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EVALUATION AND FORMATION MECHANISM OF SURFACE CONTAMINANTS AND STRATIFICATION ON THE ROCK PAINTINGS OF HUASHAN MOUNTAIN (GUANGXI, CHINA)

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Abstract

The Rock Paintings of Huashan Mountain dated back ~1620 to ~4800 years ago provide clear and definite information on the history of ancient Luoyue people. Investigation shows that a great amount of water drops attached to the rock surface combining with dusts resulted in the formation of mud wrapping layers covering the rock paintings. Yellow thick and dense calcium based stratification on the limestone due to the karst water seepage are very commonly observed as well. Both are main factors that are ascribed to the spallation of the rock painting from the limestones. Combining with on-site and laboratory measurements using SEM with EDS, X-ray diffraction, portable XPS, and stereoscopic microscopy, this work aims to characterize the mud wrappings and dense calcium based stratification on the surface of the rock painting and clarify the underlying mechanisms that cause a large scale spallation on the rock paintings, a phenomenon that has to be resolved or retarded urgently. This work allows the execution of specifically directed conservation strategies and chooses the most appropriate cleaning technique. Especially, it has provided a solid technological support to the restoration project conducted from 2010 to 2013.

Keywords*: Cultural heritage; Limestone monuments; Rock paintings; Surface stratifications*

Introduction

The aim of this work is to present a complementary analytical approach to characterize the surface contaminants and stratification, clarify the processing and mechanism of their formation, and evaluate the conservation status of the Rock Painting of Huashan Mountain in Guangxi, China, which has been listed as UNESCO World Heritage in 2016. The herein results provide a significant technological support to the phase III of the restoration project beginning in 2013, allow the execution of specifically directed restoration strategies, and choose the appropriate cleaning technology. This paper also aims to present information that aids to the interpretation of the techniques used during their creation.

The origin, component, and degradation of ancient rock paintings have attracted significant interest among scientists and archaeologist s in both laboratory and in-field studies [1-3]. As an extensive assembly of historical rock artifacts painted on the limestone cliffs

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located in Guangxi, southern China, the rock paintings of Huashan Mountain indicated by carbon dating could be dated back from ~1620 to 4200 years ago [4]. The total painting area is of ~170 meters in width and ~40 meters in height. It covers an area of ~8000 square meters. In addition to blurred ones, there are still more than 1900 identifiable images that can be divided into about 110 groups. It has been shown by archaeological evidence that the rock paintings were created by the Luo Yue people, who are considered as ancient of the Zhuang minority in modern China. We would like to mention that the rock paintings provide clear and definite evidence of the history and culture of the disappeared ancient Luoyue people. The rich content and information of the rock paintings provide reliable proof for the research and exploration of this cultural heritage as well.

As the key constituent unit of the rock paintings, all the human sketches are barefooted and in the gesture of half squat with the raised hands and bended knees. They accompany with the sketches of horses, dogs, timbales, knives, swords, clocks, ships, roads and the suns, etc. They are typically between 60 cm and 150cm tall. Preliminary investigation has shown that the red paintings should be painted using a mixture of red ochre (hematite), animal glue, and blood [5].

Overall, the rock paintings still present a momentum of grand, broad, and magnificent spectacular views at a first glance. Figure 1a and b shows panorama and partial view of the Rock Paintings of Huashan Mountain, respectively [6]. However, the degradation characteristics of these artifacts are significant after they were aged for thousands of years. A survey carried out in 2008 showed that there are seven main types of diseases that could result in the spallations and falling-offs of the rock paintings [7]. In addition to the geological factors that caused the instability of the limestone substrate [8, 9], main degradation characteristics include the peeling-off of the pigment layers from weathered rock, the fading of the petro-glyphs pigments, water erosion, contaminants and stratification on the surface of the rock paintings, and biological attacking, etc.

