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Micro-Raman analysis of the pigments on painted pottery figurines from two tombs of the Northern Wei Dynasty in Luoyang

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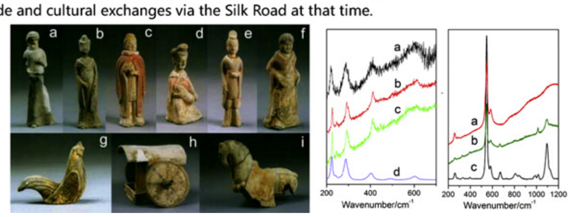
HIGHLIGHTS

- The pigments on the painted pottery figurines were identified by Raman microscopy.
- Pottery figurines of two tombs used similar pigments despite the style difference.
- Pigment lapis lazuli and pottery figurine of Sogdians are of great significance.

GRAPHICAL ABSTRACT

Pigments on the painted pottery figurines from two tombs of Northern Wei Dynasty were analyzed by Raman microscopy. All the pigments were identified. For the first time, lapis lazuli was found as blue pigment on painted pottery figurines. The discovery of this pigment and the pottery figurine of Sogdians revealed significant information about the trade and cultural exchanges via the Silk Road at that time.



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ABSTRACT

The pigments on the painted pottery figurines from two tombs of Northern Wei Dynasty (AD 386-534) in Luoyang were analyzed by Raman microscopy. All the pigments were identified compared with the Raman spectra of standard pigments. The red pigments were identified as haematite, the blue pigment as lapis lazuli, the green pigment as malachite, the black pigment as carbon black and the white pigment as calcite. Similar pigments were used in the two tombs despite the pottery figurines were very different in artistic style. The use of lapis lazuli as blue pigment on Chinese painted pottery figurines was found for the first time. This pigment and the painted pottery figurine of Sogdians are of great archaeological significance because it demonstrated that the trade and cultural exchanges via the Silk Road had extended to Luoyang city in the Northern Wei Dynasty. The result also confirms that micro-Raman spectroscopy is a powerful analytical method for the identification of pigments on ancient artworks.

Introduction

Ancient Chinese tombs were prevalently decorated with mural paintings and painted pottery figurines. The custom using painted pottery figurines as burial artifact started from the Warring States period, reached the climax by the Terracotta Army of China's first Emperor Qin-Shi-Huang and ended by the late Ming Dynasty.

Luoyang, known as the capital by 13 dynasties starting from the Xia Dynasty (21st-16th century BC), is regarded as the central zone of the birth and development of Chinese civilization. In the archaeological excavations recent years, a large amount of mural paintings and painted pottery figurines were unearthed in Luoyang. These cultural relics were of vital importance to the study of the politics, military, culture and custom of that era. The research results can help us to understand the ancient Chinese burial culture and Chinese art history and offer much information for the preservation and restoration.

Pigment is a key constituent of the ancient artworks. In the past decades, Raman spectroscopy has been increasingly used by many researchers to study the pigments on ancient artworks [1–8]. This is chiefly because that Raman analysis is nondestructive and can be carried in situ without sample preparation. Recently, aided by the

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Luoyang Ancient Tombs Museum, a project was launched to make a systematic study of the pigments on the artworks unearthed in Luoyang. This paper is devoted to the identification of the pigments on the painted pottery figurines from two tombs of the Northern Wei Dynasty (AD 386-534). The usage of pigments and its archaeological significance were also discussed.

Experimental

Samples

The painted pottery figurines studied were excavated from two adjacent tombs located at the north bank of the Yellow River near Luoyang [the location of the tombs on the map can be found in Fig. S1 (Supporting Information)]. According to the epitaphs, the two tombs both belong to the Northern Wei Dynasty and the owners buried in are father–son relationship. The father, Lv-Da, official as "Wei-Yuan General" and "Ji-She General", died in Zheng-Guang fifth year (AD 524) of Emperor Xiao-Ming. The son, Lv-Ren, as "Ning-Yuan General", died in Pu-Tai second year (AD 532) of Emperor Jie-Min. Thirty painted pottery figurines were excavated from the former, including 24 human figurines, one tomb-guarding beast figurine and five animal figurines. Thirty-nine painted pottery figurines were excavated from the latter, including 23 human figurines, 11 animal figurines and five living utensil figurines. Some of the painted pottery figurines are shown in Fig. 1. More photos of the painted pottery figurines are presented in Fig. S2 (Supporting Information).

Raman measurement

The Raman spectra were recorded on a Horiba Jobin–Yvon HR-800 micro-Raman spectrophotometer equipped with an air-cooled CCD detector and an 1800 groove/mm dispersive grating. A 50× long working distance objective was used to perform an 180° backward scattering configuration and the pinhole diameter was set at 300 μm. The excitation source was the 514.5 nm line of an Ar^+ laser.

