete communities of practice or trade networks could be reasonably separated – such as a comparison between potters on opposite ends of the Valley – differences in primary glaze components, lead sources/forms/mixtures, colorants, and/or trace elements could provide provenance determinations for more samples.

Conclusion

As noted in the introduction, previous studies have not used the geochemical composition of lead glazes to determine the provenance of lead-glazed earthenwares. In this article, we demonstrated that the composition of lead glazes can be used to make provenance determinations for lead-glazed earthenwares made within a single region and that at times glaze composition can let us identify the individual towns vessels were made in. While our analysis was limited by the movement of common knowledge, widespread materials, and itinerate potters throughout our study area, we argue that this analytical technique can be successfully applied to other regions, especially when combined with paste characterization by NAA.

References

Abrajevitch A (2020) Diagenetic formation of bedded chert: Implications from a rock magnetic study of siliceous precursor sediments. *Earth and Planetary Science Letters* 533: 116039.

Beck ME and Neff H (2007) Hohokam and Patayan interaction in southwestern Arizona: evidence from ceramic compositional analyses. *Journal of Archaeological Science* 34(2): 289–300.

Brill RH and Rising BA (1999) *Chemical Analyses of Early Glasses, Vol. 2.* Corning, New York: Corning Museum of Glass.

Comstock HE (1994) *The Pottery of the Shenandoah Valley Region*. Winston-Salem, North Carolina: Museum of Early Southern Decorative Arts.

Druc I (2013) What is Local? Looking at Ceramic Production in the Peruvian Highlands and Beyond. *Journal of Anthropological Research* 69(4): 485–513.

Druc IC, Inokuchi K and Dussubieux L (2017) LA-ICP-MS and petrography to assess ceramic interaction networks and production patterns in Kuntur Wasi, Peru. *Journal of Archaeological Science: Reports* 12: 151–160.

Eckert SL and James WD (2011) Investigating the production and distribution of plain ware pottery in the Samoan archipelago with laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Journal of Archaeological Science* 38(9): 2155–2170.

Glascock MD (1992) Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics. In: Neff H (ed.) *Chemical Characterization of Ceramic Pastes in Archaeology*. Madison, Wisconsin: Prehistory Press, pp. 11–26.

Glascock MD and Neff H (2003) Neutron activation analysis and provenance research in archaeology. *Measurement Science and Technology* 14(9): 1516–1526.

Gratuze B, Blet-Lemarquand M and Barrandon J-N (2001) Mass spectrometry with laser sampling: A new tool to characterize archaeological materials. *Journal of Radioanalytical and Nuclear Chemistry* 247(3): 645–656.

Greer MC (Forth.) *Assembling Enslaved Lives: Labor, Consumption, and Landscapes in the Northern Shenandoah Valley*. Ph.D. Dissertation. Syracuse University, Syracuse, New York.

Greer MC and MacDonald BL (2020) Which town did it come from?: Sourcing locally-made ceramics in the Mid-Atlantic. *North American Archaeologist* 41(4): 135–167.

Greer MC, MacDonald BL and Stalla D (2021) Cobalt, lead, and borax: Preliminary LA-ICP-MS and SEM-EDS analysis of Late-18th- to Mid-19th-century British refined earthenware glazes. *Journal of Archaeological Science: Reports* 37(June): 1–11.

Heath BJ (2004) Engendering Choice: Slavery and Consumerism in Central Virginia. In: Galle JE and Young AL (eds) *Engendering African American Archaeology: A Southern Perspective*. Knoxville: University of Tennessee Press, pp. 19–38.

Hill Edwards J (2021) *Unfree Markets: The Slaves' Economy and the Rise of Capitalism in South Carolina*. New York: Columbia University Press.

Joyce RA (2006) The Monumental and the Trace: Archaeological Conservation and the Materiality of the Past. In: Agnew N and Bridgland J (eds) *Of the Past, for the Future: Integrating Archaeology and Conservation*. Los Angeles, California: Getty Conservation Institute, pp. 13–18.

