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Blue pigments in Cave 256, Mogao Grottoes: a systematic analysis of murals and statues in 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 in multilayer murals which reflects the social development at that time to a certain extent. 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. Smalt used in statues of the Qing Dynasty was first discovered in Mogao Grottoes. It can be inferred from the discovery of smalt that statues of the Qing Dynasty in Cave 256 were repainted in the first half of the nineteenth century.

Keywords: Mogao Grottoes, Murals, Statues, Cave 256, Lazurite, Azurite, Smalt

Introduction

Dunhuang Mogao Grottoes (莫高窟) is 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 fourth century to the fourteenth century. There was no new cave were excavated after the Ming Dynasty (明, 1368–1644 A.D.). A large number of murals and statues were repainted in the Qing Dynasty (清, 1636–1912 A.D.). There are about 45,000 m^2 of murals and over 2200 statues in Mogao Grottoes [1], which are important physical materials for studying the history of materials and craftsmanship of ancient Chinese murals and statues.

Mogao Grottoes is located 24 km southeast of present-day Dunhuang City. The caves are distributed in four layers. Cave 256 is located on the second floor of the central area of the southern area of Dunhuang Mogao Grottoes, about 200 m north of the nine storeys pagoda (九层楼) of Mogao Grottoes (Fig. 1). It has a relatively large area, with over 500 m^2 of murals and seven statues [2]. According to scholars, Cave 256 was built by Cao Yuanshen (曹元深), the third military governor of Guiyi (归义) Army (a local armed regime that originated from the Tang Dynasty (唐, 618–907 A.D.). It was founded in the Five Dynasties (五代, 907–960 A.D.) [3] and repaired during the Zhenzong (真宗) period of the Northern Song Dynasty (北宋, 960–1127 A.D.) by Murong Yanchang (慕容言长), the military director of Yu Men (玉门) Town of the Guiyi Army, and his wife Yan (阎氏). The bottom layer was covered and

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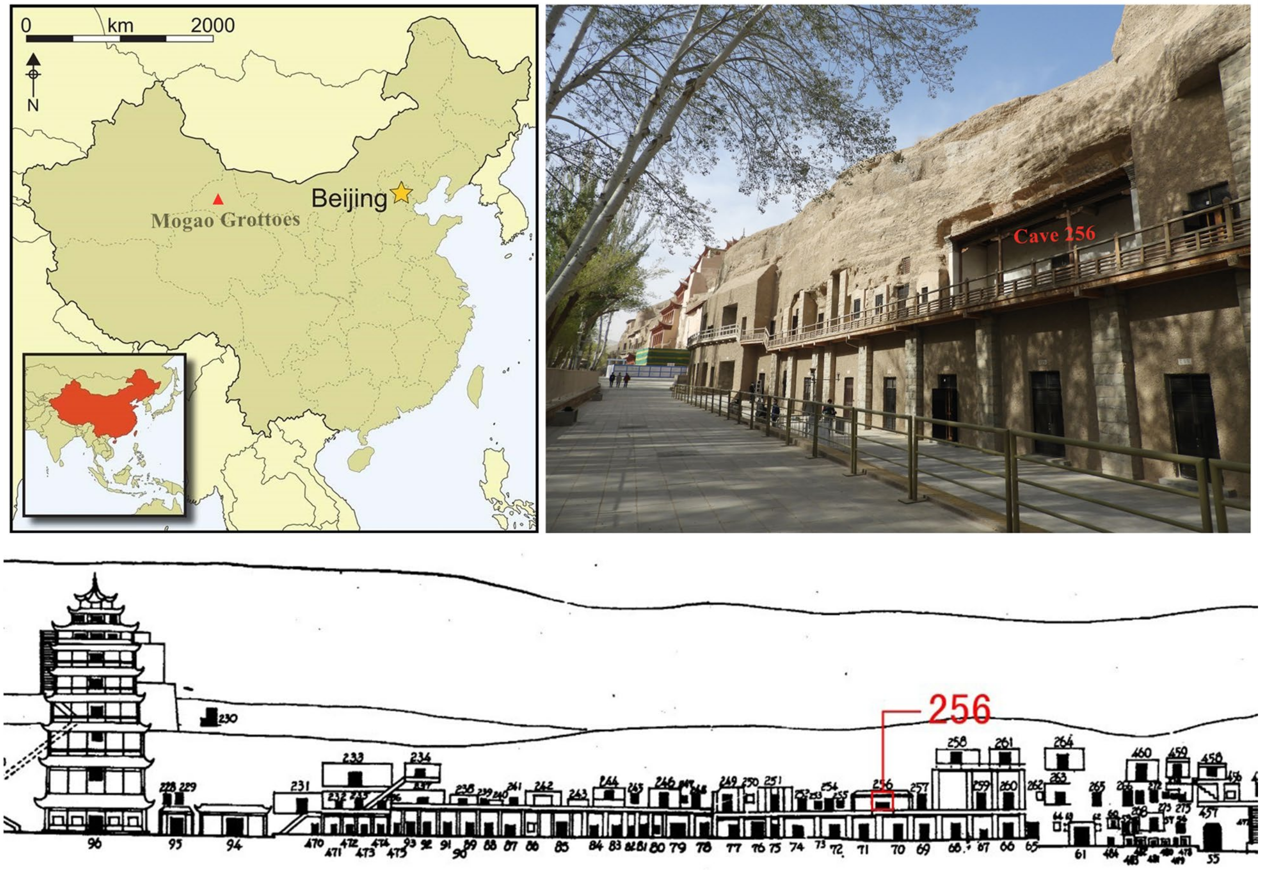


