Study on blue pigments in Cave 256, Mogao Grottoes: Five dynasties, Song Dynasty and Qing Dynasty

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Abstract

Murals of Cave 256, Mogao Grottoes consist of several layers, with the outermost layer overlays all others. The bottom layer was painted in the Five Dynasties. The outermost layer was mural of the Song Dynasty. Statues were repainted in the Qing Dynasty. We found that different blue pigments are used through research of murals and statues of different dynasties in Cave 256. In order to know the type of blue pigments, technology such as X-ray diffraction, microscopic FTIR spectroscopy and polarizing microscope were used for analysis of trace samples based on non-destructive research through the portable X-ray fluorescence. As a result, we know that Lazurite was used as blue pigment in murals of the Five Dynasties and Azurite was used in the Song Dynasty. Small used in statues of the Qing Dynasty was first discovered in Mogao Grottoes. Difference in blue pigments reflects the social development at that time to a certain extent. It can be inferred from the discovery of small that statues of the Qing Dynasty in Cave 256 were repainted in the first half of the 19th century.

Introduction

Dunhuang Mogao Grottoes is located 24 kilometers southeast of present-day Dunhuang City. As a comprehensive art combining architecture, sculpture and mural painting, it is the largest, longest lasting and the most informative site of grottoes temples in China and the whole world. Construction of Mogao Grottoes lasted for almost a thousand years from the second half of the 4th century to the 14th century. There was no new cave were excavated after the Ming Dynasty. A large number of murals and statues were repainted in the Qing Dynasty. There are about 45,000m² of murals and over 2,200 statues in Mogao Grottoes[1], which are important physical materials for studying the history of materials and craftsmanship of ancient Chinese murals and statues.

Cave 256 is located on the second floor of the central area of the southern area of Dunhuang Mogao Grottoes, about 200 meters north of the nine storeys pagoda of Mogao Grottoes(Fig. 1). It has a relatively large area, with over 500m² of murals and 7 statues[2]. According to scholars, Cave 256 was built by Cao Yuanshen, the third military governor of Gуйyи Army (a local armed regime that originated from the Tang Dynasty). It was founded in the Five Dynasties[3] and repaired during the Zhenzong period of the Northern Song Dynasty by Murong Yanchang, the military director of Yu Men Town of the Gуйyи Army, and his wife Yan. The bottom layer was covered and a new layer of murals was painted[4–6]. Statues were repaired and repainted in the Qing Dynasty.

Blue is highly regarded in ancient Chinese culture[7]. As one of the three primary colors, it is the most basic color in painting. It symbolizes eternity, nobility and purity and is loved by people in different times. It is also one of the most important colors of murals in the Mogao Grottoes. Based on previous research results, blue pigments used in murals and statues of the Mogao Grottoes are Lazurite[8, 9] (from the Sixteen Kingdoms to the Northern Zhou Dynasty), Azurite[10] (the Sui Dynasty to the Five Dynasties), indigo blue[11] found in individual caves and artificial ultramarine used in repainting in Qing Dynasty[12].

In this study, scientific analysis methods are used to study types, usage techniques and sources of different blue pigments used in murals and statues of Cave 256 in the Five Dynasties, the Song Dynasty and the Qing Dynasty, providing new ideas for analysis of history of blue pigments used in the Mogao Grottoes.

Materials And Methods

Analysis equipment and parameters

(1) Portable X-ray fluorescence analyzer

The Thermo XL3t-600 Portable X-ray fluorescence analyzer is used for element analysis of pigments. It uses silver target. The spot diameter is 1 cm. The analysis condition is 50kV/40µA (maximum), the detection time is 1 min, and the soil mode is used.

(2) Digital microscope

VHX-600E digital microscopes manufactured by KEYENCE are used. Microscope lens model is VH-Z20R (20X-200X). VHX-600E built-in floodlight is used for observation.

(3) X-ray diffraction analyzer

The Rigaku Dmax/2500X X-ray diffraction analyzer is used for phase analysis of pigments. It has copper target. The analysis voltage is 40kV and the current is 100mA. Scanning is continuous. The scanning range is 5°-70°. Graphite monochromator is used for filtering.

(4) Microscopic FTIR spectroscopy

The Thermo Scientific Nicolet iN10 MX Microscopic FTIR spectroscopy is equipped with liquid nitrogen cooled MCT/A detector and has transmission mode. The measuring range is 4000-675cm⁻¹, and the spectral resolution is 4cm⁻¹, with 128-time scanning.

