Rapid Qualitative Compositional Analysis of Ceramic Paints

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Abstract

In previous research Van Keuren and colleagues used time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS) to infer distinct paint composition groups in glaze-painted White Mountain Red Ware (WMRW) from late pre-Hispanic villages in eastern Arizona. This analytical approach cannot be reasonably applied (in a non-destructive way) to the study of paint composition on whole vessel collections. To expand the earlier study and examine the link between compositional group and whole vessel decoration, we used portable x-ray fluorescence (pXRF) to qualitatively examine the composition of glaze-painted designs on a large corpus of WMRW whole vessels curated at the National Museum of Natural History. This paper summarizes the previous ICP research, explains the methodology behind the qualitative XRF analysis, presents the results of the whole vessel analysis, and proposes additional applications for the qualitative analysis of ceramic paints using pXRF.

Key Words

Portable X-ray fluorescence (pXRF); time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS); ceramic paints; White Mountain Red Ware; Ancestral Pueblo

1. Introduction

Archaeologists working in the American Southwest have made great strides in the compositional analysis of ceramic paints (Cordell and Habicht-Mauche 2012, Huntley, et al. 2007, Huntley 2006, Fenn et al. 2006, Speakman and Neff 2002, Van Keuren et al. 2013), and much of this work utilizes laser ablation-inductively coupled plasma-mass spectrometry (LA-

ICP-MS) to precisely and accurately measure the chemical composition of paints via tight control of the location and depth of sample locations on the painted surfaces of ceramics (Speakman and Neff 2005, Duwe and Neff 2007). The resulting data have been useful for inferring pigmentation techniques, potter learning networks, and other dimensions of ceramic production in many areas of the world (e.g., Vaughn et al. 2005, Backes et al. 2012, Cecil and Neff 2006).

Despite its utility for inferring ancient paint recipes, LA-ICP-MS has been largely limited to the analysis of sherd samples. Assays require analytical equipment that is non-portable and requires the removal of small fragments for efficient analysis of multiple specimens. As such, it cannot be readily applied to whole vessels curated in museums and other research facilities that generally do not permit destructive analysis of whole vessels. This presents an obstacle with respect to inferring the fuller socio-economic context of production since whole vessels provide the clearest picture of decorative variation and overall vessel use. Thus, LA-ICP-MS analysis of sherd samples has limited applicability when archaeologists are interested in linking technological diversity of paints with the stylistic behavior of potters in the past.

In this paper we illustrate how portable X-ray fluorescence (pXRF) can extend sherd-based LA-ICP-MS to the characterization of paints on whole vessels. In an earlier project, Van Keuren and colleagues used LA-ICP-MS to identify the basic paint “recipes” of glaze-painted red ware sherds from fourteenth-century Ancestral Pueblo sites (Van Keuren et al. 2013). In this paper, we use these data as a baseline for examining a large corpus of painted whole vessels using pXRF. Our results illustrate both the use of pXRF for studying the paints in museum whole vessel collections and the efficacy of pairing quantitative and qualitative measures of elemental

composition in ceramic paints. The study also further clarifies the social contexts of ancient Pueblo pottery during an important period of cultural change.

2. Research Background

2a. Archaeological context

Our study concerns the production of glaze-painted White Mountain Red Ware (hereafter “WMRW”) in east-central Arizona during the early Pueblo IV period (AD 1275/1300-1400). Pottery types in this ware sequence were red-slipped and decorated with black and white designs (Fig. 1). Potters experimented with pigments and firing regimes to yield a lustrous (or glazed) effect with black paints by using key minerals as fluxing agents and colorants. Lead was the primary fluxing agent but copper and manganese were also added as both colorants and possible fluxing agents. Beyond these technological innovations, potters also began to apply new types of decorative subject-matter on painted bowls (Crown 1994). Potters at a handful of large Silver Creek villages (Fig. 2) produced a new representational-style pottery type (Fourmile Polychrome or FP) by the 1320s (Carlson 1970). The type is distinguished from earlier Pinedale-style vessels by its presentation of masked figures, macaws, and other iconographic forms on bowl interiors. Regional scholars attribute this ceramic transition along with other archaeological evidence to the emergence of new religious traditions and practices (Crown 1994, Adams 1991, Van Keuren and Glowacki 2011). The vessels may have been produced by specialists working in a handful of Silver Creek villages (Van Keuren et al. 2013), and a recent use-wear analysis demonstrates that they were used less intensively than earlier WMRW types (Van Keuren and Cameron 2015).

