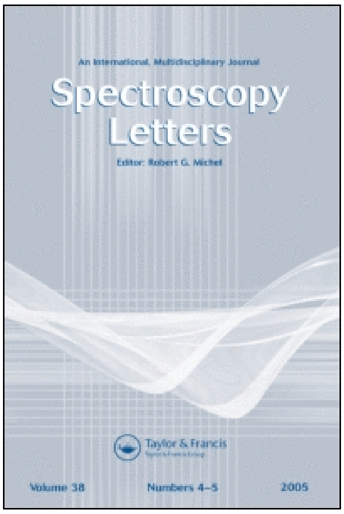

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Non-Destructive *In-Situ* Study of White and Black Coating on Painted Pottery Sherds From Bancun Site (Henan, China) by Raman Microscopy

Zuo Jian[a]; Wang Changsui[a]; Xu Cunyi[a]
[a] Structure Research Laboratory, University of Science and Technology of China, Anhui, P R China

To cite this Article Jian, Zuo , Changsui, Wang and Cunyi, Xu(1998) 'Non-Destructive *In-Situ* Study of White and Black Coating on Painted Pottery Sherds From Bancun Site (Henan, China) by Raman Microscopy', Spectroscopy Letters, 31: 7, 1431 — 1440

To link to this Article: DOI: 10.1080/00387019808001650

URL: http://dx.doi.org/10.1080/00387019808001650

SPECTROSCOPY LETTERS, 31(7), 1431-1440 (1998)

NON-DESTRUCTIVE *IN-SITU* STUDY OF WHITE AND BLACK COATING ON PAINTED POTTERY SHERDS FROM BANCUN SITE (HENAN, CHINA) BY RAMAN MICROSCOPY

Key Words : Raman Spectra, Ancient Painted pottery, Pigment

Zuo Jian Wang Changsui Xu Cunyi

Structure Research Laboratory
University of Science and Technology of China, Academia Sinica
Hefei, Anhui, 230026, P R China

ABSTRACT

Pottery sherds from the archaeological site of Bancun (Henan,China) were analyzed by Raman microscopy and the pigments used in the coating of this ancient (*c*. 4000-5000 BC) pottery were determined . It was found that bauxite was used to make the white pigment. The black coating was identified as a magnetite and its particle size was in the nanometer range.

This work also showed that the size of pigment had influence on the color of the coating. In principle, Raman spectra could be used not only to identify the mineral source of the pigment but also to estimate the particle size of the pigments.

INTRODUCTION

In 1991, Professor Yu Weichao , the director of Chinese History Museum, organized and led a synthetically archaeological research into the Bancun Site of Mianchi, Henan Province for the purpose of probing new methods of Chinese archaeology. Bordering on Yangshao village, the Bancun Site is a typical site of the Yangshao Cultural , which is world-famous, especially for its art and technology of ancient painted pottery. For many years, people have paid special attention to ancient painted pottery, mainly to its form and artistic style. The invention, spread and mutual influence of the technology of Yangshao painted pottery is extremely complex and important for archaeological research. Obviously, pottery coating is the key to inquire into these problems. The raw material and technology of the coatings is more complex than that of the pottery body. So it has obvious archaeological meaning to seek the mineral origin of pottery's coating.

Raman spectroscopy is known as a convenient nondestructive tool to characterize materials. It has been reported that Raman microscopy is the analytical procedure which is most exact, sensitive, spatially resolution for the *in situ* analysis of inorganic pigment on pottery, manuscripts, and paintings. Many papers have been published on its use in this field[1-5] . In this work, five painted pottery sherds from the Bancun Site (henan, China) were analyzed by Raman Microscopy. This study was devoted to identification of the white and black coating on the sherds and demonstration of the mineral source of the pigments.

EXPERIMENTAL AND RESULTS

The specimens to be studied were three black coating sherds (sample A, B and C) and two white coating sherds (sample D and E). All of the samples were analyzed, nondestructively and *in situ*, by Raman microscopy. A Raman microscopy coupled to a Spex 1403 Monochromator was used and 514.5nm radiation from a argon ion laser was used for excitation and the laser power at the sample was about 80 mw.

Figure 1 shows the Raman spectra of the black coating on painted pottery (sample A、 B and C) and natural magnetite standard. From Figure 1, we can see that the features of the Raman spectra of the black coating are similar to those of natural magnetite standard, but there are some differences about the position and width of the peaks . Compared with natural magnetite standard, the peak at 654 cm^{-1} of the sample C is red shifted by about 19 cm^{-1} and the full width at half - maximum is broadening by 24 cm^{-1}. The shifting and broadening of the Raman spectra can be due to the particle size effect. It was confirmed that particle size effects can produce large shifting and broadening of Raman spectra in some nanometer materials[6-9]. When the particle size is smaller, the shifting and broadening will get larger, this can be explained by a phonon confinement effect[9,10]. The phonon confinement model is based upon the fact that, in an infinite crystal, only phonons near the center of the Brillouin zone (q ~ 0) contribute to the Raman spectrum

