RESEARCH

Study of barium copper silicate pigments on painted pottery from the Qinhan Xincheng, Western Han Dynasty (207 B.C.–8 A.D.), Xi'an, Shaanxi province, China

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Abstract

Lead-barium silicate system products, represented by barium copper silicate and lead-barium glass, epitomize a unique artistic craftsmanship of ancient China. Specifically, barium copper silicate products were the only known artificially synthesized blue-purple inorganic pigments in ancient China. Painted pottery decorated with barium copper silicate pigment, predominantly found in elite tombs after 2nd century B.C., is exceedingly rare and holds immense archaeological significance. This case employed multi micro-scale analytical techniques, such as ultra-depth-of-field microscopy, Raman spectroscopy, μ X-ray Diffraction, and electron probe microanalysis, for comprehensive microscopic examination of a rare Chinese Purple (CP, $BaCuSi_2O_6$) pigments on painted pottery. The analytical results confirm that the purple pigment is $BaCuSi_2O_6$, accompanied by cinnabar for the red and bone white for the white sections, suggesting the probable use of organic residues as an adhesive. Additionally, the study reveals microstructural characteristics in CP faience and CP pigments, notably the encapsulation of CP particles by quartz particles. Therefore, it can be hypothesized that the process of manufacturing purple pigment was achieved by grinding faience into fine particles and then using an organic-based adhesive to adhere these particles to the pottery. This implies that the evolutions in CP products circa the 2nd century B.C. were driven not by technological advances from lead-barium glass, but rather by shifts in application methods, reflecting an adaptation process among different cultures. This study provides new perspectives and significant insights for comprehending the interplay between barium copper silicate and lead-barium glass, reconstructing ancient pottery painting techniques, and exploring the era's technological and cultural interactions.

Keywords Chinese Purple, Painted pottery, Lead barium silicate system, Mapping, Cultural exchange

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Introduction

Barium copper silicate system, lead barium glass etc., are part of ancient China's distinctive silicate system, defined by employing barium and lead as fluxes. Artificial barium copper silicate is produced by processing minerals such as quartz, along with materials containing copper and barium, using lead as a flux. Similarly, lead barium glass utilizes lead, alongside barium and quartz sand, as key ingredients, melting them together with other materials to form a special type of glass. Products made from lead barium silicate are unique to China. These materials represent a significant hallmark in the history of ancient Chinese technological innovation. A profound investigation into these materials can aid in comprehending the crystallized wisdom of ancient ancestors, enrich the understanding of the scientific and technological essence of ancient civilizations, and explore underlying issues related to cultural exchanges and technological dissemination.

Chinese Purple and Chinese Blue (CB, $BaCuSi_4O_{10}$), representative of barium copper silicate pigments, are unique as the only example of artificially synthesized purple and blue inorganic pigments in ancient China. This represents a remarkable milestone in the historical chronology of ancient Chinese pigments. CB and CP were recognized and named in 1983 [1] and 1992 [2] respectively by E. W. Fitzhugh of the Freer Gallery of Art Washington, D.C., during her research on Han Dynasty (207 B.C.–220 A.D.) artifacts (painted pottery and octagonal stick) in the museum's collection. Previous studies have concentrated on several key aspects of barium copper silicate, such as its chemical properties [3], methods of simulated preparation [4, 5], and exploration of its sources [6–8].

The emergence and sequence of these pigments have long been subjects of considerable debate. Previous research confirms that CB is chemically more stable than CP, which can transform into CB under specific conditions [9]. Despite the superior chemical stability of CB, archaeological evidence reveals that artifacts of CP have been found in greater quantities and variety. This discrepancy may be attributed to the specific production conditions required for these pigments. Research indicates that their synthesis required temperatures between 900 and 1000 degrees Celsius, beginning with the formation of $BaCuSi_2O_6$ as a kinetic product, which subsequently transformed into $BaCuSi_4O_{10}$ through further reactions. The production of pure CB, in particular, necessitated prolonged high temperatures, reflecting its more complex manufacturing process. Therefore, some scholars suggest that due to the technological limitations, these pigments were likely produced as a mixture rather than separately [10].

In the previous study, the origin of barium, whether from barite ($BaSO_4$), witherite ($BaCO_3$), or barium oxide (BaO), has long been a contentious issue in the study of these ancient materials. Although barite is more prevalent in geological conditions, simulation experiments have shown that synthesizing CP using $BaSO_4$ presents considerable challenges. In contrast, utilizing $BaCO_3$ significantly simplifies the synthesis process [5]. Nevertheless, some scholars [11] have detected sulfur elements within the samples, suggesting that barite may be the source, though this hypothesis remains contested. Given that ancient CP samples were produced at high temperatures, the original mineralogical information may have disappeared or changed. Furthermore, the mineralogical symbiosis between barite and witherite further complicates the identification of the primary source of barium. Therefore, studying different samples may lead to varying conclusions, potentially influenced by geological symbiosis or the characteristics of the samples themselves.

From the archaeological findings of barium copper silicate artifacts, their evolution can be divided into two developmental stages based on archaeological materials: the Spring and Autumn Period and the Warring States Period (770 B.C.–221 B.C.), and the Qin and Han dynasties (221 B.C.–220 A.D.), with the Qin dynasty (221 B.C.–207 B.C.) being the critical point in its developmental transformation. Some archaeological sites are shown in Fig. 1, while Fig. 2 illustrates the evolution process of barium copper silicate products.

The earliest known CP particle was found on a spindle-shaped faience bead that was discovered during the Spring and Autumn Period (770 B.C.–476 B.C.) in the Dabaozishan Cementry [12] in Lixian County, Gansu. However, it is widely known that the bead's creation was accidental, as evidenced by its low lead content. During the Warring States era (476 B.C.–221 B.C.), distinct barium copper silicate products were found, the majority of which were thousands of faience beads discovered in the Majiayuan site [11]. In addition, barium copper silicate products were also found in several sites including the Zhaitouhe Cemetery [13] in Shaanxi, the Hejia Qin Tomb [14] in Mausoleum of Zhou in Shaanxi and the Xigong District [15] in Luoyang. The shape of barium copper silicate objects during this period is primarily that of faience beads, though there are other faience objects as well, including octagonal sticks, earrings, and Chess Pieces of Liubo [16].

