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Combined technique analysis of the composition of Punic make-up materials

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ABSTRACT Ten archaeological Punic make-up samples from Tunisia dating from the 4th to the 1st centuries BC were analysed by several techniques including Raman microscopy and synchrotron X-ray diffraction in order to determine their compositions. Eight samples were red and found to contain either quartz and cinnabar or quartz and haematite. The remaining two samples were pink, the main diffracting phase in them being quartz. Examination of these two samples by optical microscopy and by illumination under a UV lamp suggest that the pink dye is madder. These findings reveal the identities of the materials used by Carthaginians for cosmetic and/or ritual make-up purposes.

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1 Introduction

Little significant material is available which reveals much about Punic society and civilization compared to other contemporary Mediterranean cultures. The scientific examination of material from Carthaginian sites is thus of particular interest to archaeologists and historians. During the excavation of Carthaginian tombs in modern day Tunisia and documented in 1898 [1], small vessels containing residues of cosmetic products (make-up, perfumes or cleansing oils) were found. Small quantities of several types of pigmentary material, possibly used as cosmetics, were discovered in receptacles such as sea-shells [2]. The use of pigmentary materials as make-up components is indirectly confirmed by the examination of human remains in several Punic tombs, which have revealed that some bones show traces of pigments [3]. It would be invaluable to be able to differentiate between make-up used on living people (cosmetic) and that used to vivify and embellish the dead (ritual). Some unguents containing cinnabar or ochre were used as ‘mourning reds’ and were applied on the face and the forehead of people at the point of death. The finding of traces of red pigmentation on bones and particularly skulls suggests that this ritual was common in Punic and Roman periods. The identification of the pigmented materials found in vessels in tombs and on bones may help

in confirming the function of the pigments and possibly in indicating cultural or trade exchanges with other cultures using similar practices.

Natural colorants used in antiquity include red pigments such as cinnabar [4] and ochre, and pink dyes such as madder [5], such materials having served as constituents of ritual and cosmetic make-up. The Greeks used *miltos* (translated variously as “red ochre”, “vermilion” or “red lead”) as a face cosmetic [6] and reported its use as an ingredient for body and face paint in other cultures [7]. The Romans are known to have used a red cosmetic make-up for cheeks [8–10]. Ochres are abundant materials of mineral origin and have been used since prehistoric times. They range in colour from yellow to red to brown and consist predominantly of clay mixed with iron oxides in various states of oxidation and hydration. They were used in cosmetic make-up because of their abundance and the variety and richness of their hues.

The fact that archaeological material believed to be make-up from Punic and Roman periods has been described in the past simply as “red-coloured” has not helped in discriminating between ritual and cosmetic make-up, which are difficult to characterise by visual inspection. The objective was therefore the physico-chemical analysis of archaeological colorants and pigments considered by archaeologists to be make-up products; a characterisation of the components of these products might suggest their original function.

2 Experimental

Ten samples from archaeological excavation sites or museums in Tunisia were selected for this study, eight being red (B1, B2, B3, B10, OCRB, FCC4, FCC5 and FCC6) and two pink (C41C and FCC2). These samples were in the form of dry powders in very small quantity. This necessitated the use of micro-sampling techniques. Several techniques were used: elemental analysis was performed by using atomic absorption spectroscopy (AAS); optical and Raman microscopy were used to characterize the mixtures and identify their components; the mineralogical analysis of the samples was performed by using synchrotron radiation X-ray diffraction (XRD) in two modes: a) moderate resolution XRD employing a CCD detector to obtain two-dimensional powder patterns and to identify quickly the major mineral phases present within each sample and b) high resolution powder

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diffraction in stepping mode to obtain high quality data for quantitative determination of phase abundance.

The optical microscopy analysis of a few particles from each sample was performed using a Leica Aristomet microscope in the transmitted light mode. Extreme care was taken to avoid any mechanical crushing likely to cause any modification of particle size and shape. Raman microscopy was performed using a Renishaw Raman System 1000, equipped with a He-Ne laser source irradiating at 632.8 nm and with a Leica microscope attachment. The X-ray diffraction patterns were collected on beamline X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory at a wavelength 0.7 Å. The samples were loaded in 0.5 mm diameter quartz capillaries and mounted on the horizontal axis of the diffractometer. By using the peak positions obtained from the data it was possible to identify the major constituents with the help of the powder diffraction database (PCPDF) and to carry out quantitative phase analysis on eight samples. The same capillaries used at NSLS were used to obtain diffraction patterns at station 9.6 at the synchrotron radiation source (SRS) at Daresbury Laboratory at $\lambda = 0.87$ Å. Two-dimensional diffraction patterns were collected in transmission geometry by a QUANTUM-4 CCD area detector with a typical acquisition time of 1–3 min.

