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## **Phoenicians preferred red pigments: chemical compositions of make-up powders found in archaeological sites from Sicily**

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### **Abstract**

Little is known concerning Phoenician and Punic cosmetics and pertinent studies and analyses on archaeological finds are particularly scanty. The present study has taken into account 22 archaeological red and pink Punic make-up samples collected in several Sicilian museums. The samples were analyzed by infrared spectroscopy, Raman microscopy and SERS (Surface Enhanced Raman Spectroscopy). The analyses revealed an interesting and unusual variability in the use of raw materials, ranging from the mineral to the organic world. Not only traditional dye-based pigments were identified, but also rare ones never reported previously for this use. We show also an occurrence unusual in Antiquity of a lead chromate block presumably intended to be ground just before its use as a make-up.

## Keywords

Phoenicians, make-up, pigments, Raman spectroscopy, SERS

## Introduction

Phoenicians are known to have preferred bright colors in their dress and to love luxury. The term itself *Phoenician* derives from the Greek word "*phoenix*" that is "red", like the shell purple, the commerce of which Phoenicians, a people of merchants and sailors, had monopoly for a long time. The Phoenicians were also closely linked to the movement of Arabia and East caravans carrying varied raw materials, which the Phoenicians elaborated according to their particular taste, assuming the function of authentic mediators of civilizations. They themselves were known makers of the cosmetics (ointment) containers in glass paste and in alabaster produced in Tyre, Sidon and Rhodes and exported all over the Mediterranean world. Carthage laboratories were also celebrated for their capabilities to prepare medicines and cosmetics. From Phoenicians, western Sicily settlements knew welfare and prosperity, in particular in the Mozia island (founded in the eighth century B.C.) and in Lilybeum (nowadays Marsala), founded after the Mozia destruction in 397 B.C. Significant findings and symbols related to Phoenicians culture and civilization are relatively few, unlike other contemporary Mediterranean cultures, for which archaeological and textual evidence are more abundant.<sup>1,2</sup> Furthermore, in relation to a topic such as Punic cosmetics, scarce is the information provided by classical sources and generally from Greek or Latin authors<sup>3,4</sup> or through scientific studies on archaeological materials.<sup>5-7</sup> Therefore, it could be assumed that the analyses of materials from the Punic sites may be of particular interest and relevance to both archaeologists and historians. Here we have taken into account a large number of containers stored at the Whitaker Museum (Island of Mozia, Trapani, Italy), Museo Salinas (Palermo, Italy), Baglio Anselmi Museum (Marsala, Trapani, Italy) and Conte Agostino Pepoli Museum (Trapani, Italy) to understand the type of materials used in cosmetics in the Punic sites of Mozia, Lilibeo, Palermo, Selinunte and Soluntum. The large

number of unguentaries, pyxis and *alabastra* made of glass or ceramics was studied: 202 items from Salinas, 210 from Mozia, 14 from Pepoli and 119 from Baglio Anselmi. The present work is exclusively focused on 22 samples of red and pink cosmetics, that are presented as particularly significant and interesting among those sampled. Whereas these containers, like *alabastron* and *lekythos*, are usually considered as vessels used for storing oil and ointments, we observed they are containing remains of colored materials, which were likely used as make-up.

## Historical Background

The museums from which the samples studied are as follows: the museum Giuseppe Whitaker (Mozia); the Regional Archaeological Museum "Antonio Salinas" (Palermo, Italy); the Archaeological Baglio Anselmi Museum (Marsala, Sicily, Italy); and the regional Pepoli Trapani Museum. These museums house finds from various periods from the excavations of Mozia, Birgi, Lilibeo and Selinunte archaeological sites (Fig. 1).

[insert Figure 1.]

Mozia, one of the Phoenician colonies of western Sicily, was founded before 600 B.C. The majority historic information comes from the funerary areas: the findings from the Tophet (enclosed place of sacrificial burials) and Birgi necropolis (settlement on the mainland overlooking the island of Mozia, connected to this by a road now submerged) are both rich, among other things, of cosmetic containers.<sup>6</sup> They are dating from a period of about five centuries, i.e. not only during the development of Mozia after its foundation by the Phoenicians, but also after its destruction and the rise of the new city Lilibeo.

