

## RAMAN SPECTROSCOPIC ANALYSIS OF ANCIENT EGYPTIAN PIGMENTS\*

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*The application of FT-Raman spectroscopy and visible Raman microscopy to the non-destructive analysis of pigment specimens excavated from Tell el Amarna by Flinders Petrie in the 1890s has provided information about the chemical composition of the materials used by XVIIIth Dynasty artists in the New Kingdom at the time of King Akhenaten, c. 1340 BC. Comparison of the Raman spectra of the samples labelled 'red and yellow ochre' with documented, archival material from geological collections provided a clear indication of the materials used in the iron(III) oxide/hydroxide system, including  $\alpha$ -hematite, goethite, maghemite, magnetite and lepidocrocite. The yellow–orange specimen labelled 'realgar' proved to be a mixture of realgar and pararealgar; since the specimen had been sheltered from light since its excavation, this could indicate that the ancient Egyptian artists recognized the colour variation and may have used this to effect in their decorations. A specimen of yellow ochre contained goethite,  $\alpha$ -FeO.OH, with particles of crystalline, highly ordered graphite; in contrast, the red ochre specimens contained amorphous carbon particles.*

**KEYWORDS:** EGYPT, MIDDLE KINGDOM, TELL EL AMARNA, PIGMENTS, RAMAN SPECTROSCOPY, NON-DESTRUCTIVE ANALYSIS, REALGAR, OCHRES

### INTRODUCTION

Raman spectroscopy has been applied with demonstrable success to the study of pigments in historiated ancient manuscripts (Best *et al.* 1992, 1993, 1995; Clark *et al.* 1995, 1997, 1998; Burgio *et al.* 1997a), medieval cantorals (Edwards *et al.* 1999c), polychrome statuary (Edwards *et al.* 2000) and wall-paintings (Coupry *et al.* 1994; Russ *et al.* 1995; Edwards *et al.* 1997, 1998, 1999a–c; Edwards 1998; Edwards and Rull Perez 1999; Smith *et al.* 1999). A wealth of information about ancient technology used in the preparation of pigments and their subsequent interactions with substratal material has emerged from these studies, including mineral instability due to the presence of neighbouring pigments and changes in their molecular structures with time. A major advantage of Raman spectroscopic techniques over infrared absorption is the simplicity of presentation of complex artefacts to the spectrometer in the

\* Received 26 October 2000; accepted 8 May 2001.

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former, which requires little or no sample preparation. The wavenumber coverage of the Raman spectra, typically 50–3500 cm<sup>-1</sup> in one instrument, also provides a unique means of analysis for inorganic minerals (especially heavy metal salts, oxides or sulphides) and organic dyes and binders (Vandenabeele *et al.* 2000), which may occur together in works of art.

Although organic dyes and colorants were recognized as 'fugitive' by ancient artists, nevertheless they are still found in manuscripts, especially those that have been preserved in libraries. The situation is different in the case of prehistoric rock art, since the colour palette is strictly limited (Russ *et al.* 1995; Smith *et al.* 1999) to naturally occurring metal oxides and charcoal or bone white (calcined ivory or bone). However, the exposure of these paintings to environmental climatic changes such as temperature and humidity, and colonization by algae, fungi and lichens, creates new problems for conservators, which Raman spectroscopy is addressing (Seaward and Edwards 1995, 1997; Edwards and Rull Perez 1999).

Tomb paintings, wall-paintings and frescoes in public buildings that are visited by members of the public provide other biodeteriorative scenarios for archaeologists, art historians and conservators. Although colonization by biologically active organisms was thought to occur slowly over long periods of time, recent reports indicate that destructive invasion of paintings and their substratal rock or plaster is now proceeding at alarming rates, often fuelled by hydrocarbon emissions and pollutants in urban environments. Our earlier Raman studies (Seaward and Edwards 1995) on the colonization of the Zuccari 16th-century frescoes in the Palazzo Farnese in Caprarola, Italy, by *Dirina massiliensis* forma *sorediata*, which was first recognized in 1986 and is now responsible for the permanent disfigurement of over 80% of the painted surfaces, have indicated the complexity of the biodeteriorative process. Molecular spectral identification of key biomarkers such as whewellite, weddelite, carotenoids, polyphenolic acids and lichen pigments has assisted in the recognition of biodeteriorative erosion of frescoes and wall-paintings elsewhere, so providing an early warning device for curators of these works of art.

Although the ancient Egyptian artists clearly used an extensive palette, as shown by tomb-paintings, papyri, decorative ceramics and coloured funerary artefacts, there have been few Raman spectroscopic studies. Clark and Gibbs (1997) have reported a non-destructive Raman study of coloured ancient Egyptian faience fragments from Amarna (in the Petrie Collection at University College London), and Coupry *et al.* (1994) and Coupry (1998) have reported Raman spectroscopic studies of blue pigments from the Egyptian New Kingdom. In the present study, we have taken the opportunity to analyse non-destructively, for the first time, using Raman spectroscopy the pigments excavated from Tell el Amarna by Sir William Flinders Petrie in 1891–2, which are now housed in the Manchester Museum.

