

Article

A Study of Song Dynasty Polychrome Statue-Making Techniques and Materials in the Sage Mother Hall of the Jinci Temple, Shanxi, China

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Abstract: The polychrome statues of the Sage Mother Hall at the Jinci Temple in Taiyuan city are recognized as one of the three masterpieces of the Jinci Temple. They are also regarded as an outstanding representative of ancient Chinese temple statues. These statues possess great historical, artistic, scientific, cultural and social values, and they are an important physical material for the study of ancient Chinese history, culture, religion, politics and economy, as well as science and technology. The internal structure, plaster layer samples and surface pigments of the polychrome statues of the Sage Mother Hall were analyzed by optical microscope (OM) scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS), X-ray powder diffraction (XRD), Raman spectroscopy (Raman), X-radiography and other analytical methods in order to gain an understanding of the production process and pigment composition of the polychrome statues of the Sage Mother Hall. According to the findings, the following steps were taken during the production of the polychrome statues that decorate the Sage Mother Hall at Jinci Temple: building a wooden skeleton, fixing the skeleton with rivets or twine, shaping the clay form with coarse clay, shaping the appearance with fine clay, refining the molded appearance, and white substrate layer painting. The majority of the pigments are inorganic mineral pigments: the red pigments include cinnabar and minium; the blue pigments include ultramarine; the green pigments include lavendulan; the yellow pigments include yellow ochre; the black pigments include carbon black; and the white pigments and substrate layers include white lead and lead sulfate. Some of the pigment layers can be seen in multiple layers, which indicates that over the history of the painted statues of the Sage Mother Hall, they have been subject to a series of repainting, with the more recent repainting time perhaps having taken place during the late Qing Dynasty and the following time period.

Keywords: Jinci Temple; Song dynasty; polychrome statues; production techniques



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1. Introduction

Shanxi, also known as “Jin (晋)” for its abbreviated name, is a province in the People's Republic of China. Its capital is Taiyuan, and it is situated in northern China. The location of Shanxi province can be found in Figure 1a. It shares borders with the provinces of Hebei to the east, Shaanxi to the west, Henan to the south and Inner Mongolia to the north. This province is the site of the Jinci Temple. The ancient Chinese ritual architecture, gardens, polychrome statues, murals and inscriptions that constitute this site make it a precious piece of historical and cultural heritage. In 1961, it was labeled as a major historical and cultural site that should be protected at the national level unit.

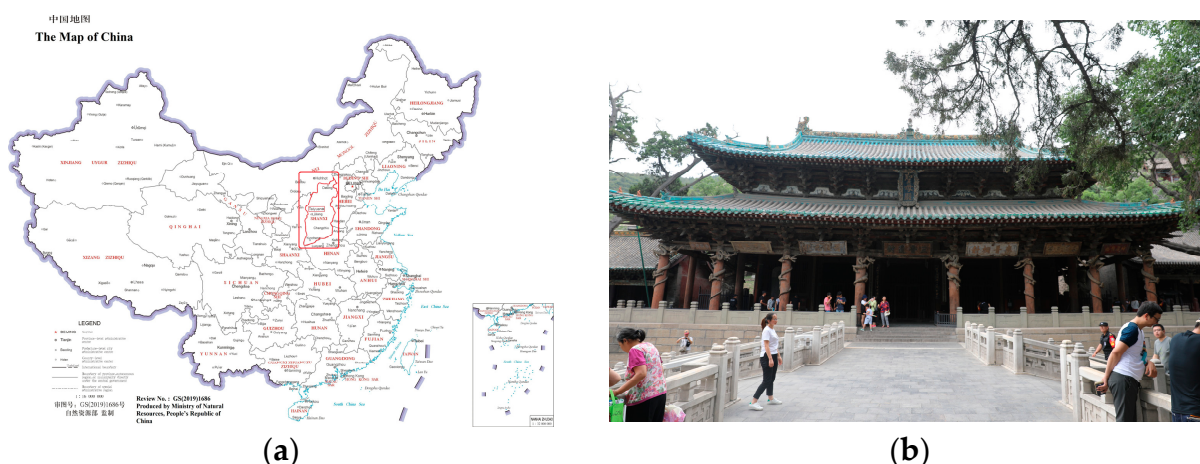


Figure 1. (a) Location of Shanxi province within China; (b) exterior view of the Sage Mother Hall.

The Sage Mother Hall (圣母殿) is the shrine's main hall. It has typical Song Dynasty architecture, standing west to east and at the back of the center axis, and is a representative of China's cultural heritage. The exterior view of the Sage Mother Hall can be found in Figure 1b. It was constructed in the Northern Song Dynasty's year of Taiping Xingguo (A.D. 984) and repaired in the Song Dynasty's first year of Chongning (A.D. 1102). It was initially a hall dedicated to Tang Shuyu (唐叔虞), but in the Song Dynasty, it was altered to be a hall dedicated to the Sage Mother, and then became a hall dedicated to Yi Jiang (邑姜), the empress of King Wu and Tang Shuyu's mother. It is the Jinci Temple's oldest surviving building [1,2].

The statues in the hall serve as objects of worship, ritual, and veneration, while the building serves as a venue for religious events and as a home to these polychrome statues. The Sage Mother Hall contains 45 statues in all, including 43 inside the hall and 2 outside. Outside the temple, there are statues of the General of the Temple on both sides of the main corridor; the northern statue is an original Song Dynasty statue, and the southern statue is from the 1950s. Most of the statues depict maids from the Song dynasty, and the layout is reflected not only in the relationship between the statues and the building space but also in the arrangement and configuration of the statues, as well as differences in the size between the statues. The maids are positioned in front of the main statue shrine, as well as on the left and right sides, according to responsibility, status and rank. Additionally, the statues are organized and distributed in a “concave (凹)” shape to create a clustering effect. Each statue in the temple, with the exception of the main statue, is larger than the last. Highlighting the importance of the main statue, the others are designed to look like ordinary people. This reflects the secularized and realistic qualities of Song Dynasty designs. The distribution and a group image of the polychrome statues of the Sage Mother Hall of Jinci Temple can be found in Figure 2a,b, respectively.

The polychrome statues of the Jinci Temple reflect the emotions that were poured into them by folk artisans, and their realistic expressions are unsurpassed, giving life to the statues and allowing their beauty to express their lives and emotions despite changes that have occurred over time. The statue group in the Sage Mother Hall of Jinci Temple is considered a landmark statuary piece with respect to ancient China, and it has epoch-defining significance in the history of art.

