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https://doi.org/10.1038/s40494-025-01800-0

Nondestructive analysis of architectural decorative patterns in Prince Kung's Palace by Raman and XRF

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This study used portable Raman spectroscopy and X-ray fluorescence to non-destructively analyze pigments in the architectural decorative patterns of Prince Kung's Palace, Beijing. Focusing on eight representative patterns, it identified a complex palette of pigments, including historical mineral, modern synthetic, and plant-derived ones. The mineral pigments identified are cinnabar, red lead, hematite, orpiment, lead white, chalk, carbon black, azurite, and atacamite. Synthetic pigments include Hansa red, chrome yellow, titanium white, Prussian blue, ultramarine blue, phthalocyanine blue, emerald green, and phthalocyanine green. Indigo was found in certain areas. Degradation products such as lead sulfate and gypsum were also detected. The analysis suggests multiple creation periods for the patterns, providing evidence of historical restorations. Some patterns date to around the 45th year of the Qianlong period, while others might be from the Republic of China period (1912–1949 CE). This research offers insights into the conservation and restoration of the decorative patterns.

Prince Kung's Palace, located in the Xicheng District of Beijing, stands as the most exquisite princely residence in Qing Dynasty (1644–1912 CE). With significant historical and cultural values, it has been designated as a first-class national museum and a 5A-class tourist attraction of China. The construction of the palace was initiated around 1780 CE by Ho-Shen, a minister under Emperor Qianlong. It nowadays spans an area of approximately 60,000 square meters[1]. The residence has housed notable figures including Minister Ho-Shen (1750–1799 CE), Princess Gulunhexiao (1775–1823 CE), Prince Qing Yonglin (1766–1820 CE), and Prince Kung Yixin (1833–1898 CE). As a fusion of a ministerial residence and a royal family mansion, Prince Kung's Palace encapsulates a wealth of historical, cultural, and artistic legacies.

The architectural complex of Prince Kung's Palace is adorned with a plethora of decorative patterns, which have undergone numerous restorations from the Qing Dynasty to the present, preserving a trove of historical information. The decorative patterns encompass the three official types commonly used during the Qing Dynasty: tangent circle pattern, dragons pattern, and Suzhou-style pattern. These patterns not only accentuate the noble status of the residents but also serve as invaluable resources for studying the cultural and artistic milieu of the era while preserving key information about the pigments prevalent during the Qing Dynasty. However, the enduring effects of natural elements, including rain, wind, sand, and sunlight, as well as human-induced factors, have led to significant degradation of the decorative patterns. The degradation is manifested as flaking, peeling, fading, and powdering, severely impacting the aesthetic appeal and value of the patterns. Consequently, there is an imperative need for identification and preservation measures for the decorative patterns. Pigment analysis is pivotal for the effective protection and restoration of these decorative patterns[2–4].

Raman spectroscopy is a rapid, non-destructive, and micro-regional analytical technique. Combined with XRF, the multimodal method enables the swift and precise identification of the molecular fingerprints and elemental composition of materials[2,4,5]. At present, the combined use of portable Raman spectroscopy and handheld X-ray fluorescence (XRF) spectrometry has been well-established in the field of mural research. For instance, M. Sawczak et al. used portable XRF and Raman techniques for non-destructive analysis of the murals of the Little Christopher chamber in the Main Town Hall of Gdańsk, Poland and successfully identified the pigments[6]. R. Alberti et al. analyzed archaeological samples from the Villa dei Quintili (II/III century A.D.) using handheld XRF and Raman spectrometer, identifying key pigments and their distribution in frescoes, pottery, and statues[7]. J. M. Madariaga et al. conducted in-situ analyses on the

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walls and wall paintings of two Pompeian houses using portable Raman and ED-XRF spectrometers, identifying key compounds in the efflorescence and assessing the effect of environmental factors on their formation[8]. These advanced techniques facilitate the non-invasive analysis of the paintings, allowing for the accurate identification of pigments without compromising the integrity of these invaluable artifacts.

This research represents the first application of portable Raman spectroscopy and handheld X-ray fluorescence for the non-destructive analysis of the architectural decorative patterns of Prince Kung's Palace. The investigation primarily targets the pigments utilized in the artistic creation process, uncovering the embedded historical and cultural information. Furthermore, this research provides a scientific foundation for the conservation and restoration of these painted artworks.

Methods

Architectural decorative patterns of Prince Kung's Palace

The research conducted a comprehensive scientific examination of the representative architectural decorative patterns within Prince Kung's Palace. Figure 1 shows the architectural plan of Prince Kung's Palace, in which architectures that have undergone non-destructive investigation are marked with colored boxes. The pictures of the decorative patterns in these architectures are shown in Fig. 2, which included the Baoguang Hall (Fig. 2a, g), the First Palace Gate (Fig. 2b), the East Imperial Gate Two (Fig. 2c), the West Imperial Gate Two (Fig. 2h), the Hall of Mental Purification (Fig. 2d), the aisle of Baoguang Hall (Fig. 2e), and the Duofu Hall (Fig. 2f). These structures are located on the east, west and middle roads of the palace, as well as the gardens, encompassing a broad area and showcasing a diverse array of decorative patterns. All *in-situ* measurement locations are marked with red boxes in Fig. 2, facilitating the precise documentation and analysis of the pigments without causing any disturbance to the integrity of the patterns.These locations encompass most of the colors that can be observed, including red, yellow, white, black, blue, and green.

Experimental techniques

The Raman spectroscopic analysis was conducted utilizing a portable spectrometer from EmVision LLC., America, which incorporates a thermoelectrically cooled charge-coupled device (CCD) detector. This detector is capable of achieving a cooling temperature as low as −60 °C, minimizing thermal noise thus enhancing the detection sensitivity. The spectrometer is designed to operate over a spectral range from 100 cm^{-1} to 2000 cm^{-1} with a resolution of 4 cm^{-1}. The system is equipped with a 785 nm semiconductor laser, which serves as the excitation source with an adjustable power output of up to 300 mW. Careful selection of the laser power during the measurement process is essential to prevent laser-induced damage to the decorative patterns, ensuring the preservation of the artwork's integrity.

XRF analysis was performed using the Thermo Scientific Niton XL3t spectrometer, manufactured by Thermo Fisher Scientific in the USA. This high-performance handheld instrument employs a miniature X-ray tube with a gold target as the excitation source and was operated in soil mode during the *in-situ* analysis. The spectrometer is equipped with a high-performance silicon photodiode (Si-Pin) detector, which is capable of quantifying 32 elements across the atomic measurement range from sulfur (S) to bismuth (Bi). This comprehensive analytical capability provides valuable insights into the elemental composition of the pigments and substrates within the architectural decorative patterns.

Results

Through in-situ non-destructive analysis of the painted artwork in various buildings in the Prince Kung's Palace, the pigments used in the different decorative patterns were successfully identified.