## EXPERIMENTAL

### *Samples*

The pigment samples studied in the present work were excavated by Sir William Flinders Petrie at Tell el Amarna in Middle Egypt in 1891–2 (Petrie 1894). The site consists of the remains of a royal city which was constructed, occupied and then deserted within the very short time of 20 years or so during the reign of Amenhotep IV (Akhenaten), c. 1350–1334 BC, in the XVIIIth Dynasty. Akhenaten is now considered as a pioneer of a beautiful culture, whose art forms were quite distinct from those that had preceded it. The 'Amarna culture', as it became known, came into conflict with the orthodox priesthood, who saw it as a heresy and supervised

the destruction of the city on the pharaoh's death in 1334 BC (Sanson 1972; Phillips 1998). Samples from the Amarna cultural period excavations can hence be realistically dated to a very narrow period of occupation. In the present study, some coloured pigments from Petrie's excavations at Amarna (Drawer 1985) were deposited in the Manchester Museum of Egyptology in 1896 and have not been examined since. Their rarity and special significance therefore lend themselves to non-destructive Raman spectroscopic analytical examination for the first time.

Details of the specimens presented for Raman spectroscopic analysis are given in Table 1; the samples are believed to be mineral pigments of colours yellow, red, red-brown, green, orange, orange-yellow, blue and yellow-brown, from the remains of artists' palettes used in decoration of this vibrant artistic period of Dynastic Egyptian history. In some cases, the samples were found adhering to fragments of stone mortars, which presumably were used to produce the fine pigment powders required for the art work. The Raman spectroscopic technique did not necessitate the detachment of the minerals from their associated artefacts; nor did it involve the pulverizing or grinding of archival material.

The mineralogical descriptions of the specimens in Table 1 are based only upon the initial examination prior to cataloguing for the Museum collection; it is stressed that chemical analysis has not been carried out on these specimens hitherto.

### *Raman spectroscopy*

Raman spectroscopy is a vibrational spectroscopic technique that depends on the analysis of the wavenumbers of scattered laser radiation. The pattern of the scattered radiation wavenumbers is characteristic of the molecular composition of the material being studied, and in this respect the Raman spectrum is complementary to the infrared. Since infrared and Raman spectroscopy arise from different physical processes, however, the information acquired from Raman spectra is not identical to that obtainable from the infrared spectra in band appearance, intensity and often wavenumbers. The application of near-infrared laser excitation for the recording of Raman spectra provides a useful means of minimizing the fluorescence that can occur along with the Raman spectra of organic materials, and which effectively swamps the weaker Raman signals. A particular advantage of Raman spectroscopy in the characterization of pigments is the wealth of information about geological and synthetic minerals and biological materials which can be gathered from the same spectrum over the extended wavenumber range offered by the Raman technique in comparison with the infrared. This has a special application for the non-destructive analysis of sensitive archaeological materials and artefacts. In addition, the

Table 1 *Samples from Tell el Amarna studied in the present work*

| <i>Sample code</i> | <i>Colour</i> | <i>Classification</i>      | <i>Number of specimens studied</i> |
|--------------------|---------------|----------------------------|------------------------------------|
| Uncat NCR Ore      | Yellow        | Yellow ochre               | 1                                  |
| NCR Ore            | Red-brown     | –                          | 2                                  |
| –                  | Green         | Malachite (?)              | 1                                  |
| 7458               | Orange        | Red ochre                  | 1                                  |
| 5664               | Orange-yellow | Realgar                    | 1                                  |
| 2478               | Blue          | Frit                       | 1                                  |
| 1964               | Blue          | Fragment                   | 1                                  |
| 1129               | Yellow-brown  | Ochre (glass fruit colour) | 1                                  |

weak response of the Raman technique to water means that desiccation of specimens need not be undertaken which, in conjunction with the versatile sampling arrangements that require no mechanical or chemical pre-treatment of specimen surfaces, means that there are a host of applications in the field of archaeological science.

#### *FT-Raman spectroscopy*

Fourier-transform Raman spectra were obtained using a Bruker IFS 66 infrared spectrometer with an FRA 106 Raman module attachment and dedicated Raman microscope. Excitation was effected using 1064 nm radiation from a Nd<sup>3+</sup>/YAG laser operating with a maximum power of 750 mW, although laser powers at the sample of about 100–200 mW were typical of those used here. Spectra were recorded at 4 cm<sup>-1</sup> spectral resolution over the wavenumber range, 100–3500 cm<sup>-1</sup>, to check for any organic components, such as resins, which would be indicated by  $\nu(\text{CH})$  scattering near 3000 cm<sup>-1</sup> and  $\delta(\text{CH}_2)$  modes near 1400 cm<sup>-1</sup>. Co-accumulation of spectral scans was undertaken to provide improvement in signal-to-noise ratios; typically, about 100–200 scans were made, representing a total accumulation time of  $\sim 3$  min for each specimen, to provide good-quality Raman spectra.