Fig. 1 Location of Cave 256

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 ($(NaCa)_8(AlSiO_4)_6(SO_4, Cl, S)_2$) [8, 9] [from the Sixteen Kingdoms (十六国, 304–439 A. D.) to the Northern Zhou Dynasty (北周, 557–581 A.D.), azurite ($Cu_3(CO_3)_2(OH)_2$] [10] [the Sui Dynasty (隋, 581–618 A.D.) to the Five Dynasties (五代)], indigo blue ($C_{16}H_{10}N_2O_2$) [11] found in individual caves and artificial ultramarine used in repainting in Qing Dynasty [12]. In terms of analytical techniques used to characterize pigments, since most of the above literatures are relatively early, XRD, XRF and SED-EDS are mainly used, and Raman spectroscopy is used for the characterization of indigo in Cave 465.

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(宋, 960–1279 A.D.) 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-800 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 50 kV/40 μA (maximum), the detection time is 1 min, and the soil mode is used.
2. X-ray diffraction analyzer

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

3. 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 4000–675 cm^{-1}, and the spectral resolution is 4 cm^{-1}, with 128 time scanning.
4. Polarizing microscope.
DM2700P polarizing microscope (Leica, Germany) is equipped with DMC 2900 camera (magnification 50×, 100×, 200×, 500× and 1000×). M256-03 sample is mounted as cross section, the minute pigments are embedded in epoxy resin and polished with dry abrasive papers down to 0.5 μm to obtain sufficiently polished surface, and then observe it under a microscope.
5. Micro-area X-ray fluorescence spectrometer
As for German Bruker ARTAX-400 mobile micro-area X-ray fluorescence spectrometer, input voltage is 30 kV, input current is 900 μA, test time is 300 s, 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 sample M256-06.

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 blue pigment areas in the bottom layer, dark blue pigment and blue pigment areas in the surface layer, and blue pigments used in statues repaired in the Qing Dynasty. Moreover, taking the pXRF detection results as a reference, only one sample was taken from the area with the same elemental composition, and four blue and one green pigment trace samples were obtained. Table 1 and Fig. 2 for details of non-destructive testing location and micro-destructive sampling information.

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 (Fig. 3a). The chemical composition of blue pigment cannot be determined through XRF results. 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 (Fig. 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 (Fig. 3c), which are possibly cobalt-containing compounds, the high signal of Pb in the spectrum comes from the lead-containing white pigment in the prime-coat layer.

XRD phase analysis

The XRD phase analysis results of the trace samples are shown in Table 2 and Fig. 4. The result shows that the blue pigments used in the Five Dynasties (M256-01) 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 ($Mg_3Si_4O_{10}(OH)_2$), calcite ($CaCO_3$), and quartz (SiO_2), all of which come from the white background layer of the mural. The XRD pattern of statues repainted in the Qing Dynasty (M256-07) shows a dispersive peak, and

Table 1 pXRF non-destructive testing location and micro-destructive sampling information

No.	Location and color	Dynasty	Sample property	Analytical methods
M256-01	The bottom layer of the damaged part of the north wall of the main room. Blue	The Five Dynasties	Powder	pXRF, XRD and PLM
M256-02	The bottom layer of the damaged part of the east wall of the main room. Blue	The Five Dynasties	–	pXRF
M256-03	The third Donor Portraits ears from the west on the south wall of the tunnel. Dark blue	Song Dynasty	Powder + block	pXRF and XRD μ-FTIR and PLM
M256-04	The third Donor Portraits costume from the west on the south wall of the Tunnel. Blue	Song Dynasty	Powder	pXRF and XRD
M256-05	Next to sample M256-04. Green	Song Dynasty	Powder	XRD
M256-06	Head halo of Thousand-Buddha on the east wall of the main room. Blue	Song Dynasty	–	pXRF
M256-07	Left knee of the Buddha statue in the main room. Blue	Qing Dynasty	Powder	pXRF, XRD, μ-FTIR, PLM and ED-XRF

– means that no sampling

Fig. 2 pXRF testing and micro-sampling location of Cave 256

the color rendering component was amorphous, which cannot be determined for the time being. The deep blue pigment used in the Song Dynasty (M256-03) 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 of 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 ($Cu_2Cl(OH)_3$). Other phases include small amounts of quartz and calcite. The color rendering component of the blue pigment used in the Song Dynasty (M256-04) is only azurite. Other phases include talc, calcite, quartz, and mica from the background layer. Sample M256-05 is the green pigment next to Sample M256-04, and the XRD results show strong diffraction peaks of atacamite.

