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Surface treatment of red painted and slipped wares in the middle Yangtze River valley of Late Neolithic China: multi-analytical case analysis

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Abstract

Red slipped and painted wares (RSW and RPW) were manufactured to cook, serve, or store foods and liquids in the middle Yangtze River valley (MYRV) of China some 8500 and 7800 years ago, respectively. Their primary use narrowed down to serving and drinking in the Upper Qujialing (5300–4500 cal BP) and Shijiahe (4500–4200 cal BP) periods when initial states (*bang guo*) took shape and developed in the region. The increasing social complexity in MYRV correlated with the formation of community and neighborhood identity through rituals and socio-economic ties involving the widespread use of RSW and RPW. How the two wares were produced and used helps us understand the relationships among productive activities, identity, and social inequality in MYRV. This paper presents the first overview of RSW and RPW in the Neolithic MRYV. It introduces a multi-analytical study of the two wares—mostly dating to the Shijiahe period—unearthed from the site of Fenghuangzui in Xianyang City of Hubei Province, China. Optical microscopic examination revealed that the paint of RPW—50 μm thick on average—was applied using a brush while the slip of RSW is thinner and finer and possibly formed by self-slipping. Handheld X-ray fluorescence (hhXRF) and benchtop micro-XRF analyses ascribed the red paint or slip to iron and iron oxide. Raman and X-ray absorption fine structure analyses confirmed that iron was present in the paint or slip in the form of hematite with a poorly developed crystalline structure. Furthermore, thin-section petrography implied that different pastes were used to produce RPW and RSW, and hhXRF data indicated that the Upper Qujialing and Shijiahe pottery differ in the concentrations of five elements (Zr, Fe, Mn, Ti, and Ba), which might be helpful in future provenance studies of RSW and RPW. Our study discloses the complexity of the manufacture of RSW and RPW at Fenghuangzui. More details of RSW and RPW production and use from our ongoing project shall reveal the role of the two wares in the social dynamics of the Late Neolithic MYRV.

Keywords: Middle Yangtze River valley (MYRV), Red slipped ware (RSW), Red painted ware (RPW), Fenghuangzui, Surface treatment, Chemical composition, Thin-section petrography, X-ray absorption fine structure (XAFS)

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Graphic Abstract

Introduction

The middle Yangtze River valley (MYRV) is a crucial region for understanding social complexity and state formation in early China. This region underwent dramatic socio-political, demographic, and ideological changes in the Upper Qujialing (5300–4500 cal BP) and Shijiahe (4500–4200 cal BP) periods. Nineteen man-built walled towns have been identified in this water-abundant environment, which was rare in Neolithic East Asia, and 18 of them are dated to the Upper Qujialing to Shijiahe times [1]. Also remarkable is that beginning in the Upper Qujialing period, community and neighborhood identity, social inequality, and complex economic systems were integrated on a regional scale in MYRV, leading to the formation of, as some would call it, initial states (*bang guo*). All features above continued into the Shijiahe period with further development [e.g., 2–7]. Compared to the pottery of previous periods, the Upper Qujialing and Shijiahe red slipped or painted pottery was used mainly for serving and drinking purposes. The two wares were manufactured with considerable labor investment. Their use was distributed over a vast landscape and often associated with feasts or rituals, potentially indicating some widely shared identities and beliefs [7, 8]. In more than one aspect, how they were produced and used is essential and offers clues for understanding the relationships among productive activities, identity, and social inequality in MYRV.

Nearly a century of archaeological investigations and excavations has been carried out in MYRV; however, scientific analysis of prehistoric pottery unearthed from this region—red slipped wares (RSW) and red painted wares (RPW) in particular—has received little attention, thus contributing little to the understanding of ceramic production and its role in social dynamics. Grounded in the first overview of Neolithic red slipped and painted wares in MYRV, the present paper reports a technical investigation of the Upper Qujialing and Shijiahe RSW and RPW recently unearthed from the site of Fenghuangzui in the Xiangyang City of Hubei Province, central China. The slipping and painting of both wares are discussed based on a multi-analytical study, and so are their implications for the production of RSW and RPW. Our study is an essential start for a fuller understanding of the relations among ceramic production, identity, and social complexity in MYRV during the Neolithic times.

RSW and RPW in MYRV during the Neolithic times

Surface treatment techniques such as slipping and painting have received relatively little attention in comparison to other steps of the pottery-making process [e.g., 9, 10]. According to Vladimir J. Fewkes (1942), a 'slip' is prepared from clay, but it differs in composition, texture, and color from the clay from which the pottery is made [11]. Others also defined 'slip' as the thin-layered, fine clay applied on the vessel's surface before the vessel is painted or fired [e.g., 8, 9, 12], which may show the same color as the body fabric or a different color [13: 175]. Often, slip can be identified visually by the thin layer, finer texture, and distinct color contrast to the vessel body [14: 149–150]. On the other hand, paint refers to the inorganic (mineral) pigment applied on the vessel to create, for example, motifs and patterns [8, 12]. An organic dye can sometimes be used as paint before or after firing [e.g., 14, 15].

The present paper focuses on the Neolithic red slipped and painted wares unearthed from MYRV. It began with an overview of RSW and RPW through the Pengtoushan (8500–7800 cal BP) to Shijiahe (4500–4200 cal BP) periods. This is the first overview of archaeological discoveries of the two wares in MYRV. Table 1 lists the primary regional cultures during which RSW and RPW were produced and used in the Neolithic middle Yangtze River valley.

Table 1 Chronological sequence and major cultures in the middle Yangtze River valley during the Neolithic times. Modified from Table 2 in Shan et al. (2021)

Culture/period	Dates (cal BP)
Shijiahe 石家河	4500–4200
Upper Qujialing 屈家岭上层	5300–4500
Late Daxi 大溪晚期, Lower Qujialing 屈家岭下层	5500–5300
Early Daxi 大溪早期, Youziling 油子岭	5900–5500
Tangjiagang 汤家岗	6900–5900
Chengbeixi 城背溪, Lower Zaoshi 皂市下层	7800–6900
Pengtoushan 彭头山	8500–7800

RSW (red slipped ware)

As early as in the Pengtoushan period (8500–7800 cal BP), RSW was already widespread in MYRV [16], with the red slip being applied on cooking vessels (e.g., *guan*-jar, *fu*-cauldron, and *zhizuo*-pot support) and serving vessels (e.g., *pen*-basin, *pan*-plate, and *bo*-bowl) [17]. In the subsequent Lower Zaoshi/Chengbeixi period (7800–6900 cal BP), most utilitarian potteries had a red, thin-layered slip, and many Chengbeixi RSW were either *fu*-cauldron or *pan*-plate [18]. RSW continued to be produced and used in the Tangjiagang period (6900–5900 cal BP). Most fine-paste and coarse-paste pottery at the time—including *fu*-cauldron, *weng*-urn, *pen*-basin, and *dou*-stemmed bowl—had a red slip on the exterior surface of the vessel [19]. Pottery of more diverse shapes and forms was noticed for the Daxi period (5900–5300 cal BP), which consisted of (1) cooking vessels such as *fu*-cauldron and *guan*-jar; (2) serving vessels such as *dou*-stemmed bowls, *pan*-plate, *wan*-bowl, and *bo*-bowl; and (3) drinking vessels such as *hu*-jar and *ping*-vase. As noticed in the Tangjiagang period, most of the Daxi pottery had a red slip on its exterior surface [20]. RSW was also popular in the Youziling period (5900–5500 cal BP), in the form of *ding*-tripod and *fu*-cauldron for cooking foods and *pan*-plate and *pen*-basin for serving purposes [21, 22].

A significant shift was noticed in the Lower Qujialing period (5500–5300 cal BP) when red pottery decreased in quantity and gave way to gray and black wares. Only a few RSW date to this period, including *ding*-tripod, *gui*-tureen, *dou*-stemmed bowl, *guan*-jar, *weng*-urn, and *fu*-cauldron [23, 24]. This tendency continued through the Upper Qujialing (5300–4500 cal BP) to the Shijiahe period (4500–4200 cal BP), when a smaller proportion of the pottery had a (red) slip. The Upper Qujialing RSW consists of *ding*-tripod (cooking), *guan*-jar (storage), and *hu*-jar and *bei*-cup (drinking) [24, 25]; in contrast, *bei*-cup of the Shijiahe period most often tends to have a red slip, and its contextual use usually indicates feasts or ritual events [26, 27].

To conclude, RSW was manufactured and widely used in the earliest Neolithic culture of MYRV mainly for food preparation and serving. By the Daxi period, RSW was used for cooking, serving, storage, and drinking purposes, indicating that its use context greatly expanded and so did its function. Beginning in the Lower Qujialing period, the importance of RSW decreased and the red slip was applied only on a few known vessel shapes and forms. RSW were used as drinking vessels more often than other types of vessels in the Shijiahe period. Our observations above are very descriptive due to the lack of quantitative data on pottery production and use. However, a pattern seems recognizable that over time, RSW gave way to gray and black pottery and its primary use narrowed down eventually to mainly serving and drinking.

RPW (red painted ware)

In MYRV, red painted ware (RPW) was manufactured and used in small quantities as early as in the Lower Zaoshi/Chengbeixi period [18]. Reddish pottery was applied with a red or white slip but also painted to create a red stripe pattern at the time. Typical RPW was the ring-foot *pan*-plate. Occasionally, some Chengbeixi potteries were painted to form a stripe or string pattern [28]. During the Tangjiagang period, red or brown paint was often applied on *guan*-jar and *dou*-stemmed bowls to create dot, grid, swirl, and wave patterns [19].

The subsequent Daxi culture is well-known for its painted pottery which shows strong regional styles. During this period, black, red, and ocher paints were used together for the first time in MYRV. The paint was often applied on the rim or shoulder of cooking vessels *guan*-jar and *fu*-cauldron, but it was also present on other cooking, serving, and drinking vessels (*ding*-tripod, *pen*-basin, *bei*-cup, *ping*-vase, and *hu*-jar) [20]. The paints were applied to create the wide stripe, link-hooked, wave, grid, dot, and other patterns [20]. Painted potteries of the Youziling culture are also well developed in MRYV, mainly in the form of *wan*-bowl or *bei*-cup for serving or drinking purposes. Black paint was most popular during the Youziling period but the red painted pottery does exist. Typical patterns for the Youziling painted pottery (including RPW) include stripes, diamond-shaped grids, horizontal stripes, dots, slanted string, or curly string patterns [21, 22].

In the Lower Qujialing period, most painted pottery (including RPW) was *wan*-bowl. A few *hu*-jar, ceramic spindle whorls, and clay balls were painted black. Red

paint was usually applied on the rim or bottom of some vessels [23, 24]. Most of the Upper Qujialing painted pottery (e.g., *wan*-bowl, *bei*-cup, and *hu*-jar) used black pigment but a few ceramic spindle whorls and *bei*-cup were painted with red pigment. RPW consists of mainly *wan*-bowl, *hu*-jar, *bei*-cup, and spindle whorls. Black or red paint was applied to create wide stripe, grid, swirl patterns, and short-straight or arched lines [24, 25]. In the Shijiahe period, red or black paint was applied on *bei*-cup, *hu*-jar, and spindle whorls, just as in the Upper Qujialing period; however, RPW accounted for a smaller portion of the pottery at this time. Red or black paint was applied to create the grid, stripe, and shading patterns [26, 27].