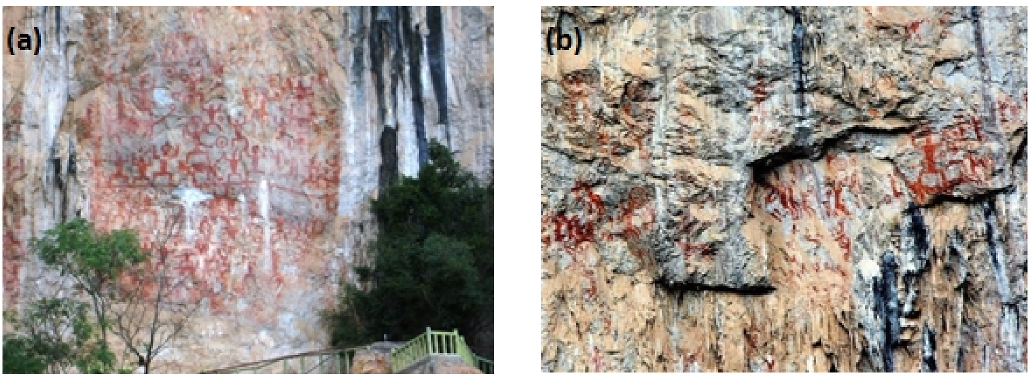

Fig. 1. The Rock Paintings of Huashan Mountain:
a. panorama view; b. partial view

It should be stressed that the geological stability of limestone substrate, surface hollowing, and large-scale scaly falling-offs of the rock paintings are under effective control after an urgent conservation project were finished in 2008, but there are still serious surface contaminants and stratification that must be uncovered. Especially, due to the local environment with alternating temperature and humidity, the mud wrappings on the surface of the rock paintings can result in the scaly peeling-off of the rock paintings. Additionally, gray or black dense calcium based coverings on the limestone, another important degradation characteristic that is ascribed to the falling-off of the rock paintings, are very common. We would like to point out that these surface contaminants and stratification have significantly degraded the aesthetics of the rock paintings. In some cases, the thick layered sediments even made some sketches on the rock paintings illegible.

The traditional chemical paste methods for the removal of the surface contaminants on the rock paintings are relatively simply and effective, but the cleaning processing could be corrosive and accompanied with by-products that are not environmentally benign. Therefore, their practical applications for the surface cleaning of the paintings have not been recommended or even prohibited. This led us to select the laser surface cleaning technique. It is stressed that it has been extensively applied for the surface cleaning of the painted marble or limestone [10-12]. Especially, the core goal of the phase III of the urgent restoration project is to effectively and safely clean the mud wrappings and gray or black dense calcium based coverings on the Rock Paintings of Huashan Mountain.

Several studies reported the successful applications of the laser cleaning technique for uncovering the wall paintings of the Sagrestia Vecchia and the Cappella del Manto in Santa Maria della Scala, Siena [13]. However, the cleaning of the paintings surface is still considered as a big challenge for laser cleaning technique. It is crucial in laser cleaning to control the inhomogeneity of optical properties along the cross section of the irradiated stratification. For example, an increasing diffusivity moving from the outer black crust to the inner Ca-oxalates film, and then to the sulfated stone underneath has been observed [14]. It also is of a fundamental importance to choose suitable criteria to successfully uncover the stratification on the rock paintings surface. Therefore, the identification of materials originally used and components of the surface contamination is of a crucial importance before the practical applications of the laser cleaning technique.

In this context, the components of surface contaminants and stratifications are characterized by a detailed study by scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS), X-ray diffraction (XRD), portable XPS, and stereoscopic microscopy. This work also clarifies the formation mechanism of these contaminants and stratifications that result in a large scale of the spallation of the rock paintings, a phenomenon that has to be resolved or retarded urgently. Especially, this work is helpful to execute the specifically directed conservation strategies and chooses the most appropriate cleaning technique.

Experimental

Pigment samples for component analysis were collected from the Rock Paintings of Huashan Mountain. Extra samples were collected by carefully scraping the weakly bonded surface of the rock paintings as well. Rock samples were carefully collected from rock debris falling off from the cliff. Especially, small limestone pieces with paintings on the surface were collected. Samples were subsequently characterized by on-site portable X-ray fluorescence (Bruker-Tracer III, Germany) and stereoscopic microscopy system (Hirox-KH7700, Japan), respectively.

