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Slips, films, and material choice: Long-distance hydrothermal pigments on Middle Mississippian red ware

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ABSTRACT

Using laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) and Raman spectroscopy, we investigate red pigment applied to ceramic vessels as a slip or film (pigment + liquid + binder mixture) in the midcontinental United States. We find that during the CE 1000–1200 period, potters at Cahokia and nearby sites in the American Bottom region of the Middle Mississippi Valley used pigments originating from hydrothermal deposits. The closest hydrothermal deposits are located over 50 km away in the Ozark Highlands and the pigments may have been collected from areas already exploited for other resources. Approaching slips or films as pigment + liquid + binder mixtures integrates ceramic raw materials research with pigment research and encourages us to consider a variety of pigment options, some of which require binders for use on ceramics.

1. Introduction

Pigmented surface coatings on ceramic vessels, known as slips or films, are understudied from a materials perspective compared to pottery clay and temper. Here we address slips or films as pigment + liquid + binder mixtures and investigate pigments on archaeological ceramics through laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) and Raman spectroscopy.

Indigenous North American potters used red slips or films along the west-central Gulf Coast of Florida after AD 200 (Pluckhahn et al., 2018), in the Central Mississippi Valley between the Ohio and Arkansas Rivers after AD 400 (McNutt, 1996), and in the American Bottom region of the Middle Mississippi Valley just before CE 1000 (Kelly, 1991; Pauketat, 1998b; Stoltman et al., 2008; Pauketat, 1998a). We find that during the period CE 1000–1200, potters at the large urban center of Cahokia and nearby sites in the American Bottom (Fig. 1) covered vessels with red pigments that originated from hydrothermal deposits—minerals precipitated from hot water circulating in the Earth's crust. The use of hydrothermal pigments here is a surprising and novel finding, given the emphasis on shale (sedimentary rock) in the ethnographic literature for vessel coatings and the distance to the closest hydrothermal activity in the Ozark Plateau.

We begin below by defining the terms "slip" and "film" and describing differences in their pigment + liquid + binder mixtures. We then consider the geological setting and potential pigment resources for potters in the American Bottom region of the Middle Mississippi Valley before presenting our LA-ICP-MS and Raman results. Further pigment characterization should yield interesting data on Middle Mississippian resource acquisition patterns. More broadly, we argue that our approach to slips and films as pigment + liquid + binder mixtures will better integrate ceramic raw materials research with pigment research and prove useful for slip or film analyses in other regions.

2. Background

2.1. Definitions

This paper concerns ceramic vessels covered with red pigment—-specifically a red mineral colorant (pigment) applied when suspended in a liquid medium (Rapp, 2009), often with a binder to help the mixture adhere to the underlying surface (pigment + liquid + binder). Red pigment has also been labeled "ochre" (see discussion in Beck et al., 2022). When mineral pigment (red ochre) is applied in a pigment + liquid + binder mixture across an entire ceramic vessel surface, we describe it as "slip" or "film.".

The terms "slip" and "film" both describe vessel surface coatings but

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refer to different pigment materials in the pigment + liquid + binder mixture. A slip is technically a "fluid suspension of clay in water" used to cover vessel surfaces before firing (Rye and Owen, 1981:41). In this pigment + liquid + binder mixture, water is the liquid and clay serves as both pigment and binder (Eiselt et al., 2011; Shepard, 1985). The clay in the slip layer fires together with the clay in the vessel wall, creating a durable pigmented surface (Weiss, 2019).

A film is essentially paint, another pigment + liquid + binder mixture (Munson, 2020; Rapp, 2009) but potentially with low to no clay content. There is relatively little clay in the red film on Hiwassee Island Red-Filmed pottery (Bow, 2020:146), for example. Red pigment or ochre may be high in clay (Beck et al., 2022) but not necessarily (Hays-Gilpin and Neitzel, 2020; Munson, 2020; Eiselt et al., 2011). When paints or films include mineral pigments with low to no clay content, they incorporate liquids or binders such as blood, plant juices, fish and bird eggs, oil, fat, and saliva (Ancheta, 2013; Eiselt et al., 2011, 2019; Fralick et al., 2000; Morrow, 1975; Munson, 2020; Rapp, 2009; Scott et al., 1996). Informal experiments by Eiselt et al. (2011) and by the authors suggest that clay-rich sediment is unlikely to be added to pigment as a binder because its color quickly overwhelms the color of the pigment before affecting its binding properties.