Wavenumbers are correct to better than  $\pm 1$  cm<sup>-1</sup> for sharp bands. For macroscopic sampling, each specimen was mounted directly and vertically in the sample illuminator; fragile samples could be studied using a 90° illuminator attachment and horizontal mounting. In each case, the sample ‘footprint’ studied was about 100  $\mu\text{m}$  diameter. For microscopic studies, samples were held horizontally on a microscope stage, and a ‘footprint’ of about 8  $\mu\text{m}$  was obtained using a 100 $\times$  objective lens.

#### *Visible Raman microscopy*

The visible Raman measurements were performed using a Renishaw microscope system fitted with a Peltier-cooled CCD detector (Wright, 600 $\times$ 400 pixels) and with an Olympus metallurgical microscope. The spectra were excited with the 632.8 nm line of a He–Ne laser (Spectra Physics, model 127) which was focused on a *c.* 1–2  $\mu\text{m}$  (micrometre) spot, with an average spectral resolution of about 2–4 cm<sup>-1</sup> over the wavenumber range of 100–1800 cm<sup>-1</sup>.

Laser powers were kept as low as possible (*c.* 0.7 mW) to avoid sample degradation. Co-accumulation of spectral scans over 5–50 s was effected to provide good spectral signal-to-noise ratios.

It is important to note that in all cases no prior mechanical or chemical treatment of the specimens was necessary; hence, the mineral pigments could be returned to their museum archive in exactly the same condition as they left it.

## RESULTS AND DISCUSSION

For the purpose of discussion, the results from the red, orange and yellow pigments and from the blue and green samples (shown in Table 1) will be presented separately.

#### *Red, orange and yellow samples*

These samples had been archived (Table 1) as ochres (uncat NCR,7458), realgar (5664) or had no identification at all (NCR Ore, 1129). As part of our Raman spectroscopic studies designed to provide a database of pigments used in Antiquity, we have included work on the iron(III) oxide/hydroxide system that forms the basis of ochre pigment coloration (de Faria *et al.* 1997;

Clark and Curri 1998; Bersani *et al.* 1999). In prehistoric cave-paintings, the limited palette available to the artists usually consisted of red, yellow, white and black colours, which are normally comprised of red and yellow ochres, gypsum or calcite, carbon or pyrolusite and manganese(IV) oxide (Coupry *et al.* 1994; Russ *et al.* 1995; Smith *et al.* 1999). The colours of the ochres are of particular relevance in the current work, since admixture of raw pigments with sands or clays and heating to various temperatures was a technology that was available even in prehistoric times.

Some of the compounds in the iron(III) oxide/hydroxide system of relevance to the present study include minerals such as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), goethite ( $\alpha$ -FeO.OH), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and lepidocrocite ( $\gamma$ -FeO.OH). In the construction of our Raman spectroscopic database, mineral samples from the geological collections of the National History Museum, London, were analysed non-destructively. Key papers on the Raman spectra of iron oxides and oxyhydroxides have recently appeared in the literature (de Faria *et al.* 1997; Smith *et al.* 1999; Bikiaris *et al.* 2000). Much careful interpretation of the pigments in this system has been undertaken with regard to their mineralogical classifications. The visible Raman spectra of some of these system components using 632.8 nm excitation are illustrated in the stack plot in Figure 1, and the key wavenumbers that can be used to characterize these materials are given in Table 2. Having established the database for these minerals, it is appropriate to apply the analysis to the Amarna ochre samples, bearing in mind that small wavenumber shifts due to environmental effects can be expected between the pure mineral and the same mineral found in admixture with clays and sand. Raman spectra of the ochre samples were obtained using 633 nm and 1064 nm excitation, but the spectra obtained at 633 nm were stronger. A stack plot of the FT-Raman spectra of the Amarna ochre specimens is given in Figure 2. Comparison of the Raman band wavenumbers of the Amarna ochres in Figure 2 (Table 3) with the iron(III) oxide/hydroxide standards in Figure 1 (Table 2) provides the following conclusions:

- (i) *Sample 7458*: red ochre. This can clearly be assigned to  $\alpha$ -hematite, but the presence of the features at  $462\text{ cm}^{-1}$  and  $252\text{ cm}^{-1}$  in some spectra (not shown here) is indicative of  $\alpha$ -quartz, probably from admixture with sand. Sand was normally used as an aid to fine particle production through grinding (Best *et al.* 1995).
- (ii) *NCR Ore*: red-brown ochre. This may also be assigned to  $\alpha$ -hematite but, unlike sample

