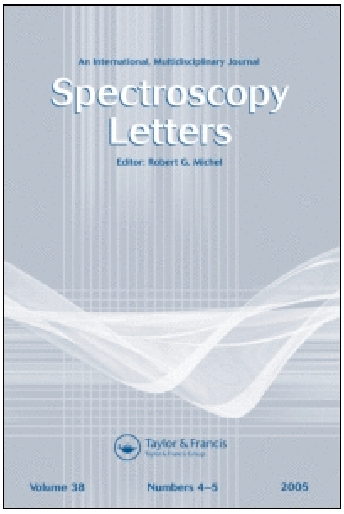

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Raman Microscopy Study of the Pigments on the Ancient Wall Painting from the Large Grave in Wanzhang (Hebel, China)

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RAMAN MICROSCOPY STUDY OF THE PIGMENTS ON THE ANCIENT WALL PAINTING FROM THE LARGE GRAVE IN WANZHANG (HEBEL, CHINA)

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abstract

Fragments of the ancient wall painting (*c.* 550 - 580 AD) from the archaeological site of Wanzhang (Heibei, China) were analyzed by Raman Microscopy. The pigments with different colors were identified by Raman Microscopy, which are respectively cinnabar, goethite, carbon black and calcite doped with other metal atoms.

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INTRODUCTION

The scientific examination of the pigments used in archaeological findings such as wall paintings, have been proven to be important in revealing information for the characterization, restoration and preservation concerns. They provide information that is useful in the evaluation of cultural and economic features of earlier civilizations and can be used to build up an overview of the artistic materials and methods.

Analysis of archaeological objects by Raman spectroscopy is a rapidly developing field. The Raman microscopy is recognized to be a very important non-destructive analytical technique for the *in situ* characterization of pigments in works of art [1-3]. In this work, two pieces of fragments of the ancient wall painting from the Large Grave in Wanzhang (Hebei, China) were analyzed, non- destructive and *in situ*, by Raman microscopy and a small part of pale blue pigment was removed for X- ray fluorescence (XRF) spectroscopy analyzation. This study was devoted to identification of the pigments used on this ancient wall painting.

ARCHAEOLOGICAL BACKGROUND

The wall painting in graves are very brilliant and plentiful with distinctive local features, especially those excavated from Hebei province. The fragments of wall painting from the Large Grave in Wanzhang (Heibei, China) were analyzed . This tomb lies in the south of Cixian (a county in Hebei), where the graveyard of imperial families and nobles of the Dongwei Beiqi Dynasty are found. It is inferred that this is the tomb of the Beiqi Wenxuan emperor - Gao yang[4]. The tomb is composed of the aisle leading to the coffin chamber and the coffin chamber. All of these were decorated with wall painting, but now only the frescoes on the aisle were preserved entirely. The aisle is 37 meters in length, 3.62 to 3.88 meters in width , 0.36 to 0.42 meters in height at the end of the south and 8.86 meters in height at the end of the north. Lime plaster was used as the ground coating, then the artist drew on it. The wall paintings of Wanzhang are in plentiful colors showing superb skill and workmanship.

EXPERIMENT AND RESULTS

The specimens to be studied were two fragments of the frescoes with four kinds of colors. These pigments on the wall painting were analyzed, non-destructively and *in situ*, by Raman microscopy separately. A Raman microscopy coupled to Spex-1403 monochromator was used and 514.5 nm radiation from an argon ion laser was used for excitation and the laser power at sample was about 40 - 100 mw. A small part of the pale blue pigment was removed for X- ray fluorescence spectrum measurements. X- ray fluorescence spectrum was tested using a Japan Shimaoku VF320 X-ray Fluorescence Spectrometer, with analyzing crystals as LiF, Ge, PET, and TAP, the detector was a Scintillation Counter Tube (S.C.) and a gas flow type Proportional Counter Tube, tube voltage and tube current were 40KV and 40mA respectively.