Ethnographic and ethnoarchaeological literature on red-pigmented pottery usually lacks any explanation of the geological raw materials used for the pigment (e.g., Birmingham, 1975; Batmaz, 2019). The available information is almost exclusively from the U.S. Southwest, where 20th-century Indigenous potters on the Colorado Plateau used shale-derived clays for slips (Colton and Harold, 1953). Contemporary Hopi, Acoma, and Laguna potters have all used shales as red slip material (Blair and Blair, 1999; Dillingham, 1999), including Late Cretaceous Mancos shale (Blair and Blair, 1999). Potters at San Ildefonso "obtain [red slip material] near Santa Fe" (Guthe, 1925:23) collected from "red-burning Pennsylvanian shales" (Hawks, 1970:27). It would be tempting to conclude, based on the above, that all pigmented vessel surface coatings are slips that use clay-rich pigments from shales.

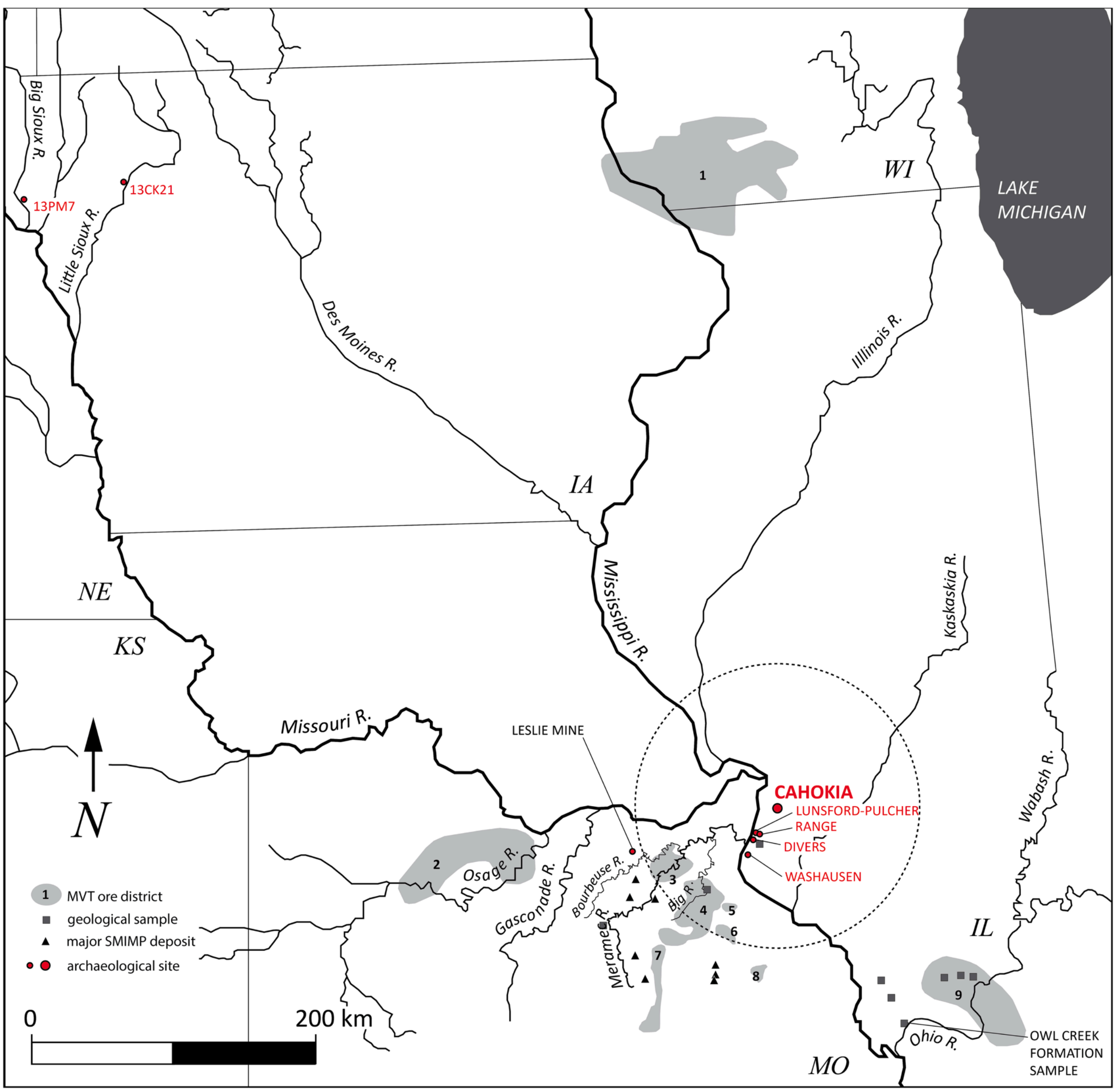

Fig. 1. Locations of archaeological sites, geological samples, Mississippi Valley-type (MVT) ore districts and deposits (Garven et al., 1993:Fig. 1; Lasemi, 2010: Fig. 16-2; Mugel and Douglas, 2017:Fig. 1), and Southeast Missouri Iron Metallogenic Province (SMIMP) deposits (Starkey and Seeger, 2016:Fig. 1). MVT districts and deposits shown are the Upper Mississippi Valley District (1), Central Missouri Barite District (2), Franklin County Mines (3), Southeast Missouri Barite District (4), Valles Mines (5), Old Lead Belt (6), Viburnum Trend (7), Mine La Motte subdistrict (8), and the Illinois-Kentucky Fluorspar District (9). The dashed circle represents a 100-km radius around Cahokia.

2.2. Regional geology and potential pigment resources

Cahokia and other sites in the American Bottom region of the Middle Mississippi Valley are located near the western border of the Illinois Basin, an intracratonic basin developed on Precambrian crust and filled with Paleozoic sedimentary rocks (Panno et al., 2013,2022). The bedrock within a 30-km radius of Cahokia consists of Mississippian and Pennsylvanian limestones, sandstones, and shales (Kolata, 2005; Starbuck, 2017), and Pennsylvanian shales in Illinois have been mined for brick production (Lasemi et al., 2010).

