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AN ANALYTICAL STUDY OF PIGMENTS IN QING DYNASTY MURALS OF LONGWANG TEMPLE, XIAZHUANG, XINRONG DISTRICT, DATONG

ABSTRACT The frescoes of Xia Zhuang Longwang Temple in Xinrong District, Datong, were Ming Dynasty frescoes of the Qing Dynasty. To understand their pigment composition, this work used a combination of scanning electron microscopy-energy spectrometry and laser micro Raman spectroscopy to analyze the pigment samples. The results show that the murals of Xia Zhuang Longwang Temple are all inorganic pigments. The white pigment is hard gypsum, the red pigment is mainly cinnabar, the green pigment is alkaline copper chloride, the blue pigment is cobalt blue, the black and gray pigments are mainly carbon black, the pink pigment coloring component is iron red, and the yellow pigment contains coloring components cinnabar and lead. The results of the study are important for understanding the production process of folk murals and the use of pigments in the Qing Dynasty.

Key words: frescoes, pigments, SEM-energy spectroscopy, Raman spectroscopy

ABSTRAKT Freski dynastii Ming w świątyni Xia Zhuang Longwang w dystrykcie Xinrong w Datong pochodzą z okresu z dynastii Qing. Aby poznać skład ich pigmentów wykorzystano kombinację skaningowej mikroskopii elektronowej, spektrometrii energetycznej i laserowej mikrospektroskopii Ramana do analizy próbek pigmentu. Wyniki pokazują, że wszystkie malowidła ścienne świątyni Xia Zhuang Longwang wykonane zostały za pomocą pigmentów nieorganicznych. Biały pigment to twardy gips, czerwony to głównie cynober, zielony to alkaliczny chlorek miedzi, niebieski to kobaltowy błękit, czarne i szare pigmenty to głównie sadza, komponentem różowego pigmentu jest żelazo, zaś na pigment żółty składa się cynober i ołów. Wyniki badań są ważne dla zrozumienia procesu tworzenia fresków w czasach dynastii Qing.

1. Introduction

Xinrong District is located in the northernmost part of Shanxi Province, the north and northwest to the Great Wall as the boundary with the Inner Mongolia Autonomous Region, Fengzhen City and Liangcheng County, is the throat of Shanxi to Inner Mongolia, but also Beijing and the North China Plain side back, since ancient times, strategic and economic location is very important.

Xia Zhuang Dragon King Temple is located in the southeast of Xia Zhuang, Xin Rong District, Datong City, 1272 meters above sea level. The temple is separated from the village by a deep east-west ditch, surrounded by ditch isolation, becoming an isolated building, county (district) level cultural relics protection units. Dragon King Temple southeast facing northwest, the middle with the wall interval, divided into two rooms in the east and west, each room four walls have murals, the content is basically complete. East painted Erlang God of merit map, for Erlang Temple; West painted Dragon King cloth rain map, for the Dragon King Temple. Mural for the Qing Dynasty, a total area of 59 square meters.

Frescoes as a painting art, pigment is the most essential part of the fresco production materials, so in the frescoes for restoration work before the fresco production process and materials must be analyzed and studied. With the continuous development of science and technology, the use of a variety of means to analyze the structure of ancient frescoes and pigment composition, determine its preservation status, is an important basis for the implementation of conservation and restoration work. The present work analyzes and studies the pigments of Xia Zhuang Longwang Temple to determine their composition, which is important for understanding the use of pigments for folk murals in the Qing Dynasty (Fig. 1-3).

2. Experimental samples and instruments

2.1. Experimental samples

The samples used for the experiments were taken from the broken location of the frescoes in Xia Zhuang Longwang Temple, and a total of nine experimental samples were collected according to the layout of the fresco contents and hues, including white, gold, red, green, blue, black, gray, pink and yellow, and the sampling locations are shown in Figure 2, Figure 3 and Table 1.