(5) Polarizing microscope

DM2700P polarizing microscope (Lycra, Germany) is equipped with DMC2900 camera (magnification 50×, 100×, 200×, 500× and 1000×).

(6) Micro-area X-ray fluorescence spectrometer

As for German Bruker ARTAX-400 mobile micro-area X-ray fluorescence spectrometer, input voltage is 30kV, input current is 900µA, test time is 300s, X-ray tube uses Mo target with fine focal spot and helium gas environment is used for test. The analysis and test results are compared with the standard working curve fitted by glass standard samples (Corning-B, Corning-C, Corning-D glass). Quantitative analysis is made to element contents of samples.
Non-destructive testing location and micro-destructive sampling information

The portable XRF is used to perform non-destructive analysis and testing of blue pigments used in murals of different eras in Cave 256, including two blue pigment areas in the bottom layer, one dark blue pigment and two blue pigment areas in the surface layer, and blue pigments used in statues repaired in the Qing Dynasty. Moreover, four blue pigment trace samples were obtained taking the pXRF test results as a reference. Table 1 and Figure 2 for details of non-destructive testing location and micro-destructive sampling information.

<table>
<thead>
<tr>
<th>No.</th>
<th>Location and color</th>
<th>Dynasty</th>
<th>Sample property</th>
<th>Analytical methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>M256-01</td>
<td>The bottom layer of the damaged part of the north wall</td>
<td>The Five Dynasties</td>
<td>Powder</td>
<td>pXRF, XRD and PLM</td>
</tr>
<tr>
<td></td>
<td>of the main room</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M256-02</td>
<td>The bottom layer of the damaged part of the east wall</td>
<td>The Five Dynasties</td>
<td>—</td>
<td>pXRF</td>
</tr>
<tr>
<td></td>
<td>of the main room</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M256-03</td>
<td>The third person's ears from the west on the south wall of the tunnel</td>
<td>Song Dynasty</td>
<td>Powder + block</td>
<td>pXRF and XRD µ-FTIR and PLM</td>
</tr>
<tr>
<td>M256-04</td>
<td>The third person's costume from the west on the south wall of the tunnel</td>
<td>Song Dynasty</td>
<td>Powder</td>
<td>pXRF and XRD</td>
</tr>
<tr>
<td>M256-05</td>
<td>Head halo of Thousand-Buddha on the east wall of the main room</td>
<td>Song Dynasty</td>
<td>—</td>
<td>pXRF</td>
</tr>
<tr>
<td>M256-06</td>
<td>Left knee of the main statue in the main room</td>
<td>Qing Dynasty</td>
<td>Powder</td>
<td>pXRF, XRD, FTIR, PLM and ED-XRF</td>
</tr>
</tbody>
</table>

Note: “—” means that no sampling

Results

**XRF fluorescence spectrum analysis**

XRF analysis results show that the two blue pigments used in murals of the Five Dynasties of Cave 256 mainly contain Fe and Ca (Figure 3a). It is supposed that Lazurite pigment may have been used. In murals of the Song Dynasty, the dark blue is similar in composition to the blue pigments, mainly containing Cu and a small amount of Fe and Ca (Figure 3b). The color rendering component may be copper-containing Azurite. The blue pigments in the statue of the Qing Dynasty mainly contain Pb, Fe, and Co (Figure 3c), which are possibly cobalt-containing compounds.

**XRD phase analysis**

The XRD phase analysis results of the trace samples are shown in Table 2 and Figure 4. The result shows that the blue pigments used in the Five Dynasties have strong diffraction peaks when 2θ is 23.999, 19.393 and 13.694, and corresponding d values are 3.704, 4.571 and 6.441, which is consistent with characteristics of diffraction peak of Lazurite. Other phases include talc, calcite, and quartz, all of which come from the white background layer of the mural. The dark blue pigment used in the Song Dynasty has strong diffraction peaks when 2θ is 25.193, 17.033, 24.240, and the corresponding d values are 3.534, 5.181, and 3.675, which are consistent with the characteristic diffraction peaks of azurite. It also has strong diffraction peaks when 2θ is 16.223, 17.697 and 32.375 and the corresponding d values are 5.480, 5.018, and 2.771, which are consistent with the characteristic diffraction peaks of atacamite. Other phases include small amounts of quartz and calcite. The dark blue pigment is the result of joint use of azurite and atacamite. However, it is still uncertain whether these two pigments are used separately or mixed with each other. The color rendering component of the blue pigment used in the Song Dynasty is only azurite. Other phases include talc, calcite, quartz, and mica from the background layer. The XRD pattern of statues repainted in the Qing Dynasty shows a dispersive peak, and the color rendering component was amorphous, which cannot be determined for the time being.
atacamite particles. It can be determined that the dark blue pigment used in the Song Dynasty is the mixture of green pigment and blue pigment (Figure 7).

