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Multi-analytical investigation into the materials and techniques of paintings on Northern Wei Dynasty (398–494 CE) coffin planks excavated from Shanxi, China

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This study combined various non-invasive and micro-invasive analytical techniques to investigate the production process of coffin plank paintings excavated from a Northern Wei tomb in Zhijiabao Village, Datong City, Shanxi Province. Fiber-optic reflectance spectroscopy, portable Raman spectroscopy, and portable X-ray fluorescence spectroscopy were employed for in-situ non-invasive detection of coffin panel paintings. On that basis, micro-samples in smaller amounts than that of previous studies of the same type were collected and analyzed through optical microscopy, confocal micro-Raman spectroscopy, and scanning electron microscopy-energy dispersive spectroscopy. The results showed that the studied coffin plank decoration was painted after applying a layer of yellow primer to the plank surface. Specifically, cinnabar was used as the red material, pararealgar was used as the yellow color, an indigo and orpiment mixture was used as the green substance, the blue pigment was most likely an indigo and lead white mixture, gypsum was used the white material, and carbon black was used as the black pigment. Notably, the studied coffin plank was painted with a mixture of inorganic and organic materials to present the green and blue colors. This study provided not only a scientific basis for the conservation and restoration of this artifact but also new information for the research on Northern Wei art history.

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Introduction

As products of secular culture, painted wooden coffins are characteristic funerary boxes with decorative paintings, mostly figures, social customs, material culture, funerary beliefs, and so on (Yu and Qin, 2006). Published archeological data covered excavations of painted wooden coffins in the Mediterranean and East Asia, mainly in Egypt and China. Egyptian-painted wooden coffins appeared during the Old Kingdom period, flourished during the Middle Kingdom period, and still received wide usage during the New Kingdom period (Cooney, 2014). Painted wooden coffins in China first appeared in the Han culture region (Xu, 2011), and those unearthed from the Tomb of Marquis Yi of Zeng in Sui County, Hubei Province, during the Warring States period (475-221 BCE) are the earliest physical objects found to date (Tong, 2007). During the Han Dynasty (202 BCE-220 CE), the custom of lavish burials was popular in the Central Plains, and the decorative technique of paintings on wooden coffins was also prevalent (Wu, 2007). As wars plagued the Central Plains in the Wei and Jin Dynasties (220-420 CE), this decorative tradition was brought into coetaneous tombs in the Hexi Corridor as the noble clans from the Central Plains moved in to seek refuge (Lin, 2020). Meanwhile, the southward migrating Xianbei people absorbed this decorative tradition into their funeral customs and started using wooden coffins for burials (Tong, 2007; Wu, 2008). Painted wooden coffins from different times and places took on different forms and features, reflecting the different historical and cultural backgrounds. Studying the painting decoration techniques can reveal the evolution of funerary beliefs and the social structure and economic system changes in different periods.

At present, the study of techniques adopted on Egyptian painted wooden coffins has evolved into a technical system combining non-invasive and micro-invasive analyses. For example, Bracci et al. (2015) combined these analyses to study the materials and cross-sectional characteristics of a late 22nd Dynasty / early 25th Dynasty Egyptian painted wooden coffin in the collection of the Archaeological Museum of Bologna, confirming that the coffin had undergone several restorations. Zidan et al. (2018) and Abdrabou et al. (2022) adopted various analytical methods, such as multispectral imaging, infrared spectroscopy, and Raman spectroscopy, to identify the pigments and wood materials of ancient Egyptian painted wooden coffins in the collections of the Egyptian Museum in Cairo. Bonizzoni et al. (2018) characterized the pigments and adhesives from the 21st Dynasty wooden coffins in the collection of the Royal Museums of Art and History of Brussels using imaging techniques, multiple spectral analyses, and gas chromatography - mass spectrometry. Based on case studies, scholars proposed constructing pigment libraries of different periods (Scott, 2016) to provide strong empirical evidence for the research on Egyptian painting history.

Most studies on the painted wooden coffins in China have focused on analyzing the images of the paintings to reveal the influence of Han culture on non-Han cultures, the phenomenon of multi-ethnic cultural integration, and the artistic characteristics (Kong and Hou, 2006; Tong, 2012; Xin and Ma, 2017). Meanwhile, the times and regions covered in previous studies mainly included the Hexi and Xinjiang regions during the Han and Jin Dynasties (202 BCE-420 CE), the Qinghai region during the Tibetan Empire and Tuyuhun Dynasty (313-842 CE), and the Inner Mongolia region during the Liao Dynasty (907-1125 CE). The establishment and development of the Northern Wei Dynasty (386-534 CE) were accompanied by the intermingling of different cultures, and setting the capital in Pingcheng was an important symbol of the Tuoba regime's transition from a nomadic country beyond the Great Wall to a Central Plains

dynasty (Peng, 2018). While absorbing Han culture and cultures of other ethnic groups, the Xianbei ruling class in that period retained the cultural characteristics of their own people, showing obvious characteristics of the times. However, only four sets of painted wooden coffins from the Pingcheng Period (398-494 CE) of the Northern Wei Dynasty were excavated (Gao, 2004; Han and Han, 1984; Liu and Gao, 2004; Shanxi Provincial Institute of Archaeology, Datong Municipal Museum, 1992). Despite the few studies on the content of the paintings (Hu et al., 2015; Sun, 1989), the raw materials and techniques of the painted wooden coffins of this period remain unclear due to the lack of scientific analysis. In addition, non-invasive analytical methods have not yet been reported in the existing scientific analyses of painted wooden coffins in China, which generally require the extraction of samples larger than 1 cm in size for research (Fan et al., 2012; Hao et al., 2017; Jiang et al., 2020; Liu et al., 2016; Zhang, 2015), and excessive sampling may adversely affect the preservation of the artifacts.

In September 1997, Datong Municipal Institute of Archaeology discovered a disturbed earthen cave tomb with a sloping path in the north of Zhijiabao Village in Datong City (Fig. 1), which was identified as a cultural relic from the Pingcheng Period of the Northern Wei Dynasty. Three pieces of painted wooden coffin planks, painted in red, white, black, green, blue, and gray, were unearthed. The subjects of the paintings were actual scenes from the secular life of the northern ethnic groups, including carriage and horse travels, hunting activities, guards at feasts, decorative patterns, etc., making them outstanding masterpieces of paintings in the Pingcheng Period (Liu and Gao, 2004). Due to the damage from tomb raiding prior to excavation and the lack of professional conservation, the coffin plank paintings exhibited surface cracking, pigment shedding, wood degradation, etc.

To fill in the gaps between previous and current research, i.e., the lack of research on the production techniques of coffin plank paintings in the Northern Wei Dynasty, this study combined various non-invasive and micro-invasive analytical techniques to investigate the pigments and production process of those coffin plank paintings. This study provided not only a reliable basis for the conservation and restoration of such coffin plank paintings, but also new information for the research on Northern Wei art history. To balance between maximizing information revelation and maintaining the integrity of cultural relics, we first conducted portable X-ray fluorescence (p-XRF) spectroscopy, portable micro-Raman spectroscopy (p-RS), and fiber-optic reflectance spectroscopy (FORS) for the initial identification of coffin plank painting pigments, and located sampling sites with sufficient necessity and representativeness. On this basis, we attempted to reduce the sampling volume below that in previous studies and precisely identify the pigment compositions and the production techniques via optical microscopy (OM), scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS), and confocal micro-Raman spectroscopy (micro-RS). The data from multiple instruments can complement and corroborate each other, thus extracting rich information from cultural relics more effectively.