Overall, RPW dates younger than RSW in MYRV and the red paint was often used along with the black or white paint. Like RSW, RPW decreased in frequency over time and their primary use gradually narrowed down to serving and drinking. The Upper Qujialing ceramic spindle whorl is an exception and interesting to investigate: spindle whorls were tools related to the spinning and threading of fibers and the patterns or motifs on them conveyed symbolic meanings. By the Shijiahe period, only a tiny portion of the pottery was painted, consisting of about the same vessel forms as in the Upper Qujialing period, but the drinking vessels dominated RPW. Again, our descriptive statements about RPW will need to be checked with site-specific quantitative data in future studies.

Previous analytical studies of painted and slipped wares

Since the 1980s, many analytical studies have investigated the pigments or the slip applied on Neolithic pottery from the Yellow River valley, a region well-known for painted and slipped pottery (e.g., the Yangshao and Majiayao pottery). RSW and RPW of MYRV have only been occasionally studied, which mostly focused on the Daxi period. Analytical approaches did not investigate the Upper Qujialing pottery until very recently and only the black wares, slipped or painted, were analyzed and discussed [29]. Our discussion below focuses on MYRV and whenever possible, plays an emphasis on RSW and RPW.

Li and Huang conducted a chemical compositional analysis of 37 sherds of the Daxi culture pottery unearthed from the Guanmiaoshan site in Zhijiang County of southern Hubei [30]. Seven were sampled from slipped and/or painted wares, and five were RSW or RPW. Using wet chemistry, Li and Huang confirmed that both the red and brown paint are rich in iron (Fe) while the black and brown-black paint are explained by iron and manganese (Mn). Li and Huang suggested that the Daxi potters made the black paint from Fe–Mn nodules procured locally and that they may have mixed the local red clay with Fe–Mn nodules to make the brown paint. This was the first scientific investigation of Neolithic RSW and RPW in MYRV.

Focusing on Zhongbaodao, another Daxi culture site discovered in Yichang City of western Hubei, Yu et al. analyzed 28 RSW and RPW sherds as well as ten others from gray and black-burnished pottery, using an Energy Dispersive X-ray fluorescence analyzer (EDXRF), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDS), and Raman spectroscopy [31]. Principal component analysis of the chemical compositional (EDXRF) data suggests that RPW and gray pottery were both locally produced but likely used different clays. SEM–EDS results indicate that the black paint is rich in iron (Fe) and manganese (Mn). Raman analysis confirms that raw umber ($Fe_2O_3 \cdot xMnO_2$) is present in the black paint. The red slip is also rich in iron and could have been prepared from fine clay rich in iron oxide.

Scientific methods and techniques in MYRV have investigated only a few RSW and RPW; however, the topic has been extensively explored in other regions of China, especially the upper and middle Yellow River valley. For example, Zhou et al. carried out spectroscopic analyses of the pigments on pottery of the Yangshao culture. They argued that the red color is ascribed to iron (Fe) while the black color is ascribed to iron (Fe) and manganese (Mn) [32]. Ma and Li investigated 25 vessel sherds of the Yangshao, Miaodigou, Banshan-Machang, Majiayao, and Qijia cultures in Gansu of northwestern China [33]. Compositional analysis and phase identification by X-ray fluorescence (XRF) and X-ray diffraction (XRD) confirmed that the red paint was prepared from hematite (α-Fe_2O_3) while the black paint was prepared from magnetite (Fe_3O_4) and manganese oxide (MnO). Wang et al. analyzed the painted Miaodigou pottery unearthed at the Bancun site in Henan Province of central China. XRF and XRD confirmed that the red paint was prepared from hematite (α-Fe_2O_3) while the black paint was prepared from maghemite (γ-Fe_2O_3) [34].

The case studies above, and others not reviewed here due to the word limit [e.g., 35–38], disclose to us the chemical and mineralogical compositions of the red paint/slip most commonly seen on painted and slipped pottery of Late Neolithic China. This information is valuable for understanding the surface treatment of RSW and RPW unearthed in MYRV.

Materials and methods

We are particularly interested in understanding how the surface treatment was applied on wares to form a red slip or paint. This information is important because it (1) discloses the ceramic production and technological style, and (2) helps us understand why specific wares were

more often slipped and/or painted than others. The present paper focuses on the red slipped and painted wares (RSW and RPW) recently unearthed from the site of Fenghuangzui in MYRV. We emphasize the Shijiahe period but also included a few sherds from the Upper Qujialing period for initial comparison.

The Fenghuangzui site and its significance

The Fenghuangzui site (111° 59′ 20.39″ N, 32° 14′ 42.67″ E) refers to a Late Neolithic walled settlement in the middle Hanshui River valley, which is also close to the southern edge of Nanyang Basin, in central China. Figure 1 shows the geographic location of the Fenghuangzui site in MYRV and the layout of the walled settlement, revealed by shovel probes, at the site.

As shown in Fig. 1a, the walled settlement at Fenghuangzui is located the furthest away from other contemporaneous walled settlements in MYRV. Archaeological evidence suggests that this walled settlement was on the periphery of the Upper Qujialing and Shijiahe cultures because the two cultures took shape and developed on the Jianghan Plain and neighboring regions far to the south of the Fenghuangzui site.

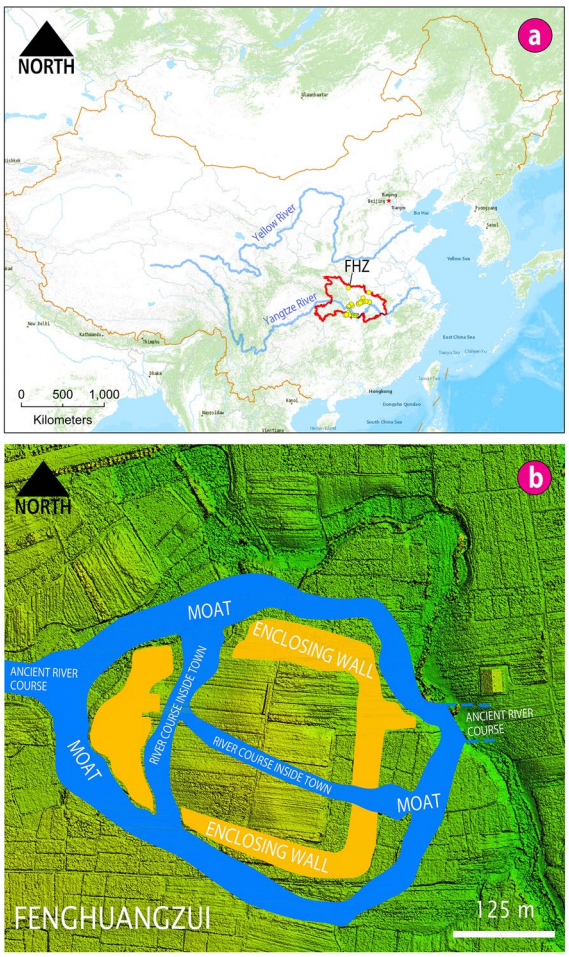

Fig. 1 **a** The geographic location of the site of Fenghuangzui in MYRV and **b** the layout of the walled town revealed by shovel probes at the site. Red, thick lines on the map delineate the provincial boundary of Hubei

Regarding the modern administrative division, the site of Fenghuangzui is spread over two villages (Qianwang and Yanying) of the Xiangzhou District in Xiangyang City of Hubei Province. The site was discovered in a national survey on cultural heritage in 1958 but subject to no proactive excavation until 2016, when local archaeological units carried out a 250-m^2 test excavation in the northeastern part of the site (surveys carried out later on in the region confirmed that this excavation area lied beyond the walled settlement). Pottery assemblages from the 2016 excavation, and further finds from a field survey by shovel probes in 2018, helped identify an approximately square-shaped Neolithic walled town at the site, with a walled town size of 15 ha and surrounded by a moat (see Fig. 1b).

More proactive, extensive excavations led by the Wuhan University's Department of Archaeology began at the site of Fenghuangzui in August 2020, revealing unexpectedly important features (an enclosing wall, a moat, houses with plaster walls, kilns, burials, large pits supposedly related to feasting activities, and so on) and finely crafted artifacts (i.e., jade and turquoise ornaments, red slipped and painted *bei*-cups, and black-burnished wares) within the walled town area. Pottery typology suggests human occupation at the site over three cultural periods: Upper Qujialing; Shijiahe; and Meishan.

Charcoal samples were collected from ash pits with precise stratigraphic contexts for accelerator mass spectrometry (AMS) radiocarbon dating, and the results are shown in Table 2 and Fig. 2. The town, as Fig. 2 suggests, was constructed and occupied mainly between 5300 and 3900 cal BP, corresponding to three significant cultural periods identified for the middle Yangtze River valley—Upper Qujialing (5300–4500 cal BP), Shijiahe (4500–4200 cal BP), and Meishan (4200–3900 cal BP) [39]. The absolute dates perfectly match the relative dating results by pottery typological analysis.

Fenghuangzui is one of the few walled towns in MYRV that have been well radiocarbon dated. In addition, the dating results placed the Fenghuangzui site among the earliest walled towns in present-day Xiangyang City, which could well mean an early form of urban planning.

RSW and RPW unearthed from Fenghuangzui

Two seasons (2020 to 2021) of excavations have been carried out in the walled settlement at the site of

Table 2 AMS 14C dating results of 16 charcoal samples

Lab. No.	Sample code	AMS 14C age (yr BP)	Cal radiocarbon age (2σ range, cal yr BP)
Beta-577497	2020XRD4TG2H13(1)(No. 4-1)	3850 ± 30	4407–4218 (75.6%)
			4209–4155 (19.8%)
Beta-577498	2020XRD4TG2H13(1)(No. 4-2)	3880 ± 30	4416–4235 (94.1%)
			4196–4185 (1.3%)
Beta-577499	2020XRD4TG2H13(2)(No. 10)	3880 ± 30	4416–4235 (94.1%)
			4196–4185 (1.3%)
Beta-577500	2020XRD4TG2H13(2)(No. 11)	3870 ± 30	4414–4227 (89.6%)
			4200–4178 (4.4%)
			4169–4160 (1.4%)
Beta-577501	2020XFD4T1551C50	3890 ± 30	4418–4240 (95.4%)
Beta-577502	2020XFD4T1551B50	3910 ± 30	4422–4248 (95.4%)
Beta-597333	2020XFD4TG7(17)	3640 ± 30	4008–3868 (76.4%)
			4084–4031 (18.0%)
			3858–3849 (1.0%)
Beta-597334	2020XFD4TG7(21)	3740 ± 30	4156–3984 (90.5%)
			4226–4204 (4.9%)
Beta-597335	2020XFD4TG7(26)	4430 ± 30	5060–4873 (67.7%)
			5277–5176 (23.5%)
			5133–5104 (4.2%)
Beta-597336	2020XFD4TG3H7(1)	4240 ± 30	4861–4806 (61.9%)
			4756–4701 (27.7%)
			4672–4651 (5.8%)
Beta-597337	2020XFD4TG3H110	4310 ± 30	4960–4834 (95.4%)
Beta-597338	2020XFD4TG2H137	4120 ± 30	4725–4526 (69.0%)
			4817–4751 (26.4%)
Beta-597339	2020XFD4TG2(8)	4330 ± 30	4970–4840 (95.4%)
Beta-597340	2020XFD4TG1(11)	4370 ± 30	4983–4856 (85.4%)
			5039–5004 (10.0%)
Beta-597341	2020XFD4T1548H17(3)	3980 ± 30	4525–4403 (93.0%)
			4321–4305 (1.4%)
			4367–4357 (1.0%)
Beta-597342	2020XFD4T1548H17(9)	3960 ± 30	4451–4349 (52.5%)
			4520–4464 (32.6%)
			4332–4296 (10.3%)

Fenghuangzui, which produced the pottery (or sherd pool) that the present paper is based on.