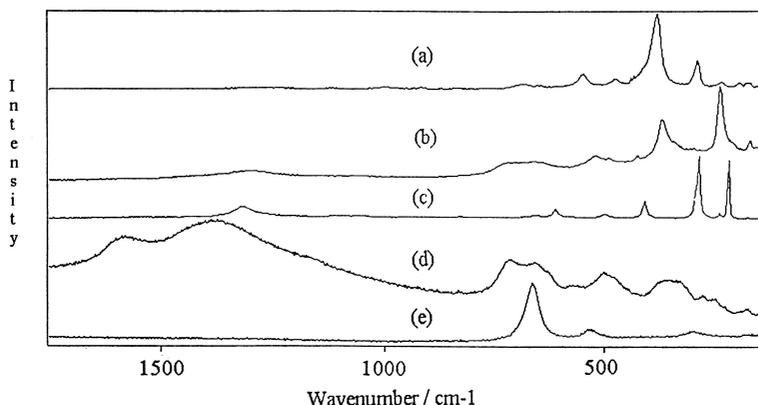


Figure 1 An FT-Raman spectral stack plot of minerals in the iron(III) oxide/hydroxide system: a, goethite; b, lepidocrocite; c, hematite; d, maghemite; e, magnetite. 633 nm excitation, wavenumber range  $150\text{--}1700\text{ cm}^{-1}$ , 30 s spectral accumulation,  $2\text{ cm}^{-1}$  spectral resolution.

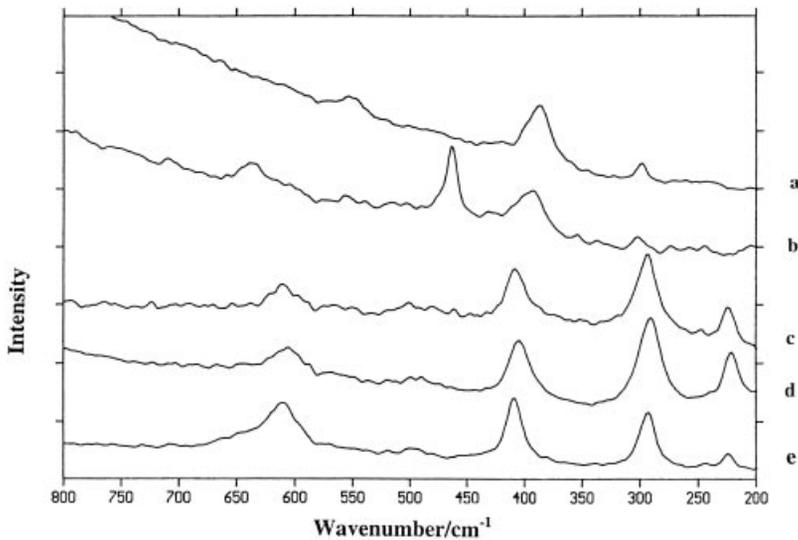


Figure 2 An FT-Raman spectral stack plot of archival ochre pigment specimens from the Amarna excavations: a, yellow-brown ochre (1129); b, yellow ochre (Uncat NCR Ore); c, red ochre (7458); d, red ochre (Uncat NCR Ore); e, red-brown ochre (NCR Ore). 1064 nm excitation, Wavenumber range 200–800  $\text{cm}^{-1}$ , 4  $\text{cm}^{-1}$  spectral resolution, 1000 scans spectral accumulation.

7458, there is no indication of  $\alpha$ -quartz present in any of the specimen regions sampled. However, at larger wavenumber shifts this sample gave bands at 1043, 1280, 1330, 1453, 1669, 2937, 2978 and 3016  $\text{cm}^{-1}$ . These are assignable to an organic resin that contains CO, aliphatic  $\text{CH}_2$  and  $\text{C}=\text{C}$  groups. A possible candidate for this is a terpene such as abietic acid or resinous gums such as colophony, dammar and pinene. It is suggested that this specimen has possibly been prepared for some special use—perhaps involving decoration of a sarcophagus or wooden item, where a resin binding medium would assist in the adhesion of the pigment to the substrate. Alternatively, the admixture of resin and hematite produces a brown pigment, which could have been the colour desired by the ancient artists. Small black particles in the specimen were identified as carbon from characteristic bands in the Raman spectrum.

(iii) *Uncat NCR Ore*: yellow ochre. This is very inhomogeneous. Two characteristic spectra were obtained from different regions of the specimen; one, of distinctly red particulates, matches an assignment to  $\alpha$ -hematite, but the other contains a large quantity of sand, as shown by the Raman bands at 252 and 464  $\text{cm}^{-1}$ , and has a yellow colour that fits better with goethite, a hydrated iron(III) oxide/hydroxide. On heating, goethite produces hematite (de Faria *et al.* 1997; Bersani *et al.* 1999). Hence, the *Uncat NCR Ore* (yellow ochre) specimen is very different from the similarly catalogued *NCR Ore* (red–brown ochre) specimen described above and they were probably designed for different artistic purposes, in that the *Uncat NCR Ore* (yellow ochre) has been subjected to a simple preparation technology involving heating, whereas the *NCR Ore* (red–brown ochre) involves mixing with a resin binder, which may have involved a heating or melting process.