Red pigments

The red pigments were predominantly identified in the patterns of the intermediate purlin of the Baoguang Hall (Fig. 2a–A4, A5, A7), the First Palace Gate (Fig. 2b–B6, B9), the East Imperial Gate Two (Fig. 2c–C3, C8), the Hall of Mental Purification (Fig. 2d–D2, D6, D8, D9), and the eaves outside the Aisle of Baoguang Hall (Fig. 2e–E4, E7, E8). The corresponding

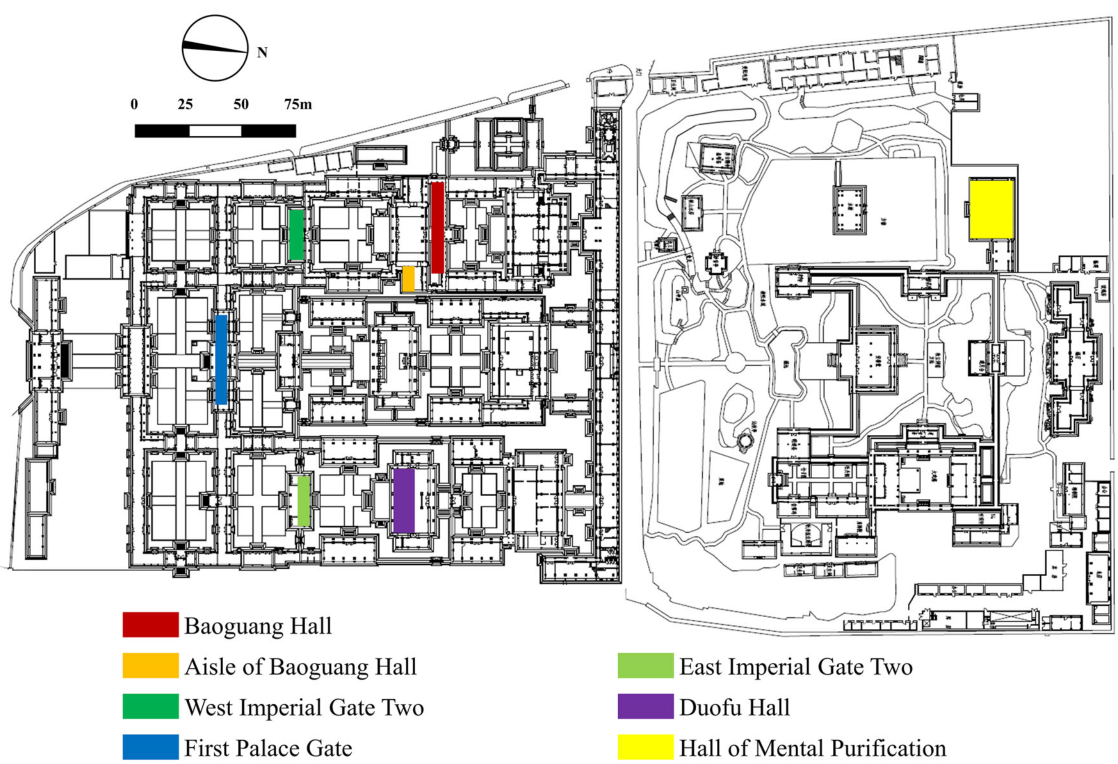

Fig. 1 | Architectural plan of Prince Kung's Palace (The architectural plan was provided by the Prince Kung's Palace Museum). Architectures that have undergone non-destructive investigation are marked with colored boxes.

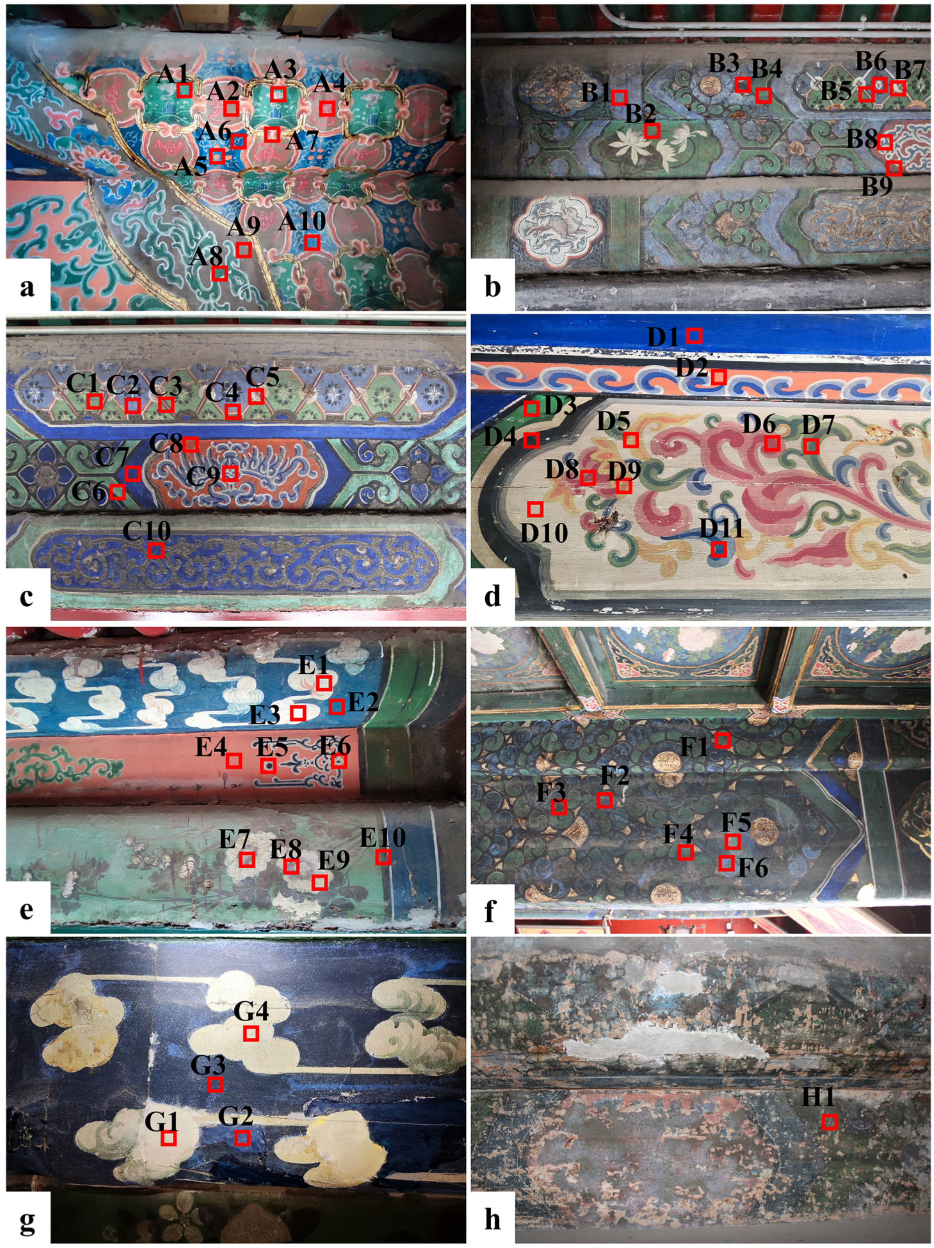

Fig. 2 | The pictures of decorative patterns in Prince Kung's Palace. a The intermediate purlin of the Baoguang Hall, (**b**) First Palace Gate, (**c**) East Imperial Gate Two, (**d**) Hall of Mental Purification, (**e**) Aisle of Baoguang Hall, (**f**) Duofu Hall, (**g**) The beam of the Baoguang Hall, (**h**) West Imperial Gate Two

Raman spectra for these areas are depicted in Fig. 3. The Raman bands at 252, 284, and 343 cm^{-1} in Fig. 3a align with those of cinnabar (HgS), induced that cinnabar was employed as the red pigment in these areas (as detailed in Table 1). The characteristic Raman peaks at 120, 150, 313, 390, and 548 cm^{-1} (Fig. 3b) confirm the presence of red lead (Pb_3O_4), thus affirming that red lead was used as a red pigment in the specified locations (points A5, A7, B9, C8, D2, D9, and E4 in Fig. 2). The Raman bands at 226, 294, 411, 497, and 615 cm^{-1}, as illustrated in Fig. 3c, are distinctively attributed to haematite (Fe_2O_3)[9], which were collected from the red area (point C3) in the East Imperial Gate Two. Furthermore, the bands observed at 341, 617, 797, 986, 1126, 1185, 1215, 1254, 1331, 1383, 1445, 1495, 1554, and 1617 cm^{-1} in Fig. 3d, obtained from the red areas (points D6 and D8) in the decorative patterns of the Hall of Mental Purification, are assignable to Hansa red ($C_{17}H_{13}N_3O_3$)[9,10], with the band at 1087 cm^{-1} corresponding to chalk ($CaCO_3$).