Selinunte was founded by the Greeks of Megara in the second half of the 7th century BC. From 409

BC it became an important Punic commercial center. Some of the Selinunte containers, finely crafted, were excavated from the Demetra Malophoros sanctuary, whereas others were from the acropolis or the necropolis dating from the 6th to the 5th century BC. The sanctuary area seems to have been a meeting point between indigenous, Greek and Panhellenic peoples. In the area where once the acropolis rose, the remains indicate a village with Phoenician and Greek inhabitants.<sup>8,9</sup>

## **Methods**

### **IR with attenuated total reflection (FT-IR/ATR)**

The spectra were recorded with a VERTEX 70 (Bruker) FT-IR spectrophotometer, equipped with a deuterium triglycine sulphate (DTGS) detector. Setting parameters are: resolution 4 cm<sup>-1</sup>; apodization weak. The spectral range was 4000-600 cm<sup>-1</sup> with 32 scans for each spectrum. The ATR spectra were recorded using the Golden-Gate accessory. The Golden Gate™ Single Reflection Diamond ATR Series MkII was used mainly because it does not require sample preparation and the sample could be recovered after the measurement.

### **Raman microscopy**

The Raman spectra were recorded with a confocal Labram instrument (Jobin Yvon-Horiba) equipped with a He-Ne laser at 632.8 nm and a CCD detector (256x1024), cooled by the Peltier effect. The spectra were recorded in backscattering after focalization in several positions within a small area (ca. 100 μm x 100 μm) of the sample. The maximum laser power employed was 5 mW and the usual recording time for good signal-to-noise ratio was 10-30 s. The identification of the components was carried out by comparison with databases and literature references. Furthermore, GRAMS / AI 2.7 was used for the elaboration of the spectra (baseline correction and smoothing).

### **Surface enhanced Raman spectroscopy**

The aqueous silver colloid used in the SERS experiments was prepared by reduction of silver nitrate

(Aldrich, 99.998% purity) by sodium citrate (Aldrich, 99% purity), following the Lee–Meisel method<sup>10</sup>, and 18 MΩ/cm water was used. A rate of colloid (2 mL) was centrifuged at 3000 rpm for 30 minutes. The supernatant was eliminated to have 0.2 mL and ultrapure water was added up to 0.5 mL. The colloid remained in the refrigerator overnight and was used the next day. For the analysis, 2 μL of colloid were added directly to the sample on a glass slide and then 2 μL of a 0.2M KNO<sub>3</sub> solution as aggregating agent. After 1 minute the analysis took place with the instrument cited above. The power employed was 0.6-2 mW and the recording time was 10 s.

## Results and Discussion

In Table I, the inventory numbers with brief descriptions of the containers and sampled powders are given, with interpretation of the micro-Raman, SERS and FT-IR/ATR spectra. The powders identified inside different type of containers were sampled with a steel spatula: a small amount was taken and put inside a plastic vial. After sampling, the ancient remains were analysed at the laboratories of the University of Modena. The data are discussed in detail below. Pictures of the containers are given in Table S1 in supplementary information.

Phoenicians' love for red is highlighted from the great number of powders of this color found in the containers. The powders were probably used to give a hue to cheeks or to lips. Besides these uses as make-up powders, we can also assume a ritual use of ointments and powders containing cinnabar or ochre, applied to the face and the forehead during preparation rituals of the bodies. The discovery of red paint traces on bones and skulls suggests that these practices were common among the Phoenicians as for other populations.<sup>6,11</sup>

[insert Table I.]