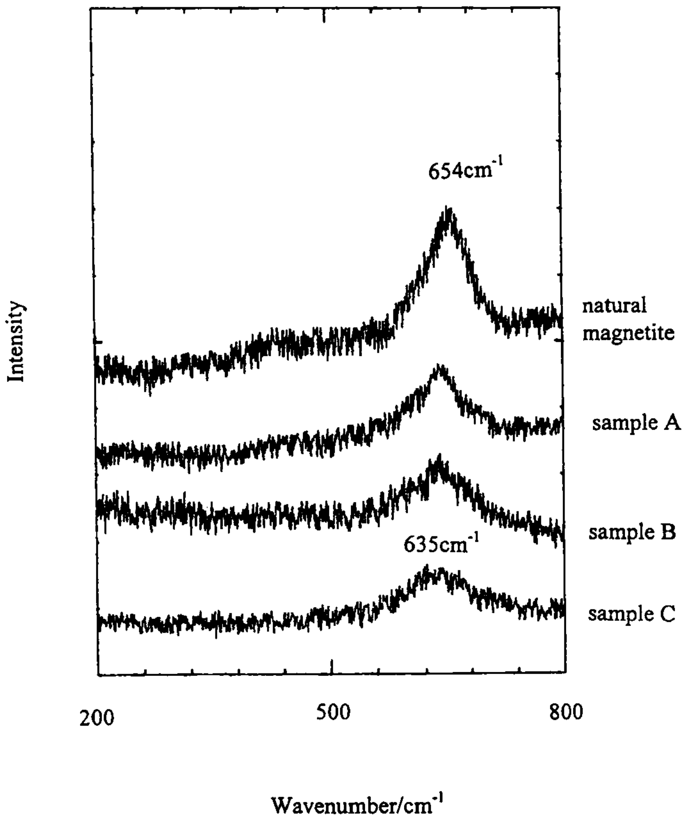

FIG. 1 The Raman spectra of the black coating on painted pottery (sample A 、 B and C) and natural magnetite standard.

because of the momentum conservation between phonons and incident light. On the other hand, in a finite crystal, phonons can be confined in space by crystal boundaries or defects. This results in uncertainty in the phonon momentum, allowing phonons with $q \neq 0$ to contribute to the Raman spectrum. G.W. Graham[8] studied the Raman spectra of nanometer ceria in automotive exhaust-gas catalysts and showed that Raman spectra is relatively simpler and easier for determination of particle sizes in comparison with TEM (transmission electron microscopy) and XRD (X-ray diffraction) methods. With this in mind, a small part of black coating was removed for XRD and TEM measurements. X-ray diffraction was carried out on Japanese Rigaku D/max-rA rotating target X-ray diffractometer With Cu Kα radiation, 40KV tube voltage and 100mA tube current. Transmission electron microscopy observation was performed by use of a Hitachi H-800 TEM. The results of XRD and TEM showed that the black coating was magnetite and the particle sizes of sample C and A were about 25nm and 60nm respectively. Accompanying the changes in the peak position and width of the Raman spectra, the optical properties and Raman scattering intensity of the black coating also showed change with the particle size decreased. The color of sample C is darker than that of sample A and the Raman scattering intensity of sample C is also weaker than that of sample A . This means that the color of the coating depends not only on the pigment composition but also on the its particle size.

Figure 2 shows the Raman spectra of the white coating on painted pottery and a natural bauxite standard. It can be seen that the Raman spectra of the white coating are in agreement with bauxite standard, only a small peak at 446cm^{-1} got blue shift. Compared with the natural bauxite, the peak at 446cm^{-1} of sample D and E were blue shifted by about 16 cm^{-1}. We also got some powder from sample D and E for XRD measurement. The results of XRD confirmed that the white coating was bauxite. It's not very clear that what cause the Raman peak at 446cm^{-1} got blue shift. There is plenty of bauxite in the north of Henan province. It seems that the raw materials made the white coating were chosen from local site. Before this work, people thought that the pigments of white coating were just Carbonate, Sulphate, Kaolin etc.[1].

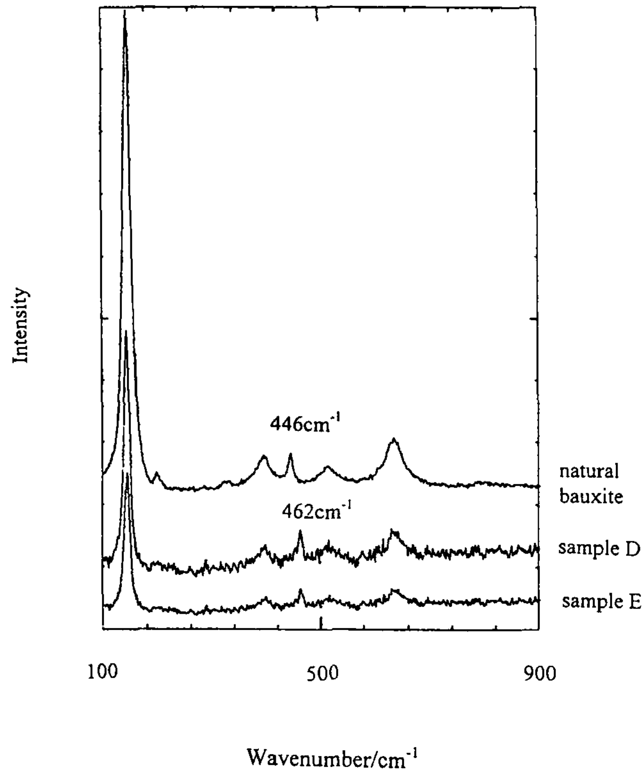

FIG. 2 The Raman spectra of the white coating on painted pottery (sample D and E) and a natural bauxite standard.

CONCLUSION

The work described here confirms that Raman microscopy is very effective to determine the pigments used in painted pottery. Bauxite has been demonstrated to be the mineral source of the white coating on the pottery. The black coating was identified as a magnetite and its particle size was in the nanometer range. Our work showed that the size of pigment has influence on the color of the coating. In principle, Raman spectra could be used not only to identify the mineral source of the pigments but also to estimate the particle size of the pigments.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China, No.29775023. The authors would like to thank the Chinese History Museum, Bancun Synthetically Archaeology team for supplying the samples.

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Date Received: April 9, 1998
Date Accepted: June 29, 1998