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Identification of the Pigments on the Mural Paintings from an Ancient Chinese Tomb of Tang Dynasty Using Micro-Raman and Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy Analysis

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Abstract: The tomb of Hanxiu, a prime minister of the Tang dynasty who died in 740 CE, was decorated with elaborate mural paintings. The pigments used in the mural paintings were collected from representative colours before a restoration process and analyzed using micro-Raman and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDS) analysis to characterize the chemical compositions. The results reveal the chromatic palette and the painting technique used in the mural paintings. Most of the pigments are natural mineral pigments similar to those excavated in previous archaeological works, except the yellow pigment is unusual. A rare mineral pigment, vanadinite [$Pb_5(VO_4)_3Cl$], was employed in a large amount as the yellow pigment. This phenomenon was analyzed and compared with tomb mural paintings from varied periods and locations in ancient China. Notably, the identification of vanadinite via Raman spectra has to be performed carefully and combined with an elemental analysis to avoid misidentification.

Keywords: mural paintings; Tang dynasty; micro-Raman; SEM-EDS; vanadinite; natural mineral pigments

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1. Introduction

The colours of paintings, by which artists can express their thoughts and feelings and make the paintings more expressive and infectious, are of great significance. Pigments are material carriers of colours. A variety of pigments are used to produce different colours with varied hue, saturation, temperature, luminosity and chroma on artworks and make them beautiful and attractive.

Before the extensive usage of synthetic pigments after the middle of the 19th century, the pigments that were used could be classified as mineral pigments, plant pigments/dyes, metal pigments (mostly gold and silver) and other pigments from animal blood, bones, shells, microbial corpses and gem powder according to the sources of the materials. Inorganic mineral pigments were the earliest and mostly used pigments among them. On the pottery of the Majiayao culture (3280 BC–2050 BC) in ancient China, natural minerals like franklinite ($ZnFe_2O_4$), magnetite (Fe_3O_4) and hausmannite (Mn_3O_4) were used for black paint, while gypsum ($CaSO_4 \bullet 2H_2O$) and calcite ($CaCO_3$) were used for white paint by early humans in the Neolithic Age [1]. On the mural paintings excavated in the Shimao site (2200 BC–1900 BC) of the late Neolithic Age, haematite (α-Fe_2O_3), goethite ($FeO \bullet OH$) and glauconite [(K, Na)(Fe^{3+}, Al, Mg)$_2$(Si, Al)$_4$O$_{10}$(OH)$_2$] were used as pigments for red, yellow and green colours [2]. On prehistoric rock paintings, haematite, gypsum, calcite, magnetite, goethite and other natural minerals were found in different areas of various countries [3–7]. With the progress of time and technology, artists and craftsmen accumulated more and more knowledge of mineral pigments. More kinds of minerals were discovered as pigments, and the technology used to process and purify mineral pigments increasingly improved. Ancient artists learned how to achieve their desired colour effect by mixing pigments and created a large number of excellent paintings.

The use of pigments has distinct chronological and regional characteristics in art history. In addition to the artistic effect, ancient artists had to consider the easy accessibility, durability and costs of the pigments. Most natural mineral pigments have the advantages of brilliant colour and chemical stability compared with other pigments/dyes. Hence, ancient artists chose pigments mainly based on costs and accessibility and were limited by the availability of local mineral resources. This is the reason that haematite and carbon from burned plants were widely used in the earliest artworks throughout the world and some precious pigments such as lapis lazuli were scarcely used. Another important factor that affected the artists' preference of colour was the cultural background of different countries and nationalities just like the image of the dragon and the yellow color was only allowed to be used for the royal family and the dignitaries in ancient China. The identification of pigments on ancient artworks is of great importance because it can help artists and archaeologists achieve a better understanding of the materials, technology, provenance, chronologies and the problems causing deterioration. The results can also benefit the restoration and conservation of valuable cultural heritages.

