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

Mark R. Schurr[a],[*], Patrick H. Donohue[b], Antonio Simonetti[c], Emily L. Dawson[d]

[a] Department of Anthropology, University of Notre Dame, 296 Corbett Family Hall, Notre Dame, IN, USA
[b] Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Manoa, 1680 East-West Road, POST 602, Honolulu, HI 96822, USA
[c] Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA
[d] Department of Anthropology, University of T University of Texas at Austin, 2201 Speedway Stop C3200 SAC 4.166, Austin, TX 78751, USA

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 (μXRF), and laser-ablation-inductively coupled mass spectrometry (LA-ICP-MS). SEM-EDS was especially useful for determining glaze composition, μXRF 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 unvitrified 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; Iñañez 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

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 Wedgewood 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 μm 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 ≤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)
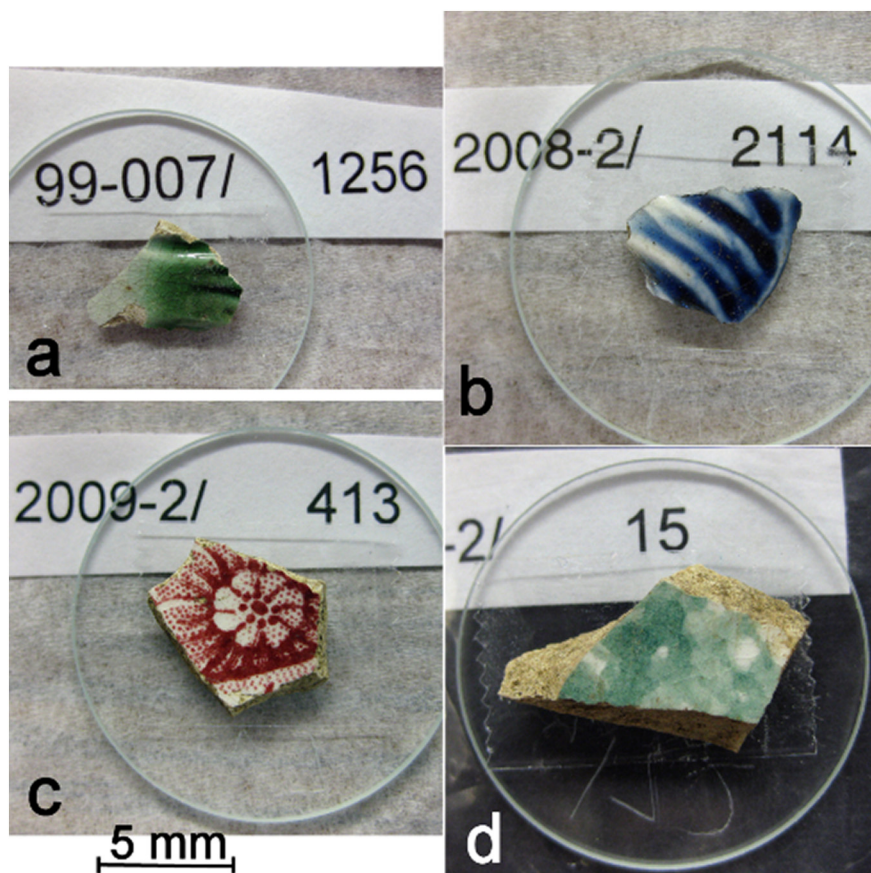
Fig. 1. Examples of sherd variants prepared for analysis, mounted with double-sided tape on 1″ rounds. Styles are (a-b) shell-edged, (c) transfer-print, and (d) sponge-print.
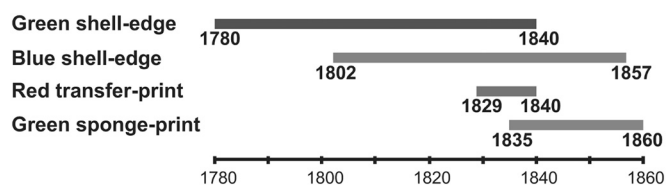

Fig. 2. Times of popularity for the decorations (Kenyon, 1985).

coupled to a NewWave Research UP213 Nd:YAG (Neodymium, Yttrium-Aluminum-Garnet) laser ablation (LA) system housed within the Midwest Isotope and Trace Element Research Analytical Center (MITERAC) at the University of Notre Dame. Trace element abundances were calculated from monitored isotopes ^{43}Ca, ^{45}Sc, ^{47}Ti, ^{53}Cr, ^{55}Mn, ^{60}Ni, ^{69}Ga, ^{85}Rb, ^{86}Sr, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{133}Cs, ^{137}Ba, ^{138}Ba, ^{180}Hf, ^{181}Ta, ^{208}Pb, ^{232}Th, ^{238}U, and rare earth elements (La to Lu). Half of the samples also included ^{53}Cr, ^{55}Mn, ^{59}Co, and ^{60}Ni in the analytical routine. The National Institute of Standards and Technology (NIST) standard reference material (SRM) 610 glass was used as an external standard to monitor instrument drift. Two repeat analyses of the external standard bracketed every 10 analyses of sherds. Calcium oxide (CaO) abundance (0.3–10 wt%) previously obtained by SEM-EDS was used for internal standardization.

Multiple regions (3 to 4 spots per pigment) were analyzed with a 40 μm diameter beam. Single points were used instead of scan lines because the samples were not flat and we did not want to risk defocusing the beam by moving the stage. Background ion signals were collected for 60 s prior to ablation, and during the final 20 s of this, the laser was "warmed up" to stabilize the fluence. During laser warm-up, an aluminum shutter is shut to prevent ablation of the sample, and

opened for lasering and sample signal acquisition for 60 s. The GLITTER© data reduction program (van Achterbergh et al., 2001) was used for examining the time-resolved data (time vs. ion signal plots) and calculation of trace element abundances, internal precision, and detection limits. The minimum detection limits (MDL) were determined by Poisson counting statistics (MDL = $2.3 * \sqrt{(2B)}$), where B is the total counts in the background interval. In this work, the MDLs for most trace elements ranged between 0.003 and 0.05 ppm, and between ~0.001 ppm for U and ~0.1 ppm for Rb. The internal precision (or relative uncertainty) varies according to the elemental abundances present within the samples since the latter influences directly the ion signal size recorded and consequently affecting counting statistics. Thus, the relative uncertainties can be effectively summarized in the following manner (from Dustin et al., 2016): for samples with reported elemental concentrations > 100 ppm, the associated relative uncertainty is between ~2 and ~5% (2σ); for determined abundances between 10 and 100 ppm, the associated uncertainty varies between ~5 and ~10% (2σ); and for concentrations < 10 ppm, the relative uncertainties range between ~10 and ~20% (2σ). The accuracy of the laser ablation protocol employed here has been verified by the repeated analysis of the NIST SRM 612 standard wafer treated as an unknown (e.g., Simonetti et al., 2008). The time resolved profiles did not reveal evidence for sampling of inclusions (e.g., soil impacted on the sherd surface). Test ablation pits on a blue shell-edge-sherd (Fig. 3) showed the 60 s ablation produced pits < 75 μm in depth, and did not reach the underlying white body. It is possible that the pigment is thinner in green sponge-printed and red transfer-printed sherds.