The temple is known as “the treasure house of ancient Chinese polychrome statues and murals art” because the ancient architectural resources of Shanxi are abundant there, and the polychrome statues attached to it express a wide range of topics. There are more than 10,000 statues that have survived. Previous studies on the polychrome statues of the Sage Mother Hall have primarily concentrated on the history of sculpture and art. The polychrome statues have been affected by pigment-layer flaking, peeling, cracks and other deterioration to different degrees. There is no detailed research on the production

process and material analysis of the polychrome statues; thus, the scientific investigation and protection of the polychrome statues of the Sage Mother Hall is urgent.

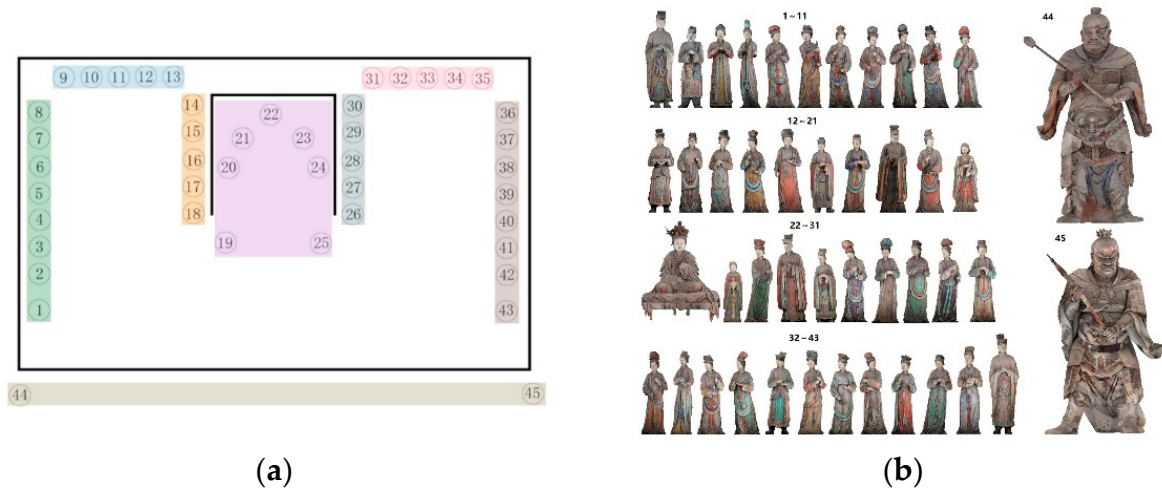


Figure 2. (a) Distribution of polychrome statues in the Sage Mother Hall; (b) depiction of the polychrome statues in the Sage Mother Hall.

This paper adopts a variety of instrumental methods to scientifically analyze the materials and processes used to create the polychrome statues of the Sage Mother Hall of Jinci as a complement to the study of Song Dynasty wood skeletons and polychrome statues, as well as to provide data support for the conservation of the Sage Mother Hall of Jinci Temple.

2. Materials and Methods

2.1. Sample Collection

As can be seen through the remnants of several polychrome statues, the construction of a polychrome statue consists of a support body (wooden skeletons), a plaster layer (composed of a coarse clay layer and a fine clay layer) and a pigment layer. This study used a combination of nondestructive testing analyses and onsite sampling/laboratory analyses, with samples taken from the pigment and plasters of the polychrome statues in The Sage Mother Hall (No.CS1) in order to reduce the damage to the information contained within the polychrome statues. This was due to the importance and special characteristics of the polychrome statues in the Sage Mother Hall. At the same time, multiple analysis methods were combined in order to obtain data that were more scientific and rigorous. The sampling information is shown in Table 1, and Figure 3 provides information regarding the locations.

Table 1. Sampling information for the polychrome statue.

Number	Samples	Analysis Method
1-1	Blue pigment	RAM, SEM-EDS
1-2	Yellow pigment	RAM, SEM-EDS
1-3	Red pigments	RAM, SEM-EDS
1-4	Green pigment	RAM, SEM-EDS
1-5	White pigments	RAM, SEM-EDS
1-6	Black pigment	RAM, SEM-EDS
1-7	Coarse clay layer	XRD
1-8	Fine clay layer	XRD

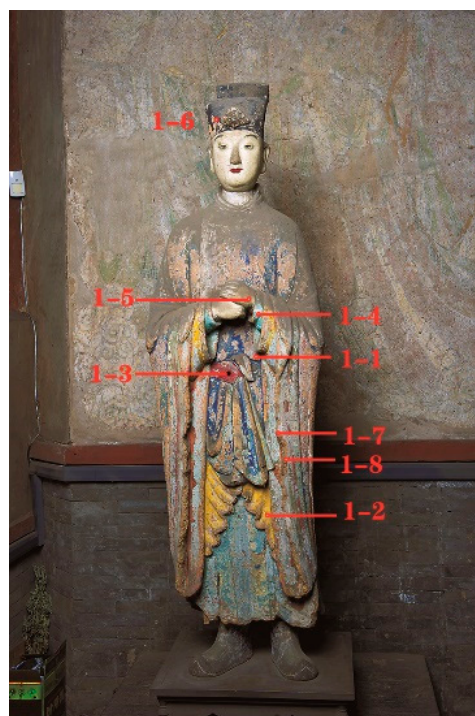


Figure 3. Statue No.CS1 in the Sage Mother Hall. Location of sampling positions.

2.2. Instrumentation and Measurements

2.2.1. Non-Invasive In Situ Study

A handheld Niton XL3t GOLDD+ ED-XRF analyzer (Thermo Fisher Scientific Inc., Waltham, MA, USA) was employed for the identification of chemical elements. The X-ray radiation was emitted by an Ag tube anode of 45 kV. It used a geometrically optimized large drift detector (GOLDD), and the radiation could reach a penetration maximum of 40 μm . It was provided with an integrated CCD camera, which allowed for the visualization of the measurement area. The diameter of the measurement spot could be reduced from the standard 8 to 3 mm thanks to a collimator. Four filters were available, namely, main (40 kV), high (30 kV), low (20 kV) and light (10 kV). Each of them could be selected specifically for the optimum excitation of a certain range of elements. The measurement method employed was “Mining and soils”. Four filters, with a measurement time of 20 s each, were used.

X-ray radiography: KF-200 X-ray machine, operating current 3 mA, maximum voltage 200 kV.

2.2.2. Laboratory Studies on Selected Samples

Cross-section sample preparation: For cross-section preparation, the minute pigments are embedded in epoxy resin (Buehler Epo Thin) and polished with dry abrasive papers down to 0.5 μm to obtain a sufficiently polished surface.

X-ray powder diffraction (XRD): Rigaku D/max 2200 X-ray powder diffractometer, Cu target, $DS = 1^\circ$, $SS = 1^\circ$, $RS = 0.15$ mm, tube voltage 40 kV, tube current 40 mA.

Optical microscopy (OM): A KEYENCE VHX-6000 ultra-depth-of-field 3D video microscope was used to observe and document the cross-sections, at magnifications from 20 to 2000 $\times$.

