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Studies of wall painting fragments from Kaiping Diaolou by SEM/EDX, micro Raman and FT-IR spectroscopy

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ABSTRACT

The multi-technique analytical approach has proved to be a very effective tool for the analysis of artwork, as demonstrated by various studies. In this work, four micro-analysis methods were used to analyze the wall painting fragments in Kaiping Diaolou, a world cultural heritage enlisted in 2007. Field-emission scanning electron microscopy (FE-SEM), energy dispersive X-ray micro-analysis (EDX), combined with micro Raman and Fourier transform infrared (FT-IR) spectroscopy, provided a vast amount of information concerning the raw materials present in the pigments, organic binder, plasters and mortars of the wall painting. Four types of pigments (goethite, lazurite, chromium green and calcite) were identified on the surface layer of the wall paintings. The substrate under the pigment layer was found to be composed of cubic-like calcite ($CaCO_3$), micro-rod bundle-shaped syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$) and silica (SiO_2). The organic binder can be attributed to animal glue (such as egg) and drying oil by micro FT-IR spectroscopy. These analysis results can provide important information for the conservation and restoration of the Kaiping Diaolou.

1. Introduction

Kaiping City lies in the southern part of the Guangdong Province in China, on the western side of the Pearl River Delta. During the Ming Dynasty (1368–1643), the area was badly ravaged by bandits and natural disasters, especially floods. Some villages decided to protect themselves against these threats by building multi-storey towers (‘Diaolou’) (Fig. 1(a)). There are currently 1833 Diaolou towers in Kaiping, which possess a mixture of both oriental and western architectural styles, and such structures have become a characteristic feature of the Kaiping region (more information on geographical region of Kaiping can be seen from the website: http://www.kaipingdiaolouandvillages.com/).

Kaiping has long been the hometown of numerous Chinese emigrants living or working overseas; those who prospered were keen to contribute to the improvement of their family in Kaiping, often by involving in the construction of Diaolou towers. Until the late 19th century, the Chinese society was basically isolated from the outside world, and the Chinese people were resistant to new things coming from aboard. Nevertheless, local Kaiping people began to initiatively accept and absorb new ideas from overseas due to influence from the large amount of emigrants from Kaiping. Some western architectural esthetics, techniques, and materials were brought into traditional Chinese architectural practices. The Diaolou towers were built using traditional Chinese architectural craftsmanship but with reference to the western style (including the building structure and material). As a result, Kaiping Diaolou towers were regarded as the product of harmonious architectural fusion in multicultural architectural esthetics. This unique cultural background caused the Kaiping Diaolou towers to be designated as a UNESCO (United Nations Educational, Scientific, and Cultural Organization) World Heritage site in 2007 [1].

Wall painting is an important component in Kaiping Diaolou. Analyses of the pigments, binder, plasters and mortars in the wall paintings can reveal the information on temporal or geographical variability of the construction materials. Based on such information, patterns of trade or cultural exchanges can be inferred. However, there are only a few historical records concerning the crafting of these wall paintings. Besides, any physical handling and natural degradation result in damages of the wall paintings. Art conservators require detailed information on the chemical composition of the materials before restoration projects can be conducted. It is therefore necessary to determine the raw materials employed in constructing the wall painting.

Some analytical techniques have been used for the characterization of pigments in artworks [2–9]. For example, the groups of Clark