In an earlier study, Van Keuren (2006) examined a large corpus of WMRW whole vessels in museums and recognized the presence of “hybrid” Fourmile-style WMRW bowls (Fig.

1b). These vessels mimic some of the fundamental decorative features of Fourmile Polychrome but lack the iconographic-style layouts of bowl interiors. Painted designs also rarely exhibit the surface luster that is commonly found on glaze-painted WMRW, suggesting technological differences in the manufacturing process. Both stylistic and technological differences thus suggest that “classic” Fourmile Polychrome (Fig. 1a) was produced by individuals with specialized skills, knowledge, or access to production resources that was not available to potters who produced hybrid versions. The chemical composition of paints on both categories of Fourmile-style WMRW is directly germane to this issue.

2b. Previous compositional research

Employing protocols established by Duwe and Neff (2007), Van Keuren and colleagues (2013) used TOF-LA-ICP-MS (time-of-flight laser ablation-inductively coupled plasma-mass spectrometry) to examine the composition of 463 sherds representing Pinedale-and Fourmile-style polychromes; the sample included sherds with two decorative features of hybrid WMRW that can be observed on rim sherds. These were recovered primarily from three possible producer villages in the Silver Creek area (Fourmile, Shumway, and Pinedale ruins). Parts per million assays of 60 elements were analyzed with principal components analysis (PCA) to define five compositional groups (Van Keuren et al. 2013:681-683). These groups were primarily defined by relative amounts of lead (Pb), copper (Cu), manganese (Mn), and antimony (Sb). The compositional groups correspond with the “recipes” used by pottery to render different hues in black paints. Based on the lack of luster, it was anticipated that Fourmile-style hybrids would have lower lead content. However, it was found that the paint composition of hybrids fell into all five of the composition groups with the majority in group 2a (high lead and copper, low manganese). The study showed that potters producing the hybrid bowls introduced lead but

failed to render the luster of glaze-painted designs observed on Fourmile Polychrome. The potters who produced hybrids apparently had access to key mineral resources, but were not rendering glaze-painted designs. Van Keuren and colleagues (2013) speculated that these potters were not able to achieve the specialized firing regime required to produce glaze-painted designs, perhaps because they lacked access to needed fuels or the required knowledge of WMRW firing techniques. At least part of this variance may also be due to the heterogeneous nature of these minerals in their raw form; ancient potters likely processed ores that were aggregates of copper, manganese, and galena (Blinman et al. 2012).

Although the type-sequence of WMRW was defined many decades ago (Carlson 1970, Colton and Hargrave 1937), large-village ceramic assemblages are notoriously complex in the Southwest (see Smith 1962). The nuances of decoration that identify WMRW hybrids can be discerned on rim sherds but are sometimes impossible to recognize on body sherds making classification of sherds problematic. WMRW hybrids are best identified through the careful observation of whole vessel design layouts as well as specific features on bowl exteriors; once fragmented, a vessel can easily yield sherds that might be assigned to different ceramic types. Whole vessel examples, for instance, combine both Fourmile-style designs with earlier elements. Fortunately, large numbers of fourteenth-century WMRW whole vessels are available for stylistic research since the key archaeological sites were targeted by early researchers. Jesse Walter Fewkes excavated a large whole vessel assemblage from Fourmile Ruin in 1896, which is now curated in the National Museum of Natural History (NMNH). In earlier research, this collection served as a foundation for defining hybrid types among late WMRW assemblages in east-central Arizona (Van Keuren 2001).