Materials and methods

Samples. The measurement points are shown in Fig. 2. First, 20-23 test points were selected on each of the three coffin planks for in-situ non-invasive analysis. Then, four micro-samples were extracted from the edge or warped areas for laboratory analysis. Based on the preliminary experimental results, simulated samples were prepared to investigate the complex pigment mixing phenomena. The specific information is presented in Table 1.

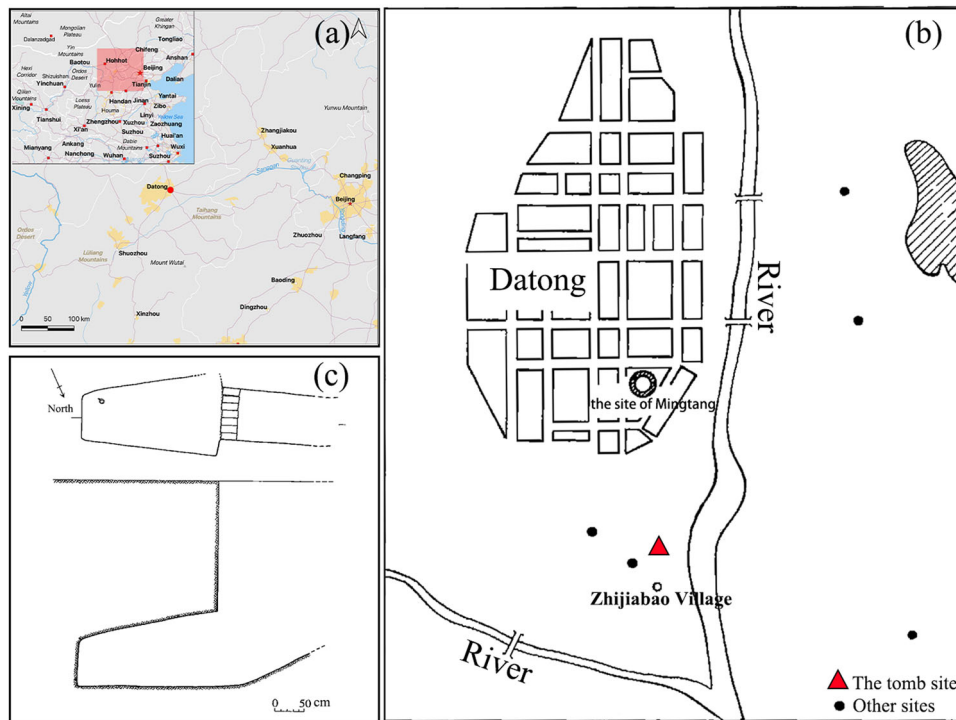


Fig. 1 The location and layout of the Zhijiabao site. **a** Zhijiabao Village on the map of China, located in Datong City, Shanxi Province. The maps were created using QGIS 3.12 (<https://qgis.org/en/site>) and use Natural Earth vector map data from (<https://www.naturalearthdata.com/downloads/>). **b** The location of the Northern Wei tomb within the Zhijiabao Village. **c** The plan and section view of the tomb. The location and layout of the tomb correspond to the archeological report on this Northern Wei tomb.

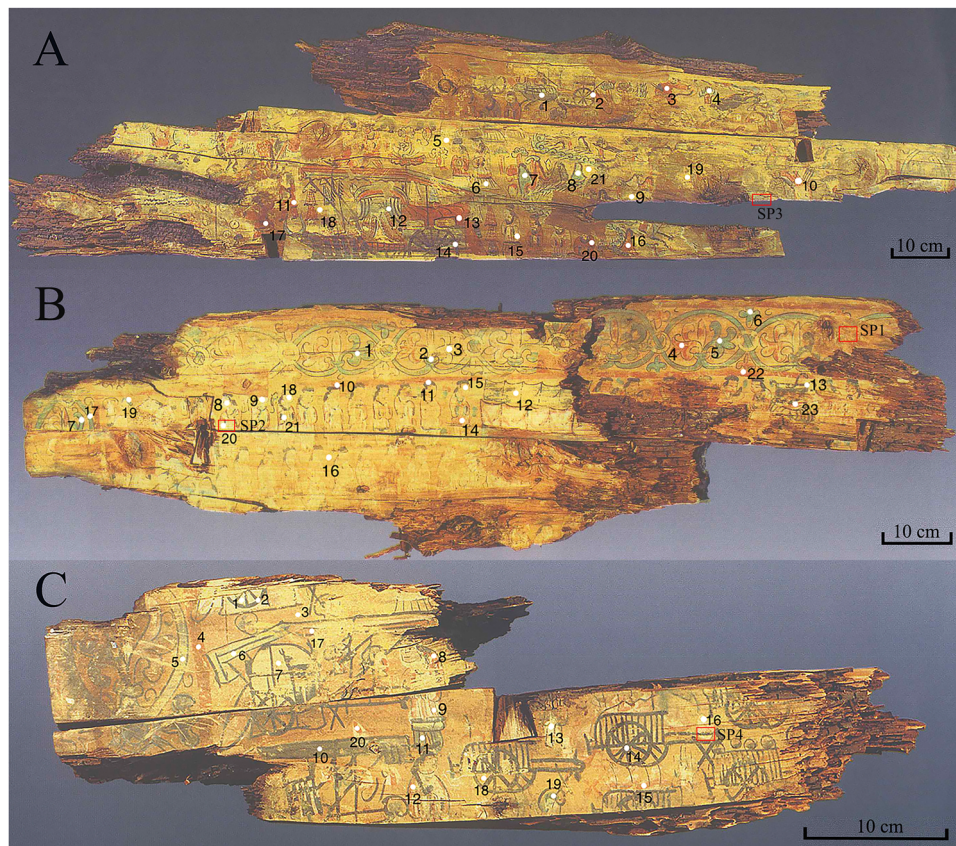
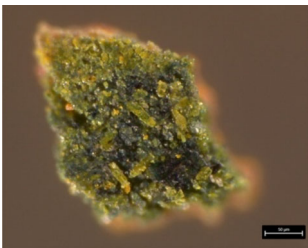
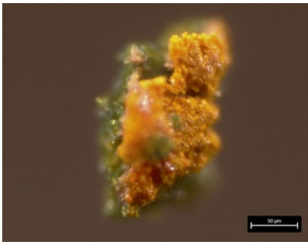
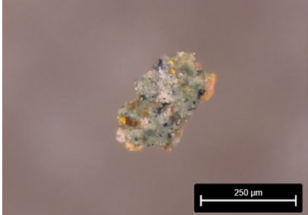
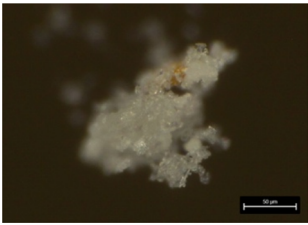




Fig. 2 Zhijiabao coffin plank paintings. Plank A, 1.53 × 0.42 m, Plank B, 1.33 × 0.44 m, Plank C, 0.60 × 0.18 m; Points 1 to 23 are non-invasive test points, and SP1 to SP4 are sampling locations.