Table 1. Xia Zhuang Longwang Temple fresco pigment sampling table

Number	Name	Sampling location
1	White pigment	The lower right corner of the painting on the main wall in the west room is missing
2	Golden Layer	The second Dragon King under the skirt to the right of the Mother of Dragons on the main wall in the west room
3	Red pigment	On the right side of the main wall of the west room, at the sleeve of the small dragon
4	Green Pigment	The second Dragon King to the left of the Mother of Dragons on the main wall of the west room at the sleeve of the right major arm
5	Blue pigment	The abdomen of the third Dragon King to the left of the Mother of Dragons on the main wall in the west room
6	Black pigment	In the upper left corner of the border of the main wall of the west room
7	Grey pigment	Lower right side of the main wall of the west room
8	Pink pigment	Painted floor on the lower right side of the main wall in the west room
9	Yellow pigment	The feet of the figures in the lower middle of the East Room East Wall screen (counting from the left of the screen, the fifth figure's feet)

2.2. Analytical instruments and principles

Scanning electron microscope – energy spectrometer (SEM-EDX): 3600N scanning electron microscope produced by Hitachi, Japan, operating at 20kv.

The energy spectrometer was a Genesls2000 made by EDAX; the sample surface was sprayed with gold.

Micro confocal Raman spectrometer: XploRA Raman spectrometer made by JYBIN YVON, France.

3. Results and Discussion

3.1. Scanning electron microscopy-energy spectrometry analysis results

The samples No. 1, No. 2, No. 5, No. 8 and No. 9 were examined by scanning electron microscopy-energy spectrometry, and the results are shown in Figs. 4 to 15.