The Olympus BXFM microscope without bottom frame can offer a large free space under the objective turret. Thus, the pottery figurines sized about 40 cm can be placed on a sample holder with XY motorized stage. Laser focus can be achieved by adjusting the height of the microscope objectives instead of the sample stage.

Considering the tiny laser spot and the mixture nature of the pigment, several measurements had to be made around each acquisition spot to get the signals from pigments and exclude the signals from the impurities or contaminants on the surface. To avoid any possible photo-induced degradation of the pigment samples during the measuring process, a set of neutral filters was employed to decrease the laser power on sample less than 1 mW. The integral time was prolonged to 60 s and 10 acquisitions were averaged in order to improve the spectral signal–noise ratio. Over fifty spectra were recorded from pigments on different pottery figurines.

Results and discussion

According to the historical materials excavated from the year-numbering tombs of Northern Wei Dynasty in Luoyang, after the capital was moved to Luoyang from Pingcheng in AD 494, the period between Northern Wei Xiao-Ming emperor (AD 516) and Eastern Wei Xiao-Jing emperor (AD 534), was the transformation period of the artistic styles of burial pottery, especially the pottery figurines. This was also proved by the present work. In general, the artistic styles of the pottery figurines from two tombs differed considerably though they were only eight years apart. Most of the human figurines from Lv-Da's tomb were produced with only a face mold. The backs of the human figurines were flat and the color decorations were relatively simple. In stark contrast, the human and animal figurines from Lv-Ren's tomb were molded and the living utensil figurines were wheel-turned. The artistic style was more realistic and the color decorations were relatively rich and bright. This can be seen from the front and side views of them in Fig. S3 (Supporting Information).

We made a comparative Raman study on the pigments from the two tombs. The result showed that the painted pottery figurines used similar pigments despite their style difference.

Red pigment

Red is the most common color painted on the pottery figurines from both tombs. All the Raman spectra recorded showed similar characteristics except small frequency shift and different fluorescence background. Fig. 2 shows the Raman spectra of the red pigment on the pottery figurines and haematite (α-Fe_2O_3). It is evident that haematite were used as red pigment.

Fig. 1. Some of the painted pottery figurines: (a, e and h) from Lv-Da's tomb; (b–d, f, g and i) from Lv-Ren's tomb.

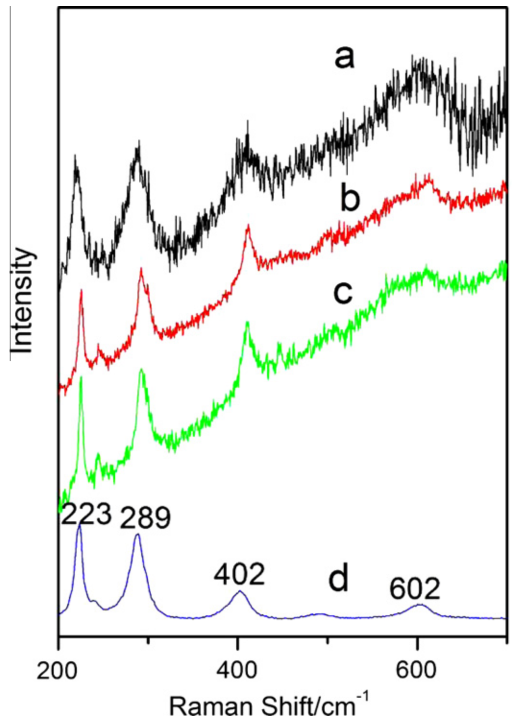

Fig. 2. Raman spectra of the red pigment from (a) the overcoat of a civil officer figurine from Lv-Da's tomb, (b) the fur coat of a male figurine from Lv-Ren's tomb, (c) the skirt of a dancing female figurine from Lv-Ren's tomb and (d) haematite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cinnabar (HgS) and minium (Pb_3O_4) were frequently used as red pigment in ancient Chinese artworks [3,5]. In Ref. [3], Zuo et al. reported the use of cinnabar as red pigment on painted pottery figurines of Han Dynasty (BC 208-AD 220). But they were not found in these of Northern Wei Dynasty.

Blue pigment

Bright blue pigments appeared on seven pottery figurines and can be easily identified as lapis lazuli by their Raman spectra. Fig. 3 shows some of the Raman spectra of the blue pigment on the pottery figurines and lapis lazuli.