Cinnabar, red lead, and hematite have historically been common red pigments used in ancient times. Hematite and red lead were found in Cappadocian churches from the 6th to 13th centuries[11]. There are also many records of the application of cinnabar, red lead and hematite in archaeological materials[12–15]. Hansa red, a synthetic organic pigment derived from β-naphthol, was first synthesized in the early 20th century; however, it is rare to find Hansa red used as a red pigment in artworks[10].

Yellow pigments

The Raman spectra of the yellow pigments, as depicted in Fig. 4, were collected from various locations, including the intermediate purlin of the Baoguang Hall (Fig. 2a–A2, A9), the First Palace Gate (Fig. 2b–B5), the East Imperial Gate Two (Fig. 2c–C4), and the Hall of Mental Purification (Fig. 2d–D5). The Raman spectrum presented in Fig. 4a, obtained from the decorative patterns of the Baoguang Hall, First Palace Gate, and East Imperial Gate Two, exhibits characteristic bands at 136, 152, 177, 201, 291, 309, 354, and 382 cm^{-1}, which are assignable to orpiment (As_2S_3)[16]. Therefore, we believe that orpiment is used as a yellow pigment in these places. In contrast, the Raman spectrum displayed in Fig. 4b, obtained from the Hall of Mental Purification (Fig. 2d–D5), reveals a distinct band at 841 cm^{-1}, tentatively attributed to chrome yellow ($PbCrO_4$)[9,17]. Complementary X-ray fluorescence spectroscopic analysis, as illustrated in Fig. 5, offers elemental confirmation of the presence of Pb and Cr elements

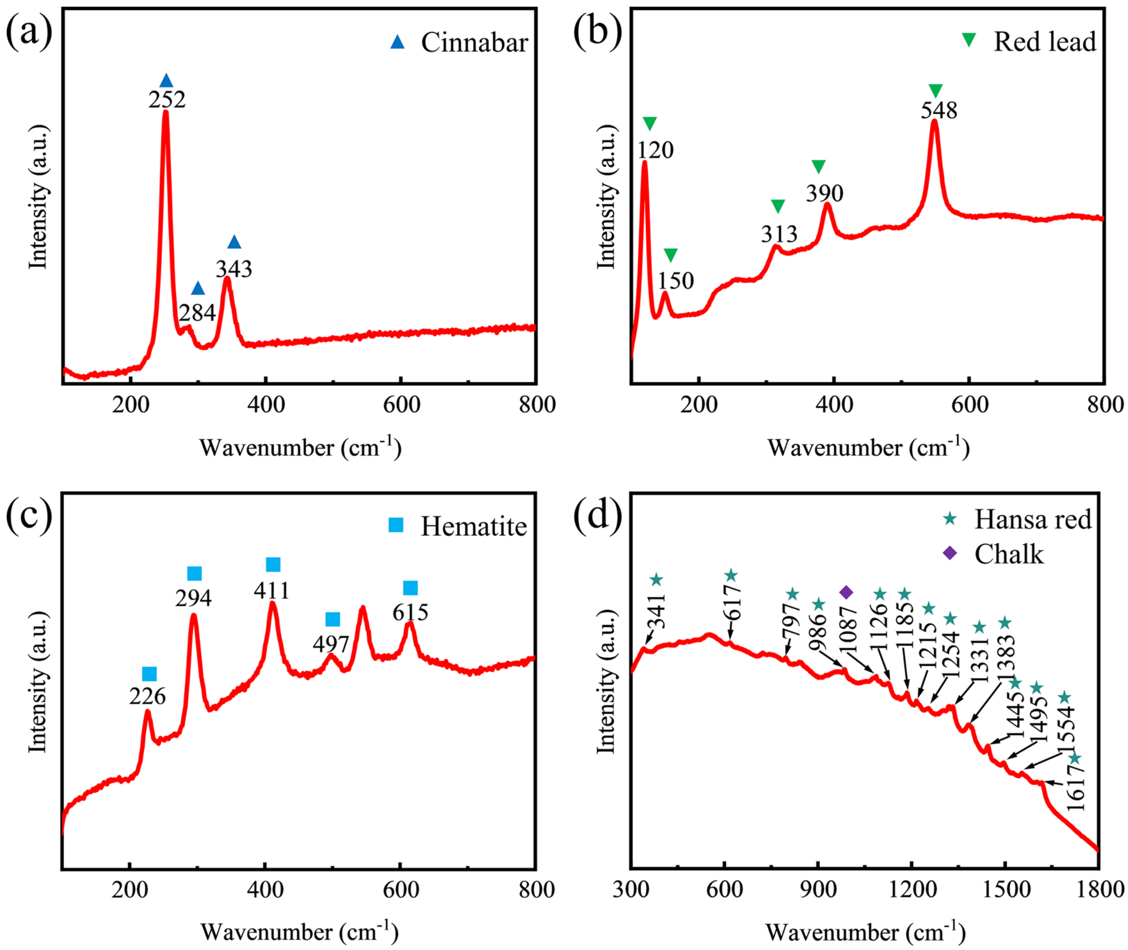

Fig. 3 | Raman spectra of red pigments acquired from different areas. **a** Raman spectrum acquired from points of A4, B6, E7, E8; **b** Raman spectrum acquired from points of A5, A7, B9, C8, D2, D9, E4; **c** Raman spectrum acquired from point of C3 and (**d**) Raman spectrum acquired from points of D6, D8 (All the point labels A-H are shown in Fig. 2, the legends below is the same).

in the yellow region at point D5 in Fig. 2d. This finding is consistent with the in-situ Raman analysis result, thereby confirming that chrome yellow is used as the yellow pigment in the decorative patterns of the Hall of Mental Purification.

White pigments

The in-situ analysis of white pigments has been carried out across the white areas of the seven decorative patterns, which include the intermediate purlin of the Baoguang Hall (Fig. 2a–A3), the First Palace Gate (Fig. 2b–B7), East Imperial Gate Two (Fig. 2c–C5, C9), the Hall of Mental Purification (Fig. 2d–D10), the eaves exterior of the Aisle of Baoguang Hall (Fig. 2e–E1, E3, E6, E9), the beam of the Baoguang Hall (Fig. 2g–G1, G4), and West Imperial Gate Two (Fig. 2h–H1). Totally, five different Raman results were found in these white areas (Fig. 6). Some white areas (points A3, B7, C5, C9, E1, E3, and E9) present a Raman band at 1050 cm^{-1} (Fig. 6a). It can be attributed to the v(CO_3^{2-}) vibrational mode characteristic of lead white ($2PbCO_3{\cdot}Pb(OH)_2$)[15,18,19]. As illustrated in Fig. 6b, the Raman bands at 281, 711, and 1086 cm^{-1}, assignable to chalk, were found in the most white areas (as detailed in Table 1). Specially, it is inferred that chalk is the component of the ground layer material due to the peeling off of the pigment layer at the West Imperial Gate Two (Fig. 2h–H1).