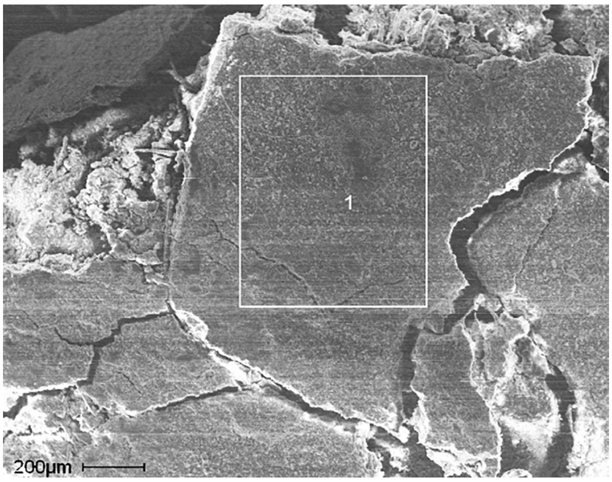

Fig. 4. Scanning electron microscope photo
of sample No. 1

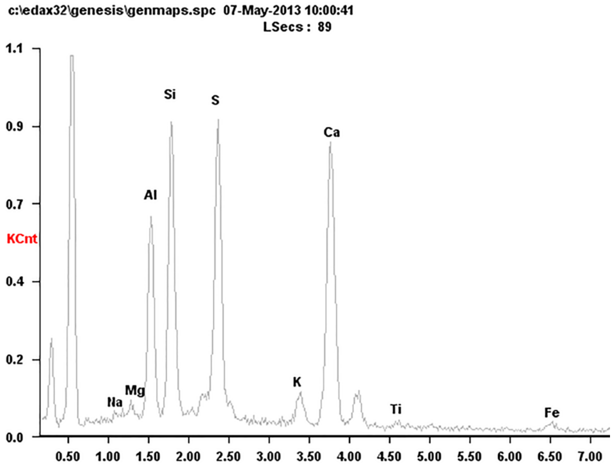

Fig. 5. Energy spectrum of sample No. 1

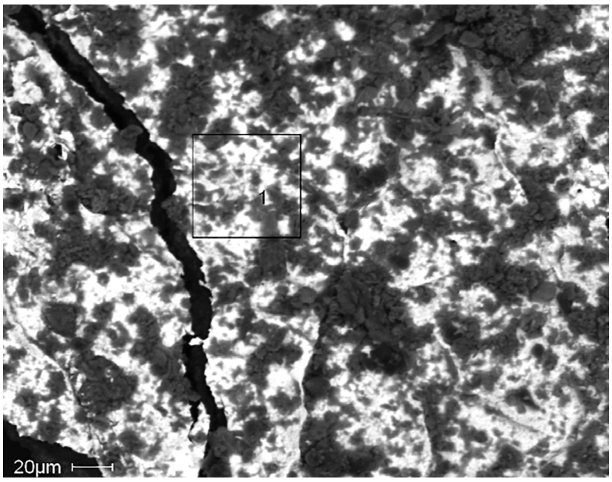

Fig. 6. Overall scanning electron microscope photo
of sample No. 2

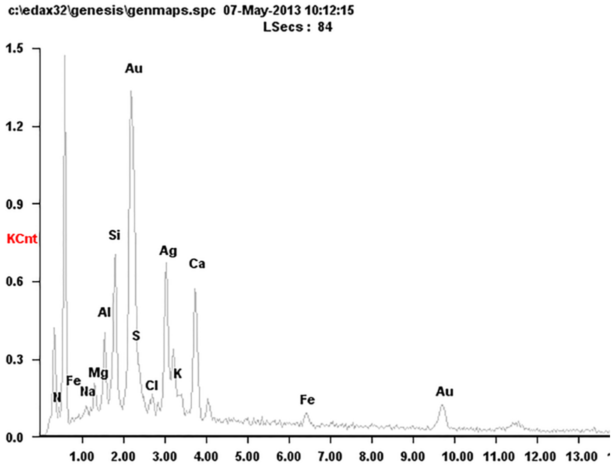

Fig. 7. Overall scanning energy spectrum
of sample No. 2

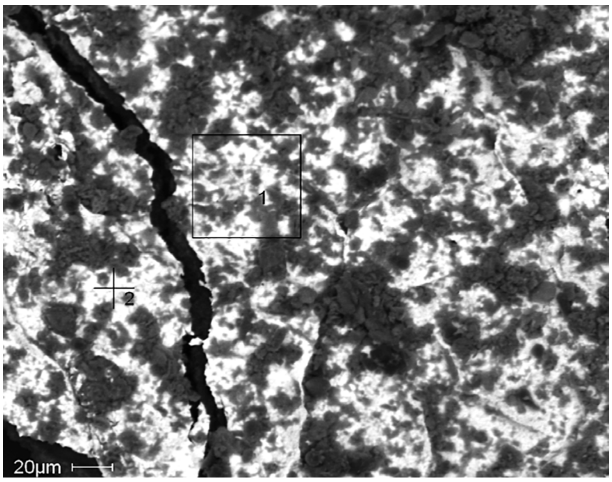

Fig. 8. Local scanning electron microscope photo
of sample No. 2

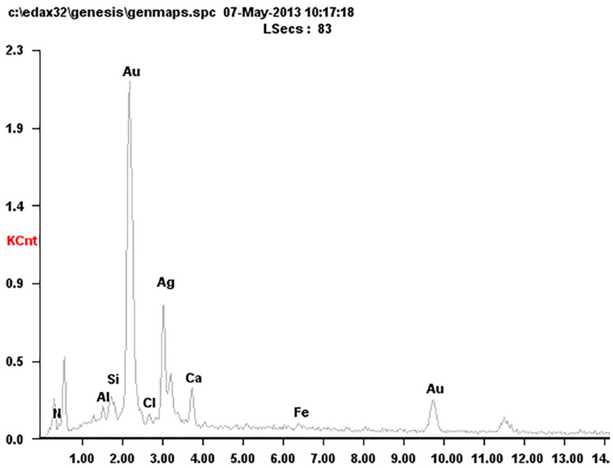

Fig. 9. Local scanning energy spectrum
of sample No. 2

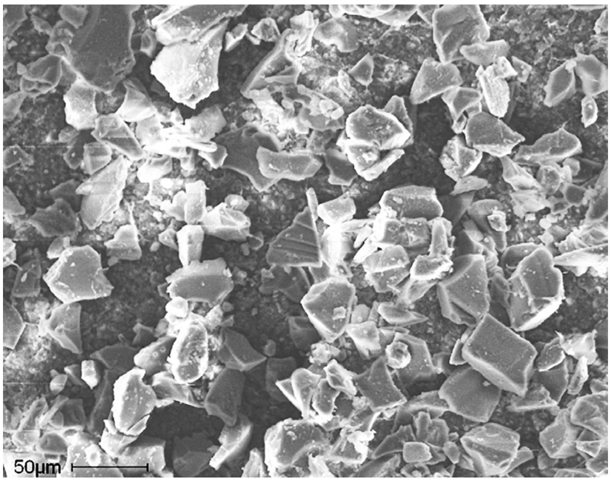

Fig. 10. Scanning electron microscope photo of sample No. 5

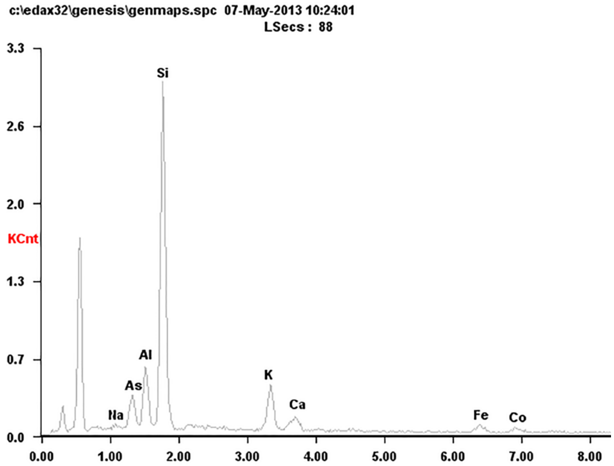

Fig. 11. Energy spectrum of sample No. 5

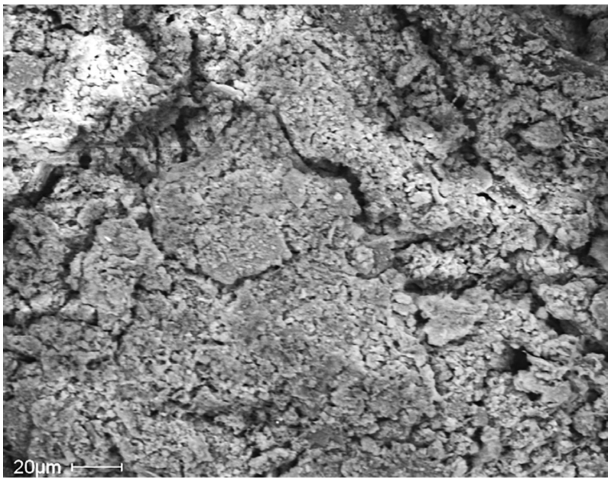

Fig. 12. Scanning electron microscope photo of sample No. 8

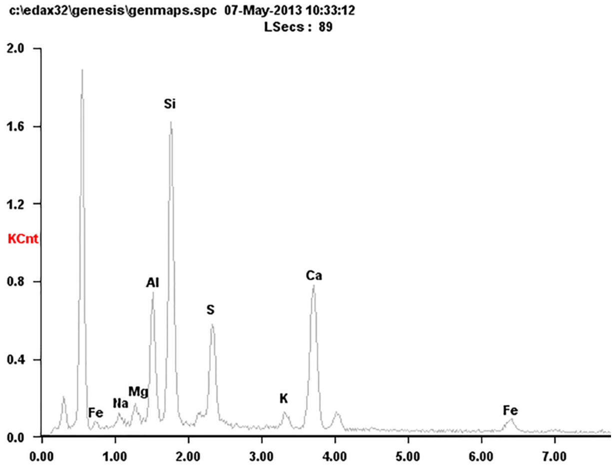

Fig. 13. Energy spectrum of sample No. 8

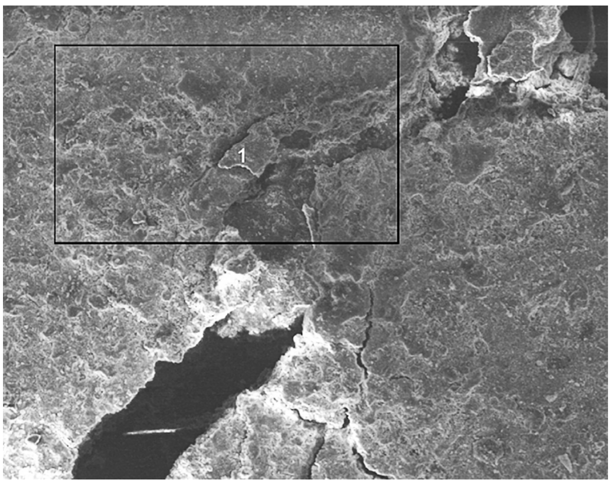

Fig. 14. Scanning electron microscope photo of sample No. 9

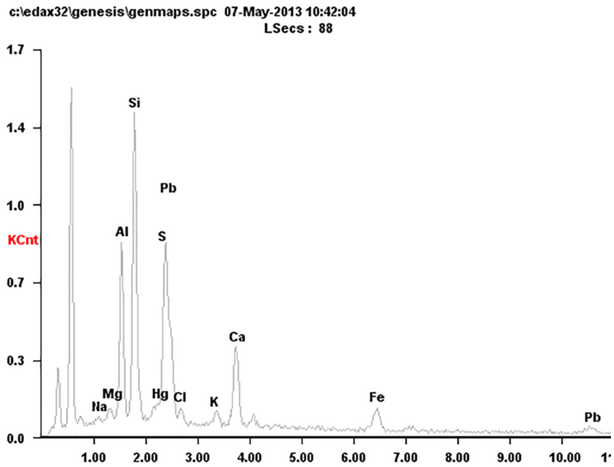

Fig. 15. Energy spectrum of sample No. 9

