



Multi-element and lead isotope characterization of early nineteenth century pottery sherds from Native American and Euro-American sites

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ABSTRACT

Fine earthenwares imported from England are a distinctive artifact type frequently found on early nineteenth century Native American and Euro-American sites in eastern North America. Relatively rapid changes in decorative motifs and technologies can easily be identified by eye and provide information about site chronology and economic status. However, visual analyses of sherds usually can provide only general information because most assemblages are very fragmented. We present the chemical composition of pigments and glazes from sherds from two sites occupied during the first half of the nineteenth century: Pokagon Village, a Native American site (southwestern Michigan); and Collier Lodge, a Euro-American site (northwestern Indiana). Multi-element compositions of glazed portions of 12 sherds (with 3 different decorations, 2 specimens from each site of each pattern) were determined by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), micro X-ray fluorescence (μ XRF), and laser-ablation-inductively coupled mass spectrometry (LA-ICP-MS). SEM-EDS was especially useful for determining glaze composition, μ XRF rapidly provides information on pigment composition and Pb content, and LA-MC-ICP-MS provides information on trace elements and Pb isotopes that reflect different raw material sources.

1. Introduction

Fine earthenwares are tablewares with unvitriified bodies. During the early 19th century, the region of Staffordshire, England was the source for decorated fine earthenware pottery now found on archaeological sites in eastern North America (cf., Majewski and O'Brien, 1987). During the late eighteenth and early nineteenth century, ceramic technology evolved rapidly. New manufacturing methods produced new ware types, with the goal of producing whiter and more durable bodies, and new colors and styles of decoration went in and out of style. Changes in ware types and decorative methods and motifs over time have been used to determine provenance (e.g., Huntley et al., 2007; Iñáñez et al., 2010) and study topics such as economic class (Kenyon, 1985; Majewski and O'Brien, 1987; Miller, 1980; Samford, 1997).

Pearlware is a type of early 19th century fine earthenware manufactured with a lead glaze which contains a small amount of cobalt oxide to counteract a yellow tint (Majewski and O'Brien, 1987). Of all the fine earthenwares of the 19th century, pearlware is the most likely to have been decorated. Decorative methods changed rapidly, and the evolution of decorative styles has received much attention (Kenyon,

1985; Samford, 1997). Decoration is usually studied on relatively large sherds or complete vessels. However, most pottery is recovered only as small sherds. It is often difficult to distinguish the ware type of such sherds, so decoration is often more useful than ware type for determining both chronology and the economic value of 19th century ceramic assemblages (Majewski and O'Brien, 1987; Miller, 1980). Yet, there are often numerous recovered sherds that are too small to contain identifying marks (e.g., backmarks or characteristic pattern designs) for this categorization. With small sherds, visual examination is stronger when complemented by chemical composition investigations. Chemical characterization is widely applied in studies of ceramic components, which consist of bodies (Attaelmanan and Mouton, 2014; Bloch, 2016; Cantisani et al., 2012; Guirao et al., 2014; Holmqvist et al., 2014), pigments (Coentro et al., 2012; Dell'Aquila et al., 2006; Domoney et al., 2012; Roldán et al., 2006), and glazes (Miao et al., 2010; Reiche et al., 2009).

We used multiple methods to characterize shell-edge decorated ware, transfer-printed, and sponge-printed sherds from two early 19th century archaeological sites in the North American Midwest. As far as we can determine, there are no published descriptions of the material

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recipes that were used to produce the sherds. The recipes for glazes and the raw materials (and their sources) are unknown, except in the most general sense (e.g. crushed flint provided silica and white lead provided lead) according to sources published long after the pottery was made (Binns, 1910). It is therefore necessary to use analytical methods to determine the composition. By comparing four different styles with three different pigment colors from two early 19th century sites that were slightly separated in time, we evaluate the potential for the various analytical methods, alone and in combination, to determine aspects of chemical composition that can be used to date small sherds or to identify sherds from different manufacturers.

Although much attention has been paid to decorative methods and motifs from Staffordshire ceramics, relatively little is known about their chemical composition, especially pigments and glazes (Maggetti et al., 2015). Douglas (2000) used an electron microprobe to examine glazes and pigments on blue, green, and red/purple transfer-printed and hand-painted sherds, as well as blue transfer-printed sherds. These sherds were manufactured by the Spode pottery and had known manufacturing dates that ranged from 1813 to possibly as late as 1970. Glaze compositions were primarily SiO_2 , PbO , and Al_2O_3 (totaling > 75% by weight), with minor amounts of CaO , K_2O , and Na_2O , and perhaps some SnO . Lead contents were variable and generally decreased over time, ranging from 29.1% to 5.8%. Prior to 1833, glazes tended to have higher PbO abundances (> 20 wt%; (Douglas, 2000)) compared to those manufactured later, with the lowest PbO content (5 wt%) identified in a sherd from 1890. The decrease after 1833 coincided with a change in factory ownership. Douglas's analysis of the pigments also confirmed that Co was the blue pigment, and determined the intensity of the color was related to pigment concentration. Green decorated sherds used two different pigment recipes depending on the style of decoration. Green transfer-print pigments contained high Cr and Sn , whereas hand-printed green pigments were produced by Cu . The red/purple pigment recipe was more difficult to determine, but was probably produced by Sn in the hand-painted designs, and supplemented with Co in the transfer-printed ones. The findings of Douglas (2000) provide an important baseline for pigmentation formulas, but coloration is produced by a potentially wide variety of recipes (Newcomb, 1947). Maggetti et al. (2015) analyzed three Wedgwood sherds from a town waste-dump in Berne, Switzerland that was filled between 1787 and 1832 using multiple methods (XRF, XRD, SEM-BSE and SEM-EDS). Transparent lead alkali glazes were applied over siliceous-aluminous bodies. They compare body compositions to published recipes but found no comparable published information on glazes.