Micro-Raman spectroscopy (Raman): A Thermo Nicolet Almega type micro confocal laser Raman spectrometer configured with an Olympus microscope and an integrated motorized stage were used to qualitatively analyze the mineral composition of different layers under 50 $\times$ and 100 $\times$ objective lenses. The blue and green pigments were analyzed using a 532 nm laser, and the other pigments were analyzed using the 785 nm laser. The laser output power ranged from 15–30 mW (532 nm) to 10–50 mW (785 nm), the spectral

range was 50–2000 cm^{-1} , and the collection time was 15–25 s with 2 accumulations. The instrument was calibrated using the 520 cm^{-1} silicon Raman band.

Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS): Hitachi S-3600 N scanning electron microscope equipped with a Genesis 2000 XMS type X-ray energy spectrometer was used to analyze the microstructural characteristics of paint layers and semi-quantitatively analyze the relative contents of major elements in pigment minerals in different layers. Analyses were carried out in a high vacuum environment with a scanning voltage of 20 Kv and 90 s of acquisition time at a 15 mm working distance.

3. Results

3.1. Surface Elemental Information of Polychrome Statue

There is a large quantity of pigment used in the polychrome statue of the Sage Mother Hall. The six colors are red, yellow, blue, green, white and black. Firstly, the XRF detection was carried out on CS1; the detection position is shown in Figure 4, and the data were normalized and processed, with the results displayed in Table 2.

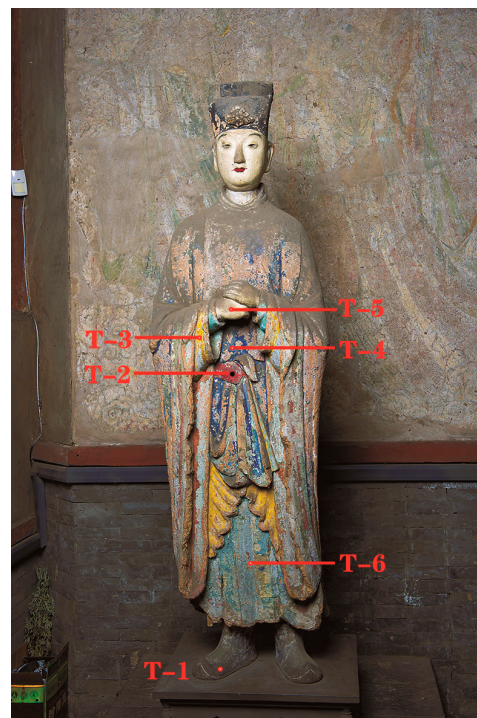


Figure 4. Statue No.CS1 in the Sage Mother Hall. Location of testing positions.

Table 2. Statue No.CS1, Sage Mother Hall: XRF analyses results.

Color	Point Number	Pb	As	Hg	Cu	Fe	Ca	S
Black	T-1	0.1%	0%	0%	0.1%	8.3%	51.0%	40.4%
Red	T-2	33.5%	8.3%	39.9%	1.4%	1.2%	0.4%	15.3%
Yellow	T-3	30.4%	1.6%	0%	13.6%	31.1%	3.2%	20.1%
Blue	T-4	10.3%	0%	0.8%	63.6%	3.3%	5.2%	16.9%
White	T-5	77.2%	6.2%	0%	0.1%	1.6%	1.3%	13.6%
Green	T-6	26.5%	4.2%	0%	22.6%	2.3%	10.6%	33.7%

The data received from the portable XRF detection conducted on the CS1 polychrome statue were used to determine the elemental composition of the pigments. According to the data in the table, the black pigment contains a high concentration of Ca and S elements, which may be the main components of the white substrate layer material under the black pigment. No obvious Pb elements were detected, excluding the black pigment as lead dioxide (PbO_2). Lead pigments, e.g., white lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and red lead (Pb_3O_4), were employed owing to their bright colors and high covering power in paintings. Lead pigments turn black, which is caused by reactions between sulfur-containing compounds and black galena (PbS) and oxidation in the black-brown plattnerite (PbO_2) [3,4]. The red pigment has Hg and Pb color-exhibiting elements, implying that the red pigment contains cinnabar (HgS) and minium (Pb_3O_4), but whether it is a mixed layer or a heavy layer requires more experimental verification. The yellow pigment has high Pb, As and Fe content, and it is presumed that the yellow pigment may be realgar (As_4S_4), mars yellow ($\text{Fe}(\text{OH})_3$) and artificial chrome yellow (PbCrO_4). There is a high Cu content in the blue pigment, with Cu being the main element responsible for imparting color; consequently, it is hypothesized that the blue pigment is azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$); conversely, Pb is the primary element implicated for white pigment, and it also contains a small amount of As and S. It is suspected that the white pigment is white lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) or lead sulfate (Pb_3SO_4); the Cu content of the green pigment is relatively high, but considering that the majority of green mineral pigments contain Cu, it is impossible to make a decision regarding the green pigment.

After a comprehensive analysis of the XRF data, the types and compositions of the pigments used in the polychrome statue of the Sage Mother Hall were initially clarified. According to the pigments commonly used in ancient China, the red pigment was judged to be cinnabar and minium, the yellow pigment was realgar and mars yellow, the blue pigment was probably azurite, the white pigment was white lead or lead sulfate, and the green and black pigments were not determined.

3.2. Microstructure of the Polychrome Statues

The cross-sections observed under the optical and scanning electron microscope clearly show that the structure of the painted sculpture is composed of three layers: a plaster layer, a white substrate layer, and a pigment layer. Most pigment samples have overlap layers and multilayers. OM and BSE images of the sample cross-sections are shown in Figure 5. The results of the SEM-EDS of the samples are listed in Table 3.

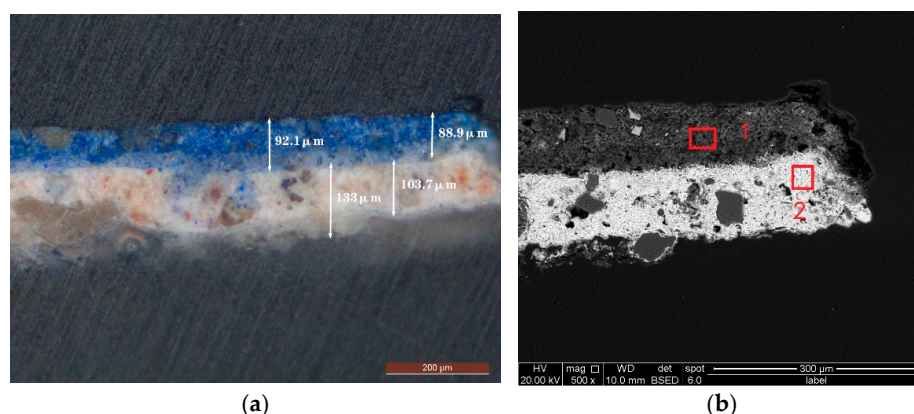


Figure 5. Cont.