Microscopic FTIR spectroscopy analysis

Microscopic FTIR spectroscopy is used to study the dark blue pigment samples (M256-03) 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. The blue pigment particles have absorption peaks at 3427 cm^{-1}, 1463 cm^{-1}, 1408 cm^{-1}, 1090 cm^{-1}, 948 cm^{-1}, 837 cm^{-1} and 767 cm^{-1}, which are very close to the peak positions of azurite in the literature (Fig. 5a). Among them, 3427 cm^{-1} should belong to the O–H stretching mode, the absorption at 1463, 1408 cm^{-1} is the asymmetric stretching of carbonate C–O(ν_3), the absorption peak at 1090 should belong

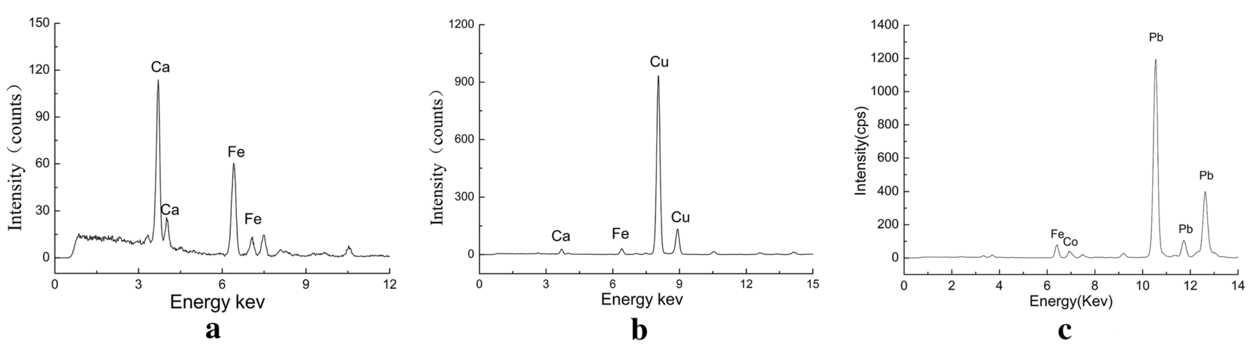


Fig. 3 XRF patterns of blue pigments used in different dynasties in Cave 256. **a** Murals of the Five Dynasties. **b** Murals of the Song Dynasty. **c** Statues of the Qing Dynasty

Table 2 XRD phase analysis results of trace samples in Cave 256

No.	M256-01			M256-03			M256-04			M256-05			Lazurite (17–0749)			Azurite (11–0682)			Atacamite (25–0269)		
	2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0
1	9.420	9.361	51	16.223	5.480	54	8.727	10.131	75	16.137	5.494	56	13.761	6.430	40	17.204	5.150	55	16.161	5.480	100
2	10.590	8.465	18	17.033	5.181	77	9.337	9.418	64	17.653	5.040	30	18.239	4.860	6	17.443	5.080	30	17.618	5.030	70
3	13.694	6.441	11	17.697	5.018	36	12.323	7.151	42	20.903	4.258	19	19.537	4.540	18	17.760	4.990	11	21.928	4.050	12
4	17.480	5.076	11	24.240	3.675	99	17.133	5.176	56	21.857	4.063	17	23.966	3.71	100	24.205	3.674	50	31.520	2.836	50
5	18.953	4.682	15	25.193	3.534	79	20.860	4.263	42	24.283	3.657	20	24.992	3.56	6	25.310	3.516	100	32.184	2.779	50
6	19.393	4.571	12	26.667	3.343	33	21.077	4.212	40	26.580	3.345	100	25.955	3.430	6	28.709	3.107	11	32.424	2.759	55
7	23.999	3.704	11	28.660	3.112	34	24.067	3.693	51	27.620	3.227	18	27.769	3.21	16	34.604	2.590	11	32.630	2.742	25
8	26.623	3.346	15	30.957	2.886	36	25.150	3.534	41	29.483	3.027	19	29.454	3.030	6	35.307	2.540	25	33.014	2.711	20
9	28.530	3.123	100	32.375	2.771	47	26.493	3.368	59	31.563	2.838	41	31.115	2.872	45	35.553	2.523	20	33.915	2.641	14
10	29.440	3.030	53	34.597	2.595	30	28.443	3.127	69	32.170	2.781	45	32.472	2.755	4	35.743	2.510	35	35.524	2.525	14
11	30.957	2.886	16	35.244	2.543	34	29.440	3.037	71	35.680	2.516	20	34.168	2.622	80	35.846	2.503	30	35.670	2.515	40
12	36.070	2.490	14	35.680	2.512	38	30.913	2.891	31	39.667	2.267	37	37.009	2.427	16	38.506	2.336	17	39.527	2.278	70
13	39.450	2.281	12	38.453	2.341	100	32.343	2.766	37	42.440	2.127	19	39.636	2.272	25	39.151	2.299	13	39.763	2.265	45
14	43.307	2.093	18	39.147	2.301	55	39.407	2.287	39	44.433	2.037	26	42.173	2.141	35	39.365	2.287	35	41.029	2.198	17
15	44.520	2.033	12	39.840	2.265	62	39.753	2.266	44	50.067	1.825	26	51.222	1.782	30	39.763	2.265	25	42.401	2.130	25
16	47.597	1.190	15	40.533	2.227	42	43.133	2.095	35	50.977	1.791	21	57.322	1.606	20	40.528	2.224	70	44.300	2.043	17
17	48.723	1.872	20	46.557	1.948	43	44.867	20.020	33	53.403	1.716	20	59.219	1.559	10	41.623	2.168	15	49.960	1.824	35
18	57.433	1.604	9	49.980	1.824	40	47.467	1.917	43	57.220	1.609	19	61.164	1.514	10	46.584	1.948	20	50.166	1.817	25
19	60.727	1.525	8	57.780	1.595	30	48.507	1.675	44	67.747	1.382	77	62.963	1.475	14	49.960	1.824	17	53.310	1.717	20
20	64.887	1.437	11	64.757	1.438	30	49.937	1.827	100	67.963	1.378	47	68.423	1.370	18	57.743	1.595	15	57.322	1.606	55