From the energy spectrum of the above samples, we can see that all five samples contain Si, Al, Ca, Mg and Na elements, which may be mixed with the ground battle layer or the substrate layer below the pigment during the sampling process. 1 sample is white, and from the energy spectrum shown in Figure 5, we can see that the sample contains S elements and the content is high, but it is difficult to speculate its color development composition, and further testing and analysis are needed.

The atomic percentages of gold and silver were 13.03% and 12.19%, respectively, when the whole area of gold layer sample No. 2 was surface scanned. When the brighter areas were scanned, the main components were Au, Ag, Ca, etc. Among them, the atomic percentages of gold and silver were 35.06% and 24.94%, as shown in Figs. 6 to 9. The appearance of silver in the gold layer samples may be due to the ancient frescoes, architectural painting in the paste gold use of gluing materials for gold glue oil or gold glue paint, the ancients in the preparation of gold glue oil or gold glue paint, will add silver beads to set off the color of gold, but also easy to know whether the gold glue oil hit uniform.[1]

From Figure 11, it can be seen that the blue sample No. 5 contains As, Co, Fe and other elements, which is consistent with the composition of the blue pigment (smalt) imported from Europe, which is a kind of cobalt glass with Co as the coloring agent, and the cobalt blue pigment is a kind of ground cobalt glass powder,[2] therefore, it is presumed that the blue pigment is cobalt blue. From the middle of the 15th century cobalt blue was used as a pigment, gradually replacing the scarce lapis lazuli and blue bronze ore at this time, and was widely used in European paintings and frescoes.[3]

The energy spectrum of No. 8 pink pigment sample showed the presence of Fe element, as shown in Figure 13. From this, it can be presumed that its color-rendering component may be iron red. Iron red, also known as hematite, is simple to prepare, strong in coverage, stable in color, and cheap, and was used in large quantities in ancient paintings.[4]

From Figure 14, it can be seen that the yellow sample No. 9 contains Pb and Hg elements, and it can be tentatively inferred that its color-rendering components may be Pb_3O_4 and HgS, and the specific components need to be combined with its Raman spectrum to make an accurate judgment.