Klesner C, Renson V, Akymbek Y, et al. (2021) Investigation of provenances of Early Islamic lead glazes from northern Central Asia using elemental and lead isotope analyses. *Archaeological and Anthropological Sciences* 13(11): 203.

Klesner CE, MacDonald BL, Dussubieux L, et al. (2019) Local production and long-distance trade of Islamic glazed ceramics in Central Asia: A compositional analyses of ceramics from Southern Kazakhstan by NAA and LA-ICP-MS. *Journal of Archaeological Science: Reports* 26(August): 1–22.

Minc LD, Sherman RJ, Elson C, et al. (2016) Ceramic provenance and the regional organization of pottery production during the later Formative periods in the Valley of Oaxaca, Mexico: Results of trace-element and mineralogical analyses. *Journal of Archaeological Science: Reports* 8: 28–46.

Molera J, Pradell T, Salvadó N, et al. (2001) Interactions between Clay Bodies and Lead Glazes. *Journal of the American Ceramic Society* 84(5): 1120–1128.

Mommsen H (2004) Short Note: Provenancing of Pottery— The Need for an Integrated Approach? *Archaeometry* 46(2): 267–271.

Monette Y, Richer-LaFlèche M, Moussette M, et al. (2007) Compositional analysis of local redwares: characterizing the pottery productions of 16 workshops located in Southern Québec dating from late 17th to late 19th-century. *Journal of Archaeological Science* 34(1): 123–140.

Neff H (2012) Comment: Chemical and Mineralogical Approaches to Ceramic Provenance Determination. *Archaeometry* 54(2): 244–249.

Niculescu T (2017) Tides of Celadon: Glaze Color Chronology from the Edgefield Pottery District, South Carolina. *Journal of African Diaspora Archaeology and Heritage* 6(3): 196–224.

Park S (2001) *The Life of a Potter, Andrew Pitman*. Research Report Series. Richmond: Virginia Department of Historic Resources.

Pearce NJG, Perkins WT, Westgate JA, et al. (1997) A Compilation of New and Published Major and Trace Element Data for NIST SRM 610 and NIST SRM 612 Glass Reference Materials. *Geostandards Newsletter* 21(1): 115–144.

Pezzarossi G (2015) A Spectral Haunting of Society: Lounge Duree Archaeologies of Capitalism and Antimarkets in Colonial Guatemala. In: Leone MP and Knauf JE (eds) *Historical Archaeologies of Capitalism*. 2nd Edition. New York: Springer International Publishing, pp. 345–374.

Schurr MR, Donohue PH, Simonetti A, et al. (2018) Multi-element and lead isotope characterization of early nineteenth century pottery sherds from Native American and Euro-American sites. *Journal of Archaeological Science: Reports* 20: 390–399.

Stahl AB, Cruz MD, Neff H, et al. (2008) Ceramic production, consumption and exchange in the Banda area, Ghana: Insights from compositional analyses. *Journal of Anthropological Archaeology* 27(3): 363–381.

Stark BL, Speakman RJ and Glascock MD (2007) Inter-Regional and Intra-Regional Scale Compositional Variability in Pottery from South-Central Veracruz, Mexico. *Latin American Antiquity* 18(1). Cambridge University Press: 59–84.

Stoner WD (2016) The analytical nexus of ceramic paste composition studies: A comparison of NAA, LA-ICP-MS, and petrography in the prehispanic Basin of Mexico. *Journal of Archaeological Science* 76: 31–47.

Tite MS, Shortland AJ, Schibille N, et al. (2016) New Data on the Soda Flux Used in the Production of Iznik Glazes and Byzantine Glasses. *Archaeometry* 58(1): 57–67.

Trouillot M-R (1995) *Silencing the Past: Power and the Production of History*. Boston, Massachusetts: Beacon Press.

US Bureau of the Census (1810a) *United States Federal Census, Frederick County, Virginia*. Washington D.C.: National Archives and Records Administration.

US Bureau of the Census (1810b) *United States Federal Census, Shenandoah County, Virginia*. Washington D.C.: National Archives and Records Administration.