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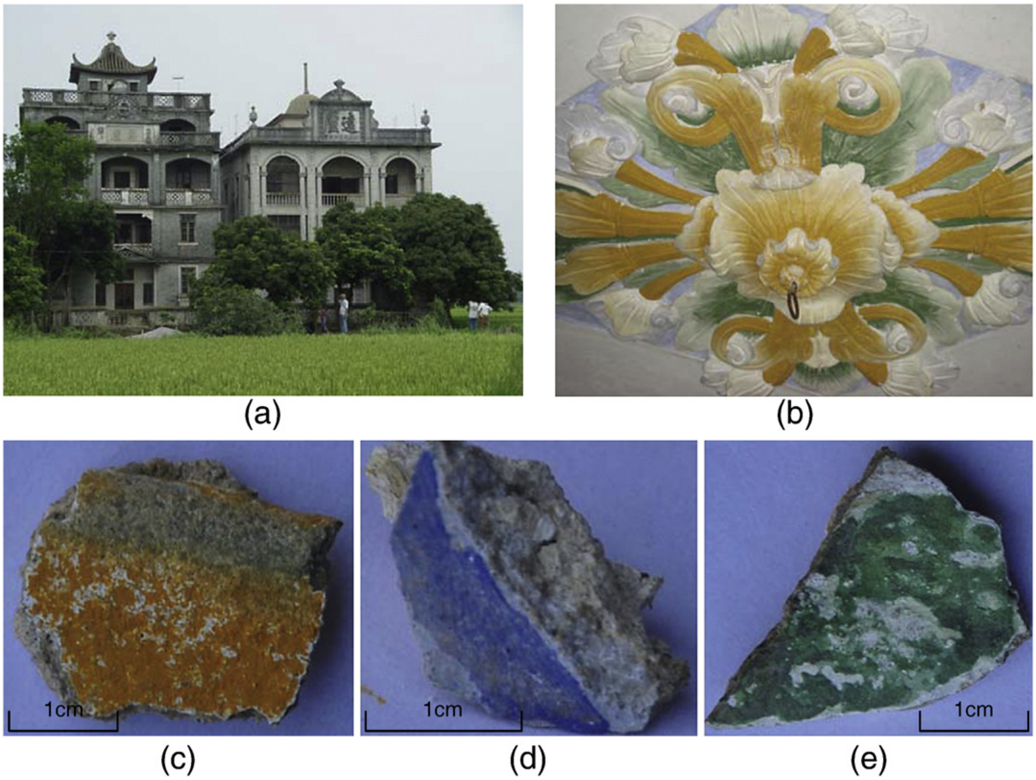

Fig. 1. Optical photograph of Kaiping Diaolou (a). Three colored fragments from a wall painting (b) in Kaiping Diaolou: yellow (c), blue (d) and green (e). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and Edwards investigated a large number of pigment materials used in ancient artwork such as illuminations, inks, ceramics, maps and statues by Raman spectroscopy [7–10]. Synchrotron radiation-based X-ray techniques were also used to characterize 16th-century wall paintings [11,12]. These studies indicated that scientific analytical techniques are important for the identification of pigment materials of artwork. In the case of wall painting, except identification of pigment, the analysis of the binder, plasters and mortar materials are also important for the conservation and restoration. It have been demonstrated that the binder, plasters and mortar materials played significant roles in the preservation of artworks [13,14], but until now very few analyses of Chinese artifacts are available.

The chemical compositions of material used in artwork are generally very complex, and their characterization is a challenging task. Besides, the extraction of samples for examination is often forbidden or highly limited in quantity. Analysis techniques with high spatial resolutions are therefore required for such investigations. It is well-known that scanning electron microscopy (SEM) and energy dispersive X-ray micro-analysis (EDX) can provide information about the surface morphology and the elemental compositions of the artwork over micron or even sub-micron areas. Whereas micro Raman and Fourier transform infrared (FT-IR) spectroscopy are considered as ideal tools because it can be applied in micron-sized area for identifying individual grains made of different raw materials [5–9]. Therefore, a multi-technique analytical approach can provide more complete information on the chemical compositions of an artifact.

In this work, some fragments (as shown in Fig. S1 (Supporting Information)) of wall paintings with different color were retrieved from a Diaolou tower. They were analyzed by FE-SEM, EDX, micro Raman and FT-IR spectroscopy. FE-SEM and EDX can provide the data related to the morphology and elemental composition, while micro Raman and FT-IR spectroscopy can identify directly the molecular structure of the samples in micrometer scale. Detailed information about pigments, binders, plasters and mortars employed in the wall painting were extracted by these micro-analysis methods.

2. Experiment

The particular Diaolou tower (Fig. 1(a)) studied in this work was built in 1900 A.D, with some paintings (Fig. 1(b)) decorating the surface of the walls. Some small fragments of the wall painting with different color (yellow in Fig. 1(c), green in Fig. 1(d), blue in Fig. 1(e)) and white in Fig. S1 (Supporting Information) were investigated. Although the data presented in this work were extracted from these four colored specimens, we also have measured several fragments (as shown in Fig. S1 (Supporting Information)) in the same Diaolou tower before preparing this manuscript. It was found that fragments with the same color yielded similar results. These four samples were presented in this work due to their relatively large size and hence clearer signals that could be obtained. All of the fragments examined in this work contained the original pigments and the underlying plaster and substrate. In order to obtain information about the original materials used in the plasters and mortars, part of the surface of the yellow fragment was slightly scratched to expose the grey plaster layer (Fig. 1(c)).