3.2. Raman spectrometer analysis results

Raman spectroscopy was used to detect and analyze No. 1, No. 3, No. 4, No. 6, No. 7 and No. 9, and the results are shown in Figure 16 to Figure 22.

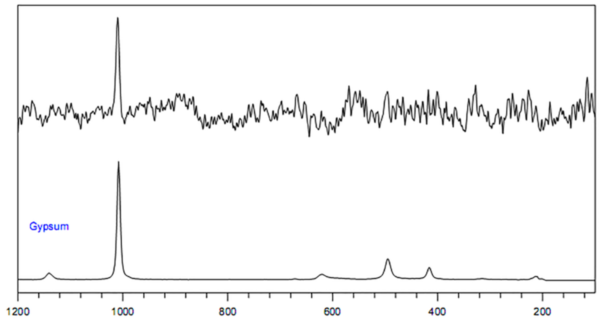

Fig. 16. Raman spectrum of No.1 white sample

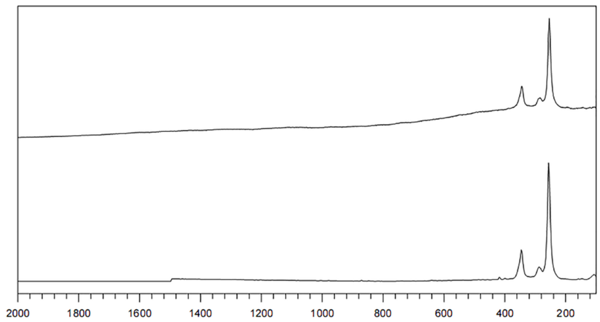

Fig. 17. Raman spectrum of No.3 red sample

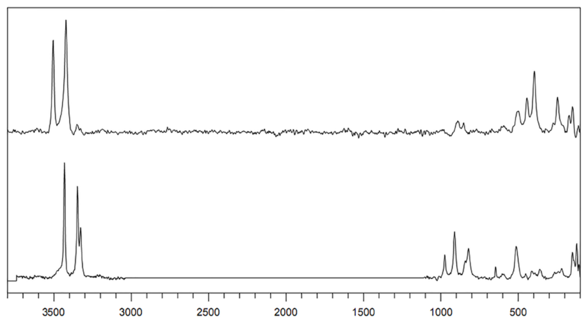

Fig. 18. Raman spectrum of No. 4 green sample

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[1] Hu Kejia, Bai Chongbin, Ma Linyan 2013: 65-72.
[2] Lei Y, Cheng S-L, Yang H. 2010: 140-156.
[3] Yan, H., Sun, K., Tang, J. 2019.
[4] Zheng Tengteng 2011.