VanValkenburgh P, Kelloway SJ, Dussubieux L, et al. (2015) The production and circulation of indigenous lead-glazed ceramics in northern Peru during Spanish colonial times. *Journal of Archaeological Science* 61: 172–185.

Figures

Figure 1. Location of Belle Grove Plantation, the city of Winchester, and the towns of Newtown (now called Stephens City), Strasburg, and Woodstock. Map by Erica Moses.

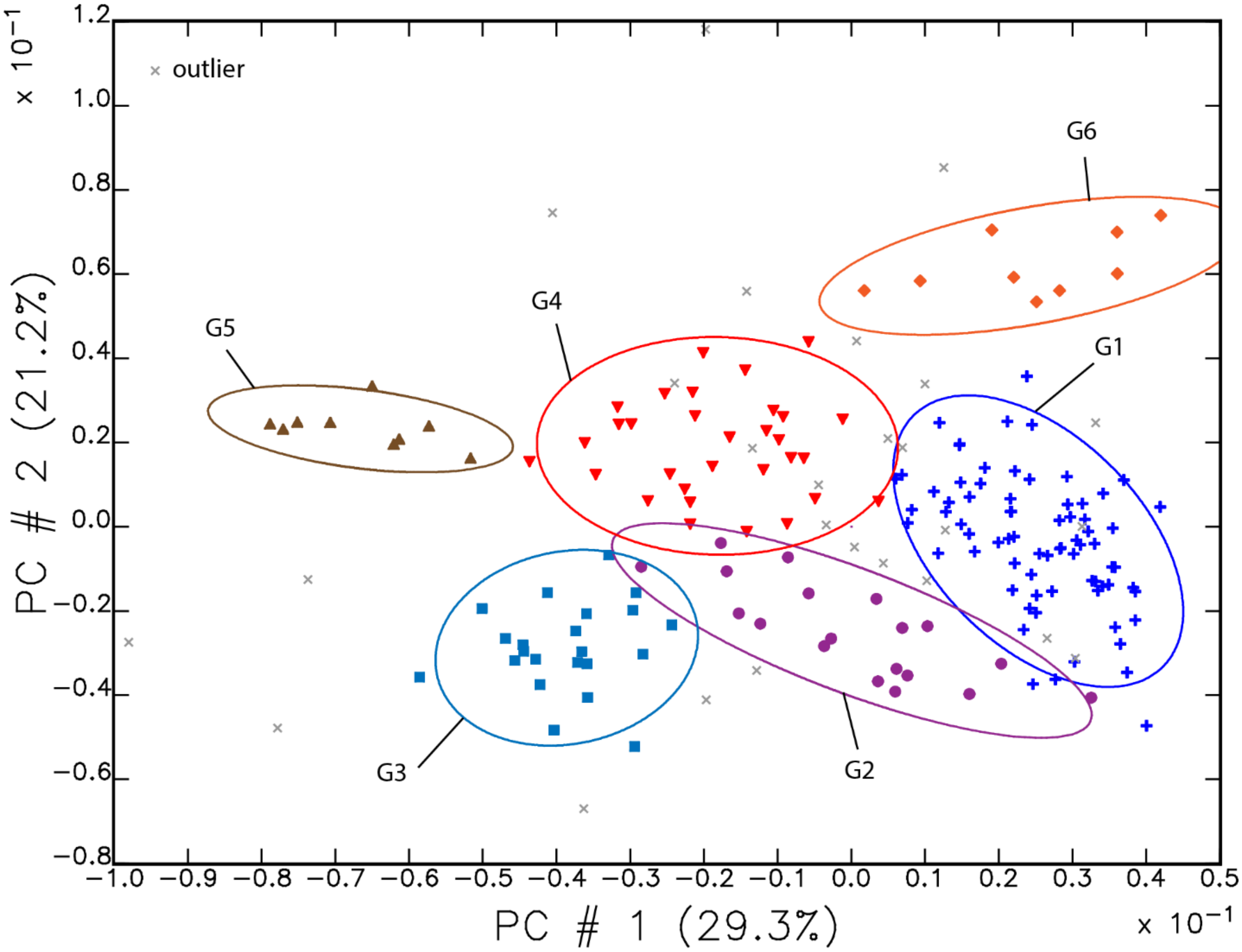

Figure 2. Scatterplot of PC1 (29.3%) versus PC2 (21.2%), showing the distribution of NAA Paste Groups 1–6. Ellipses are drawn at 90% confidence. Originally published in (Greer and MacDonald, 2020: 151).