Microstructure and chemical composition were characterized by scanning electron microscope (SEM) coupled with X-ray energy dispersive spectrometer (EDS) (JEOL JSM 6400). Gold was sputtered on the sample surface. Determination of mineralogical components was performed using an X-Ray Diffractometer (Rigaku, Japan) with Cu K_α radiation. XRD data were collected at 40kV with a scanning step of 0.02°/second in a range of 5-55°. Identification of crystalline compounds was performed by software (MDI Jade), and then verified manually with the JCPDS database.

Results

Limestone substrate

The stone substrate of the Rock Paintings of Huashan Mountain is identified as bioclastics micro-micrite calcite and fine sand-like structure. Main component includes ~95vol% calcite and ~5vol% dolomite. Figure 2a and b shows the SEM pictures of the microstructure of non-degraded limestone substrate and the surface of degraded one with obvious erosion holes, respectively. As shown, the non-degraded limestone is dense. In contrast, the degraded one is relatively loose. Especially, the shape of erosion holes is generally irregular and there are a large number of intergranular pores and seams.

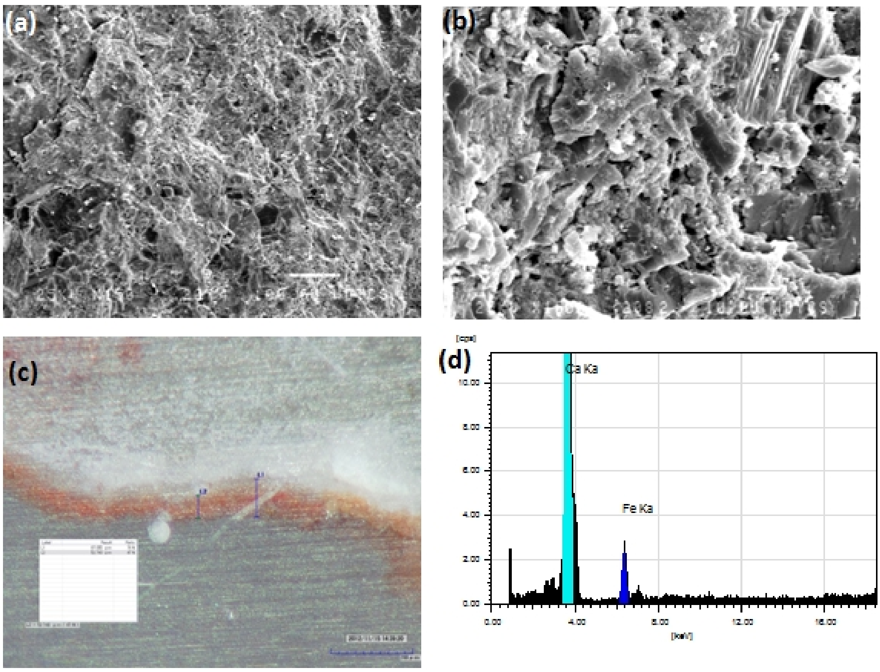

Fig. 2. SEM pictures of the microstructure:
a. non-degraded limestone substrate; b. the surface of degraded one with obvious erosion holes;
c. stereoscopic image of cross sectional limestone with pigment layer;
d. EDX patterns of pigments from the rock paintings

Component of pigments

Figure 2d is the XRF patterns of the pigment layer on the limestone substrate, showing that only iron (~95at %) and calcium (~5at %) can be detected. Lead and mercury that are very common in red pigments have not been observed within the detectable range. We would like to mention that the creation of the Rock Paintings of Huashan Mountain mainly happened in Han Dynasty. The most common minerals used as red pigments at that time were identified as red lead-lead tetroxide (Pb_3O_4) and cinnabar-vulcanization mercury (HgS) in addition to iron oxide (Fe_3O_4) [15].

These results are consistent with previous reports by electron microprobe [16]. It was indicated that only iron oxide was detected in samples collected from the Rock Paintings of Huashan Mountain as well. It is well known that iron oxide has been an important natural red mineral pigment. Figure 2c is the image of a very thin pigment layer by stereoscopic microscopy, indicating that its thickness is between 50-80μm. It is clear that the Rock Paintings of Huashan Mountain were painted directly using red iron oxide on the limestone substrate without additional surface polishing processing by the ancient Luoyue people.