The Raman spectrum depicted in Fig. 6c exhibits bands at 142, 396, 513, 637, 684, 739, 773, 839, 1214, 1287, 1338, and 1538 cm^{-1}. The bands at 142, 396, 513, and 637 cm^{-1} are attributed to titanium white (TiO_2)[20,21], while those at 684, 739, 773, 1214, 1287, 1338, and 1538 cm^{-1} correspond to the characteristic vibrational modes of phthalocyanine green ($Cu(C_{32}Cl_{16}N_8)$)[9]. The bands at 839 cm^{-1} belong to chrome yellow. Titanium white, phthalocyanine green and chrome yellow are all modern synthetic pigments, with synthetic dates of 1923, 1936 and 1809, respectively[9], imply that the decorative patterns have been restored, and the restoration works must have occurred post-1936, as the pigments employed in these works were not available before this period. Hence, the white pigment used in the restoration process of the white area on the beam of the Baoguang Hall (point G1 in Fig. 2g) is titanium white, while phthalocyanine green and chrome yellow were accidentally mixed in. This hypothesis is substantiated by the observable presence of light green and yellow hues in the vicinity of the measuring point.

The Raman spectrum of the white regions within the decorative patterns of the Aisle of Baoguang Hall (Fig. 2e) is showed in Fig. 6d. The Raman bands at 977, 1053, and 1086 cm^{-1} suggest different chemical compositions. Specifically, the bands at 1053 and 1086 cm^{-1} correspond to the vibrational modes characteristic of lead white ($2PbCO_3{\cdot}Pb(OH)_2$) and chalk, respectively, while the band at 977 cm^{-1} is assigned to lead sulfate ($PbSO_4$)[22]. The discovery of lead sulfate suggests the potential chemical degradation of lead white due to the presence of sulfur-containing pollutants[23].

Furthermore, the Raman spectrum depicted in Fig. 6e presents a band at 1087 cm^{-1}, which is assignable to chalk, and a band at 1008 cm^{-1}, which is belong to gypsum ($CaSO_4{\cdot}2H_2O$)[24]. The spectrum was obtained from the green area of the West Imperial Gate Two (point H1 in Fig. 2h), however only white pigments were identified. It is therefore inferred that the pigment layer in the measured area has peeled off, revealing the underlying ground layer, which is composed of chalk. The presence of gypsum is likely due to the chemical transformation of chalk, a process that is consistent with the degradation pathways described in the literature[23,25].

Table 1 | The information on the pigments identified from the decorative patterns in Prince Kung's Palace

Color	Pigments Identification	Formula	Raman bands (cm^{-1})	Position in decorative patterns[a]
Red	Cinnabar	HgS	252, 284, 343	A4, B6, E7, E8
	Red lead	Pb_3O_4	120, 150, 313, 390, 548	A5, A7, B9, C8, D2, D9, E4
	Haematite	Fe_2O_3	226, 294, 411, 497, 615	C3
	Hansa red	$C_{17}H_{13}N_3O_3$	797, 986, 1126, 1185, 1215, 1254, 1331, 1383, 1445, 1495, 1554	D6, D8
Yellow	Orpiment	As_2S_3	136, 152, 177, 201, 291, 309, 354, 382	A2, A9, B5, C4
	Chrome yellow	$PbCrO_4$	841	D5, F5, G1
White	Lead white	$2PbCO_3{\cdot}Pb(OH)_2$	1050	A3, B7, C5, C9, E3, E9, G4
	Chalk	$CaCO_3$	281, 711, 1086	A3, C5, C9, D10, E1, E3, E6, E9, G4, H1
	Gypsum	$CaSO_4{\cdot}2H_2O$	1008	H1
	Lead sulfate	$PbSO_4$	977	E9
	Titanium white	TiO_2	142, 396, 513, 637	G1
Black	Carbon black	C	1322, 1583	B3, D4, E10, F3
Blue	Azurite	$2CuCO_3{\cdot}Cu(OH)_2$	no	A6, A10
	Prussian blue	$Fe_4[Fe(CN)_6]_3{\cdot}14\text{-}16H_2O$	272, 537, 2133	B1, B8, E2, E5, F2; G3
	Indigo	$C_{16}H_{10}N_2O_2$	549, 1312, 1571	E6
	Ultramarine blue	$Na_{6\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$	547	C2, C7, C10, D1, D11, F6
	Phthalocyanine blue	$CuC_{32}H_{16}N_8$	592, 682, 747, 775, 841, 953, 1142, 1342, 1451, 1529	G2
Green	Atacamite	$CuCl_2{\cdot}3Cu(OH)_2$	no	A1, A8, B2, B4, F1, F4
	Emerald green	$Cu[C_2H_3O_2]_2{\cdot}3Cu[AsO_2]_2$	no	C1, C6, D3, D7
	Phthalocyanine green	$Cu(C_{32}Cl_{16}N_8)$	684, 746, 775, 1211, 1339, 1538	F5, G1

[a]Correspond to the points in each picture in Fig. 2.

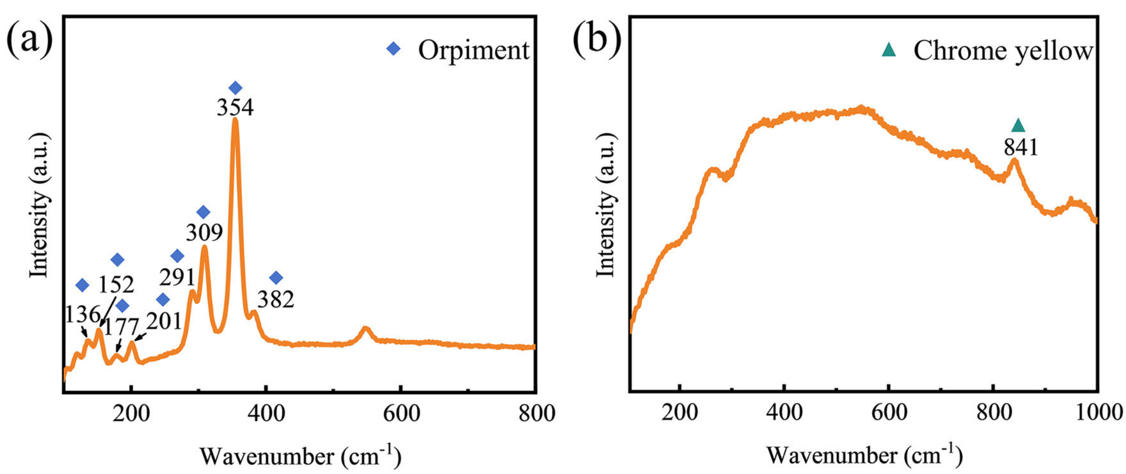

Fig. 4 | Raman spectra of yellow pigments acquired from different areas. a Raman spectrum acquired from point of A2, A9, B5, C4, and (**b**) Raman spectrum acquired from point of D5.

Black pigment

The measurement points for the black areas are limited in number and are specifically situated at the First Palace Gate (Fig. 2b–B3), Hall of Mental Purification (Fig. 2d–D4), the eaves exterior of the Aisle of Baoguang Hall (Fig. 2e–E10), and Duofu Hall (Fig. 2f–F3). The Raman spectrum of these black areas, as shown in Fig. 6f, reveals broad spectral bands centered at approximately 1322 and 1583 cm^{-1}, which belong to characteristic Raman bands of amorphous carbon (C). The similar Raman spectra across all measured black areas suggest the employment of carbon black as the primary black pigment in these artworks. Historically, in ancient China, carbon black was a prevalent choice for black pigment in a diverse array of artistic creations, encompassing decorative patterns, murals[26], and sculptures[16,27].