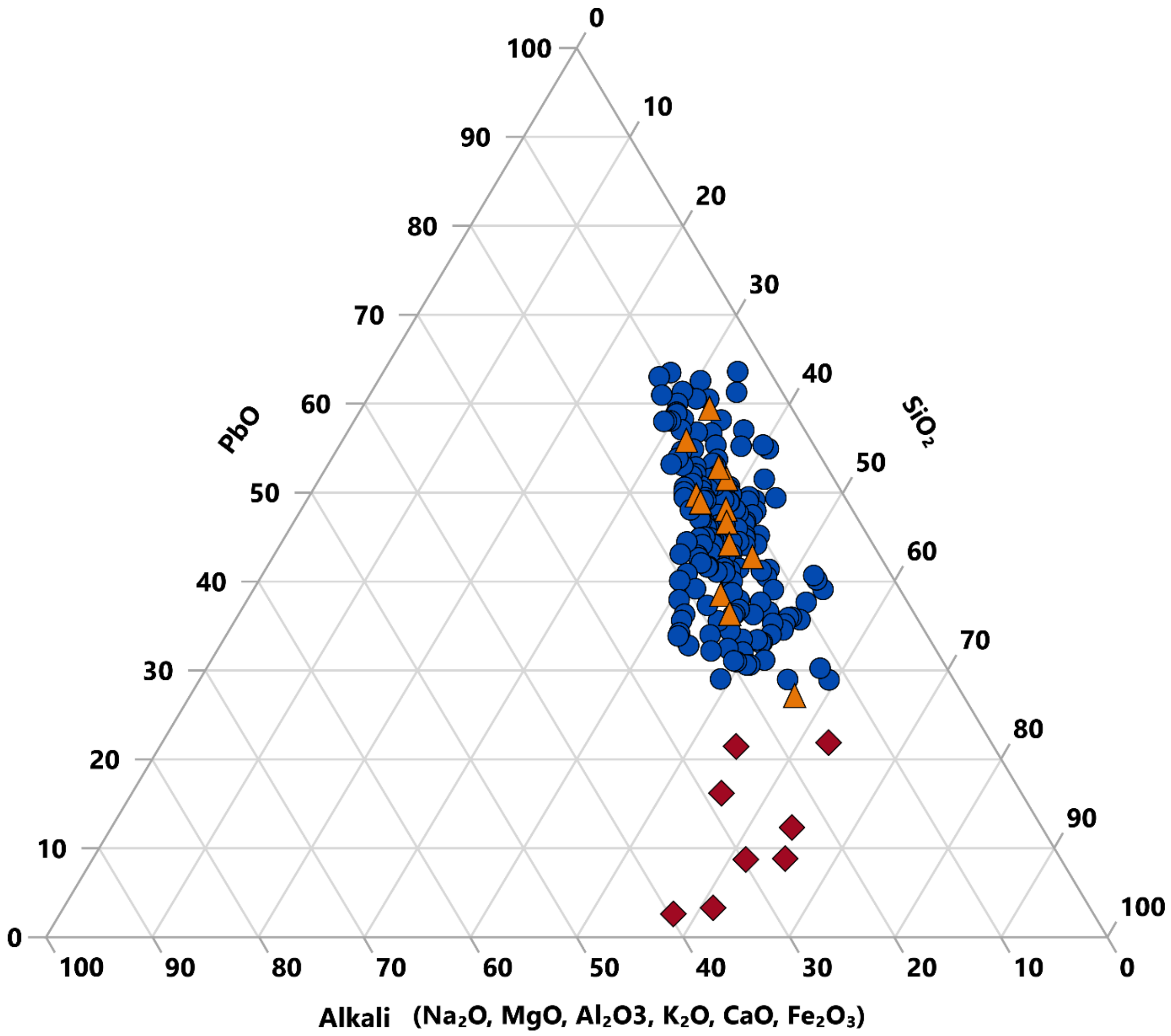

Figure 3. Ternary plot comparing the amount of PbO, SiO_2, and alkali oxides among high lead (blue circles), lead-tin (orange triangles), and low lead (red diamond) samples. Low lead samples are SYU009, SYU022, SYU069, SYU117, SYU133, SYU173, SYU184, and SYU223.