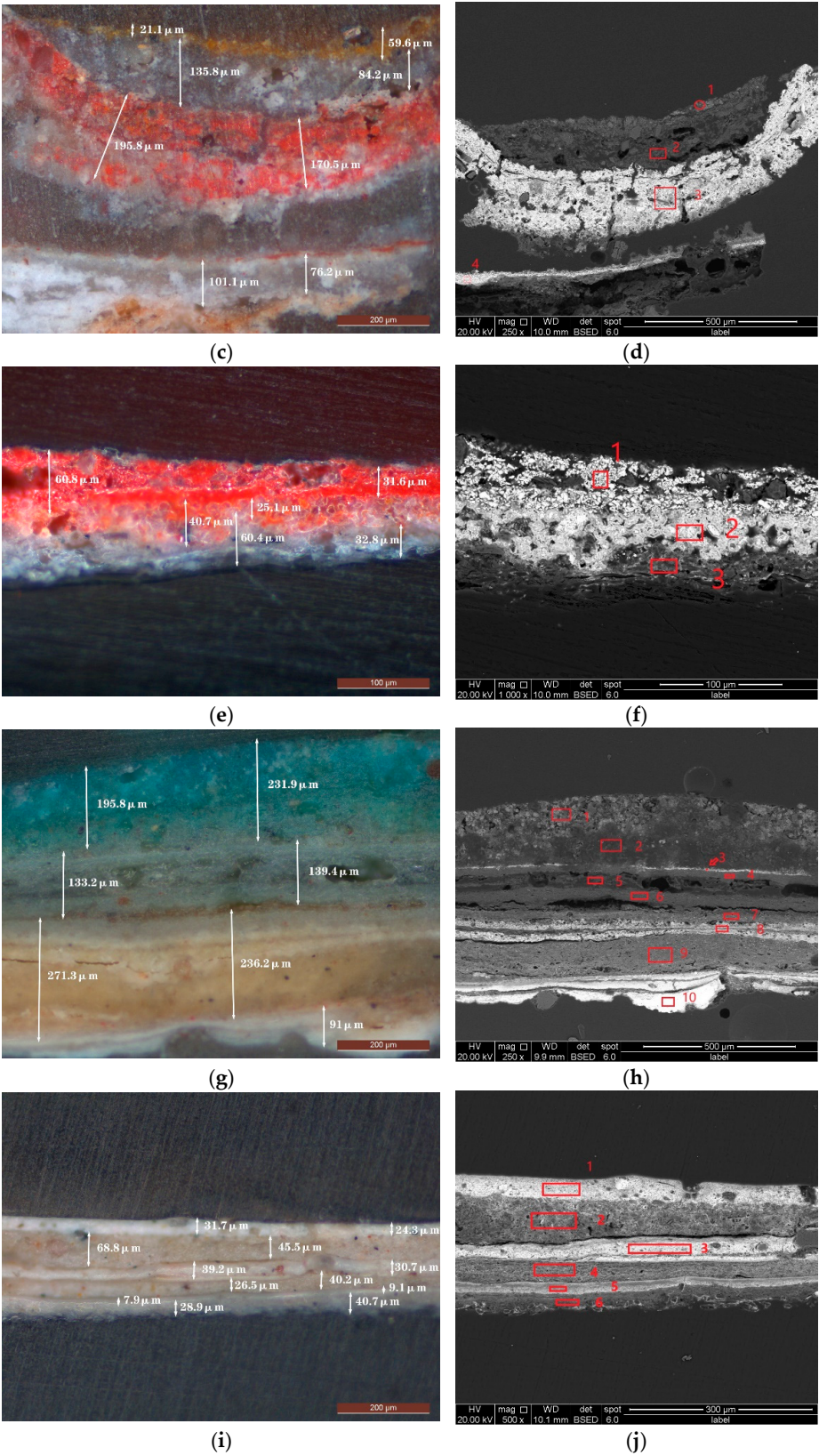


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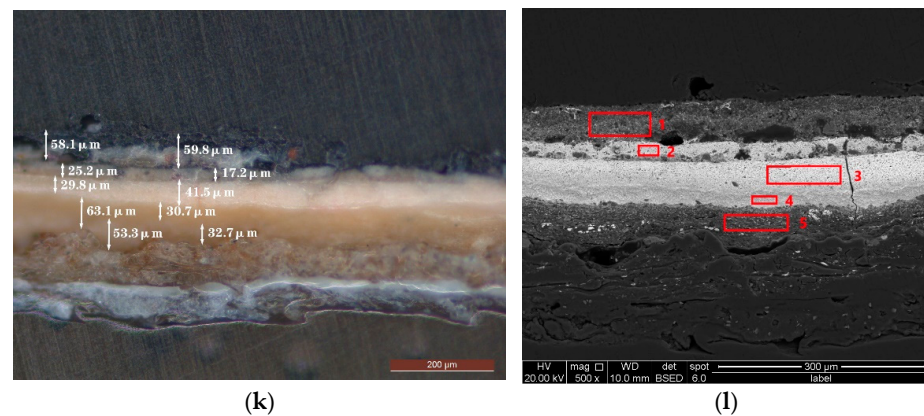


Figure 5. OM and BSE images of the sample cross-sections revealing paint stratigraphy. (a) OM images of 1-1 blue sample; (b) BSE images of 1-1 blue sample; (c) OM images of 1-2 yellow sample; (d) BSE images of 1-2 yellow sample; (e) OM images of 1-3 red sample; (f) BSE images of 1-3 red sample; (g) OM images of 1-4 green sample; (h) BSE images of 1-4 green sample; (i) OM images of 1-5 white sample; (j) BSE images of 1-5 white sample; (k) OM images of 1-6 black sample; (l) BSE images of 1-6 black sample.

Table 3. Statue No.CS1, Sage Mother Hall: SEM-EDS and cross-section results.