The Qin Dynasty (221 B.C.–207 B.C.) was an important part of the development of artificial barium copper silicate, which was first employed as a pigment in the painting of Terracotta Warriors of the Mausoleum of the First Qin Emperor [17]. In addition, CP particles were also found on the bronze waterfowl painting
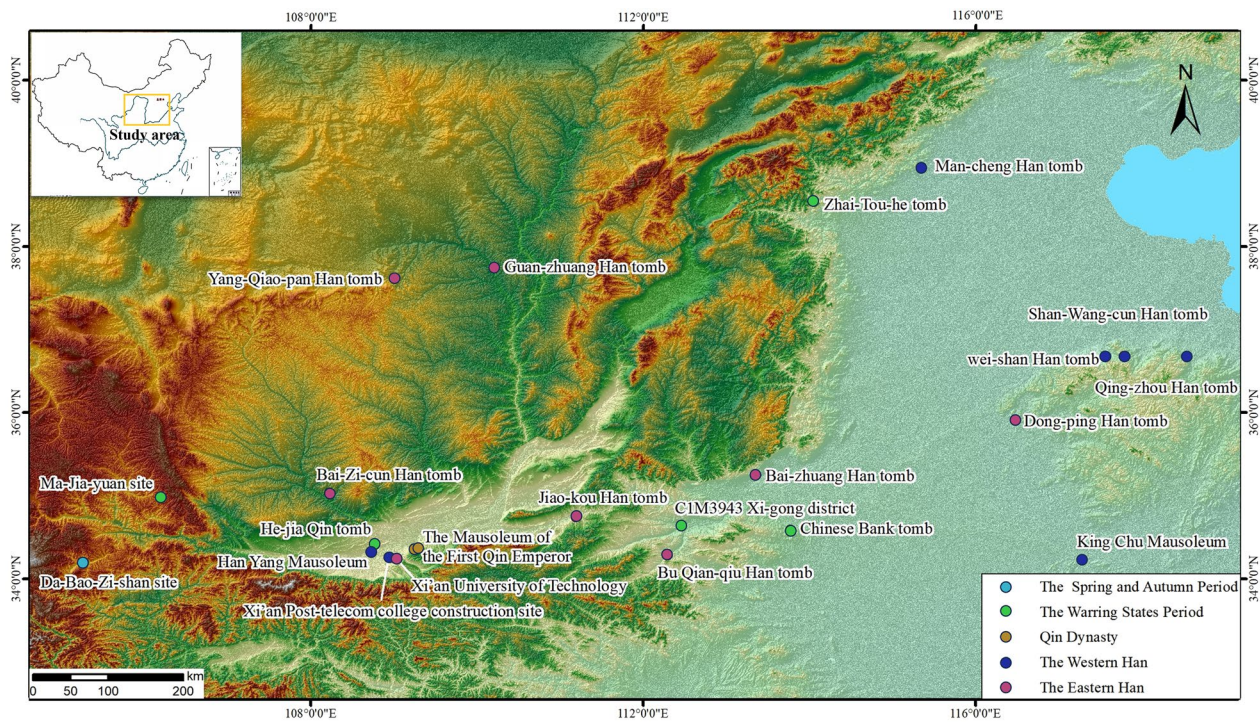
Fig. 1 Map of Archaeological findings of barium copper silicate products. Blue circles indicate archaeological sites from the Spring and Autumn period (770 B.C.–476 B.C.), green circles denote sites from the Warring States period (476 B.C.– 221 B.C.), dark yellow circles identify sites from the Qin dynasty (221 B.C.–207 B.C.), dark blue circles represent sites from the Western Han period (207 B.C.–8 A.D.), and red circles stand for sites from the Eastern Han period (25 A.D.–220 A.D.)

Fig. 2 The image illustrates the principal forms and developmental evolution of barium copper silicate products across various historical periods. In the Spring and Autumn (771 B.C.–476 B.C.) and Warring States (476 B.C.–221 B.C.) periods, faience was the predominant material. During the Qin dynasty (221 B.C.–207 B.C.), barium copper silicate was applied as colored paint on the Terracotta Army. In the Han dynasty (207 B.C.–220 A.D.), it was primarily used as pigment in pottery and murals. Image from published articles and doctoral dissertations [4, 12]

unearthed in the K0007 burial pit of the Mausoleum of the First Qin Emperor, appearing changes in its use. The Western Han Dynasty (207 B.C.–8 A.D.) was the peak of the development of barium copper silicate products. In ten archaeological sites, including Han Yangling Mausoleum [18], Chang-le Palace [7], King Chu Mausoleum [19], and Man-cheng Han Tomb [7], barium

copper silicate products were discovered, 60% of which were used as pigments in the painted pottery. Notably, pottery painted with CP is more commonly found in tombs of high status. During the Eastern Han Dynasty (25 A.D.–220 A.D.), new barium copper silicate items, such as pigment blocks [4] and pigments on the stone carvings [7], began to emerge. Barium copper silicate

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products mysteriously vanished after the Eastern Han Dynasty (25 A.D.–220 A.D.), and hardly any archaeological records were discovered. In the painted murals of the Gao-chang State Cemetery [20] from the Tang Dynasty (618 A.D.–907 A.D.) only one instance has so far been discovered. It is evident that artificial barium copper silicate products underwent significant transformation during the Qin Dynasty (221 B.C.–207 B.C.). Their forms evolved from faience beads and octagonal sticks, typical of various faience products, to a purple pigment used in painted pottery and murals. After the Qin period (221 B.C.–207 B.C.), faience products essentially disappeared. This period (Qin Dynasty) marks an important time for the transformation of artificial barium copper silicate products.

Therefore, the change in the use of artificial barium copper silicate products around 2nd century B.C. poses questions. It's unclear whether this change represented a direct continuation of traditional faience technology, or if it was a transformation and enhancement by the people of Qin dynasty (221 B.C.–207 B.C.) after mastering the production process. Understanding this shift is crucial to comprehending the development, dissemination, and evolution of this technology.

To further investigate the technical characteristics of barium copper silicate and clarify its developmental evolution in relation to lead barium glass, this study employed electron probe micro-analysis (EPMA) and μ X-ray diffraction (μ-XRD) techniques for a detailed analysis of selected barium copper silicate samples. EPMA, integrating backscattered electron imaging (BSI) and wavelength dispersive spectroscopy (WDS), combines microscopic imaging with micro-area compositional analysis. It can obtain imaging and quantitative compositional data with high quality in meanwhile. It offers significant advantages over traditional methods in analyzing microscopic structures and chemical compositions. μ-XRD analysis employs an extremely fine beam for XRD measurements, suitable for analyzing the microstructure and composition of precious samples like high-value artifacts. Its non-destructiveness and applicability are major advantages over traditional diffraction methods. This is crucial for valuable artifacts that cannot withstand conventional destructive analysis techniques, as exemplified by the painted pottery discussed here. Two analytical techniques, EPMA [21, 22] and μ X-ray Diffraction [23, 24], have long been utilized in the identification of pigments. Thus, the integration of EPMA and X-ray Diffraction with μ-scale techniques, through detailed structural and micro-area compositional analysis, effectively infers the technical processes of raw material preparation and craftsmanship. This approach

provides solid details for in-depth discussions on the craft techniques and cultural connotations of barium copper silicate products from the Qin and Han dynasties (221 B.C.–220 A.D.).

Materials and methods
### Archaeological background
The Shaanxi Jinghe New City Equestrian Site, unearthed in 2020 amidst infrastructure development in Xi'an New District, Shaanxi province, stands as a significant segment of the Qinhan Xincheng site. Notably, a variety of artifacts were unearthed from Tomb No. 6, dating to around 200 B.C. These include painted pottery pots, faience beads, compound eye beads, copper, and jade items. This study focuses on polychrome pigment samples from a painted pottery pot found in the tomb. The pot, when discovered, displayed distinct polychrome decorations with white, purple, and red pigments. These decorations, mainly cloud patterns arranged in three layers separated by red painted lines, extend from the neck to the belly of the pot. The cloud patterns alternate between purple and white in each layer. Figure 3a presents the map of the site location, while Fig. 3b illustrates a photograph of the sample along with its sampling location.

Methods
Microscopic observation was performed with a Keyence VHX-6000 ultra-depth-of-field three-dimensional video microscope, which provided a magnification range maximum up to 3000×.