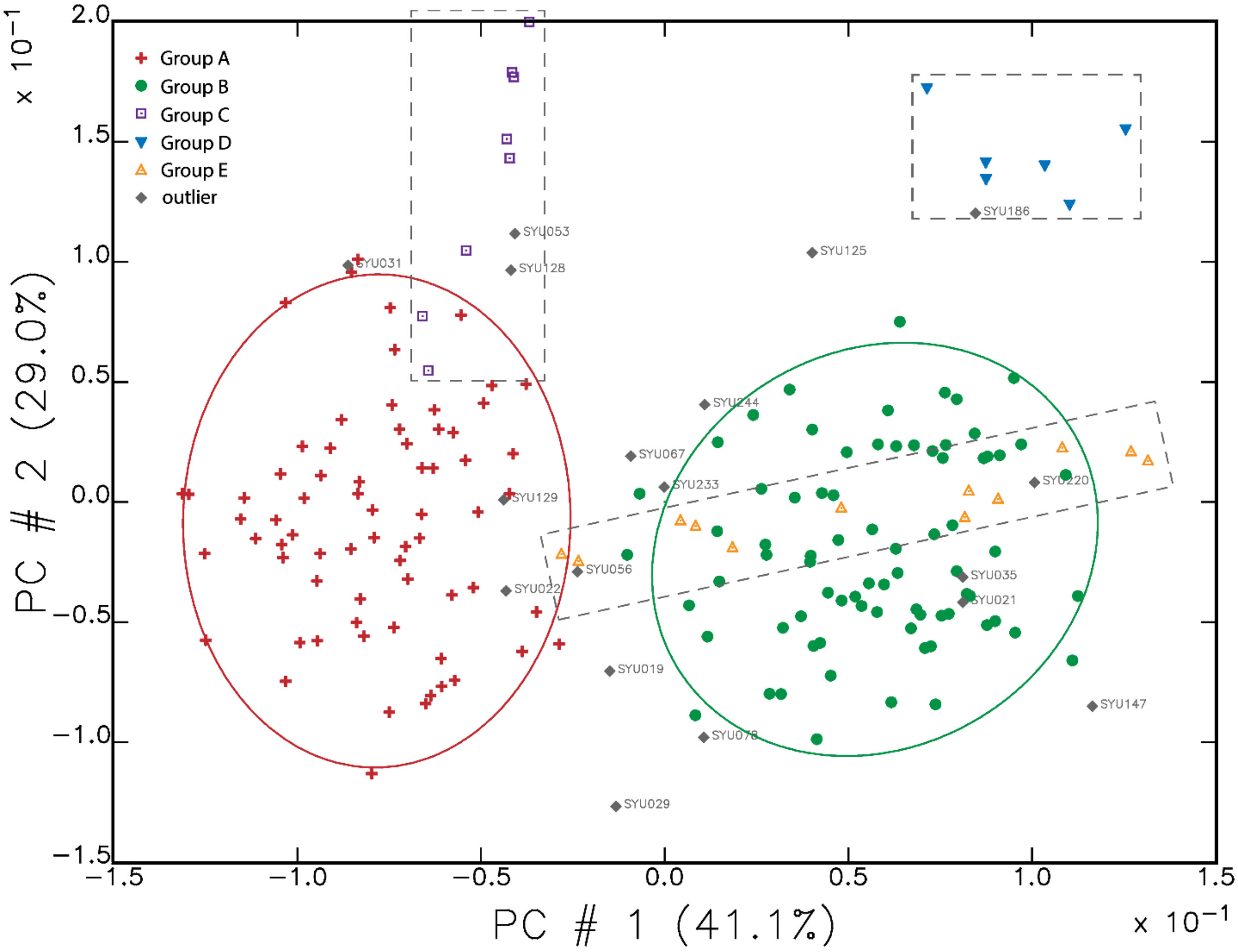

Figure 4. Scatterplot of PC1 (41.1%) and PC2 (28.9%) showing the distribution of possible lead sources/forms/mixtures in the dataset. Outlier samples are individually marked. Ellipses are drawn at 90% confidence and show the groups associated with each workshop. Lead Groups C-E indicated by dashed boxes.

Table 1. Samples analyzed by NAA and LA-ICP-MS.

Site	Site Number	Location	Date Range	NAA Samples	LA-ICP-MS Samples
Quarter Site B (QSB)	44FK520	Belle Grove Plantation, VA	c. 1800 – 1850s	100	125
Peter Lauck Pottery	44FK552	Winchester, VA	1780 to 1839	20	20
Anthony Bacher Pottery	44FK550	Winchester, VA	1862 to 1889	13	10
Andrew Pitman Pottery	44FK528	Stephens City, VA	c. 1782 to 1838	16	16
John Pitman Pottery	44FK547	Stephens City, VA	1794 to 1820s	20	18
Strasburg Steam Pottery	44SH482	Strasburg, VA	1890 to 1897	20	0

Table 2. Paste groups organized by site. Table from (Greer and MacDonald, 2020: 152)

Site	Location	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Outlier
Peter Lauck Pottery	Winchester	2	3		4		8	3
Anthony Bacher Pottery	Winchester	4	5	1				3
Andrew Pitman Pottery	Stephens City	13	1	1				1
John Pitman Pottery	Stephens City	9	4	2				5
Strasburg Steam Pottery	Strasburg	1			13	2		4
Quarter Site B	Belle Grove	44	6	18	14	7	1	10
Total		***73***	***19***	***22***	***31***	***9***	***9***	***26***