Inorganic mineral pigments with a variety of colours, including red, green, blue, white and black, were widely used by ancient Chinese artists to make mural paintings in tombs [8–16]. However, yellow was rarely employed in most of the tomb mural paintings excavated in China. In the cases that yellow pigment was used, the amount was very limited [14]. It is known that several kinds of yellow pigments, including yellow ochre ($FeO \bullet OH$), orpiment (As_2S_3), pyrite (FeS_2), massicot (PbO), pararealgar (As_4S_4), chrome yellow ($PbCrO_4$) and sulfur, were used by ancient Chinese artists and craftsman in artworks. Hence, Guo [13] et al. attributed the limited use of yellow in tomb mural paintings to religion and funeral culture. Even on a worldwide scale, yellow was scarce in mural paintings [17–19]. But as shown in the following section, the use of yellow colour/pigment in a tomb mural painting of the Tang dynasty (618–907 CE) was totally different from others. This paper presents a scientific study of this tomb mural painting. The pigments from the mural painting were analyzed using micro-Raman and scanning electron microscopy/energy dispersive X-ray spectroscopy. We aim to identify the pigments and possible degradations and to support further restoration and conservation works of mural paintings. Furtherly, we want to understand the use of yellow pigment in that period and that location.

2. Archaeological Context

The tomb mural painting studied in this work is located in the southeast rural area of Xi'an City, China. The archaeologists of Shaanxi History Museum had to carry out a rescue excavation after it was plundered by grave robbers in February 2014. Based on the inscriptions carved on the epitaphs found in the tomb, the deceased masters are Hanxiu, a prime minister of the Tang dynasty who died in the 28th year of Kaiyuan Emperor's era of the Tang dynasty (740 CE), and his wife, Mrs. Liu, who died 8 years later. This single chamber brick tomb is about 11 m deep underground with a stone door facing south. With a long ramp tomb passage of about 40.6 m to one chamber, it is a high-grade Tang dynasty tomb consisting of four tunnels, five patios and one chamber. The burial chamber is roughly square with a side length of about 4 m.

The four side walls of the chamber are decorated with 21 pieces of elaborate mural paintings summed over 40 m^2, and one painting on the east wall of the tomb is shown in Figure 1. It is noteworthy that, firstly, the subject matter of the mural paintings is markedly different from the others that were previously excavated in China. The top of the tomb is painted with a sun, moon and stars chart. The walls of the tomb are painted with Zhuque (God of the South in ancient Chinese myth, shaped like a phoenix), Xuanwu (God of the

North in ancient Chinese myth, shaped like a tortoise and a snake), landscape, Gao Shi (profound scholars) and people playing music and dancing. Secondly, the predominant colour of the mural paintings is yellow, which is rarely found in the tomb mural paintings excavated in China.

Figure 1. Painting of people dancing and playing music on the east wall of the tomb.

3. Materials and Methods

The pigment samples were collected in two ways: the first method was picking the residuals and the detached layer for the least interventions on the paintings; the second method was scraping the surface of the paintings, with a very thin scalpel, from carefully selected places. The former method obtained bulk samples with the pigment layer and the ground layer together, which were 5–20 mm in width and 2–10 mm in thickness, while the latter obtained tiny pigment powders. Three to five samples were collected for each colour to ensure true representation of the pigments used.

Raman spectra were recorded on a Horiba Jobin-Yvon HR-800 micro-Raman spectrometer (Horiba scientific Co., Paris, France) equipped with an Olympus BXFM microscope (Olympus Co., Tokyo, Japan), an air-cooled CCD detector and an XY motorized stage. The 514.5 nm line from an Ar^+ laser was used as excitation source. A 50× long-working-distance objective was used to perform a 180° backward scattering configuration. The 1800 line/mm dispersive grating and 300 μm pinhole diameter resulted in a spectral resolution better than 2 cm^{-1}. The pigment samples were put on a microscope slide for Raman analysis. To avoid the laser-induced degradation of the samples, a set of neutral filters was used to decrease the laser power on samples less than 1 mW. The integral time varied from 10 s to 60 s depending on the sample, and 3 to 10 acquisitions were averaged to improve the spectral signal/noise ratio. For each sample, 3 measurements were made on different spots to obtain the signals from samples and exclude those from impurities or contaminants [14].

The micromorphology and elemental analyses were conducted using a Zeiss SIGMA 500 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) coupled with an Oxford energy-dispersive X-ray micro-analyzer (Oxford Instruments, Abingdon, UK). Pigment particles scraped from the samples were attached to a sample holder with carbon conductive tapes and then coated with gold film of about 10 nm in thickness for measurement. Observations were performed at 10 KV acceleration voltage and 136.1 μA beam current. The qualitative elemental distributions were performed in mapping modes within a squared area (20–200 μm in length depending on the homogeneity of samples), and the results were summed as the final elemental composition.