Pigment identification employed confocal Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), and micro X-ray Diffraction (μ-XRD). Raman spectroscopy was performed with a Horiba LabRAM SoLeil, utilizing laser wavelengths of 532 nm and 785 nm. X-ray diffraction (XRD) analysis utilized a Rigaku Smartlab system, featuring Cu $K\alpha$ radiation and a maximum power of 9 KW. This XRD process encompassed two-theta angles from 5° to 75°, scanning at 10°/min and advancing in 0.02° steps. The resulting diffraction patterns were processed and identified using MDI Jade 6.0 Software and the powder Diffraction file database. The infrared spectroscopic analysis was conducted using the Fourier Transform Infrared (FTIR) Spectrometer Nicolet 8700. The samples were meticulously analyzed under a controlled temperature setting of 25 °C. For data acquisition, the OMNIC system was employed, targeting a comprehensive spectral range spanning from 4000 to 400 cm^{-1}.

Chemical composition analysis utilized a SHIMADZU EPMA-8050G at the Instruments Center for Physical Science, University of Science and Technology of China,

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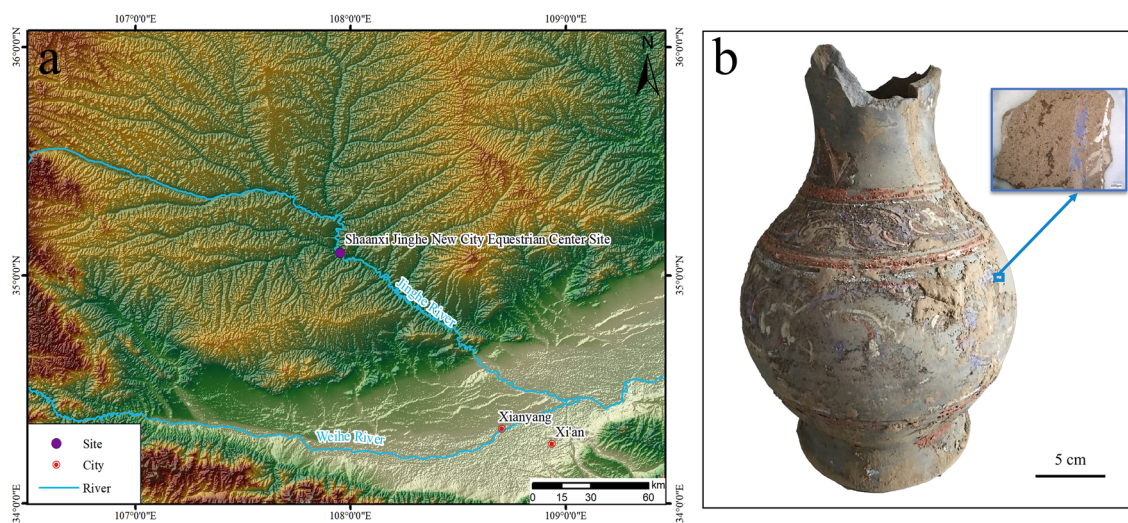
Fig. 3 Archaeological site location, sample collection, and sampling process at Shaanxi Jinghe New City Equestrian. **a** Site location: Geographic positioning of the Jinghe New City Equestrian archaeological site. **b** Sample Illustration: This photo shows a photograph of a painted pottery pot excavated from the Jinghe New City Equestrian site in Xi'an, Shaanxi province. The artifact, dating back to the Western Han Dynasty (207 B.C.–8 A.D.), exhibits intricate decorations using red, white, and purple pigments. Accompanying the photo is a schematic diagram of the sampling site

including a microbeam diameter of 50 μm, an accelerating voltage of 20 kV, a beam current of 20 μA, an element characteristic peak spectrum acquisition time of 30 s, and a background spectrum acquisition time of 20 s.

Results

Microscopic observation

Figure 4 presents the observation results of the pigments of polychrome decoration pottery under a digital
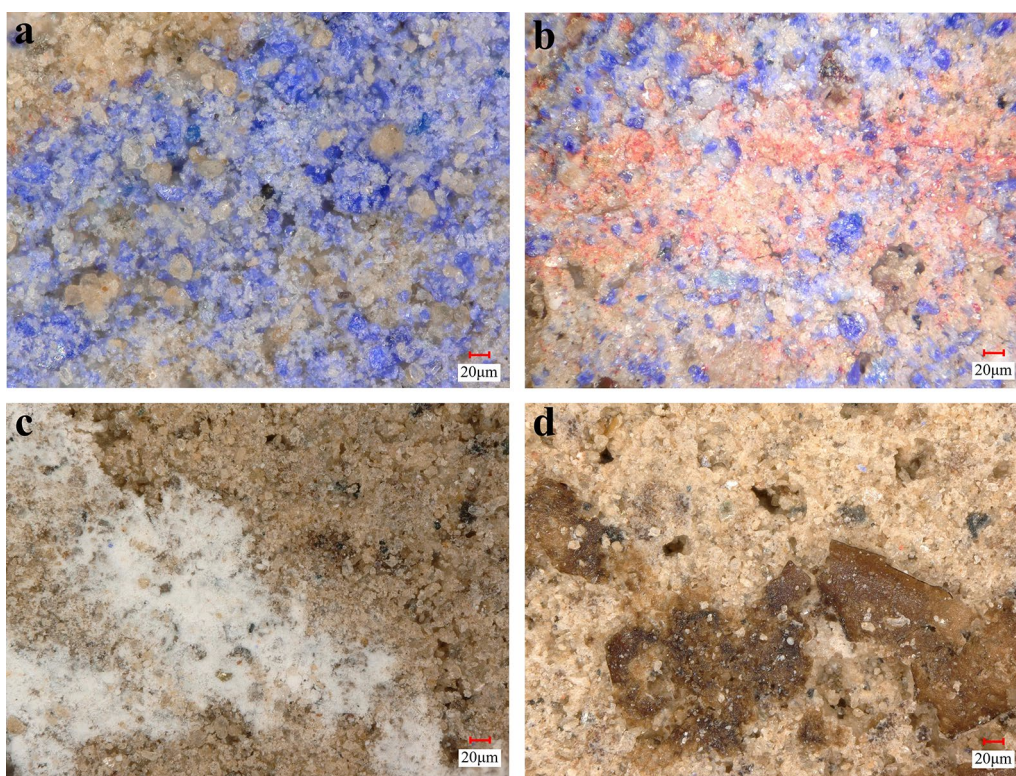
Fig. 4 Microscope photographs of the samples. **a** Purple pigment; **b** Red pigment; **c** White pigment; **d** Yellow-brown substance

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microscope. Microscopic observation indicates that the distribution of the purple pigment (Fig. 4a) is uneven and speckled, and its scale is noticeably larger than that of the red pigment (Fig. 4b), exhibiting a granular texture. The white pigment (Fig. 4c) is the most delicate. Additionally, a yellow-brown substance with a slightly curled appearance was also observed on the surface of the pottery (Fig. 4d), which phy-chemical characters requires to be identified.

Pigment identification

To investigated the pigment types, analyses were conducted using confocal Raman spectroscopy, infrared spectroscopy, and μ X-ray diffraction.