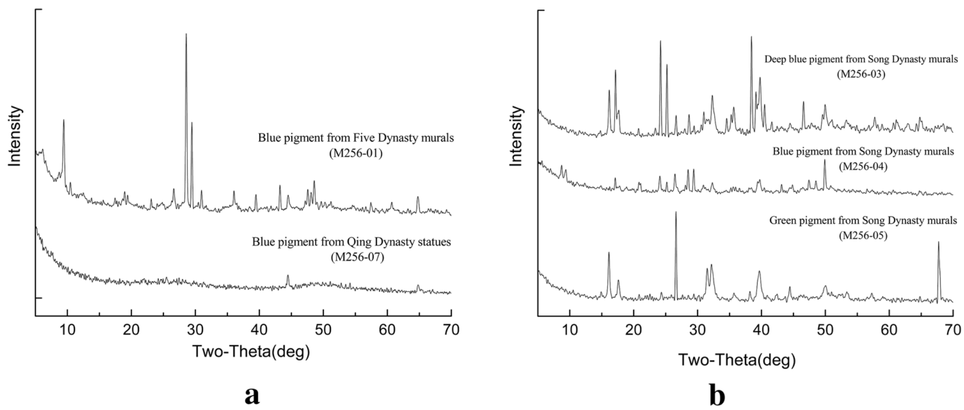


Fig. 4 XRD patterns of pigments used in different dynasties in Cave 256. **a** Five Dynasties and Qing Dynasty. **b** Song Dynasty

to the C–O symmetric stretching mode(ν_1), 948 cm^{-1} is the out of plane bending vibration of O–H, the signal at 837 cm^{-1} is the out of plane bending of CO_3^{2-}(ν_2), and the peak at 767 cm^{-1} belongs to in-plane bending (ν_4) [13]. The green pigment particles showed the characteristic O–H stretching modes at 3441, 3346 cm^{-1} and a series of weak bands due to the O–H bending modes between 800 and 1000 cm^{-1}, which are close to the peak position of atacamite (Fig. 5b) [14, 15]. Figure 5c shows the infrared spectrum of blue pigments used in statue repainted in the Qing Dynasty (sample M256-07). Through the absorption bands observed at about 1053 cm^{-1} can be assigned to the Si–O antisymmetric stretching band. Two bands located at 3309 cm^{-1} and 1652 cm^{-1} can be assigned to the adsorbed water during the exposure of dried powder to air. The bands present at 795 cm^{-1} may be attributed to the vibrations of aluminosilicate compounds in the glass pigment. A weaker Co–O band is found at 578 cm^{-1} as shown. The presence of the blue pigment smalt was identified with μ-FTIR spectroscopy [16, 17].

Microscopic analysis

The blue pigment used in the Five Dynasties (M256-01) shows a very uniform bright blue under single polarized light, with different particle sizes, and is completely extinct under orthogonal polarized light, which is consistent with the XRD analysis result, and so it is lazurite mineral (Fig. 6a and b). There are blue and green particles in the dark blue pigment used in the Song Dynasty (M256-03). Under single polarized light, the blue pigment particles are of different sizes. Large particles are dark blue and small particles are light blue. Blue particles mostly extinct under orthogonal polarized light and should be azurite. Under single polarized light, the green pigment particles are in the form of massive rocks, which should be natural atacamite (Fig. 6c and d). Blue pigment used in the Qing Dynasty (M256-07) looks like sharp-edged glass shards under single-polarized light, varying from light blue to dark blue. They are completely extinct under cross-polarized light, with a refractive index of 1.55, which are identified as smalt (Fig. 6e and f).

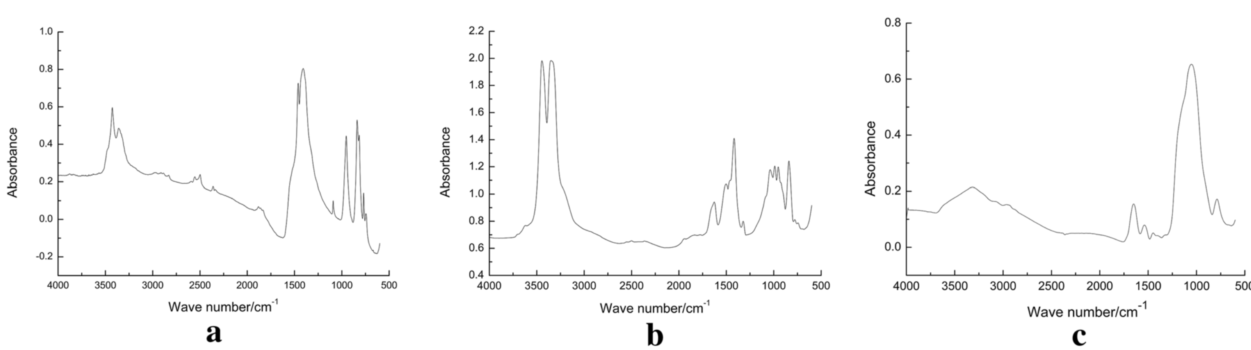


Fig. 5 Infrared spectrum of blue pigment used in Cave 256. **a** Infrared spectrum of blue pigment particles. **b** Infrared spectrum of green pigment particles. **c** Infrared spectrum of blue pigment used in the Qing Dynasty