Table 1 Sample information.

Sample	Picture	Description
Green (SP1-1)		The front side of SP1 is green, with unevenly distributed yellow crystals on the surface, measuring ~0.20 mm.
Green (SP1-2)		The back side of SP1 has yellow crystals stained with traces of green particles, measuring ~0.15 mm.
Blue (SP2)		SP2 is light blue overall, with aggregated dark blue dots and white attachments on the surface, measuring ~0.25 mm.
White (SP3)		SP3 is in the form of white crystals with traces of yellow particles, measuring ~0.15 mm.
Black (SP4)		SP4 preserves a complete cross-section from the wood to the pigment layer, which could be used for cross-section and black pigment analyses, measuring <3 mm in length.
Simulated sample		It is prepared by applying two layers of pigment on the surface of standard wood blocks, the first layer being a mixture of orpiment and realgar while the second layer being a mixture of orpiment and indigo, serving as a simulated sample of the green pigment in the coffin plank paintings.

In-situ non-invasive analysis

p-XRF. A portable X-ray fluorescence spectrometer (Niton XL3t 950, Thermo Fisher Scientific, USA) was used to analyze the elementary composition of the pigments. The specific settings were X-ray excitation of the Ag target with an excitation energy of 50 kV/40 μ A and a detection time of 30 s, and the mode of analysis was set to mining. Data were downloaded using the Thermo Fisher Scientific Niton Data Transfer (NDT 8.2) software and used without further processing on other software.

p-RS. A portable Raman spectrometer (HE785, Horiba Scientific, France) was employed to analyze the samples. A 785 nm laser served as the excitation source. The fiber-optic probe was equipped with a high-sensitivity CCD detector covering the UV-visible spectral band, which was thermoelectrically cooled to -50 $^{\circ}$ C, and an objective lens of 50 times was installed. The signal acquisition time was 5 s, and the number of accumulations was two times. Sulfur powders were used for calibration. The spectral testing range was 100-1000 cm^{-1} . LabSpec 6 (Horiba Scientific) was employed for data acquisition, and figures were plotted using OriginPro 2022 (Origin Lab Inc.).

FORS. In situ reflectance spectroscopy was performed using a spectrometer (FX2000, Ideaoptics Instruments, China) with an HL2000 halogen light source, a Y-type quartz fiber, and a wavelength range of 200-1100 nm. STD-WS series standard whiteboards were used for calibration. The light probe was kept on a surface about 0.5 cm from the sample, and the analyzed area was about 2 mm in diameter. The integration time was 40 to 50 ms, and each spectrum was the average of five acquisitions. Morpho (Ideaoptics Instruments) was employed for data acquisition, and figures were plotted using OriginPro 2022 (Origin Lab Inc.).

Laboratorial microanalysis

OM. A three-dimensional digital microscope (DVM6, Leica Microsystems, Germany) was used to observe the microscopic morphology of the pigment particles and the distribution of layers in the cross-section. Prior to cross-sectional observation, SP4 was encapsulated with light-curing resin (Technovit 2000LC) and polished with 500, 800, 1200, and 2000 grit sandpapers.

SEM-EDS. Elemental analysis was conducted using a benchtop SEM (Phenom XL, Thermo Fisher Scientific, USA) in the back-scattering probe mode, with an accelerating voltage of 15 kV and a vacuum degree of 10 Pa. The samples were not subjected to surface treatment prior to analysis.

micro-RS. The molecular structure of the samples was analyzed with a laser confocal micro-Raman spectroscopy (LabRAM HR Evolution, Horiba Scientific, France). For optimal experimental results, 532 nm and 633 nm lasers were used as excitation sources, respectively. The objective lens was 50 times. The signal acquisition time was 5 s, and the number of accumulations was five times. The resolution was 2 cm^{-1} , and the spot size was 1 μm . Single-crystal silicon wafers were employed for calibration. The spectral testing range was 100-2000 cm^{-1} . LabSpec 6 (Horiba Scientific) was employed for data acquisition, and figures were plotted using OriginPro 2022 (Origin Lab Inc.).

Results and discussion

Cross-section. Cross-sectional analysis explore the artifact production technique by observing the number, sequence, and thickness of layers. As shown in Fig. 3, the first layer on top of the

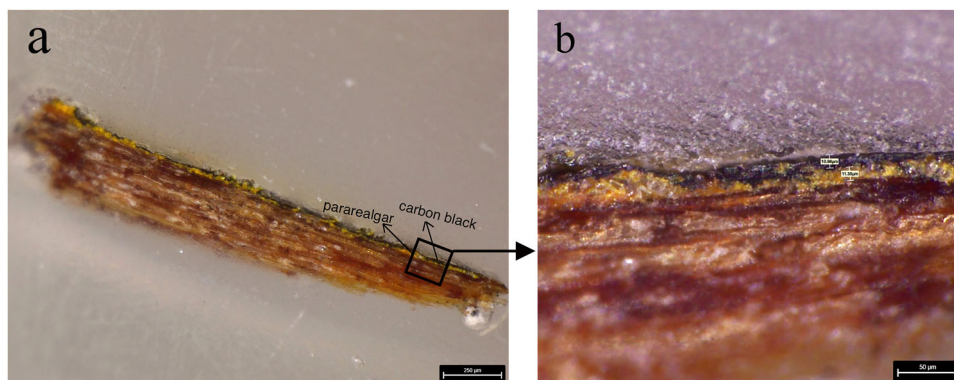


Fig. 3 Micrographs of SP4. Cross-sections magnified **a** 380 × and **b** 1700 ×.

Table 2 The p-RS and p-XRF analytical results of different test points.

Hue	Measurement spots	Major elements	Main Raman bands (cm^{-1})	Attribution
Red	A3, A10, A11, A13, A16, A17, A20; B4, B14, B22, B23; C4, C8, C9, C12, C15, C17, C20	Hg, As	255, 348	Cinnabar (HgS)
Yellow	A5, A9, A15, A18, A19, A21 B3, B12, B15, B16; C3, C7, C18	As	188, 233, 344	Realgar or Pararealgar (As_4S_4)
Green	A1, A4, A7, A8, A12; B1, B2, B5, B6, B7, B17, B19; C5, C6, C10, C11, C19	As	188, 293, 310, 354	Orpiment (As_2S_3)
Blue	B20, B21	As, Pb	192, 250, 350, 550	/
White	A6; B8, B9, B18; C1, C13, C16	As, Pb, Ca	190, 233, 348	/
Black	A2, A14; B10, B11, B13; C2, C14	As	/	/

wood substrate is a yellow pigment, and the second layer is black material, both with a thickness of 10–12 μm . This technique of priming with one kind of pigment (white) before painting was also identified in previously excavated painted wooden coffins from the Xinjiang region (Jiang et al., 2020) and Hexi Corridor (Zhao et al., 2017) during the Han and Jin Dynasties. The purpose is to cover and even out the base color to facilitate the subsequent color rendering of the painted layer, while filling in the wood grooves to make the painting surface smoother. Similar to this case, the practice of using a yellow pigment as the primer layer was also found in the painted wooden coffin discovered in M229 of the Northern Wei tomb complex (School of History and Culture - Shanxi University, Shanxi Provincial Institute of Archaeology and Datong Municipal Museum, 2006), located in the southern suburbs of Datong City. It can be inferred that this may represent a unique type of artistic style during the Northern Wei Period in Pingcheng. However, based on the existing data, it is not yet possible to determine whether it also carries other specific meanings.