The Raman spectral analysis conducted on the purple sample, as illustrated in Fig. 5a, has successfully identified seven distinct peaks located at 179, 273, 352, 458, 512, 586, and 986 cm^{-1}. Notably, the peak at 986 cm^{-1} is a clear indication of the a_{1g} ν(Si–O) vibrational mode. The peaks at 586 cm^{-1} and 512 cm^{-1} are attributed to the $\delta s(SiO_2)$ bending mode within silicate groups. Additionally, the vibrations occurring at 273 cm^{-1} and 179 cm^{-1} are indicative of Cu–O vibrations, which closely align with the known properties of standard CP ($BaCuSi_2O_6$) [9]. Similarly, the Raman spectrum of the light blue sample, as depicted in Fig. 5b, displays nine identical peaks at the frequencies of 126, 344, 381, 425, 459, 558, 792, 991, and 1097 cm^{-1}. The band observed at 1097 cm^{-1} is attributed to the a_{1g} ν(Si–O) vibration, and the band at 425 cm^{-1} is consistent with the symmetric Si–O bridging vibrations. The band at 383 cm^{-1} is specifically assigned to Cu–O vibrations, which are in agreement with the characteristics of the standard Chinese Blue ($BaCuSi_4O_{10}$) sample [9]. Furthermore, the Raman spectrum for the dark blue particles, presented in Fig. 5c, exhibits notable peaks at 122, 158, 314, 358, 458, 560, 660, 672, 896, and 1017 cm^{-1}. The peak at 1104 cm^{-1} is correlated with α_{1g} ν(Si–O) vibrations, while the peak at 672 cm^{-1} is in line with symmetric Si–O bridging vibrations. The peak at 458 cm^{-1} is indicative of symmetric Si–O–Si deformation, which closely resembles the traits of the standard Chinese Dark Blue ($BaCu_2Si_2O_7$), a derivative of CP's production process [25]. The Raman spectrum of the white particles sample, as depicted in Fig. 5d, showcases five distinctive peaks at 127, 200, 263, 356, and 463 cm^{-1}. The peak at 463 cm^{-1} is identified as the Si–O–Si bending vibration in quartz. Additionally, the bands at 127 cm^{-1} and 200 cm^{-1} are recognized as the low-frequency peak positions characteristic of Si–O. These combined spectral features strongly suggest that the particles in question are indeed quartz [26].

For the red part on sample, illustrated in Fig. 5e, the Raman spectrum identifies bands at 254 cm^{-1}, 288 cm^{-1}, and 344 cm^{-1}, which are in line with Hg-S stretching vibrations, matching the standard Cinnabar (HgS) sample [27]. Lastly, the Raman spectrum for the white sample, presented in Fig. 5f, displays bands at 440 cm^{-1} and 588 cm^{-1}, representing PO_4^{3-} bending vibrations, and a band at 964 cm^{-1} denoting the symmetric stretching vibration of PO_4^{3-}. These features accord with the standard Calcium Phosphate ($Ca_3(PO_4)_2$) sample [28].

In the FTIR analysis of the white sample, detailed in Fig. 6a, several distinct bands are identified at the following wavenumbers: 466 cm^{-1}, 875 cm^{-1}, 1052 cm^{-1}, 1436 cm^{-1}, 1631 cm^{-1}, and 3445 cm^{-1}. The peak occurring at 3445 cm^{-1} is characteristic of O–H vibrations. At 1436 cm^{-1}, an asymmetrical C–O stretching vibration is observed. The presence of a CO_3^{2-} bending vibration in the plane is indicated by the band at 875 cm^{-1}. The band at 1052 cm^{-1} corresponds to a symmetrical stretching vibration of PO_4^{3-}, and the band at 466 cm^{-1} is associated with a symmetric bending vibration of the same group. These spectral features suggest the sample comprises calcium carbonate and calcium phosphate, as evidenced by their respective infrared signature peaks [29].

In the infrared spectroscopic examination of the yellow-brown substance, detailed in Fig. 6b, key absorption bands are discerned at the wavenumbers: 1405 cm^{-1}, 1634 cm^{-1}, 2851 cm^{-1}, 2925 cm^{-1}, and 3427 cm^{-1}. The absorption at 3427 cm^{-1} is notably associated with hydroxyl (OH) vibrations. The presence of methylene (CH_2) stretching vibrations is confirmed by the peaks at 2925 cm^{-1} and 2851 cm^{-1}, whereas the peak at 1634 cm^{-1} is characteristic of esters or carboxylate functionalities. Additionally, the band at 1405 cm^{-1} is attributed to methine (CH) vibrations. These characteristic peaks closely align with the infrared spectral features of ancient Chinese lacquer [30].

To further determine the composition of the purple pigment, CP particles were analyzed by μ X-ray diffraction. The results, shown in Fig. 7a, indicate that the main phase of the purple pigment is CP ($BaCuSi_2O_6$). Additionally, diffraction peaks of quartz were detected in separate purple particles. The μ X-ray diffraction analysis revealed that the primary component of the white pigment is calcium phosphate, as shown in Fig. 7b. Combined with the Raman analysis results, it is suggested that the white sample may be bone white.

Quantitative and mapping by EPMA

Through the mapping analysis of EPMA, it is possible to rapidly obtain the compositional characteristics and distribution of substances in different forms within the matrix. This information aids in identifying the original substances or processing methods under conditions of morphologically similar residues, allowing for further

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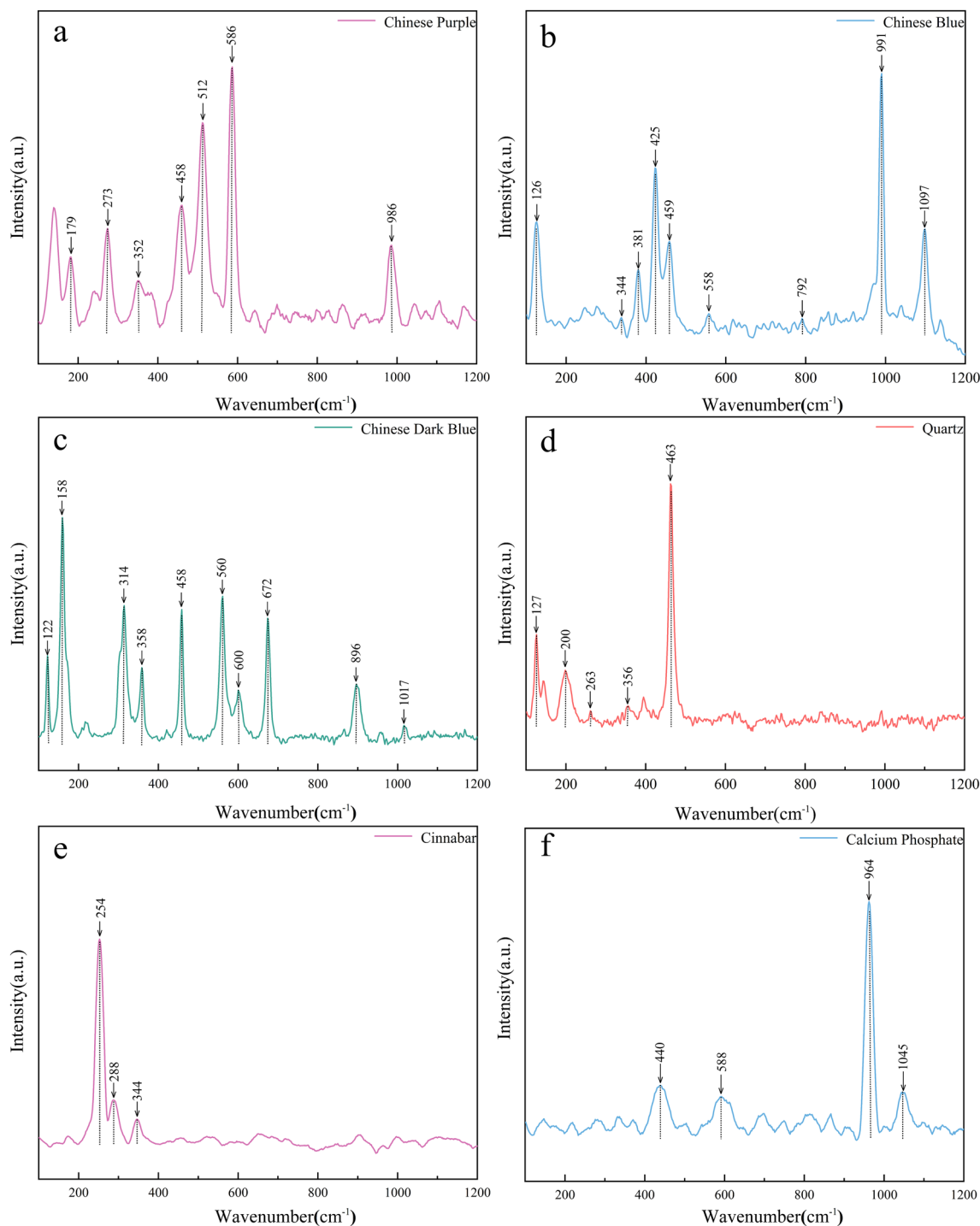
Fig. 5 Raman spectra of purple sample. **a** Purple pigment; **b** Light blue particle; **c** Dark Blue particle; **d** White particle; **c** Red pigment; **f** White pigment. The excitation wavelengths for **a**–**d** samples were 532 nm, and for **e** and **f** were 785 nm