Table 3. Oxides associated with primary glaze components. All averages and Standard Deviations (STD) are presented in ppm unless indicated in weight percent.

	Al_2O_3 (wt%)		**SiO_2 (wt%)**		**K_2O (wt%)**		**CaO (wt%)**		**SnO_2**		**PbO (wt%)**	
Glaze Group	***Mean***	***STD***	***Mean***	***STD***	***Mean***	***STD***	***Mean***	***STD***	***Mean***	***STD***	***Mean***	***STD***
Pb-Si (n=14)	4.901	1.397	38.35	7.201	.03170	0.1848	0.3480	0.1861	208.8	301.4	50.74	8.642
Pb-Si-Al (n=102)	11.38	2.601	37.32	5.134	0.4351	0.1974	0.2765	0.1859	411.4	648.9	45.87	6.973
Pb-Sn-Al (n=10)	11.19	2.361	38.47	6.114	0.5266	0.2421	0.3993	0.2157	22327	8983	42.37	8.404
Pb-Sn (n=1)	5.592	n/a	30.46	n/a	0.4176	n/a	0.8139	n/a	42388	n/a	55.10	0.000
Pb-Sn-Al-Alkali (n=2)	7.897	1.501	39.16	2.705	1.905	1.405	0.7130	0.4825	27916	10473	40.62	2.597
Pb-Si-Al-K (n=48)	12.94	3.331	43.85	5.804	1.691	1.096	0.3728	0.2140	284.7	501.3	35.26	7.407
Pb-Si-Al-Ca (n=5)	11.72	3.099	44.72	7.608	0.3605	0.1069	1.459	0.1447	345.2	545.8	37.44	6.061
Pb-Si-Al-Mixed Alkali (n=7)	16.70	6.257	54.29	5.831	4.812	1.890	0.8265	0.5797	349.9	345.3	12.32	11.05
Pb-Si-K (n=8)	5.889	n/a	49.64	n/a	0.5419	n/a	0.1326	n/a	37.5	n/a	38.84	0.0

Table 4. Lead groups by site. The MD-GMP calculation show that over 80% of the samples in each group have strong membership probabilities (>20%) (see Online Resource 7).