Red. The red pigment was present in all three planks and applied to larger areas in Plank A. Hg element was detected at all red test points listed in Table 2, and the corresponding Raman spectra showed the same characteristics. Taking the Raman spectrum of test point C4 as an example (Fig. 4), the peaks near 254 cm^{-1} and 343 cm^{-1} are attributed to the stretching vibration of HgS , confirming the presence of cinnabar (Zhu et al., 2022). As a common mineral pigment in ancient times, cinnabar was commonly used

in murals, paintings, and other painted relics. In terms of wooden coffins, it could be used directly as a painting pigment or a coloring substance for the lacquer film.

Yellow. The yellow pigment was used as the base color of the painted wooden coffin. As shown in Table 2, the As element is present at all yellow detection points, and the corresponding Raman spectra show the same characteristics. Taking test point B15 as an example (Fig. 5a), the peaks at 190 cm^{-1} , 233 cm^{-1} , and 344 cm^{-1} are characteristic peaks of arsenic-sulfur compounds (As_4S_4). On this basis, we performed micro-RS tests on the underlying yellow pigment of SP1 to accurately identify the crystal structure of As_4S_4 in the studied artifact (Table 1. SP1-2), and the results (Fig. 5b) agreed well with the characteristic peaks of pararealgar (Bell et al., 1997). Among them, the peak near 232 cm^{-1} is attributed to the symmetric stretching vibration of As-As-As, and the peak near 345 cm^{-1} is attributed to the symmetric stretching vibration of S-As-S. The most distinctive feature distinguishing pararealgar from realgar is the characteristic band near 273 cm^{-1} . In addition, pararealgar has more strong- and moderate-intensity bands on the Raman spectrum compared to realgar, reflecting its reduced molecular symmetry (Vermeulen et al., 2018). Considering the elemental composition and molecular structure, it can be determined that the underlying pigment of SP1 contains pararealgar. However, this does not exclude the possible presence of realgar in the yellow pigment since pararealgar is a polymorph of realgar and can be easily converted from realgar by the action of light (Trentelman et al., 1996).

Green. The green pigment was present in all three planks, either as a filler color for pattern decoration or a decorative color for the figures' costumes. A comparative analysis was conducted between the reflectance spectra of the simulated sample (Table 1) and

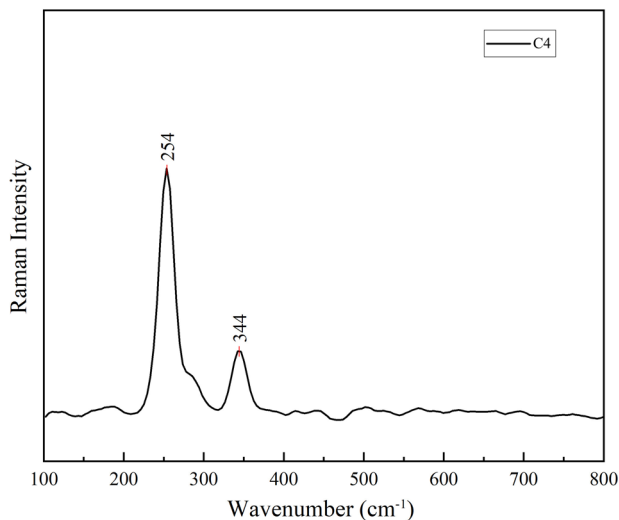


Fig. 4 Raman spectrum of C4. Obtained through p-RS with a 785 nm excitation source.

standard orpiment and indigo samples (Fig. 6a). For the standard samples, the maximum absorption peak of orpiment was near 450 nm, and the maximum absorption peak of indigo was near 660 nm, with the inflection point around 710 nm (Aceto et al., 2014; Tamburini and Dyer, 2019). In contrast, the simulated sample had absorption peaks at 450 nm as well as around 660 nm, with the inflection point near 690 nm. Thus, the reflection spectrum of the mixed sample showed a shift in the inflection point compared to the single-component indigo sample but still had the basic characteristics of the two pigments (Delaney et al., 2014; Xu et al., 2021). A comparison between the reflectance spectra of the simulated samples and the in-situ test points (Fig. 6b) suggested that their reflectance trends were approximately the same. Thus, it is presumed that the components of the green pigment are basically the same as those of the simulated samples.

As shown in Table 3, the elements detected by EDS include As, S, C, N, and O, but not Cu (Figure S1, Supplementary Material). Therefore, the green pigment was not the copper-based ones commonly used in ancient Chinese paintings but possibly arsenic-based or organic. As shown in Fig. 7, the Raman spectra of the green pigment and the simulated sample show consistent results. The peaks at 136 cm^{-1} , 154 cm^{-1} , 202 cm^{-1} , 294 cm^{-1} , 311 cm^{-1} , 354 cm^{-1} , and 383 cm^{-1} corresponded to orpiment, among which the peaks at 202 cm^{-1} and 383 cm^{-1} were attributed to the symmetric and antisymmetric stretching vibrations of As-S-As, respectively (Zhu et al., 2022). In addition, the peaks at 546 cm^{-1} and 599 cm^{-1} corresponded to the vibrations of $\delta\text{C}=\text{C}-\text{CO}-\text{C}$, $\delta\text{C}-\text{N}$, and $\delta\text{C}-\text{Cring}$, $\delta\text{C}-\text{N}$, respectively; the peaks at 1224 cm^{-1} and

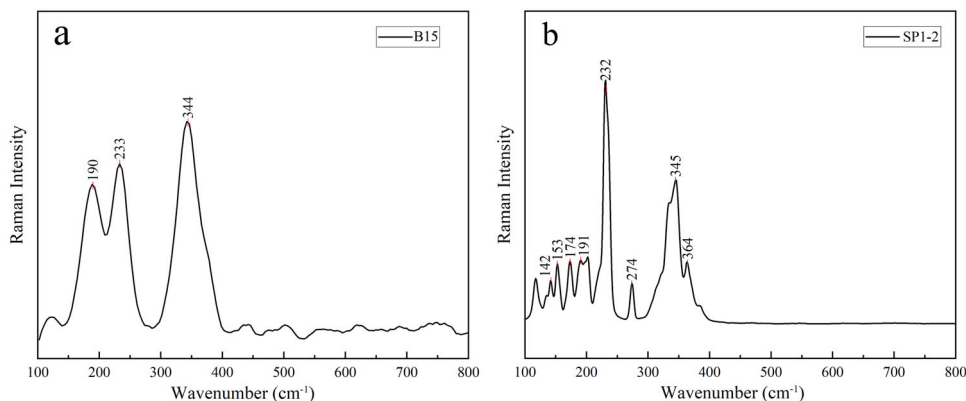


Fig. 5 The p-RS and micro-RS analysis of yellow pigment. **a** Raman spectra of test point B15 obtained through p-Raman with a 785 nm excitation source; **b** Raman spectra of yellow pigment detection points SP1-2 obtained through micro-Raman with a 633 nm excitation source.