analysis of their manufacturing techniques and cultural significance.

To explore the relationship between form and composition further, EPMA mapping and quantitative analysis were used to determine the distribution characteristics of different elements at the microscopic level. Elements such as Al, Si, S, Cu, Ba, and Pb, identified based on the WDS spectrum, were analyzed for their distribution, with the

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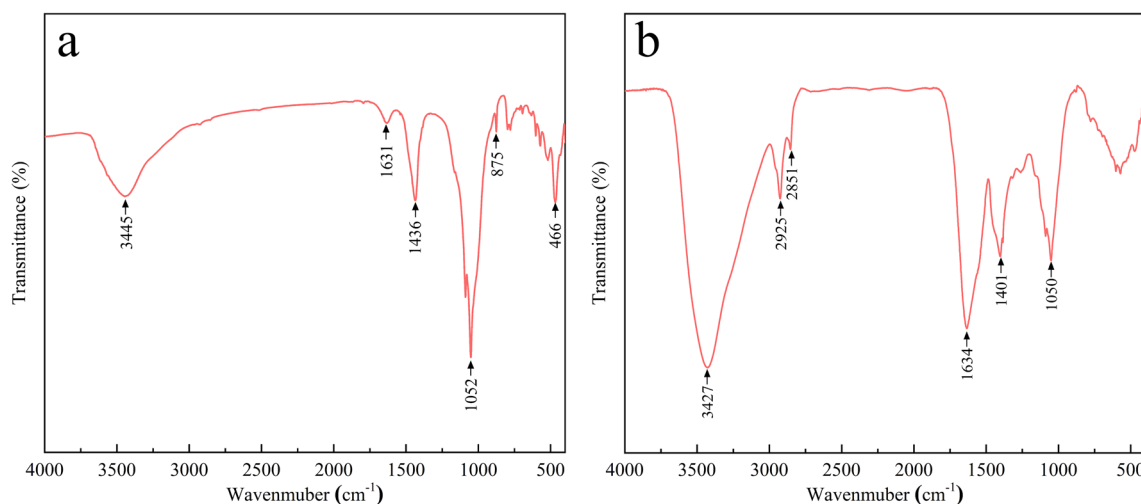
Fig. 6 FTIR spectra of white and yellow-brown substance sample. **a** White pigment **b** Yellow-brown substance
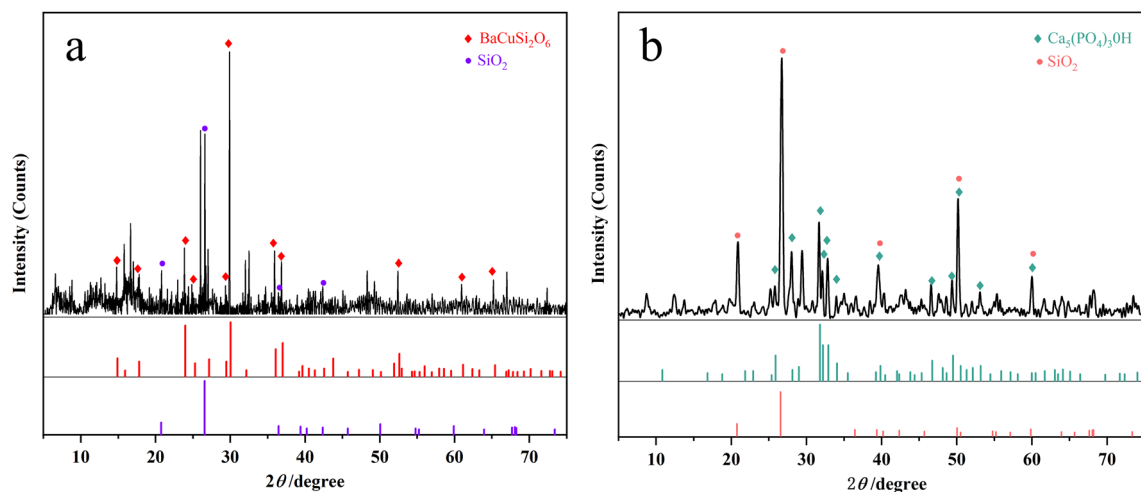
Fig. 7 The μ-XRD pattern of the samples. **a** Purple sample; **b** White sample. Circles represent silica crystals, and diamonds indicate another major phase

results displayed in Fig. 8c–i. Nine spots were selected for quantitative analysis, and the outcomes, along with their locations, are presented in Table 1; Fig. 8a, b.

According to the EPMA mapping results, Cu and Ba exhibit a strong correlation in purple pigments, while there is no significant correlation for Si and Al. Furthermore, there is a low degree of overlap between the distribution of these elements and that of Pb, which can be attributed to the crystal structure of the pigment. Although S is present in the sample, it is unevenly distributed and shows a low correlation with other elements. Additionally, mapping and quantitative measurements of the Sn element indicate that the sample contains negligible amounts of Sn.

The WDS quantitative analysis shows that the primary components at points 6–9 are Si, Ba, and Cu. The chemical composition and ratio closely resemble those of CP ($BaCuSi_2O_6$), confirming the presence of barium copper silicate. Integrating these findings with previous results, it can be concluded that the purple pigment in the pottery pot unearthed at the Shaanxi Qinhan Xincheng is CP. The red pigment is identified as cinnabar, and the white pigment as bone white.