1. Analysis of Red Pigment

Raman spectrum for the red pigment of the wall painting was recorded between Raman shifts of 100 to 500 cm^{-1} , which yielded three significant peaks at 252, 284 and 343 cm^{-1} (Fig. 1a). It is in good agreement with natural cinnabar standard (Fig. 1b). R.J.H. Clark had done some research on ancient chinese manuscripts, eight paper fragments with a trace of red ink and one textile sample with red pigmentation were analyzed by Raman microscopy. Cinnabar was unambiguously identified on the four paper samples with red calligraphy and on the textile fragment with red pigmentation. Clark thinks that cinnabar was the most important component of red ink in pre - tenth century China [5]. Our work further supports this conclusion and shows that cinnabar could be used not only to make red ink for writing manuscripts, but also to make red pigment for wall painting .

2. The Discovery of Goethite in Yellow Pigment

The Raman spectrum of the yellow pigment, between 100 cm^{-1} and 600 cm^{-1}, was recorded. There are three significant peaks at 214, 277and 390 cm^{-1} (Fig. 2). Figure 2 (a) shows the Raman spectrum of the yellow pigment and figure 2 (b) shows the Raman spectrum of natural goethite standard. It can be seen that the Raman spectrum of the yellow pigment is in good agreement with that of natural goethite standard. This confirmed the presence of goethite in yellow pigment.

3. Analysis of black pigment

Figure 3 shows the Raman spectrum of the black pigment. Under Raman microscopy analysis, the sample showed peak at 1350 and 1600 cm^{-1} indicating that the pigment used was the carbon material[6]. The fundamental and most frequently cited work concerning the application of Raman spectroscopy investigation of different carbon materials is that of Tuinstra and Koenig[7,8]. These researchers have

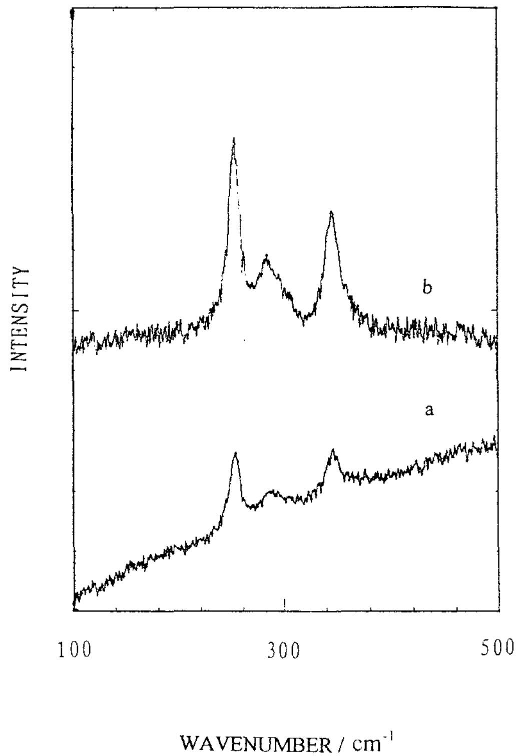

Fig.1 (a) The Raman spectrum of the red pigment on ancient wall painting.
(b) The Raman spectrum of the natural cinnabar standard.

shown that the main line of the first order Raman scattering of a graphite single crystal appears at 1575 cm^{-1} . This line is usually called the G - line. The appearance of this line is ascribed to normal vibrations of carbon atoms in a graphite plane assigned to the E_{2g} symmetry mode. In addition to the G - line of graphite materials, there is also a line in the Raman spectra at 1350 cm^{-1} which is often called the D - line in literature. Comparing the Raman spectrum of the black