(iv) In both the *NCR Ore* (red–brown ochre) and *Uncat NCR Ore* (yellow ochre) specimens, small black particles were identified as carbon from the Raman spectra recorded. In Figure 3, a Raman spectrum typical of the *NCR Ore* (red–brown ochre) is seen to be amorphous carbon with the characteristic twin peaks at 1580 and 1340  $\text{cm}^{-1}$ , whereas the carbon particles in the

Table 2 Key Raman wavenumbers/cm<sup>-1</sup> characteristic of minerals in the iron(III) oxide/hydroxide system\*

| <i>Fe</i> <sub>2</sub> <i>O</i> <sub>3</sub> <i>α</i> -hematite<br>(BM 58103, Isere, Fr) | <i>α</i> - <i>FeO.OH</i> goethite<br>(BM 26844,<br>Restormel, UK) | <i>γ</i> - <i>Fe</i> <sub>2</sub> <i>O</i> <sub>3</sub><br>maghemite<br>(BM 1929, 1690,<br>Pretoria, SA) | <i>γ</i> - <i>FeO.OH</i><br>lepidocrocite<br>(Seigen, Germany) | <i>Fe</i> <sub>3</sub> <i>O</i> <sub>4</sub><br>magnetite<br>(BM 1989, 209,<br>Kinumarau, Kenya) |
|--|---|--|--|--|
| <b>226 ms</b> <sup>†</sup>   |   |  |  |  |
| <b>246 w</b>   | <b>243 mw</b>   |  | <b>245 ms</b>  |  |
| <b>293 s</b>   | <b>300 m</b>  |  |  | <b>302 m</b>   |
|  |   |  | 310 mw, sh   |  |
|  |   |  | 347 m  |  |
|  |   | <b>350 m, br</b>   | <b>373 ms</b>  |  |
|  | <b>385 mw, sh</b>   |  |  |  |
| <b>411 ms</b>  | <b>479</b>  |  | <b>493 mw</b>  |  |
| 500 w  |   | <b>500 m, br</b>   |  | <b>513 w</b>   |
|  |   |  | <b>522 w</b>   | <b>534 w</b>   |
|  | <b>550</b>  |  |  |  |
| <b>610 ms</b>  |   |  | 650 mw   |  |
|  |   |  |  | <b>663 ms, br</b>  |
|  | <b>685 mw</b>   | <b>700 m, br</b>   | <b>719 w</b>   |  |

\*Raman bands suitable for non-destructive characterization purposes are shown in **bold** type.

<sup>†</sup>Key: s, strong; ms, medium-strong; m, medium; w, weak; mw, medium-weak; br, broad.

Uncat NCR Ore (yellow ochre) specimen exhibit just the 1580 cm<sup>-1</sup> band, which is also much narrower in spectral bandwidth than the more typical carbon spectra. This result, which indicates that the carbon particles in the Uncat NCR Ore (yellow ochre) arise from a highly crystalline, ordered graphite, whereas those in the *NCR Ore* (red-brown ochre) specimen arise from an amorphous carbon, indicates that the two specimens probably originate from different sources. Alternatively, there is a possibility that the *NCR Ore* (red-brown ochre) red pigment has been made from the yellow specimen. It is clear that the yellow goethite in the Uncat NCR Ore (yellow ochre) has not been subjected to thermal or mechanical processing, which would have destroyed the highly oriented graphitic carbon particles. Hence the presence of red hematite particles within this specimen can be attributed to natural geological contamination and not to residual processing.

(v) *Sample 1129*: yellow-brown ochre. This is believed in the cataloguing to be the origin of 'glass fruit' colours found in the Amarna excavations. The Raman spectrum of this specimen best matches that of goethite in our database. However, there is no indication of the presence of highly crystalline carbon particles in this specimen, so it is likely that this goethite has originated from a different source from that which comprises the Uncat NCR Ore (yellow ochre) specimen.

(vi) *Sample 5664*: orange-yellow; labelled 'realgar'. Under the microscope, this sample clearly consists of two components, reddish-orange crystals and bright yellow crystals. The FT-Raman microscope spectra of these components are shown in Figure 4. The two spectra are quite different and may be assigned to pararealgar (yellow component) and realgar (orange-red component) which are two polymorphic forms of As<sub>4</sub>S<sub>4</sub>. The band wavenumbers for pararealgar and realgar are given in Table 4, from which it is seen that these chemical specimens