3.4. Pb isotopic analysis

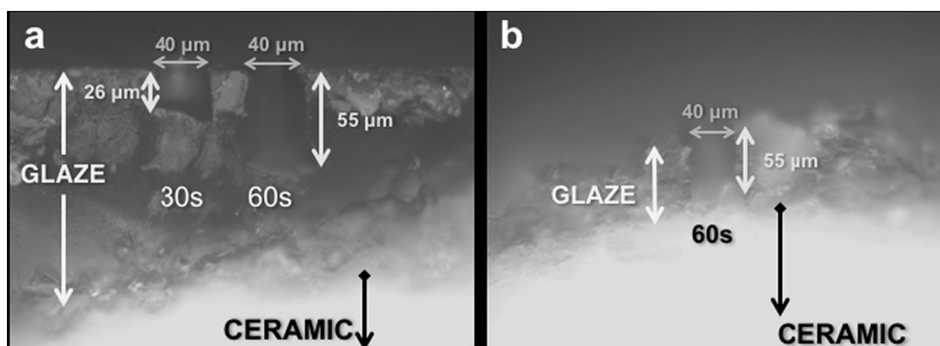Points proximal to LA-ICP-MS spots were analyzed for Pb isotope

Fig. 3. Photomicrographs (40×) of test ablation pits in a blue shell-edge sherd, viewed in cross-section. (a) Two pits on a thick portion of glaze. 30 s ablation reached ~35–40 μm depth, 60 s pit reached 65–70 μm depth. (b) 60 s ablation pit (60 μm deep) made in the thinnest glaze did not reach underlying body layers.

ratios on a Nu Instruments *Nuplasma II* multicollector (MC)-ICP-MS coupled to a New Wave 193 nm excimer LA-system housed within the Midwest Isotope and Trace Element Research Analytical Center (MITERAC) at the University of Notre Dame. Ablated particles are carried by He, flowing at 1 L/min, and combined downstream with mixed Ar gas and ionized by the plasma torch. All measured isotopes of Pb (204, 206, 207, 208) were collected simultaneously in Faraday cups. Because of the high Pb concentration in the sherds, the laser was set at a low power (65%) and pulse rate of 2 Hz and spot sizes of 25 and 35 μm. Pb ion signals were collected using the Nu Instruments time-resolved analysis (TRA) software, with acquisition of ~60 s for background measurement and ~60 s of ion signals during lasering. Prior to each analysis, the laser was warmed up for ~30 s to achieve a stable beam by leaving the shutter closed prior to ablation. Instrumental mass bias and drift were monitored and corrected for using a conventional 'sample-standard' bracketing technique (e.g., Chen and Simonetti, 2015), with several analyses of an Amazonite feldspar standard (Schmidberger et al., 2007) from the Broken Hill deposit (Australia) that bracketed every 6 analyses of sherds. Pb isotope values reported for the Amazonite feldspar standard by Schmidberger et al. (2007), and adopted for the instrumental drift and mass bias corrections in this study are the following (associated relative uncertainties are at 2σ level): $^{206}Pb/^{204}Pb = 15.99 \pm 0.03$, $^{207}Pb/^{204}Pb = 15.37 \pm 0.05$, $^{208}Pb/^{204}Pb = 35.59 \pm 0.14$, $^{207}Pb/^{206}Pb = 0.9611 \pm 0.0011$, $^{208}Pb/^{206}Pb = 2.2260 \pm 0.0043$; these are indistinguishable (given the associated relative uncertainties) compared to those obtained for sulphides from the Broken Hill deposit (Gulson, 1984), which are as follows: $^{206}Pb/^{204}Pb = 15.97 \pm 0.02$, $^{207}Pb/^{204}Pb = 15.35 \pm 0.02$, $^{208}Pb/^{204}Pb = 35.54 \pm 0.06$, $^{207}Pb/^{206}Pb = 0.9609 \pm 0.0006$, $^{208}Pb/^{206}Pb = 2.2248 \pm 0.0023$.

3.5. Statistical tests

One-way analysis of variance (ANOVA) using SPSS Version 20 was used to test for statistically significant different elemental concentrations between pigmented and unpigmented portions of the sherds using a significance level of $p < 0.05$.

4. Results and discussion

4.1. SEM-EDS

Glaze compositions were determined by measuring unpigmented portions of the sherd while the pigmented portions of the sherds provide information about the glaze and the pigment underneath. Table 1 lists the mean oxide compositions for major and minor elements in the pigmented and unpigmented portions for each type of decoration. Silicon and lead oxides are the major components, with lesser amounts of aluminum, potassium, calcium, and sodium, with even lower amounts

of iron and copper (in all but the green shell-edge sherds). The amounts are generally similar to those reported by Douglas (2000) and both data sets reflect a similar range of values (Fig. 4). The data also indicate that Pb contents decreased over time as green shell-edge sherds, the earliest style, contained the most Pb. The blue shell-edge sherds from Pokagon Village also contained high amounts of lead, so they were likely manufactured around the same time as the green versions. The blue shell-edge sherds from Collier Lodge contained less Pb, indicating they were probably manufactured later than those at Pokagon Village. The absence of green shell-edge pottery at Collier Lodge is probably because the site was inhabited after 1820 when the popularity of blue shell-edged decoration supplanted green shell-edge decoration. The two latest styles of red transfer-print and green sponge-print contained the least Pb (around 10%). The lower glaze Pb content of the sherds from the slightly later Collier Lodge site, compared to the higher glaze Pb content of sherds from the earlier Pokagon Village, shows that glaze Pb content decreases over time in the first few decades of the 19th century. Glaze Pb content can therefore be used to date early 19th century fine earthenware sherds, even those that are undecorated.

Douglas (2000) attributed a similar decrease in Pb content over time in wares from the Spode factory to new ownership in 1933. We have no evidence our samples were made at the Spode factory so the decrease in Pb content may have been an industry-wide trend. Lead was replaced by Si and to a lesser extent Al, suggesting the lower Pb glazes were probably less expensive to produce. This would have incidentally produced a somewhat healthier product. The use of lead in pottery production was clearly recognized as a health hazard as early as 1700 CE but legislature to protect British industrial workers from lead was not passed until 1883 (Riva et al., 2012), decades after the glaze composition changed. The role of health concerns in the observed reduction of Pb in the glazes remains ambiguous, although it cannot be ruled out.

Comparison of the Co content of the white and blue portions of the blue shell-edge sherds by a one-way ANOVA test confirms that Co was the primary blue pigment. There is a statistically significant difference in Co concentration between the pigmented and unpigmented areas ($F_{(1,29)} = 43.119$, $p < 0.001$). One-way ANOVA tests of the Cu concentrations in the green and white portions of green decorated shell-edge and sponge-print sherds indicate a significant difference ($F_{(1,52)} = 12.73$, $p = 0.001$); however, ANOVA tests do not indicate a significant difference for the pigmented and "unpigmented" areas of the green sponge-print ($F_{(1,45)} = 1$, $p = 0.374$). This result could indicate a change in green pigment composition over time (see below), or that the "unpigmented" portions of the green sponge-print contained significant amounts of pigment; the main reason for the latter being that the decoration tended to be very diffuse and it was not possible to find completely undecorated areas on the very small sherds examined by SEM-EDS. There is no obvious time trend in other major elements, except that all of them were lowest in the green shell-edge sherds where Pb is at the highest concentration in the glaze.