4. Results and Discussion

Micro-Raman spectroscopy has been proven to be a powerful method to identify the chemical nature of mineral pigments and the degradation products of paintings due to its advantages such as being non-destructive, having a little sample requirement, not needing special sample preparation and having high specificity and high sensitivity. But in some cases, the Raman spectra of certain samples might be obscured by fluorescence or the signal from impurities and could not give enough signal/noise ratio for identification, or the Raman spectra could not give an ambiguous identification (as in the case of yellow pigment in this study); therefore, SEM-EDS analysis was used as a supplement to confirm the identification of the key elements of the pigments. In this work, the identifications of the pigments were firstly made by comparing the measured Raman spectra with references [20–23] and our previous results. The EDS results were secondly employed to confirm or clarify the Raman identifications.

4.1. Yellow Pigment

As can be seen from Figure 1, yellow is the dominant colour in all the mural paintings. Yellow pigment was used to paint the clothes of the people, the clouds, the dragon, the tortoise, the snake, etc. The Raman spectra of five yellow pigment samples from different positions of the mural painting are shown in Figure 2. Based on the Raman spectra results, we deduced three candidate minerals, crocoite ($PbCrO_4$), vanadinite [$Pb_5(VO_4)_3Cl$] and mimetite [$Pb_5(AsO_4)_3Cl$], which were possibly used as the yellow pigments.

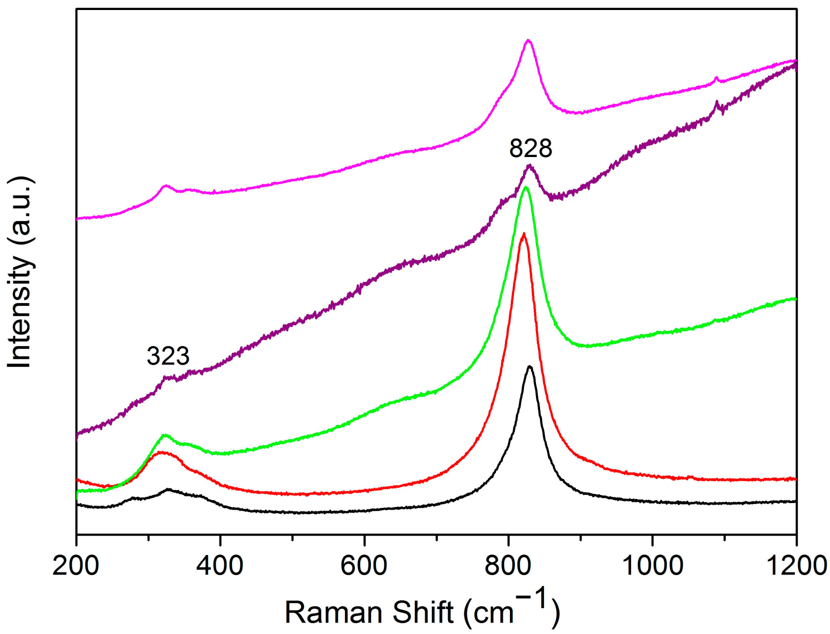

Figure 2. Raman spectra of five yellow pigment samples from different positions of the mural paintings.

Crocoite, vanadinite and mimetite are all rare secondary minerals formed in the oxidation zone of lead deposits, and often associated with other secondary minerals such as pyromorphite, cerussite, anglesite, galena, barite, etc.

Crocoite is monazite-type with a tetrahedral anion group, CrO_4. The transparent prismatic to acicular crystals display bright colours from red to reddish orange, orange and yellow. The colour is due to the O^{2-} to Cr^{6+} charge transfer within the CrO_4 group, which causes a strong absorption of the visible light in the violet–green domain [24]. Natural crocoite was likely used as a pigment before the introduction of the artificial product lead chromates ($PbCrO_4$) in 13th century in Europe [25,26]. The only report of crocoite being used as a pigment in 14th century paintings in China [27] is suspected to be a pigment imported from Europe for subsequent repairs.