Discussion

Chemical composition analysis

The data can be categorized into four groups based on the quantitative WDS results. Points 1 are characterized

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Table 1 WDS result of purple sample (wt%). A dash (-) represents uncalculated data

Posi	Si	Al	S	Cu	Pb	Ba	Mg	Fe	K	Ca	Ni	Cu/Ba	Si/Cu	Si/Ba
1	5.74	1.02	11.65	1.22	1.43	74.91	0.23	0.36	0.09	0.40	2.93	–	–	–
2	15.33	0.29	0.00	2.10	48.33	31.43	0.07	0.17	0.02	0.08	2.18	–	–	–
3	16.21	0.56	0.00	1.85	48.67	28.28	0.28	2.10	0.02	0.24	1.79	–	–	–
4	21.27	1.12	0.00	2.21	46.56	26.00	0.39	0.72	0.16	0.32	1.25	–	–	–
5	31.50	23.46	0.02	0.06	0.18	0.08	0.75	14.59	1.00	28.31	0.04	–	–	–
6	26.46	2.39	0.27	18.67	1.40	44.10	0.36	0.82	0.32	4.03	1.17	0.82	2.94	2.40
7	24.70	1.54	0.17	22.16	1.05	47.88	0.34	0.53	0.13	0.14	1.35	0.89	2.31	2.06
8	23.38	0.81	0.16	23.23	1.03	49.51	0.10	0.22	0.07	0.14	1.34	0.91	2.08	1.89
9	25.60	0.50	0.04	22.43	0.90	48.62	0.08	0.26	0.04	0.09	1.43	0.89	2.36	2.11
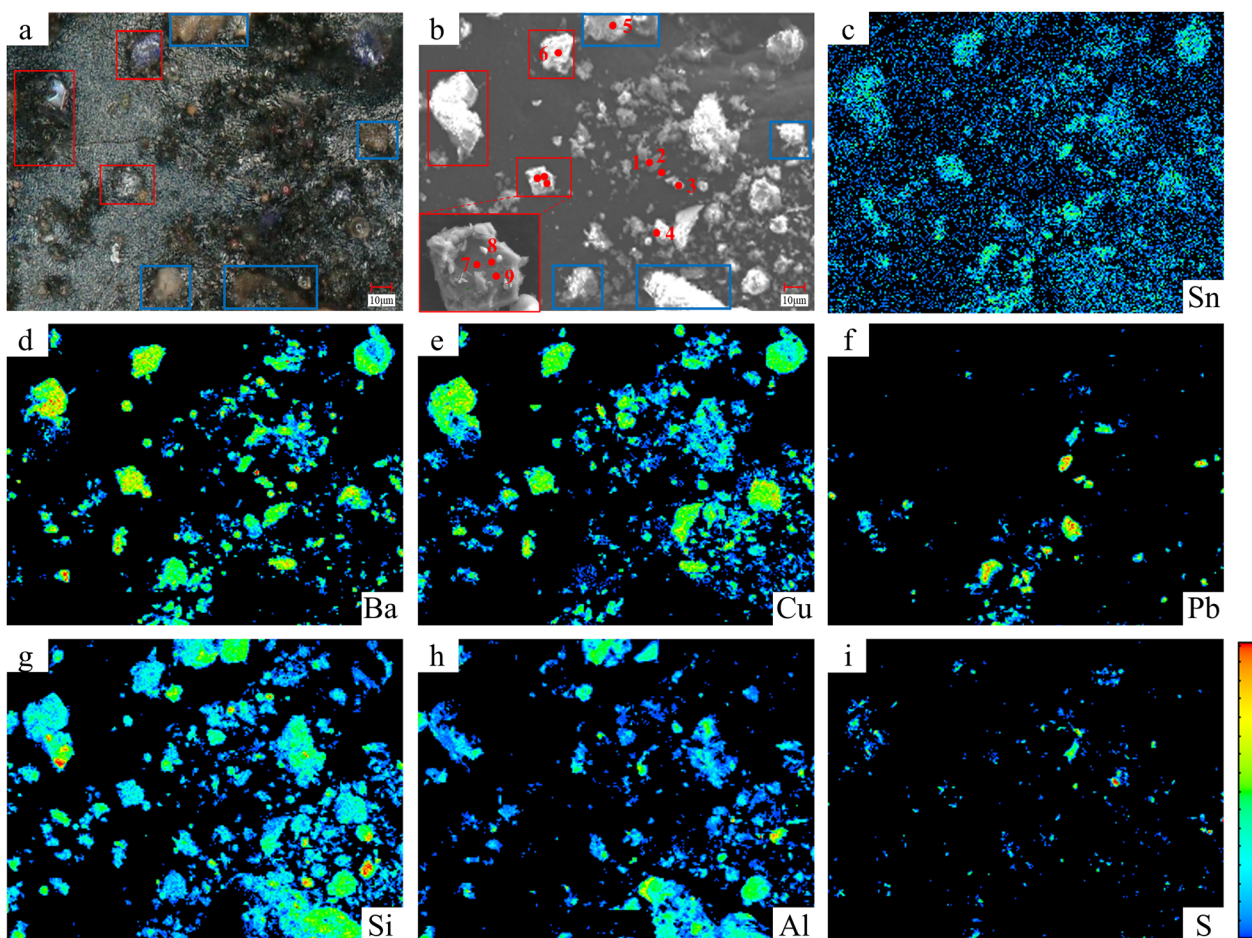
Fig. 8 Visualizing the mapping area and mapping results for different elements. **a** EPMA mapping area under an optical microscope **b** EPMA quantification position map of purple sample. The mapping area micro-photo clearly shows the purple pigment and the accompanying clods of soil; the nine points were selected based on the EPMA mapping results. The red boxes represent the CP particles, the blue boxes represent the soil. **c**–**i** are EPMA mapping results of the purple sample, featuring seven elements: Al, Si, S, Sn, Cu, Ba, Pb. Blue to red represents the level of element concentration, with blue being lower and red being higher

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by low Si, high S, and high Ba. Points 2–4 are notable for high Pb and medium Ba. Point 5 is distinguished by high Si, high Al, high Fe, and high Ca. Points 6–9 are marked by high Si, high Cu, low Pb, and medium Ba. Additionally, Points 6–9 further confirm the presence of barium copper silicate.

The characteristics of point 1 data are: the content of Si and Cu is pretty low, while the content of S and Ba is high, may indicate residual barium sulfate minerals. As mentioned in the introduction, some scholars have disputed the source of barium- containing mineral raw materials in previous studies [3, 5]. In principle, barite ($BaSO_4$), witherite ($BaCO_3$), and barium oxide (BaO) can be used as barium sources. However, simulation experiments [4, 5] have shown that when $BaSO_4$ is used as the barium source, whether used directly or converted into calcined ash, it is challenging to synthesize CP. In contrast, using $BaCO_3$ makes the process much easier. On the other hand, some scholars [11], using chemical analysis of materials such as Majiayuan faience beads and Western Han (207 B.C.–8 A.D.) CP pigments, found them to contain S and Ba, with a ratio close to 1:1, indicating the use of barite. Hence, it is suggested that witherite was used as a raw material in ancient times. Nonetheless, whether point 1 implies the use of barite as a barium source in ancient times remains questionable, due to the close physical properties and common co-existence of witerite and barite. In the mapping results, the distribution of S and other elements does not overlap significantly, and the amounts are not substantial, suggesting that the content is relatively low. Therefore, whether barite was an ancient barium source material or merely an accidental impurity still requires further investigation.