3. Methodology

LA-ICP-MS provides accurate quantifiable paint composition data due to the ability to control the precise location and penetration depth of the laser. Typical analysis requires the removal of small (~4mm x ~4mm) pieces of the artifacts to fit into the standard ablation chamber. While there have been some efforts to develop laser ablation chambers capable of sealing to the external surfaces of whole ceramic vessels and thus limiting the sample destruction to nearly invisible ablation marks (Laure Dussubieux, personal communication 2014), the entire system is not portable and the ability to standardize and normalize the data from multiple vessels is difficult. For the non-destructive on-site analysis of museum collections of complete vessels we have developed a method utilizing qualitative pXRF spectra analysis.

The pXRF is a small handheld instrument that can be taken directly to ceramic collections for analysis. The small size and completely non-destructive nature of the pXRF allow for rapid analyses of interior and exterior paints on whole vessels, and is particularly useful when examining the metallic components of surface paints. While the depth and location of analysis in LA-ICP-MS can be controlled entirely by the regulation of the laser, the location and depth of the pXRF analysis is a function of beam placement and size as well as energy of the resulting fluorescent X-rays. Beam sizes on pXRF instruments are typically about 5mm in diameter (a 2mm x 3mm oval in the case of the Bruker Tracer used in this study), and can be restricted to individual design elements in most cases. The major limitation to quantitative analysis is the depth of X-ray penetration. The depth of penetration and the ability of resulting fluorescent X-rays to escape the matrix are largely a function of energy. Low energy X-rays that are most likely to fluoresce elements at the low end of the 0-40 keV scale are not able to penetrate deep into the sample. In addition, any generated low-energy fluorescence is unable to escape the matrix from greater depths. Thus, the greater an element's peak energy, the greater the depth of matrix

included in the spectra. This is particularly problematic for surface paints as low-energy elements might derive from only the surface paint, while higher energy elements may include x-rays from the underlying slip or paste. The situation is further complicated by the highly variable paint thickness within and between vessels. The qualitative method we have developed to adjust for the quantitative limitations of surface XRF analysis is outlined below.

All pXRF measurements were taken with a Bruker Tracer III-V handheld spectrometer operated at 40KeV and 15 μ A using a Cu (6 mil thick), Ti (12 mil thick), and Al (2 mil thick) secondary target (filter) to reduce background throughout the lower-energy portion of the spectrum. In all measurements, the instrument window was within 5mm of the vessel surface. Distances were minimal for measurements of the convex exteriors and higher in the concave interiors. Comparison of each interior and exterior measurement from each vessel showed no changes (except for those rare cases of clearly different paint recipes) indicating minimal, if any, impact as a result of variations in sample geometry. To control for variable paint thickness and slip and paste compositions, a background spectra was collected from the slip adjacent to the paint. The overlay of the adjacent slip and paint spectra reveal the additional components of the paint. XRF is particularly sensitive to metals, and thus only 10 second analyses were required to visually identify the primary metallic components (Mn, Cu, and Pb) that are pertinent to the recipes of ancient glaze-painted ceramics. At minimum, two unique paint features were analyzed on both the interior and exterior of the bowls. If additional features of interest were noted, such as color or luster variations, more analyses were conducted. Changes in the observed peaks for manganese, copper, and lead were recorded as no change (1), small peak (2) or large peak (3). The peaks seen in the paint spectra that are not present in the adjacent slip are proportional to the relative concentration of that element as well as the thickness of that area of paint.