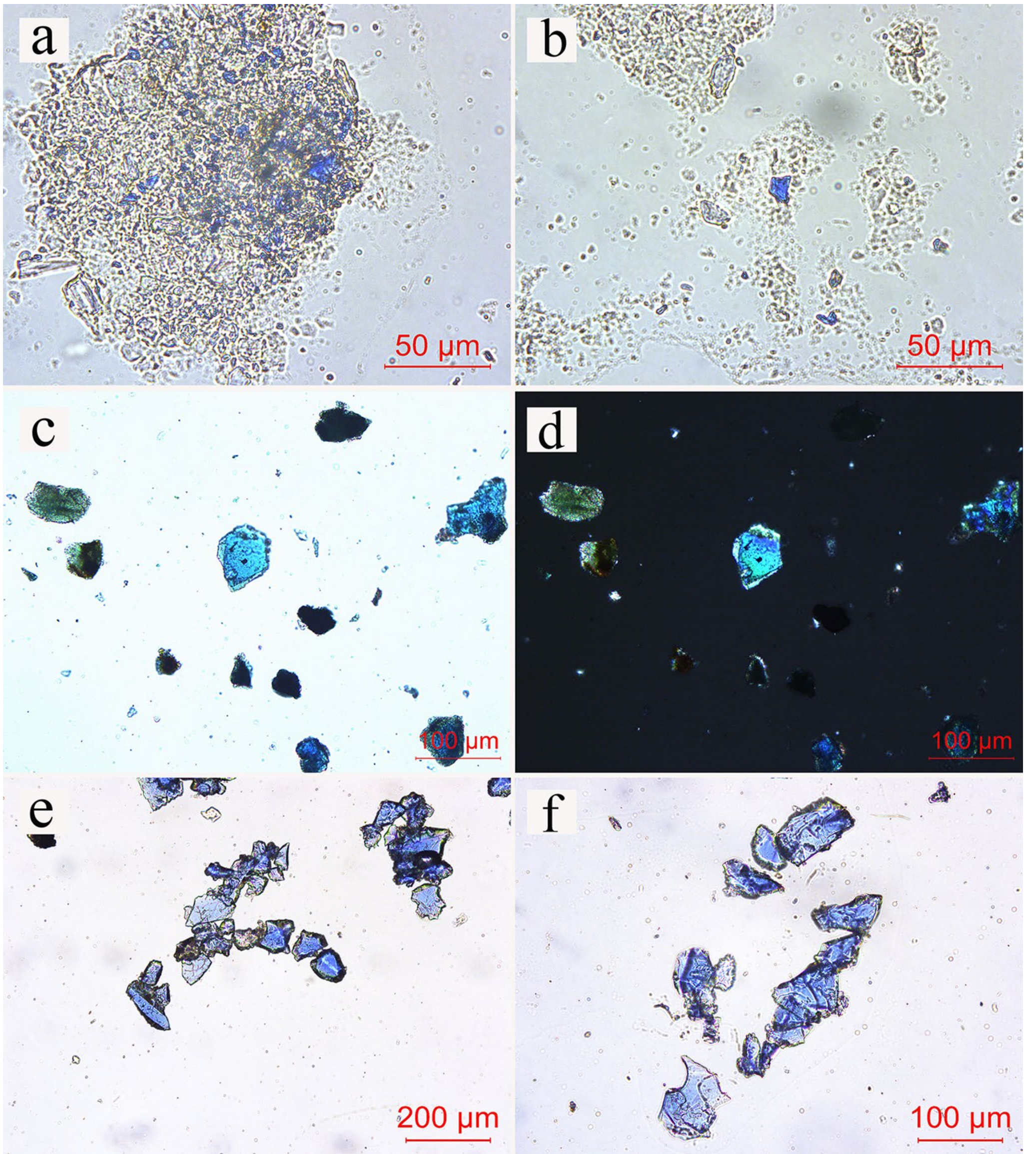
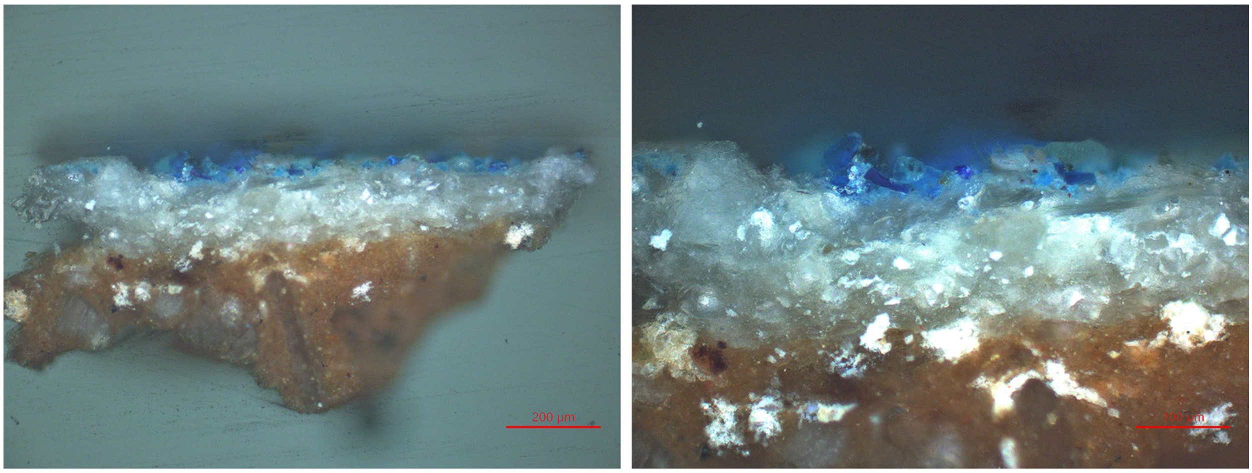