Pottery artifacts are the most abundant, followed by stone tools. A few artifacts of bone, jade, and turquoise are also unearthed. Pottery dating to the Upper Qujialing period are characterized by *ding*-tripod (a cooking vessel), *guan*-jar (a storage vessel), *shuangfudou*-double bellied stemmed bowl and *hongdingbo*-red-rimmed bowl (both for serving purpose), and drinking vessels such as a tall, ring-footed cup. By contrast, pottery of the Shijiahe period shows a greater diversity in shape and form, including vessels for cooking (*ding*-tripod, *yan*-steamer, supporting base), storage (high-necked *guan*-jar and medium-mouthed *guan*-jar), serving (ring-footed *pan*-plate, *pen*-basin), and drinking (*gui*-tripod pitcher and red cup) purposes. Although nearly all pottery we have examined has a utilitarian function, small, handmade clay bird, turtle, dog, caprine, and elephant figures were recovered, which are the physical representations of man's sense of nature and may be used as toys for fun.

Many Upper Qujialing and Shijiahe pottery vessels unearthed at Fenghuangzui do not have a paint or slip, and those with a slip or paint are mainly serving or

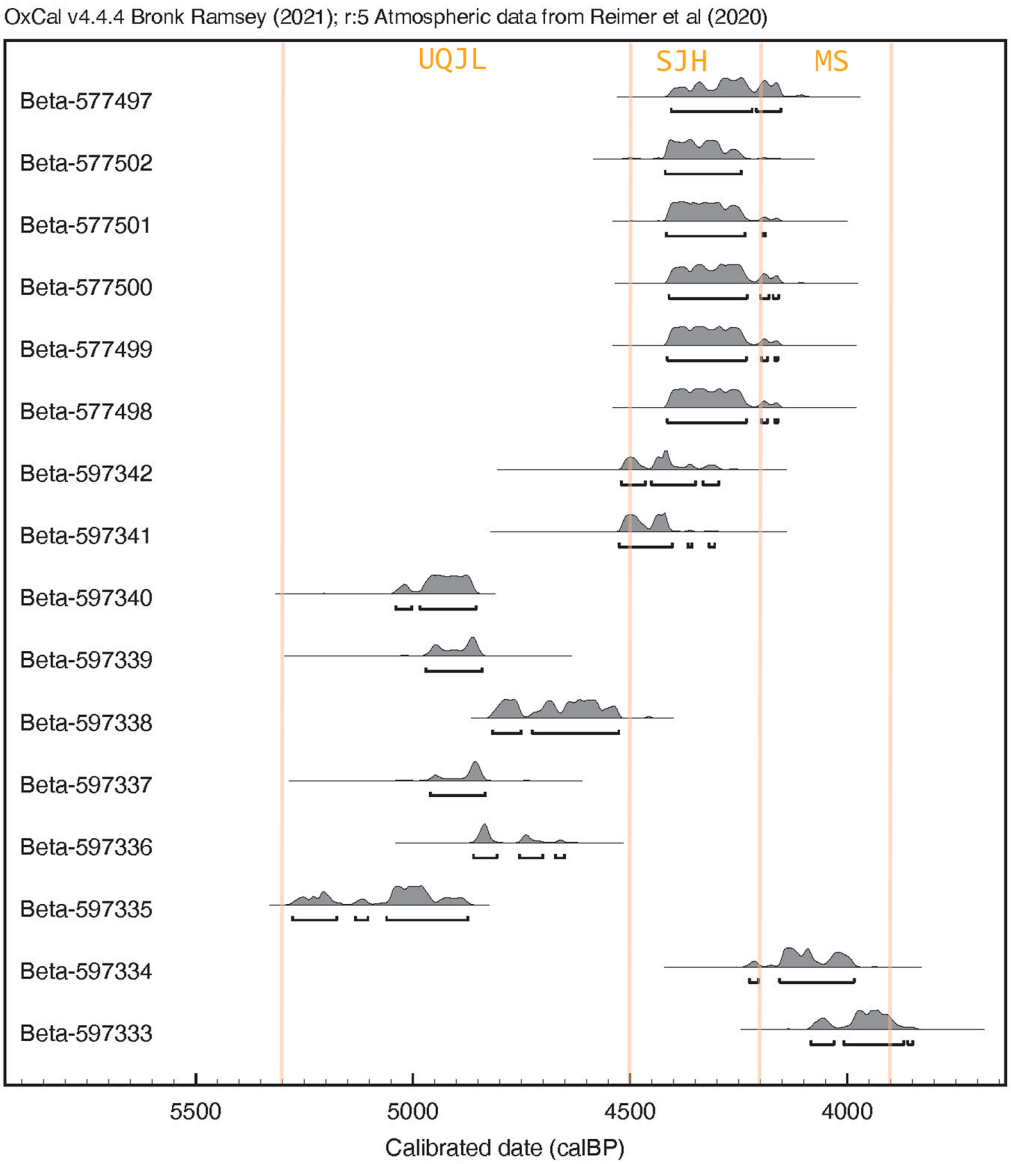

Fig. 2 AMS 14C dating results of the 16 charcoal samples collected from the 2020 and 2021 field excavations at the Fenghuangzui site

drinking vessels such as *bo*-bowl, *hu*-jar, and red *bei*-cups (see Fig. 3 for some red slipped and painted *bei*-cups and Fig. 4 for some fragments). "Painted pottery," as we use it to describe the pottery from Fenghuangzui, refers to the pottery that was brushed with a red or black pigment before being fired, to create red or black stripe pattern on the exterior surface of the vessel after the firing. A slipped surface is characterized mainly by its reddish color against the body fabric (usually whitish or orange) and its thinner layer and finer texture.

The red slipped and painted wares (RSW and RPW) unearthed at Fenghuangzui are essential in two aspects. First, they were less abundant but were manufactured with considerable labor, time, and a higher level of crafting skills compared to other utilitarian vessels. This is especially clear in serving (e.g., *wan*-bowl) and drinking (red *bei*-cups and *hu*-jar) vessels. Second, slipping/painting has been noticed on pottery with a slightly whitish body fabric and a form-deduced function of serving or drinking. We propose that the slipped

Fig. 3 Red slipped ware (**a** fully applied with a red slip) and red painted ware (**b**–**f** partially applied with stripes of a red paint), both being bei-cup unearthed from the site of Fenghuangzui in 2020–2021 excavations

or painted pottery was associated with identity, status, or feasts at the household level and beyond. By the time this study was carried out, most RSW and RPW were unearthed from important features such as ash pits H13 and H17. Both pits contained large amounts of fine pottery, jade ornaments, charred rice and millet grains, and animal bones related to food sharing and feasts. This strengthens our argument above.

Sampling strategy

Our sampling targets the pottery that has a red slip or paint. Sample selection was conducted at the Fenghuangzui Conservation Center from October to December 2021. Vessels (or vessel sherds) were selected mainly from the Shijiahe remains because they were most abundant in this study. But we managed to include a few Upper Qujialing vessels, too.

The RSW and RPW we selected were unearthed from important features such as ash pits H13, H17, and H166, and burial M3. We had a sample size of 20, all of which are complete or fully restored vessels and retain the red paint and/or slip (see Table 3 for sample information). Our sample consists of 15 Shijiahe pottery and five Upper Qujialing pottery. One *wan*-bowl, two *hu*-jar, and 17 *bei*-cup were selected for analysis, all being vessels to serve food or liquids.

Our project prefers non-destructive analysis for complete or fully restored vessels, for which handheld X-ray fluorescence analyzer was applied. But we also select sherds for destructive analysis to provide complementary information whenever necessary. Specifically, we selected three sherds (two belonging to RPW, labeled as RPW01 and RPW02; and one to RSW, labeled as RSW01) for microscopic examination, and two of them (RPW02 and RSW01) were analyzed by micro-XRF analysis, Raman spectroscopy, and X-ray-absorption fine-structure. In addition, one RPW sherd and one RSW sherd were selected for thin-section petrography. Details of the five sherds for destructive analysis are described along each analytical method.

Optical microscopy (OM)

The exterior surfaces and cross-section of three sherds (RPW01, RPW02, and RSW01) were examined under an Olympus SZX7 stereo microscope, to reveal the microstructure and manufacture of the slip or paint. The sherds, belonging to *bei*-cup or *hu*-jar, were unearthed from ash pit H17 that were very likely related to feasts. They were selected because they show characteristics typical of RSW or RPW.

Fig. 4 Three RPW and RSW sherds selected for destructive analysis in the present study

Table 3 Information on the 20 complete or fully restored vessels investigated in the present study

Lab No.	Test unit	Form	Fabric color	Culture/period
FHZ01	TG2H13②	*bei*-cup	Reddish	Shijiahe
FHZ02	TG2H13②	*bei*-cup	Reddish	Shijiahe
FHZ03	TG2H13②	*bei*-cup	Reddish	Shijiahe
FHZ04	TG2H13②	*bei*-cup	Reddish	Shijiahe
FHZ05	T1748M3	*bei*-cup	Whitish	Shijiahe
FHZ06	T1548H17①	*bei*-cup	Whitish	Shijiahe
FHZ07	T1548H17①	*bei*-cup	Reddish	Shijiahe
FHZ08	T1548H17⑨	*bei*-cup	Reddish	Shijiahe
FHZ09	T1548H17⑥	*bei*-cup	Reddish	Shijiahe
FHZ10	T1548H17⑥	*wan*-bowl	Reddish	Shijiahe
FHZ11	T1548H17⑥	*hu*-jar	Reddish	Shijiahe
FHZ12	TG2S16	*hu*-jar	Orange	Upper Qujialing
FHZ13	T1651⑧	*bei*-cup	Reddish	Shijiahe
FHZ14	T1847⑤	*bei*-cup	Whitish	Upper Qujialing
FHZ15	T1748H25②	*bei*-cup	Whitish	Shijiahe
FHZ16	T1847H166③	*bei*-cup	Reddish	Upper Qujialing
FHZ17	T1847H166③	*bei*-cup	Whitish	Upper Qujialing
FHZ23	T1548H17⑦	*bei*-cup	Reddish	Shijiahe
FHZ24	T1651H180	*bei*-cup	Reddish	Shijiahe
FHZ32	T1847H166③	*bei*-cup	Reddish	Upper Qujialing

Handheld X-ray fluorescence analysis (hhXRF)

A Thermo Fisher Scientific Niton XL3+ 950 handheld X-ray fluorescence (hhXRF) analyzer was used to collect compositional data from the paint, the slip, and the sherd's plain surface. The hhXRF analyzer, in comparison to other analytical methods for compositional analysis, provides semi-quantitative data in a short time and can be carried out in situ and with a relatively large number of samples. In archaeological studies, the hhXRF analyzer is useful especially for studying pottery, metal, obsidian, rock, and stone artifacts.

The analyzer was equipped with a 50 kV X-ray tube (max. 50 kV, 100 μA, 2 W) with an Ag anode and a Large Drift Detector (LDD) with an active area of 7 mm^2 fitted with a polymer winder (MOXTEK AP 3.3 film), which provides superior X-ray transmission in the low-energy range down to the Mg Kα. The X-ray beam spot focusing on the sample was about 3 mm in diameter. The detection limits for analyzing sherds were based on a 90-s total analysis time (30 s for the high filter; 30 s for the low filter; and another 30 s for the main filter) in the Soil mode.

We collected the hhXRF readings from two or more spots on each complete or fully restored RSW or RPW (sample information shown in Table 3). Only the best two hhXRF readings were kept to represent the sherd's most likely chemical composition. Although the hhXRF reading consists of concentrations of up to 33 elements, most elements are excluded from further analysis for their considerably large relative standard deviation. Following the protocol described elsewhere [40, 41], the final compositional dataset consists of ten major, minor, and trace elements (zirconium, strontium, rubidium, zinc, iron, manganese, titanium, calcium, potassium, and barium), whose concentrations remain stable and show an overall relative error of less than 15%.