## Inorganic components

In many cases, hematite (Inv N. 807-Mozia, 2309-Mozia, 4268-Baglio) was detected as main pigment. The iron oxide, shown in Fig. 2a, was used, either as it was or after being heated to high temperatures to transform yellow goethite into hematite. Recognizing whether it is natural or artificial hematite is complex and it is a much debated issue. In fact hematite can be obtained by heating goethite up to moderate temperatures (300–350°C). The newly formed hematite lattice is inherently quite defective and all peaks are much broader than those of the natural hematite. Furthermore, for the hematite obtained by heating the goethite, a peak appears in the spectrum at 660 cm<sup>-1</sup>, attributable to magnetite, the intensity of which is very sample dependent. The intensity ratio of this peak with respect to the 600 cm<sup>-1</sup> intensity peak has been used as a measure of the impurity content.<sup>12,13</sup> Another parameter used to measure the defect structures is the width of the Raman lines. The full-width at half maximum (FWHM) of the peak at 223 cm<sup>-1</sup> is function of the intensity I(660)/I(600) ratio and it is related to the treatment temperature. The ‘artificial’ hematite specimens display higher values of FWHM, owing to a higher concentration of chemical impurities. Already other authors also reported that it is possible to differentiate the main types of iron oxide using Raman spectroscopy,<sup>14,15</sup> with a very careful experimentation, taking care not to exceed 0.7 mW power as the excitation could induce an enlargement of some Raman bands in the hematite and magnetite spectrum. Thus, in our samples we can see the presence of this band at 660 cm<sup>-1</sup>, which may indicate the presence of traces of magnetite with hematite since this is present together with an enlargement of the Raman bands. This therefore indicates a probable synthetic origin of the hematite present in the samples. Hematite was renowned in Roman culture for its medical use as purgative, corrosive<sup>16,17</sup> and in dermatology.<sup>18</sup>

Other pink and red powders contained cinnabar (unguentaries Inv N. 6480-1-Pepoli, 34396-Salinas, alabastra Inv. N. 7317/7-Salinas, 482-Mozia, 1255-Salinas). Its presence in *alabastra* is interesting because this shape of container is, according to archaeologists as well as ancient texts like those of Pliny the Elder, typically dedicated to the preservation ointments and perfumes. Pliny wrote in Book XIII, 7 of the “*Naturalis historia*” that the perfumes was composed of “*sucus et corpus*” (oil and flavors), but also of the little mentioned colour. “*Cinnabaris et anchusa*” were used to this aim. The

“anchusa” is a well-known organic dye from the *Alkanna tinctoria*, while it is more controversial to indicate unequivocally what the Romans meant by “cinnabaris”. In fact, Pliny himself treats (NH XXXIII, 115 and XXIX, 25) the serious confusion between the Indian cinnabar (called “dragon blood”, red resin from *Dracena cinnabaris* or *Calamus draco*) and the Latin “minium” which today is called cinnabar (HgS), whose toxicity was known. Having to color an oily matrix, such as perfume, organic dyes must be used, so in this specific passage Pliny means the resin. But we have found the HgS pigment. It could therefore be an ingredient exchange in the perfume preparation, or the containers was intended to store a red powder for make-up. The powder 7317/7-Salinas (Fig. 2b) is particularly interesting, with its bright red tint, consisting of HgS (bands at 255 and 344  $\text{cm}^{-1}$ ) with traces of anatase, calcite (band at 1089  $\text{cm}^{-1}$ ), gypsum and quartz. Mixture of cinnabar with crystalline and heated hematite is found inside several containers including two shells (Inv. N. 34396-Salinas) coming from the tomb 138 (burial chamber with a sarcophagus) in Corso Calatafimi-Corso Pisani necropolis, excavated in Palermo in 1953 (Fig. 3, color picture available as Fig 1S in supplementary information online). The many grave goods found are dated from the first half of the 5th century B.C. to the end of the third century A.D. This mixture is also sometimes associated to white minerals, like gypsum or cerussa, to produce a pink color. In other cases, carbon black and pyrolusite (a black manganese oxide) were added probably to darken the mixtures. By these mixtures, many hues were prepared. Hematite and cinnabar are pigments commonly used during Antiquity all over the Mediterranean area and beyond. Although their cosmetic use in the ancient world is widely cited, few studies have actually identified their presence in cosmetic archaeological finds. Pompeian unguentaries, for example, kept a few red pigments consisting mainly of hematite,<sup>19</sup> the ten red Punic cosmetics of Tunisia analyzed by Huq et al. revealed cinnabar and hematite,<sup>5</sup> similarly to Mesoamerican funeral ritual contexts,<sup>20</sup> and again a hematite-based lipstick was found in a Chinese burial.<sup>21</sup>

Minium, the lead oxide  $\text{Pb}_3\text{O}_4$ , is another red pigment observed in one alabastron (Inv. N. 1606-Salinas). Its use as a pigment for lipstick was previously described,<sup>22</sup> but it was also known as an



ingredient in medicines because of its purgative effects and its potential action to treat bites. It was usually synthesized by the thermal transformation of lead compounds (in particular lead carbonates composing lead white), and its natural form was rarely used.<sup>23,24</sup>

[insert Figure 2.]