Both vanadinite and mimetite belong to the apatite group with the general formula $M_5(ZO_4)_3X$, where M = Ca, Sr, Pb or Na; Z = P, As, Si or V; and X = F, OH or Cl. Vanadinite occurs as short prismatic crystals, massive granular masses and crusts with red-orange-yellow colours. Mimetite is usually found in the form of small hexagonal crystals with colours ranging from pale to bright yellow, orange, yellowish-brown and white, and are translucent to opaque. Their colours are due to the oxygen-to-metal charge transfer within the ZO_4 group, which determines a strong absorption of visible light in the violet–green domain [24]. Natural vanadinite is rare, and there are very few reports about its usage as pigment. In China, researchers reported vanadinite as the yellow pigment used on one pottery of the Terracotta Warriors of the Qin dynasty [28], in the tomb mural paintings of the Western Han dynasty [29], the Wei and Jin dynasty [30] and the Tang dynasty [31]. The descriptions of mimetite as a pigment are very scarce in the literature, and only one report can be found [30]. In other countries, there are also very few reports of vanadinite and mimetite as pigment or degradation in the literature [26,32–37]. According to the review article by Kakoulli [38], vanadinite and mimetite were found as yellow pigments on a painted grave stelai at the Louvre Museum in 1998, but it is worth noting that Gliozzo [39] stated that so far in the literature, vanadinite has not been confirmed as an intentional pigment in the review article published in 2022.

Based on the published data [40,41] and our previous works, as shown in Figure 3, the three minerals presented similar Raman spectra with two groups of characteristic Raman bands, weak multiple bands around 320 cm^{-1} and strong overlapped bands around 830 cm^{-1}. The former is attributed to the degenerate bending vibrations, and the latter is attributed to the degenerate stretching vibrations of the XO_4 (X = Cr, V, As) group.

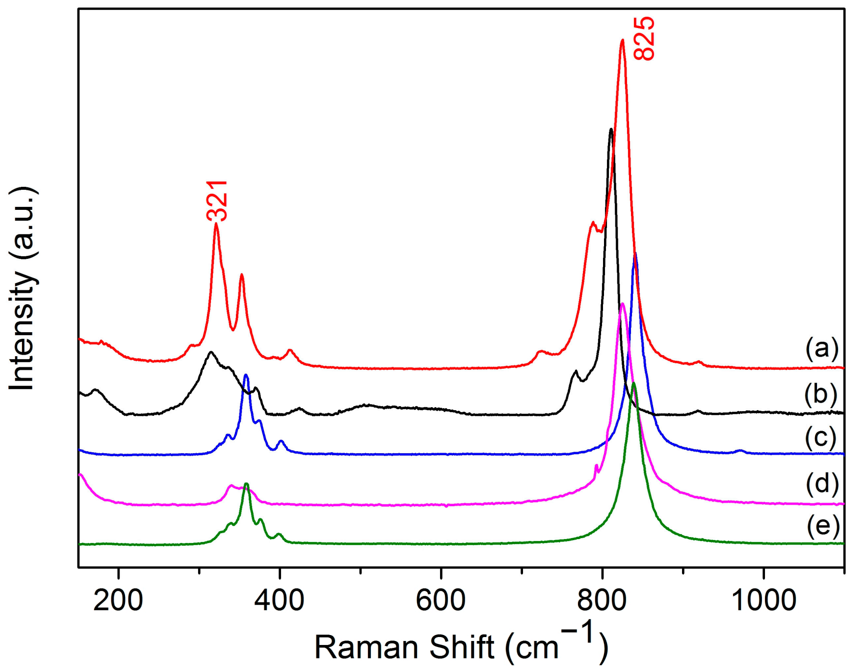

Figure 3. Raman spectra of mineral (**a**) vanadinite, (**b**) mimetite, (**c**) crocoite and synthetic pigments; (**d**) chrome yellow-orange and (**e**) chrome yellow deep.

The Raman spectra of two synthetic pigments, chrome yellow orange ($PbCrO_4{\cdot}PbO$) and chrome yellow deep ($PbCrO_4$ + $PbCrO_4{\cdot}PbO$), are also presented in Figure 3 together with the three natural minerals for comparison. Their Raman spectra are so similar that it is difficult to distinguish them. For the pure minerals, it is possible to distinguish them by the frequency difference of the Raman spectra. But for the pigments in the paintings, the spectral signal-to-noise ratio can be reduced because of the impurities or contaminations and can make it very difficult to distinguish them. Additionally, the Raman band shapes and frequencies can be changed and shifted via atomic substitutions, sample orientation and temperature variations [39]. In the RRUFF online database [23], the Raman spectra of these minerals showed considerable variations with the samples and the experimental setup. Hence, the similarities of the Raman spectra of these yellow pigments make it practically impossible to distinguish them using only the frequencies and shapes of their Raman spectra.