We aimed to collect hhXRF data from the paint/slip and the body for the 20 vessels. But this data collection strategy failed to work on three of the 20 vessels because only the paint/slip or the body of the three vessels can be analyzed by hhXRF. These three vessels were thus excluded from further discussions. Table 4 shows the concentrations of the ten elements for the 17 RSW or RPW.

Micro-X-ray fluorescence (μ-XRF)

The hhXRF data can be best interpreted as the averaged concentration of elements within a small area, and they may reveal little information regarding the compositional variations at a small scale. In addition, hhXRF does not detect light elements such as carbon (C), oxygen (O), sodium (Na), and magnesium (Mg), and it has to be performed under vacuum conditions if elements such as aluminum (Al), silicon (Si), sulfur (S), and prosperous (P) are to be determined [42]. The microanalysis offers more accurate and conclusive information on elemental compositions and thus on the coloring mechanism.

We selected two vessel sherds (RPW02 and RSW01) and performed the micro-XRF (μ-XRF) analysis on their exterior surface and cross-section. The microanalysis was carried out on a benchtop Orbis micro-XRF (μ-XRF) elemental analyzer (EDAX, Germany) with a Rhodium source operating under a vacuum. The spot size of the X-ray beam used for the analysis is about 1 mm. The operating voltage of the X-ray tube is 50 kV and the tube current is 800 mA, and the dead time is about 20% of the total analysis time.

Thin-section petrography

Two additional vessel sherds (one from RPW and the other from RSW, sample images not shown here) were also sampled from ash pit H17 for thin-section petrography. They were cut, mounted, polished, and prepared into 30 μm (0.03 mm) thick slices. Thin sections were examined under a Leica DMS1000 digital microscope, with 6× to 300× magnifications. Identification of minerals was carried out on the basis of the optical properties of the mineral (such as cleavage, steak, interference color, and relief). As the two sherds are fine-paste, thin-section

Table 4 hhXRF data (concentrations of ten elements) of the 17 RSW and RPW

Lab No.	Spots	Zr	Zr_E	Sr	Sr_E	Rb	Rb_E	Zn	Zn_E	Fe	Fe_E	Mn	Mn_E	Ti	Ti_E	Ca	Ca_E	K	K_E	Ba	Ba_E
FHZ01	B	197.0	5.0	232.4	4.8	104.2	3.8	108.3	9.6	3.3	0.025	396.5	50.2	0.5	0.010	0.6	0.015	2.3	0.034	1692.5	32.5
FHZ01	P/S	191.6	4.9	245.9	4.8	101.9	3.7	108.9	9.5	3.8	0.027	431.8	50.7	0.5	0.011	0.8	0.018	2.5	0.038	1580.0	31.2
FHZ02	B	203.8	5.0	180.2	4.3	77.1	3.3	44.1	7.5	2.0	0.020	165.6	42.2	0.4	0.007	0.4	0.010	1.2	0.019	1195.5	32.9
FHZ02	P/S	211.8	4.9	219.9	4.5	78.1	3.2	53.2	7.5	2.7	0.022	217.5	42.6	0.5	0.011	0.9	0.017	1.8	0.030	1144.5	28.1
FHZ03	B	192.9	5.0	194.7	4.5	105.1	3.9	110.4	9.9	3.2	0.026	1212.6	68.5	0.5	0.010	0.9	0.017	2.3	0.034	1466.6	31.1
FHZ03	P/S	190.2	4.8	184.7	4.3	110.6	3.9	113.3	9.8	4.1	0.028	409.1	51.2	0.5	0.011	0.9	0.019	2.4	0.037	1162.1	29.3
FHZ04	B	193.8	5.2	174.2	4.4	94.2	3.8	76.3	9.3	3.0	0.026	475.8	55.4	0.4	0.008	1.2	0.017	1.7	0.026	1157.7	34.6
FHZ04	P/S	209.7	5.4	163.0	4.3	107.7	4.1	85.3	9.6	4.1	0.031	479.2	57.4	0.4	0.011	3.3	0.032	2.1	0.036	1031.4	28.9
FHZ05	B	140.8	4.3	288.6	4.9	132.4	3.9	101.7	8.7	1.9	0.018	421.9	46.0	0.6	0.010	1.0	0.016	2.2	0.030	1470.4	29.7
FHZ05	P/S	149.2	4.3	283.7	4.9	135.6	4.0	109.2	8.9	2.5	0.020	118.3	37.4	0.6	0.012	1.4	0.020	2.2	0.032	1419.5	29.2
FHZ06	B	153.5	4.2	276.7	4.7	81.5	3.1	76.5	7.8	1.9	0.018	176.4	37.9	0.5	0.010	2.1	0.021	1.7	0.026	1239.0	28.4
FHZ06	P/S	155.5	4.2	260.4	4.6	83.0	3.1	76.1	7.7	2.6	0.021	128.2	37.0	0.5	0.011	1.6	0.021	1.9	0.030	1049.8	27.0
FHZ07	B	204.0	4.8	164.5	4.0	100.5	3.6	71.4	8.2	2.4	0.021	560.2	51.7	0.5	0.010	1.1	0.016	1.8	0.027	1116.3	29.8
FHZ07	P/S	201.2	4.7	156.0	3.8	107.3	3.7	73.8	8.2	2.8	0.022	373.1	47.1	0.5	0.010	2.2	0.024	1.8	0.029	1152.5	29.9
FHZ08	B	186.2	5.1	209.7	4.8	96.6	3.9	91.2	9.6	2.1	0.021	247.7	47.2	0.5	0.009	1.4	0.018	2.0	0.028	1035.5	28.2
FHZ08	P/S	195.5	4.6	231.0	4.4	94.3	3.3	82.9	8.1	2.7	0.021	229.9	40.7	0.5	0.011	2.4	0.026	2.4	0.035	937.1	26.4
FHZ10	B	159.4	4.2	141.2	3.5	138.4	3.9	82.2	8.1	3.2	0.023	336.6	43.5	0.6	0.011	2.7	0.028	2.8	0.038	465.6	24.2
FHZ10	P/S	143.7	4.1	189.0	4.0	127.7	3.8	98.5	8.5	3.3	0.023	304.1	42.9	0.5	0.011	2.4	0.026	2.6	0.036	599.4	25.4
FHZ11	B	204.8	4.9	200.6	4.4	100.2	3.6	105.0	9.2	2.8	0.023	1817.4	75.5	0.5	0.010	0.8	0.016	1.9	0.029	1276.3	30.2
FHZ11	P/S	205.0	4.7	246.0	4.6	100.4	3.5	96.3	8.6	3.2	0.023	1598.2	65.8	0.4	0.011	3.9	0.034	1.8	0.032	1185.8	28.0
FHZ12	B	219.2	4.6	298.2	4.7	98.1	3.2	68.1	7.2	1.5	0.015	275.9	38.3	0.6	0.010	1.7	0.019	1.9	0.027	524.0	23.2
FHZ12	P/S	225.1	4.6	246.6	4.3	96.1	3.2	77.7	7.5	1.8	0.016	480.8	43.4	0.6	0.010	1.2	0.017	1.9	0.027	561.3	23.7
FHZ13	B	206.1	4.9	185.4	4.3	98.5	3.7	88.0	8.9	3.0	0.024	534.3	53.2	0.5	0.010	1.0	0.017	2.6	0.034	1626.5	33.0
FHZ13	P/S	203.7	5.0	194.6	4.4	101.9	3.8	102.3	9.5	4.2	0.029	666.5	58.1	0.4	0.012	1.6	0.024	2.8	0.040	1452.1	31.7
FHZ14	B	260.7	4.9	173.8	3.8	85.3	3.2	61.9	7.4	1.6	0.016	527.6	47.9	0.5	0.009	1.0	0.015	1.9	0.027	1096.9	27.5
FHZ14	P/S	248.4	5.0	186.4	4.1	83.7	3.3	69.3	7.9	1.8	0.018	690.0	52.8	0.5	0.009	1.0	0.016	2.1	0.029	1145.1	27.5
FHZ15	B	231.8	4.7	247.5	4.4	79.2	3.0	74.7	7.6	2.0	0.018	284.8	40.9	0.7	0.011	1.1	0.017	2.4	0.032	1319.6	28.3
FHZ15	P/S	240.5	4.9	195.0	4.1	80.2	3.1	78.9	8.0	2.4	0.020	294.7	42.8	0.7	0.011	1.2	0.019	2.3	0.033	1158.0	27.4
FHZ16	B	251.2	5.1	119.0	3.4	103.6	3.7	95.3	9.0	2.8	0.023	604.6	53.9	0.6	0.010	1.9	0.023	2.1	0.032	751.7	26.6
FHZ16	P/S	246.6	5.1	128.5	3.6	101.6	3.7	82.5	8.6	3.3	0.025	651.3	55.5	0.4	0.010	4.4	0.034	2.1	0.034	885.8	28.2
FHZ17	B	247.2	5.8	185.2	4.7	91.1	3.9	92.4	9.9	1.5	0.019	961.1	68.9	0.5	0.009	1.1	0.016	2.1	0.027	1250.2	28.4
FHZ17	P/S	252.2	5.1	194.5	4.2	87.8	3.3	98.2	8.8	1.7	0.017	1303.6	65.9	0.5	0.009	0.9	0.015	2.0	0.028	1222.4	27.9
FHZ32	B	217.4	5.9	180.2	4.9	77.6	3.8	87.6	10.5	2.0	0.023	2491.0	107.6	0.4	0.008	1.3	0.017	1.7	0.025	1143.6	31.0
FHZ32	P/S	235.3	5.0	184.9	4.1	88.4	3.4	85.6	8.5	2.4	0.021	1994.9	78.5	0.5	0.010	1.0	0.017	2.2	0.032	1082.7	28.0

*(1) The concentrations of iron (Fe), titanium (Ti), calcium (Ca), and potassium (K), as well as their measurement errors (represented as Fe_E, Ti_E, Ca_E, and K_E), are in wt% while others in ppm; (2) 'B' in spots refers to the body fabric of the sherd, ' P/S' to the red paint or slip

petrography focuses on the silt- and sand-sized mineral inclusions occurring naturally in the clay-rich sediments [43].

Raman spectroscopy

Raman analysis can provide data complementary to the compositional analysis by μ-XRF, which helps characterize and identify the colorant materials in the slip or paint. The confocal XploRA PLUS Raman microscope (Horiba Jobin Yvon, France) was used, and three excitations (532, 638, and 785 nm) were tried to obtain the best Raman signals for the red slip or paint. Raman spectra were recorded in wavenumber between 100 and 3000 cm^{-1}, with spectral accuracy of about 2 cm^{-1}. An optical microscope was used to focus the laser on samples, at ×50, throughout the analysis. Background spectra of water and carbon dioxide are obtained in ambient air. Raman spectra presented here were smoothed without baseline correction.

X-ray-absorption fine-structure (XAFS)

XAFS has been extensively used to characterize the short-range structure of coloring materials in cultural heritage for its advantages such as element-specificity, sensitivity to the short-range order, and chemical state [e.g., 44–47]. This study measured Fe K-edge XAFS spectra at the BL11B beamline of Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring of SSRF was operated at 3.5 GeV with an electron current of 200 mA. The hard X-ray was monochromatized with a Si(111) double crystal monochromator and the crystals were detuned to remove the high harmonics from the incident X-rays. In XAFS measurements, the position of the absorption edge was calibrated with Fe foil. XAFS data for model compounds (Fe_2O_3) were measured in transmission mode and the red slipped and painted wares were measured in fluorescence mode with Lytle detector.