However, it should be mentioned that the study by Tang [16] indicated that red pigment layer with ~ 5μm average thickness actually does not come directly into contact with the limestone substrate. In contrast, a very thin transient layer exists between the pigment layer and substrate revealed by polarized microscopy. However, further investigation shows that the optical properties and composition of this thin gray layer is very similar to that of calcite. Therefore, it is believed that main component of the thin transient layer should be calcium oxalate due to the reaction between calcite and oxalic acid. It is well known that oxalic acid is very rich in subtropical plant roots, stems, and fruits.

Surface contaminants and stratifications

Surface contaminants and stratifications on the Rock Paintings of Huashan Mountain mainly include the endogenous white karst stratification (porphyritic or banded shell), the exogenous dust stratification, yellow calcareous stratification, and the anthropogenic pollutants, such as ink marks and spotted cement and/or limewash.

Anthropogenic pollutants

A few mural surfaces were contaminated by spotted cement and/or limewash, which were identified as a kind of aluminosilicate, a primary component in modern cement. In the entrance of the visiting corridor, obvious graffiti left by visitors using black ink brush can be seen. FTIR analysis (not shown) indicates that the components of the graffiti are made up of glutinous rice juice and amorphous carbon black. Figure 3a and b shows the traces of spotted cement and/or limewash and ink marks, respectively.

Microbial erosion

It is well known that the stone monuments can be attacked by biota [17, 18]. For example, significant damages or degradation can be caused by oxalic acid produced by microorganisms. Especially, the microbial erosions on the limestone surface due to lichens, mosses, and algae are very common. Main microorganisms in Huashan Mountain include the *Clepraria sp, Verrucaria sp, Rachythecium rotaeanum,* and *Weisiopsis anomala et.al*. However, they usually are bonded loosely with limestone substrate and can be removed relatively easily. Therefore, they are still in an active state, but they are relatively easy to be removed. Figure 3c shows the image of the eroded surface of the rock paintings by microorganisms. Figure 3d further shows the typical *Lepraria sp* on the surface of the paintings by stereoscopic microscopy.

Karst-related white stratification

The endogenous white point-like and/or striped karst stratifications are very common on the surface of the Rock Paintings of Huashan Mountain. Main components revealed by XRD include ~0.7wt% quartz, ~4.8wt% gypsum, ~calcite 91.7wt %, and ~2.8wt% aragonite. Investigation showed that there are more than 50 seasonal water seepages on the vertical cliffs. It was further revealed that the origin of the white stratifications is directly related to the calcite of the limestone substrate, which is dissolvable in water. Huashan Mountain is located in a typical Karst landscape in Southern China and the fissure water seepages are very common. However, the white stratifications are unique in the limestone, cliff inscriptions and cave. As shown in Figure 3e, on-site investigation further showed that lots of white patchy stratifications and coagulations were formed in the point-like water seepage sites. In contrast, a large amount of white striped karst stratifications were formed in the water seepage sites with exudation as shown in Figure 3f.