In order to unambiguously confirm the composition of the yellow pigment, elemental analyses of the yellow pigment samples were conducted via SEM-EDS. The SEM image of the yellow pigment (sample 6#) and the selected area (square about 10 μm) for EDS analysis are shown in Figure 4. Prismatic, granular and massive crystals can be observed in the SEM image.

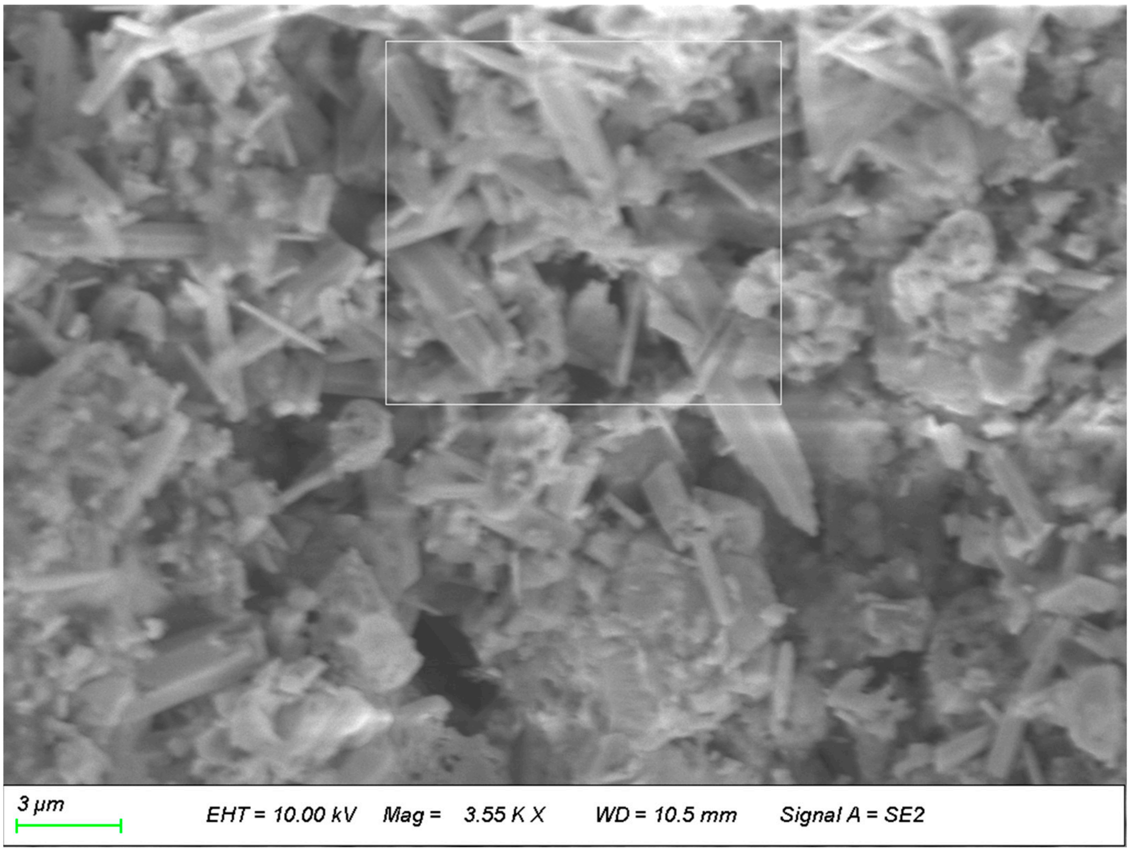

Figure 4. SEM image of the yellow pigment (sample 6#) and the selected area (the boxes) for EDS analysis.

The EDS spectrum of the yellow pigment collected from the selected area is shown in Figure 5, and the elemental analysis results of the five yellow pigment samples are summarized in Table 1. It should be noted that the elemental analysis results came from the yellow pigment, the lime-based ground layer, the carbon conductive tape and the gold coating within the selected area. So, they were just qualitative, and the element concentrations varied a lot within the selected area.