The blue pigment used in the Five Dynasties shows a very uniform bright blue under single polarized light, with different particle sizes, and is completely extinct under cross-light, the green pigment particles are in the form of massive rocks, which should be natural atacamite (Figure 8).

Microscopic analysis

Microscopic FTIR spectroscopy is used to study the dark blue pigment samples of the donor's streamers on the south wall of the tunnel. Under the microscope, it can be seen that there are blue and green pigment particles distributed. These two kinds of particles are analyzed separately, and the results are shown in Figure 5a. The blue pigment particles have absorption peaks at 3427cm\(^{-1}\), 1463cm\(^{-1}\), 1408cm\(^{-1}\), 1090cm\(^{-1}\), 948cm\(^{-1}\), 837cm\(^{-1}\) and 767cm\(^{-1}\), which are very close to the peak positions of azurite in the literature. The green pigment particles have absorption peaks at 3441cm\(^{-1}\), 3346cm\(^{-1}\), 983cm\(^{-1}\), 951cm\(^{-1}\), 927cm\(^{-1}\) and 837cm\(^{-1}\), which are close to the peak position of atacamite[13] and is consistent with the XRD results. Figure 5b shows the infrared spectrum of blue pigments used in statue repainted in the Qing Dynasty. There are absorption peaks at 3309cm\(^{-1}\), 1652cm\(^{-1}\), 1534cm\(^{-1}\), 1053cm\(^{-1}\), 795cm\(^{-1}\), and 593cm\(^{-1}\), which are very similar to smalt[14, 15].

Quantitative analysis of micro-area X-ray fluorescence spectrometer
The micro-area X-ray fluorescence spectrometer is used for quantitative analysis of smalt pigment used in the Qing Dynasty. The result shows that the percentage of oxides in smalt pigment is: SiO$_2$: 72.13%, K$_2$O: 15.90%, CaO: 5.03%, Fe$_2$O$_3$: 2.83%, CoO: 1.26%, NiO: 0.23%, and PbO: 2.62.

**Discussion**

Based on the results of XRF, XRD, M-FTIR and PLM analysis, the blue pigments used in the murals and statues of Cave 256 at different periods are different. Natural lazurite minerals were used as blue pigment in the Five Dynasties. Azurite was used as blue pigment in murals of the Song Dynasty. People also used the mixture of azurite and atacamite as dark blue. Smalt was used as the blue pigment in the Qing Dynasty.

In the 3rd century AD, the lazurite pigment was introduced into the Western Regions from Afghanistan through the Silk Road, and then to the Central Plains through the Hexi Corridor[16]. Mr. Su believes that lazurite was used as a pigment from the Jin Dynasties (265-420 AD). Since then, lazurite pigments have been found in major grottoes in the northern region[17–19]. A large number of lazurite were also used in the early Dunhuang murals. However, it gradually decreased after the 7th century, and the use of azurite gradually increased. Azurite has already occupied a dominant position in Dunhuang murals of the Tang Dynasty, which might be related to the discovery of azurite in the Qilian Mountains of Gansu in the Tang Dynasty[20]. Cave 256 of Mogao Grottoes was built in the Five Dynasties. Azurite was used as the blue pigment in most caves at that time. However, expensive lazurite was used in Cave 256. The repainting period of murals on the surface layer was about 60 years later than the excavation of Cave 256. Azurite used here instead of lazurite. There are two main reasons for this difference. Firstly, Cave 256 was the merit cave of Cao Yuanshen, the third military governor of Guiyi Army (a local armed regime that originated from the Tang Dynasty). During this period, the regime of Guiyi Army was stable and the economy developed rapidly. As the supreme ruler at the time, Cao Yuanshen had sufficient funding support to build caves and paint. The repainted cave belonged to Murong Yanchang, the military director of Yumen Town of the Guiyi Army, and his wife Yan in the Song Dynasty during the Cao Zongshou period. At this time, the Guiyi army regime began to go downhill. The Ganzhou Uighurs and Gaochang Uighurs continued to invade, and internal contradictions were numerous. As a result, they were short of money. They only afforded repainting an old cave because it cost too much to open a new one. Moreover, the cheaper azurite was used in a large area. Secondly, due to the unobstructed Silk Road, flourishing trade and the prosperity of the pigment market during the Cao Yuanshen period, lazurite was also relatively easy to obtain as an imported pigment. In the Cao Zongshou period (after the 11th century), frequent battles in the Hexi Corridor, traffic obstruction and social restlessness affected the source of pigments used in Dunhuang murals[21].