Blue pigments

As shown in Fig. 2, it is evident that blue and green are the most prevalent colors in the decorative patterns. The in-situ analysis of blue areas was conducted across seven distinct decorative patterns, encompassing the intermediate purlin of the Baoguang Hall (Fig. 2a–A6, A10), the First Palace Gate (Fig. 2b-B1, B8), East Imperial Gate Two (Fig. 2c–C2, C7, C10), Hall of Mental Purification (Fig. 2d–D1, D11), the eaves outside the Aisle of Baoguang Hall (Fig. 2e–E2, E5, E6), Duofu Hall (Fig. 2f–F2, F6), and the beam of the Baoguang Hall (Fig. 2g–G2, G3). We found four different blue pigments in the blue areas. The typical Raman spectra are presented in Fig. 7.

As depicted in Fig. 7a, the spectrum obtained from the blue areas (points C2, C7, C10, D1, D11, and F6 in Fig.1), exhibits a Raman band at 547 cm^{-1}, which is assignable to the symmetric stretching vibration of S_3^-

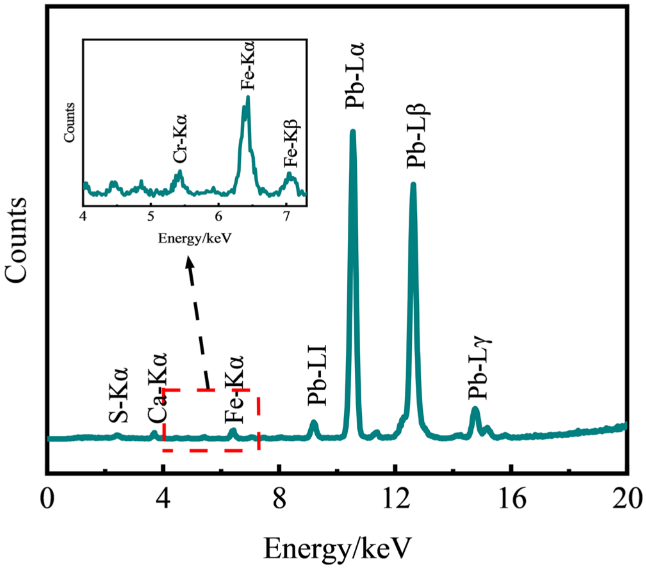

Fig. 5 | XRF spectrum of the yellow area (D5) in the decorative patterns of the Hall of Mental Purification (Fig. 2d).

radical[4,28]. The presence of the S_3^- radical is characteristic of several blue pigments, including natural lapis lazuli ($(Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)_{1-2}$), synthetic ultramarine blue ($Na_{6-10}Al_6Si_6O_{24}S_{2-4}$), and haüyne ($Na_6Ca_2(Al_6Si_6O_{24})(SO_4)_2$). Together with S_2^- ions, these S_x^- species constitute the chromophores responsible for the vibrant blue coloration of these minerals. However, distinguishing among these potential pigment sources based solely on the S_3^- signature presents significant challenges. Accurate differentiation requires complementary ultraviolet (UV)-excited Raman spectroscopy, which can suppress chromophore resonance effects and provide detailed insights into the structural characteristics of the host aluminosilicate matrix[29,30]. Unfortunately, the portable Raman spectrometer employed in this study operates at a wavelength of 785 nm, limiting its capability to unequivocally assign the S_3^- anion to a specific pigment. Despite this analytical limitation, historical and economic considerations offer valuable context for pigment identification. Historically, lapis lazuli as a precious semiprecious stone, was extensively utilized in China prior to the Tang Dynasty. Its application in artwork declined due to its high cost, leading to the adoption of more economical alternatives such as azurite ($2CuCO_3{\cdot}Cu(OH)_2$)[31–34]. Additionally, haüyne, recognized as one of the rarest gem varieties globally, has not been documented as a blue pigment in Chinese polychrome artworks[35]. In contrast, synthetic ultramarine blue, which closely mimics the color properties of natural lapis lazuli, was first synthesized in France in 1828. Its superior affordability and vivid coloration facilitated its widespread use during the late Qing Dynasty in China[36]. Empirical evidence supporting the prevalence of synthetic ultramarine blue includes its identification in numerous significant artworks, such as the murals of the Guandi Temple at Hujiapu, Xi'an—painted in 1881 CE during the Guangxu reign of the Qing Dynasty[37]—as well as in portraits of Taoist figures from the late Qing Dynasty[38] and statues restored in the Dunhuang Grottoes during the same period[39]. Furthermore, ultramarine blue has been detected in numerous decorative motifs from the Qing Dynasty era[4,40,41]. Given these historical precedents and the spectral data obtained, it is thus reasonable to infer that these blue areas analyzed predominantly employed synthetic ultramarine blue as the pigment. In Fig. 7b, the Raman bands at 549, 1086, 1312, and 1571 cm^{-1} are considered as indigo ($C_{16}H_{10}N_2O_2$), with the band at 1086 cm^{-1} correspond to chalk within the ground layer. Therefore, indigo is used as the blue pigment at point E6. Indigo, a plant-derived pigment renowned for its vivid blue hue and durability in artistic applications, extensively employed in murals, textiles, and other artifacts, such as those found in Cave 465 of the Mogao Grottoes[42] and Tang Dynasty wooden painted artifacts from Xinjiang[43].

The spectrum obtained from the areas corresponding to points B1, B8, E2, E5, F2, and G3 in Fig. 2, displays the bands at 272, 537, and 2133 cm^{-1}, which are characteristic of Prussian blue ($Fe_4[Fe(CN)_6]_3{\cdot}14\text{-}16H_2O$)[17,44]. For further confirmation, the XRF spectrum of the corresponding blue area is presented in Fig. 8a, revealing a pronounced Fe-Kα peak, thereby confirming that the blue pigment contain Fe element. This result is consistent with the Raman analysis. Prussian blue was first synthesized in Germany in 1704, then brought in China and extensively utilized in Qing Dynasty artworks, such as the blue pigments on the lacquer and gilded ink boxes from the Qianlong period (1736–1796 CE)[45] and the restored Yongxin Palace in the Palace Museum during the Daoguang period (1821–1850 CE)[40].

The Raman spectrum of the blue area (Fig. 2g–G2) is presented in Fig. 7d, with bands at 592, 682, 747, 775, 841, 953, 1142, 1342, 1451, and 1529 cm^{-1}, which are assignable to phthalocyanine blue ($CuC_{32}H_{16}N_8$)[9]. Phthalocyanine blue, synthesized in the early 20th century, is a prominent organic pigment. Due to its low cost and vibrant color, it is widely used in coatings, printing inks and fiber tinting, etc[46–48].

In the blue areas of the intermediate purlin of the Baoguang Hall (Fig. 2a–A6, A10), no corresponding Raman spectra were detected. However, the XRF spectrum, as shown in Fig. 8b, reveals a significant Cu element, indicating that the blue pigment used should contain Cu element. Given the historical context of the Qing Dynasty, where the widely used blue pigments included lapis lazuli, azurite, smalt ($CoO{\cdot}nSiO_2$), indigo, Prussian blue, and ultramarine blue[36]. Among these pigments, azurite is the only copper-containing pigment among them, it is deduced that the blue pigment in this instance is likely azurite. Azurite has been widely used in ancient colored paintings. It have been found in the murals of the Qutan Temple in Qinghai Province[49] and the A-Er-Zhai Grottoes in Inner Mongolia[50].