The chemical and Pb isotopic composition of the sherd glazes and pigments in our sample were obtained by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), micro-X-ray fluorescence (μXRF), and laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) for major and trace elements, and LA-multicollector (MC)-ICP-MS for lead isotopes. The methods (a) confirmed that lead glaze content decreases over time, (b) were able to identify the pigments used in the decorations, and (c) identified variations in pigment composition, trace element content and lead isotopes that likely reflect different factories or changes in raw material sources over time.

2. Materials

Twelve refined earthenware pottery sherds with three different types of decoration (shell-edge, transfer-printed and sponge-printed) in three colors (blue, green, and red) were selected for analysis (Fig. 1). The sherds were decorated using the underglaze method. In underglazing, the pigmented decoration is applied to a pre-fired body and then covered with a transparent lead glaze.

The sherds were retrieved from two archaeological sites in the Midwestern United States. The Pokagon Village (PV) site, in southwestern Michigan, was inhabited by a band of Native American Potawatomi between about 1825 and 1839. Excavations at the site

recovered fine earthenware sherds from two middens dating to this time period (Schurr et al., 2006). The Collier Lodge (CL) site, in northwestern Indiana, had a long occupation history, spanning most of the prehistoric and historic periods in the region (Schurr and Rotman, 2010). The sherds used here came from an early nineteenth Euro-American occupation that occurred between about 1828 and 1850. The general chronological sequence of the decorative patterns, from earliest to latest, is shown in Fig. 2. The ceramics from the sites are consistent with a slightly earlier date for Pokagon Village because it yielded green shell-edge ware, the earliest pattern examined here. Green shell-edge decorated sherds were not found at Collier Lodge. Instead, Collier Lodge excavation produced sponge-printed sherds, a late style of green decorated pottery that was not present at Pokagon Village. Comparing sherds from the two sites allows us to explore changes in composition over a short period of time (two to three decades). All the sherds were very small (< 1 cm wide) so traditional methods of sourcing and precise dating by manufacturer's backmarks or the scenes on transfer-prints are not useful.

3. Methods

3.1. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS)

Regions of interest on the pottery sherds were imaged using an EVO50 Leo Zeiss Environmental SEM equipped with an Oxford Instrument electron dispersive spectrometer (EDS) at the Notre Dame Integrated Imaging Facility. Due to the fragmental nature and burial history of the sherds, high-magnification images ($100\times$ to $300\times$) were necessary to avoid cracks, pits, and dirt embedded in the glaze in subsequent analyses. Semi-quantitative SEM-EDS analyses of the glaze and pigmented regions, at least three points each, were conducted on every sample. Minimum detection limits (MDL) for SEM-EDX analyses are typically around the level of 10s to 100s of ppm (Kuisma-Kursula, 2000). The 2 sigma reproducibility for major and minor elements (> 1 wt%) is expected to be better than 5% relative standard deviation (RSD) (Kuisma-Kursula, 2000). The RSD for trace elements present at concentrations between 0.1 and 1 wt% is typically ~10%, and for concentrations < 0.1 wt% the RSD may be upwards of 60–70%.

3.2. Micro X-ray fluorescence (μXRF)

Semi-quantitative measurements of glaze and pigment elements of the pottery sherds were made using an EDAX Orbis μXRF system at the Center for Environmental Science and Technology (CEST) at the University of Notre Dame. Analyses were performed in a vacuum, which theoretically allowed for monitoring of elements between Na and Np (Np is an artificial element and would not be expected in these samples). High spatial resolution was achieved by using a spot size of $30\ \mu\text{m}$ at 25–35 kV and 300–350 μA . The μXRF measurements of major and minor elements were conducted on the pigmented and unpigmented portions of the sherds (except for PV676, a blue shell-edge sherd that was completely pigmented) with replicate measurements (3–5) for most samples. Typical uncertainties (2 sigma) on measurements were based on counting statistics, and were $\leq 5\%$ (for elements present at > 1 wt% abundance), 1.3–10% (0.2 to 1 wt%), and 10–30% (0.05 to 0.2 wt%). Internal reproducibility (precision) was ~10%, based on replicate measurements, and detection limits were ~0.01 wt% (see Table 2). The accuracy and precision of μXRF is expected to be comparable to or better than SEM-EDX (Kuisma-Kursula, 2000; Trejos et al., 2013).

3.3. Trace element analysis

Thirty-two trace elements were quantified on a ThermoFinnigan Element2 inductively coupled plasma mass spectrometer (ICP-MS)

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