3 Results and discussion

The elemental composition obtained by AAS showed that some samples were rich in mercury, suggesting the presence of cinnabar, and others were rich in iron, suggesting the presence of an ochre or haematite. The levels of aluminium and silicon indicate the presence of clay minerals, either coincidental (contamination from excavation soil) or intentional, i.e. part of the recipe for the preparation of the cosmetic powder or simply present in the raw material from which the pigments were prepared. The remaining two samples, C41C and FCC2, were pink and showed a pink-orange fluorescence when examined under ultraviolet illumination, indicating that they contain madder [5].

In accordance with the AAS analysis, mercury(II) sulfide and iron oxide particles were observed only in samples rich in mercury or iron, respectively. Mercury(II) sulfide was always found as crystals of variable particle size. Several bigger particles show the striations typical of both cinnabar (mercury(II) sulfide of natural origin) and synthetic vermilion prepared by the dry process. It is very difficult to discriminate unambiguously between ground cinnabar and ground dry-process vermilion [4]. However, considering the age of these samples (4th–1st century BC) and the presence of several mineral impurities, such as quartz and calcite, mixed with the mercury(II) sulfide it is reasonable to identify these samples with natural cinnabar.

All samples with a high content of iron exhibit a variety of particle sizes. Within each sample the shade of the particle varies, and in one sample yellow particles of hydrated iron oxide were also found. This evidence suggests that all iron oxides present in the samples are of mineral origin.

Calcium carbonate, CaCO_3 , appears to be abundant only in one sample, OCRB, although occasional particles are found

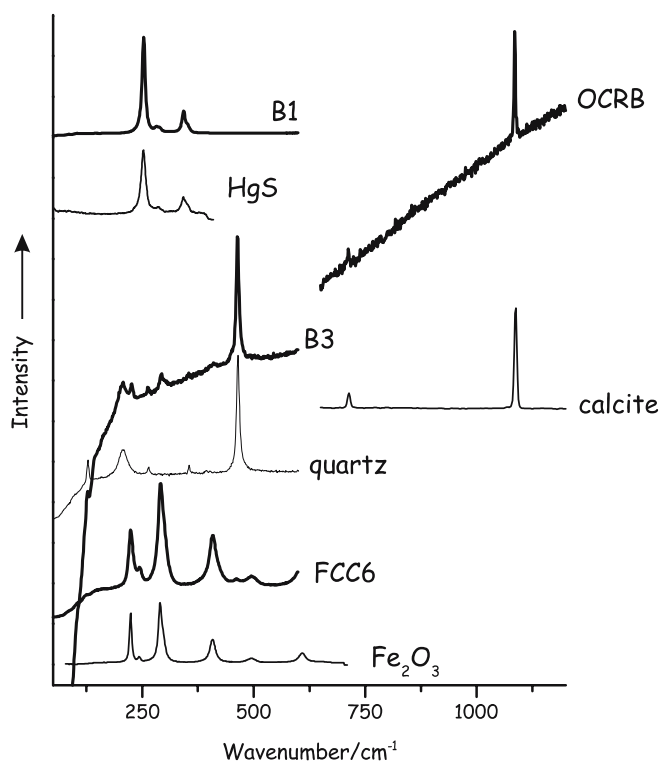


FIGURE 1 Raman spectra of selected Punic samples, compared to those of reference materials

in other samples as well. Occasional coccoliths can be seen, especially in samples B3 and OCRB¹.

Figure 1 shows the Raman spectra of some of the samples, compared to those of reference materials. The strongest bands in the spectra correspond to those of α -quartz, mercury(II) sulfide, and iron(III) oxide and in one case calcite, calcium carbonate CaCO_3 (OCRB) [11, 12]. The two samples for which optical microscopy indicated the presence of madder did not yield any identifiable Raman spectra because of the strong fluorescence excited by the laser beam.

Samples B1, B2, B3 and FCC5 are characterized by diffraction patterns that are almost exclusively derived from cinnabar and quartz. Rietveld analysis of the patterns reveals that the relative mass abundance of cinnabar to quartz ranges from 12:88 to 75:25 with no significant amounts of other mineral phases needing to be included in the fitting. Figure 2 shows such a fitted pattern. There are hardly any reflections that cannot be indexed to cinnabar or quartz. The corresponding two-dimensional pattern shows that the cinnabar diffraction rings are fine and continuous, indicating particles of small size, while the quartz rings contain more distinct diffraction spots indicating the presence of sizeable crystallites of a given orientation relative to the beam. Close inspection of the line shape of the quartz reflections in both sets of profiles shows that there is significant asymmetry. This is typical of cases where the crystal grains have been subjected to stress [13] indicating that the pigment must have been carefully ground to produce a fine powder. By contrast,

¹ Coccoliths are microscopic skeletal plate made of calcite that protect certain marine phytoplankton. In a fossilized state they form chalk and limestone deposits.