4. Results

4a. Pilot Study

To explore the feasibility of applying the pXRF to identifying compositional groups in whole vessel collections, a blind trial sample of WMRW sherds (n=25) was selected (by VanKeuren) from the larger ICP-MS sample published by Van Keuren and colleagues (2013). Using pXRF, Ferguson was able to predict most of the four primary TOF-LA-ICP-MS compositional groups defined by relative amounts of lead (Pb) and manganese (Mn) (Table 1). The technique was less successful at identifying those sherds with low copper (Cu) previously assigned to Group 1, which was not surprising given the loose membership of samples in this group from the earlier LA-ICP-MS analysis. Table 1 illustrates the similar results between the pXRF pilot study and the LA-ICP-MS analysis. The minor differences are likely the result of a difference between the qualitative and nominal data from the pXRF methodology compared to the quantitative and continuous nature of the LA-ICP-MS analysis. Figures 4 and 5 illustrate the association between the compositional groups identified in the LA-ICP-MS analysis and the qualitative groups identified by pXRF.

4b. Whole Vessel Study

Our primary goal of this research was to build on the pilot study and assess compositional variability in a large corpus of whole WMRW vessels. The ceramic types were previously identified by Van Keuren in a stylistic analysis that relied on the structural organization of design layouts on both bowl interiors and exteriors. Van Keuren and others (2013) relied on these stylistic definitions to categorize sherds for the LA-ICP-MS study, but the study of paint composition had not yet been conducted on a whole vessel sample where distinctions between “classic” and “hybrid” WMRW are recognizable based on decorative layout and execution. In

addition to Fourmile Polychrome and the Fourmile-style hybrids, we included Pinedale-style vessels that were produced prior to the 1320s. Our results are summarized in Table 2 and largely correlate with the patterns identified in the earlier LA-ICP-MS study. Based on the percentages listed in Table 3, the compositional grouping of the pXRF data versus earlier LA-ICP-MS analyses compares favorably. The exception is the larger percentage of Pinedale-style types assigned to groups 3b in the earlier analysis, which we suspect this is due to sampling differences between the two studies, or perhaps variance in the ceramic type designations of sherds in the previous analysis. Two additional pXRF groups were also defined in the broader whole vessel analysis. These groups are represented by five vessels that are defined by low Cu and high Pb and variable amounts of Mn (Table 2; Fig. 4). Three of these samples may correspond with LA-ICP-MS Group 1, which included a diverse population of sherds with lower amounts of Cu and variable Pb and Mn.

The majority of Pinedale-style whole vessels in the NMNH collection fell within two low-Mn pXRF groups D and E that correspond to LA-ICP-MS Groups 2a/2b. Many of the Fourmile Polychrome bowls were squarely assigned to high-Mn pXRF groups B and C (LA-ICP-MS Groups 3a/3b). The latter vary in relative amounts of Pb, but the temporal trend in increasing introduction of Mn is clear. Van Keuren and colleagues' (2013) suggest that this may be related to conscious efforts on the part of potters to subtly alter the hue of black paints, in some cases, rendering purplish sub-glazes. The Fourmile-style hybrids were produced concurrently with Fourmile Polychrome, but exhibit primarily low-Mn recipes (32 percent versus 71 percent of FP). One of the primary goals of the study was to assess the relationship between "classic" and "hybrid" Fourmile Polychrome. The vessels that we identified as Fourmile-style hybrids in the NMNH collection were primarily decorated with a low-Mn, high-Pb paint recipe

that corresponds with LA-ICP-MS Group 2a. This group is the predominant “recipe” for earlier Pinedale-style pottery made at these villages, suggesting that the individuals who manufactured Fourmile-style hybrids were drawing on an earlier paint recipe.