The micro-morphology and distribution of elemental components in the samples were analyzed by means of a FEI Nova NanoSem 430 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive analysis system of X-ray spectrometer (EDX) accessory (EDAX Inc., ISIS with Si detector system). As the samples need to be analyzed repeatedly by several analysis techniques, the sample surfaces cannot be coated with carbon or Au/Pt as in typical SEM imaging processes. Therefore, the SEM images and EDX of the samples were obtained under low vacuum conditions (water vapors pressure in the chamber set to 50 Pa). A low accelerating voltage (5–

10 kV) was used for avoiding discharges from the sample surfaces in SEM image measurement. EDX analyses were performed with an accelerating voltage of 15 kV for the electron beam (beam current 2 nA), using a variable microscope magnification and a data collection time of 100 s.

Micro Raman spectroscopic study was carried out with a Jobin Yvon LabRam UV-IR HR-800 spectroscopy coupled to an Olympus BX41 microscope. Samples were illuminated using a near-IR laser diode emitting at 785 nm. Laser power at the sample was reduced to 1 mW or less for the analysis of the samples. The average spectral resolution in the Raman shift range of 100–2000 cm^{-1} was 1 cm^{-1} (grating 600 grooves/mm). These conditions gave spectral footprints of ~1–2 μm (50× microscope objectives) in diameter at the specimens. Owing to the relatively weak Raman signal of the samples, long integration times (typically>80 s) were used to achieve acceptable signal-to-noise ratios. Calibration of the instrument was carried out daily with the 520 cm^{-1} silicon Raman band. The Raman spectra were recorded for the identification of the compounds, with the selection of the sampling points being assisted by *in situ* optical microscopy.

The samples were examined between 4000 and 600 cm^{-1} by a Vertex 70 (Bruker Optics) FT-IR spectrometer, equipped with nitrogen cooled MCT detector. Micro FT-IR spectroscopy allows the identification of inorganic and organic materials on a very small area of a sample (up to 10×10 μm) by the use of a coupled Hyperion 2000 infrared microscope. The spectra of the samples were collected as received in the reflectance mode.

3. Results and discussions

Kaiping Diaolou towers are extensively decorated with wall paintings, which is the result of the incorporation of Western architectural esthetics, techniques and materials into traditional Chinese architectural practices. The particular wall paintings in Fig. 1(b) consist of four colored fragments of yellow, blue, green and white. Investigations by micro-analysis (SEM/EDX and micro Raman and FT-IR spectroscopy) were focused on the yellow fragment, and the results are presented here. The other three fragments were also examined by micro Raman and FT-IR spectroscopy and the results are discussed in the following.

4. Yellow fragment

The optical photograph of the yellow fragment is shown in Fig. 2(a). The surface of the fragment can be separated into two regions, one being the yellow region with the surface covered by yellow pigment, the other being the grey region.