Sample Number	Test Number	Elemental Content (wt%)											Thickness (um)
		Na	Al	Si	S	Cl	Ca	Cu	Pb	Fe	Hg	As	
1-1	1	8.6	21.4	35.6	23.5	2.0	1.4	7.5	-	-	-	-	89~92
1-1	2	-	-	-	17.9	-	-	-	82.1	-	-	-	104~133
1-2	1	-	11.1	16.9	4.9	-	1.9	-	-	56.4	-	8.8	21~60
1-2	2	-	44.3	48.5	-	-	4.0	-	-	3.2	-	-	84~136
1-2	3	-	-	2.6	-	-	1.9	4.3	88.6	2.6	-	-	171~196
1-2	4	1.6	-	-	8.6	2.8	4.7	-	82.3	-	-	-	72~101
1-3	1	-	-	-	10.7	-	-	-	-	-	89.3	-	32~61
1-3	2	-	-	-	12.6	-	-	-	82.6	4.8	-	-	25~41
1-3	3	-	19.0	21.2	8.8	-	7.4	-	41.5	2.1	-	-	33~60
1-4	1	-	13.06	21.3	2.0	3.2	2.9	34.1	-	1	-	21.9	196~232
1-4	2	5.0	15.7	28.6	12.2	3.6	-	20.5	-	3.2	-	11.2	
1-4	3	-	-	-	8.7	3.6	-	3.9	63.2	-	-	20.6	133~139
1-4	4	3.9	29.7	33.5	20.6	-	8.3	4.0	-	-	-	-	
1-4	5	-	10.0	12.2	34.6	14.7	10.9	17.6	-	-	-	-	
1-4	6	1.9	28.0	41.1	-	-	2.1	14.0	-	2.3	-	8.5	
1-4	7	-	17.8	33.5	18.5	1.7	-	7.8	-	2.9	-	17.8	236~271
1-4	8	-	8.9	19.7	17.1	-	-	25.9	28.4	-	-	-	
1-4	9	4.5	26.8	50.4	-	-	3.2	-	-	2.0	-	13.1	
1-4	10	-	-	-	8.3	-	1.6	-	90.1	-	-	-	≈91
1-5	1	-	-	-	11.3	-	-	-	88.7	-	-	-	24~32
1-5	2	-	15.8	30.1	7.1	-	12.5	-	31.3	3.2	-	-	46~69
1-5	3	-	-	-	19.2	-	-	-	80.8	-	-	-	31~39
1-5	4	-	21.7	24.7	12.4	-	1.8	-	39.4	-	-	-	27~40
1-5	5	-	1.8	2.8	21.4	-	1.4	-	58.0	14.6	-	-	8~9

Table 3. Cont.

Sample Number	Test Number	Elemental Content (wt%)											Thickness (um)
		Na	Al	Si	S	Cl	Ca	Cu	Pb	Fe	Hg	As	
1-5	6	-	30.2	37.9	6.3	-	1.1	-	24.5	-	-	-	29~41
1-6	1	-	13.5	22.7	11.7	-	8.5	-	43.6	-	-	-	58~60
1-6	2	-	-	-	19.4	-	2.1	-	78.5	-	-	-	17~25
1-6	3	-	-	-	19.9	-	-	-	80.1	-	-	-	30~42
1-6	4	-	33.1	40.8	-	-	-	-	26.1	-	-	-	≈63
1-6	5	-	33.3	35.5	4.3	-	2.2	-	8.7	16.0	-	-	

“-” means not detected.

As shown in Figure 5 and Table 3, Sample 1-1's layer structure distribution is as follows: L1 blue pigment layer → L2 white substrate layer, with the whole being flat; via EDS analysis, the Al and Si content in the blue pigment layer was found to be high, and Cu and Na elements were also detected, so the blue pigment was initially assumed to be ultramarine. No other elements were detected in the white substrate layer except Pb and S elements, so we can deduce that it is composed of lead sulfate.

Sample 1-2 has the following structure: L1 yellow pigment layer → L2 plasters layer → L3 red pigment layer → L4 white substrate layer. The color-revealing element Fe accounts for 56.44% of the yellow pigment layer. While it contains a small amount of As, combined with the same high Fe content found by the XRF, it was assumed that the yellow pigment was yellow ochre or orpiment. The Al and Si elements in the layer account for 92.82% of the total percentage, and thus, their composition should be kaolinite and quartz; the color-emitting element Pb was detected in the lower red pigment layer of the sample, but Hg was not measured, effectively ruling out the possibility that the red pigment in Sample 1-2 is a mixture of cinnabar and minium; in the bottom white powder layer, Pb accounts for 84.72%. While it contains a small amount of Ca and S elements, it is assumed that the white substrate layer is a mixture of lead sulfate or white lead and gypsum, which needs to be determined by other methods.

Sample 1-3 is divided into three layers under BSE (two red pigment layers and a white substrate layer), with no white substrate layer between the two pigment layers. The surface red pigment layer mainly contained elements Hg and S, and in the middle red pigment layer, Pb was detected in 82.62% of the surface. Pb, Al and Si were found in the bottom white substrate layer. Since there was no white substrate layer between the two pigment layers, it was deduced that the white substrate layer was a mixture of white lead, kaolinite and quartz.

Sample 1-4 has a four-layer structure: L1 green pigment layer → two plaster layers → white substrate layer. This sample, with Cu and As as color ingredients, is more complicated, and it mainly includes cornwallite ($\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$), lavendulan ($\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$), emerald green ($\text{Cu}(\text{CH}_3\text{COO})_2\cdot 3\text{Cu}(\text{AsO}_2)_2$) [5] and so on.

Sample 1-5 has a total of six layers, and each plaster layer is painted with a white pigment layer. Pb and S are abundant in the white pigment layer. We believe lead sulfate was used for the white pigment. The plaster layer between the pigment layers is dominated by Pb, Al and Si, so we inferred that the plaster layer is a mixture of lead pigment, kaolinite and quartz.

From outside to inside, Sample 1-6 has four layers: L1 black pigment layer → white substrate layer → white pigment layer → plasters layer. Via EDS analysis, the white substrate layer was found to contain a lot of Pb and S, which is likely lead sulfate. The plaster layer is mainly Al and Si, except for the above two elements, and it is presumed that the plaster is a mixture of kaolinite and quartz.

3.3. Internal Structure of Polychrome Statues

X-ray radiography is a nondestructive testing method that uses X-rays with a high penetrating ability to detect the internal structure of materials without destroying them [6], and has been widely used in the conservation and restoration of cultural relics and archaeological research [7,8]. Because of the unique production process of the polychrome statue, the internal skeleton and the preserved wooden bone needed to be detected with the lap method. The internal structures of three polychrome statues were photographed and imaged with the X-ray radiography method, as shown in Figure 6.