Smalt is a glassy pigment that develops color with cobalt element. It has been industrialized in Europe since the 15th century and it has been widely used in European oil paintings and church murals[22–27]. In the 19th century, it was gradually replaced by other inexpensive artificial blue pigments. The usage of small pigment in China mostly occurred in the Qing Dynasty. The earliest evidence at present is the land-and-water drawing of Luochuan, Shaanxi painted in the thirtieth year of Kangxi (1691AD) [28]. This pigment is concentrated in Beijing and Shanxi and scattered in other areas [29–31]. The forms of cultural relics are mainly architectural murals, colored paintings and statues. The small pigment used in statue of the Qing Dynasty in Cave 256 is reported for the first time in the murals and statues of Mogao Grottoes.

Oxide percentages of the small pigment used in colored paintings founded in Beijing, Shanxi, Inner Mongolia and Sichuan, blue and white porcelains of the Yuan Dynasty and the Ming Dynasty, Greek murals and European oil paintings are listed in Table 3. It can be seen that the oxide content of small pigment used in China was close to that of European murals and oil paintings: they all contained about 70% SiO$_2$, the content of K$_2$O generally exceeded 10%, and the content of the color rendering element Co was 1%-5%. In addition, they also contained Fe, Ca, Ni, As, Pb and other elements. The small pigment found in Cave 256 is also one of this type of material. However, as for the small pigment used in blue and white porcelains of the Yuan Dynasty and the Ming Dynasty, the content of SiO$_2$ was close, K$_2$O was relatively low, Al$_2$O$_3$ was about 15% and the content of the color rendering element Co was generally lower than 0.5%. In summary, the small pigment used in statue of Cave 256 should be imported from Europe.

In this study, the small pigment is firstly founded in statues of the Qing Dynasty in Mogao Grottoes in Dunhuang. According to previous literature, artificial ultramarine pigments were generally used for remodeling and repainting of statues of Mogao Grottoes during the Qing Dynasty. The small pigment discovered this time can be used as a reference for us to study the history of repainting and repairing of statues in Cave 256. The small pigment was a very important blue paint in the history of European art. It was regarded as the only artificial substitute for azurite and Lazurite until the invention of artificial ultramarine. There is evidence that the export of small pigment from Europe to China covered almost the entire 18th century and continued into the 19th century[34,35]. After the mid-19th century, artificial ultramarine entered China. With low price and strong hiding power, it quickly replaced small. Kangxi actively explored the Western Regions in his later years. Taking this as a chance, he began to manage the area west of Jiayuguan. During the 5th-6th year of Yongzheng, 2405 households, about 10,000 people, immigrated to Dunhuang. The arrival of immigrants laid the foundation for the development of Dunhuang in the Qing Dynasty and even in modern times[36]. According to Inscriptions for Donors of Mogao Grottoes in Dunhuang (Cave 454), the pedagogue Lei Jixiang completed his donation on February 15th of the lunar calendar in the first year of Yongzheng[37]. It can be concluded that the first year of Yongzheng (1723 AD) should be the earliest date for the reconstruction of the Mogao Grottoes in the Qing Dynasty. Based on the history of the introduction of small into China and the history of the reconstruction of Mogao Grottoes in the Qing Dynasty, it is believed that the statues of Cave 256 were rebuilt in the first half of the 19th century, that is, during the reign of Qianlong and Daoguang in the Qing Dynasty.
Table 3
Comparison of element content of smalt pigment in different regions[28][32, 33]

