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Article

Analysis and Protection of One Thousand Hand Buddha in Dazu Stone Sculptures

WANG, Li-Qin[a,b](王丽琴) DANG, Gao-Chao*[,c](党高潮) WANG, Xiao-Qi[a](王晓琪)
XI, Zhou-Kuan[d](席周宽) LIANG, Guo-Zheng[b](梁国正)

[a] *College of Culture and Museology, Northwest University, Xi'an, Shaanxi 710069, China*
[b] *College of Chemical Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, China*
[c] *Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, China*
[d] *Dazu Rock Carvings Art Museum, Dazu, Chongqing 632360, China*

The components of the rock, the pigments, the gold foils and the adhesive of One Thousand Hand Buddha in Dazu stone sculptures, Chongqing, China, have been analyzed by X-ray diffraction (XRD), X-ray fluorescence (XRF), infrared spectroscopy (IR), energy dispersive X-ray analysis (EDX) and fiber optics reflectance spectroscopy (FORS). Furthermore, the weathering and degeneration of One Thousand Hand Buddha have been discussed and the protective methods have been provided. In this work some useful information to study on conservation of stone relics is given.

Keywords stone, relic, analysis, component, protection

Introduction

Dazu stone sculptures, mainly being composed of the cliffside sculptures, lie in Dazu county, 160 kilometer east from Chongqing, China. In December 1999, Dazu stone sculptures were enlisted in the list of the Cultural Heritage in the World by UNESO. One Thousand Hand Buddha (see Figure 1) is a typical representative in so many stone sculptures in Dazu. It was sculptured in the South Song period (1127-1179A.D.). The niche is more than seven meter high, over twelve meter wide and covers nearly 90 square meters. One Thousand Hand Buddha was sculptured according to Thousand Hand Sutra. The 3-meter-high Buddha sits on the lotus flowers, with 48 crowns on the head. Because 1007 hands, with one eye on one hand, were sculptured on the left, right and upper directions on the Buddha's back, the statue was called Buddha with numerous hands and eyes. The whole statue, the biggest Buddha with one thousand hands, is like a tail-extending peacock. Its hands and eyes respectively symbolize the boundless dharma power and intelligence.

The making of the Buddha is very refined. Its surface is covered with the gold foils, which makes the statue brilliant and elegant. And the pigments are painted on parts of the statue, which also adds its aesthetic value. However, because of the high humidity, low evaporation there, and the gold foils on the rock's surface, a great deal of congealed water in the rock with the gold foils is hard to vapor, which makes the rock become loose, the gold foils peel off, even some fingers of the Buddha break apart. Therefore, it would be valuable to do the scientific analysis on the materials of the Buddha and make out the related protection. So far as we know that there is little research and conservation on this precious Buddha. In this paper, many analytical methods, such as X-ray diffraction (XRD), X-ray fluorescence (XRF), infrared spectroscopy (IR), energy dispersive X-ray analysis (EDX) and fiber optics reflec-

Figure 1 One Thousand Hand Buddha in Dazu Chongqing, China.

* E-mail: dll523@sohu.com; Tel.: +86-29-88373032; Fax: +86-29-88302976
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tance spectroscopy (FORS), have been used to measure the components of the rock, pigments, gold foils and the adhesive. The scientific foundation has been provided for the selection of protective substances, techniques and methods.

Experimental

Apparatus

D/max-3c X-ray Diffractometer (Rigaka, Japan), RIX-2100 X-ray Fluorescence Spectrometer (Rigaka, Japan), EDAX-Dx-4 Energy Dispersive Spectrometer (Philips, Japan), Equinox 55 FT-IR Spectrometer (Bruker Instruments LTD. Germany), Fiber Optics Reflectance Spectrophotometer (Self-Developed).[1]

Relic samples

Rock material It comes from a finger cracked from the Buddha. The rock is gray, badly weathered and the rock powders will drop when touched.

Gold foils They are also from the finger. Several layers of the gold foils have been found on the finger's surface. They are very thin. Each layer of gold foil has two sides. The right side has gold luster, while the back side has lost the luster and there are some earthy substances here which stick to the gold foil tightly. Some parts of the gold foils have bent upwards, even peeled off.

Color pigments The green and bright red colors have been measured. They were copied in Qing Dynasty.