The acquired XAFS data were processed according to standard procedures using the ATHENA module implemented in the DEMETER software. The Fe K-edge k^3-weighted $\chi(k)$ data in the k-space ranging from 2.5 to 11 $Å^{-1}$ were Fourier-transformed to real (R) space using a Hanning windows to separate the EXAFS contributions from the different coordination shells. To obtain the detailed structural parameters around the Fe atom in the samples, quantitative curve fittings were carried out using the ARTEMIS module of DEMETER. Theoretical EXAFS amplitude and phase functions for Fe–O, Fe–Fe single scattering paths were generated using the FEFF6 program in Athena software. Hematite was used as the model crystallographic compound for EXAFS fitting. The S_0^2 was set as 0.75 during the EXAFS fitting procedure and was established by fitting the EXAFS data for the α-Fe_2O_3 standard compound. All EXAFS data were fitted in q space and structural parameters obtained here consisted of the amplitude reduction factor (S_0^2), the Fermi energy shift (E_0), interatomic type and distance (Å), coordination number and the Debye–Waller factor (σ^2).

Results and discussion

Microscopic examination

Under the optical microscope, the exterior and interior surfaces and the cross-section of the three sherds (RPW01, RPW02, and RSW01) were examined. The microscopic examination reveals that RPW and RSW were produced from fine clay because of the (near) absence of large inclusions or tempering materials.

As shown in Fig. 5a, the red paint on RPW01 was brushed over the vessel's surface. The paint layer, about 50 μm thick on average, was so unevenly brushed over that some cracks are obvious in certain areas, revealing the lighter color of the body. The same observation was made on RPW02 (see Fig. 5b). The cracks could also have been caused when the paint layer underwent a higher thermal expansion than the body in the firing [48]. This often happens when the paint and the body fabric differ in chemical and mineralogical composition. The uneven distribution of the red paint layer can also be noticed by the varying thickness or different shades of the red color; that is, some parts of the red paint are thicker than others and so is the color of the paint. The paintbrush (or tools that serve the same function, such as bamboo or wooden strips) offers a brush stroke that is about 0.5 mm, as indicated in Fig. 5a, which is thinner than the 1 to 2 mm brush stroke noticed for the painted wares unearthed from Guanmiaoshan, a Daxi culture site [49: 94–95]. Li proposes that the 1 to 2 mm brush stroke indicates the use of an animal hair brush [49]. Experimental studies are required to test the validity of this assumption. Judging from the cross-section of RPW (Fig. 5e), the vessel's body is overall fine-paste and shows a whiter color towards the exterior or interior surface, in contrast to the grayish core in the middle. A few holes, in varying sizes, are also noticed on the cross-section, which were formed during the firing.

Compared to RPW, RSW shows a less intense reddish color on the surface (Fig. 5c). The slip, in orange color, is applied only on the exterior surface of the

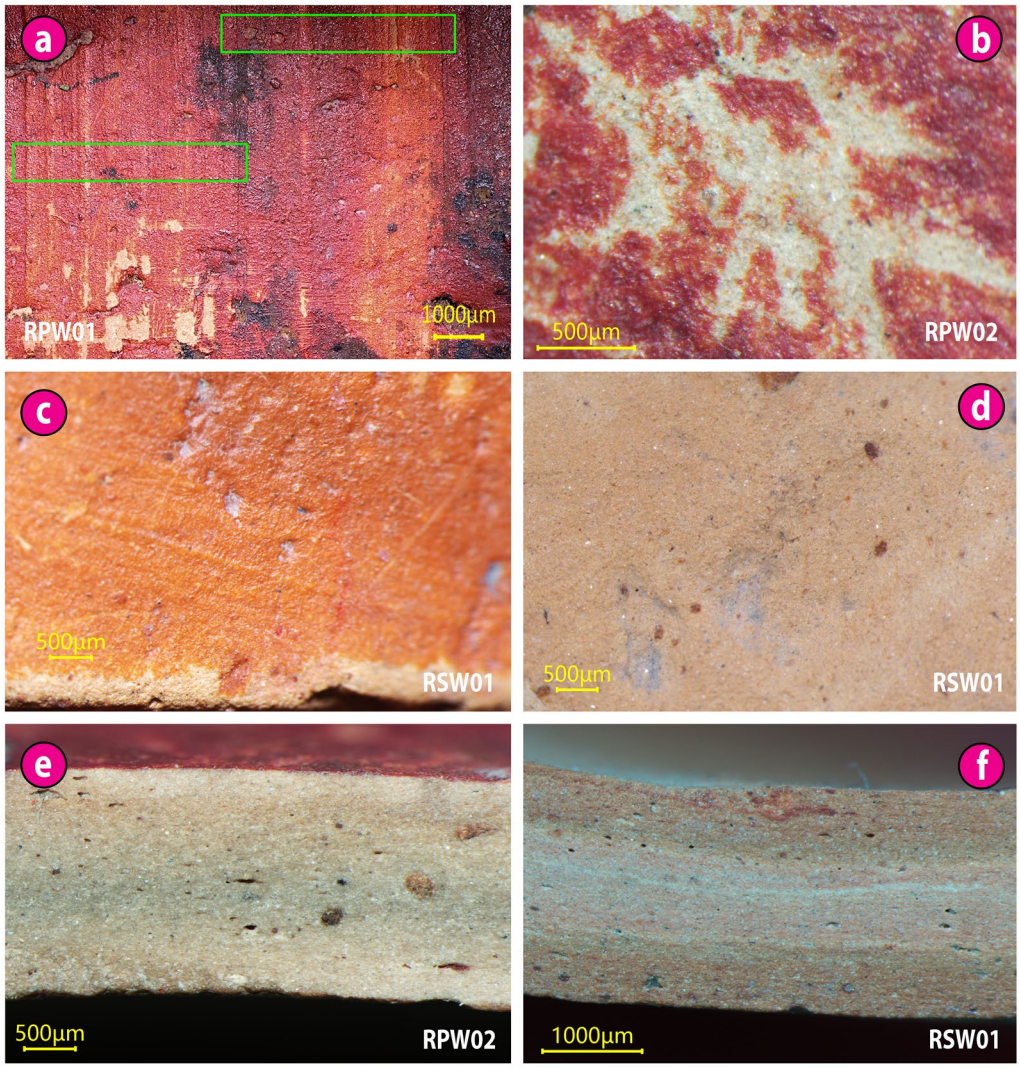

Fig. 5 Microscopic examination of RPW01 (**a** exterior surface with brush strokes indicated by rectangles); RPW02 (**b** enlarged area showing the whitish body color underneath the cracked paint), RSW01 (**c** exterior surface with no clear brush strokes; **d** the unslipped interior surface showing a slightly reddish color). The cross-section of RPW02 (**e**) shows a red paint layer of about 50-µm thick; by contrast, no clear slip layer is noticed on the cross-section of RSW01 (**f**)

vessel (Fig. 5c, d). The slip is much thinner than the red paint layer on RPW; however, the slip is smooth, tight, and fine-textured, with no cracks. The slip and the body fabric do not seem to differ much in their chemical or mineralogical composition. Moreover, no clear brush strokes are noticed on the exterior surface of RSW but some use-wear marks are evident (Fig. 5c). Unlike RPW, RSW shows on the cross-section a lighter core in the middle and a darker, more reddish color towards the exterior and interior surfaces of the sherd (Fig. 5f). The higher level of iron towards the two surfaces may explain this (see Table 5).

Surface chemical composition revealed by hhXRF

Concentrations of ten major, minor, and trace elements—i.e., zirconium, strontium, rubidium, zinc, iron, manganese, titanium, calcium, potassium, and barium—were determined for each of the 20 wares. Dividing the semi-quantitative hhXRF data into two sub-groups (the paint/slip vs. the body fabric), we compared the paint/slip and vessel body for their elemental compositions, in the hope of understanding which element(s) may be responsible for the red color. The results are shown in Fig. 6.

The overall concentrations of iron (Fe) and calcium (Ca) are much higher in the red paint/slip than in the body

Table 5 μ-XRF results of the red paint/slip (concentrations in wt%)

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Exterior surface										
RPW0**2**										
Paint	3.32	1.41	22.20	60.22	3.55	2.46	1.96	0.70	0.01	4.07
Body	7.37	0.76	12.78	67.06	4.93	2.17	1.56	0.74	0.01	2.63
RSW0**1**										
Slip	4.09	0.95	19.78	64.31	0.98	2.48	1.76	0.79	0.02	4.83
Body	3.00	1.45	14.78	73.73	0.74	1.71	0.78	0.79	0.02	2.98
Cross-section										
RPW0**2**										
Exterior	3.08	1.23	14.98	69.79	4.76	1.96	1.17	0.74	0.01	2.25
Middle	1.89	1.10	14.40	71.88	4.97	1.69	1.53	0.65	0.01	1.81
Interior	2.58	1.06	14.16	72.03	4.27	1.72	1.70	0.68	0.01	1.71
RSW0**1**										
Exterior	2.23	1.72	15.45	71.20	2.00	1.72	1.46	0.90	0.02	3.30
Middle	2.96	1.89	16.34	70.82	1.38	1.79	0.97	0.73	0.02	3.08
Interior	1.95	1.83	16.24	72.26	1.12	1.75	0.86	0.72	0.02	3.24

fabric of the same vessel; in the meanwhile, the concentration of barium (Ba) is lower in the red paint/slip than in the body fabric. The paint/slip and body fabric seem to be similar in terms of other elements. We could then ascribe the redness of the paint/slip to iron. The higher calcium in the paint/slip *vs* the lower calcium in the body fabric may relate to the refinement of the paint/slip [50].

Micro-XRF (μ-XRF)

The μ-XRF analysis offers compositional information regarding the color of the red paint or slip at a higher spatial resolution (with an X-ray focal spot size of 0.3 mm, 1/10 of the size of hhXRF). Using μ-XRF, we first analyzed the red paint and the body fabric of RPW02 and RSW01. We refer to these data as 'Exterior surface' because they were obtained from the exterior surface (see Table 5). Our investigation went on by performing another μ-XRF analysis on the cross-section of RPW02 and RSW01. Mainly, we collected compositional data from the spots close to the exterior (with the paint or slip) and the interior (with no paint or slip) surfaces as well as from the middle (or the core) of the cross-section. We refer to this second batch of data as 'Cross-section' because they were obtained on the cross-section of the sherd (also in Table 5). Ideally, the Cross-section data reveal the compositional variations between the two surfaces and the body fabric of the same vessel.

As shown in Fig. 7 and Table 5, the red paint on RPW02 has a higher concentration of iron oxide (Fe_2O_3, 4%, wt%) than the body (2.6%, wt%). In the meanwhile, the paint layer contains less sodium oxide (Na_2O, 3.3%) and phosphorus pentoxide (P_2O_5, 3.6%) than the body (7.4% and 4.9%, respectively). But, compared to RSW01, RPW02 contains substantial higher concentration of phosphorus pentoxide. On the cross-section of RPW02, the exterior surface—brushed over with the red paint—is more elevated in sodium oxide (3.1%) and iron oxide (2.3%) but lower in calcium oxide (CaO, 1.2%), and it differs little from the core and the interior surface in other oxides (except silicon dioxide and aluminum oxide). Overall, the red paint of RPW02 is characterized by a higher concentration of iron oxide which, once again, is compatible with hhXRF data.