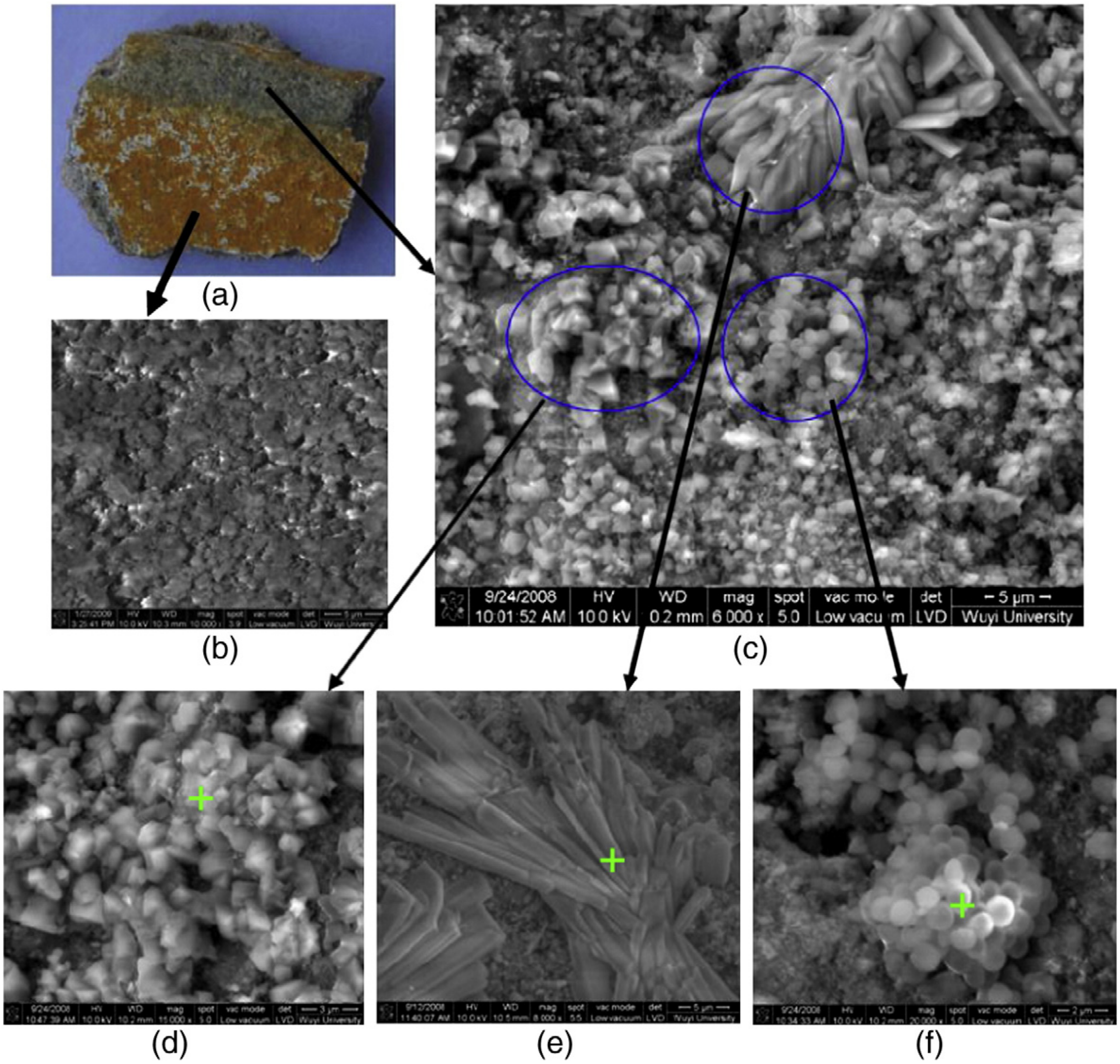

Fig. 2. (a) Optical photograph of a yellow fragment from the wall painting, with two areas (yellow and grey) observed. SEM images of the yellow pigment and grey area are shown in (b) and (c).Three micro-morphologies are observed in the grey area of the yellow fragment specimen. The SEM images with higher magnification for the three micro-morphologies show cubic (d), micro-rod (e) and spherical (f) features. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.1. SEM and EDX analysis

The yellow pigment appears to be homogeneous from the SEM image shown in Fig. 2(b). EDX measurement of the pigment (as shown in Fig. S2(a) (Supporting Information)) shows that the main elemental compositions of the yellow area includes Fe, Ca, C and O. The yellow pigments commonly used in the period between the Middle Ages to ca. 1700 A.D include orpiment (As_2S_3), yellow iron oxide (FeO(OH)), lead tin yellow types I and II, lead tin antimony yellow (Pb_2SnSbO_6) and para-realgar (As_4S_4) [15]. The significant quantity of Fe and O suggested that the yellow pigment was probably Fe_2O_3 or FeO(OH). More definitive identification requires further analyses by Raman spectroscopy (see later sections).

The SEM image of the grey region is shown in Fig. 2(c). It is interesting that three distinct micro-morphologies (highlighted in the figure) such as cubes, rods and spheres are observed. This observation may provide information on materials used in the binder, plaster and mortar under the pigment layer. FE-SEM images of the highlighted features in Fig. 2(c) with higher magnifications are shown in Fig. 2(d), (e) and (f). The size of the cube-like features is in the range of hundreds of nanometers, as shown in Fig. 2(d). The main elemental compositions of such cubes are shown in the EDX results in Fig. S2(b) (Supporting Information). The existence of C, O, Ca and Si is verified, suggesting it is a mixture of $CaCO_3$ and SiO_2. Such two materials are the major components of plaster and mortar. For the rod-like structures (Fig. 2(e)), they exist in the form of bundles with length of several microns and width of hundreds of nanometers. EDX measurements on these micro-rods (as shown in Fig. S2(c) (Supporting Information)) have detected six major elements (C, S, O, Ca, K and Si). Further analysis using Zeeman anisotropy fluorescence (ZAF) method revealed the atomic concentration of these elements: C (21%), S (9%), O (53%), Ca (7%) and K (8%), accompanied by a small amount of Mg, Al and Si. The predominant components in the micro-rod bundles are O, S, Ca and K, which may be identified as $CaSO_4$ or K_2SO_4 or $K_2Ca(SO_4)_2\cdot H_2O$. The other components that can be present include SiO_2 and $CaCO_3$. As recorded in Chinese literature, cement was seldom used in wall paintings due to the limited production in ancient China, while gypsum ($CaSO_4\cdot 2H_2O$) was instead frequently used for the same purpose. In addition to cubes and micro-rods, some spherical particles with diameter of 1 μm were found embedded in the supporting medium (Fig. 2(f)). The predominant elements of such spheres (as shown in Fig. S2(d) (Supporting Information)) were C and O, which indicated that the material could be organic compounds such as binders.