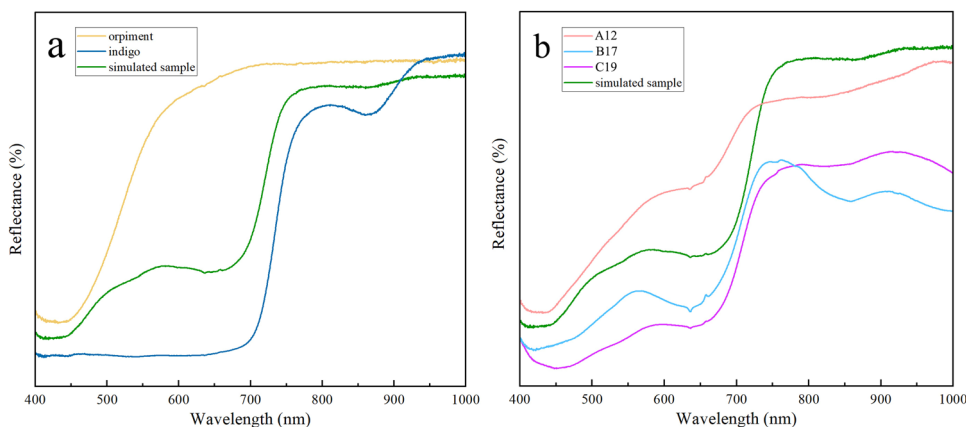


Fig. 6 Reflectance spectra of standard samples and measurement points. **a** Standard orpiment and indigo samples as well as the simulated sample; **b** test points A12, B17, C19, and simulated sample.

1248 cm^{-1} were attributed to the vibrations of $\delta\text{C-H}$, $\delta\text{C-Crings}$, and $\delta\text{C-H}$, $\delta\text{C}=\text{C}$, $\delta\text{N-H}$, respectively; the peaks at 1574 cm^{-1} and 1582 cm^{-1} were ascribed to the vibrations of the $\delta\text{N-H}$, $\delta\text{C-H}$, $\delta\text{vC-Crings}$ and $\text{vC}=\text{C}$, $\text{vC}=\text{O}$, $\delta\text{N-H}$ group conjugation systems, respectively (Fiedler et al., 2011; Rio et al., 2006; Tatsch and Schrader, 1995), which corresponded to the characteristic peaks of indigo (Caggiani et al., 2016). Based on the above data, it can be concluded that the green pigment is a mixture of orpiment and indigo.

The use of the orpiment and indigo mixture as a green pigment by medieval Persian painters has been documented (Purinton and Watters, 1991). Such mixed pigments have recently been found in the pigments of Northern Liang (397-460 CE) Cave murals in the Tiantishan Grottoes, suggesting that this technique was already present in China as early as the 5th century CE (Zhang et al., 2019). In addition, this mixture pigment has also been found in 15th century Tibetan manuscript illustrations (Wu, Lv and Cuojimeiduo, 2021) as well as 16th century painted lacquer coffins excavated at Gaoling County, Xi'an City (Zhang, 2015). Blending organic dyes with inorganic pigments for more appropriate colors was not an unusual practice (Fu et al., 2021; Mahmoud, 2014; Medhat et al., 2014; Pereira-Pardo et al., 2019).

Blue. Blue pigment was used sparingly in the studied coffin plank paintings, only in Plank B for the portraits of the figures. Such

pigment particles showed a light blue color overall with obvious aggregated dark blue dots (Table 1), which may be a coloring phenomenon caused by mixing colorants. In addition, the number of layers in this part of the painting increased to three, as can be clearly observed in the micrograph (Fig. 8).

According to Table 3, the main elements at SP2 are C, N, O, and Pb (Figure S2, Supplementary Material), indicating the possible presence of organic dyes and lead-containing pigments. In the Raman spectra (Fig. 9), the peaks at 546 cm^{-1} , 599 cm^{-1} , 1224 cm^{-1} , 1248 cm^{-1} , 1574 cm^{-1} , and 1582 cm^{-1} correspond to the characteristic peaks of indigo (Fiedler et al., 2011; Rio et al., 2006; Tatsch and Schrader, 1995). Moreover, the small amount of Al and Si peaks on the EDS spectrum may be ascribed to residual salts and oxides of the indigo plant. Ca and P may be associated with the high content of such elements in indigo leaves (Abdel-Ghani et al., 2012). Therefore, the blue pigment contains indigo (Caggiani et al., 2016; Marucci et al., 2018). The Pb element peaks on the EDS spectrum may be due to the addition of lead white to the pigment during its preparation. Mixing indigo with lead white to improve its brightness is a somewhat common practice (Abdel-Ghani, 2022; Abdel-Ghani et al., 2012). However, the characteristic peak of lead white at 1048 cm^{-1} in the Raman spectrum of the sample was covered by fluorescence, which may be due to the low content of lead white and the presence of contamination on the sample surface.

Indigo is the oldest known organic dye and is mainly extracted from plants containing indole acids, such as knotweed, woad, and Indigofera. Indigo production was mastered in China by the Warring States Period at the latest, and the traditional process of producing indigo from plants was well documented in books from the Northern Wei Dynasty (Cheng et al., 2007). Indigo is mostly used in textiles and paper artifacts in China and is also found in ancient murals (Yan et al., 2016; Zhang et al., 2019; Zhang et al., 2010). In addition, the usage of indigo in murals and painted sculptures in Shanxi has been reported (Hu and Wang, 2012; Ma et al., 2015). The indigo found in the coffin plank paintings of Zhijiabao confirmed that such blue pigment was also used to decorate coffins.

White. The white pigment was mainly found in the portraits and some of the edges of the paintings. Table 3 shows that the elements detected by EDS include Ca, S, and O (Figure S3, Supplementary Material). According to the micro-RS data (Fig. 10),

Table 3 Micro-RS and EDS analysis results of SP1 to SP4.