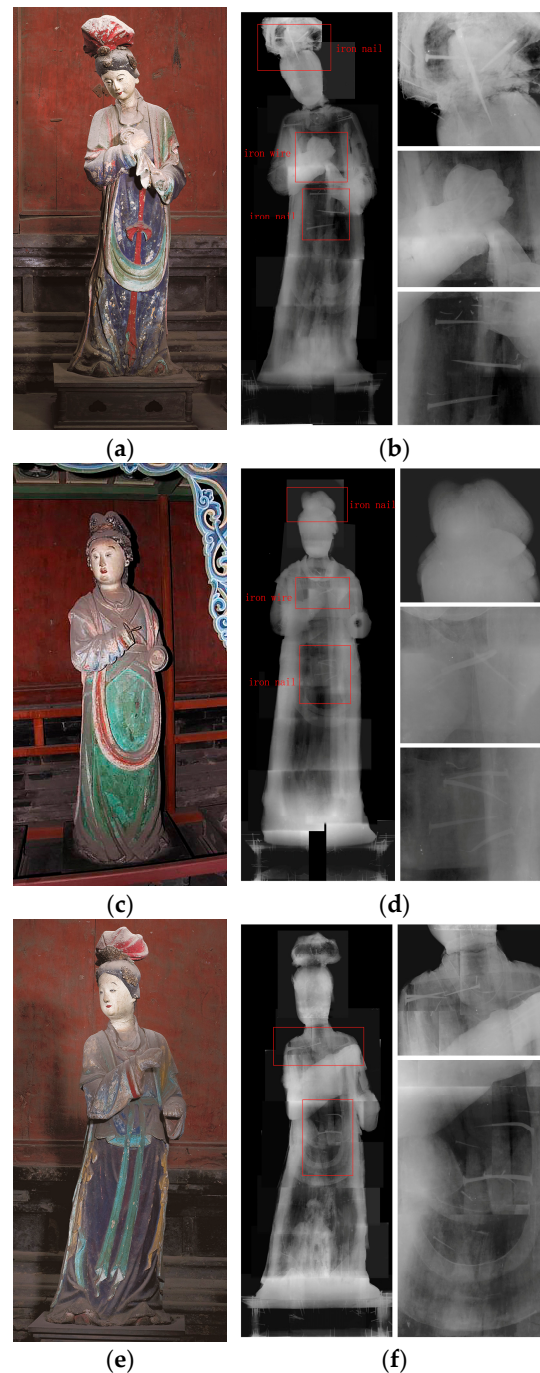


Figure 6. Visible and X-ray images of the polychrome statues. (a,c,e) CS27, CS29, CS30, visible light photographs; (b,d,f) CS27, CS29, CS30, X-radiographic images.

X-radiography was unable to generate the desired image effect because of the statues' material qualities, namely, their thicker clay layers. The results of X-radiography show that the wooden bones of the statues are vertically connected by iron nails. Additionally, the wooden skeleton of the CS30 statue can be clearly seen to be built in the shape of a “cross” to support the lower half of the body in situations where it is subjected to stress. Iron nails join the head, shoulders and elbows, while iron wires form the contour of the hands. In addition, in CS27 and CS30, it can be clearly seen under the X-ray that their preparation layers are cracking at the neck, with CS27 having the more serious damage of the two. The heads and bodies are currently only relying on the pulling force of the preparation layer to support them, which poses a serious threat to the stability and long-term preservation of the statues. This test was conducted not only to investigate the manufacturing process of the polychrome statues but also to provide a reference basis for the internal preservation of these cultural relics.

3.4. Analysis of Plaster Layer

The preparation layer is not only bonded to the wooden skeleton; it is also the carrier of the pigment layer, which is one of the key factors to determine whether or not a polychrome statue can be preserved over a long time. The production of polychrome statues is usually divided into the following steps: standing bone (立骨), fitting flesh (贴肉) and decorating (穿衣). The plaster layer of the polychrome statues consists of two distinct layers, namely, the coarse clay layer and the fine clay layer. Each of these materials was analyzed with XRD, and their main components are quartz (SiO_2), sanidine $\text{K}(\text{AlSi}_3\text{O}_8)$, calcite (CaCO_3) and a small amount of kaolinite and other clay minerals. The analysis results are shown in Table 4.

Table 4. Statue No.CS1, Sage Mother Hall: XRD analyses results.

Sample Number	Sample Name	Phase
1-7	Coarse mud layer	quartz, sanidine, calcite
1-8	Fine clay layer	quartz, kaolinite, calcite

1-7 XRD profile

1-8 XRD profile

In addition, a comparative analysis of the XRD profile of the samples from the coarse clay layer and the fine clay layer reveals that, although the main components of the two are very similar, the content of the non-crystalline clay minerals in the coarse clay layer is significantly higher than that of the fine clay layer. This finding suggests that the clay in the fine mud layer has been subjected to a screening process, such as elution.

3.5. Analysis of Pigment Layers

Raman is commonly used in the conservation of cultural relics and works of art because of the tiny quantity of the required sample, the convenience of the sample's preparation and the capacity to collect comprehensive information on both the structure and composition of the sample in the analysis [9].

Microstructural observation and SEM-EDS analysis were used to determine the elemental content of the different pigment samples of the polychrome statues. Raman was adopted to further determine the main mineral phase of the pigments, as shown in Figure 7.