Green pigments

The nondestructive analysis of green areas within the decorative patterns was conducted at multiple locations, including the intermediate purlin of the Baoguang Hall (Fig. 2a–A1, A8), the First Palace Gate (Fig. 2b–B2, B4), East Imperial Gate Two (Fig. 2c–C1, C6), Hall of Mental Purification (Fig. 2d–D3, D7), and Duofu Hall (Fig. 2f–F1, F4, F5). The Raman spectrum of the green area corresponding to point F5 is presented in Fig. 9, revealing the bands at 684, 746, 775, 841, 1211, 1339, and 1538 cm^{-1}. Among them, the bands at 684, 746, 775, 1211, 1339, and 1538 cm^{-1} belong to phthalocyanine green, while the band at 841 cm^{-1} is attributed to chrome yellow. The Raman spectrum of phthalocyanine green, as shown in Fig. 6c, was also detected at point G1 within decorative patterns on the beam of the Baoguang Hall (Fig. 2g).

Due to the stronger fluorescent background, suitable Raman spectra could not be obtained from other green areas. Consequently, elemental analysis of these regions was performed using XRF spectroscopy, with the corresponding spectra displayed in Fig. 10. The XRF spectrum obtained from the green areas (points A1, A8, B2, B4, F1, and F4 in Fig. 2), as shown in Fig. 10a, reveals the presence of Cu, and Cl elements. It indicates that the green pigment used should contain these elements. The XRF spectra of other green areas (points C1, C6, D3, and D7 in Fig. 2) reveal that the green pigment of these areas contains Cu and As elements (Fig. 10b). In ancient painting art, the common green pigments include malachite ($CuCO_3{\cdot}Cu(OH)_2$), emerald green ($Cu[C_2H_3O_2]_2{\cdot}3Cu[AsO_2]_2$), and atacamite ($CuCl_2{\cdot}3Cu(OH)_2$)[51]. Among them, atacamite is characterized by the presence of both Cu and Cl elements, while emerald green contains both Cu and As elements. Therefore, the XRF spectra in Fig. 10a, b obtained from the green areas correspond to the pigments of atacamite and emerald green, respectively. Atacamite, a green pigment frequently employed prior to the late Qing Dynasty, has been identified in temple murals in Datong[52] and in the ancient architectural decorative patterns of the Confucius Temple in Qufu[53]. Emerald green, a synthetic green pigment synthesized in 1814, was extensively utilized during the late Qing Dynasty due to its affordable price[51]. The use of two different green

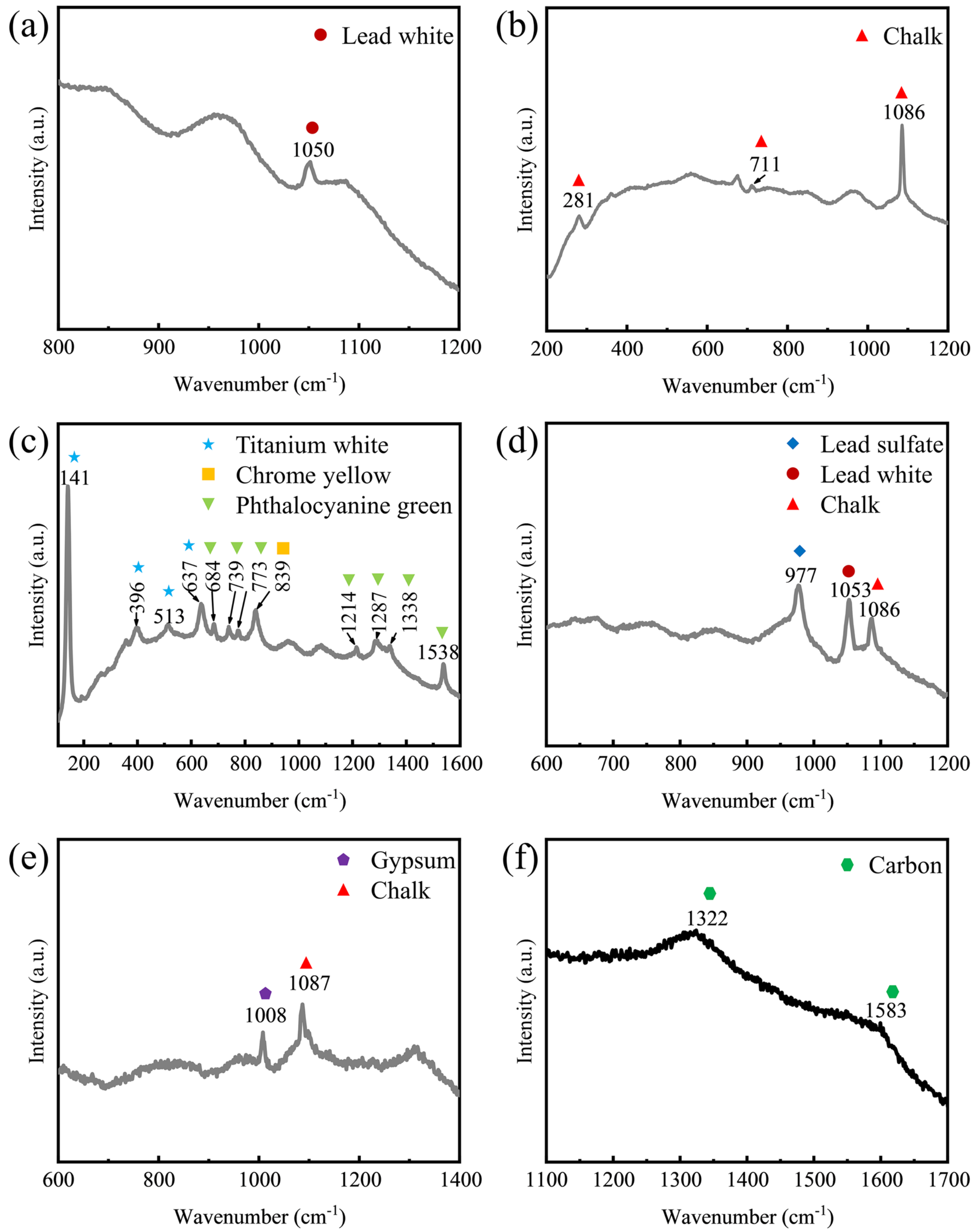

Fig. 6 | Raman spectra of white and black pigments acquired from different areas. **a** Raman spectrum acquired from white areas of A3, B7, C5, C9, E3, E9, G4; **b** Raman spectrum acquired from white areas of A3, C5, C9, D10, E1, E3, E6, E9, G4, H1; **c** Raman spectrum acquired from white area of G1; **d** Raman spectrum acquired from white area of E9; **e** Raman spectrum acquired from white area of H1; **f** Raman spectrum acquired from black areas of B3, D4, E10, F3.

pigments with distinct time periods can serve as a marker for distinguishing the age of murals.

Discussion

The pigments characterized within the architectural decorative patterns of Prince Kung's Palace are delineated in Table 1, It is observed that the pigments used in different decorative patterns are not consistent. Among the identified pigments, cinnabar, red lead, haematite, orpiment, lead white, chalk, lead sulfate, gypsum, and carbon black are prevalent in pre-modern artifacts, which complicates the precise dating of the decorative patterns. Nevertheless, the presence of contemporary synthetic pigments, including ultramarine blue, emerald green, Hansa red, Prussian blue, phthalocyanine green and phthalocyanine blue, provides pivotal evidence for discerning between modern restorations and ancient paintings.