In order to obtain detailed information on the molecular structure, micro Raman spectroscopy was employed to further characterize the yellow fragment. Although the small regions observed in FE-SEM cannot be located by optical microscopy due to the limited spatial resolution, useful information can still be given by Raman spectra by selecting micro region with the help of optical microscope.

4.2. Micro Raman spectroscopy analysis

A detailed study by Raman microscopy of the yellow fragment sample is shown in Fig. 3(a), (b) and (c). The Raman spectra are recorded in selected areas (as indicated in the optical images (I) and (II) on the left of Fig. 3), located by *in situ* optical microscopy. For the yellow region in Fig. 3(I), five bands at 250, 304, 389, 483 and 554 cm^{-1} are observed (curve 1 in Fig. 3(a)). These bands can be assigned to goethite (α-FeOOH) [4]. The band at 1087 cm^{-1} is due to the presence of calcite. At the white region of Fig. 3(I), strong Raman bands of calcite ($CaCO_3$) (282, 714 and 1087 cm^{-1}) and silica (SiO_2) (130, 207 and 466 cm^{-1}) are identified (curve 2 in Fig. 3(a)). These results are consistent with those from the previous EDX analysis.

Fig. 3(II) shows the optical image of the yellow fragment specimen at the grey area. Three areas (corresponding to curves 3, 4 and 5) can be distinguished in this photograph, and the corresponding Raman spectra are presented in Fig. 3(b) and (c). Raman bands in the black area (at 127, 206, 263, 354, 393, 464, 806, and 1161 cm^{-1}, as shown in curve 3) are assigned to silica silicon oxide (SiO_2) [16]. The appearance of the band at 1087 cm^{-1} implies the presence of calcite. In curve 4, the Raman bands at 415, 490, 620, 670, 1010 and 1133 cm^{-1} indicate that the material is gypsum ($CaSO_4\cdot 2H_2O$) [16]. The other four bands observed at 250, 304, 389 and 552 cm^{-1} are assigned to goethite (α-FeOOH). Therefore, the mixtures of gypsum, goethite and calcite (1087 cm^{-1}) are found in curve 4.

In order to accurately assign the Raman bands in curve 5, the reference Raman spectra of goethite, calcite and syngenite are listed in Fig. 3(c). Apart from the Raman bands of calcite (Raman bands at 280, 714 and 1087 cm^{-1}) and goethite (Raman bands at 250, 304, 389 and 552 cm^{-1}), there are some strong bands centered at 440, 641, 1138, 1165, 980 and 1004 cm^{-1}, respectively, which are assigned to syngenite ($K_2Ca(SO_4)_2\cdot H_2O$) [17]. As suggested by the results of EDX analysis as shown in Fig. S2(c) (Supporting Information), the molar ratio of S and K is about 1:1, which is consistent with the ratio between S and K in $K_2Ca(SO_4)_2\cdot H_2O$. Therefore, one conclusion that can be drawn is that the micro-rod bundles in Fig. 2(e) are syngenite $K_2Ca(SO_4)_2\cdot H_2O$. It may be produced during hydration processes of high-K cements, often leading to the so-called false or flash set and during the storage of clinkers [18]. However, the cement was seldom used in wall paintings of Kaiping Diaolou due to the limited production in China during late 19th century, as confirmed by old handicraftsmen and local historians. That the syngenite is regarded as a raw material is a more possible explanation. Moreover, the distribution of the syngenite in China is very rare, and there are very few records on syngenite production in China. Therefore, the syngenite may have come from abroad, but the exact origin of the syngenite is very difficult to be determined based on the above analysis.