Site	Location	Lead Group A	Lead Group B	Lead Group C	Lead Group D	Lead Group E	Unassigned
Lauck	Winchester	8	10			1	1
Bacher	Winchester		3			6	1
A. Pitman	Newtown	10	1	1		1	3
J. Pitman	Newtown	1	8	1		2	6
QSB	Belle Grove	50	54	6	6	2	7
Total		69	76	8	6	12	18

Table 5. Mean concentrations of colorants. All averages are presented in ppm unless indicated in weight percent.

Colorant Group	MnO (wt%)	Fe_2O_3 (wt%)	CoO	Sb_2O_5	SO_3	CuO	MgO	TiO_2	Cr_2O_3	ZnO	As_2O_3
High Mn (n=29)	1.496	2.096	14.34	576.0	749.2	245.0	4817	5899	79.87	157.6	41.14
Low Mn (n=13)	0.3060	2.373	10.17	460.5	652.5	446.3	3711	5057	94.49	169.4	54.33
Fe (n=23)	0.0180	3.176	7.60	599.1	669.4	245.3	4064	6167	55.36	241.2	79.10
Fe & High Mn (n=31)	1.376	3.372	15.91	315.1	672.1	257.6	5397	6482	86.76	199.5	84.79
Fe & Low Mn (n=14)	0.3090	4.247	12.18	203.1	910.4	330.2	5269	6248	88.47	245.8	23.37
Co & Mn (n=10)	2.173	2.142	115.9	263.1	521.2	192.1	3327	2783	39.03	513.1	59.50
Co, Mn, & Fe (n=23	1.462	6.369	73.07	175.2	609.7	920.6	4838	5685	101.2	500.0	19.46
Fe & Stibnite (n=1)	0.0584	5.485	11.81	14096.2	20635	76.62	5561	7700	85.26	452.2	15.56
Clear (n=23)	0.0219	2.646	8.43	490.6	774.3	235.3	4418	6410	57.14	177.4	22.42

Table 6. Mean concentrations of selected trace elements in trace element groups. All averages are presented in ppm.

Trace Group	P		Ti		Cu		Zn		Sb		Ba	
	Mean	*STD*	*Mean*	*STD*	*Mean*	*STD*	*Mean*	*STD*	*Mean*	*STD*	*Mean*	*STD*
High Ti (n=2)	177.1	36.36	7430	2697	72.84	1.715	53.01	4.990	292.98	172.1	277.4	196.6
High Ti & High Ba (n=1)	234.2	n/a	7726	n/a	31.12	n/a	144.2	n/a	5.283	n/a	1771	n/a
High Ba & High P (n=1)	3564	n/a	3094	n/a	11.04	n/a	54.41	n/a	277.0	n/a	1007	n/a
High Zn (n=4)	170.9	266.2	2768	2902	170.2	61.63	889.2	1008	240.6	218.9	380.6	127.6
High Ba (n=14)	454.6	442.9	3650	1581	107.2	154.2	168.2	242.3	210.3	177.6	1853	675.5
High Cu (n=5)	188.1	102.8	3596	2041	1576	584.1	219.9	182.5	143.5	72.70	328.0	244.2
High Sb (n=29)	626.4	253.0	3551	1313	18.96	133.6	81.39	60.07	767.3	308.3	184.3	142.4
High Sb & High Ba (n=5)	218.4	83.12	3786	1065	76.80	158.4	74.20	161.6	1359	478.9	1021	492.7
High Sb & High Cu (n=3)	291.4	207.9	3408	594.8	1117	189.8	134.8	66.31	904.4	2514	148.9	12.64
High Sb & High Sn (n=1)	148.2	n/a	2910	n/a	242.5	n/a	41.15	n/a	2820	n/a	212.4	n/a
High Sn (n=24)	236.4	189.2	4016	1021	281.9	284.9	434.9	182.0	300.2	142.7	218.2	151.4
High Sn & High Ba (n=6)	268.3	182.1	4801	1213	154.1	151.9	155.0	75.34	227.7	99.09	1779	462.2