Table 1
Percentage composition by SEM-EDS (mean ± std. dev.)

Pattern	n	SiO_2	PbO	Al_2O_3	K_2O	Na_2O	CaO	FeO	CoO	CuO
Green-edged										
White	11	48.2 ± 3.6	42.9 ± 6.1	3.4 ± 1.2	1.2 ± 0.5	0.6 ± 0.2	1.3 ± 0.5	0.10 ± 0.04		2.4 ± 2.6
Green	20	44.4 ± 5.0	40.0 ± 3.3	5.6 ± 1.6	1.1 ± 0.4	0.4 ± 0.3	1.7 ± 0.5	0.6 ± 0.6		6.9 ± 1.3
Blue-edged										
White	18	54.4 ± 9.6	29.4 ± 5.7	9.0 ± 1.4	3.5 ± 2.0	0.6 ± 0.3	1.7 ± 1.8	0.7 ± 0.3	0.7 ± 0.6	0.8 ± 1.0
Blue	46	56.4 ± 8.6	28.2 ± 8.3	7.9 ± 1.3	2.8 ± 1.9	0.5 ± 0.3	2.0 ± 2.0	0.3 ± 0.2	1.9 ± 1.3	0.2 ± 0.3
Red transfer-print										
White	27	70.3 ± 6.8	9.4 ± 0.8	10.5 ± 1.5	2.8 ± 0.3	1.2 ± 0.5	5.5 ± 2.2	0.3 ± 0.2		0.3 ± 0.2
Red	35	70.4 ± 8.1	9.7 ± 1.5	9.8 ± 0.9	2.5 ± 0.6	1.1 ± 0.7	6.5 ± 3.4	0.3 ± 0.2		0.1 ± 0.1
Green sponge										
White	3	71.0 ± 3.6	10.0 ± 1.0	9.9 ± 0.7	3.4 ± 0.5	0.5 ± 0.2	5.0 ± 0.5	0.3 ± 0.1		0.2 ± 0.1
Green	3	71.3 ± 4.1	10.1 ± 1.4	9.6 ± 0.9	2.8 ± 0.8	0.7 ± 0.2	5.2 ± 1.1	0.3 ± 0.1		0.3 ± 0.1
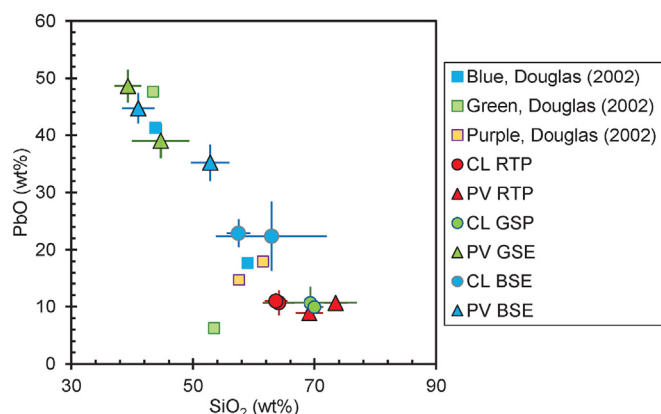
Fig. 4. Average SEM-EDS measurements of lead versus silica content in the pottery sherd glazes (pigmented regions only) for red transfer-print (RTP), green sponge-print (GSP), green shell-edge (GSE) and blue shell-edge (BSE). Uncertainties shown are 2 standard deviations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.2. Micro-XRF

The μXRF measured a different suite of elements than the SEM-EDS (Table 2). It was not able to detect Al or Na but did detect a wider range of metal oxides used as pigments, so the μXRF and SEM-EDS results are not directly comparable (the compositional results for each instrument are normalized to 100%). However, the relative proportions and trends for the detected elements should be the same. Elements present at low concentration, below the 0.1 wt% range, may represent less precise analyses but still provide important qualitative information. Elements with X-ray energies below about 1.7 keV (i.e., lighter than Al) could not be reliably detected with this instrument and operating conditions. The μXRF measurements confirm the reduction in Pb content over time identified by SEM-EDS.

Comparisons of pigmented and unpigmented region compositions were performed by one-way analysis of variance (ANOVA) tests. The ANOVA test highlights several elements with significantly different abundance between the unpigmented and pigmented areas of the sherds by pattern (Table 2). Colored pigments were produced by a variety of elements, including Co and Cu (as found by SEM-EDS) and also Mn, Ni, Sn, Cr, Zn, and perhaps Fe. In general, white areas tend to have slightly more Ti than pigmented areas. This suggests that the measurements on the white areas may be sampling a bit of the sherd body beneath the glaze, a likely location for trace amounts of TiO_2 used as a white pigment. This is consistent with the larger excitation volume of the μXRF (i.e. the beam penetrates deeper into the sample) compared to SEM-EDS analysis. In subsequent analyses by LA-ICP-MS and

investigation of the time-resolved signal (see Section 4.3.1), there was certainly TiO_2 added to the glaze. This may be akin to modern potters using rutile or ilmenite (ores containing Ti and Fe) in glazes to obtain specific effects (Rhodes, 1957). However, as Fe in the ores produces tan to brown tones or black specks that were not observed in our samples, the use of rutile or ilmenite appears unlikely and TiO_2 might have been present in the body or the glaze as a trace mineral from the raw materials. A more likely source of TiO_2 for the unglazed portions is in the underlying body where it is not masked by pigment. English ball clays contain about 1 to 2% TiO_2 (Maggetti et al., 2015, Table 5) and the body beneath the glaze could therefore be the source of the TiO_2 we detected in the unpigmented areas.

Green pigmentation was produced using different recipes for the shell-edge and sponge print sherds. As the actual recipes are not known, we can only provide possible elemental compositions for the pigments. Differing compositions suggest different recipes. It appears Cu was the primary pigment in green shell-edge sherds, perhaps with small amounts of Fe. The use of Cu as the primary pigment in the green shell-edge sherds is consistent with the tendency of the green decoration to be very intense along the rim edge and gradually lighten toward the center of the vessel because Cu diffuses very easily in Pb glazes (Coentro et al., 2012). Douglas (2000) also found different recipes for green pigments in different patterns, and that Cu alone was used in shell-edged designs, while green transfer-print pigments contained Cr and Sn. The green pigment used on the CL sponge-print was primarily a mixture of Cu, Co, and Zn (± Cr). One of the sponge print sherds (CL985) contained Cr, with higher Cr in the green pigmented regions. The presence of Zn may indicate that the Cu pigment was manufactured from brass ash, which is documented in some porcelain overglaze enamels (Domoney et al., 2012). It is also possible that the green pigment was produced from a mixture of CuO, Cr_2O_3, and ZnO (Parry and Coste, 1902). Domoney et al. (2012) reported Sb in combination with Cu creates a yellowish green, but Sb was not detected in these sherds.

Micro-XRF confirms the primary pigment in the blue shell-edge sherds was Co, with minor additional Ni (Table 2). Low levels of Ni have been found associated with Co in some blue pigments used on majolicas from Italy (Dell'Aquila et al., 2006) and in Valencian ceramics (Roldán et al., 2006). These Co-Ni pigments can be produced by roasting of *zaffre* (Co-Ni-As minerals) at high temperature (Roldán et al., 2006), providing some insight into the method that may have been used to produce the Co-blue pigment used in the Staffordshire potteries. Another possible source of Co-Ni pigments were mines in the region of Freiberg-Erzgebirge (Gratuze et al., 1996).