Fig. 6 Polarized microscope photos of blue pigments used in different dynasties in Cave 256. **a**, **b** blue pigment used in the Five Dynasties; **c**, **d** dark blue pigment used in the Song Dynasty; **e**, **f** blue pigment used in the statue in the Qing Dynasty

In order to make out whether azurite and atacamite in the dark blue pigment are used separately or mixed with each other, the M256-03 dark blue block sample is embedded with resin. The result shows that green atacamite and blue azurite particles mixed with each other (Fig. 7). It can be speculated that the dark blue pigment used in the Song Dynasty is the mixture of green pigment and blue pigment. There are three reasons. First, the dark blue pigment has good uniformity and their positions are regular. It is mainly used to express the hair and clothing edges of the donor. Second, there are large areas of blue pigment and green pigment on this portrait of the donor. According to the XRD results, the blue pigment is pure azurite, and the green pigment is pure atacamite. Except for the dark blue pigments, no atacamite was found in other blue pigments areas. Finally, according to the literature, high pH value, humid environment and chloride invasion are the main reasons why azurite discolor into atacamite [18]. The high pH value and humid environment are difficult to achieve in Mogao cave 256. The current research has not found any evidence that azurite in the murals of the Mogao Grottoes has discolored into atacamite. In conclusion, it is more convincing that the dark blue pigment is the result of the mixed use of azurite



a b

Fig. 7 Cross-section photos of dark blue pigment used in the Song Dynasty in Cave 256. **a** 100×. **b** 200×

and atacamite than the result of the discoloration of the azurite.

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_2O: 15.90%, CaO: 5.03%, Fe_2O_3: 2.83%, CoO: 1.26%, NiO: 0.23%, and PbO: 2.62%.

Discussion

Actually, the lazurite pigment was introduced into the Western Regions from Afghanistan through the Silk Road in the third century A.D., and then to the Central Plains through the Hexi (河西) Corridor [19]. Mr. Su believes that lazurite was used as a pigment from the Jin (晋, 265–420 A.D.) Dynasties. Since then, lazurite pigments have been found in major grottoes in the northern region [20–22]. Lazurite were also used in the early Dunhuang murals. However, it gradually decreased after the seventh 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 (祁连) Mountains of Gansu in the Tang Dynasty [23]. 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 was 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 (曹宗寿) period. At this time, the Guiyi army regime began to go downhill. The Ganzhou (甘州) Uighurs and Gaochang (高昌) 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 eleventh century), frequent battles in the Hexi Corridor, traffic obstruction and social restlessness affected the source of pigments used in Dunhuang murals [24].

Smalt is a glassy pigment that develops color with cobalt element. It has been industrialized in Europe since the fifteenth century and it has been widely used in European oil paintings and church murals [25–30]. In the nineteenth century, it was gradually replaced by other inexpensive artificial blue pigments. The usage of smalt pigment in China mostly occurred in the Qing Dynasty. The earliest evidence at present is the land-and-water

Table 3 Comparison of element content of smalt pigment in different regions [31, 35, 36]

Source	Oxide percentage (Wt%)													
	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	MnO	C_oO	NiO	CuO	MgO	BaO	As_2O_3	PbO
Cave 256 of Mogao Grottoes			72.13	15.90	5.03	2.83		1.26	0.23					2.62
Cining Palace, Forbidden City, Beijing	0.18	1.27	72.90	10.35	0.53	0.62		2.35				5.24	6.54	
Chengqing Palace, Xiannong Temple, Beijing	0.19	1.50	73.32	8.64		0.84		0.49	1.03				4.60	
Jingxin Temple, Taigu, Shanxi	0.47	0.67	66.41	11.99	0.25	2.99		3.15	0.08				12.46	1.22
Sanqing Palace, Shanxi	0.16	0.53	73.00	11.41		2.79		3.40	0.12	0.02		0.09	8.36	
Qianfo Cliff, Guangyuan, Sichuan	0.25	0.33	80.67	8.44	0.04	3.59		3.90		0.47	0.08		2.30	
Dazhao Temple, Inner Mongolia	0.91	0.12	77.63	13.82		1.77		1.00	0.77				3.89	
Cobalt of blue and white porcelain of the Yuan Dynasty	3.14	15.22	68.05	2.74	8.78	1.73	0.09	0.37			0.39			
Cobalt of blue and white porcelain of the Yuan Dynasty	2.68	14.79	66.76	4.39	6.98	2.83	0.11	0.47			0.36			
Cobalt of blue and white porcelain of the early Ming Dynasty	2.84	15.35	68.94	3.16	5.98	2.17	0.25	0.24						
Greece murals			68.93	22.59	2.16	2.49		4.09						
European oil painting			66–72	10–21				2–18						