Within a 100-km radius of Cahokia, the only accessible alternatives to limestones, sandstones, and shales (or to iron-rich concretions within them) occur in the Ozark Highlands, a region of uplifted Ordovician and Cambrian sedimentary rocks surrounding Precambrian igneous mountains (Day et al., 2016; Kisvarsanyi et al., 1981). Where regional faults and fracture zones formed paths for heated mineral solutions, hydrothermal alteration of igneous and sedimentary rock created large deposits of iron ore, barite, lead (galena), and zinc (Keller, 2004; Mugel and Douglas, 2017). The geological diversity of the Ozark Highlands provides multiple raw materials important to Cahokia and the American Bottom (Pauketat, 1994, 1998b), such as galena (Walthall, 1981), flint clay for figurines (Emerson and Hughes, 2000), diabase for celts (Koldehoff and Wilson, 2010; Pauketat and Alt, 2004), and Burlington chert from the Crescent Quarry area (Ray and Jack, 2007). There is one known pre-Columbian ochre mine in the Ozark Highlands, the Leslie Mine (Crane, 1912; Holmes, 1903; Moorehead and Warren, 1912), hinting to some researchers (Emerson and Hughes, 2000; Pauketat, 1998b) that the red pigment so common in Middle Mississippian sites (e.g., Baltus and Baires, 2012) may also come from this region.

Raw material source areas within the Ozark Highlands can be further distinguished based on previous mining activity and associated geological investigation. One possible way to classify source areas would rely on defined Mississippi Valley-Type (MVT) ore deposits in carbonate rock (Gregg and Shelton, 2012; Wilkinson, 2014). The closest MVT ore district to the American Bottom is the Southeast Missouri Barite District and adjacent Franklin County and Valles mines (see Fig. 1). Almost all the galena characterized from the Cahokia area came from "the Southeastern Missouri Potosi deposits" (Walthall, 1981:41), the boundaries of which include the Southeast Missouri Barite District. Iron ore occurs in some MVT ore districts (St. Marie et al., 2001). In Illinois, the only Euroamerican iron ore mining took place in Hardin County in the MVT Illinois-Kentucky Fluorspar district (Starke, 1935). MVT ore districts are not useful for categorizing all iron pigment sources, however, because iron ore also occurs in other areas of hydrothermal activity.

