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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.

1. Introduction

Archeologists 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 pigmenting 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 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 archeologists 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

2.1. Archeological 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. 1a). 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,

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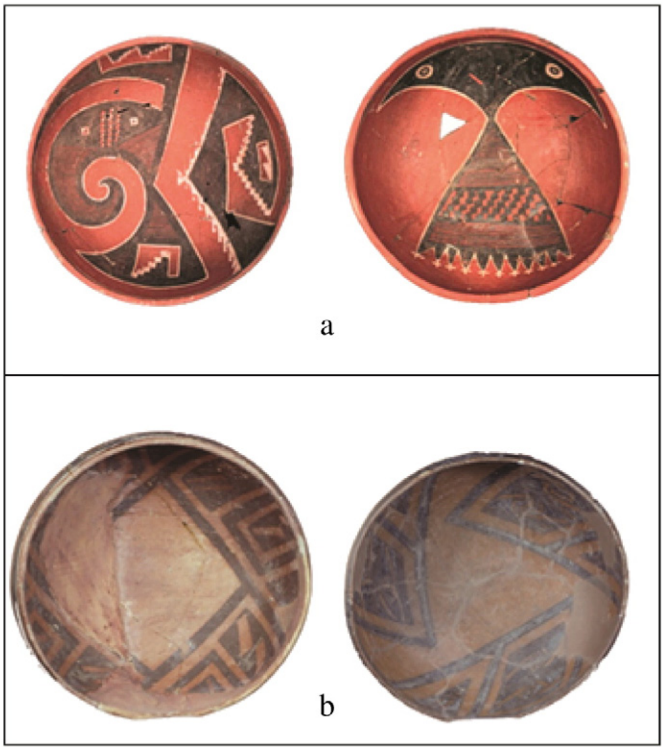

Fig. 1. White Mountain Red Ware (WMRW) bowl interiors. Examples of both "classic" (a) and "hybrid" (b) Fourmile Polychrome.

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 archeological 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.

2.2. 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 did not render the luster of glaze-painted designs observed on Fourmile Polychrome. Van Keuren et al. (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 archeological 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 (~4 mm × ~4 mm) 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