Table 3 Raman band wavenumbers/cm<sup>-1</sup> in spectra of 'ochres' from Amarna excavations

| Sample 7458,<br>red ochre | NCR Ore,<br>red-brown ochre | Uncat NCR Ore, yellow ochre |               | Sample 1129,<br>yellow-brown ochre<br>(glass fruit colour) |
|---------------------------|-----------------------------|-----------------------------|---------------|--|
|                           |                             | Red region                  | Yellow region |  |
|                           |                             |                             | 115 w         |  |
|                           |                             |                             | 143 ms        |  |
|                           |                             |                             | 205 w         |  |
| 225 m*                    | 225 mw                      | 222 m                       |               |  |
| 252 w                     |                             |                             | 252 w         |  |
| 294 ms                    | 293 ms                      | 291 ms                      |               |  |
|                           |                             |                             |               | 299 mw   |
|                           |                             |                             | 303 w         |  |
|                           |                             |                             | 388 ms        |  |
|                           |                             |                             | 393 ms        |  |
| 409 m                     | 410 ms                      | 405 ms                      |               |  |
| 462 w                     |                             |                             | 464 ms        |  |
| 501 w                     | 500 w                       | 495 w                       |               |  |
|                           |                             |                             |               | 525 w, br  |
| 612 mw, br                | 611 ms                      | 608 mw, br                  |               |  |
|                           | ...†                        |                             | 639 mw        |  |

\*Key: s, strong; ms, medium-strong; m, medium; w, weak; mw, medium-weak; br, broad.

†Additional bands, found at 1043 mw, 1280 m, 1330 m br, 1453 m, 1669 m, 2937 m, 2978 m and 3016 m cm<sup>-1</sup>, are indicative of an organic component mixed with the pigment.

may be differentiated from each other by strong or medium-intensity bands at 332, 309, 202, 151 and 116 cm<sup>-1</sup> (Bell *et al.* 1997). Pararealgar is formed from realgar by a light-induced transformation, particularly by radiation in the green–yellow region of the electromagnetic spectrum, near 530–560 nm, and both have the chemical formulation As<sub>4</sub>S<sub>4</sub>, arsenic (III) sulphide. There are thus bands which are common to both species in their Raman spectra—for example, 353, 220, 191, 182 cm<sup>-1</sup>—which may be assigned to  $\nu(\text{As-As})$  and  $\nu(\text{As-S})$  modes. The radiation-induced transformation of realgar to pararealgar involves the breaking and re-formation of As–As bonds.

The use of orpiment, arsenic(III) sulphide (As<sub>2</sub>S<sub>3</sub>), as a yellow pigment in ancient times has long been recognized. The differentiation of this pigment and of the two polymorphs of realgar by their Raman spectra is quite straightforward, since orpiment has strong and medium-intensity bands at 154, 292 and 353 cm<sup>-1</sup>. A stack plot of some yellow and red natural sulphide pigments in use in Antiquity has been published previously (Edwards *et al.* 2000), in which the Raman spectra of the arsenic sulphides orpiment and realgar were plotted with those of mosaic gold (tin sulphide) and cinnabar (mercury sulphide) to illustrate the potential for unambiguous discrimination between these minerals using this technique.

In a Raman microscopic study of a 13th-century Byzantine/Syriac Gospel Lectionary (Burgio *et al.* 1997b), the presence of pararealgar was identified in some 32 of 60 yellow illuminations. This was the first time that pararealgar had been observed in any manuscript, and the usage of this rich, yellow coloration in the correct context and alongside orpiment indicated that the artist made a deliberate choice of pigments for his illustrative work, which had hitherto not been realized. By the same token, it would be relevant to examine specimens of bright-yellow and orange decorative pigments from artefacts of the Amarna culture, in an

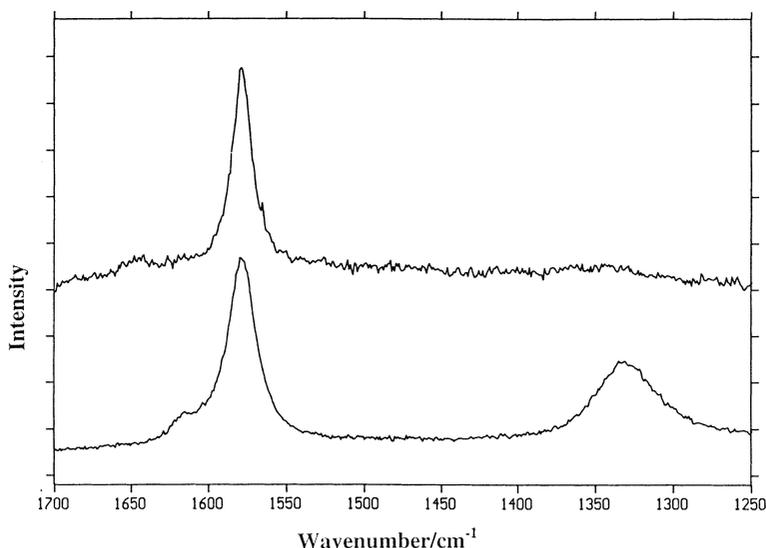


Figure 3 Raman spectra of carbon particles using 633 nm excitation from NCR Ore (hematite) and Uncat NCR Ore (goethite/hematite) specimens; the single sharp peak at  $1580\text{ cm}^{-1}$  in the Uncat NCR Ore sample indicates that the carbon is a highly crystalline form of graphite.

attempt to identify the differential usage of yellow and orange-red realgar, orpiment and pararealgar. The observation of pararealgar in decorated artefacts points to the recognition of this pigment in ancient Egypt and to a possible early technology for its preparation. Pararealgar has been recognized on an XVIIIth Dynasty Egyptian papyrus from the Petrie Museum Collection (University College London: Burgio and Clark 2000) and on two Egyptian funerary masks dating from about 200 BC (Vandenabeele *et al.* 2001).