The literature on iron ore distribution in Missouri's Ozark Highlands indicates two types of sources, both of which have hydrothermal deposits. The first type is the Southeastern Missouri Iron Metallogenic Province, an area with eight major iron oxide deposits in Precambrian igneous rocks in the St. Francois mountains (Kisvarsanyi et al., 1981; Nuelle et al., 1992; Starkey and Seeger, 2016). The second type is the Filled Sink (Central) District, covering an area of over 10,000 square kilometers south of the Missouri River but with most iron ore deposits "in the area drained by the upper Meramec River in Phelps, Crawford, and Dent counties" (Crane, 1912:85). The Filled Sink (Central) District overlaps with the northern part of the Southeastern Missouri Iron Metallogenic Province and the area of the Franklin County MVT ore mines. Although filled sink deposits have been described as sedimentary (Hayes, 1959; Starkey and Seeger, 2016), the ore-bearing sediments show evidence of hydrothermal alteration by "fluids related to Mississippi Valley-type deposits and(or) hydrothermal fluids which interacted with the underlying Precambrian volcanic rocks" (Asher-Bolinder, 1992:1).

Examples of filled sink iron ore deposits include the Leslie Mine (Crane, 1912), located in Franklin County near the Bourbeuse River, and the iron ore deposit at the Maramec Iron Works (now within Maramec Spring Park) in the Meramec River Valley (Norris, 1964). Popelka-Filcoff (2006; Popelka-Filcoff et al., 2007) sampled several iron ore deposits from Euroamerican mines, including the Maramec deposit. The Maramec deposit does not appear to be a source of hematite or other iron-rich rock for sampled Archaic and Woodland archaeological tools and fragments in the American Bottom (Pierce et al., 2020; Pierce and Popelka-Filcoff, 2023).

No previous research indicates how potters might have engaged with any of the resources described above. Although red pigment on Mississippian palettes (Steponaitis et al., 2011), knives (Vermilion et al., 2003), rock art (Blankenship, 2015; Bow, 2020), stone statues (Bow, 2020), and pottery (Bow, 2020) has been characterized, these studies conclude that the pigment contains iron without making comparisons to possible geological sources.

2.3. Red ceramics in this study

Just before CE 1000, potters at Cahokia and elsewhere in the American Bottom began making red ware (Holley and George, 1989; see Griffin and James, 1949; Vogel, 1975). Monks Mound Red, an early limestone-tempered red ware type, was produced at sites to the south of Cahokia and circulated throughout the American Bottom as part of widespread ceramic exchange, perhaps linked to the transport of food for feasts (Kelly, 2002). It may have been "manufactured by a limited number of potters and distributed… in a manner that also would have transmitted potent central themes throughout Greater Cahokia" (Pauketat, 1998b:70).

By CE 1050, red ware was transported along with other Middle Mississippian material culture to the Upper Mississippi Valley (Green and Rodell, 1994; Pauketat et al., 2015; Stoltman et al., 2008). Within a few decades, potters in the northeastern Great Plains began making a local version of Monks Mound Red known as Mill Creek Red (Beck and Hannus, 2020; Ives, 1962). Archaeologists identify these potters as part of the Mill Creek culture of northwestern Iowa (CE 1100–1250; Lensink, 2005). Red ware technology probably spread into the northeastern Plains through pilgrimages, visits, and exchanges with Mississippian groups (Pauketat, 1998b; Stoltman and Tiffany, 2016), some resulting in "the movement of a small number of women as marriage partners" (Beck and Hannus, 2020:39).

Red ware ceramics were common in the American Bottom; between CE 1000–1100, they comprised roughly 30–40 percent of ceramics at sites in the southern American Bottom (e.g., Barrier, 2014; Freimuth and Glen, 2010: table 40) and were even more common at Cahokia in the same period (Holley and George, 1989; Pauketat, 1998b; Pauketat, 1998a). In contrast, red ware is rare in Mill Creek sites, comprising less than three percent of the ceramics (Fishel, 1997; Ives, 1962; Tiffany, 2021). At one Mill Creek site (13CK21), over half of the red ware ceramics were found in one feature with raptor bones and other items linked to Mississippian interaction (Fishel, 1997).