The Baoguang Hall exhibits a diversity of blue pigments across its different sites, including azurite on the intermediate purlin (Fig. 2a) and a combination of Prussian blue and phthalocyanine blue on the beams (Fig. 2g). Azurite, a prevalent mineral pigment in antiquity, has a

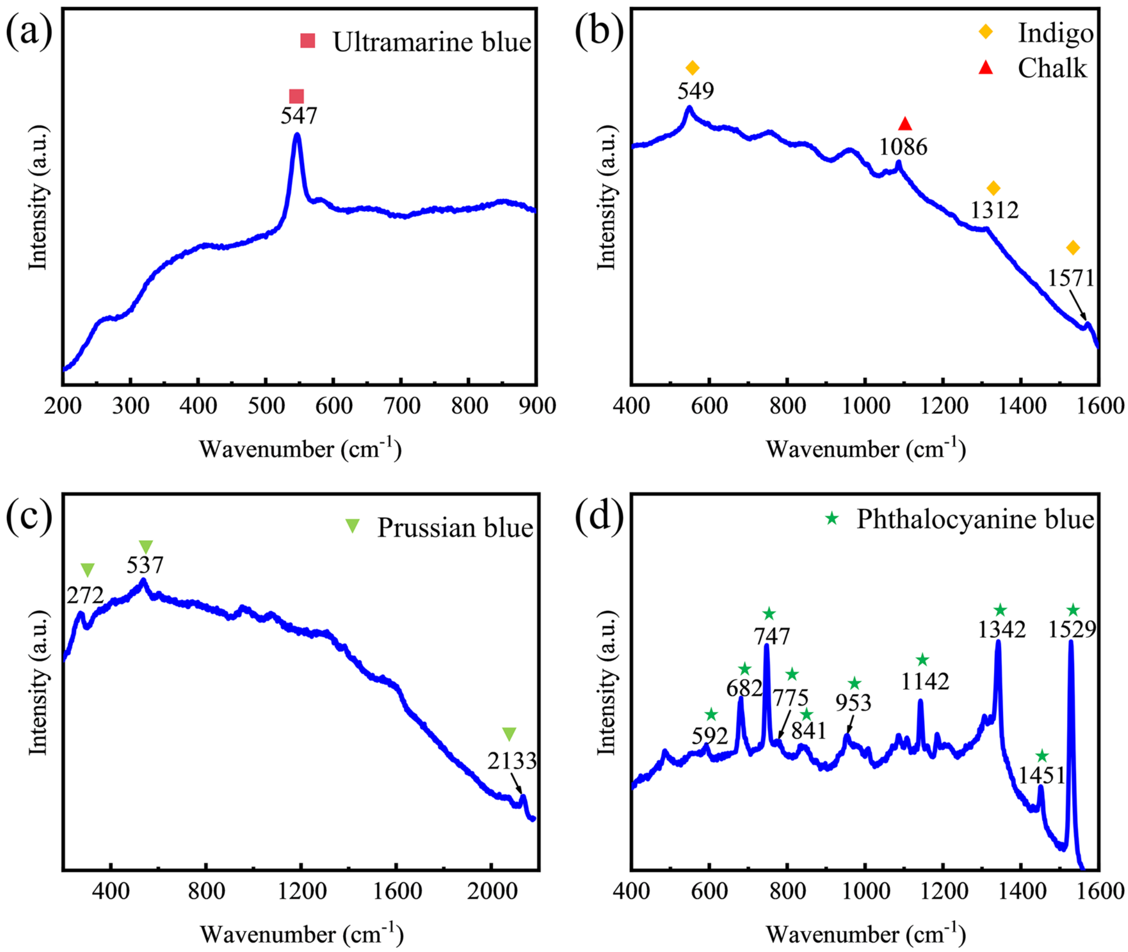

Fig. 7 | Raman spectra of blue pigments acquired from different areas. a Raman spectrum acquired from points of C2, C7, C10, D1, D11, F6; (**b**) Raman spectrum acquired from point of E6; (**c**) Raman spectrum acquired from points of B1, B8, E2, E5, F2, G3; (**d**) Raman spectrum acquired from points of G2.

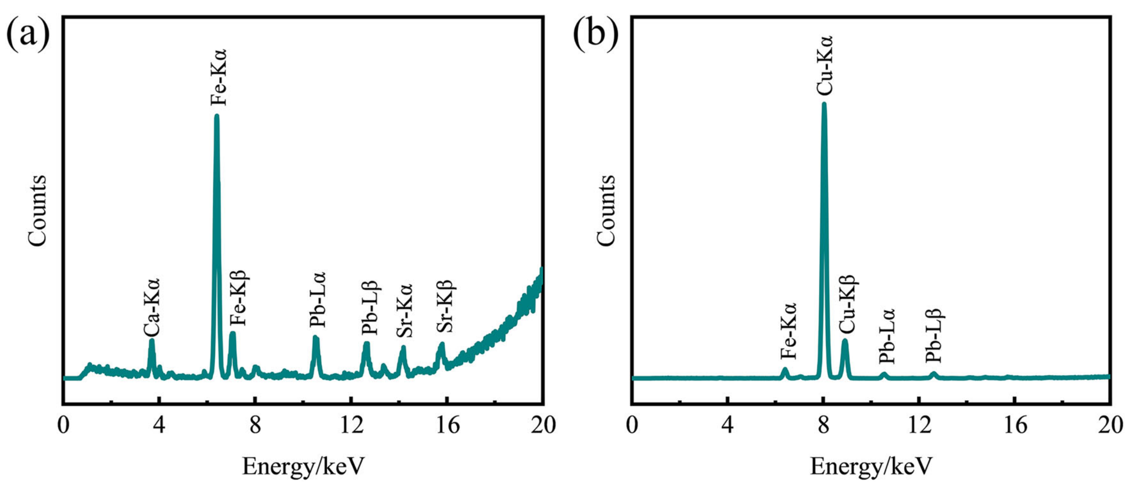

Fig. 8 | The XRF spectra collected from the blue areas. a XRF spectrum collected from points of B1, B8, E2, E5, F2, G3 and (**b**) XRF spectrum collected from points of A6, A10.

documented presence in the Tianti Mountain Grottoes[54], A-Er-Zhai Grottoes in Inner Mongolia[50], and the Eastern Thousand Buddha Caves in Guazhou[55]. Prussian blue, first synthesized in 1704, was introduced to China around 1775 and achieved domestic production by 1827[45,56,57]. Phthalocyanine blue, synthesized in 1936, marks a more recent addition to the palette. The use of these three pigments, each from distinct historical periods, indicates that the decorative patterns in the Baoguang Hall underwent restoration on at least two occasions. The azurite-containing patterns on the intermediate purlin are likely original artworks from the Qianlong period around 1780 and have been well-preserved due to their elevated position above the ceiling. In contrast, the Prussian blue-adorned beams, situated below the ceiling, were likely repainted post-1827, with partial restoration employing titanium white and phthalocyanine blue post-1936. Collectively, the decorative patterns within the Baoguang Hall exhibit a combination of at least three periods of artworks, each utilizing distinct blue pigments.

The Prussian blue identified in the decorative patterns of First Palace Gate (Fig. 2b) aligns with that used in the unrestored areas of the beams of Baoguang Hall (Fig. 2g) and Duofu Hall (Fig. 2f) and is consistent with the blue pigment on the outer eaves of the aisle of Baoguang Hall (Fig. 2e). Notably, there is no evidence of other modern synthetic pigments in these areas except for the repair areas. This suggests that the decorative patterns in these locations should be painted during the same time range, specifically after 1827.