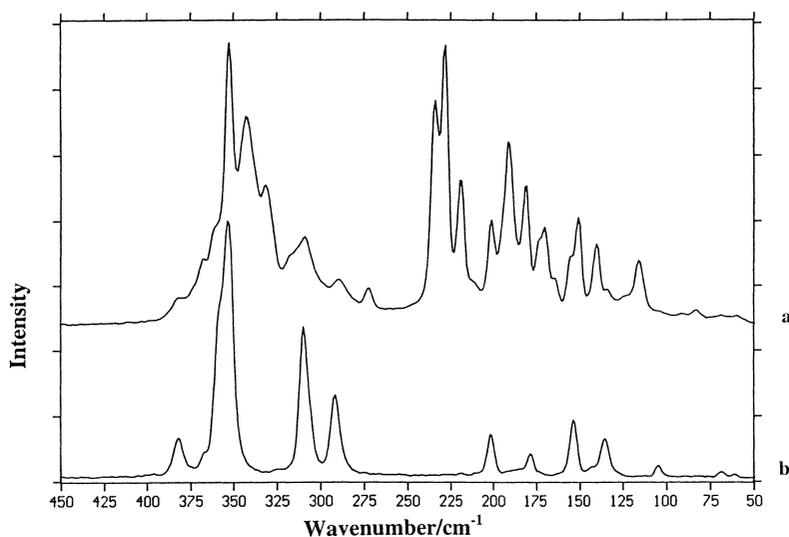


Figure 4 FT-Raman microscope spectra of yellow Amarna pigment specimen: a, pararealgar; b, realgar. 1064 nm excitation, wavenumber range  $50\text{--}450\text{ cm}^{-1}$ , 200 scans, spectral accumulation  $4\text{ cm}^{-1}$  spectra resolution.

Table 4 Raman band wavenumbers/cm<sup>-1</sup> for realgar and pararealgar, As<sub>4</sub>S<sub>4</sub>

| Pararealgar (yellow) | Realgar (orange-red) |
|----------------------|----------------------|
| 116 m*               |                      |
| 141 m                | 142 m                |
| 151 m                |                      |
| 171 m                | 171 m                |
| 182 m                | 182 m                |
| 191 m                | 191 m                |
| 202 m                |                      |
| 219 m                | 220 ms               |
| 229 s                |                      |
| 234 ms               | 233 w                |
| 273 w                |                      |
| 290 w                |                      |
| 309 mw               | br                   |
| 332 m                |                      |
| 343 m                | 342 m                |
| 353 s                | 353 s                |

\*Key: s, strong; ms, medium-strong; m, medium; w, weak; mw, medium-weak; br, broad.

### Blue-green samples

Three samples were studied in the blue-green category: a green uncoded specimen labelled 'Malachite (?)' and blue samples no. 2478, labelled 'Frit', and no. 1964, labelled 'Fragment'.

Raman spectra were obtained using visible laser excitation at 633 nm and 514.5 nm and near-infrared excitation at 1064 nm. The specimen labelled 'Malachite (?)' gave a Raman spectrum (Fig. 5) with characteristic peaks at 154, 179, 215, 269, 352, 430, 509, 535, 1051 and 1490 cm<sup>-1</sup> of basic copper(II) carbonate, CuCO<sub>3</sub>.Cu(OH)<sub>2</sub>, a mineral known in Antiquity. The questionable identification label of this pigment is therefore clarified and the specimen confirmed as malachite.

The specimen coded no. 2478, a blue pigment sample, gave a spectrum that was assignable to Egyptian blue from features at 430, 470, 572, 789, 992, 1012 and 1086 cm<sup>-1</sup>. Egyptian blue, a synthetic pigment that has been identified in early Pharaonic burial sites dating from the IVth Dynasty (c. 2613–2494 BC), has a long history of decorative use in Egypt. The features in our Amarna specimen clearly match those reported in a recent comprehensive study of Egyptian blue and green pigments reported by Pagès-Camagna *et al.* (1999). It is believed that the Egyptian green (turquoise) synthetic pigment is also chemically similar to the blue pigment. The 'frit' or glassy appearance of the Amarna blue fragment no. 2479 also correlates with our Egyptian blue reference spectrum, since the pigment is closely associated with cuproriväite, a naturally occurring form of Egyptian blue, of formulation CaCuSi<sub>4</sub>O<sub>10</sub>.