The primary pigment used in the red transfer-print was Sn, with minor (< 0.5 wt%) additional Mn and Cr. However, Sn was only quantified in two of the four red sherds. It is likely that Sn is present in the pigment, and that the absence here is probably because it was omitted from the element list during quantification as it appears that the Sn peak can be masked by K and Ca peaks. Red pigment in one

Table 2
Glaze and glaze/pigment composition determined by μXRF (as percent elements normalized to 100%, mean ± std. dev.) with significant ANOVA test probabilities. Areas with significant differences have $p \leq 0.05$, and in these cases, the area of higher concentration is indicated in parentheses.

Pattern	n	SiO_2	PbO	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO	NiO	SnO_2	Cr_2O_3	ZnO
Green-edged														
White	10	36 ± 7	59 ± 7	1 ± 1	1.7 ± 0.6	0.2 ± 0.08		0.3 ± 0.1	0.1 ± 0.08	1.6 ± 0.8				
Green	14	34 ± 5	58 ± 4	1 ± 1	1.6 ± 0.3	0.1 ± 0.1		0.20 ± 0.03	0.1 ± 0.01	4.6 ± 0.6				
p value						0.003 (white)		0.001 (green)		< 0.001 (green)				
Blue-edged														
White	18	40 ± 10	53 ± 10	4 ± 1	2.8 ± 2.2	0.20 ± 0.05		0.5 ± 0.2	0.5 ± 0.4		0.1 ± 0.1			
Blue	46	38 ± 10	55 ± 9	3 ± 1	2.4 ± 2.2	0.20 ± 0.08		0.3 ± 0.1	2.2 ± 1.0		0.3 ± 0.2			
p value				< 0.001 (white)		0.007 (white)		< 0.001 (white)	< 0.001 (blue)		< 0.001 (blue)			
Red transfer-print														
White	22	62 ± 7	19 ± 8	4 ± 1	14 ± 5	0.2 ± 0.10	0.10 ± 0.03	1.1 ± 0.6	0.10 ± 0.01	0.10 ± 0.03		0.02 ± 0.05	0.01 ± 0.06	
Red	20	60 ± 7	17 ± 7	3 ± 1	17 ± 6	0.1 ± 0.1	0.20 ± 0.05	0.8 ± 0.2	0.10 ± 0.01	0.10 ± 0.04		1.4 ± 1.3	0.10 ± 0.04	
p value				< 0.001 (white)	0.038 (red)	0.006 (red)	< 0.001 (red)					< 0.001 (red)	< 0.001 (red)	
Green sponge														
White	10	63 ± 7	21 ± 7	4 ± 1	12 ± 3	0.10 ± 0.01		0.7 ± 0.2	0.1 ± 0.01	0.10 ± 0.01		0.12 ± 0.05		0.10 ± 0.05
Green	9	58 ± 6	24 ± 4	4 ± 1	12 ± 2	0.10 ± 0.01		0.8 ± 0.2	0.5 ± 0.07	0.10 ± 0.01		0.7 ± 0.2		0.6 ± 0.2
p value														< 0.001 (green)

sherd from Pokagon Village was also supplemented with minor Ni. The pigments used in red transfer-prints have not been empirically identified before. Modern potters use Sn in combination with Cr to produce pinks and light red tints (Finkelnburg, 2011; Newcomb, 1947), thus it is possible the same combination of elements was used in these red sherds. The presence of other elements such as Mn and Ni suggests some kind of unknown impure mineral pigment was used instead of pure oxides.

4.3. LA-ICP-MS

4.3.1. Trace elements obtained by LA-ICP-MS

Pottery glazes are composites of pigments, compounds used in pottery recipes, and raw materials. In the absence of known recipes, these must be inferred from analytical data. The latter must be interpreted with care since the trace element composition of glazes, pigments and compounds may combine to produce a 'mixed' signature during a single laser ablation analysis; this feature renders geologic provenance identification and/or production-related tracing difficult to discern. However, unraveling components used in pottery sherds is in general aided by LA-ICP-MS investigation due to its high spatial resolution nature, and provides highly precise, quantifiable abundances of trace elements present at (high) ppb and ppm levels. Moreover, this technique can provide corroborating evidences for the chemical constituents associated with different pigments outlined in preceding sections. In addition, it can combine the abundances of trace elements not detectable by the other analytical methods utilized in this study. The end result is that trace element patterns are produced (Fig. 5), which can be used to compare the chemical fingerprint of different pottery sherds of the same color/print from different locations. For example, identical and/or similar trace element patterns for different fragments from Pokagon Village and Collier Lodge of same-colored sherds suggest that raw materials, pigments and manufacturing processes are identical; at the very least, this hypothesis cannot be ruled out. Contrarily, different trace element patterns indicate that at least one of the components (source of raw materials, process, pigment) involved in the sherd fabrication is distinct. As described in earlier sections and below, pigments are indeed associated with the presence of certain trace elements.

In the previous sections, several pigment chemical components were identified. Of the previously identified pigments, the LA-ICP-MS analytical method included quantification of Co, Ni, and Cr concentrations in half of the analyzed sherds. Blue colored areas yielded the highest Co (~5000–18,000 ppm) and Ni (~870–3400 ppm) abundances of any colored or uncolored areas. Lower amounts of Co and Ni were found in some other colors and in areas of glaze that otherwise appeared unpigmented. Co and Ni contents are also positively correlated in all sherds, supporting a related source for these two elements. The green sponge-print, which contains no completely unpigmented regions, also contains high Co (~200–430 ppm) and Cr (~80–460 ppm) abundances. Red pigments show Cr enrichments (> 100 ppm) relative to unpigmented regions in red transfer-prints, with one exception where a white region yielded 570 ppm. Ti contents are generally higher in unpigmented regions, as previously identified by SEM-EDS. Thus, in general the LA-ICP-MS analysis pigment-element associations corroborate and expand upon the findings by SEM-EDS and μXRF.