drawing of Luochuan (洛川), Shaanxi painted in the thirtieth year of Kangxi (康熙) (1691 A.D.) [31]. This pigment is concentrated in Beijing and Shanxi and scattered in other areas [32–34]. The forms of cultural relics are mainly architectural murals, colored paintings and statues. The smalt 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 smalt pigment used in colored paintings found in Beijing, Shanxi, Inner Mongolia and Sichuan, blue and white porcelains of the Yuan (元,1271–1368. A.D.) 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 smalt 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_2O 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 smalt pigment found in Cave 256 is also one of this type of material. However, as for the smalt pigment used in blue and white porcelains of the Yuan Dynasty and the Ming Dynasty, the content of SiO_2 was close, K_2O was relatively low, Al_2O_3 was about 15% and the content of the color rendering element Co was generally lower than 0.5%. In summary, the smalt pigment used in statue of Cave 256 should be imported from Europe.

In this study, the smalt pigment is firstly found 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 smalt 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 smalt 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 other inexpensive artificial blue pigments. There is evidence that the export of smalt pigment from Europe to China covered almost the entire eighteenth century and continued into the nineteenth century [37, 38]. After the mid-nineteenth century, artificial ultramarine entered China. With low price and strong hiding power, it quickly replaced smalt. Kangxi actively explored the Western Regions in his later years. Taking this as a chance, he began to manage the area west of Jiayuguan (嘉峪关). During the 5–6th year of Yongzheng (雍正), 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 [39]. According to *Inscriptions for Donors of Mogao Grottoes in Dunhuang* (Cave 454), the pedagogue Lei Jixiang (雷吉祥) completed his donation on February 15th of the lunar calendar in the first year of Yongzheng [40]. 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 smalt 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 nineteenth century, that is, during the reign of Jiaqing (嘉庆) and Daoguang (道光) in the Qing Dynasty.

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 studied. 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 nineteenth 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.

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

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Availability of data and materials
All data generated or analyzed during this study are included in this published article.

Declarations

Competing interests
The authors declare that they have no competing interests.