Points 2–4 exhibit Pb content close to 50%, suggesting the addition of a lead-containing mineral. Interestingly, S content measured at these points is almost zero, indicating no correlation between Pb and S. Point 5 shows a significantly high Al, along with relatively high Fe and Ca levels, which may represent the base soil samples of pottery pots. Additionally, the data from points 1–9 all exhibit a certain amount of Ni, which may be an impurity in a certain raw material ore in barium copper silicate. However, mapping and quantitative measurements of the Sn element indicate that the sample contains negligible amounts of Sn. Previous studies [31] have indicated that barium copper silicate may have used bronze scraps as a source of copper, thereby introducing Sn and Ni impurities. However, the current experimental results have no clue to that bronze scraps were not used.

The elemental composition of points 6–9 is notably consistent, with the data for each element staying within a specific range. This observation, combined with microscopic results (Fig. 9c), suggests that the crystals at points 6–9 are likely flaky in nature. Studies [31] have indicated that the chemical composition influences the crystal form of CP. For instance, when Sn is present in CP samples, the morphology typically exhibits needle-like crystals. In this analysis, the CP sample was found to contain lead (Pb) but not tin (Sn), which resulted in the formation of barium copper silicate crystals in a flake form rather than as needles. This finding underscores the diversity in the crystal characteristics of barium copper silicate.

Treating process characters

Considering that the tomb was from a critical period marking the transition in the use of barium copper artificial silicate, this study conducted a microscopic comparison between the Western Han (207 B.C.–8 A.D.) CP painted pottery pigment and the Warring States period (470 B.C.–221 B.C.) CP octagonal stick products to further clarify the technological evolution of pigments during this era. The detailed information on the CP painted pottery pigment and the comparative results are presented in Fig. 9. The blue color prominently displayed in Fig. 9 is due to the grain size of CP exceeding 40 μm, which causes it to exhibit a blue coloration [32, 33]. The purple part on painted pottery reveals pigment particles of varying sizes, (around 15–20 μm) with almost all these particles being enveloped by transparent crystalline particles on their surfaces. These transparent crystal-like substances, distinguishable in shape and exhibiting partial melting, are likely unmelted quartz particles, a situation similar to that of CP faience products. When comparing with the microstructure of the CP octagonal stick, similar transparent crystalline particles are observed, consistent in shape with the sample, but smaller in size, attributed to the precision manufacturing of faience products.

Thus, it is postulated that the raw materials of purple used in the painted pottery were based on the faience-system material production method. This implies a two-step process: initially creating CP faience-system material, and then grinding it to be used as a pigment, which is later combined with organic glue for application on pottery surfaces. Unlike lead-barium glass products, which are typically completely homogenized to glassy status without any quartz crystals or semi-fused particles, the barium copper silicate faience system incorporates quartz as the base, followed by a glazing process, making quartz particles a common feature in faience products. This is corroborated by Raman and XRD results of the CP particles, which identified the presence of quartz crystal phase (please refer to Figs. 6d and 8a).

While CP pigment technology is related to faience, it may have retained distinctive features due to specific aspects of its craftsmanship or technique. As a result, although it was used in typical Central Plains cultural

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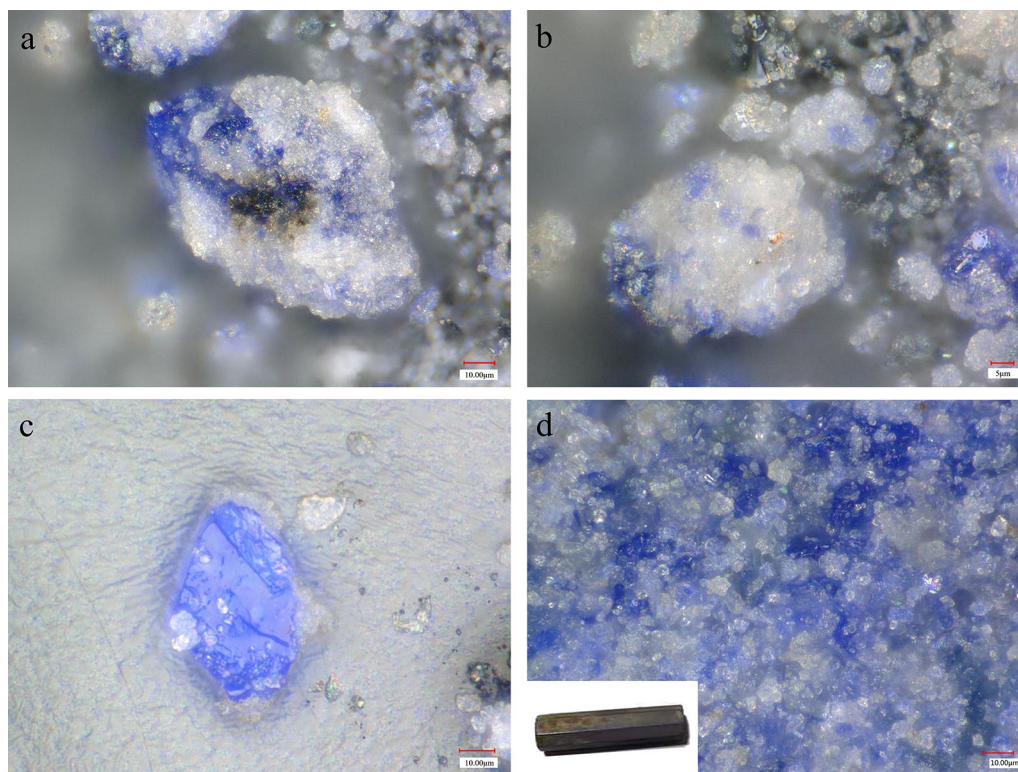
Fig. 9 Microphotographs: intricate details of CP painted pottery (**a**–**c**), highlighting a Singular Blue Particle (**c**), alongside a CP Octagonal Stick (**d**)

artifacts, its technological essence did not completely diverge from faience influence. It failed to integrate deeply with lead-barium glass technology, continuing instead the traditional faience craftsmanship.

It is evident that the CP pigment used in painted pottery and the faience production process exhibit consistency. They should be formed after the processing of faience, distinctly different from the lead-barium glass technology system. This observation underscores that in the realm of cultural exchange and mutual learning, technology transmission or integration is not a linear or simple replacement process. Instead, it represents a complex and diverse developmental process. These insights provide an important reference for understanding the introduction and influence of different technologies during the pre-Qin era (before 221 B.C.) in Northwest China, as well as their relationship with localization and adaptation.

Conclusions

Chinese Purple, a prominent purple pigment in ancient China, has historically been under-recognized in terms of its technological significance and features, hindering comprehensive discussions about its production and distribution. This research, leveraging mapping, micro-area composition analysis, and microstructural investigation,

revealed that the purple pigment in the painted pottery pot from the Qinhan Xincheng site in Shaanxi is indeed CP. Accompanying this were findings of cinnabar as the red pigment and bone white as the white pigment. The application of barium copper silicate as a pigment during the Qin and Han dynasties (221 B.C.–220 A.D.) represents a direct lineage from the faience techniques of the Warring States period (476–221 B.C.). The shift in the types of barium copper silicate products was not a result of transformation in lead-barium glass technology but a transformation in application methods, mirroring the adaptive and integrative processes among diverse cultures. These insights are invaluable for understanding the evolution of barium copper silicate products and the technological interactions across various ethnic cultures.