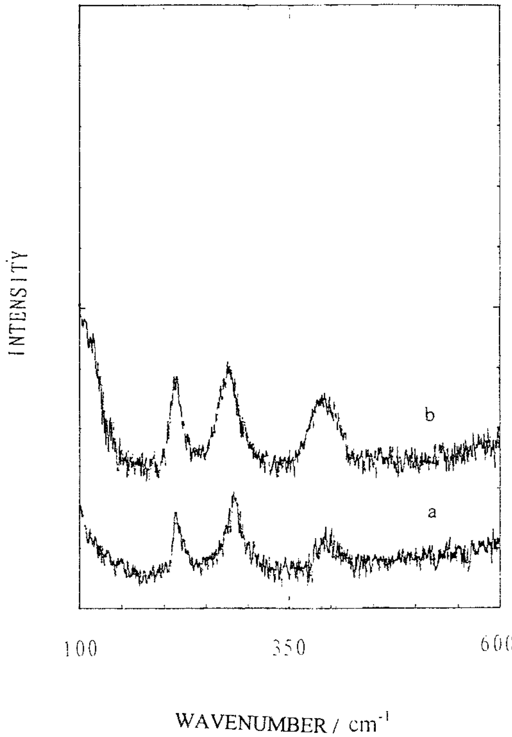

Fig.2 (a) The Raman spectrum of the yellow pigment on ancient wall painting.
(b) The Raman spectrum of the natural goethite standard.

pigment with that of graphite crystal, the half - width of both the D - line and the G - line increased and the G - line got blue shifting to 1600cm^{-1} . The broadening and blue shifting of Raman peaks were due to the structural disorder and defects[6]. So it can be confirmed that the black pigment was the graphite with some structural disorder and defects in the lattice. The carbon material used for pigment, commonly known as carbon black, has a long history of use.

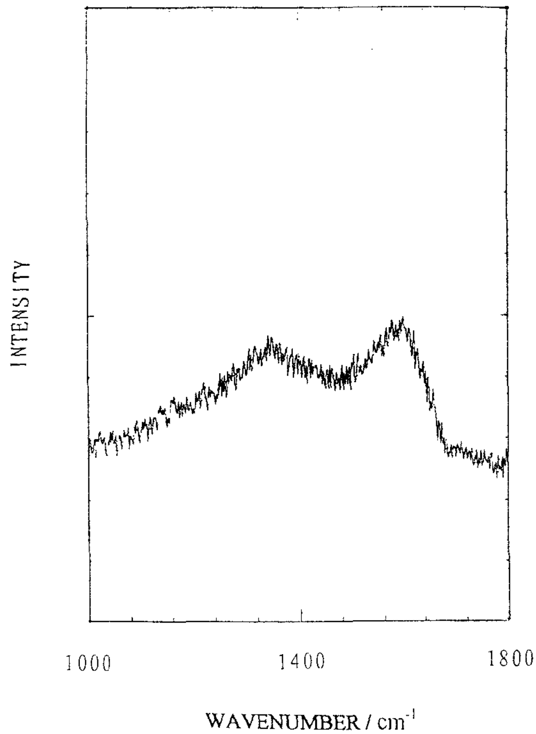

Fig.3 The Raman spectrum of the black pigment on ancient wall painting.

4. Analysis of a pale blue pigment

Figure 4 (a) shows the Raman spectrum of the pale blue pigment, which yielded a spectrum with peaks at 155, 281, 711, and 1085 cm^{-1}. Figure 4 (b) shows the Raman spectrum of the ground coating. From Figure 4 it can be seen that the Raman peak position of the pale blue pigment and ground coating are in very good agreement with that of calcite(9), only the two peaks of the pale blue pigment at 155 and 281 cm^{-1} are broadened. Compared with the ground coating, the full width at

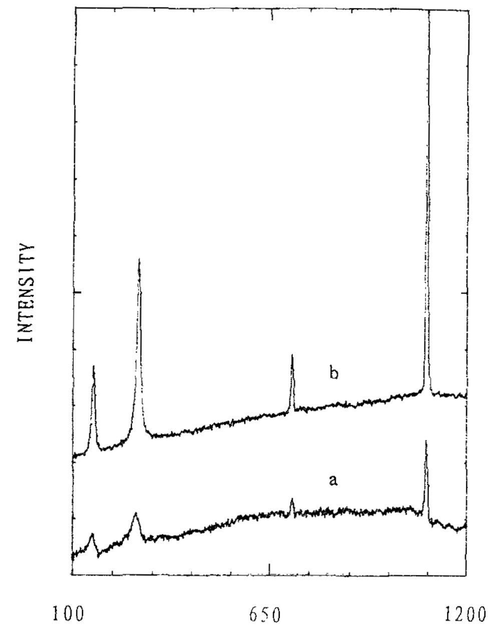

Fig.4 (a) The Raman spectrum of the pale blue pigment on ancient wall painting.
(b) The Raman spectrum of the ground coating.