Table 7. Proposed provenance of groups identified in glaze characterization. Samples are sorted into glaze types, lead source/form/mixture, colorant, and trace element group, and summarized by potter location (left column) and paste group (right column). As indicated by their headings, the right columns only contain samples from QSB. The paste and glaze groups are described above. QSB outliers are NAA outliers and LA-ICP-MS only samples were not analyzed by NAA. Provenance determinations were only made in cases where the NAA and LA-ICP-MS data aligned with one another.

Glaze Type	**Lauck**	**Bacher**	**A Pit.**	**J Pit.**	**QSB G1**	**QSB G2**	**QSB G3**	**QSB G4**	**QSB G5**	**QSB G6**	**QSB Outlier**	**QSB LA-ICP-MS Only**	**Provenance**
Pb-Si-Al	6	2	7	1	27	3	1	7	1	1	7	39	Widespread
Pb-Si-Al-K	9		8	14	9	1		1				5	Widespread
Pb-Si-Al-Ca							1	2				2	Widespread
Pb-Mixed Alkali	2		1	2			1	1					Widespread
Pb-Sn				1	4							6	Newtown
Pb-Sn-Mixed Alkali					2								Newtown
Pb-Si	2	8				1						3	Winchester
Pb-Si-K	1												Winchester
Lead Source/Mixture	**Lauck**	**Bacher**	**A Pit.**	**J Pit.**	**QSB G1**	**QSB G2**	**QSB G3**	**QSB G4**	**QSB G5**	**QSB G6**	**QSB Outlier**	**QSB LA-ICP-MS Only**	**Provenance**
Lead Group A	8		10	1	10	2	1	6	1		3	27	Widespread
Lead Group B	10	3	1	8	22	2	1	5		1	3	20	Widespread
Lead Group C	1			1	3							3	Newtown
Lead Group D					3							3	Newtown
Lead Group E	1	5	1	2		1	1						Newtown / Winchester
Colorant	**Lauck**	**Bacher**	**A Pit.**	**J Pit.**	**QSB G1**	**QSB G2**	**QSB G3**	**QSB G4**	**QSB G5**	**QSB G6**	**QSB Outlier**	**QSB LA-ICP-MS Only**	**Provenance**
High Mn	1			1	12	2		1			1	11	Widespread
Low Mn			1	1	2			2		1		6	Widespread
Fe	3		3	2	4		1	1				9	Widespread
High Mn & Fe	6		1	4	11	1		2				6	Widespread
Low Mn & Fe	1	1		6	1		1				1	3	Widespread
Mn & Co	3	7											Winchester
Mn, Co, & Fe		2		1									Newtown or Winchester
Fe & Stibnite			1										Newtown
Underglaze	6		12		11	2	1	5	1		4	21	Widespread

Trace Group	Lauck	Bacher	A Pit.	J Pit.	QSB G1	QSB G2	QSB G3	QSB G4	QSB G5	QSB G6	QSB Outlier	QSB LA-ICP-MS Only	Provenance
High Ba	3	1	1	1	3	1		1				3	Widespread
High Cu	1		1	1						1		1	Widespread
High Ba & High P							1						Ind.
High Ti												2	Ind.
High Ti & High Ba	1												Ind.
High Zn	1	1			1							1	Ind.
High Sb			2	3	9			1			3	11	Newtown or Strasburg
High Sb & High Ba					1	1		1				2	Newtown or Strasburg
High Sb & High Cu			1		1							1	Newtown or Strasburg
High Sn & High Sb			1										Widespread
High Sn	1		3	1	11	1					1	6	Newtown or Winchester
High Sn & High Ba				2	1							3	Newtown or Winchester