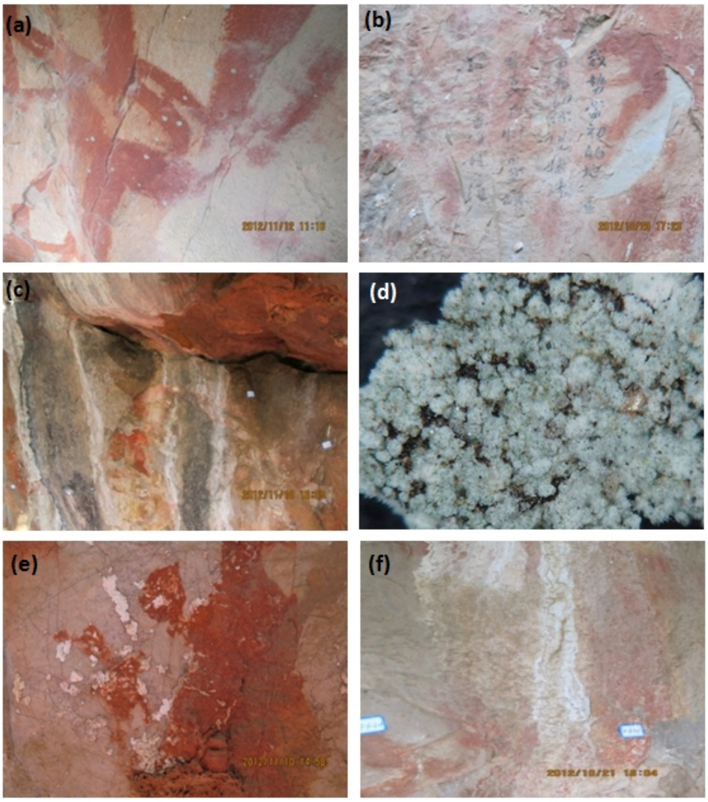

Fig. 3. Typical surface contaminants and stratifications on the Rock Paintings of Huashan Mountain: a. Gray spotted cement; b. Black ink marks left by visitors; c. Dark green microbial erosion; d. Stereoscopic image of Lepraria sp on the limestone Substrate; e. point-like; f. strip-like white karst-related stratifications

Due to the slow formation processing of the karst-related white stratification, they are dense and bonding strongly to the surface of the limestone substrate. Figure 4a further shows the cross sectional microstructure of the Karst-related stratification. The XRD patterns of the stratifications are shown in Figure 4b, indicating that the main components are calcite and gypsum.

It should be mentioned that the Rock Paintings of Huashan Mountain were painted on the top of limestone cliffs, on which a great amount of water seepages exist. Therefore, the water migrating along the fissures in the limestone gradually dissolves calcium-rich limestone to form solution containing HCO_3^-, Cl^-, and SO_4^{2-} anions and Na^+, Mg^{2+}, and Ca^{2+} ions. They finally condense on the surface of the limestone substrate to form white dot-like and/or striped calcareous stratifications.

Khaki rust stratification

In addition to loose dust agglomerates on the relatively flat surface, yellow dense khaki calcareous stratification on the projections or slightly slope areas of the rock paintings is the dominant stratification, which significantly destroys the aesthetic value of the rock paintings by masking the underlying paint layers. It is believed that they result from the chronically accumulation of the dusts. The thickness of the rust stratification can be significantly different and can change from a few micrometers to several millimeters. A typical khaki stratification is shown in Figure 4c. Figure 4d is the XRD patterns of the yellow khaki calcareous stratification, indicating that its main components include ~63.7wt% calcium carbonate, ~15.9wt% quartz,

~13.8 wt% gypsum, and ~6.6 wt% calcium oxalate. Further investigation reveals that their thickness still keep increasing due to continuous dust accumulation in the air.

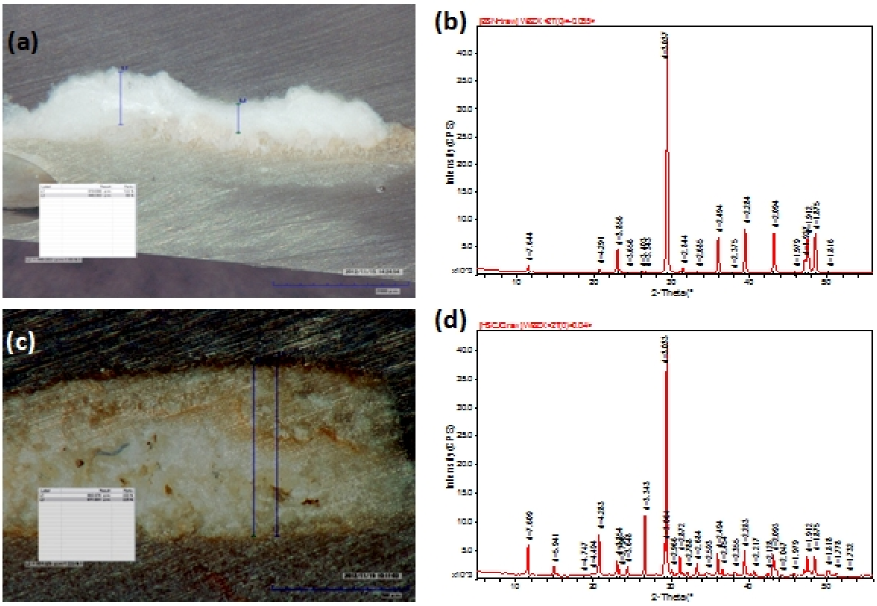

Fig. 4. The XRD patterns of the stratifications are shown:
a. cross sectional image (50×); b. XRD patterns of white karst-related stratifications;
c. Cross sectional image (50×); (d) XRD patterns of yellow dense
calcareous stratification white karst-related stratifications