As for RSW01, the slip and the body differ in the concentration of iron oxide (4.8% for the red slip *vs* 3% for the body). This confirms that the red was due to iron oxide. Furthermore, the slip of RSW01 contains higher concentrations of sodium oxide (4.1%) and phosphorus pentoxide (~1%) than the body fabric (3% and 0.7%, respectively), which is right on the opposite of what we noticed for RPW02. In addition, potassium oxide (K_2O, 2.5%) and calcium oxide (CaO, 1.8%) are higher in the slip than in the body (1.7% and 0.8%, respectively). On the cross-section of RSW01, the red slip contains higher concentrations of iron oxide (3.3%), calcium oxide (CaO, 1.5%) and phosphorus pentoxide (2%) than the body fabric or the interior surface. It is reported elsewhere that the slip sometimes tends to have lower concentrations of silicon (Si) and calcium (Ca) and higher concentrations of aluminum (Al) and potassium (K) than the body fabric; and that the depletion of silica and enrichment of alumina in the slip are due to the removal of coarse quartz grains and the enhanced amount of fine-grained clay minerals [51]. This explanation may also apply to RSW

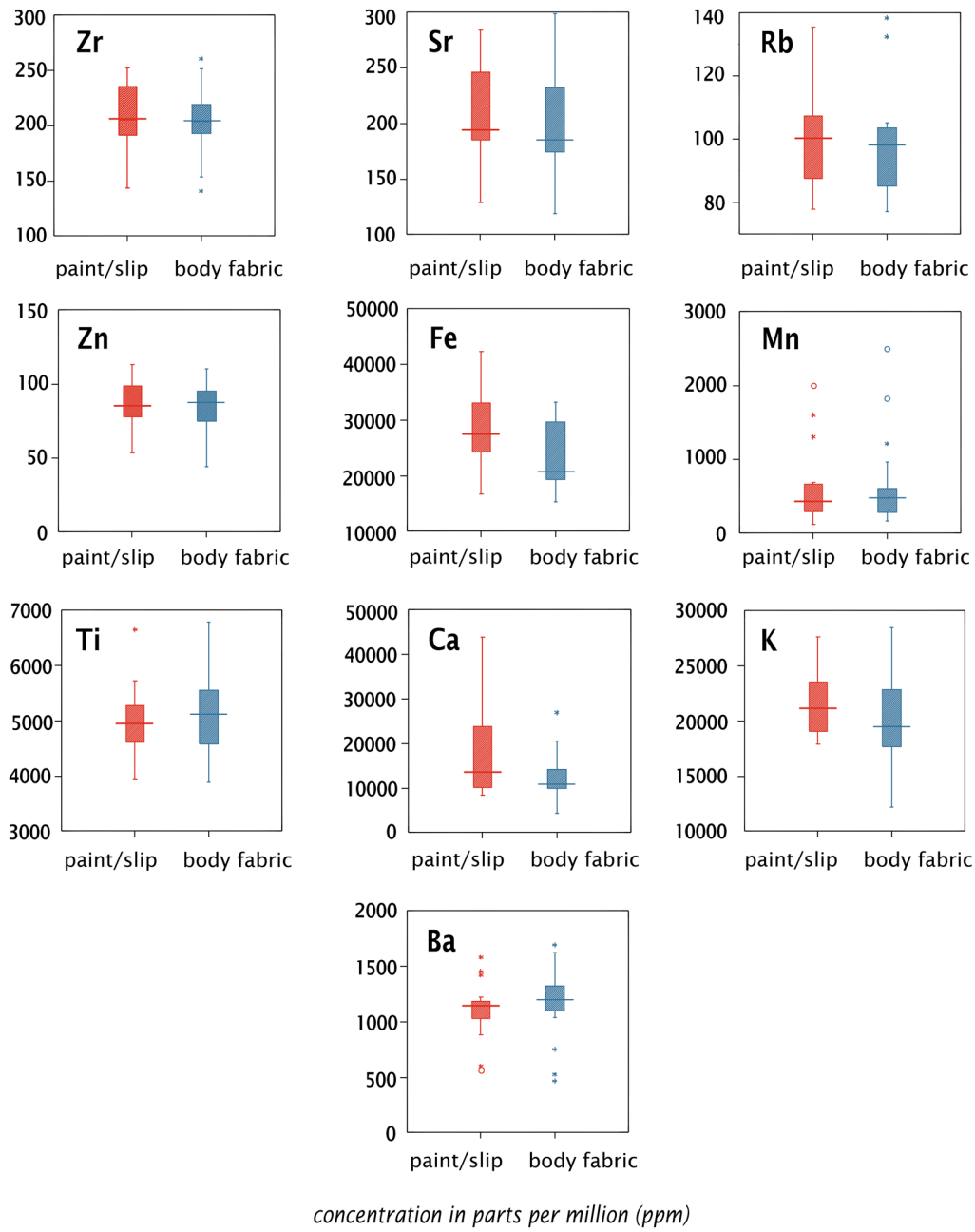

Fig. 6 hhXRF analysis reveals the overall high contents of iron (Fe), calcium (Ca), and potassium (K) in the red paint/slip than in the body fabric

because the slip contains lower concentrations of silicon and higher concentrations of aluminum and potassium than the body fabric.

Using the cross-section data of RPW02 and RSW01, we noticed that both wares have a body fabric dominated by SiO_2 (71.9% and 70.8%, respectively) and Al_2O_3 (14.4% and 16.3%). The body fabric of the two wares also contains some Fe_2O_3 (1.8% and 3.1%), CaO (1.5% and 1%), Na_2O (1.9% and 2.9%), MgO (1.1% and 1.9%), and is almost free of MnO (0.02% or less). Compared to the unslipped and unpainted pottery, RPW02 and RSW01's body fabric are characterized by relatively lower concentrations of SiO_2 and Al_2O_3 but a higher flux content (5.1% and 5.7% for RPW02 and RSW01, respectively, $CaO + Na_2O + K_2O$) [49: 169–173], indicating that RPW02 and RSW01 were produced from

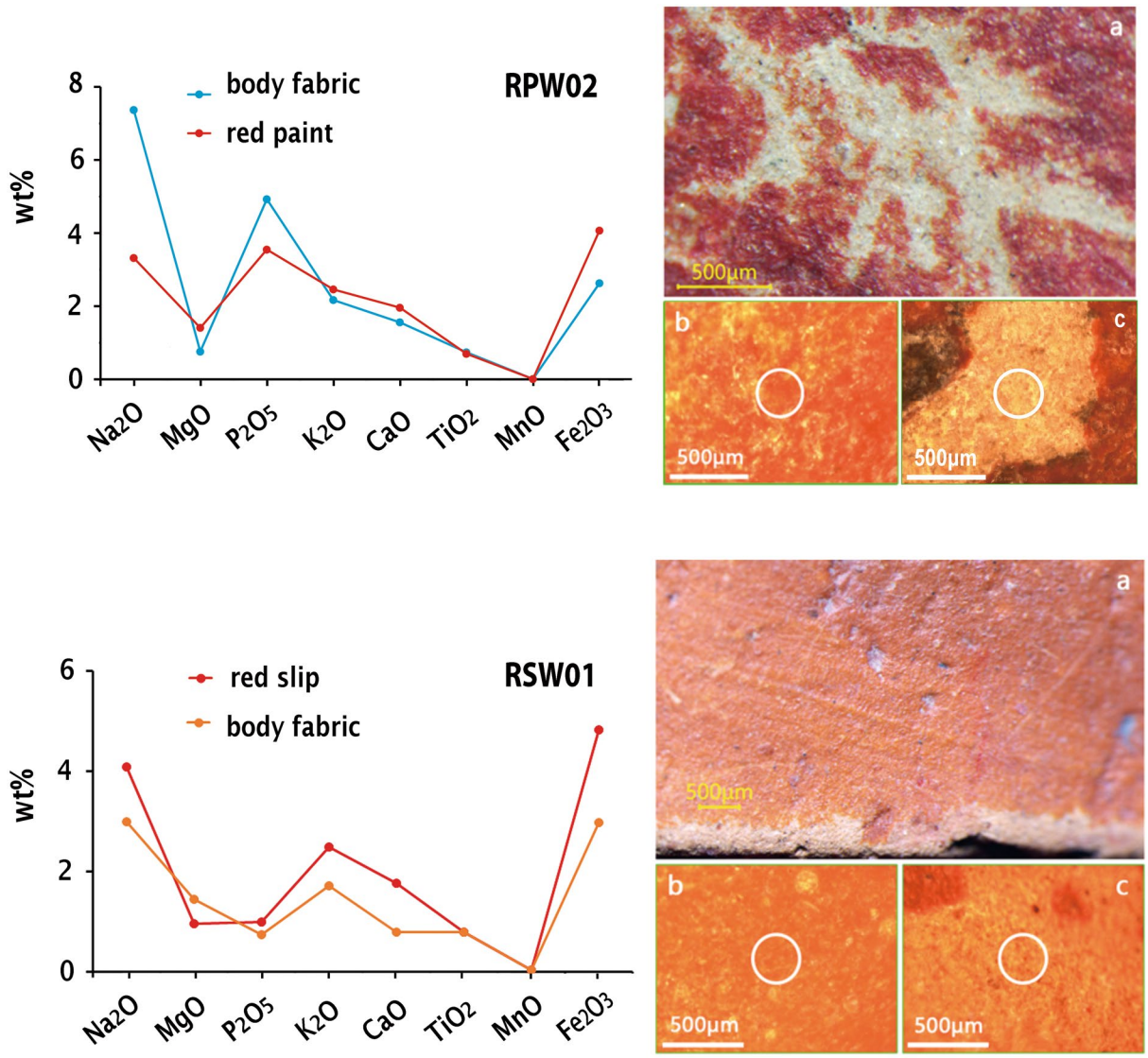

Fig. 7 Micro-XRF results of RPW02 and RSW01 reveal the difference in contents of oxides (except silicon dioxide and aluminum oxide) between the red paint/slip and the body fabric

common clays that can easily sinter at lower temperatures. This conclusion is compatible with previous compositional studies of the Daxi culture pottery in MYRV [8, 49].

Raman spectroscopy

hhXRF and μ-XRF analyses disclose the chemical compositions of the paint, the slip, and the body of the vessel and they both ascribe the red to iron and iron oxide. Raman analysis sheds additional light on the topic.

As shown in Fig. 8a, the two Raman spectra collected on RPW02—one focusing on the red paint while the other on the whitish body fabric—fail to show characteristic Raman peaks. Due to a strong Raman fluorescence effect, we did not see any meaningful Raman peaks in 100 to 1000 cm^{-1}, a range Raman peaks of common iron oxides are often noticed [52, 53]. The same observation was made for the whitish body. While some propose that the broad Raman peaks between 1150 and 1250 cm^{-1} may be attributed to, for example, organic materials with SO_2 symmetric stretch or ring breathing mode [54], we suggest that this issue awaits further exploration and explanation.