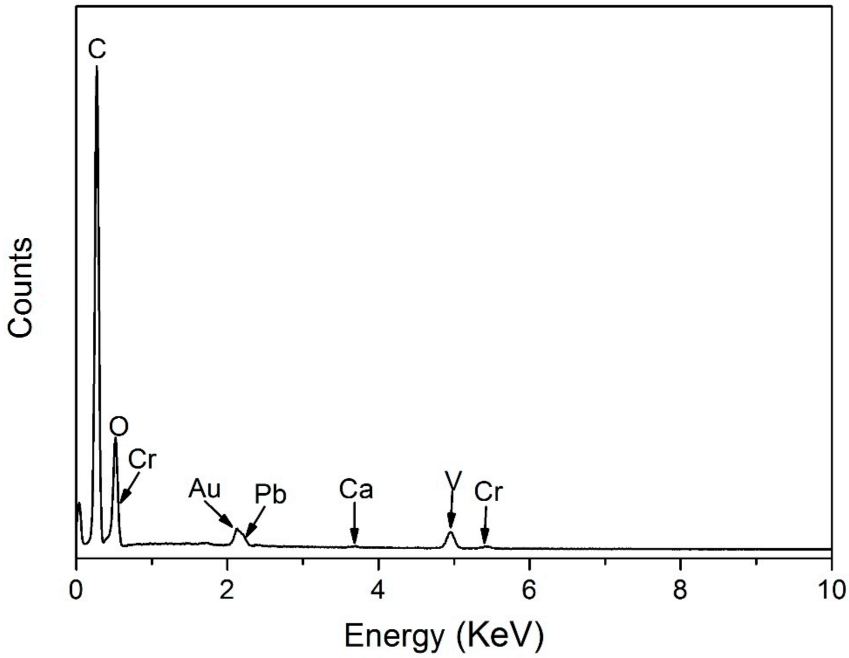

Figure 5. The EDS spectrum collected from the selected area of the yellow pigment (sample 6#).

Table 1. SEM-EDS elemental analysis results of the yellow pigment samples (Wt %).

Sample	C	V	O	Pb	Si	Ca	P	Mg	Al	Cr	Au
6#	3.94	4.31	12.27	74.00	1.44	2.17	1.11	0.36	0.39		
7#	3.01	1.00	17.2	71.62		7.17					
10# a	46.15	25.72	18.54	0.30		0.30				2.71	6.28
10# b	24.34	1.43	27.93	14.42	1.84	20.85		0.45	0.59		8.15
10# c	55.45	15.83	19.87	0.05		0.35				0.99	7.47

The presence of Pb and V in all the samples confirmed that the colourant of yellow was vanadinite and the absence of As excluded mimetite from the yellow pigment. The occasional presence of Cr indicated that crocoite possibly coexisted with vanadinite in a small amount as an associated mineral. The existence of C, O, Ca, Al, Mg, P and Si should be attributed to the mortar in the preparatory layer. Since the three samples from yellow pigment 10# were coated with gold before the SEM-EDS tests, Au occurred in the results.

The extensive use of vanadinite as a yellow pigment in this Tang dynasty tomb mural painting should be directly related to the large amounts of lead deposits in the Qinling Mountains near Xi'an city. In addition, to understand the reason why the usage of vanadinite as a yellow pigment was confined to the period between the Qin dynasty and the Tang dynasty, and why it was abandoned afterward, many works have to be conducted on ancient funeral culture, including archaeological and mineral studies.

4.2. Red Pigment

In contrast to the extensive use of red in other ancient Chinese tomb mural paintings [15,16], the use of red pigment in this mural painting is very limited. A dark red colour was used to paint the trunk of a banana tree in the east wall and to outline the border line in the west and north walls. The characteristic Raman bands at 221, 288, 406 and 610 cm^{-1} (Figure 6) indicated that haematite (Fe_2O_3) was used as a red pigment. The sharp band at 1086 cm^{-1} was due to the carbonate from the lime-based preparatory layer mixed with the sample.