In addition to pigmentation, manufacturers also added certain elements (e.g., Pb) in specific proportions to achieve a desired look, or as were required by firing methods. In contrast to these additive components, trace elements present in the raw materials reflect their geological source and were not under direct control of the manufacturer. Thus, it may be possible to distinguish pottery sources using distinctive trace element compositions. Pigments or modifying compounds with impurities may also affect trace element distributions, but these should be apparent in differences between pigmented and unpigmented regions of sherds. As noted above, the geological sources of the materials are unknown but they can be inferred from the composition.
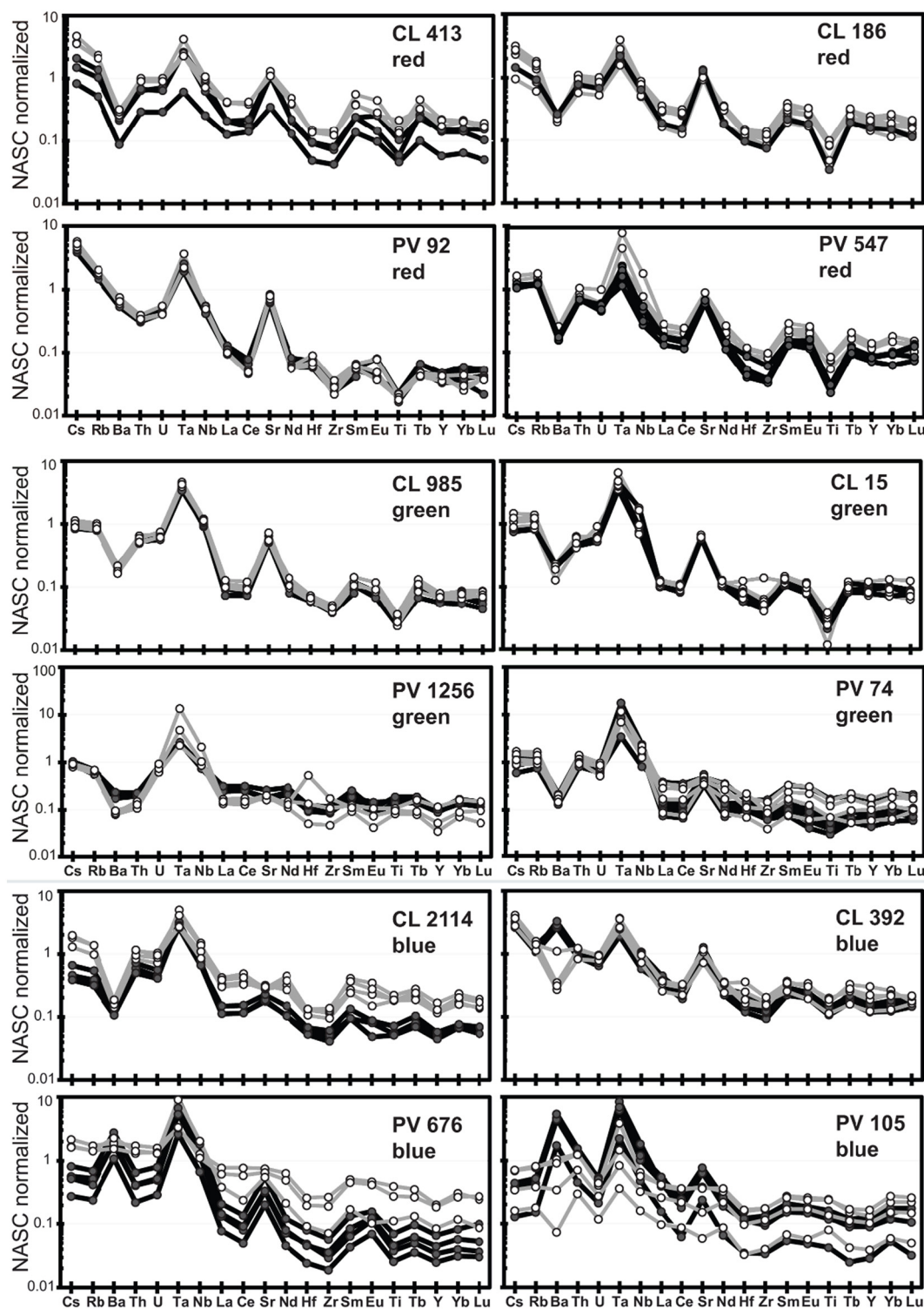
Fig. 5. Trace element patterns of individual sherds from PV and CL sites. Lines are individual analyses from pigmented (black lines) and unpigmented or lightly pigmented (gray) areas. (Normalization to North American Shale Composite values (Gromet et al., 1984)).

A common approach to evaluating geological provenance of raw materials is with the use of multi-element spider diagrams (Fig. 5), which compare the trace element concentrations of unknown samples to those for a well characterized source. In this case, the trace element abundances within the pottery sherds investigated here are normalized to the North American Shale Composite (NACS; Gromet et al., 1984); the latter represents the average composition of continental upper crust, which is an appropriate surrogate to evaluate the raw materials used in the fabrication of the sherds. This is evidenced by the fact that a majority of the normalized values plot within one order of magnitude from unity (normalized concentration = 1; Fig. 5).

The normalized patterns clearly exhibit one to two orders of magnitude variation for a given trace element within sherd groups. At least some of this variation is attributable to varying amounts of combined pigment and/or glaze ablated during LA-ICP-MS analysis since the depth of penetration/vertical profile was not examined for every

individual laser spot. Patterns identified as "unpigmented" in Fig. 5 were devoid of pigmentation and thus represent ablation of glaze and/or underlying ceramic/clay. Overall, these NASC-normalized patterns (Fig. 5) exhibit many similarities in positive and negative element anomalies, indicating similar raw materials were used in the production of all analyzed sherds. Moreover, a majority of the patterns for both unpigmented and pigmented sections of different pottery sherds are similar or identical (e.g., CL985 green, PV92 red), indicating that the glaze and/or underlying ceramic are of similar composition. However, there are sherds of similar pigment from the two sites that exhibit distinct patterns. For example, the green and red decorated sherds show distinct trace element patterns that suggest different sources for the raw materials and/or pigment at the two sites (Fig. 5). In addition, the blue decorated sherd from Pokagon Village has a higher concentration of trace elements than the blue decorated sherd from Collier Lodge.

Many of the patterns are characterized by positive Sr anomalies, which likely reflect contributions from feldspar, a common component in glazed raw materials. It is also interesting that Ba, which is substitutes for K in potassium feldspar, is rarely near unity (except in red transfer-print PV092) or "enriched" (blue-pigmented analyses). These low-Ba glazes may have instead been produced with a more sodic feldspar (i.e., albite). Blue sherd CL392 further demonstrates that Ba is a contaminant in the blue pigment, as the light blue region (i.e., thinner glazed) Ba abundance is near unity in Fig. 5, intermediate between the darker pigmented and unpigmented analyses. Relative to NASC, each sherd is depleted in rare earth elements (REEs). With the exception of green shell-edge sherd PV1256, unpigmented regions have higher (five sherds) or similar (six sherds) REE abundances compared to pigmented regions (Fig. 5; Table 3). The most likely explanation is that the addition of relatively pure pigment compounds, devoid of REEs, dilutes the REE abundance in pigmented regions.

4.3.2. Lead isotopes obtained by LA-MC-ICP-MS

The spread in Pb isotopic ratios shown in Fig. 6 is relatively restricted compared to the natural variation in Pb ore sources spanning both North American and global scales (e.g., Stacey and Kramers, 1975; Sangster et al., 2000). To our knowledge, major industrial sources of Pb ore were lacking within North America during the early-to-mid 1800s when the pottery sherds investigated here were produced (Sangster et al., 2000). Within North America, the Mississippi Valley Type (MVT; Missouri, upper Mississippi Valley, SW Wisconsin – SW Illinois, and Tri-State Oklahoma–Kansas–Missouri region, USA), and Buchans and Bathurst (Newfoundland and New Brunswick, Canada) Pb ore deposits were the main sources of industrial Pb for North America, but these

Table 3
Representative REE compositions of unpigmented and pigmented portions of sherds as determined by LA-ICP-MS. Values normalized to North American Shale Composite (NASC; Gromet et al., 1984).