By contrast, two Raman spectra were obtained from different spots on RSW01, showing almost identical Raman peaks, as shown in Fig. 8b. This suggests the

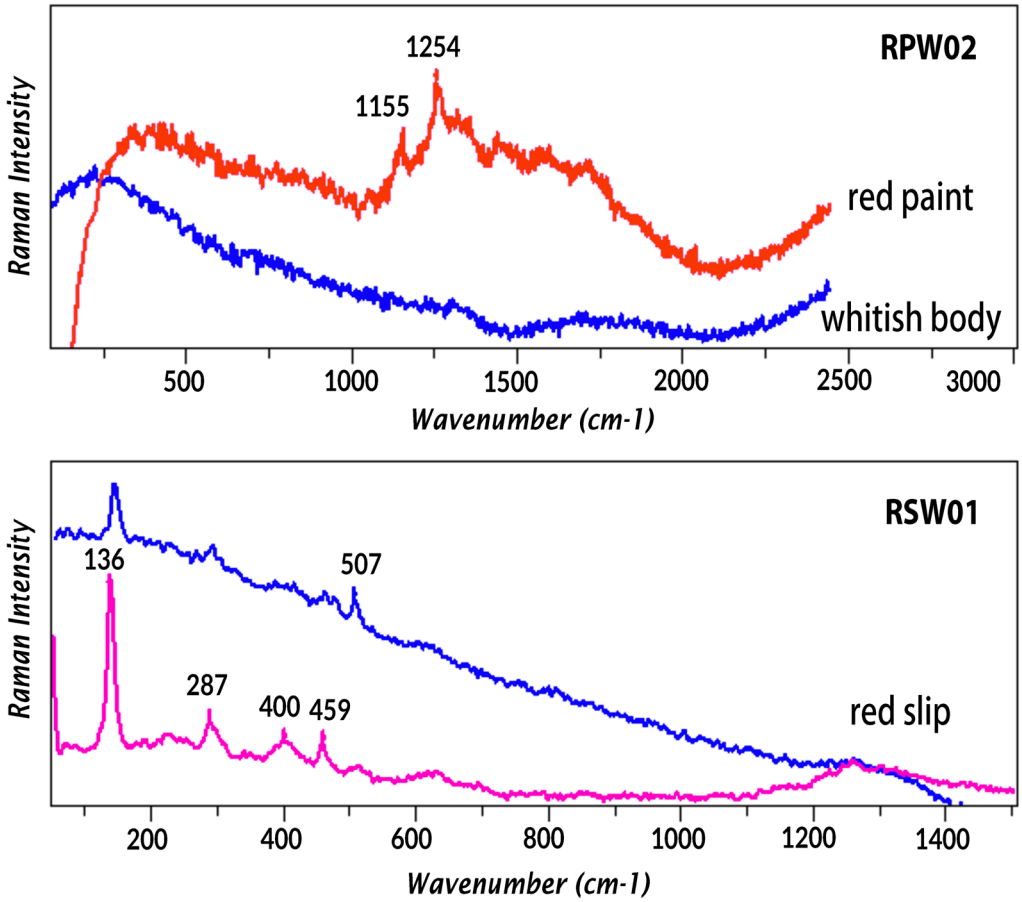

Fig. 8 Raman analysis of the red paint (RPW02) and the red slip (RSW01)

presence of the same substance(s) in different parts of the red slip. Raman peaks are noticed at 136, 287, 400, 460, and 507 cm^{-1}; however, they do not fully match with those of common iron oxides such as hematite (α-Fe_2O_3) in the mineral form, which usually show intense Raman peaks near 225, 290, 410, and 612 cm^{-1} [52, 53]. Instead, the Raman peak at 136 cm^{-1} and 460 cm^{-1} can be assigned to anatase (TiO_2) and quartz (SiO_2), respectively [55, 56]; and the Raman bands at 287, 400, 507, and ~ 1300 cm^{-1} can be characteristic of hematite (α-Fe_2O_3) [56, 57].

It is argued elsewhere that quartz can remain unchanged at high temperatures but anatase, if present, suggests a firing temperature in the range of 750 to 950 ℃ [58]. We have not applied the thermal expansion method to estimate the firing temperature of pottery unearthed at the Fenghuangzui site. But, our previous studies with the Zoumaling walled town [1] suggest that the Upper Qujialing pottery at the site was fired at a temperature of 900 to 950 ℃. The identification of anatase in RSW01 may indicate that at the site of Fenghuangzui, RSW was fired at no higher than 950 ℃.

Given the discussions above, we infer that iron oxide accounts for the red color in the slip (and the paint as well). Given the much stronger Raman fluorescence effect, iron oxide has a less well-developed crystalline structure in the paint than in the slip.

Thin-section petrography

Ceramic petrography reveals the clay matrix and inclusions, which are essential for understanding the pottery-making raw materials, the craft of pottery manufacture and even the provenance of pottery [43, 59–61]. One RPW sherd and one RSW sherd, both unearthed from ash pit H17 dating to the Shijiahe period, were selected for a pilot petrographic study. We could not compare the Shijiahe and Upper Qujialing RPW or RSW for their petrographic characteristics because at the time this study was carried out, there was no Upper Qujialing RPW/

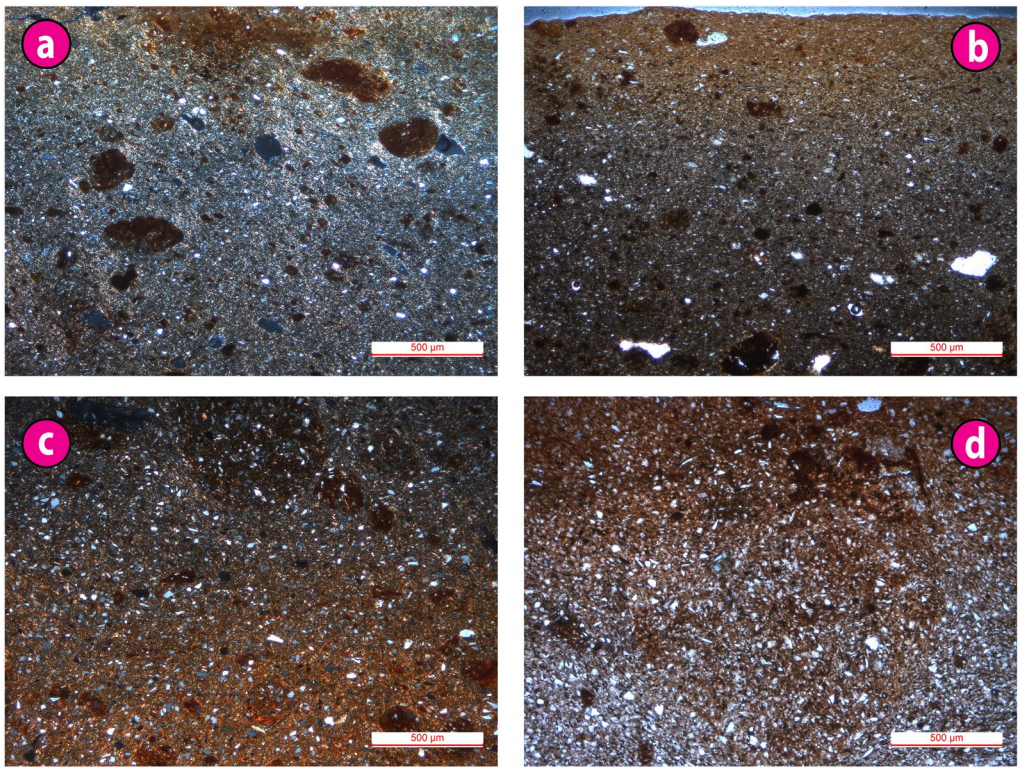

Fig. 9 Thin-section images of two additional RPW and RSW sherds (RPW: **a** and **b**; RSW: **c** and **d**)

RSW available for destructive analysis. The thin-section images are shown in Fig. 9.

The RPW sherd (Fig. 9a, b) consists mainly of clay minerals (~80%) but also a tiny amount of powdered fine sand debris (10%) and sandy debris (10%). Clay minerals are mostly leaf-shaped or rod-shaped, showing crystal orientation or alignment. Under plane-polarized light, the minerals show a light yellowish color. Most of the clay minerals, judged from their grey interference colors, belong to the kaolinite subgroup. Other clay minerals such as illite are rare. Powdered fine sand debris are mainly felsic, with a particle size of 0.04 mm or smaller. They are colorless and translucent under plane-polarized light and show characteristics of roundness. The debris shows gray and white interference colors and can hardly be subdivided due to their small particle sizes. The sandy debris consists mainly of rock debris (8%) and small amounts of quartz (2%). The rock debris has a particle size of 0.1 to 0.5 mm and show characteristics of roundness and a dark red color indicative of iron-rich mudstones. The debris of quartz has a particle size of 0.05 to 0.2 mm.

The RSW sherd (Fig. 9c, d) mainly consists of debris (70%) whose particle sizes are less than 0.01 mm, with a good size-sorting property. The particles show little roundness possibly because they are too small and lightweight and transported mainly through suspension. Most of the debris are quartz which are colorless and translucent under plane-polarized light, and they show gray and white interference colors. Also present in the RSW sherd are (1) small amounts of sericite debris (5%), whose particle size is less than 0.01 mm; (2) fine sand debris (5%), which have particle sizes of 0.1 to 0.6 mm and show a dark red color under plane-polarized light; and (3) clay minerals and rich iron oxides as binding medium, which show no clear crystal structure, with varying degrees of dark red colors depending on the content of iron oxides.

Even though only two sherds were studied by thin-section petrography, the results suggest intriguing findings. RPW was produced from the clay rich in kaolinite subgroup, indicating that a particular kind of body fabric may be preferred in producing RPW. RSW, on the other hand, contains a large number of small sandy particles and includes a higher content of iron oxide (thus explaining the orange to reddish color of the body). In short, RSW and RPW were produced from different pastes that seem to be chosen or processed on purpose. Although the sherds for thin-section petrography were not the same for μ-XRF analysis, our observations on

thin-section petrography are well compatible with, and can be explained by, the μ-XRF data shown in Table 5.

X-ray-absorption fine-structure (XAFS)

For ceramics, color is usually contributed by transition metals due to their characteristic absorption frequencies in the visible region as a result of d–d electronic transitions, which refers to the shift of electron(s) from a lower energy to a higher energy d orbital by absorption of energy (and vice versa). We have demonstrated in earlier sections that the red paint or slip was ascribed to iron (Fe). To further understand the speciation of iron (Fe) in RPW and RSW, XAFS is employed to investigate the oxidation state and local structures. The Fe_2O_3 compound (hematite phase, α-Fe_2O_3) was used as reference material.

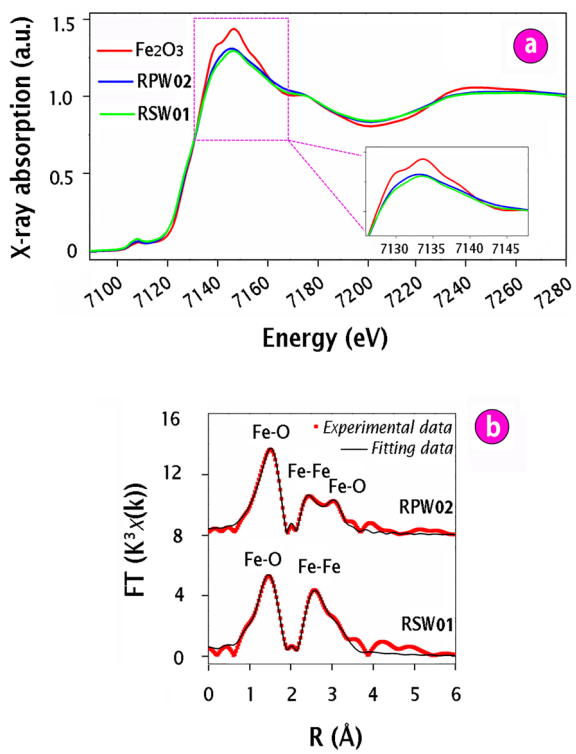

Fig. 10 XAFS characterization of RPW02 and RSW01: **a** Fe K-edge XANES spectra; **b** curve fitting results of EXAFS spectra

As shown in Fig. 10a, the X-ray absorption near edge structure (XANES) characters of RPW02 and RSW01 are similar to those of the reference material Fe_2O_3, sharing almost identical absorption edge. This indicates that ferrous iron is present in RPW02 and RSW01. Moreover, some discrepancies are noticed in the crest region, including a broad crest and weakened shoulders, when RPW02, RSW01, and referenced Fe_2O_3 compound are compared. Ferrous iron, we propose, is located in an amorphous or disordered local environment.