<table>
<thead>
<tr>
<th>Source</th>
<th>Oxide percentage (Wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂O Al₂O₃ SiO₂ K₂O CaO Fe₂O₃ MnO C₉O NiO CuO MgO BaO As₂O₃ PbO</td>
</tr>
<tr>
<td>Cave 256 of Mogao Grottoes</td>
<td>72.13 15.90 5.03 2.83 1.26 0.23</td>
</tr>
<tr>
<td>Cining Palace, Forbidden City, Beijing</td>
<td>0.18 1.27 72.90 10.35 0.53 0.62 2.35 5.24 6.54</td>
</tr>
<tr>
<td>Chengqing Palace, Xiannong Temple, Beijing</td>
<td>0.19 1.50 73.32 8.64 0.84 0.49 1.03 4.60</td>
</tr>
<tr>
<td>Jinxin Temple, Taigu, Shanxi</td>
<td>0.47 0.67 66.41 11.99 0.25 2.99 3.15 0.08 12.46 1.22</td>
</tr>
<tr>
<td>Sanqing Palace, Shanxi</td>
<td>0.16 0.53 73.00 11.41 2.79 3.40 0.12 0.02 0.09 8.36</td>
</tr>
<tr>
<td>Qianfo Cliff, Guanyuan, Sichuan</td>
<td>0.25 0.33 80.67 8.44 0.04 3.59 3.90 0.47 0.08 2.30</td>
</tr>
<tr>
<td>Dazhao Temple, Inner Mongolia</td>
<td>0.91 0.12 77.63 13.82 1.77 1.00 0.77 3.89</td>
</tr>
<tr>
<td>Cobalt of blue and white porcelain of the Yuan Dynasty</td>
<td>3.14 15.22 68.05 2.74 8.78 1.73 0.09 0.37 0.39</td>
</tr>
<tr>
<td>Cobalt of blue and white porcelain of the Yuan Dynasty</td>
<td>2.68 14.79 66.76 4.39 6.98 2.83 0.11 0.47 0.36</td>
</tr>
<tr>
<td>Cobalt of blue and white porcelain of the early Ming Dynasty</td>
<td>2.84 15.35 68.94 3.16 5.98 2.17 0.25 0.24</td>
</tr>
<tr>
<td>Greece murals</td>
<td>68.93 22.59 2.16 2.49 4.09</td>
</tr>
<tr>
<td>European oil painting</td>
<td>66-72 10-21 2-18</td>
</tr>
</tbody>
</table>

Conclusion

Pigment is an indispensable and the most important material in the process of making murals and statues. Pigments used in murals and statues in different historical periods of Mogao Grottoes are also different because of factors such as the origin of the pigments, processing techniques, prices, etc. In this paper, blue pigments used in murals and statues of the Five Dynasties, the Song Dynasty and the Qing Dynasty of Cave 256 are studies. The result shows that expensive lazurite pigment was used in the murals of the Five Dynasties and azurite was used on a large scale in the repainted murals of the Song Dynasties, which was closely related to the social status of the cave owner and the historical background at that time. The blue pigment in the repainted statues of the Qing Dynasty was smalt, which was first discovered in the Mogao Grottoes. It is judged that it is an imported pigment from Europe based on the element composition. Based on the history of the reconstruction of Mogao Grottoes in the Qing Dynasty, it is believed that the statues of Cave 256 were rebuilt in the first half of the 19th century, that is, during the reign of Jiaqing and Daoguang in the Qing Dynasty. In summary, the analysis and research of pigments in a specific historical period can reflect the social development at that time on the one hand, and on the other hand can provide scientific evidence for us to analyze the reconstruction and repainting history of the murals and statues of Mogao Grottoes.

Abbreviations

pXRF portable X-ray fluorescence
µ-FTIR microscopic fourier transformed infrared spectroscopy
XRD X-ray diffraction
PLM polarizing microscope
ED-XRF energy dispersive X-ray fluorescence.

Declarations

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Authors’ contributions

BMS and MLS provided support and guidance for this study. BWS and ZRY performed XRD, PLM and performed the analysis. QC, ZYY performed XRF and prepared the manuscript. ZW performed M-FTIR and prepared the manuscript. All authors read and approved the final manuscript.

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References


Figures

Figure 1
Location of Cave 256

Figure 2
pXRF testing and micro-sampling location of Cave 256
Figure 3

XRF patterns of blue pigments used in different dynasties in Cave 256
Figure 4

XRD patterns of blue pigments used in different dynasties in Cave 256
Figure 5
Infrared spectrum of blue pigment used in Cave 256

Figure 6
Polarized microscope photos of blue pigments used in different dynasties in Cave 256
(a and b: blue pigment used in the Five Dynasties; c and d: dark blue pigment used in the Song Dynasty; e and f: blue pigment used in the statue in the Qing Dynasty)

Figure 7
Cross-section photos of dark blue pigment used in the Song Dynasty in Cave 256