5. Blue, green and white fragment

5.1. Raman spectra of blue fragment

Fig. 4 shows the Raman spectra of the blue fragment specimen. The band at 544 cm^{-1} is assigned to a progression in the symmetric stretch of the S^{3-} ions of the lazurite ($(Na_8(Al_6Si_6O_{24})S_3)$), which acts as the blue chromophore [19,20]. Natural lazurites were traditionally obtained from the mineral lapis lazuli following a complex method of selective extraction of the blue particles. As reported in literature, this Raman band is also observed in all spectra of lapis lazuli and artificial ultramarine. On the other hand, the synthetic pigment became already available around 1830 [15]. Therefore, it is very difficult to identify whether the observed band belongs to the natural material or the synthetic pigment simply from the Raman spectra. To overcome this issue, FT-IR spectrum has been proposed for the differentiation between the natural lapis lazuli and synthetic ultramarine. It has been reported that the FT-IR spectra of natural ultramarine blue samples from Afghanistan showed a narrow band at 2340 cm^{-1}, which was absent from the spectra of the synthetic pigments [21,22]. The micro FT-IR spectra of the blue pigment were measured and the results are as shown in Fig. 5. The bands at 1070 and 960 cm^{-1} are due to the $\upsilon_{(Si-O-Si)}$ and $\upsilon_{(Si-O-Al)}$, and the bands at 1445, 880 and 719 cm^{-1} are associated to calcium carbonate. The band at 1640 cm^{-1} is due to calcium oxalate. Furthermore, the micro FT-IR spectra of blue fragment show the band at 2340 cm^{-1} [22], which indicates the presence of Afghan natural ultramarine blue. As we known, the thought of Chinese people was conservative at that time, and they often boycott the overseas products. However, the large amount (more than a million) Kaiping people working overseas in the end of 19th century bridged the local Kaiping people with the outside world socially and economically. As a result, local Kaiping people could have