half - maximum of the peaks at 155 and 281 cm^{-1} are broadened by about 12 cm^{-1} . The normal modes of the calcite structure were derived by the correlation method[10]. The low- frequency vibrations at 155 and 281 cm^{-1} belong to the external modes relating to Ca^{2+} ion, the high frequency vibrations at 711 and 1085 cm^{-1} belong to the internal modes relating to the CO_3^{2-} ion. The calcite structure carbonates are usually visualized in terms of layers of carbonate ions and layers of metal ions [11]. However the basic unit which comprises the structure is more correctly seen as a cation octahedrally coordinated with oxygen atoms , each atom being linked to a CO_3^{2-} ion. The octahedral coordination is almost perfect, the trigonal distortion being very slight. The external mode frequencies show a strong correlation with the octahedral distance, which has been noted by H.N. Rutt[9]. If some Ca^{2+} ions of calcite were replaced by other metal atoms, the distortion would be larger and the octahedral distance would change. This would result in the broadening of the external modes. With this in mind, a small part of pale blue pigment was removed for XRF analyzation. The result of XRF shows that the pale blue pigment contained a small amount of Mg, Mn and Fe besides Ca. So it is confirmed that the pale blue pigment was calcite, but some of the Ca atoms are probably replaced by Mg, Mn and Fe in the $CaCO_3$ lattice. The proper formula of this pale blue pigment should be $Ca_{1-x}(Mn,Mg,Fe)_xCO_3$.

CONCLUSION

The work described here confirms that Raman microscopy proves to be a very effective analytical method when applied to the pigments used in wall painting. Before this work, X- ray diffraction (XRD) was tried but not successful in this identification and only cinnabar was demonstrated because of the signal of ground coating was stronger .

Compared with other techniques for pigment analysis, Raman microscopy is the best single technique for this purpose[12]. It is thus attracting much interest at the frontier of the arts and sciences.

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REFERENCES

1. Clark, R .J.H. , Chem. Soc. Rev. **1995;** 24:187.
2. Clark, R.J.H.; Gibbs, P.J., J. Raman Spectrosc. **1997;** 28:97 .
3. Davey, R.; Gardiner, D.J.; Singer, B.W.; et al., J. Raman Spectrosc. **1994;** 25: 53.
4. Xu Guangji, Wenwu,**1996** ;9: 69(Chinese) .
5. Clark, R.J.H.; Gibbs, D.J.;Seddon, K.R.; et al., J. Raman Spectrosc. ,**1997;** 28: 91.
6. Fitzer, E.; Gantner, E.; Rozploch, F.;et al., High Temperature - High Pressures, **1989**; 19: 537.
7. Tuinstra, F.; Koenig, J.L., J. Chem. Phys. **1970** ;53: 1126.
8. Tuinstra, F.; Koenig, J.L., J. Compos. Mater., **1970**; 4:492 .
9. Rutt,H.N.; Nicola, J.H. , J. Phys. C: Solid State Phys., **1974**; **7**: 4522.
10. Fateley,W.G.; Mcdevitt, N.T.; Betley, F.F., Appl. Spectrosc., **1971**;25:155.
11. R.W.G. Wyckoff, Crystal Structures 2nd ed. Vol.2 (New York: Interscirnce),1964: 359.
12. Best, S.P.; Clark, R.J.H.; Withnall, R.; Endeavour, **1993**; 16: 66.

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