Sample	Color	La	Ce	Nd	Sm	Eu	Gd	Tb	Yb	Lu
Green edge-ware										
PV1256	Whitish	0.11	0.07	0.07	0.05	0.04	0.07	0.06	0.05	0.04
	Green	0.1	0.05	0.06	0.06	0.07	0.05	0.05	0.03	0.04
Blue edge-ware										
PV676	White	0.6	0.54	0.45	0.38	0.33	0.3	0.25	0.23	0.2
	Blue	0.14	0.09	0.08	0.08	0.12	0.06	0.06	0.05	0.06
CL2114	White	0.24	0.24	0.22	0.18	0.1	0.16	0.14	0.13	0.12
	Blue	0.13	0.12	0.11	0.09	0.07	0.1	0.09	0.09	0.08
Red transfer-print										
PV092	White	0.1	0.1	0.11	0.11	0.12	0.1	0.1	0.07	0.07
	Red	0.1	0.1	0.11	0.11	0.08	0.11	0.1	0.08	0.07
CL413	White	0.41	0.4	0.42	0.44	0.33	0.39	0.37	0.2	0.18
	Red	0.18	0.18	0.19	0.2	0.17	0.25	0.2	0.12	0.1
Green sponge-print										
CL985	White	0.35	0.39	0.35	0.32	0.25	0.26	0.23	0.19	0.16
	Green	0.12	0.12	0.12	0.11	0.08	0.09	0.09	0.07	0.07
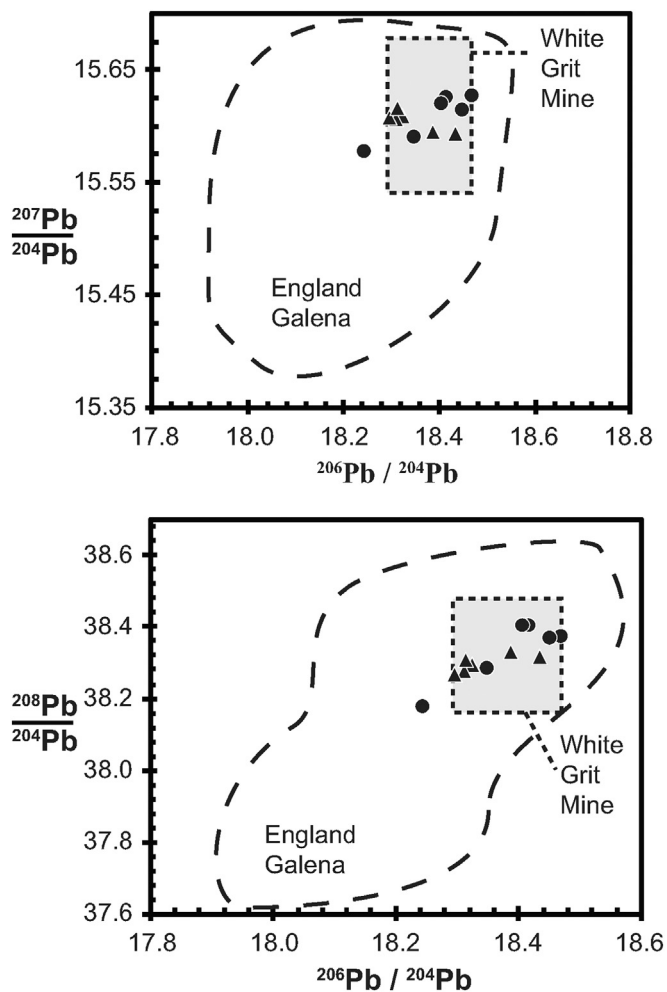
Fig. 6. Lead isotope ratios (^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb) of sherds from Pokagon Village (triangles) and Collier Lodge (circles). Data for White Grit Mine (Shropshire) and England fields from Moorbath (1962). Uncertainties on glaze measurements are smaller than the symbol size.

were exploited much later in the 1900s. In any case, the Pb isotope compositions for the sherds examined here do not overlap with any of those from MVT, Buchans, or Bathurst Pb ores (Sangster et al., 2000).

All sherd glaze isotope compositions reported here do fall within the field of Pb ore from England (Moorbath, 1962). Indeed, most of the measured lead isotopic compositions could be consistent with derivation from a single locality. This is illustrated in Fig. 6 by highlighting a locality from Shelve, Staffordshire, the White Grit Mine (Moorbath, 1962). All but one of the sherd glazes have Pb isotopic compositions similar to this source. This does not mean that all the sherd glazes were produced using ore from this same mine, but it does suggest they were produced from geologically similar areas. In the case of Pb ores, this could represent a large geographic area. Lead ore sources throughout England and Wales have Pb isotope ratios that are not systematically different, and there is also significant overlap in isotopic composition between sources in Scotland, Ireland, France, and Germany (Rohl and Needham, 1998). Thus, it is not possible to determine the specific source area of lead-containing artifacts from isotope ratios alone (Pollard, 2009). However, the Pb isotope composition of the sherds is consistent with their original production in Staffordshire, which could be expected given the region's dominance in pottery production during the time. Future work on Staffordshire ceramics with known provenance (e.g., with backmarks or more complete decorations) would be useful to determine the range in Pb isotopic variation from individual manufacturers. Archival research might also provide more information

Table 4
Pb isotopic values for glazes of Pokagon Village (PV) and Collier Lodge (CL) sherds.

Type	Color	n	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	$^{208}Pb/^{206}Pb$	2σ
Green shell-edge												
PV074	Green	3	18.299	0.006	15.608	0.001	38.269	0.008	0.8530	0.0003	2.0914	0.0002
	White	3	18.297	0.005	15.604	0.002	38.257	0.008	0.8529	0.0002	2.0910	0.0003
PV1256	Green	3	18.436	0.003	15.592	0.003	38.312	0.009	0.8457	0.0001	2.0778	0.0003
	White	3	18.438	0.004	15.596	0.003	38.323	0.011	0.8458	0.0001	2.0781	0.0002
Blue shell-edge												
CL2114	Blue	3	18.350	0.004	15.590	0.004	38.283	0.010	0.8495	0.0001	2.0862	0.0002
	White	3	18.350	0.002	15.589	0.002	38.281	0.004	0.84944	0.00003	2.0861	0.0001
CL392	Blue	3	18.248	0.003	15.577	0.001	38.180	0.004	0.8539	0.0002	2.0937	0.0004
	White	3	18.243	0.003	15.576	0.002	38.174	0.002	0.8541	0.0001	2.0939	0.0004
PV105	Blue	3	18.317	0.002	15.614	0.000	38.303	0.002	0.8527	0.0001	2.0915	0.0002
	White	3	18.314	0.002	15.616	0.001	38.304	0.004	0.8529	0.0001	2.0919	0.0002
PV676	Blue	3	18.388	0.001	15.594	0.000	38.327	0.002	0.8479	0.0001	2.0842	0.0002
	White	3	18.389	0.003	15.595	0.003	38.330	0.012	0.8480	0.0002	2.0843	0.0005
Red transfer-print												
CL186	Red	4	18.418	0.018	15.625	0.011	38.403	0.014	0.8482	0.0001	2.0849	0.0003
	White	4	18.417	0.010	15.625	0.007	38.402	0.012	0.8482	0.0001	2.0849	0.0003
CL413	Red	3	18.410	0.005	15.621	0.003	38.406	0.014	0.84819	0.00005	2.0850	0.0003
	White	3	18.404	0.002	15.617	0.002	38.402	0.005	0.8483	0.0004	2.08510	0.00003
PV092	Red	3	18.325	0.003	15.610	0.006	38.292	0.010	0.8516	0.0002	2.0886	0.0007
	White	3	18.327	0.001	15.607	0.002	38.292	0.006	0.8517	0.0001	2.0889	0.0001
PV547	Red	4	18.318	0.032	15.606	0.017	38.280	0.065	0.8520	0.0003	2.0896	0.0004
	White	4	18.308	0.003	15.603	0.002	38.259	0.008	0.8521	0.0001	2.0897	0.0002
Green sponge-print												
CL015	Green	5	18.474	0.014	15.628	0.008	38.378	0.033	0.8459	0.0001	2.0783	0.0001
	White	3	18.470	0.011	15.626	0.006	38.373	0.025	0.8459	0.0001	2.0783	0.0001
CL985	Green	3	18.452	0.007	15.614	0.006	38.365	0.012	0.8461	0.0001	2.0791	0.0003
	White	3	18.451	0.005	15.615	0.005	38.368	0.015	0.8462	0.0001	2.0793	0.0003