Hue	Major elements	Main Raman bands (cm^{-1})	Attribution
Green (SP1-1)	C, O, N, As, S	136, 154, 294, 311, 354, 383, 252, 546, 599, 1227, 1253, 1574, 1582	Orpiment + Indigo
Yellow (SP1-2)	As, S	142, 153, 174, 191, 232, 274, 345, 364	Pararealgar
Blue (SP2)	C, O, N, Pb, Al, Si, Ca	252, 546, 599, 1227, 1253, 1574, 1582	Indigo + Lead-based pigment
White (SP3)	Ca, S	413, 1008, 1132	Gypsum
Black (SP4)	/	1332, 1585	Carbon black

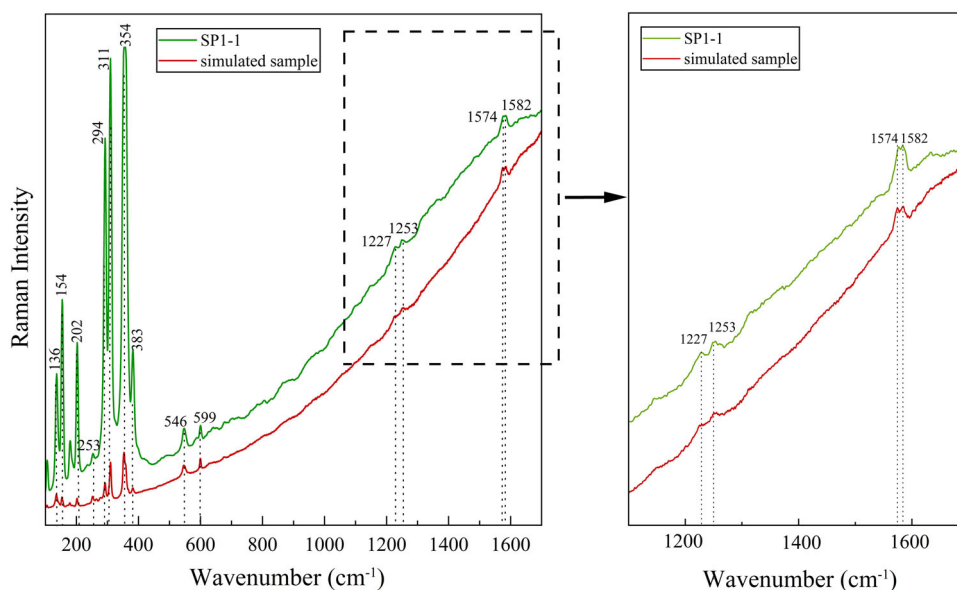


Fig. 7 The micro-RS analysis of blue pigment. Raman spectra of green particles in SP1-1 and simulated sample under a 633 nm excitation source.



Fig. 8 The middle figure of plank B and its micrograph. These graphs demonstrated the distribution of pigment layers and the extensive use of colors in the picture.

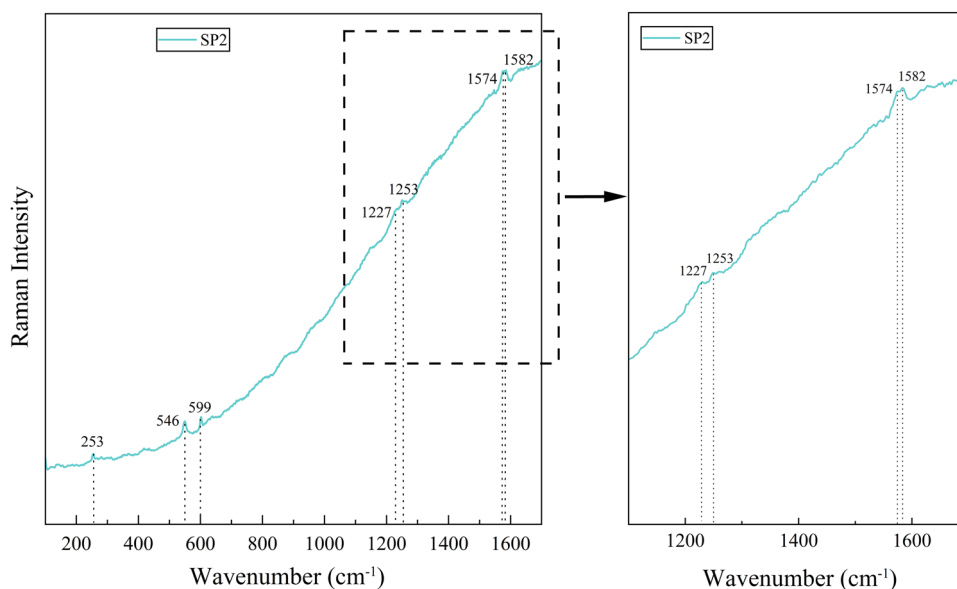


Fig. 9 The micro-RS analysis of blue pigment. Raman spectra of SP2 under a 633 nm excitation source.

the peaks at 1008 cm^{-1} and 1133 cm^{-1} represent the sulfate band of calcium sulfate dihydrate (Kanth and Singh, 2019), and the white pigment can be identified as gypsum (Bouchard and Smith, 2003). Gypsum is a common white or colorless mineral often used as a preparatory layer for murals or directly as a pigment (Li et al., 2009; Mollica Nardo et al., 2019).

Black. Black pigment was used as an outline and filler color on all three planks. As shown in Fig. 11, the characteristic peaks at 1332 cm^{-1} and 1585 cm^{-1} were assigned to the D and G peaks of carbon black (Mahmoud et al., 2019). Carbon black is the oldest black pigment used in paintings and usually consists of randomly

distributed amorphous carbon particles. Such particles are produced by the incomplete combustion of organic matter, such as plants or bone, which can serve as a pigment after drying, grinding, and washing (Van der Weerd et al., 2004; Winter, 1983). Since the Raman spectra of the samples showed no symmetric stretching vibrational band of phosphate near 960 cm^{-1} , the pigment was presumably not produced by burning bones.

Conclusion

The coffin plank paintings excavated from Zhijiabao Village, Datong City, are outstanding masterpieces from the Pingcheng period of Northern Wei and important archeological evidence for

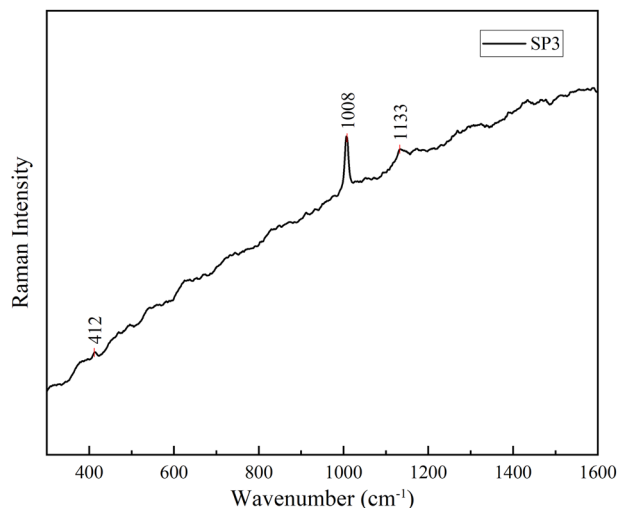


Fig. 10 The micro-RS analysis of white pigment. Raman spectra of SP3 under a 532 nm excitation source.