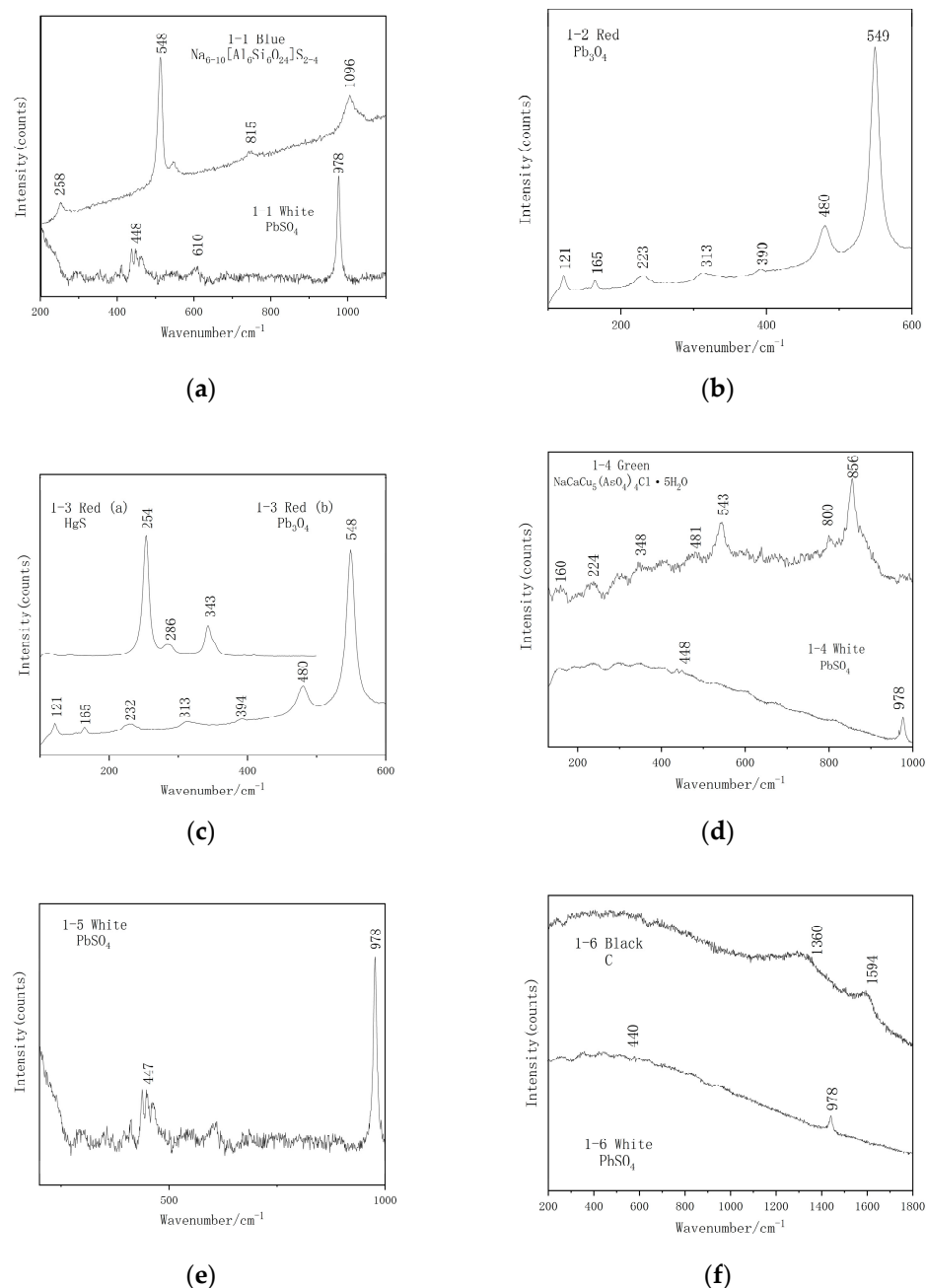


Figure 7. Raman spectra from statue No.CS1, Sage Mother Hall. (a–f) Characteristic peaks for Samples 1-1–1-6.

Raman spectra of the mineral pigments are shown in Figure 7. Raman analyses are based on the published literature [10,11].

Sample 1-1 (Figure 7a) has L1 mineral Raman characteristic bands at 258 w, 548 vs and 1096 m cm^{-1} , which are completely consistent with the characteristic bands of ultramarine. In Sample 1-2 (Figure 7b), an L1 surface yellow pigment layer was not detected, but it does have L3 mineral Raman characteristic bands at 121 vs, 223 w, 313 vw, 390 w and 549 vs cm^{-1} , which are completely consistent with the characteristic bands of minium. Sample 1-3 (Figure 7c) has L1 mineral Raman characteristic bands at 254 vs, 286 w and

343 m cm^{-1} , which are completely consistent with the characteristic bands of cinnabar; it also had L2 mineral Raman characteristic bands at 121 vs, 232 w(sh), 313 vw, 394 w, 480 vw and 548 vs cm^{-1} , which are completely consistent with the characteristic bands of minium. The characteristic bands of the particles in Sample 1-4 (Figure 7d) were detected at 160, 224, 348, 543 and 856 cm^{-1} and are completely consistent with the characteristic bands of lavendulan. The spectra consist of ν_1 (AsO_4) at 854, ν_2 at 345 and ν_4 at 545 cm^{-1} [12]. Sample 1-5 (Figure 7e) has L1 mineral Raman characteristic bands at 447 m and 978 s cm^{-1} , which are completely consistent with the characteristic bands of lead sulfate, as well as other white pigments. Sample 1-6 (Figure 7f) has L1 mineral Raman characteristic bands at 961 m (=n1(a1) PO_4^{3-}), ~1325 vs. (br) and ~1580 vs. (br), which are completely consistent with the characteristic bands of black carbon.

4. Discussion

4.1. The Production Process of Polychrome Statues

Polychrome statues can be divided into temple statues, grotto statues, tomb statues and folk statues based on the buildings to which they are attached [13]. According to the production process and materials, they can be further divided into cliff statues, grotto statues, and wooden skeleton polychrome statues [14]. Wooden skeleton polychrome statues are the most frequent among them, with a basic structure consisting of a wooden skeleton support body, a preparation layer, and a pigment layer [15]. The production process for the polychrome statues at the Sage Mother Hall is basically similar to that of other traditional wooden skeleton polychrome statues in northern China. However, as shown by the X-radiographic images, as well as by some defective and broken statues found with observation and comprehensive analysis, there are some differences; namely, the skeletons of these statues were divided into main ones and secondary ones when their basic frameworks were built. A statue's center of gravity is at the main skeleton, while the secondary skeleton aids in the overall structure of the skeleton, maintaining the balance by force. The wooden skeleton is fixed by riveting, nailing or binding, which not only strengthens the skeleton as a whole but also improves the preparation layer's adhesion and facilitates long-term preservation.

The polychrome statues must have been perfected in terms of production techniques and materials due to the status of the Sage Mother Hall in Jinci Temple and the importance of the figures enshrined in it, as well as with respect to the subject matter depicting the Song Dynasty's court rites and music system. In the current state of preservation of statues in the hall, the majority of damage to the statues is concentrated on the surface pigment layers and some mechanical damage, but none of the statues have collapsed or tilted due to their internal skeleton structures. This is the primary reason why the statues in the Sage Mother Hall have been preserved for nearly 1000 years and are still standing now.

Although the external pigment layers have been repainted many times, with most of the current paint not coming from the original era, the silhouette of the painted form, the appearance of the clothes, the posture and the charm of the statues still retain the style of the Song Dynasty, which is of practical importance to research on figure statues and the craftsmanship levels in the Song Dynasty.

4.2. The Pigments of Polychrome Statues

4.2.1. Red Pigments

Based on the results of XRF, SEM-EDS and Raman, it is clear that the majority of the pigments used in the statues are inorganic mineral pigments. Cinnabar and minium were two of the most prevalent types of red pigments used in ancient China. These pigments found widespread application in polychrome painting on ancient architecture, polychrome pottery, polychrome statues and wall painting, among other types of polychrome artwork. It was common practice to combine the two pigments in order to achieve the desired effect with respect to color modulations. For instance, the Song Dynasty polychrome statue of the Baixiang (白象) Pagoda in Wenzhou uses a mixture of both. This combination involved

using minium and then cinnabar, and then mixing the two in a certain proportion to deepen the color of the red [16]. There is a record in the literature about the process of oil painting in ancient buildings, that “the base is made of minium and the surface is covered with cinnabar” [17] (章丹打底, 银珠盖面). Similar to this, the majority of the red pigments in the polychrome statues of the Sage Mother Hall use minium in the lower layer and cinnabar in the upper layer.