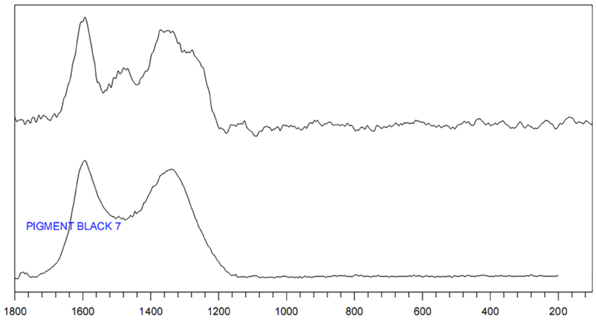

Fig. 19. Raman spectrum of No. 6 black sample

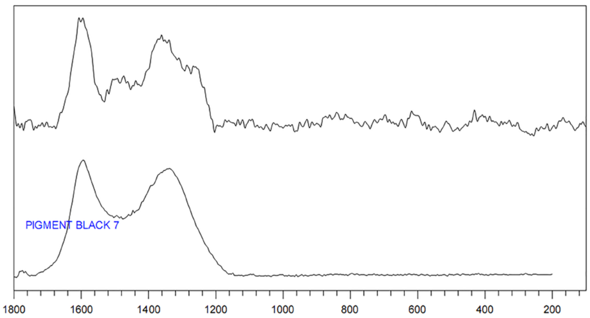

Fig. 20. Raman spectrum of No. 7 gray sample

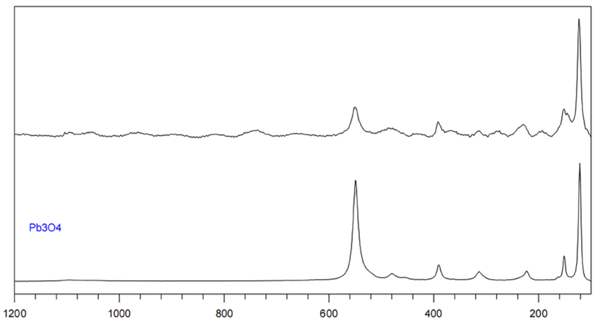

Fig. 21. Raman spectrum of No. 9 yellow sample

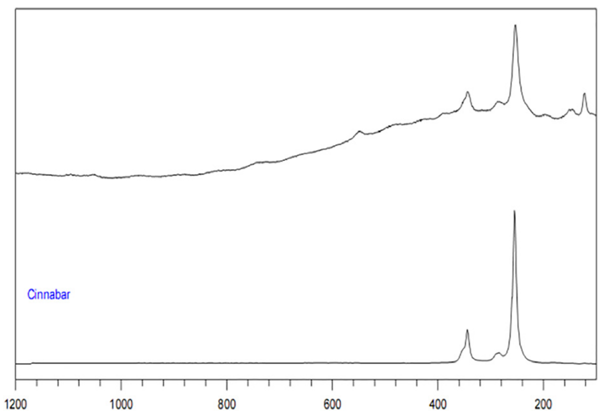

Fig. 22 Raman spectra of No. 9 yellow sample

From Figure 16, it can be concluded that the characteristic peaks of the Raman spectrogram of the white sample No. 1 are more consistent with the characteristic peaks of the standard spectrum of calcium sulfate, and combined with the results of its SEM energy spectrogram analysis, it can be inferred that the sample No. 1 contains calcium sulfate, so the white pigment may be hard gypsum ($CaSO_4$).

The characteristic peaks of the No. 3 Raman spectrum are in general agreement with the characteristic peaks of the standard cinnabar Raman spectrograms 252 cm^{-1}, 284 cm^{-1}, and 343 cm^{-1},[5] as shown in Figure 17. Cinnabar has been used as an important mineral pigment for thousands of years, mostly in the coloring of frescoes and sculptures. Cinnabar has excellent lightfastness and is a mineral pigment that can be stable and retain its vivid color over time. Although it is often confused with iron red and cadmium red due to its similarity in color, its stability, lightfastness and coverage are much better than iron red, for example.

The Raman spectrum obtained from the green sample No. 4 basically matches with the standard spectrum of alkali copper chloride, so it is inferred that the green pigment is alkali copper chloride, also called chloro-copper ore, as shown in Figure 18. The use of chloro-copper ore as a fresco pigment has not been clearly documented and is not used in modern paintings. However, the results of fresco pigment analysis indicate that chloro-copper ore was widely used in frescoes. Chalcopyrite is less stable than lime green and can either etch to lime green or absorb water to become aqueous chalcopyrite.[6] However, there are four isomers of alkali copper chloride, namely: plagioclase, para-chloroclase, chloroclase and hydroxychloroclase. Among them, oblique chloro-copperite has been found in the green pigments of some ancient wall paintings. For example, Xia Yin found a small amount of plagioclase copper ore in the analysis of the pigments of the mural painting of Fuxi Temple in Tianshui, Gansu Province.[7] In addition, Wang Jinyu, in his discussion of copper green pigments from the Dunhuang Mogao Caves, pointed out that all three isomers of alkaline copper chloride had been found in ancient fresco pigments.[8] Since the four isomers of alkali copper chloride have different stability, among which oblique chalcopyrite is