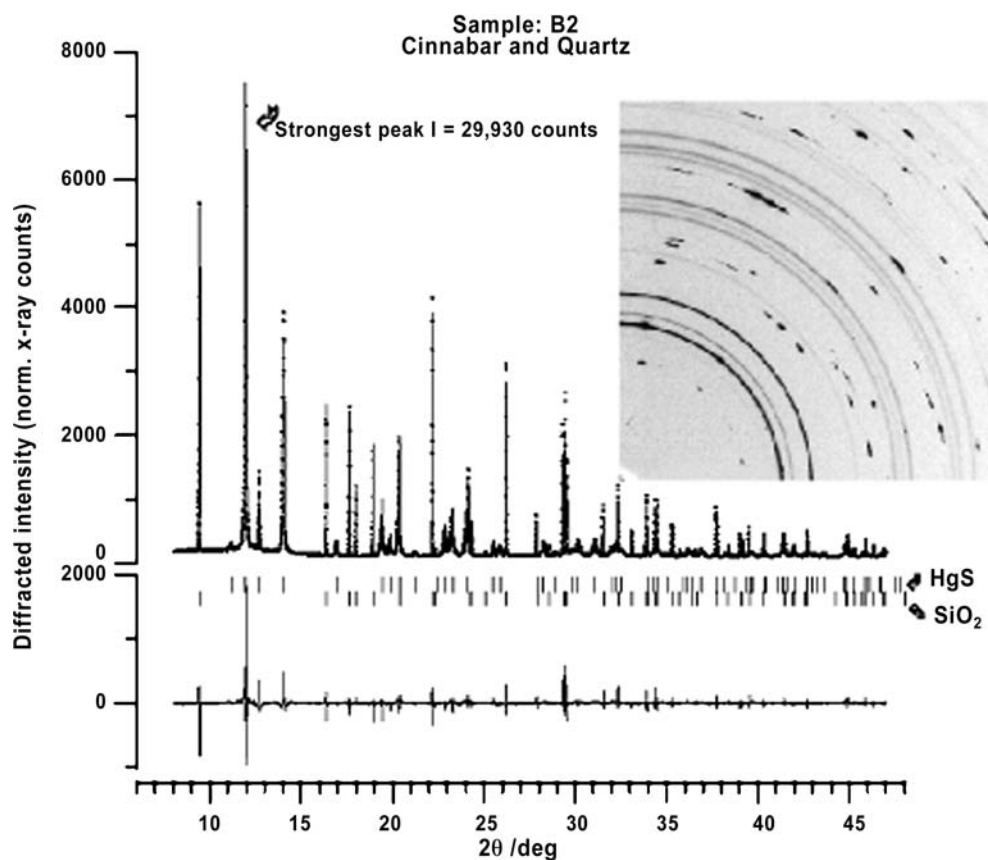


FIGURE 2 High resolution powder diffraction pattern of the cinnabar-rich sample B2. The two major phases, cinnabar and quartz, are fitted using the Rietveld procedure. The *inset* on the right shows a quadrant of the 2D pattern obtained by a CCD detector. The speckled reflections are due to quartz. Two-theta axis values for $\lambda = 0.7 \text{ \AA}$

the cinnabar and haematite in all of these samples have perfectly symmetric line profiles with linewidths twice those of quartz; this is consistent with both pigments having a much finer particle size than that of quartz, as demonstrated by the fine continuous nature of the respective diffraction rings.

Samples B10, FCC4, FCC6 and OCRB, as expected from the AAS and Raman analysis, contain haematite and quartz at a ratio ranging from 75:25 to 35:65 by mass. In one case (OCRB) significant amounts of calcite were also identified. Other reflections are also present between 3 and 5 Å, most likely arising from clay minerals present in the source material from which haematite was extracted.

The two pink samples, C41C and FCC2, exhibit similar profiles and are weakly diffracting compared to the other pigments. Small quantities of quartz are also present. The diffraction rings are all fully formed and smooth indicating a uniformly small particle size. Neither crystalline purpurin nor alizarin, the two anthraquinone dyes associated with madder, appear to fit the profile peaks. If any of these compounds are present in the samples they are not in a crystalline form. Some of the remaining reflections match quite closely in position and relative intensity those for cristobalite (SiO_2), a polymorph of quartz.

4 Conclusions

The combined scientific analysis of ten Punic make-up samples shows that the red colour of eight of them is due to the presence of cinnabar and haematite. The optical microscopy examination suggests that the cinnabar and

haematite crystals are of mineral origin. One sample contains a large quantity of calcite, which may have been used as filler added to the mixture in order to obtain a paler shade. Madder is identified in two samples.

SR-XRD has provided quantitative identification of the major diffracting phases in eight of the samples. Although it is not possible to state with certainty whether quartz is an intrinsic component of the preparative ingredients, the asymmetric profile of its reflections indicates that it is present when the starting material is ground into a powder. Similar conclusions are reached for the haematite-rich samples, which contain clay phases. SR-XRD methods applied to minute amounts of pigment are shown to allow the identification of the major diffracting phases. Raman microscopy is also capable of identifying the main components in a mixture even when only a few grains of material are available, and should be always preferred as a method for the initial characterisation of archaeological materials.

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