[insert Figure 3.]

Other materials are more unusual in a cosmetic context. The content of the glass unguentary Inv. N. 23443-Salinas revealed the mineral rhodochrosite  $\text{MnCO}_3$ , a pink mineral not previously considered in ancient cosmetics (Fig. 2c). Rhodochrosite (whose name comes from the Greek word, "rhodokhros", meaning "rose coloured") is a very attractive mineral with an absolutely one-of-a-kind, beautiful colour and is often used in jewelry. Rhodochrosite is a relatively soft stone and ranges between 3.5 and 4.0 on the Mohs scale of hardness, and therefore it is suitable to be ground to make a powder.

The observation of the yellow lead chromate crocoite  $\text{PbCrO}_4$  and the red lead chromate phoenicochroite ( $\text{Pb}_2(\text{CrO}_4)\text{O}$ ) is also a very singular finding (Fig. 4). These two rare minerals are found as major ingredients in three cosmetic containers (Inv. N. 805-Mozia, 1-98-2-Pepoli and 4386-Mozia). In fact, these minerals have never been previously attested for cosmetic use. The red-orange crystals of crocoite were described first by Lehmann in 1766 and synthesized by Vauquelin in 1809 before its use as a pigment since the 19<sup>th</sup> century.<sup>25-27</sup> It was unambiguously identified by micro-Raman spectroscopy and X-ray diffraction techniques in ancient wall paintings in the Siena Cathedral crypt<sup>28</sup> and in mediaeval murals in Northern Bohemia.<sup>29</sup> In our case we can be sure that the mineral was deliberately placed in containers, since the *amphoriskos* 805, a precious polychrome glass container, held a relatively large mineral fragment (about 2mm x 2 mm), probably intended to be ground just before its use. In the two other holders it was present as a powder.

[insert Figure 4.]

### Organic components

With regard to organic components, we note also that only one sample (N. 805-Mozia) is showing an significant presence of fatty acids. In fact, the sample infrared spectrum reported in Fig. 5 showed a preponderant presence of gypsum for the hydroxyl-stretching vibrations at  $3395\text{--}3545\text{ cm}^{-1}$ , the very strong band of water deformation at  $1629\text{ cm}^{-1}$ , the broad band at  $1135$  and the doublet at  $685\text{--}622\text{ cm}^{-1}$  due to the  $\text{SO}_4$  stretching mode. The free fatty acid presence is evident from the CH stretching modes at  $2933$  e  $2875\text{ cm}^{-1}$ , together with the C=O stretching at  $1706\text{ cm}^{-1}$ , which indicates the presence of free and non-esterified fatty acids, lacking the  $1740\text{ cm}^{-1}$  ester band. It could be a particularly degraded oil. In fact, the cosmetic formulations were extemporaneously prepared by combining powders and fats/oils or simply saliva (or water) to adhere to the face.

[insert Figure 5.]

The SERS technique is considered a technique of choice for the identification of organic dyes present in different archaeological contexts, from textiles to paintings and artefacts.<sup>30</sup> SERS technique was applied to four samples that did not provide Raman microscopy results (eg Inv. N. 802, 809, 810, 6158 from Mozia). They were first prepared by separating the red spots from the uncolored matrix. These grains were abundant and macroscopically visible (Fig. 2S available in supplementary information). SERS spectra show the presence of an organic molecule that is likely at the origin of the red color (Fig. 6). Nevertheless the bands are not corresponding to the most common organic red dyes used in antiquity. In fact, thanks to the comparison with the reference spectra of dyes, the use of madder, purple, kermes, sandalwood, brazil wood, dragonblood, carthamus, litmus (roccella),

alkanna, red beet, and rhubarb could be excluded (on the basis of the SERS spectra as suggested also by M. Leona, Metropolitan Museum, NY).<sup>31</sup> HPLC analysis performed at the Metropolitan Museum confirmed that identification of this main red dye is not possible (Data not shown).