Conversely, the decorative patterns of East Imperial Gate Two (Fig. 2c) exhibit a distinct palette, comprising ultramarine blue and emerald green. Ultramarine blue, synthesized in 1828 and introduced to China in 1860, and emerald green, synthesized in 1814 and widely adopted in the 1850s[4,9,51], indicate that these patterns were drawn during the late Qing dynasty.

The pigments employed in the decorative patterns within the Hall of Mental Purification (Fig. 2d) are predominantly modern synthetic, including Hansa red and chrome yellow. The presence of Hansa red, which emerged in the early 20th century, suggests that the decorative patterns in the Hall of Mental Purification were repainted during the Republican era. In the decorative patterns on the eaves of the aisle of Baoguang Hall (Fig. 2e), two distinct blue pigments were identified: Prussian blue and indigo. The detection of indigo beneath the white pigment layer (Fig. 2e–E6) implies that it may have been overlaid during restoration. Prussian blue, which achieved domestic production around 1827, and indigo, a plant-derived pigment frequently utilized in antiquity, indicate that the color patterns on the eaves of the outer aisle of Baoguang Hall were restored post-1827. Additionally, lead white, chalk, and lead sulfate were identified on the white floral patterns (Fig. 2e–E9), with lead white as the pigment and chalk potentially as a ground layer material. The detection of lead sulfate is indicative of the degradation of lead white due to acidic environmental exposure[23].

A variety of blue and green pigments were detected within the decorative patterns of the Duofu Hall (Fig. 2f). The extensive application of atacamite and Prussian blue suggests that the patterns were executed post-1827. Discernible traces of pigment smearing were observed in specific areas (Fig. 2f–F5, F6), where ultramarine blue and phthalocyanine green were identified, implicating subsequent restorative interventions. According to records, the Duofu Hall underwent restoration in 2003, which included the repair of its damaged and incomplete decorative patterns[1]. This historical account substantiates the aforementioned inference. The decorative patterns of West Imperial Gate Two (Fig. 2h) exhibit substantial pigment exfoliation, with chalk and gypsum detected, suggesting carbonate degradation under acidic conditions[23,58].

This investigation utilized non-destructive analytical techniques, including Raman spectroscopy and X-ray fluorescence, to perform an *in-situ* analysis of the pigments employed in the decorative patterns of Prince Kung's Palace. The results revealed that the red pigments consisted of cinnabar and red lead, with minor quantities of haematite and Hansa red. The yellow pigments were mainly orpiment, accompanied by sporadic occurrences of chrome yellow. The white pigments encompassed lead white and titanium white, while chalk was identified in the ground layer. The degradation products of chalk and lead white, such as gypsum and lead sulfate, were discovered. Carbon black was identified as the black pigment. The blue pigments comprised azurite, Prussian blue, ultramarine blue, phthalocyanine blue, and indigo. The green pigments included atacamite, emerald green, and phthalocyanine green. Among these pigments, there are commonly used historical pigments such as cinnabar, red lead, azurite, and modern synthetic pigments phthalocyanine green, Hansa red, titanium white. The application of these pigments presents valuable historical markers for creation and restoration periods of the decorative patterns. This study provides comprehensive information of the pigments used in the decorative patterns of Prince Kung's Palace, thereby enhancing the

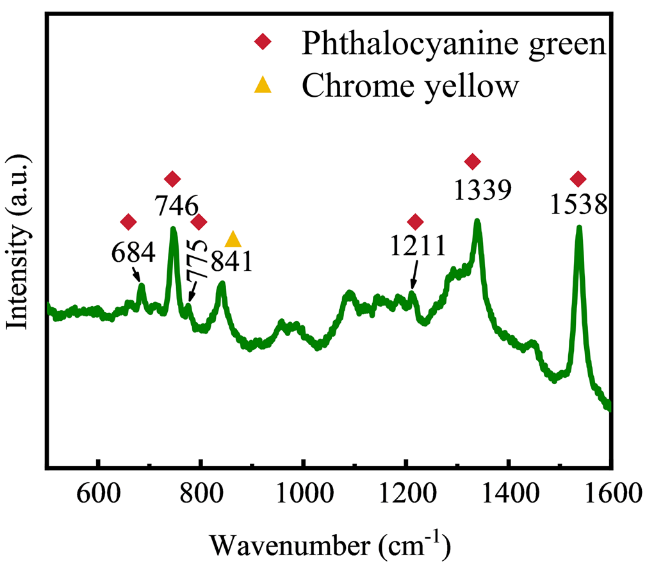

Fig. 9 | Raman spectrum of green pigment acquired from the areas of F5 and G1 in Fig. 2.

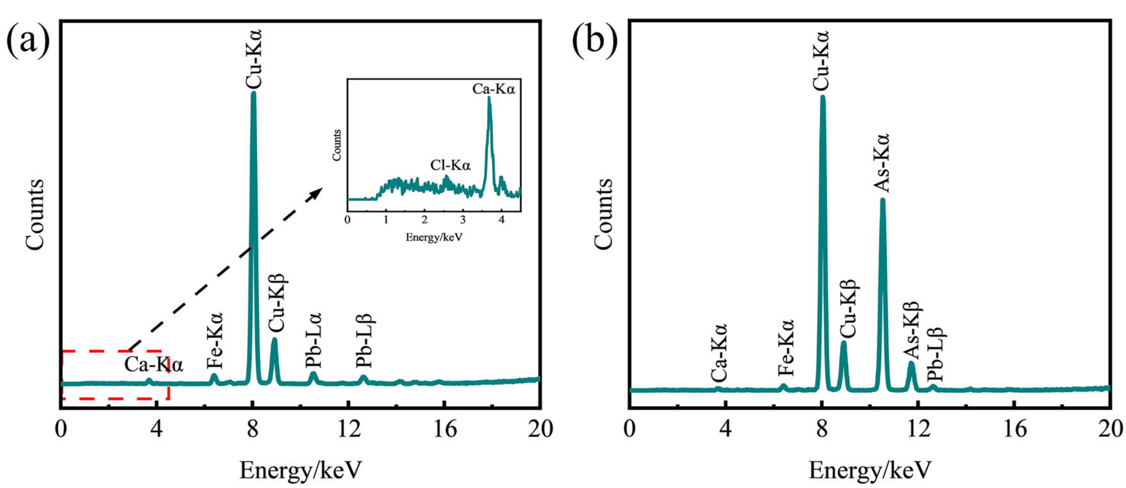

Fig. 10 | The XRF spectra collected from the green areas. a XRF spectrum collected from points of A1,A8,B2,B4, F1, F4 and (**b**) XRF spectrum collected from points of C1, C6, D3, D7.

understanding of its historical and cultural significance, and providing critical knowledge for future conservation and restoration endeavors.

Data availability

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

Received: 23 January 2025; Accepted: 19 May 2025;
Published online: 30 May 2025

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Acknowledgements

The authors would like to thank the Prince Kung's Palace Museum, Ministry of Culture and Tourism, China for providing research objects. This work is part of the project Research on Architectural Decorative Patterns in the Prince Kung's Palace (GBLXWF-2021-Z-01), and is funded by the Prince Kung's Palace Museum, Ministry of Culture and Tourism, China, and the National Natural Science Foundation of China (NO. 11874084).

Author contributions

J.M. conducted data collection, data analysis and manuscript writing; Z.C. and X.H. helped to select suitable research objects and provided research ideas; S.G. supported the relevant information of Prince Kung's Palace; J.M., Yan Li and W.Z. made in-situ measurements, including Raman and XRF experiments. F.W., Yan Li and Yu Li made revisions to the manuscript. All the authors read and approved the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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