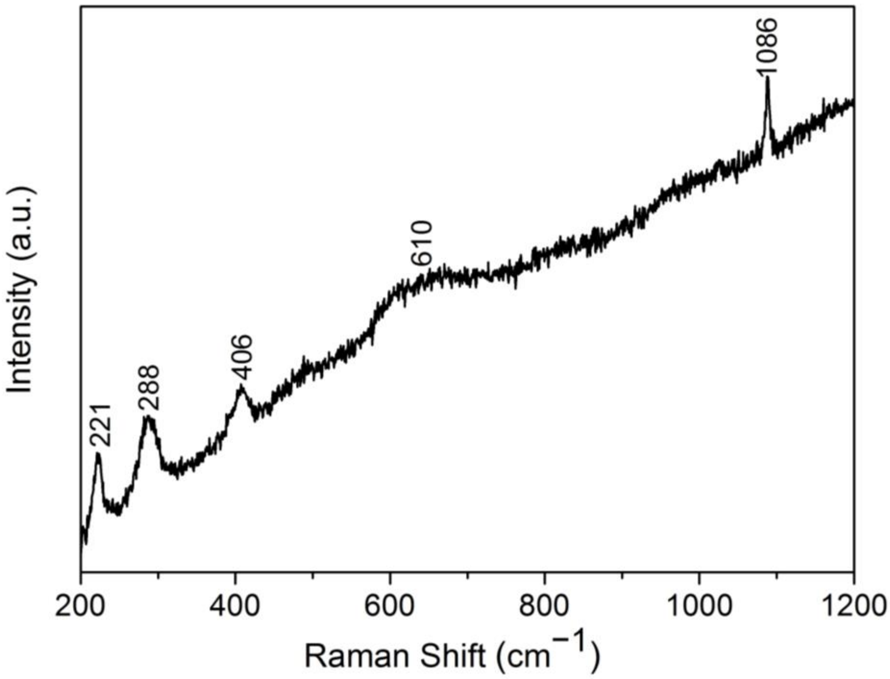

Figure 6. Raman spectra of the red pigment from the mural painting.

4.3. Green Pigment

Green pigment was used to paint the leaves of the plants in the mural paintings. One Raman spectra of the green pigment is shown in Figure 7. The green pigments are all identified as malachite [$CuCO_3$•$Cu(OH)_2$] by the characteristic Raman bands at 155, 181, 220, 270, 351, 433, 536, 720, 1059, 1098, 1368, 1496, 3310 and 3383 cm^{-1} (the last two bands are not shown in Figure 7). Malachite is a mineral that was widely used to produce green pigment with a bright green colour in ancient Chinese artworks [14].

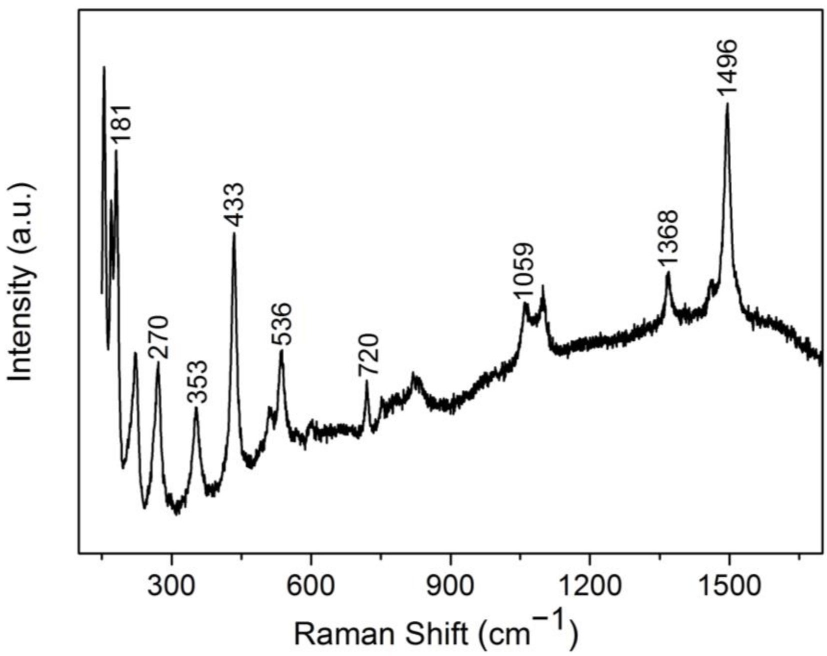

Figure 7. Raman spectra of the green pigment from the mural painting.

