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REVIEW Research on Relationships between the Pigment of Dunhuang Mogao Grottoes Frescoes and Ecological Microorganism

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ABSTRACT

Dunhuang Mogao Grottoes is one of the largest art treasures in the world. She has a large number of murals, sculptures, beautiful and vivid; There are precious Buddhist scriptures, documents, noble and elegant. Spanning more than 1,600 years, the Mogao Grottoes show the world the extensive and profound Chinese culture with a long history. But over time, the murals in the Mogao Grottoes have also changed a lot. Thousands of years of wind and rain erosion, changes in the surrounding environment, and the influence of various biological communities have caused serious color changes and fading of murals in Mogao Grottoes. To slow down the color change of Dunhuang frescoes, protection measures should be taken from the perspective of ecological microorganisms. At present, Cladosporium, Planococcus, Phoma, Chaetomium, and other strains have caused serious discoloration or discoloration of murals to a certain extent. This paper studies the main color of Dunhuang frescoes, red, and summarizes the discoloration factors and mechanism of red lead. On this level, one should try to keep the murals and control the indoor temperature. Humidity, people, and other factors slow the fading of the murals. But these are often insufficient to protect the integrity of the murals, so we have conducted a review of the literature to provide an updated overview of the available evidence on the subject.

1. Introduction

Red lead is widely used, not only in Dunhuang murals but also in any ancient painting elements. Red lead is even used in murals all over the world, both at home and abroad. However, as time goes by, red lead in murals will gradually change from red to black or fade. The main factors

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affecting the discoloration of red lead are light, humidity, microorganism, and part of salt solution. Red lead is the main part of Dunhuang murals. The color change and fading of red have a great influence on the murals ^[2].

1.1 Microorganisms Cause the Discoloration

As a strong oxidant oxidation color pigment, Pb₃O₄ is

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also known as red lead, red lead has strong stability, high corrosion, rust resistance, and high heat resistance, but not acid resistance, but because of the presence of high lead ions in the red lead, can be oxidized by a strong oxidant. This confirms that most of the black material on the mural is PbO₂^[3,6]. It is found that the microbial cause of the discoloration of Dunhuang frescoes is the oxidation of red lead into PbO₄ by Flavobacterium. Many people have also mentioned the existence of a large amount of oxalate in murals. In the disease investigation of Dunhuang murals mentioned in literature ^[11], it was found that copper oxalate was often present in the red lead and black paintings. The origin of oxalate is derived from microbial metabolites, which are often found in hydrogen peroxide. It is mentioned that the humid environment in the cave provides necessary conditions for microbial metabolic activities, organic matter in the coating layer provides sufficient nutrients for microorganisms, and darkness (or light) promotes the growth of microorganisms. As mentioned above, hydrogen peroxide exists in the metabolites of microorganisms, so it can be seen that the discoloration of red lead is partly due to hydrogen peroxide in the metabolites of Falfa bacteria, which leads to oxidation of red lead from red to black, and finally exists in the form of lead dioxide in the fresco^[5].

1.2 The Salt Solution of Carbon Dioxide Causes the Discoloration

At the same time, carbon dioxide and soluble salt also have some influence on the discoloration of red lead.

According to the sampling 98 wats ^[9] soluble salt rock is mainly sulfate and chloride salt and contains a small amount of HCO³⁻ and NO³⁻, and because the Mogao grottoes as an important cultural site, tourism, hotels increased, leading to rising carbon dioxide levels in the caves, thus rising humidity, these will make red lead is oxidation, discoloration.

Pb₃O₄+4HNO₃=PbO₂+2Pb(NO₃)₂+2H₂O^[5]

Wang Julin et al.^[5] proposed that in the environment of carbon dioxide, the discoloration of red lead is the most serious in sulfate solution, while the discoloration degree is less in a mixed salt solution. However, no matter the presence of carbon dioxide or not, the red lead will change from lead to PbCO₃ and PbO₂ after being soaked by water.

1.3 Chlorine Salts Cause Color Changes

Shimadzu, Yoshiko et al. once experimented, spraying artificial seawater on wooden objects coated with lead, and the content of salt mineral substance was 2.7wt%. After some time, they found that red lead on these

wooden objects changed color, which was inferred to be related to the crystalline salt in the seawater ^[12]. The main components of crystalline salt are NaCl and Na₂SO₄, mainly in the form of Na⁺, Cl⁻, and SO₄²⁻. Because red lead is an oxidation color change, it is speculated that Cl^{-} and $NaSO_{4}^{2-}$ may play an oxidation role. Since it is artificial seawater, it is mainly considered that the strong oxidation of Cl⁻ leads to the color change of red lead. In the experiment by Sister Daniilia and Elpida Minopoulou, they used Optical microscopy, FTIR spectroscopy and Scanning electron microscopy (SEM/EDS) was used to detect the elements in the mural, especially in the red part of the mural that has become gray. The partial alteration was found through Scanning electron microscopy (SEM/ EDS), and cinnabar mixed with calcium carbonate. At the same time, the presence and high abundance of Cl⁻ were detected ^[1], which also explained the main reason for the color change of much red lead in the seashore.