[insert Figure 6.]

The SERS spectra obtained on the four samples show the same characteristic structure and bands of red anthraquinone organic dyes. In fact dyes with chromophores having an anthraquinone structure exhibit rather similar SERS spectra,<sup>32</sup> with a weak band around  $1620\text{ cm}^{-1}$ , attributable to the rings C–C stretching mode and to the C=O group interacting with the Ag nanoparticles; a weak band around  $1550\text{ cm}^{-1}$ , due again to a ring C–C stretching mode; a medium band at about  $1460\text{--}1470\text{ cm}^{-1}$ , assigned to ring C–C stretching and to C–OH bending modes; a medium-strong band approximately between  $1390\text{ and }1420\text{ cm}^{-1}$  with a similar assignment; a strong band at  $1290\text{--}1295\text{ cm}^{-1}$  (C–OH bending modes).<sup>33,34</sup>

The anthraquinone dyes can have different origins depending on the plants or the insect species from which the dyes have been extracted: i.e. for insects: *Dactylopius coccus* (cochineal) *Kermes vermilio* and *Kerria lacca*, and for plants like wild madder (*Rubia peregrina*) and madder (*Rubia tinctorum*). The corresponding chromophore are carminic, kermesic and laccaic acids<sup>35</sup> or alizarin and purpurin.<sup>36</sup>

The measured spectra on our samples are close to those of kermesic acid,<sup>37</sup> with bands with similar intensities in the region between  $1650\text{ and }1550$  and a most intense peak that appears for kermesic acid and in our spectra at  $1367\text{--}1369\text{ cm}^{-1}$ , corresponding to the CH deformation; a band of medium intensity, characteristic for kermesic, laccaic and carminic acid, is also present for our sample, with shoulder varying from  $659\text{ to }635\text{ cm}^{-1}$  (skeletal vibration, out-of-plane bending mode of the CH and OH bonds). In our spectra, the intense band at  $1702\text{ cm}^{-1}$  has no correspondence with the other reference molecules. It can be attributed to the presence of ester groups that are not present in the structure of the other most common organic red dyes made from insects. Interestingly, an organic red

dye used for producing lakes was not identified in other archaeological Punic make-up samples and pigments from Tunisia but no SERS characterization was realized.<sup>5,6</sup>

We can hypothesize the use of a red deriving from now extinct species (animal or plant) or produced with extraction techniques that are unknown today. The insect *Kermes vermilio* living on the sap of the Kermes oak is native of the Mediterranean basin, while species such as *Dactylopius coccus* are characteristics of the Americas and *Kerria lacca* is native from Asia. Even if the SERS spectra of these dyes have a certain similarity with the red Mozia sample, it is impossible to determine its origin remains unidentified. Other measurements, for instance with HPLC-MS, would be useful for its characterization but it would need anew sampling of the containers.

## Conclusion

From an overview of the data, obtained on the Sicilian Punic red/pink cosmetics found in different sites, the heterogeneity of the raw materials used is striking. We observe that the red color was given by mineral components ranging from hematite, cinnabar, red lead, to compounds the cosmetic use of which was not ascertained so far. In fact, the identification of minerals such as rhodochroite and especially the minerals crocoite and phoenicochroite is unusual. The origin and nature of a red organic dye, the SERS spectra of which was obtained, remains without correspondent in traditional databases. Furthermore, we have not observed more common pigments like madder lake and Tyrian purple that were previously described by other works on Tunisian make-up.<sup>5,6</sup>

The type of containers containing these colors, ranging from purely Punic to Greek ones, found in tomb contexts, suggests an integration of these cultures with ancient indigenous ones in Sicily. The variety of containers on the one hand and the raw materials found on the other could then derive both from the range of the trade routes with the East, the Greeks or with indigenous populations, as already proposed by scholars.<sup>8</sup> The wide variety and sophistication of red substances used go well with the image of the Punic handed down by historians, as a society with a high standard of living, that is also reflected in the refined preparation of the cosmetic containers, and of the funerary objects that

accompanied them.