[5] Yan, H., Sun, K., Tang, J. 2019.
[6] Zhou G.X. 1984: 1-4.
[7] Xia Yin, Wang Weifeng, Liu Linxi 2007: 41.
[8] Wang Jinyu and Wang Jincong 2002: 23-31.

the least stable, it is necessary to conduct an in-depth study of the green pigment in the Xia Zhuang Longwang Temple to clarify which of the four isomers of alkali copper chloride the green pigment belongs to, and according to the difference in stability of the four isomers, effective conservation measures can be taken.

The characteristic peaks in the Raman spectra obtained from the black sample No. 6 and the gray sample No. 7 basically matched with the characteristic peaks of the standard spectrum of amorphous carbon black, from which it could be inferred that the black pigment and the gray pigment were carbon black, as shown in Figure 19 and Figure 20. Carbon black is one of the earliest painting pigments used by human. It is an amorphous carbon with the structure of graphite, not strictly amorphous, except that its grains are small and the arrangement of carbon atoms in two adjacent layers is disordered.

The characteristic peaks of the Raman spectrogram of some of the red particles in the yellow sample No. 9 coincide with the strongest characteristic peak and the second strongest characteristic peak of the standard Pb (Pb_3O_4), as shown in Fig. 21. Some of the Raman spectrograms of the red particles also appear to be in complete agreement with the characteristic peaks of the standard Raman spectrogram of vermilion, as shown in Fig. 22. Combined with the results of the elemental analysis by SEM-ESI, it can be basically inferred that this yellow sample contains both lead and cinnabar coloring components. In the ancient history of pigment development in China, in addition to using natural vermilion as a red pigment, people were able to synthesize a red mercuric sulfide artificially with mercury and sulfur to become Zhu at least in the second century BC. Based on many studies of pigments in ancient art, it is tentatively believed that the artificial Zhu, due to the presence of free sulfur in it, would darken the pigment after a long period of oxidation when mixed with lead compounds such as lead white.[9] This suggests that the yellow pigment used in the murals of Xia Zhuang Longwang Temple may have turned black after a long oxidation process.

4. Conclusion

Through the detection and analysis of the pigments used in the murals of Xia Zhuang Longwang Temple, we can roughly conclude the following.

1 Among the pigments used in the frescoes of Xia Zhuang Longwang Temple, the white pigment may be hard gypsum, the red coloring pigment is mainly cinnabar, the blue pigment coloring component is cobalt blue, the pink pigment coloring component is iron red, the yellow pigment has two coloring components, lead and cinnabar, and the black and gray pigment coloring pigment is carbon black. These are basically consistent with the mineral pigments commonly used in Chinese painting art in the past generations, but individual imported pigments cobalt blue are also found, reflecting the degree of development of the commodity economy at that time and the new changes of cultural exchanges between China and abroad.

2 The ancient Chinese gold can be divided into red gold and library gold two kinds, library gold for nine eight gold, color red; red gold for seven four gold, color white. Xia Zhuang Dragon King Temple murals in the overall gold layer of the atomic percentage of the gold content of 13.03%, the local gold content of higher places for 35.06%, gold layer also accompanied by silver atoms, very low purity, more impurities, may be related to the level of the Dragon King Temple and the financial strength of the financiers.

3 The green color pigment is alkaline copper chloride, and it is not yet possible to determine which of the four isomers of alkaline copper chloride belongs to it, and further analysis is needed.

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