Selection of analytical methods

Rock material After being ground by a grinding bowl, parts of the finger (without gold foil) are analyzed by XRD in order to determine the components of the rock.

Gold foils After being cleaned by alcohol, the surfaces of the foil's right and back are respectively analyzed EDX. It is estimated that there is an adhesive on the back side, so the earthy substances are scraped off and determined by IR spectra.

Color pigments The red and green pigments are monitored by XRF and FORS.

Results and discussion

Rock material

Figure 2 is the XRD analytical results of the rock. It is known that the contents (*w*) of quartz, albite, mica, calcite are respectively 63%, 18%, 10%, and 7%, so the components of the rock in Dazu Grotto are mainly quartz, feldspar sandstone, and earthy and calcium as the adhesive. The gypsum (with main chemical component calcium sulfate) has been not found, which is different from the reference[2] that there was much gypsum in the weathering products in Baodingshan Grotto, Dazu. There is no gypsum in the Buddha for the following reasons:

(1) Because the Buddha was sculptured in the niche, it was less influenced than that outside by acid rains and fogs. According to reports, Chongqing is one of the worst polluted areas by acid rains in China. The statistical result is that the acid rains take 70.5% the total rains, that pH value of rains is averagely 4.28, even low to 2.85. The acid rains here are sulfuric acid rains, mainly composed of sulfate ions. Therefore, the content of gypsum in the weathering products of the stone sculptures outside is higher, that of the Buddha in the niche is much lower, because it is a little influenced by sulfate ion in acid rains.

(2) On the surface of the Buddha there are gold foils, which directly prevent the rock from being contaminated.

However, despite there is no gypsum in the weathering products, the Buddha is still badly weathered, even the rock powders will drop off by a touch. Based on the analysis, it has been supposed that because of the capillarity and the seepage, a lot of water is absorbed in the rock pores and hard to vapor for the dense foils on its surface, and the water can dissolve the earthy adhesive, which causes the rock to lose the adhesion and become loose.

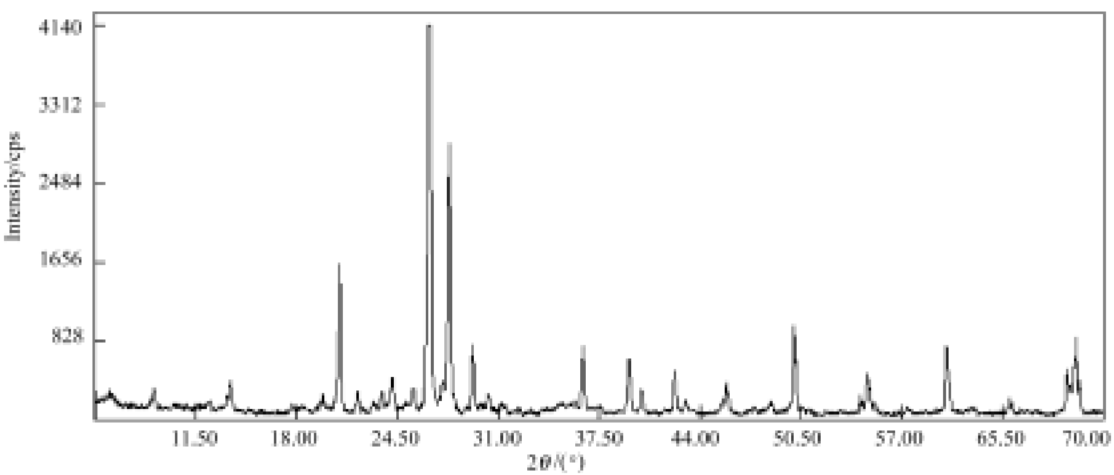

Figure 2 XRD analytical result of the rock.

Gold foils

Table 1 is the EDX analytical results of the right side of the gold foils. From the table it is known that the content of gold (*w*) is up to 68.50%. Besides gold, the content of carbon (*w*) is 27.13%. It is estimated that the high content of carbon is caused by the gold foil covering procedure. The earliest gold foil covering technology appeared in the Warring States period.[3] It was mainly used on the decoration of chariots and horses, crafts and weapons. Then it was developed in the Western Han Dynasty and used on clothes, such as the clothes unearthed from Ma Wangdui tomb in the Han Dynasty in Changsha city. Later this technology was used on the sculptures and buildings. For instance, in the proverbial Dunhuang Grotto and Dazu stone sculpture area, it was used generally. From the gold foil covering technology, we knew that the adhesive had been painted on the surface of the object and when the adhesive was almost dry, and that the gold foils were covered piece by piece. Finally, a cotton ball was used to make the foils stick to the object's surface tightly.