We included Mill Creek Red ceramics in our analysis because the surface coatings should be chemically and mineralogically distinguishable from surface coatings on Middle Mississippian red ware. Beck and Hannus' (2020) petrographic analysis confirms that the Mill Creek Red ceramics in this study were made in the Mill Creek area, a region dominated by Pleistocene deposits and Cretaceous sedimentary formations including the Dakota formation (Bain 1898; Beck et al., 2022; Macbride, 1902). Although the red surface coatings may be made from different geological materials, they are similar in appearance. The red ware ceramics in our study from the American Bottom and northeastern Plains have thin surface coatings with Munsell colors of 10R 5/6, 10R 4/6, or 10R 3/6 that wear away relatively easily.

3. Sample and methods

We characterized the red surface coatings on 44 archaeological sherds, using laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) and Raman spectroscopy, and characterized 14 geological samples using LA-ICP-MS for comparison. Both LA-ICP-MS and Raman spectroscopy were conducted at the Archaeometry Lab at the University of Missouri Research Reactor (MURR), following methods outlined in Beck et al. (2022). LA-ICP-MS was used to determine elemental chemistry of the pigmented surface coating because laser ablation can target specific regions such as ceramic slips for analysis (Neff, 2022). Raman spectroscopy was used to determine the mineral phases present in the surface coating, a common approach in pigment identification on archaeological ceramics (Bersani and Lottici, 2016).

The archaeological sherds in the LA-ICP-MS and Raman analysis (Fig. 2) are from 7 sites: Cahokia (20 sherds); Lunsford-Pulcher, Range, Divers, and Washausen to the south of Cahokia in the southern American Bottom (13 sherds); and the Mill Creek sites of 13PM7 and 13CK21 in the northeastern Plains (11 sherds). The 14 geological samples in the LA-ICP-MS analysis (Fig. 3) were collected from nine locations in Missouri and Illinois (see Fig. 1). All samples came from Mississippian and Pennsylvanian sedimentary formations with four exceptions: one sample from the Cretaceous Owl Creek Formation, two samples of residuum from Cambrian Potosi dolomite, and one sample from iron ore in the Maramec filled sink deposit. Popelka-Filcoff and colleagues (Popelka-Filcoff, 2006; Popelka-Filcoff et al., 2007) also included the Maramec deposit in their study of potential pigment sources, although the rest of their work is south of our study area.

4. Results

Four groups—Cahokia-1, Cahokia-2, Southern American Bottom, and Mill Creek—clearly separate in a plot of the first two principal components of the LA-ICP-MS element concentration data (Fig. 4). Elements that positively drive PC1 are primarily rare earth elements (Eu, Sm, Gd, Nd, Tb, Dy, and Y), and the elements that positively drive PC2 lean toward major mineral components, like CaO, MgO, Na_2O, BaO, and Al_2O_3, along with trace elements B, Tl, Mo, and Tb.

Unlike the Mill Creek group, the three Middle Mississippi Valley groups (Cahokia-1, Cahokia-2, and Southern American Bottom) show pronounced rare earth element or barium enrichment, or both, suggestive of hydrothermal origin. Raman spectroscopy reveals peaks for barite ($BaSO_4$) in multiple samples of all three groups. Two mineral phases are unique to the Cahokia groups: ilmenite, which occurs in igneous and metamorphic rocks ($FeTiO_3$; one slip in Cahokia-1 and one slip in Cahokia-2) and spinel, which also occurs in igneous and metamorphic rocks (4 slips in Cahokia-1).