Discussion

As mentioned, the Rock Paintings of Huashan Mountain were painted using natural red iron oxide as pigment. The thickness of pigment layers is generally ~50-80µm. The yellow dense khaki rust stratifications are the most prominent, followed by the karst related white stratifications and erosions by microorganisms. Table 1 describes the main degradation characteristics of typical stratifications on the Rock Paintings of Huashan Mountain. It should be mentioned that they still keep growing. Especially, the rapid development of local industry and tourism results in the accelerated growth of the stratifications.

Table 1. Description of the surface contaminants and stratification of the Rock Paintings of Huashan Mountain

Stratifications	Component	Bonding strength	Compactness	Percentage of Investigated Area	Source
Dust Agglomerate	Silty clay	Weak	Loose	All-round	Exogenous
White karst-related stratification	Calcite, gypsum	Strong	Dense	~5%	Endogenous
Yellow calcareous stratificate	Gypsum, quartz, calcite	Strong	Dense	~90%	Exogenous
Dark green microbial erosion	lepraria sp, verrucaria sp,	Weak	Dense	~4%	Exogenous
Gray spotted cement and/or limewash	Aluminosilicate	Strong	Dense	<1%	Exogenous
Black ink marks	Carbon Black	Strong	Loose	<1%	Exogenous

The Ningming County where Huashan Mountain locates is of typical subtropical humid monsoon climate. It is humid, rainy, and frost throughout the year. It is well known that the calcite in the limestone is dissolvable into water to produce Ca^{2+} and HCO_3^- aided by CO_2 in the air as described by the equation below:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (1)$$

As mentioned, oxalic acid is very rich in subtropical plant roots, stems, and fruits. Since the chemical activity of Fe^{2+}/ Fe^{3+}, Al^{3+}, and Si^{4+} ions, several other main ions in the limestone, are much lower than that of Ca^{2+}, calcium oxalate that is not easily dissolvable into the water is subsequently formed by displacing hydrogen in oxalic acid by Ca^{2+} ions as described by the equation below:

$$Ca^{2+} + H_2C_2O_4 \rightarrow Ca(C_2O_4)_2 + 2H^+ \qquad (2)$$

Additionally, Ca^{2+} ions react with sulfide in the air to form gypsum ($CaSO_4 \cdot 2H_2O$). There are several possible sulfide sources. It has been observed that the dust on the surface is the product of long-term accumulation, which reflects the time period of a general type of environmental substances. Further analysis of dust collected from the air shows that S, Cl and P content is relatively high, suggesting the contribution of exogenous acid anions.

Both calcium oxalate and gypsum can interact continuously with dehydrated calcium carbonate and khaki dust in the air to form dense stratifications on the rock paintings. It is also believed that inorganic materials containing hematite and clay slurry further react with calcium oxalate to produce Ca-rich minerals that firmly bond to the limestone substrate. However, further investigation is necessary.

Conclusion

The Rock Paintings of Mountain Huashan dated back from ~1620 to ~4800 years ago provide clear and definite information on the history of ancient Luoyue people. Surface contaminants and stratifications on the Rock Paintings of Huashan Mountain mainly include the endogenous white karst stratification (porphyritic or banded shell), the exogenous dust stratification, the yellow dense khaki calcareous stratification, and the anthropogenic pollutants, such as ink marks and spotted cement and/or limewash. The thickness of the rust stratification can be significantly different and can change from a few micrometers to several millimeters. The yellow dense khaki calcareous stratification is the dominant stratification. Main components include ~63.7wt% calcium carbonate, ~15.9wt% quartz, ~13.8wt% gypsum, and ~6.6wt% calcium oxalate. Further investigation reveals that their thickness still keep increasing due to continuous dust accumulation in the air. This study revealed that oxalic acid plays key roles in forming the yellow dense khaki calcareous stratification. This work allows the execution of specifically directed conservation strategies and chooses the most appropriate cleaning technique. Especially, it has provided a solid technological support to the restoration project conducted from 2010 to 2013.

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