about the sources areas that were exploited.

Pb isotopic ratios are indistinguishable between pigmented and unpigmented regions as the mean difference is equal to the standard deviation (Table 4). This is not surprising, since Pb is not typically added for pigmentation. However, the similarities are promising as it allows future LA-MC-ICP-MS to sample any glazed area on a recovered sherd to identify Pb isotopic compositions. The narrow range defined by individual sherd analyses most likely results from different batches of glaze used during pottery preparation. Sherds that are characterized by similar Pb isotopic and major and trace element compositions may be paired; i.e., it is possible they came from the same vessel or were manufactured in the same lot. Using these chemical and Pb isotopic criteria, there are potentially three sets of paired sherds: (1) the two Collier Lodge red transfer-prints; (2) the two Collier Lodge green sponge-prints; and (3) the two Pokagon Village red transfer-prints. At present, definitive pairing is precluded because of variations in major and trace element contents, notably the range in Cs, Rb, and Th abundances (Fig. 5). The Pokagon Village transfer-print sherd Pb isotope composition is also very similar to one green and one blue shell-edge sherd from the Pokagon Village. While they are not paired, it is possible they were produced from one or more manufacturers with access to similar Pb ore. All blue sherds appear to have been sourced from different vessels.

5. Conclusions

This study confirms that glaze Pb content decreases over time, as measured by both SEM-EDS and μXRF methods. These results are similar to those reported previously (Douglas, 2000). Lead content of the glaze can therefore be used to infer relative dates of manufacture for sherds, even those that are too small to contain maker's backmarks or datable transfer-print scenes.

Micro-XRF was very effective for identifying underglaze pigments. Results reported here indicate that green shell-edge decorated and green sponge-prints were produced with different pigments, suggesting changes in pigment composition over time, or different manufacturers

for the different patterns. As expected, the blue shell-edge sherds were decorated with Co. Moreover, red transfer-printed sherds were printed using Sn, Ni, and perhaps with minor amounts of Mn and Cr. We believe this is the first empirical determination of the pigment composition used in early 19th century Staffordshire red decoration.

SEM-EDS and μXRF are similar methods that both use X-ray spectroscopy. SEM-EDS is better at detecting lower weight metals (e.g. Al and Na) but requires a more complex sample preparation process. In our study, μXRF was not able to detect Al and Na but required less sample preparation. In addition, the EDAX instrument we used allows observing the sample in color in real time, making it very easy to sample pigmented and unpigmented areas. Both methods produce semi-quantitative results.

Lead isotope ratios reported here are determined by the batch of glaze used during firing and decoration, and are not affected by pigmentation. The sherds investigated here cover a range of ratios but are not inconsistent with sources of Pb expected for English manufacture. However, they depict a slightly different pattern of source variation than the trace elements. There were apparently two different sources for the green shell-edge sherds at Pokagon Village and for the blue shell-edge and red transfer-printed sherds at both sites. The green-sponge print sherds from CL were so similar they may have been sherds from the same vessel found during two different excavation seasons.

Unpigmented portions of the glaze are REE enriched compared to pigmented areas. This is probably due to the pigments being more refined metal oxides with fewer trace elements compared to the glaze. The trace elements in the green decorated and red transfer-print sherds suggest different sources for the glaze ingredients at the two sites. The trace element signatures of the blue shell-edge sherds demonstrate less variation, suggesting fewer sources.

Other studies have shown that the multi-method line used here is an effective approach in revealing the fabrication history of ceramics. The multiple methods used in this study for the chemical and isotopic characterization of early nineteenth century transfer-prints provided new information about their manufacture, despite the restrictive sample size of the sherds analyzed here. However, given the small size

of our sample of products that were manufactured over a period of time by multiple manufacturers, further investigations on these types of ceramics are warranted to better characterize the range and of variability of the composition of these decorated wares.

Acknowledgements

References

Attaelmanan, A.G., Mouton, M., 2014. Identification of archaeological potsherds excavated at Mleiha using XRF. J. Anthropol. Sci. 42, 519–524.

Binns, C.F., 1910. The Potters Craft: A Practical Guide for the Studio and Workshop. D. Van Nostrand Company, New York.

Bloch, L., 2016. An elemental approach to the distribution of lead-glazed course earthenware in the eighteenth-century Chesapeake. Am. Antiq. 81, 231–252.

Cantisani, E., Cavalieri, M., Lofrumento, C., Pecchioni, E., Ricci, M., 2012. Ceramic findings from the archaeological site of Aiano-Torraccia di Chiusi (Siena, Italy): a multi-analytical approach. Archaeol. Anthropol. Sci. 4, 29–46.

Chen, W., Simonetti, A., 2015. Isotopic (Pb, Sr, Nd, C, O) evidence for plume-related sampling of an ancient, depleted mantle reservoir. Lithos 216-217, 81–92.

Coentro, S., Mimoso, J.M., Lima, A.M., Silva, A.S., Pais, A., Muralha, V.S.F., 2012. Multi-analytical identification of pigments and pigment mixtures used in 17th century Portuguese azulejos. J. Eur. Ceram. Soc. 32, 37–48.

Dell'Aquila, C., Laviano, R., Vurro, F., 2006. Chemical and mineralogical investigations of majolicas (16th–19th centuries) from Laterza, southern Italy. Geol. Soc. Lond., Spec. Publ. 257, 151–162.

Domoney, K., Shortland, J., Kuhn, S., 2012. Characterization of 18th-century Meissen porcelain using SEM-EDS. Archaeometry 54, 454–474.

Douglas, M.A., 2000. An Electron Microprobe Study of 19th Century Staffordshire Glazes and Pigments Including Those of the Spode Pottery Works, Masters of Science ed. Department of Geology, University of Georgia, Athens.

Dustin, M.K., Koeman, E.C., Simonetti, A., Torrano, Z., Burns, P.C., 2016. Comparative investigation between in-situ laser ablation- vs. bulk sample (solution mode)-ICP-MS analysis of Trinitite post-detonation materials. Appl. Spectrosc. 70, 1446–1455.