4.2.2. Blue Pigments

Ultramarine is a blue pigment that comes in two varieties: natural and artificial. Natural ultramarine is a blue pigment produced by grinding and processing lazurite minerals. It has been used for at least 5000 years [18], with the earliest uses in grotto wall paintings in Xinjiang, China (5th–8th century A.D.) [19]. Because “the color like the sky” (also known as “emperor blue” or “treasure blue”) was cherished by the ancient emperors, lazurite was used to make various jade artifacts for the royal family. Many grotto paintings along the Silk Road have been found to use lazurite as a blue pigment, including in the Dunhuang Mogao Grottoes (莫高窟), the Tianshui Maiji Mountain (麦积) Grottoes in Gansu and the Kizil Cave-Temple (克孜尔) in Xinjiang [20,21]. Jean Baptiste Guimet was the first to develop an artificial ultramarine in 1828, and its commercial production evolved soon thereafter in 1830 [22]. This method significantly reduced the cost of ultramarine pigments, and artificial ultramarine has gradually replaced natural lazurite since then. Ultramarine was widely used for painting by Western European artists as soon as it appeared, and it was brought to China in the late Qing Dynasty from Europe. Chinese chemists began synthesizing artificial ultramarine using domestic raw materials in 1927, but the artificial ultramarine used in the Dunhuang Mogao Grottoes from the Qing Dynasty was imported from abroad until 1940 [23]. With respect to analyzing and identifying elemental proportions between natural lazurite and artificial ultramarine, Casellato et al. in Italy used SEM-EDS to analyze the elemental composition of natural and artificial ultramarine and found that the natural lazurite’s Na/S ratio was greater than one, while the artificial ultramarine was exactly the opposite [24]. Based on this, the ratios of Na and S in the blue pigment samples (Table 3) were 8.6% and 23.5%, respectively, and the Na/S ratio was lower than one, which was consistent with the literature findings. The blue pigments of the polychrome statues in the Sage Mother Hall were repainted in a later period, based on the date of the wide use of artificial ultramarine, with the last painting being performed after the mid-nineteenth century.

4.2.3. Green Pigments

There are three sources of lavendulan: natural mineral pigments, artificial inorganic pigments, and transformed copper and arsenic-containing pigments.

The discovery of lavendulan in Chinese paintings is seldom reported. Malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and atacamite ($\text{Cu(OH)}_3\text{Cl}$) were commonly used green pigments in ancient China, none of which contained As. It is less likely that natural lavendulan was used for the polychrome statues in the Sage Mother Hall. Artificial emerald green pigment ($\text{Cu(C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu(AsO}_2)_2$), which was first synthesized by the Germans in 1814, was used in large quantities for polychrome paintings at the Summer Palace [25] and other ancient buildings, and it is the most widely reported green pigment containing Cu and As. Murals, polychrome statues and other polychrome artifacts use lavendulan as green pigment, including the polychrome statues in Cave 11 of the Yungang Grottoes, Shanxi Province; the architectural polychrome paintings of the Nine Halls at the Kumbum Monastery in Qinghai; the Ming Dynasty polychrome statues at the Lingyan Temple in Shandong Province [26]; and the Buddha statue at Baodingshan in Dazu [27]. Using Raman, X-radiography and other techniques, it has been hypothesized in related studies that lavendulan transformed from emerald green at all of these sites. Emerald green degrades in oil paintings that are rich in relatively high concentrations of monoacids, diacids and resin acids, forming copper soaps (4Cu(FA)_2) (FA = fatty acids) and arsenic trioxide (As_2O_3), leading to transparent, discolored

brown layers [28]. Emerald green is also found to transform into mineral lammerite ($\text{Cu}_3(\text{AsO}_4)_2$) in wall paintings as a result of the migration of arsenic [29]. The formation of lavendulan needs acid environments [30]; in Taiyuan, such an environment may be supplied by polluted air and acid rain [31]. In this process, As^- migrates throughout the pigment layer, whereas Cu^- remains in situ, and the painting is supplied with lammerite produced by the emerald green. Lavendulan was found in the Sage Mother Hall's polychrome statues, as expected for its time period. Considering that the polychrome statues in the hall have been repaired many times throughout history, the use of ultramarine pigment in the polychrome statues corroborated the use of emerald green, and that it was transformed.

4.3. Multilayered Repainting

Most of the polychrome statues preserved and handed down to the present day have been repainted and repaired. The process of repainting the statues, which are tied to traditional Chinese culture and religious beliefs, did not leave detailed records every time. Repainting is generally concentrated on partial painting, resulting in varying layers of pigments among most of the polychrome statues and a gap in the repainting process. Furthermore, the application of pigments is also related to the continuity of eras; subsequent generations of repainting are superimposed on top of prior layers, and the features of the era may be determined by studying the multilayers.

Using Sample 1-2's OM images (Figure 5c) as an example, we can see that the surface yellow pigment layer differs from the red pigment layer, as well as from the white substrate layer when compared to its plaster layer. The thickness of the external pigment layer and the plaster layer varies greatly, and their processes are not uniform. The yellow pigment layer is about 60 μm deep at its thickest point, and the plaster layer is around 110 μm thick on average. The red pigment layer is quite uniform in thickness, with the thinnest point measuring at about 171 μm , approximately three times the thickness of the surface pigment layer, and the white substrate layer can be detected below it. This demonstrates that the latest repainting did not follow the traditional process of painting the white substrate layer followed by painting pigments; instead, a thicker plaster layer was directly made to cover the lower layer of the previous pigment layer. This method makes repainting easier, but the painting process is rough. The use of yellow pigment instead of the original red pigment could be linked to future generations' aesthetic preferences.

According to other research, the types of pigments used for religious statues in Shanxi change constantly. Yellow pigments were mainly made from gold foil in the Tang and Song Dynasties, and in the Ming and Qing Dynasties, the frequency of using orpiment and realgar gradually increased. Artificial pigments, such as emerald green and ultramarine, gradually replaced green and blue pigments from natural minerals such as lazurite and malachite. These phenomena reflect trends in the use of pigments.

5. Conclusions

The polychrome statues of the Sage Mother Hall in the Jinci Temple were created in the same way as other traditional northern Chinese wooden skeleton support and clay statues. First, a wooden skeleton is built and the shape of the statue is shaped at the same time. Next, the size and posture of the statue are developed. Then, the white substrate layer is painted on top of the plaster layer. Finally, painting is carried out.

Most of the pigments used in these statues are inorganic pigments. The red pigment is made from minium and cinnabar, the white pigment is lead sulfate, the green pigment is lavendulan, the yellow pigment is yellow ocher, the blue pigment is ultramarine, and the black pigment is black carbon. The pigment layers of the polychrome statues have been through both single instances of repainting and multiple instances of repainting. The main components of the plaster layer are quartz, sanidine, calcite and a small amount of clay minerals such as kaolinite.

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