To quantitatively obtained the coordination configuration of Fe in RPW02 and RSW01, extended X-ray absorption fine structure (EXAFS) was further processed and the results are shown in Fig. 10b and Table 6. For RPW02, four paths—Fe–O, Fe–Fe, Fe–Fe and Fe–O—were used during the curve fitting to obtain a nice fitting quality. In detail, the first shell was fitted with Fe–O path and the coordination number (CN) and inter-atomic distance (R) are 5.7 and 1.98 Å, respectively. The second and third shells are derived from the joint contribution of two Fe–Fe paths and one Fe–O path with inter-atomic distance (R) at 2.91 Å, 1.92 Å and 1.92 Å, respectively. For RSW01, four paths including two Fe–O paths and two Fe–Fe paths were used to get a good fitting result. The first shell was fitted with two Fe–O paths with inter-atomic distance at 1.90 Å and 2.02 Å by fixing the CN of 3. The second shell was assigned to two Fe–Fe paths with inter-atomic distances at 3.04 Å and 3.33 Å.

Given the EXAFS fitting results above, both RPW02 and RSW01 show a similar local coordination structure as that of α-Fe_2O_3, suggesting the presence of α-Fe_2O_3

Table 6 Structural parameters extracted from quantitative EXAFS curve-fitting using the ARTEMIS module of DEMETER

Sample	Atoms	Coordination number, CN	Interatomic distance (Å)	Debye–Waller factor, σ^2 (10^{-3} Å^2)	Energy shift, e0 (eV)	R-factor, r
RPW02	Fe–O	5.70 ± 0.76	1.98 ± 0.05	9.9 ± 1.4	− 3.79 ± 1.49	0.01
	Fe–Fe	0.74 ± 0.18	2.91 ± 0.02	3.4 ± 2.1	− 8.47 ± 4.42	
	Fe–Fe	1.83 ± 0.57	3.36 ± 0.02	3.4 ± 2.1	− 8.47 ± 4.42	
	Fe–O	4.88 ± 1.90	3.58 ± 0.06	9.9 ± 1.4	− 3.79 ± 1.49	
RSW01	Fe–O	3*	1.90 ± 0.04	8.1 ± 6.4	− 2.79 ± 2.03	0.016
	Fe–O	3*	2.02 ± 0.05	8.1 ± 6.4	− 2.79 ± 2.03	
	Fe–Fe	6.52 ± 2.71	3.04 ± 0.03	11.5 ± 3.0	9.19 ± 3.03	
	Fe–Fe	4.53 ± 2.70	3.33 ± 0.02	11.5 ± 3.0	9.19 ± 3.03	

*The number is fixed when fitting the experimental data

phase in the red paint or slip, which provides complementary information to the Raman results. The main difference lies in the nearest Fe–O coordination structure. For RPW02, the nearest six Fe–O have the average inter-atomic distance at 1.98 Å. By contrast, the nearest six Fe–O have two different inter-atomic distance for RSW01, closer to that of α-Fe_2O_3. This explains why the hematite in the slip shows a better crystalline structure than that in the paint.

Surface treatment of RPW and RSW at Fenghuangzui and implications

The surface treatment of RPW and RSW unearthed from the site of Fenghuangzui can be understood by synthesizing the analytical results presented above.

(1) *The coloring mechanism* Both RPW and RSW have a red color on their exterior surface but they differ in the shades of the red color. RPW has a much more intense, darker red while RSW has an orange-to-red color probably because the paint of RPW is thicker and the red slip of RSW is thinner. Given the hhXRF and μ-XRF results, the paint of RPW and the slip of RSW can both be explained by iron oxide for their red color, suggesting that both wares were fired in an oxidizing atmosphere. While iron content is slightly higher in the slip than in the paint, the flux content is higher in the paint than in the slip.

Raman analysis fails to identify the presence of iron oxide in the red paint because of the strong Raman fluorescence effect. Still, it indicates the presence of anatase, quartz, and hematite in the slip. We inferred that iron oxide in the paint has a less well-developed crystalline structure than in the slip, given the Raman results. On the other hand, XAFS analysis confirms that RSW and RPW attribute their red color to iron (III) oxide but in both cases iron (III) is in an amorphous or disordered local environment; also, it points out a better crystalline structure of α-Fe_2O_3 in the slip than in the paint, which is consistent with the Raman results. Furthermore, RSW was likely fired at temperature no higher than 950 ℃.

To conclude, RPW and RSW were both fired in an oxidizing atmosphere (with a firing temperature of 950 ℃ or lower) and they ascribed their red color to iron (III) oxide in α-Fe_2O_3 phase. However, the crystalline structure of α-Fe_2O_3 was less well developed in RPW than in RSW. The high flux content in the red paint could be one explanation but other possibilities (such as different firing temperatures and different sources of raw materials) must also be tested in further analytical or experimental studies.

(2) *Surface treatment by painting and slipping* The red paint of RPW was brushed over the vessel's exterior surface, possibly using some animal hair fiber brush. The red paint layer runs over the vessel's body consecutively and horizontally, suggesting that the potters applied the red paint while spinning the wheel or a turning table.

The slip on RSW (at least the red slipped wares examined in our sample) did not seem to be formed in the same way. The red slip was so thin (less than 20 μm thick) and may just be formed by self-slipping, in which the slip was prepared using the same material that constitutes the clay body. The μ-XRF results (Table 5) show smaller elemental variations for RSW among the exterior surface, the core, and the interior surface, which supports the self-slipping hypothesis. Quartz and anatase, both being clay minerals, are present in the red slip, which also supports self-slipping.

(3) *Implications for RPW and RSW production and use at Fenghuangzui* The 2020 and 2021 excavations at the site of Fenghuangzui have revealed kilns dating to the Shijiahe period. Thus, it is not unreasonable to assume the local production and consumption of pottery for the site. Details about pottery production and use at Fenghuangzui will rely on provenance and residue analysis. Our limited samples, however, shed some light on the topics above.

Firstly, both RPW and RSW were produced from fine clays, without tempering materials. The red paint or slip was applied to a very few vessel forms and shapes, mostly for serving and drinking purposes. This indicates that the production of RPW and RSW was intentional and so was their surface treatment, that both wares were functionally specific (especially given the feasting context in which they were discovered), and that their quantity was less than other ordinary wares. We infer that at the site of Fenghuangzui RPW and RSW was assigned symbolic meanings and/or related to specific culinary practices and social status. Some kind of community cohesion seemed to be developing at the site and this may create a centripetal force that draw people together for public affairs (e.g., labor pooled for the construction and maintenance of the enclosing wall, the moat, and river courses). The importance of RPW and RSW in the formation and development of social relations shall be more

Table 7 Five elements showing greater variations among the Upper Qujialing and Shijiahe pottery (UP = Upper Qujialing)

	Mean ± SD (Zr, Mn, and Ba in ppm; Fe and Ca in wt%)				
	Zr	Fe	Mn	Ca	Ba
Paint/slip					
UQ (n = 5)	241 ± 11	2.2 ± 0.70	1024 ± 626	1.7 ± 1.5	979 ± 265
Shijiahe (n = 12)	191 ± 28	3.2 ± 0.68	438 ± 397	1.9 ± 0.98	1156 ± 256
Body					
UQ (n = 5)	239 ± 19	1.9 ± 0.57	972 ± 883	1.4 ± 0.40	953 ± 304
Shijiahe (n = 12)	189 ± 26	2.6 ± 0.56	552 ± 484	1.2 ± 0.62	1255 ± 320

fully understood when technical studies are carried out to compare RPW, RSW, and other 'ordinary' vessels.

Secondly, while a local mode of pottery production and use is highly likely, not all pottery were produced from the same (source of) clay. Our thin-section petrography study shows that RPW and RSW, dating to the Shijiahe period, were produced from different pastes. This could mean that both wares were produced by different potters who lived at different localities and made pottery with the clay most abundant and instantly available to them, or that the two wares were produced by the same potters who produced different vessels using different paste recipes. The fewer the potters (or production units) are, the stronger the economic ties are indicated. A chemical and petrographic analysis of a larger sample size will hopefully address this issue further.

Thirdly, the surface elemental analysis by μ-XRF reveals that compared to the red slip, the red paint layer has a higher content of phosphorus pentoxide (P_2O_5, 3.5–5%, wt%). The source (or cause) of higher phosphorous in the paint require further investigation and may provide additional information for the understanding of RPW production. Nevertheless, our results point out the complexity in the manufacture of RSW and RPW and thus call for more analytical studies on the phase changes in the two wares and the determination of original firing temperatures. Experimental studies on painting and slipping are needed to test our assumptions, for example, for the coloring mechanism and the nature of compositional varaitions.

Lastly, we compared the concentrations of the ten elements (Table 4) for the Upper Qujialing and Shijiahe RPW and RSW. Five of the ten elements show greater variations between the two periods (see Table 7). Overall, zirconium (Zr) and manganese (Mn) are higher in the Upper Qujialing RPW/RSW than in the Shijiahe ones; while the opposite is true for iron (Fe) and barium (Ba). Furthermore, calcium (Ca) is higher in the body fabric of the Upper Qujialing RPW/RSW than in the the Shijiahe ones. Given the small sample size (Upper Qujialing: 5; Shijiahe: 12) in our study, we do not intend to overinterpret the implications of the compositional variations. But these five elements may be helpful for distinguishing or provenancing the Upper Qujialing and Shijiahe RPW/RSW unearthed at the site of Fenghuangzui, a topic that will be discussed on a more systematic sampling.

Conclusions

Red slipped and painted wares (RSW and RPW) were manufactured in the middle Yangtze River valley (MYRV) of China as early as some 8500 and 7800 years ago, respectively. However, few technical investigations have been made on both wares to understand their production, distribution, and use. The present paper introduces the first multi-analytical study on RSW and RPW in MYRV through a case study focusing on the site of Fenghuangzui in Xiangyang City of Hubei Province, central China. Microscopic examination and surface elemental analysis reveals that the red paint was applied on RPW possibly using an animal hair brush while the slip of RSW may have been formed by self-slipping. Raman analysis and XAFS analysis confirmed that iron was present in the paint or slip in the form of hematite with a poorly developed crystalline structure. Our pilot study has demonstrated the potential of the combined use of analytical techniques for understanding RSW/RPW production and use in MYRV. Further investigations involving a more systematic sampling shall reveal details of pottery production, distribution, and use at the site of Fenghuangzui.

Abbreviations

FHZ: Fenghuangzui; UQ: Upper Qujialing; RSW: Red slipped ware; RPW: Red painted ware; MYRV: Middle Yangtze River valley; OM: Optical microscopy; hhXRF: Handheld X-ray fluorescence analyzer; XAFS: X-ray absorption fine structure.

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Author contributions
Project leader and mainly writing, TL, GY Li, SW Shan, and LH Wang; archaeological background, ZY Li, TF Wu, SW Shan, and TH; optical microscopy, TL and GY Li; hhXRF and micro-XRF, GY Li; Raman analysis and thin-section petrography, TL and GY Li; XAFS, LH Wang; funding acquisition and supervision, SW Shan and HT. All authors contribute to the writing of earlier drafts of the manuscript and have read and approved the final manuscript. All authors read and approved the final manuscript.

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Declarations

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Competing interests
The authors declare no competing interests.

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