The fragment coded no. 1964 is also a blue pigment, but of a paler coloration than no. 2478. The Raman spectrum of the sample is also shown in Figure 5 and can be identified with the mineral azurite, a basic copper carbonate of formulation 2CuCO<sub>3</sub>.Cu(OH)<sub>2</sub>. Key Raman bands are observed at 1571, 1425, 1091, 940, 836, 762, 397 and 245 cm<sup>-1</sup>.

As an illustration of the spectral differentiation, a stack-plot of the FT-Raman spectra of the green 'Malachite (?)' and the blue fragment no. 1964 specimens is given in Figure 5.

#### CONCLUSIONS

The results from the non-destructive Raman spectroscopic study of the archival material relating to Amarna pigments in the Manchester Museum have confirmed the value of this technique for the characterization of ancient pigments. In some cases, the results point to the existence of a simple preparative technology being involved; that is, the samples have not just been mined and used without treatment.

In an earlier study of ancient Egyptian faience specimens from the Petrie Amarna collection at University College London using Raman microscopy, Clark and Gibbs (1997) were able to support the conclusions of an earlier study (Kaczmarczyk and Hedges 1983). The principal chromophore in the red faience specimens was iron(III) oxide, but the quality of the Raman spectra recorded was severely compromised by the silica glaze. The yellow pigment on the faience fragments from Amarna was identified as Naples yellow, lead(II) antimonate, and neither orpiment nor realgar/pararealgar were identified. Hence, the unequivocal presence of realgar and pararealgar in the specimens studied here from the same period indicates that a wider pigment palette was obviously available to ancient Egyptian artists during the Amarna period. It would be a logical step to study other examples of yellow or orange-red pigments from artefacts manufactured at Amarna to identify positively the application of these arsenic sulphides during this period (c. 1340 BC).

The results of the present study also demonstrate that Raman bands which arise from pigments deriving from the iron(III) oxide/hydroxide system can be used to identify pigment

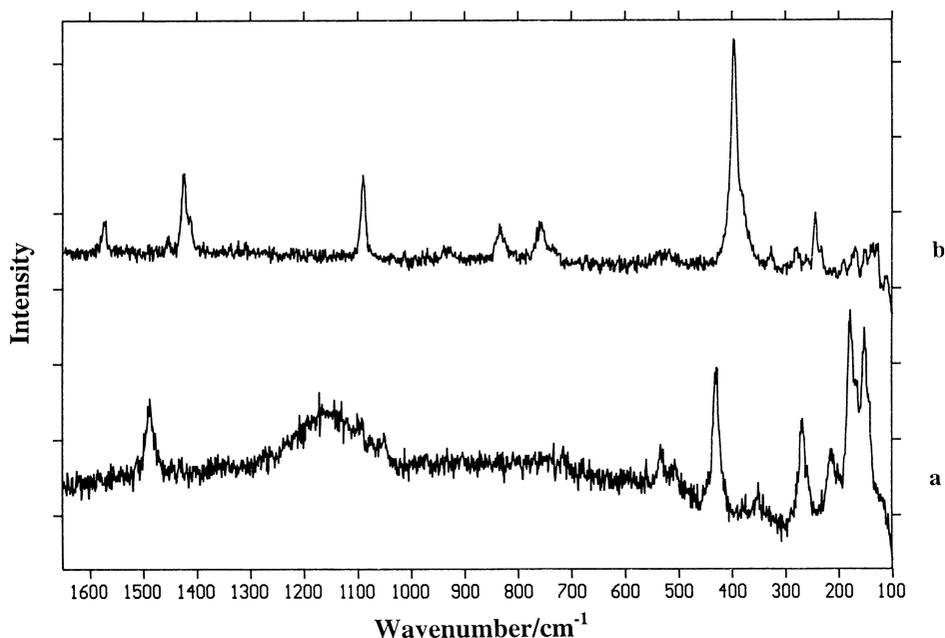


Figure 5 An FT-Raman stack plot of a green [a, 'Malachite (?)'] specimen and a blue pigment specimen [b, no. 1964] from the Amarna excavations, 1064 nm excitation, 4 cm<sup>-1</sup> spectral resolution, 1000 scans spectral accumulation.

preparation technologies. Here, we have suggested that one of our specimens had been mixed with sand, another had possibly been heat-treated and a further sample mixed with a terpene-type resin binder, presumably to increase adhesion properties for a specific application. A very significant discovery relates to the yellow ochre sample, which contains a highly ordered form of graphitic carbon. Clearly, this specimen had not been subjected to thermal or mechanical processing, which would have destroyed its orientational properties. The implication of this discovery is that a geological survey of source minerals combined with a Raman spectroscopic analysis could be undertaken to provide information about the possible location of the source of the Amarna yellow ochre excavated by Petrie.

#### ACKNOWLEDGEMENTS

H. G. M. E. and D. L. A. de F. are grateful to the British Council and CAPES (Brazil) for support during which this study was carried out.

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