Figure 1. Unoxidized red lead

Source: Baidu pictures



Figure 2. PbO₂

Source: Baidu pictures

2. Microorganisms in the Air where Dunhuang Frescoes are Located

2.1 Method

Factors affecting microbial concentration in air of Dunhuang with control variables. According to the Study

of Air Fungal Ecology in Dunhuang Mogao Grottoes, the main factors affecting the concentration of air fungi in Dunhuang Mogao Grottoes include temperature, relative humidity, and human activities.

Sample 1.

Vacuum sterile glasses were used to sample the air in the mogao grottoes four times. After sampling, sealed glasses were numbered 1,2,3,4, and the change of fungal concentration in the glasses was monitored.

(1) Place no. 1 cup in normal air to monitor its fungal concentration

(2) The no.2 cup was properly heated, other conditions were kept the same as the no.1 cup, and the change of fungal concentration in the cup was monitored.

(3) Change the relative humidity of no. 3 cup, keep other conditions the same as that of No. 1 cup and monitor the change of fungal concentration in the cup.

(4) Mix the air people have breathed into cup no. 4, keep other conditions the same as cup No. 1, and monitor the change of fungal concentration in the cup.

2.2 The Experimental Results

(1) Compared with no. 1 cup, with the increase of temperature, the fungal concentration in No. 2 cup increased in a certain range

(2) Compared with No. 1 cup, the fungal concentration in No. 3 cup increased when the relative humidity was higher, and the fungal concentration in No. 3 cup was lower when the relative humidity was lower

(3) Compared with cup 1, the concentration of fungi was higher in cup 4 mixed with air that humans had breathed

2.3 The Experimental Conclusion

(1) The concentration of fungi in the air of Dunhuang Mogao Grottoes is affected by temperature. Within a certain range, the higher the temperature is, the higher the concentration of fungi will accelerate the fading of mogao grottoes frescoes. The increase of temperature led to the increase of fungal metabolic rate, the increase of metabolites produced by fungi, and the acceleration of the redox process. If the murals are in this environment, red lead in the murals will cause a serious color change.

(2) The concentration of fungi in the air in Dunhuang Mogao Grottoes was affected by relative humidity. The higher the relative humidity was, the easier the fungi were to reproduce, and the easier the mogao grottoes murals were to fade. The relative humidity is low, the concentration of fungi in the air is low, and the mural is not easy to fade. Because the increase of humidity will lead to the increase of water molecules, and in a high humidity environment, any metal substance will be affected by the action of water molecules and oxygen in the air, to carry out redox reactions and lead to the change of lead color.

(3) The concentration of fungi in the air of Dunhuang Mogao Grottoes is affected by human activities. Human activities change the composition of gases in the air. The more people there are, the faster the growth and reproduction of fungi will be, and then the fading of murals will be accelerated. Bacteria and fungi are everywhere in the environment, especially the bacteria carried by the human body, and their metabolites will cause irreversible color changes to the murals.

(4) In fact, it is not difficult to see that the dry and cold environment is conducive to the preservation of the murals, to reduce the conditions and factors leading to the redox reaction of red lead in the murals. To protect the mural. The mogao Grottoes also use this method to protect murals under the condition of controlling temperature, humidity, and passenger flow. Although we say that we need to reduce the mural color change caused by fungi and other influencing factors in a dry environment, too dry conditions will also cause cracking, falling off and other effects on the mural, so at present, we are applicable to the way of constant temperature and humidity control

According to "Research on the Prevention and Control of Fungal Diseases in Dunhuang Murals", ^[7] inhibitors such as mercury chloride and butyl tin chloride have significant antibacterial effects, which can also affect the concentration of fungi in the air in Mogao Caves, so they are effective.

3. Protection of Dunhuang Frescoes

In fact, during the Sino-Japanese War of 1894-1895, people had already carried out the protection of the Murals in Mogao Grottoes. However, due to the poor conditions, harsh environment, and underdeveloped science and technology at that time, people could only reduce the passenger flow and limit the phenomenon of cultural relics being stolen again in the grottoes. As time went on and technology developed, people began to use existing technology to reinforce and repair the caves. At present, the protection of caves is mainly carried out from three aspects: geology, ecological environment, and human influence. For example, people use baffles and cement floors to prevent the wear of wind sand and strong ultraviolet radiation. Even though dust and sundries in the caves are cleaned, weather stations are established to monitor the harsh environment in the area in real time,

and rules and regulations are used to protect the caves and murals ^[4].