4.4. Black Pigment

Black pigment was used to paint the trees, the leaves and grass, mountains and human hairs and to outline the sketches. The Raman spectra of the black pigment (Figure 8) showed two broad bands around 1400 and 1602 cm^{-1}, which were assigned as the D and G bands of amorphous carbon. So, this black pigment is the Chinese ink that is widely used in ancient Chinese artworks.

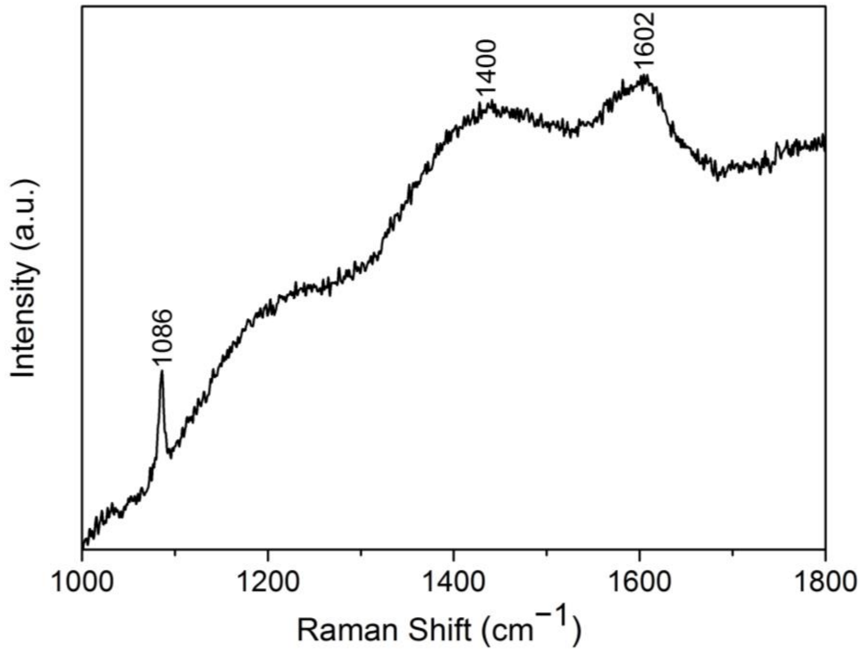

Figure 8. Raman spectra of the black pigment from the mural painting.

The SEM-EDS results of the other pigments further confirmed the identification via the Raman spectra with the key elements Fe for red, Cu for green and C for black pigment, as shown in Table 2.

Table 2. SEM-EDS elemental analysis results of the other pigment samples (Wt %).

Sample	C	O	Cu	Fe	Ca	Pb	Si	Mg	Al	K	Au
Red	24.57	27.83		14.71	10.85	5.90	3.75	0.27	3.23	0.64	8.24
Green	8.55	30.04	38.7		2.67	2.98	1.52		1.57	0.34	13.63
Black	28.75	35.50			28.18		1.36	0.61	0.37		5.23

5. Concluding Remarks

A tomb mural painting of the Tang dynasty (618–907 CE) was analyzed by means of micro-Raman and SEM-EDS analyses. It is the first excavation of a tomb mural painting that is dominated by the colour yellow. The use of natural mineral vanadinite as yellow pigment was confirmed using a combination of micro-Raman and SEM-EDS analyses. Hematite, malachite and carbon black were identified as other pigments in the mural paintings. We attribute the employment of vanadinite to the accessible mine resource and the owner's high social status. Meanwhile, more excavation cases are necessary to understand the extensive use of yellow and the use of this rare pigment in the Tang dynasty around ancient Chang'an city. Furthermore, the possible existence of other lead-based minerals and degradation products should be studied on more samples.

Micro-Raman spectroscopy has been proven to be an effective method for the identification of mineral pigments that are present in low quantities in paintings. Meanwhile, the combination of Raman spectroscopy and other complementary analytical technologies such as SEM-EDS, which can provide the most information on the least amount of samples, is indispensable to reach unambiguous assignments, especially in the case of distinguishing yellow mineral pigments as crocoite, vanadinite and mimetite.

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Conflicts of Interest: The authors declare no conflict of interest.

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