Table 2 is the EDX results of the back side of the foil. The total content of carbon and oxygen (*w*) is 86%, indicating that the content of some organic substance is very high. The IR results of the powders from the back side of the foil is shown in Figure 3. From Figure 3 it has been showed that there is a strong absorption in 3410.85 cm^{-1}, indicating that the existence of the hydroxyl group, and that there are the methene absorption in 2927.74 and 2855.90 cm^{-1}, whereas the absorptions in 1709.55 and 1646.67 cm^{-1} indicate the existence of carbonyl group and the functional group of double band. Figure 3 is very similar to the infrared spectrum[4] of the lacquer of the excavated lacquer coffin in the Han tomb in Xuzhou city (Figure 4). And the adhesive on the lacquer of the Han tomb has been identified the raw lacquer. Therefore, the adhesive on the back side of the foil is also like the raw lacquer.

Table 1 EDX analytical results of the right side of the gold foils

Components	Au	C	Hg	Ca	Cu
w/%	68.5	27.13	3.94	0.29	0.13

Table 2 EDX analytical results of the back side of the gold foils

Components	C	O	Hg	S	Ca	Si	Al
w/%	64.14	21.95	3.44	2.99	2.42	2.40	1.28

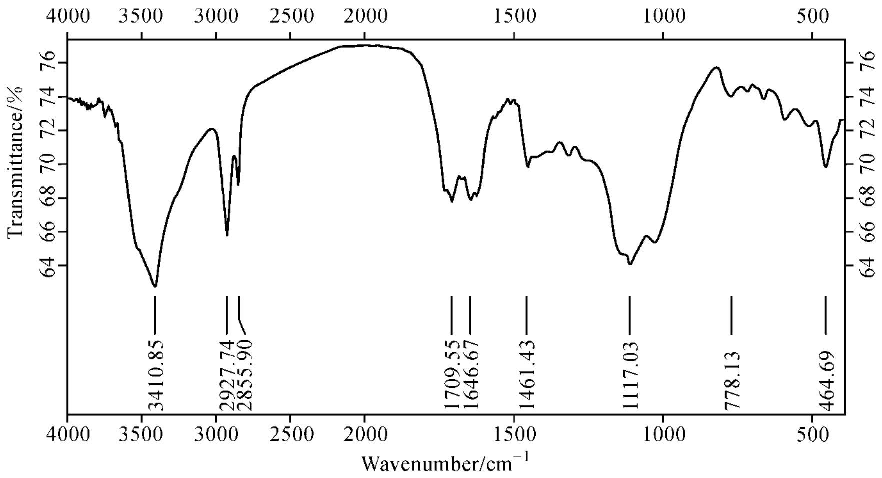

Figure 3 IR spectrum of the powders from the back side of the foil.

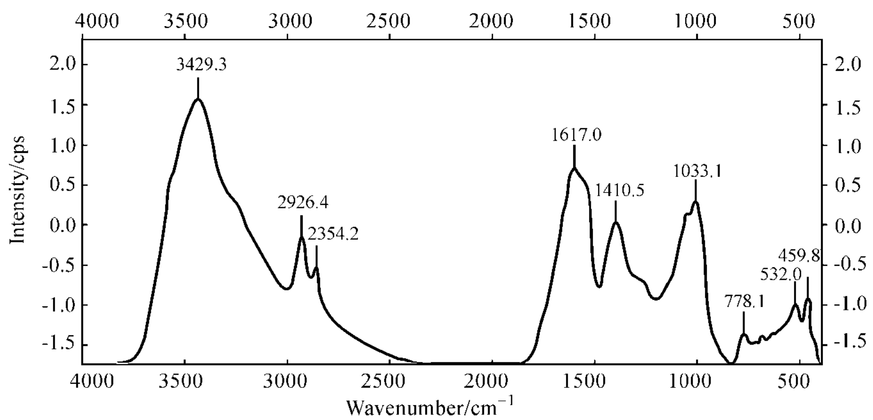

Figure 4 IR spectrum of the lacquer of the excavated lacquer coffin in the Han tomb in Xuzhou city.