The Mill Creek group includes almost all Mill Creek Red ceramics from the northeastern Plains and two ceramics from the southern American Bottom sites. We do not suggest that the two southern American Bottom ceramics in this group were made in the Mill Creek area in Iowa; instead, we suspect that these samples cluster because they lack evidence of hydrothermal origin. The Mill Creek group probably represents more than one pigment source area. Notably, although pigments may move over long distances (Arnold, 1988), it does not appear

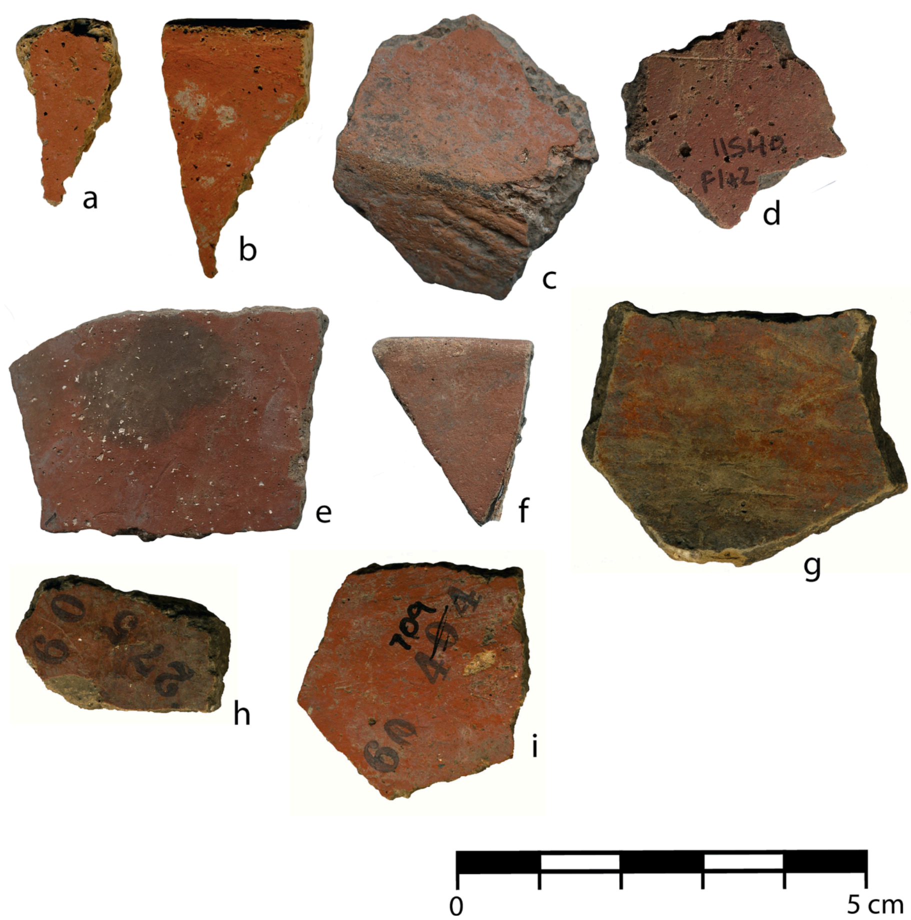

Fig. 2. Examples of analyzed red ware: (a) Cahokia, Tract 15A, F326 (MEB-219, group Cahokia-1); (b) Cahokia, Tract 15A, F203 (MEB-201, group Cahokia-2); (c) Lunsford-Pulcher, Unit 1, FS 5 (MEB-63, group Southern American Bottom); (d) Lunsford-Pulcher, F1 + 2 (MEB-64, group Southern American Bottom); (e) Washausen, F6, FS 149 (MEB-72, group Southern American Bottom); (f) Divers, F138 (MEB-68, group Southern American Bottom; image courtesy of the Illinois State Archaeological Survey); (g) 13CK21, cat 60–143-2 (MEB-1, group Mill Creek); (h) 13CK21, cat 60–275-1 (MEB-3, group Mill Creek); 13CK21, cat 60–709-1 (MEB-5, group Mill Creek).

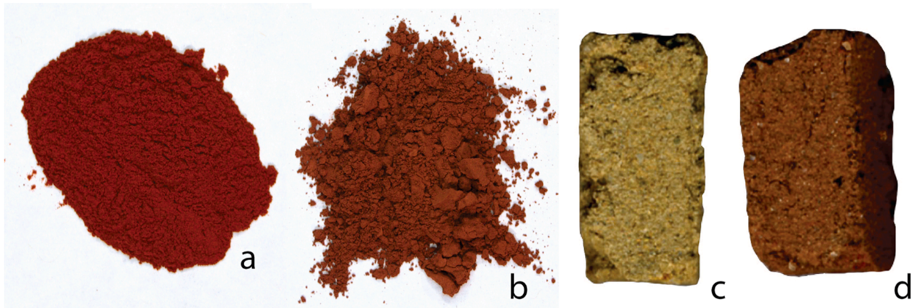

Fig. 3. Examples of analyzed geological samples: (a) residuum of Cambrian Potosi dolomite, unfired powder (MEB-229, unassigned group); (b) Maramec filled sink deposit, unfired powder (MEB-232, unassigned group); (c) Cretaceous Owl Creek Formation, unfired test tile (MEB-228, group Cahokia-2); (d) Cretaceous Owl Creek Formation, test tile fired to 800 degrees Celsius.