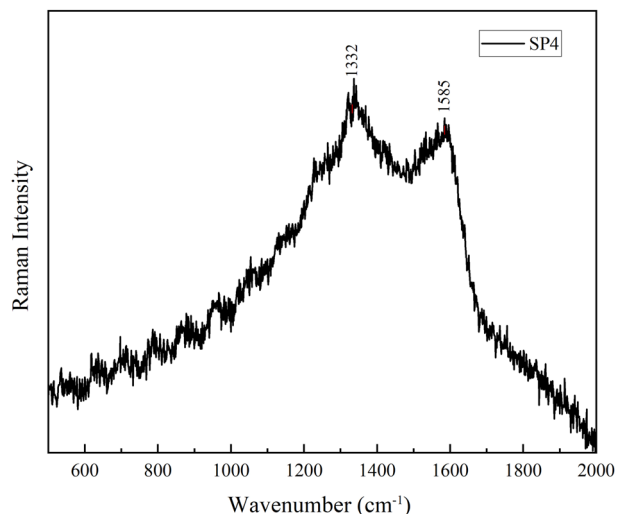


Fig. 11 The micro-RS analysis of black pigment. Raman spectra of SP4 under a 532 nm excitation source.

studying the Northern Wei funerary culture, artistic style, science, technology, etc. This study combined in-situ non-invasive analysis and laboratorial microanalysis to draw the following conclusions about the chemical composition and production techniques of coffin plank paintings.

The coffin planks were painted with a total of six colors. Cinnabar (HgS) was used as the red pigment, pararealgar (As₄S₄) was used as the yellow material, an indigo and orpiment mixture (C₁₆H₁₀N₂O₂ + As₂S₃) was used as the green substance, the blue color was most likely a mixture of indigo and white lead (C₁₆H₁₀N₂O₂ + 2PbCO₃·Pb(OH)₂), gypsum (CaSO₄) was used as the white pigment, and carbon black (C) was used as the black material. The production technique was to paint after applying a layer of pararealgar on the coffin plank surface as a primer. Most parts of the paintings had two layers, and some parts depicting figures had up to three layers. We found a mixture of organic dyes with inorganic pigments for different colors from the painted wooden coffin.

Since materials and techniques are crucial in studying ancient artworks, this research provides a strong scientific basis for selecting conservation materials and restoration methods for these precious cultural relics. Moreover, this study enriches the

understanding of pigment types and mixing methods during the Northern Wei Dynasty, providing new data for studying art history of that period from the perspective of painting materials and color matching.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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References

- Abdel-Ghani M (2022) Multidisciplinary study of a Qajar lacquered painting: technology and materials characterization. *Vib Spectrosc* 119:103355
- Abdel-Ghani M, Stern B, Edwards HGM et al. (2012) A study of 18th century Coptic icons of Ibrahim Al-Nasekh using Raman microscopy and gas chromatography-mass spectrometry: Indigo as an organic pigment in Egyptian panel paintings. *Vib Spectrosc* 62:98–109
- Abdrabou A, Hussein A, Sultan GM et al. (2022) New insights into a polychrome Middle Kingdom palette applied to a wooden coffin: a multidisciplinary analytical approach. *J Cult Herit* 54:118–129
- Aceto M, Agostino A, Fenoglio G et al. (2014) Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. *Anal Methods* 6(5):1488–1500
- Bell IM, Clark RJH, Gibbs PJ (1997) Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD). *Spectrochim Acta A* 53(12):2159–2179
- Bonizzoni L, Bruni S, Gargano M et al. (2018) Use of integrated non-invasive analyses for pigment characterization and indirect dating of old restorations on one Egyptian coffin of the XXI dynasty. *Microchem J* 138:122–131
- Bouchard M, Smith DC (2003) Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. *Spectrochim Acta A* 59(10):2247–2266
- Bracci S, Caruso O, Galeotti M et al. (2015) Multidisciplinary approach for the study of an Egyptian coffin (late 22nd/early 25th dynasty): combining imaging and spectroscopic techniques. *Spectrochim Acta A* 145:511–522
- Caggiani MC, Cosentino A, Mangone A (2016) Pigments Checker version 3.0, a handy set for conservation scientists: a free online Raman spectra database. *Microchem J* 129:123–132
- Cheng X, Xia Y, Ma Y et al. (2007) 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* 38(10):1274–1279
- Cooney KM (2014) Coffins, cartonnage, and sarcophagi. In: a companion to ancient Egyptian Art, Wiley-Blackwell, Hoboken, pp 269–292
- Delaney JK, Ricciardi P, Glinsman LD et al. (2014) Use of imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence to map and identify pigments in illuminated manuscripts. *Stud Conserv* 59(2):91–101
- Fan X, Wang L, Zhao X et al. (2012) Study of techniques and materials used to manufacture a lacquer coffin unearthed from a Ming Dynasty tomb in Shanxi. *Sci Conserv Archaeol* 24(4):95–102
- Fiedler A, Baranska M, Schulz H (2011) FT-Raman spectroscopy—a rapid and reliable quantification protocol for the determination of natural indigo dye in Polygonum tinctorium. *J Raman Spectrosc* 42(3):551–557
- Fu P, Teri G, Li J et al. (2021) Analysis of an ancient architectural painting from the Jiangxue Palace in the Imperial Museum, Beijing, China. *Anal Lett* 54(4):684–697
- Gao F (2004) Northern Wei Tomb 1 at Hudong, Datong, Shanxi. *Cult Relics* (12):26–34+1
- Han K, Han Z (1984) Excavation brief for the Northern Wei Tomb in Guyuan, Ningxia. *Cult Relics* (6):46–56+104–105
- Hao X, Wu H, Zhao Y (2017) Analysis on the composition/structure and lacquering techniques of the Coffin of Emperor Qianlong Excavated from the Eastern Imperial Tombs. *Sci Rep* 7(1):8446
- Hu W, Wang Y (2012) Analysis of Raman spectroscopy in pigments of wall paintings from Northern Qi Tombs in Shuiquanliang. *Silicon Valley* 5(17):153–154. +176
- Hu Y, Shao Y, Pan T (2015) A comparison of Kilim's decorative painting with the coffin painting in Guyuan. *J Shaanxi Normal Univ (Philosophy and Social Sciences Edition)* 44(4):125–131
- Jiang J, Shang Y, Hu X et al. (2020) Scientific research of colored coffin excavated from Bizili cemetery in Luopu County of Xinjiang, China. *Spectrosc Spect Anal* 40(7):2296–2300