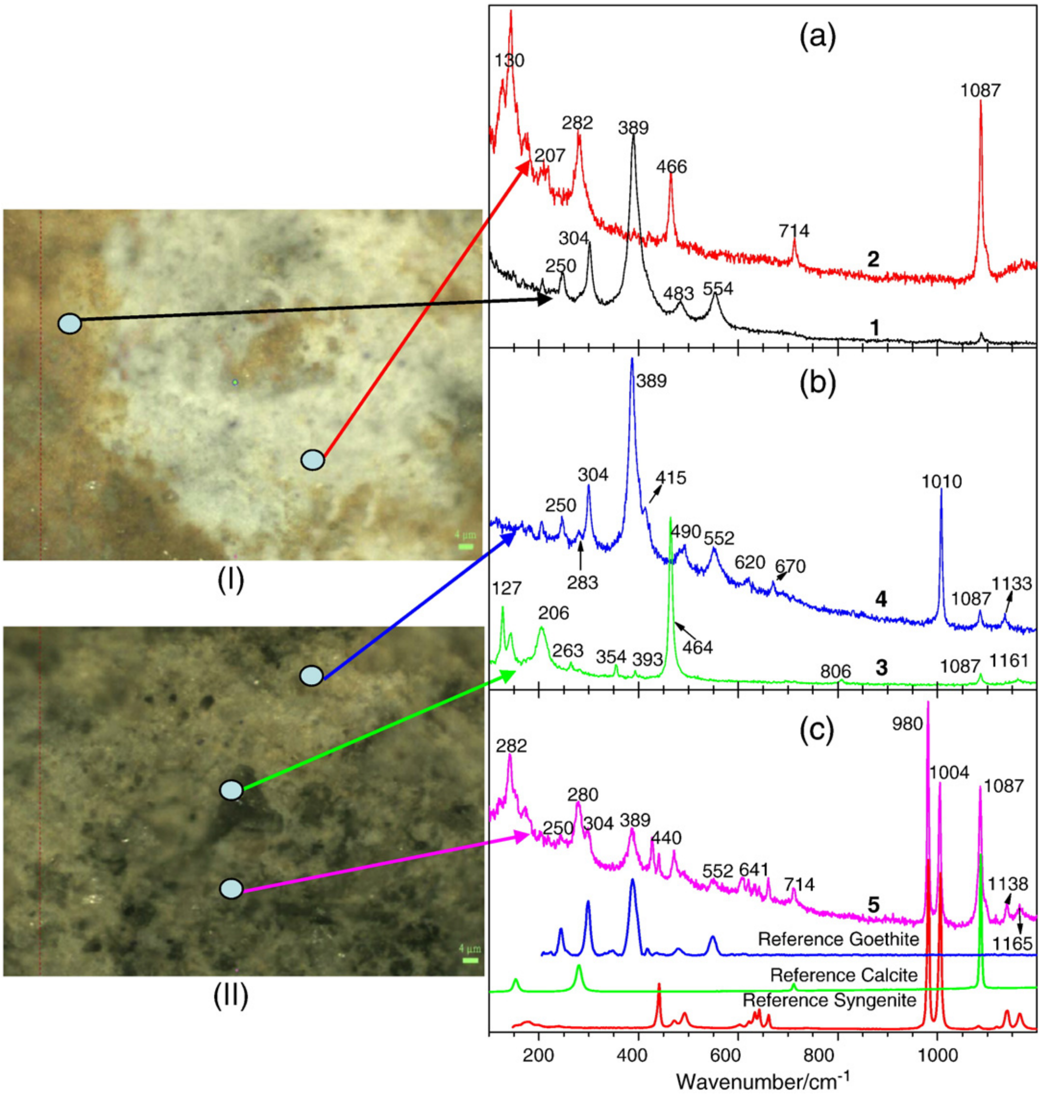

Fig. 3. Raman spectra of the yellow fragment from wall painting in Kaiping Diaolou. (a): yellow area; (b) and (c): grey area. The reference Raman spectra of goethite, calcite and syngenite are obtained from http://rruff.info/index.php. The selected positions in pictures (I) and (II) are used for Raman spectra measurement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

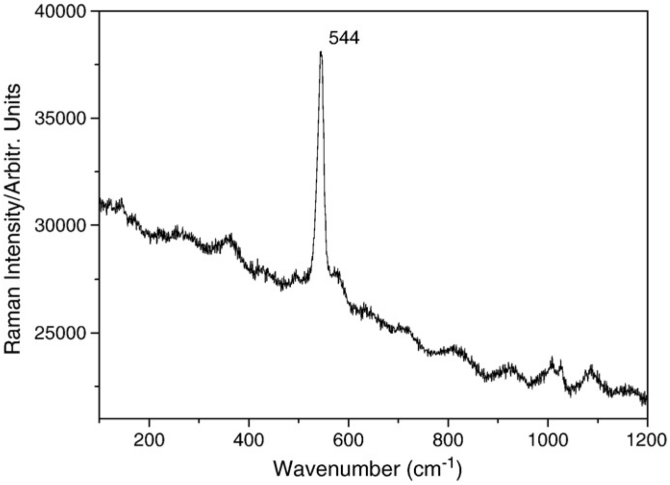

Fig. 4. Raman spectra of the blue fragment.

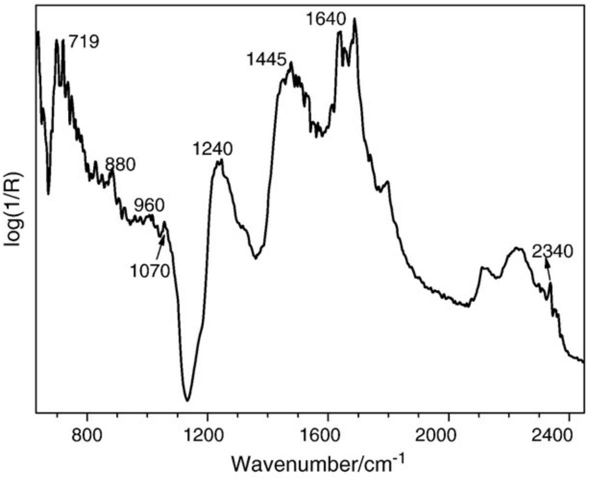

Fig. 5. Micro FT-IR spectra of the blue pigment. The spectra of the samples were collected as received in reflectance mode. “R” in vertical ordinate represents reflectance.

purchased foreign architectural materials from Hong Kong or overseas. Therefore, as above mentioned, the blue pigment may have come from Afghan, which is one representative case about the local Kaiping people initiatively accepting new things from overseas. It also could supply a scientific basis for studying the history and culture of China through the analysis of the pigment fragment.

5.2. Raman spectra of green and white fragment

The Raman spectra of green and white pigment are present in Fig. 6. For the green specimen, four characteristic Raman bands of Cr_2O_3 at 348, 552 and 615 cm^{-1} are observed [19]. The Raman bands at 154, 280, 710 and 1087 cm^{-1} of the white fragment are assigned to calcite.

Here, the analysis on the architectural craft of wall paintings in Kaiping Diaolou can be summarized as follows:

1. Plasters, mortars and binder were used as binder between the pigment and the wall. Yellow, blue, green and white pigments were identified as goethite (α-FeOOH), lazurite ($(Na_8(Al_6Si_6O_{24})S_3)$), Cr_2O_3 and calcite, respectively. Such kind of analysis can provide a scientific basis for studying the history and cultural exchange between China and overseas.
2. The main components of the plasters and mortars were determined as a mixture of calcite, silica, gypsum and syngenite. The observation the former three materials (calcite, silica and gypsum) in the mixture means that the painters used a transitional approach of substrate preparation, which was a combination of the Romanesque and the Renaissance methods [8]. However, the presence of syngenite together with calcite, quartz and gypsum as original plaster materials in wall paintings was seldom reported in literature.
3. The organic binder may be aged due to the oxidation and other environment contamination factors. So it was very difficult to obtain the exact Raman signals of the organic binder. However, information about the organic binder can be obtained by measuring the micro FT-IR spectra of the yellow fragment. In Fig. 7, Due to the existence of bands at about 2980, 2928 and 2870 cm^{-1} (assigned to the asymmetric and symmetric CH_2 stretching modes, respectively) and at 1790 cm^{-1} (assigned to the carbonyl stretching mode of the ester group) and 1620 cm^{-1} (Amide I), the organic binder can be attributed to drying oil and animal glue (such as eggs) [2,22,23]. According to historical literature on ancient Chinese architectural techniques, and from interview with old craftsman, 'dry oils' (such as tung oil and glutinous rice) were often used as binders in ancient Chinese architectural craft [13]. Furthermore, as observed by FE-SEM and EDX in Fig. 2(f) and Fig. S2 (Supporting Information), the molar ratio of the majority elements (C and O) in the spherical organic compound is about 2:1, which is close to the ratio of the tung oil [24]. The presence of animal glue could be due to a consolidation treatment of the wall painting surface. In addition, the bands at 1465, 875, 713 cm^{-1} are due to calcium carbonate, and the bands at 1650(υ_{asym}COO) and 1321 cm^{-1} (υ_{sym}COO) come from calcium oxalate, which may be the result of decomposition of organic materials.

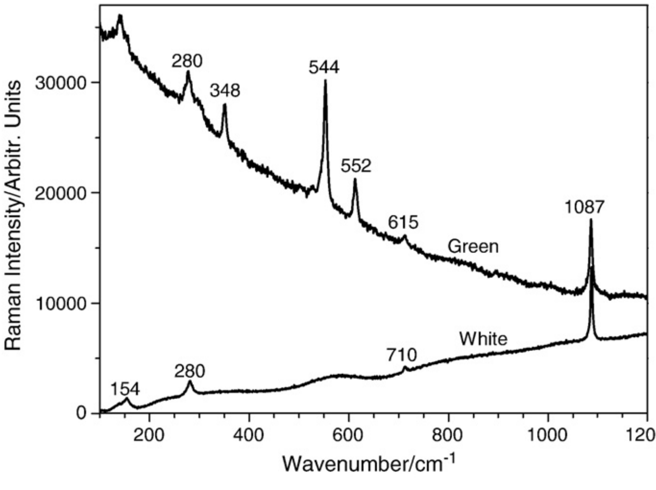

Fig. 6. Raman spectra of the green and white pigments.

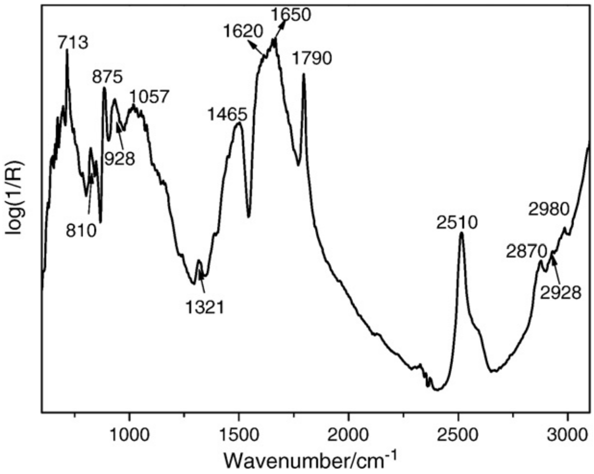

Fig. 7. Micro FT-IR spectra of the yellow fragment. The spectra of the samples were collected as received in reflectance mode. "R" in vertical ordinate represents reflectance.

6. Conclusion

Wall painting fragments in a Kaiping Diaolou tower were investigated in this work. The colored pigments (yellow, blue, green and white) were identified as goethite (α-FeOOH), lazurite ($(Na_8(Al_6Si_6O_{24})S_3)$), Cr_2O_3 and calcite ($CaCO_3$), respectively. The plasters and mortars materials were analyzed as a mixture of cubic-like calcium carbonate ($CaCO_3$), gypsum ($CaSO_4\cdot 2H_2O$), micro-rod bundles of syngenite ($K_2Ca(SO_4)_2\cdot H_2O$) and silica (SiO_2). Spherical-like organic binding medium with diameter of 1 μm was found in plasters and mortars. After further analyzed by micro FT-IR spectroscopy, the organic binders were determined as animal glue (such as egg) and drying oil. These above analyses were valuable for the conservation and restoration of the wall painting in Kaiping Diaolou.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.microc.2010.05.013.

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