WMRW is invariably painted with black designs on red slip (with or without white outlines), but some of the whole vessels exhibited color differences in the paints (Van Keuren et al. 2013). There were occasionally variations in the intensity and color of the darker paints. In fact, multiple paint compositions were found on 12 out of 189 of the vessels analyzed, and these different compositions were obviously different recipes – not minor variations in the same basic mix of minerals. The majority of the paints on the WMRW vessels we examined contained varying concentrations on Mn, Cu, and Pb. The general lack of Fe-based paints is expected due to the difficulty in getting an oxidized Fe paint to visually stand out from the high-Fe slips used to create the red background colors. The exterior designs on the vessel in Figure 5 reveal an attempt to use Fe and the more typical Mn-Cu-Pb paints to achieve multiple colors. The vessel displays what may represent a large bear and four deer on the exterior. The bear is painted in a high Cu and Pb paint with some white clay accents while the deer is painted in a Fe-based paint with the hooves in black Cu-Pb paint and the tail and antlers in white slip. The rendering of Fe-based paints are apparent in some of the deer images as they appear to have mostly oxidized the same color as the slip, leaving only the hooves and tail to indicate the deer form.

5. Discussion/conclusions

This preliminary study demonstrates the utility of studying glaze-paint composition on whole vessels with pXRF. Our work shows that pXRF can identify groups that were previously defined on the basis of quantitative data. In the case of WMRW, we were able to recognize specific paint “recipes” on NMNH whole vessels that were defined by the earlier LA-ICP-MS

analysis of sherds. Although the latter is a far superior approach to defining ancient paint recipes, it cannot feasibly be applied to the analysis of whole vessels. This presents a conundrum since we can only appreciate and document the diversity of decorative motifs and design layouts by analyzing whole vessels (versus sherds). The combination of both qualitative and quantitative methods permitted us to move beyond traditional typologies and investigate how paint composition relates to variation within singular ceramic types. More important, the pXRF analysis corroborated Van Keuren and colleagues' suggestion that iconographic-style pottery involved diverse paint recipes in east-central Arizona. The potters who produced the NMNH whole vessel assemblage were clearly working with different sets of technical knowledge as well as raw materials. Potters regularly used Cu as a colorant and perhaps a flux along with variable amounts of Pb. In "classic" WMRW vessels (Pinedale-style bowls and Fourmile Polychrome in our sample), the result was lustrous black paints. By the 1320s, Fourmile Polychrome potters additionally introduced Mn as a colorant. The interiors of hybrid bowls are typically painted with earlier Pinedale-style designs (Van Keuren 2006), and our analysis show that these vessels typically used the same low-Mn recipe that characterizes Pinedale-style types (Table 2). Taken together, these patterns suggest that the makers of hybrid Fourmile-style pottery drew on preexisting bodies of manufacturing knowledge. Surface luster is absent on the black painted designs of these hybrids (as is Mn). The community of potters who produced these vessels may not have acquired the technological expertise of other WMRW-potters at Fourmile Ruin. Van Keuren and colleagues' (2013) suggest that Fourmile Polychrome was produced by potters who controlled access to manufacturing knowledge or raw materials.

The pXRF analysis of whole vessels further revealed a compositional pattern not accounted for in the earlier ICP-MS analysis. WMRW potters were at times using multiple paint

mixtures on single vessels presumably to achieve variable hues. This confirms what archaeologists have long suspected: compositional differences may exist within individual vessels. The use of multiple chemically-distinct paint recipes is most clearly evident in one vessel in which certain elements of the deer and bear on the exterior of the bowl were painted in a typical high Mn and Cu paint, while the bodies of the deer were painted in a high Fe paint that faded to varying degrees due to the oxidation firing needed to achieve the red color desired in the high Fe slip. There is great potential to explore the variability of paint composition within single vessels, which is typically impossible with small sherds.

This study establishes a protocol for extending LA-ICP-MS studies of sherds to non-destructive pXRF analyses of both whole vessel collections, and perhaps more equally important, rapid field analyses at archaeological sites where sherds cannot be collected for off-site compositional analyses. The latter provides the additional opportunity to radically increase our sample sizes in research on ancient pottery paint recipes. With further refinement, we anticipate that pXRF can be used to non-destructively and expediently analyze both sherds in field settings and whole vessels in museum collections (including those subject to imminent repatriation).

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Table Captions

- Table 1. Comparison of ICP-MS and pXRF groups in pilot study (n=20 samples).
- Table 2. Elemental proportions of pXRF groups and counts of compositional groups by ceramic type.
- Table 3. Row percentages of compositional groups by ceramic type for pXRF and ICP-MS (parentheses) analyses.