3.1 Protection of Murals in Caves

According to the experimental results, high temperature, high humidity and more people flow will increase the concentration of fungi in the air to a certain extent, and then accelerate the color change and fading of Dunhuang murals. Therefore, relevant departments in Dunhuang should take measures to control the temperature, relative humidity, and the number of tourists in the Mogao Grottoes, strengthen the behavior management of touristsreal-tim and avoid uncivilized behaviors that further harm the murals.

Inhibitors such as mercury chloride and tributyltin chloride were used to inhibit the growth and reproduction of bacterial microorganisms. Generally, bacteria and viruses are made up of proteins. Mercury chloride is a heavy metal salt, and mercury ions are heavy metal ions. Protein molecules can combine with positively charged metal ions to form protein salts, and irreversible precipitation of proteins occurs (heavy metal ions precipitate proteins). Butyltin chloride can be effectively anticorrosive, and protect murals from corrosion^[8].

Through the correlation analysis of information decoding and digital construction, the digital integration technology is applied to integrate multidimensional architectural information into graphic image recombination processing to realize the digital regeneration of Dunhuang mural architecture. Explore the technical methods, realization approach,hes and application values of digital reproduction and reconstruction, and expand the methods and paradigms of preservation and inheritance of mural architecture in the new context^[10].

Dunhuang locals should pay attention to ecological construction, establish a good ecological environment, to improve the air inside the Mogao Grottoes, and then reduce the concentration of fungi and microorganisms, to slow down the fading effect of the frescoes.

The restoration of Dunhuang murals should be increased. The faded murals should be restored to their original colors and protected.

3.2 The Protection of the Overall Environment for the Murals

The number of daily visitors should be controlled to reduce the CO_2 concentration and humidity in the cave at the same time. Establish a natural ecological protection area^[13]. The geographical position of Dunhuang is easily

affected by wind and sand.

4. Conclusions

According to literature review and simulation experiments, hydrogen peroxide, carbon dioxide, sulfate, nitrate and chloride are the main causes of lead discoloration in our daily life. Based on these mechanisms, these methods have also been used for heritage conservation.

The natural color red lead in Dunhuang frescoes is a kind of chemical change. Despite the influence of microorganisms, the discoloration mechanism caused by red lead and microorganisms can be attributed to REDOX reaction, which can also be in ecology and microbial metabolism, and finally lead to color change or microbial metabolites.

The world is big, the development of science and is constantly, technology in the unceasing evolution, mural color changes in the city, I don't know what exists in China, more exist all over the world, the color of the murals are different, this article briefly summarizes the main color change and response mechanism of red lead, now people are constantly trying to protect cultural relics, it is not only a symbol of culture and history of each country, It is also the cultural heritage of the whole human world, which deserves protection. Although it cannot show the glory of the past, it is worth people to protect the murals and cultural relics of the present and future, so that they can be handed down forever.

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References

- Daniela, S., Minopoulou, E., 2009. A study of smalt and red lead discoloration in Antiphonitis wall paintings in Cyprus. Applied Physics A. 96(3), 701-711.
- [2] Gong, M.T., Xin, X.H., Han, F., et al., 2009. Study on the color change of lead. Culture and Museum. 6, 8.
- [3] Hideki, N., Changlong, K., 1991. Reactivity of lead lead. Huafeng Information. 2, 15. (in Chinese)
- [4] Jinshi, F., June 1997. Fifty years of protection of the

Dunhuang Grottoes. In Conservation of Ancient Sites on the Silk Road: Proceedings of an International Conference on the Conservation of Grotto Sites, ed. Neville Agnew. pp.12-22.

- [5] Wang, J.L., 2014. Corrosion science and protection technology. 02, 159-162.
- [6] Wang, L.W., 2008. Western archaeology. 00, 293-298.
- [7] Zhang, M.L., 2012. Study on the control of mold diseases in Dunhuang murals. Lanzhou Jiaotong University.
- [8] Ma, Z.Y., Wu, X.M., 1981. Antibacterial activity of dichloroethylsalicylamides. Chemical World. 10, 9-10.

- [9] Guo, Q.L., 2009. Journal of rock mechanics and Engineering. S2, 3769-3775.
- [10] Li, Q.Q., Chao, Zh., Chao, W.B., Chao, J., 2019. Digital protection of cultural Heritage. Southeast Culture. S01, 4.
- [11] Rachael D Wakefield, Melanie S Jones : Quat J Eng Geol. 1998. pp. 30l.
- [12] Shimadzu, Y., Morii, M., Kawanobe, W., 2002. A study of discolouration of the red lead coating (ni-nuri) on historical wooden buildings in a seafront environment [Original title and text in Japanese]. Science for conservation. 41, 113-120.
- [13] Lv, X.Y., 2019. On the construction of Dunhuang Cultural and Ecological Reserve. Yanshan University.