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References

1. Chen GQ. Study on salting damage analysis and treatment of wall paintings at Mogao Grottoes, Dunhuang. Lanzhou: Lanzhou University; 2016. p. 1–4 (**in Chinese**).
2. Academy D. Summary of the contents of the Dunhuang Grottoes. Beijing: Cultural Relics Press; 1996. (**in Chinese**).
3. He SZ. More about the cave built by Cao Yuanshen. Dunhuang Res. 1994;3:33–6 (**in Chinese**).
4. Chen M. The travel map of Murong family. Dunhuang Res. 2006;4:25–31 (**in Chinese**).
5. Cheng JJ. Research on the control of the Murong family in Yumen area during the Late Tang to the early Song Dynasty: centered on the Dunhuang documents and Murals. J Dunhuang Stud. 2020;2:108–16 (**in Chinese**).
6. Zheng BL. Ethnic population in the Western Corridor during the Late Tang and the Five-Dynasty period. J Lanzhou Univ Soc Sci. 2006;02:9–21 (**in Chinese**).
7. Chen XM. Preferences to color of Cerulean blue in ancient Chinese culture. J Nantong Univ Soc Sci Ed. 2008;3:78–81 (**in Chinese**).
8. Wang JY. Study on Lazurite pigments in Grottoes of Dunhuang, Maiji mountain and Bingling temple. Archeology. 1996;10:77–92 (**in Chinese**).
9. Wang JY. Pigment of for polychrome arts on ancient China summary. Wenbo. 2009;6:396–402 (**in Chinese**).
10. Li ZX. Pigment analysis on Tang dynasty Murals at The Mogao Grottes. Dunhuang Res. 2002;4:11–8 (**in Chinese**).
11. Kogou S, Shahtahmassebi G, Lucian A, Liang HD, Shui BW, Zhang WY, Su BM, Van Schaik S. From remote sensing and machine learning to the history of the Silk road: large scale material identification on wall paintings. Sci Rep. 2020;10:1–4.
12. Wang JY. Study on synthetic Ultramarine pigment in Dunhuang Grottoes. Dunhuang Res. 2000;1:76–81 (**in Chinese**).
13. Miliani CF, Rosi F, Daveri A, Brunetti BG. Reflection infrared spectroscopy for the non-invasive in situ study of artists' pigments. Appl Phys. 2012;106:295–307.
14. Emilio C, Giorgia S, Silvia P, Jia Y, Rocco M. Characterization of outdoor bronze monument patinas: the potentialities of near-infrared spectroscopic analysis. Environ Sci Pollut Res. 2018;25:24379–93.
15. Hedegaard SB, Delbey T, Brns C, Rasmussen KL. Painting the Palace of Apries II: ancient pigments of the reliefs from the Palace of Apries, Lower Egypt. Herit Sci. 2019;1:7–54.
16. Jonynaite D, Senvaitiene J, Beganskiene A, Kareiva A. Spectroscopic analysis of blue cobalt smalt pigment. Vib Spectrosc. 2010;52:158–62.
17. Sfarra S, Cheilakou E, Theodorakeas P, Paoletti D, Koui M. S.S. Annunziata Church (L'Aquila, Italy) unveiled by non- and micro-destructive testing techniques. Appl Phys. 2017;123:215.
18. Ma Q, Pan L. Translators. In: Scott D, editor. Copper and bronze in art: corrosion, colorants, conservation. Beijing: Science Press; 2009. p. 86.
19. Li HL. The study on color technology and application of Mural paintings in Northern China in 4–6th century. Shanghai: Shanghai University; 2019. p. 152 (**in Chinese**).
20. Su BM, Li ZX, Ma ZF, Li S, Ma QL. Study on the Pigments used in Murals of Kizil Grottoes. Dunhuang Res. 2000;1:65–75 (**in Chinese**).
21. Xia Y. Exploring Chinese historical pigments by optical microscopy. Wenbo. 2009;6:342–5 (**in Chinese**).
22. Chen GL. Analysis of pigments and clay of the polychrome statue and wall paintings in the No. 9 Tiantishan Grottoes. Sci Conserv Archeol. 2010;4:91–6 (**in Chinese**).
23. Xu Y. Study of pigments used in Dunhuang in the Late Tang Dynasty and the Five Dynasties. J Dunhuang Stud. 2006;4:80–4 (**in Chinese**).
24. Academy D. Chinese Grottoes: Anxi Yulin Grottoes. Beijing: Cultural Relics Press; 2012. (**in Chinese**).
25. Corregidor V, Oliveira AR, Rodrigues PA, Alves LC. Paintings on copper by the Flemish artist Frans Francken II: PIXE characterization by external microbeam. Nucl Instrum Methods Phys Res Sect B. 2015;1:291–5.
26. Kalinina KB, Bonaduce I, Colombini MP, Artemieva IS. An analytical investigation of the painting technique of Italian Renaissance master Lorenzo Lotto. J Cult Herit. 2012;3:259–74.
27. Rebollo E, Nodari L, Russo U, Bertoncello R, Scardellato C, Romano F, Ratti F, Poletto L. Non-invasive multitechnique methodology applied to the study of two 14th century canvases by Lorenzo Veneziano. J Cult Herit. 2013;3:153–60.
28. Civici N. Non-destruction identification of inorganic pigments used in 16–17th century Albanian icons by total reflection X-ray fluorescence analysis. J Cult Herit. 2006;4:339–43.
29. Daniilia S, Minopoulou E, Andrikopoulos KS, Tsakalof A, Bairachtari K. From Byzantine to post-Byzantine art: the painting technique of St Stephen's wall paintings at Meteora. Greece J Archaeol Sci. 2008;6:1695–707.
30. Bianchin S, Favaro M, Vigato PA, Botticelli G, Germani G, Botticelli S. The scientific approach to the restoration and monitoring of mural paintings at S. Girolamo Chapel-SS. Annunziata Church in Florences. J Cult Herit. 2009;3:379–87.
31. Hui N. Analysis and research on Smalt pigment in the Ming dynasty and Qing dynasty of China. Xi'an: Northwest University; 2015. p. 18–21.
32. Lei Y, Qu L, Cheng XL, Yang H, Wang SW. The discovery of Smalt in Jianfu palace in Forbidden city. Wenbo. 2009;6:276–9 (**in Chinese**).
33. Xu N. Analysis of the production technology of the painted statues at Qinglian temple in Jincheng Shanxi and a preliminary study on its virtual restoration. Xi'an: Northwest University; 2014. (**in Chinese**).
34. Liu MY, Lei YX. A preliminary exploration of Colored drawings on Rafters in Wanfo Hall of Zhenguo temple, Pingyao county. Shanxi Prov Archit Hist. 2012;3:36–54 (**in Chinese**).
35. Du F. Two different imported Smalt pigments: ("Samarra" and "Sumatra"). Science in China (Series E). Tech Sci. 2007;5:636–43 ((**in Chinese**)).
36. Riedrerer J. Die Smalte Sammelmappe - DEUTSCHE- ZEITSCHRIFT. Wissenschaftliche Verlagsgesellschaft. 1968;9:386–95.

37. Giannini R, Freestone IC, Shortland AJ. European cobalt sources identified in the production of Chinese famille rose porcelain. J Archaeol Sci. 2017;80:27–36.
38. Liu MY. 2019. Research on pigments for decorative polychrome painting in official handicraft regulations and precedents of Qing dynasty. Beijing, Tsinghua University. 318 (in Chinese).
39. Chen GW. Study on Dunhuang population issues in Qing dynasty. J Dunhuang Stud. 2018;1:55–67 (**in Chinese**).
40. Academy D. Inscriptions for Donors of Mogao Grottoes in Dunhuang. Beijing: Cultural Relics Press; 1986. (**in Chinese**).