- Kanth AP, Singh MR (2019) Vibrational spectroscopy and SEM-EDX analysis of wall painted surfaces, Orchha Fort, India. *J Archaeol Sci Rep* 24:434–444
- Kong L, Hou J (2006) Newly-discovered wooden painting of the Wei-Jin period found in Maozhuangzi Village, Jiayuguan City. *Cult Relics* (11):75–85+71
- Li T, Xie Y, Yang Y et al. (2009) Pigment identification and decoration analysis of a 5th century Chinese lacquer painting screen: a micro-Raman and FTIR study. *J Raman Spectrosc* 40(12):1911–1918
- Lin X (2020) The study on the coffin painting in the Hexi of Wei-Jin and Sixteen States Period. Dissertation, Northwest Normal University, Xi'an
- Liu L, Wu H, Liu W et al. (2016) Lacquering craft of Qing Dynasty lacquered wooden coffins excavated from Shanxi, China - a technical study. *J Cult Herit* 20:676–681
- Liu J, Gao F (2004) Excavation of a Northern Wei Tomb with a Painted Coffin. *Cult Relics* (12):35–47+31
- Ma Y, Zhang J, Hu D (2015) Scientific analysis of a Ming Dynasty polychrome star sculpture from Shanxi Art Museum, Taiyuan, China. *Sci Conserv Archaeol* 27(4):50–60
- Mahmoud HHM (2014) Investigations by Raman microscopy, ESEM and FTIR-ATR of wall paintings from Qasr el-Ghueta temple, Kharga Oasis, Egypt. *Herit Sci* 2(1):18
- Mahmoud HHM, Hussein M, Brania A (2019) Pigments and plasters from the Roman temple of Deir El-Hagar, Dakhla Oasis, Egypt: vibrational spectroscopic characterization. *Rend Lincei Sci Fis* 30(4):735–746
- Marucci G, Beeby A, Parker AW et al. (2018) Raman spectroscopic library of medieval pigments collected with five different wavelengths for investigation of illuminated manuscripts. *Anal Methods* 10(10):1219–1236
- Medhat AR, Ali M, Abdel-Ghani M (2014) Analytical investigation on a coptic wooden icon from the 18th century using SEM-EDX microscopy and FTIR spectroscopy. *Mediterr Archaeol Archaeometry* 15:151–161
- Mollica Nardo V, Renda V, Bonanno S et al. (2019) Non-invasive investigation of pigments of wall painting in S. Maria Delle Palate di Tusa (Messina, Italy). *Heritage* 2(3):2398–2407
- Peng F (2018) From Shengle to Pingcheng: National construction and political transformation of the Northern Wei Dynasty. *J Southwest Minzu Univ (Humanities and Social Science Edition)* 39(7):16–21
- Pereira-Pardo L, Tamburini D, Dyer J (2019) Shedding light on the colours of medieval alabaster sculptures: scientific analysis and digital reconstruction of their original polychromy. *Color Res Appl* 44(2):221–233
- Purinton N, Watters M (1991) A study of the materials used by medieval Persian painters. *J Am Inst Conserv* 30(2):125–144
- Rio MSD, Picquart M, Haro-Poniatowski E et al. (2006) On the Raman spectrum of Maya blue. *J Raman Spectrosc* 37:1046–1053
- School of History and Culture - Shanxi University, Shanxi Provincial Institute of Archaeology, Datong Municipal Museum (2006) The Northern Wei Period tomb complex in the southern suburbs of Datong City. Science Press, Beijing, p 316–318
- Scott DA (2016) A review of ancient Egyptian pigments and cosmetics. *Stud Conserv* 61(4):185–202
- Shanxi Provincial Institute of Archaeology, Datong Municipal Museum (1992) Excavation brief of the Northern Wei Tomb Group in the Southern Suburbs of Datong. *Cult Relics* (8):1–11+97–98
- Sun J (1989) A study of lacquer coffin painting in the Northern Wei of Guyuan. *Cult Relics* (9):38–44+12
- Tamburini D, Dyer J (2019) Fibre optic reflectance spectroscopy and multispectral imaging for the non-invasive investigation of Asian colourants in Chinese textiles from Dunhuang (7th–10th century AD). *Dyes Pigments* 162:494–511
- Tatsch E, Schrader B (1995) Near-infrared Fourier transform Raman spectroscopy of indigoids. *J Raman Spectrosc* 26(6):467–473
- Tong T (2007) The tradition of the wooden coffin painting - an element of the Xianbei Culture in the Early Middle Age. *J Tibetology* (1):165–170+235–236
- Tong T (2012) A study on the funeral scenes depicted in Golmud Tubo Coffin paintings from Qinghai. *Archaeol* (11):76–88+71
- Trentelman K, Stodulski L, Pavlosky M (1996) Characterization of pararealgar and other light-induced transformation products from realgar by Raman micro-spectroscopy. *Anal Chem* 68(10):1755–1761
- Vermeulen M, Saverwyns S, Coudray A et al. (2018) Identification by Raman spectroscopy of pararealgar as a starting material in the synthesis of amorphous arsenic sulfide pigments. *Dyes Pigments* 149:290–297
- Van der Weerd J, Smith GD, Firth S et al. (2004) Identification of black pigments on prehistoric Southwest American potsherds by infrared and Raman microscopy. *J Archaeol Sci* 31(10):1429–1437
- Winter J (1983) The characterization of pigments based on carbon. *Stud Conserv* 28(2):49–66
- Wu N, Lv X, Cuojimeiduo (2021) In-situ non-destructive analysis and testing of pigments used in the illustration of a 15th century Tibetan manuscript. *China Cult Herit* 4:87–93
- Wu S (2008) Comparing study on the Xianbei and Hans tombs dated to Northern Wei Period in Shengle and Pingcheng area. *Northern Cult Relics* (4):22–29
- Wu Y (2007) Research on Han dynastical style painted coffins with colour drawing style in Xinjiang. *J Xinjiang Arts Univ* (3):13–18
- Xin F, Ma D (2017) The studies on coffin paintings in Wulan Chaka of Qinghai. *J Qinghai Minzu Univ (Social Sciences)* 43(3):1–9
- Xu X (2011) Colorful top board of the coffin unearthed in Chaqia. *J Qinghai Minzu Univ (Social Sciences)* 37(1):88–90
- Xu Z, Li D, Shen L (2021) Study on diffuse reflection and absorption spectra of organic and inorganic Chinese painting pigments. *Spectrosc Spect Anal* 41(12):3915–3921
- Yan J, Liu D, Zhao X et al. (2016) Study the material and drawing techniques of the mural paintings of Tang prime minister Hanxiu's tomb. *Archaeol Cult Relics* (2):117–127
- Yu Z, Qin D (2006) Preliminary investigation of colorful coffin burials in the Yingshan Cemetery M15 and the Loulan Region. *West Archaeol* 1:401–427
- Zhang W, Su B, Yin Y et al. (2019) In situ nondestructive analysis of the mural pigments in the Northern Liang Caves at the Tiantishan Grottoes. *Dunhuang Res* 4:128–140
- Zhang X, Wei X, Lei Y, Cheng X, Zhou Y (2010) Micro and nondestructive analysis of blue dyes from silk fabrics and decorative painting of historic building. *Spectrosc Spect Anal* 30(12):3254–3257
- Zhang T (2015) Study on making Processes and material of painted lacquer coffins in Gaoling during Ming Dynasty. Dissertation, Northwest University, Xi'an
- Zhao J, Xie Y, Liu Y (2017) The excavation brief of Sunjiashitan Family Cemetery in Suzhou District, Jiuquan City, Gansu. *Archaeol Cult Relics* (3):21–34
- Zhu Z, Wang J, Yao X et al. (2023) Multi-analytical study on the Tara Thangka at Daxingshan Temple in Xi'an, Shaanxi, China. *Stud Conserv* 68(6):602–613
- Zidan EH, Mosca S, Bellei S et al. (2018) In situ imaging, elemental and molecular spectroscopy for the analysis of the construction and painting of a Late Period coffin at the Egyptian Museum of Cairo. *Measurement* 118:379–386

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