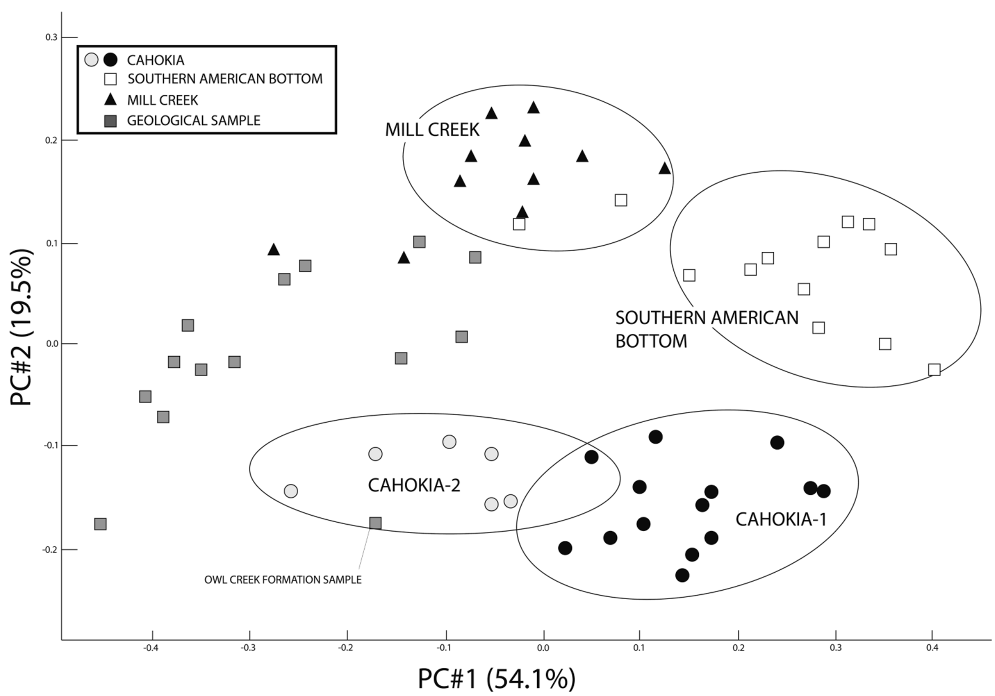

Fig. 4. Scatterplot showing the results of a principal component analysis (PCA) of the LA-ICP-MS results.

that the pigments used on the Middle Mississippi Valley red ware were transported to the northeastern Plains.

Only one of the 14 geological samples clusters with any archaeological groups: the sample from the Cretaceous Owl Creek Formation (Cahokia-2 group). This sample is located outside the Illinois-Kentucky Fluorspar District, but pronounced rare earth element enrichment in this sample suggests the deposit was affected by hydrothermal activity. We have not yet collected enough samples to distinguish between different regions of hydrothermal activity, so we are cautious about linking the Cahokia-2 ceramics to this specific deposit along the Ohio River. Notably, the sample from the Maramec filled sink deposit is low in rare earth elements as previously observed (Pierce and Popelka-Filcoff, 2023) and does not cluster with any archaeological groups.

5. Discussion

5.1. *Slip vs film*

Given the ethnographic record of Indigenous potters in North America and the abundance of sedimentary rocks in the Middle Mississippi Valley, we initially assumed that Middle Mississippi potters covered vessels with clay-rich slips made from red-firing shale. Instead, the pigments in the three Middle Mississippi Valley compositional groups (Cahokia-1, Cahokia-2, and Southern American Bottom) originated from hydrothermal deposits.