Supplementary Information

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Supplementary Material 1.

Declarations

Competing interests
The authors declare no competing interests.

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References

1. FitzHugh EW, Zycherman LA. An early man-made blue pigment from China—Barium copper silicate. Stud Conserv. 1983;28(1):15–23.
2. FitzHugh EW, Zycherman LA. A purple barium copper silicate pigment from early China. Stud Conserv. 1992;37(3):145–54.
3. Berke H. The invention of blue and purple pigments in ancient times. Chem Soc Rev. 2007;36(1):15–30.
4. Zhang ZG. Research on ancient Chinese artificial copper barium silicate pigments. Dissertation, University of Science and Technology Beijing. 2011 (in Chinese).
5. Qin Y, Wang YH, Chen X, et al. A discussion on the emergence and development of ancient Chinese artificial barium copper silicate pigments from simulation experiments. Archaeometry. 2016;58(5):796–806.
6. Liu Z, Mehta A, Tamura N, et al. Influence of Taoism on the invention of the purple pigment used on the qin terracotta warriors. J Archaeol Sci. 2007;34:1878–83.
7. Xia Y, Ma QL, Zhang ZG, et al. Development of Chinese barium copper silicate pigments during the qin empire based on raman and polarized light microscopy studies. J Archaeol Sci. 2014;49:500–9.
8. Wang R, Xu Y, Zhou X. Study on the related problems of lead-barium imitating-jade glass in the Warring States period of China. Archaeol Anthropol Sci. 2022;14(8):159.
9. Berke H. Chemistry in Ancient times: the development of Blue and Purple pigments. Angew Chem Int Ed. 2002;41(14):2483–7.
10. Wiedemann HG, Berke H. Chemical and Physical investigations of Egyptian and Chinese Blue and Purple. Monuments Sites. 2015;3:154–71.
11. Lin YX, Zhou GJ, Ian F. Research on glass and related materials unearthed from Majiayuan warring states cemetery in Zhangjiachuan. Cult Relics. 2008;(3):71–83 (in Chinese).
12. Ma QL, Portmann A, Wild F, et al. Raman and Sem studies of man-made barium copper silicate pigments in ancient Chinese artifacts. Stud Conserv. 2006;51(2):81–98.
13. Huang XJ, Wang LQ et al. Analysis and study of silicate decorative beads unearthed from Zhaitouhe cemetery in northern Shaanxi. Archaeol Cult Relics. 2018; (2):129–35. (in Chinese).
14. Wang YS, Ling X, Xu WH, et al. Scientific analysis of a purple octagonal stick unearthed from a qin tomb at Hejia village of Zhou Mausoleum. Sci Conserv Archaeol. 2020;32(3):28–37 (in Chinese).
15. Ma QL, Zhang ZG, Gao XS. Study on the Chinese blue and Chinese purple in the octagonal stick unearthed from the Warring states tomb in luoyang. Cult Relics. 2008;8:83–8 (in Chinese).
16. Huang XJ, Yan J, Zhang YLZ, et al. Technological analysis of the chess pieces of Liubo uncovered from the warring states tomb in Shaanxi province. Spectrosc Spectr Anal. 2022;42(10):3187–92 (in Chinese).
17. Thieme C, Emmerling E, Herm C et al. Research on paint materials, paint techniques and conservation experiments on the polychrome terracotta army of the first emperor Qinshihuang. In The ceramics cultural heritage: proceedings of the international symposium The Ceramics Heritage of the 8th CIMTEC-World Ceramics Congress and Forum on New Material.1994; (6): 591–601.
18. Zuo J, Zhao XC, Wu R, et al. Analysis of the pigments on painted pottery figurines from the Han dynasty's Yangling tombs by raman microscopy. J Raman Spectrosc. 2003;34(2):121–5.
19. Cheng XL, Xia Y, Ma YR, et al. Three fabricated pigments (Han purple, indigo and emerald green) in ancient Chinese artifacts studied by raman microscopy, energy-dispersive x-ray spectrometry and polarized light microscopy. J Raman Spectrosc. 2007;38(10):1274–9.
20. Gao YM. Analysis of mural pigments unearthed from Astana tombs in Turpan, Xinjiang. Turfanological Res. 2021; (2):108–12. (in Chinese).
21. Baziotis I, Xydous S, Manimanaki S, et al. An integrated method for ceramic characterization: a case study from the newly excavated Kastrouli site (late Helladic). J Cult Herit. 2020;42:274–9.
22. Shalvi G, Shoval S, Bar S, et al. Pigments on late bronze age painted canaanite pottery at Tel Esur: new insights into canaanite–Cypriot technological interaction. J Archaeol Science: Rep. 2020;30:102212.
23. Mozgai V, Topa BA, Weiszburg TG, et al. SEM–EDS and μ-XRD study of the Niello inlays of a unique late roman silver augur staff (lituus) from Brigetio, Pannonia (Hungary). Archaeol Anthropol Sci. 2019;11(4):1599–610.
24. Shen L, Wang C, Zhang J, et al. Cu and as containing pigments in Zhejiang architecture polychrome paintings: a case study of degradation products of emerald green. Herit Sci. 2023;11(1):9.
25. Berke H, Corbiere T, Portmann A, et al. Man-made ancient Chinese blue and purple barium copper silicate pigments. Wenbo. 2009;6:251–65.
26. Skultéti Á, Tóth TM, Fintor K, et al. Deformation history reconstruction using single quartz grain Raman microspectroscopy data. J Raman Spectrosc. 2014;45(4):314–21.
27. Botticelli M, Maras A, Candeias A. μ-Raman as a fundamental tool in the origin of natural or synthetic cinnabar: preliminary data. J Raman Spectrosc. 2020;51(9):1470–9.
28. Mendili YE, Vaitkus A, Merkys A, et al. Raman open database: first interconnected raman–x-ray diffraction open-access resource for material identification. J Appl Crystallogr. 2019;52(3):618–25.
29. Corrêa THA, Holanda JN. F. Fish bone as a source of raw material for synthesis of calcium phosphate. Mater Res. 2019;22:e20190486.
30. Liu L, Wu H, Liu W, et al. Lacquering craft of Qing Dynasty lacquered wooden coffins excavated from Shanxi, China–A technical study. J Cult Herit. 2016;20:676–81.
31. Zhang ZG, Ma QL, Berke H. Man-made blue and purple barium copper silicate pigments and the Pabstite ($BaSnsi_3O_9$) mystery of ancient Chinese wall paintings from luoyang. Herit Sci. 2019;7:1–9.
32. Rieck B, Pristacz H, Giester G, Colinowensite. $BaCuSi_2O_6$, a new mineral from the Kalahari Manganese Field, South Africa and new data on wesselsite, $SrCuSi_4O_{10}$. Mineral Mag. 2015;79(7):1769–78.
33. Nicola M, Gobetto R, Masic A. Egyptian blue, Chinese blue, and related two-dimensional silicates: from antiquity to future technologies. Part A: general properties and historical uses. Rend Lincei Scienze Fis E Naturali. 2023;34:369–413.

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