Ancient Chinese held the color blue in very high regard because it's the color of heaven. Blue pigments, such as azurite, lapis lazuli and Han blue, were frequently used in mural painting and building decoration [9–11]. But there were hitherto very few report about blue color on painted pottery figurines. Zuo et al. reported azurite as blue pigment on painted pottery figurines of Han Dynasty [3]. FitzHugh reported Han blue, an early man-made blue pigment, on painted pottery figurines of Han Dynasty [12]. This work is the first time that lapis lazuli was found as blue pigment on ancient Chinese painted pottery figurines up to our knowledge.

Lapis lazuli is a rare and expensive pigment extracted from the blue mineral lazurite $[(Na, Ca)_{4-8}(AlSiO_4)_6\ (SO_4, S, Cl)_{1-2}]$. Few countries, such as Afghanistan and Russian, own their lazurite mineral deposit while no mineral deposit have been found in China up to now. It was only after 1828 that the artificial form of this pigment, ultramarine, was synthesized in Europe. Lapis lazuli was reported to be used as blue pigment on the mural paintings of Dunhuang Mogao grottoes [9,10] and Bingling Temple grottoes [9]. The researchers demonstrated that they originated from Afghanistan and exported to China through the trading via the Silk Road. Hence, we believe that, the pigment lapis lazuli and the

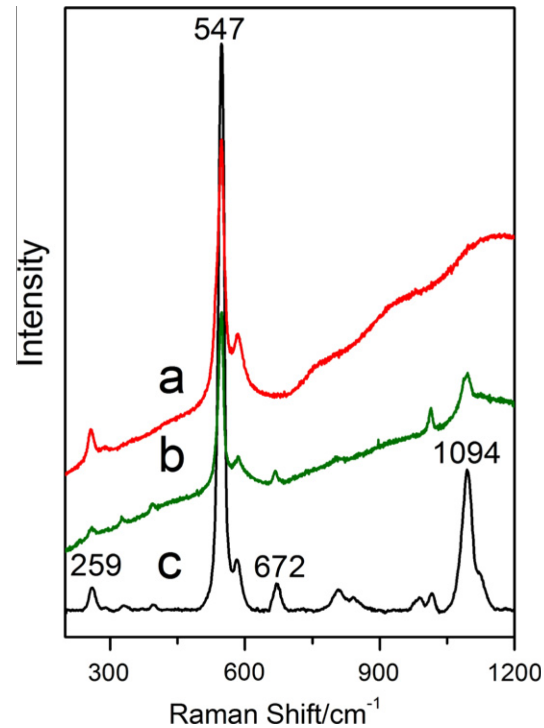

Fig. 3. Raman spectra of the blue pigment from (a) the jacket of a pottery figurine of Sogdians from Lv-Da's tomb, (b) the neck of a horse figurine from Lv-Ren's tomb and (c) lapis lazuli.

painted pottery figurine of Sogdians (Hu man) excavated from the Northern Wei Dynasty tombs are of great significance to the study of the East–West trade and cultural exchanges via the Silk Road at that time. Preliminarily, it proved that the eastern terminal of the Silk Road had extended to Luoyang after the Northern Wei Dynasty moved its capital to Luoyang in AD 493.

Green pigment

Green pigment only appeared on the coat and trousers of a civil official pottery figurine from Lv-Da's tomb. Fig. 4 shows the Raman

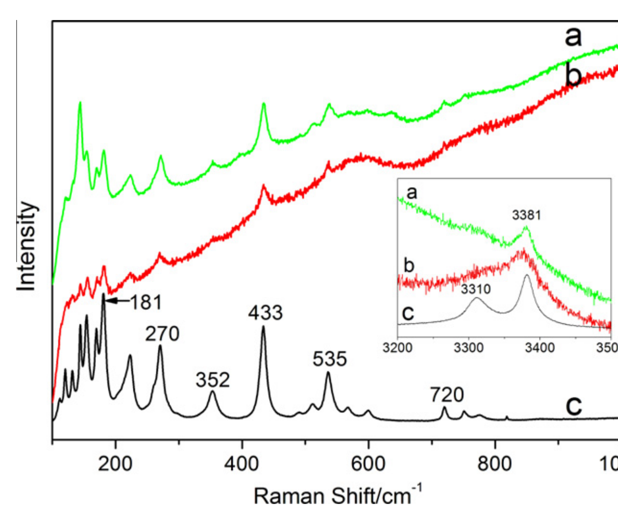

Fig. 4. Raman spectra of the green pigment from (a) the coat, (b) the trousers of a civil official pottery figurine from Lv-Ren's tomb and (c) malachite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