Color pigments

The green and red pigments on the Buddha are measured by FORS and XRF.

FORS analysis FORS is a new kind of method to measure the relic pigments.[5-7] It is quick and non-destructive. The principle to identify pigments by this method is as following:

First, get reflectance spectra, regular reflectance spectra (R-λ)or first derivative spectra (D'-λ), of both standard pigments and color pigments on ancient relics, here R is the reflectance value, D' is the first derivative ($D'=dR/d\lambda$) of the pigments and λ is the wavelength. Second, compare the reflectance spectra of unknown pigments with those of standard pigments. Third, identify pigments depending on shapes of reflectance spectra and positions of reflectance peaks on R-λ or D'-λ curves.

Generally speaking, reflectance spectrum shapes (R-λ curves) of pigments can be divided into three groups.[6] Group one: approximately bell-shaped. Reflectance spectrum shapes of blue or green pigments are like this, but the top of the bell that is the reflectance peak of each pigment is different from those of the others. Then blue or green pigments can be identified by positions of the reflectance peaks of R-λ curves directly. Group two: nearly S-shaped, Such as red, yellow or brown pigments. Although there are no reflectance peaks on R-λ curves, there must be peaks on D'-λ curves, where are the central positions on the S-curves on R-λ curves. Therefore, red, yellow and brown color pigments can be identified by their first derivative peaks. Group three: approximately linear. The reflectance and first derivative spectra are nearly linear and there are no peaks. The related pigments are usually white, black or gray.

With our self-developed Fiber Optics Reflectance Spectrophotometer,[1] the reflectance spectra of the green and red pigments are measured (See Figure 5 and Figure 6). From Figure 5, it can be seen that the R-λ curve of the green pigment is bell-shape. Its peak of the reflectance spectrum is 535 nm, which totally coincides with that of malachite, so the green one is judged as malachite. The R-λ curve of the red pigment is S-shape. Figure 6 is its first derivative spectrum. In the Figure there is a strong absorption of cinnabar nearly 600 nm and a weak absorption of hematite in the range of 670—700 nm, which also coincides with the absorption peaks of cinnabar and hematite. Therefore, the red pigment should be a mixture of cinnabar and a slight amount of hematite.

XRF analysis Because FORS can only be used to measure the color substances in pigments, therefore, the XRF analysis is also done here. The instrument is RIX-2100 X-ray fluorescence spectrometer, which can be used to measure the elements (whose atomic number is over 9) and their contents.

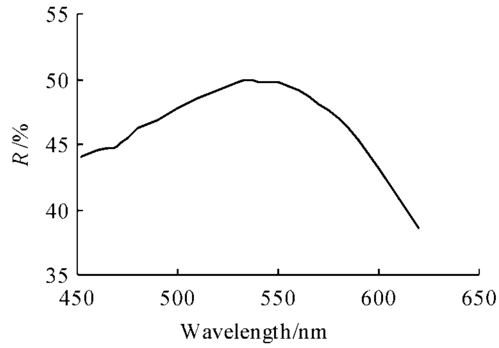

Figure 5 Reflectance spectrum of the green pigment.

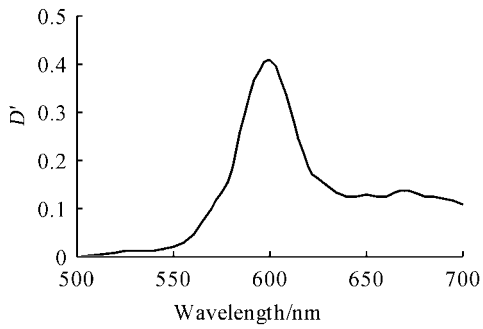

Figure 6 Reflectance spectrum of the red pigment.

Table 3 is the analytical results of both pigments by XRF. For the green pigment, the contents of silicon and aluminum are higher, which indicates some earth or dust could be mixed with pigments. The high contents of calcium and sulfur are probably caused by gypsum, which has been proved by XRD analysis. It is very common for the ancient people to add white color gypsum to the red, green and other pigments for the different bright and dark colors. There is much copper in the sample, which coincides with the malachite by FORS. Malachite [its molecular formula is [$CuCO_3 \cdot Cu(OH)_2$]]is a kind of generally used mineral pigment in the ancient times for its stability. Therefore, the green color substance in the pigment on the Buddha is identified to be malachite.