Figure Captions

- Figure 1. White Mountain Red Ware (WMRW) bowl interiors. Examples of both “classic” (1a) and “hybrid” (1b) Fourmile Polychrome.
- Figure 2. The Silver Creek area, east-central Arizona.
- Figure 3. (Right) Bivariate plot of copper and lead showing the separation of ICP Group 1. The spectra on the left are examples from the three pXRF groups (A, F, and G) that match with ICP Group 1.
- Figure 4. (Center) Bivariate plot of manganese and lead showing the separation of ICP Groups 2a, 2b, 3a, and 3b. The four spectra match the corresponding pXRF and ICP groups.
- Figure 5. Detail of bowl exterior design with Fe-based paints. The bear on the left is painted with a high copper and lead paint while the multiple deer bodies are painted with a high iron paint. The deer on the right was likely exposed to higher oxygen levels during the firing and the paint on the body oxidized to the same color as the slip. The hooves were painted with the same mineral paint as the body of the bear.

Table 1. Comparison of ICP-MS and pXRF groups in pilot study (n=20 samples).

ICP-MS Groups	pXRF Groups				
	A	B	C	D	E
1	2	1	1	1	-
2a	-	-	-	5	-
2b	-	-	1	1	3
3a	-	4	-	1	-
3b	1	1	3	-	-

Table 2. Elemental proportions of pXRF groups and counts of compositional groups by ceramic type.

ICP-MS Groups	1?	3a	3b	2a	2b	1?	1	
pXRF Groups	A	B	C	D	E	F	G	
Mn	+	+	+	-	-	+	-	
Pb	-	+	-	+	-	+	+	
Cu	-	+	+	+	+	-	-	n
Pinedale-style types ^a	-	14	6	<u>39</u>	3	-	-	62
Fourmile Polychrome	1	27	<u>45</u>	17	6	4	1	101
Fourmile-style hybrids	0	4	3	<u>17</u>	4	-	-	28

^a Include Pinedale Black-on-red/Polychrome and Cedar Creek Polychrome

Table 3. Row percentages of compositional groups by ceramic type for pXRF and ICP-MS (parentheses) analyses.

	TOF-LA-ICP-MS / pXRF groups					n
	1 / G	2A / D	2B / E	3A / B	3B / C	
Pinedale-style types ^a	- (1.0)	<u>62.9</u> (48.5)	4.8 (4.1)	22.6 (15.1)	9.7 (31.3)	62 (99)
Fourmile Polychrome	4.2 (7.1)	17.8 (24.6)	6.3 (5.2)	28.1 (26.6)	<u>46.9</u> (36.5)	95 (252)
Fourmile-style hybrids	- (10.6)	<u>60.7</u> (50.0)	14.3 (1.9)	14.3 (25.0)	10.7 (12.5)	28 (104)

Figure 1a and 1b. White Mountain Red Ware (WMRW) bowl interiors. Examples of both “classic” (1a) and “hybrid” (1b) Fourmile Polychrome.

Figure 2. The Silver Creek area, east-central Arizona.

Figure 3. (Right) Bivariate plot of copper and lead showing the separation of ICP Group 1. The spectra on the left are examples from the three pXRF groups (A, F, and G) that match with ICP Group 1.

Figure 4. (Center) Bivariate plot of manganese and lead showing the separation of ICP Groups 2a, 2b, 3a, and 3b. The four spectra match the corresponding pXRF and ICP groups.

Fig. 6. Detail of bowl exterior design with Fe-based paints. The bear on the left is painted with a high copper and lead paint while the multiple deer bodies are painted with a high iron paint. The deer on the right was likely exposed to higher oxygen levels than the deer in the center during the firing and the paint on the body oxidized to the same color as the slip. The hooves were painted with the same mineral paint as the body of the bear.