The hydrothermal pigment + liquid + binder mixture on the vessel surface is best described as a “film” rather than a “slip” when pigment clay content is low. For example, when making test tiles with collected pigments in the laboratory, we found that some hydrothermal pigment from the Maramec filled sink deposit does not work as a slip when mixed only with water; because of its low clay content, it can be washed off the underlying ceramic surface after firing to 800 degrees Celsius. In contrast, the same pigment mixed with an organic binder (4 parts pigment:1 part gum arabic) resists removal even after firing. We suggest an organic binder was a necessary addition to at least some of the hydrothermal pigments used for red ware. We cannot estimate the effect of such a binder on our chemical analyses, although it may be one of several factors that make it difficult to chemically match archaeological ceramics with the source areas for raw materials.

5.2. *Directions for future research*

More precision in source areas might reveal whether slip or film materials moved with other Ozark Highland resources or followed other paths to the Middle Mississippi Valley. Iron ore to the south of our study area can be chemically distinguished by mine (Popelka-Filcoff, 2006; Popelka-Filcoff et al., 2007), suggesting that we could distinguish between possible source areas in our study area with additional samples. Such distinctions include hydrothermal deposits in Missouri's Ozark Highlands vs. Illinois-Kentucky Fluorspar District. Within the Ozark Highlands, they include the Southeastern Missouri Iron Metallogenic Province (iron ore in Precambrian igneous rock) vs. the Filled Sink (Central) District.

Within Missouri's Ozark Highlands, people from Cahokia colonized the Big River Valley, establishing Long Mound and Village (Adams, 1949) after CE 1100 as an administrative center for mining and distribution (Koldehoff and Wilson, 2010; Milner, 1990; Pauketat, 1994). The Big River flows through the MVT Southeast Missouri Barite District or Walthall's (1981) "Potosi" galena source and just north of diabase exposures in the St. Francois Mountains (Koldehoff and Wilson, 2010). Pigment acquisition in the Big River Valley might indicate organized collection and transport routes shared with galena and diabase.

Cahokian occupation did not extend west of the Big River in the Ozark Highlands, however, and the Meramec, Bourbeuse, and Gasconade River valleys were instead occupied by local Late Woodland populations of the Maramec Spring phase (Collins and Henning, 1996; Koldehoff and Wilson, 2010; Wettstaed, 2000). Pigments acquired here might represent interactions with local groups such as Late Woodland-Early Mississippian interaction near the Maramec deposit, assuming the "red ocher outcropping… [was] the desired resource that attracted the Village Farmers so far up the [Meramec] valley" (Chapman, 1980:155).

The Leslie Mine is also west of the area occupied by Cahokian groups. It is not clear that this mine was active in the Mississippian period; the points recovered by Holmes (1903) in the Smithsonian Institution Museum of Natural History's collections are Middle-Late Archaic types.

We cannot yet rule out the possibility that pigments were acquired within the Illinois-Kentucky Fluorspar District instead of the Ozark Highlands. Pigments from the Illinois-Kentucky Fluorspar District would represent another set of interactions and movements altogether.

6. Conclusions

We find that potters in the American Bottom region of the Middle Mississippi River Valley made red-surfaced vessels using films with hydrothermal pigments rather than shale-based slips. Hydrothermal deposits only occur over 50 km away, with the closest sources in Missouri's Ozark Highlands. Further pigment characterization should yield interesting data on American Bottom resource acquisition patterns, including differences between communities of practice.

Our approach should be useful for red slip or film analyses in other regions as well. Describing slips or films as pigment + liquid + binder mixtures integrates ceramic raw materials research with pigment research and encourages us to consider shale as just one of multiple pigment options. It also highlights the potential need for binders, which hold pigment on ceramic surfaces even after firing at 800 degrees Celsius. These decisions about material choice and manipulation are part of the *chaîne opératoire* (e.g., Beck et al., 2016) and worth considering in studies of resource use and technological choice.

CRediT authorship contribution statement

Margaret E. Beck: Funding acquisition, Project administration, Supervision, Writing – original draft, Writing – review & editing. **Glen A. Freimuth:** Funding acquisition, Investigation, Resources, Writing – review & editing. **Brandi L. MacDonald:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Authors' statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript.

Appendix A. Supplementary material

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