Table 3 Analytical results of the pigments on the Buddha by XRF

Components	SiO_2	Al_2O_3	SO_3	CaO	Fe_2O_3	K_2O	ZnO	PbO	Na_2O	Cl	CuO	P_2O_5	HgO	MgO	Au_2O	As_2O_3	Others
w/% (Green)	33.0	16.5	9.9	7.5	1.7	2.0	0.2	4.2	0.8	1.4	14.2	0.4				7.5	0.8
w/% (Red)	5.3	2.4	18.6	10.9	2.1	0.8	1.7	0.8	1.5	2.3	0.2	0.2	50.5	1.1	1.3		0.3

Cinnabar is also a common red pigment in ancient times. Its molecular formula is HgS. The XRF analytical results of the red pigment show that the contents (w) of mercury oxide and sulfur oxide are very high, about 70%. Therefore, there is probably a great deal of cinnabar in the red pigment. The molecular formula of hematite is Fe_2O_3 and XRF results show the content (w) of the red pigment is 2.1%. Together with FORS result, it is concluded that the red pigment should be cinnabar and a small amount of hematite.

The protective research on the Buddha

Because the rock material has been partly powdered and this is caused by the adhesive lost for water's effects. It is advised that the statue should be reinforced and protected from water, or else it might be destroyed soon.

Reinforcing As the stone sculptures in Dazu are the sandstones, Funcosil Stone Strengthener, Remmers 300 may be chosen to reinforce them. Remmers 300, made in Germany, is composed of ethyl silicate [$Si(OC_2H_5)_4$], which has been used in many areas in the world.[8,9] such as Dayan Pagoda in Xi'an, Shaanxi Province, Diplomatic Mansion in Singapore and so on. The mechanism of reinforcement is:

$$Si(OC_2H_5)_4 + 2H_2O = SiO_2 + 4C_2H_5OH$$

Remmers 300 enters the pores in organic state and reacts slowly with the vapor in air and the capillary water in the rock, then produces the inorganic and mineral SiO_2 gel, which deposits in the pores of the rock and forms the new adhesive in order to reinforce the rock. In fact, we have already used Remmers 300 on the reinforcement on the Five Hundred Arhans in the cave No. 136 in North Mountain, Dazu stone sculptures and achieved good results.

Resisting water The weathering products are not caused by the industrial pollution, but the water for the high humidity, so resisting water is necessary. After the reinforcement, resisting water should be carried. It is suggested that WD-10 (made in Wuhan, China) can be taken. It is made of $C_{12}H_{25}Si(OCH_3)_3$ and can produce $C_{12}H_{25}Si(OH)_3$ after hydrolysis. There are two parts in $C_{12}H_{25}Si(OH)_3$. One is very active —$Si(OH)_3$ group, which will react with some groups in the rock's surface, such as hydroxyls, while the dodecyl is a hydrophobic group, which will form a hydrophobic protective membrane on the rock's surface. WD-10 has been used on Grottoes at the Grand Temple in Shaanxi[10] and Five Hundred Arhans in Dazu. The resisting water result is content.

Restoration After reinforcing and resisting water, the restoration of the Buddha will be carried on:

(1) The upward-bend gold foils will be resticked to and the dropped-off foils adhered to again. It is good to use raw lacquer or some similar kind of macromolecular materials as an adhesive.

(2) According to the analysis of the pigments, parts with color-dropping are repainted with the related mineral pigments because the endurance of the mineral pigments is better than that of the organic ones or dyestuffs.

Conclusions

Based on the scientific analysis of the Buddha by XRD, XRF, IR, EDX and FORS, it can be concluded that: (1) The rock's components are mainly quartz, and albite. (2) The gold foils are gold with high purity. On their back sides, there is an adhesive like raw lacquer. (3) On the surface of the Buddha, the red pigment is cinnabar and a small amount of hematite, whereas the green one is malachite.

The protection of the Buddha probably consists of three aspects mainly: Remmers-300 can be taken in order to reinforce the rock; WD-10 is used in resisting water treatment; the gold foils must be resticked and the pigments repainted.

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