Finkelnburg, D., 2011. Four ways to red. Ceram. Mon. 59 (4), 14–15.

Gratuze, B., Soulier, I., Blet, M., Vallauri, L., 1996. De l'origine du cobalt: du verre à la céramique. Rev. Archéométrie 20, 77–94.

Gromet, L.P., Dymek, R.F., Haskin, L.A., Korotev, R.L., 1984. The "North American Shale Composite": its compilation, major and trace element characteristics. Geochim. Cosmochim. Acta 48, 2469–2482.

Guirao, D., Pla, F., Acosta, A., 2014. The archaeometric characterization of majolica ceramics from Talavera de la Reina and El Puente del Arzobispo (Toledo, Spain). Archaeometry 56, 746–763.

Gulson, B.L., 1984. Uranium-lead and lead-lead investigations of minerals from the Broken Hill lodes and mine sequence rocks. Econ. Geol. 79, 476–490.

Holmqvist, E., Väisänen, R., Koivisto, A., 2014. Redwares from Gubbacka's medieval village: regional and inter-regional views on ceramic networks and technology (SEM-EDS). Estonian J. Archaeol. 18, 86–101.

Huntley, D.L., Spielmann, K.A., Habicht-Mauche, J.A., Herhahn, C.L., Flegal, A.R., 2007. Local recipes or distant commodities? Lead isotope and chemical compositional analysis of glaze paints from the Salinas pueblos, New Mexico. J. Archaeol. Sci. 34, 1135–1147.

Iñañez, J.G., Bellucci, J.J., Rodríguez-Alegría, E., Ash, R., McDonough, W., Speakman, R.J., 2010. Romita pottery revisited: a reassessment of the provenance of ceramics from Colonial Mexico by LA-MC-ICP-MS. J. Archaeol. Sci. 37, 2698–2704.

Kenyon, I., 1985. A history of ceramic tableware in Ontario, 1780–1840. Arch Notes:

Newslett. Ont. Archaeol. Soc. 85 (3), 41–57.

Kuisma-Kursula, P., 2000. Accuracy, precision and detection limits of SEM-WDS, SEM-EDS and PIXE in the multi-elemental analysis of medieval glass. X-Ray Spectrom. 29, 111–118.

Maggetti, M., Heege, A., Serneels, V., 2015. Technological aspects of an early 19th c. English and French white earthenware assemblage from Bern (Switzerland). Period. Mineral. 84, 139–168.

Majewski, T., O'Brien, M.J., 1987. The use and misuse of nineteenth-century English and American ceramics in archaeological analysis. In: Schiffer, M.B. (Ed.), Advances in Archaeological Method and Theory. vol. 11. Academic Press, New York, pp. 98–210.

Miao, J., Yang, B., Mu, D., 2010. Identification and differentiation of opaque Chinese overglaze yellow enamels by Raman spectroscopy and supporting techniques. Archaeometry 52, 146–155.

Miller, G.L., 1980. Classification and economic scaling of 19th century ceramics. Hist. Archaeol. 14, 2–39.

Moorbath, S., 1962. Lead isotope abundance studies on mineral occurrences in the British Isles and their geological significance. Philos. Trans. R. Soc. Lond. A: Math. Phys. Eng. Sci. 254, 295–360.

Newcomb Jr., R., 1947. Ceramic Whitewares: History, Technology, and Applications. Pitman Publishing Corporation, New York.

Parry, E.J., Coste, J.H., 1902. The Chemistry of Pigments. Scott, Greenwood and Co., London.

Pollard, A.M., 2009. What a long, strange trip it's been: lead isotopes and archaeology. In: Shortland, A.J., Freestone, I.C., Rehren, T. (Eds.), Advances in the Study of Ancient Technology. Oxbow Books, Oxford, pp. 181–188.

Reiche, I., Röhrs, S., Salomon, J., Kanngießer, B., Höhn, Y., Maizer, W., Voigt, F., 2009. Development of a nondestructive method for underglaze painted tiles - demonstrated by the analysis of Persian objects from the nineteenth century. Anal. Bioanal. Chem. 393, 1025–1041.

Rhodes, D., 1957. Clay and Glazes for the Potter. Chilton Book Company, Philadelphia.

Riva, M.A., Lafranconi, A., D'Orso, M.I., Cesana, G., 2012. Lead poisoning: historical aspects of a paradigmatic occupational and environmental disease. Saf. Health Work 3 (1), 11–16.

Rohl, B., Needham, S., 1998. The circulation of metal in the British Bronze Age: the application of lead isotope analysis. In: Occasional Paper 102. British Museum Press, London.

Roldán, C., Coll, J., Ferrero, J., 2006. EDXRF analysis of blue pigments used in Valencian ceramics from the 14th century to modern times. J. Cult. Herit. 7, 134–138.

Samford, P.M., 1997. Response to a market: dating English underglaze transfer-printed wares. Hist. Archaeol. 31 (2), 1–30.

Sangster, D.F., Outridge, P.M., Davis, W.J., 2000. Stable lead isotope characteristics of lead ore deposits of environmental significance. Environ. Rev. 8, 115–147.

Schmidberger, S.S., Simonetti, A., Heaman, L.M., Creaser, R.A., Whiteford, S., 2007. Lu-Hf, in-situ Sr and Pb isotope and trace element systematics for mantle eclogites from the Diavik diamond mine: evidence for Paleoproterozoic subduction beneath the Slave craton, Canada. Earth Planet. Sci. Lett. 254, 55–68.

Schurr, M.R., Rotman, D.L., 2010. The collier lodge archaeological site: why it belongs on the national register of historic places. Indiana Archaeol. 5 (1), 93–112.

Schurr, M.R., Martin, T.J., Secunda, W.B., 2006. How the Pokagon band avoided removal: archaeological evidence from the faunal assemblage of the Pokagon village site (20BE13). Midcont. J. Archaeol. 31, 143–164.

Simonetti, A., Buzon, M.R., Creaser, R.A., 2008. In-situ elemental and Sr isotope investigation of human tooth enamel by laser ablation-(MC)-ICP-MS: successes and pitfalls. Archaeometry 50, 371–385.

Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet. Sci. Lett. 26, 207–221.

Trejos, T., Koons, R., Becker, S., Berman, T., Buscaglia, J., Duecking, M., Eckert-Lumsdon, T., Ernst, T., Hanlon, C., Heydon, A., Mooney, K., Nelson, R., Olsson, K., Palenik, C., Pollock, E.C., Rudell, D., Ryland, S., Tarifa, A., Valadez, M., Weis, P., Almirall, J., 2013. Cross-validation and evaluation of the performance of methods for the elemental analysis of forensic glass by μ-XRF, ICP-MS, and LA-ICP-MS. Anal. Bioanal. Chem. 405, 5393–5409.

van Achterbergh, E., Ryan, C.G., Jackson, S.E., Griffin, W.L., 2001. Data reduction software for LA-ICP-MS: appendix. In: Sylvester, P.J. (Ed.), Laser ablation-ICP-mass spectrometry in the earth sciences: principles and applications. vol. 29. Mineralogical Association of Canada, Short Course Series, Québec, pp. 239–243.