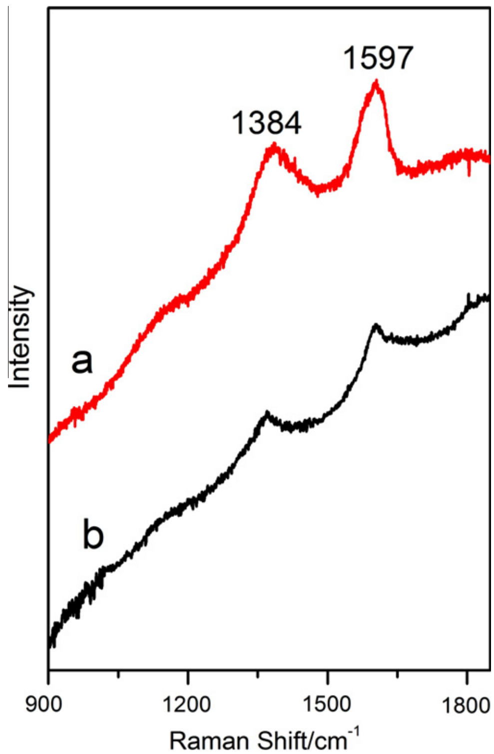

Fig. 5. Raman spectra of the black pigment from (a) the oxcart wheel spoke from Lv-Da's tomb and (b) the wing of a cock pottery figurine from Lv-Ren's tomb.

spectra of the green pigment and malachite [$CuCO_3 \cdot Cu(OH)_2$]. Obviously, the color green was painted with malachite. Malachite has a bright green color as the peacock feather and was reported to be used as green pigment on the mural paintings of Dunhuang Mogao grottoes [11] and Kizil grottoes [13]. The reason remained unknown that malachite was so less used in these two tombs. Perhaps it is for lack of the mineral deposit nearby at that era.

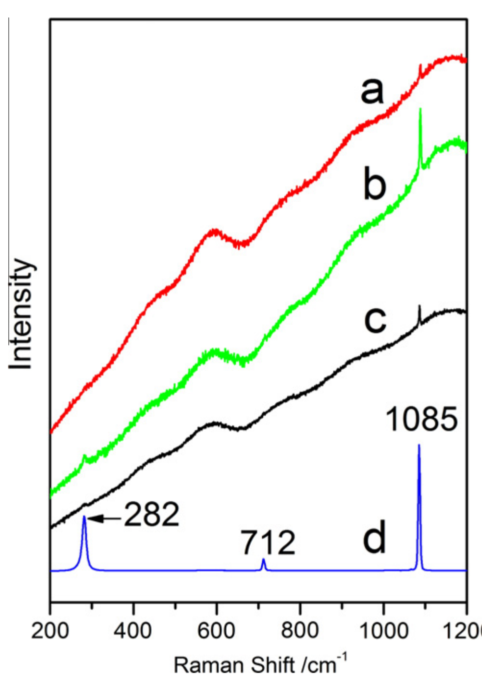

Fig. 6. Raman spectra of the white pigment from (a) the oxcart wheel from Lv-Da's tomb, (b) the skirt of a dancing female pottery figurine from Lv-Ren's tomb, (c) the underclothes of a male figurine from Lv-Ren's tomb and (d) calcite.

Black pigment

Black pigment appeared on several pottery figurines. Fig. 5 shows two Raman spectra of the black pigment. They can be easily identified as amorphous carbon black for the broad *D* band around 1384 cm^{-1} and *G* band around 1597 cm^{-1}. Carbon black used as black pigment usually came from the incomplete combustion products of organic material such as plants, oil and bones in ancient China. In Ref. [3], Zuo et al. confirmed a soot (carbon black, product of the burning of organic matter) origin of the black pigment based on the positions and half-widths of the *D* and *G* bands. In Ref. [14], Parras et al. excluded, not totally, the bone origination of the black pigment for the absence of the *P–O* stretching band at 960 cm^{-1}, which is the characteristic band of phosphate from bones [15,16]. Hence, the black pigment here should probably originate from charcoal, soot or lampblack.

White pigment

White pigment appeared on many pottery figurines. Fig. 6 shows the Raman spectra of white pigment and calcite for comparison. The characteristic bands at 281, 712 and 1086 cm^{-1} revealed the calcite nature of the white pigment. Calcite was widely used as white pigment and supporting layer and came from slaked lime in ancient China.

Conclusion

Pigments on the painted pottery figurines from two Northern Wei Dynasty tombs were analyzed by micro-Raman spectroscopy. All the pigments were identified comparing with the Raman spectra of standard pigments. Although the artistic types differed greatly, the painted pottery figurines from two tombs used similar pigments. For the first time, lapis lazuli was found as blue pigment on burial painted pottery figurines. This pigment and the painted pottery figurine of Sogdians demonstrated that the trade and cultural exchanges via the Silk Road had extended to Luoyang city in the Northern Wei Dynasty. The result confirms that micro-Raman spectroscopy is a powerful analytical method for the identification of pigments in ancient artworks and will be useful to art historians, restorers and conservators studying or working on them.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.02.015.

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