The present study was limited to a first group of 22 samples with a red color, and a research on the archaeological findings of the Phoenicians in Marsala, Trapani and Palermo is in progress. With the permission, the interest and the support of the various museums, we intend to extend the research in order to arrive at an overview of the nature and the functionality of the cosmetic and ointments residues.

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### **Supplemental Material**

All supplemental material mentioned in the text, (Tab. S1) containers' pictures of samples analyzed, (Fig. 1S) shell 34396 having traces of red color and microphotograph of the mixture and (Fig. 2S) image of the mysterious red point (sample 809) are available in the online version journal.

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## Table

Table I: Containers and description of samples analyzed and identified minerals by FTIR, Raman, and SERS spectroscopies.

Museum/ Inventory	Description	Content	Results
Mozia 801	<i>Alabastron</i> , polychrome glass, Birgi Necropolis, 5th cent. BC	Black-grey powder with bright red little grains	Red pigment: organic red (SERS) Other: Quartz, calcite, carbon
Mozia 805	<i>Amphoriskos</i> , polychrome glass, Birgi Necropolis, 5th cent. BC	Brown-red grains	Red pigment: crocoite, phoenicochroite, Other: Gypsum, free fatty acids
Mozia 807	<i>Aryballos</i> , Polychrome glass Birgi necropolis, 5th cent. BC	Abundant fine reddish powder	Red pigment: Hematite Other: Quartz, TiO <sub>2</sub> , MgOxalate, feldspar, calcite, magnetite
Mozia 809	<i>Aryballos</i> , Polychrome glass. Birgi necropolis, 5th cent. BC	Brownish-red powder with bright red little dots.	Red pigment: Hematite, organic red (SERS) Other: Quartz, calcite, magnetite, feldspar
Mozia 810	<i>Aryballos</i> , Miniaturistic polychrome glass, Birgi necropolis, 6th-4th cent. BC	Brown powder with iridescent and red dots.	Red pigment: Hematite, organic red (SERS) Other: Quartz, magnetite, corundum
Mozia 813	<i>Oinochoe</i> , Polychrome glass, Birgi necropolis, 6th-4th cent. BC	Reddish fine powder.	Red pigment: Hematite Other: Quartz, calcite, magnetite
Mozia 6158	<i>Alabastron</i> , painted Corinthian ceramics, 7th-6th cent. BC (infant burial)	Black-grey powder with bright red little grains	Red pigment: organic red (SERS) Other: carbon, quartz, calcite
Mozia NI 482	<i>Alabastron</i> . Alabaster, Birgi necropolis	Very white powder with red grains	Red pigment: cinnabar Other: Gypsum, quartz, calcite, anhydrite, charcoal
Mozia 4386	<i>Balsamarium</i> , terracotta,	Brown powder with pink,	Red/orange pigment: phoenicochroite

	7th-6th cent. BC	beige, blacks, browns, red-orange grains.	Other: Quartz, calcite, carbon, TiO <sub>2</sub> , apatite
Mozia NI 3455	Bottle, terracotta with painted decoration, 3th cent. BC	Reddish powder.	Red pigment: Hematite, cinnabar  Other: Calcite, apatite, CuO, magnetite, pyrolusite (MnO <sub>2</sub> )
Mozia NI 2284	<i>Oinochoe</i> , Female head shape, 5th cent. BC	Red residue.	Red pigment: Hematite, cinnabar  Other: Calcite, quartz, gypsum, anhydrite, magnetite
Mozia NI 2309	<i>Lekythos</i> , Attic terracotta, 5th cent. BC	Pink powder	Red pigment: Hematite  Other: Carbon, TiO <sub>2</sub> , magnetite
Salinas 1606	<i>Alabastron</i> , Corinthian (Astuto collection), 630-590 BC	Dark red residue	Red pigment: Minium, hematite  Other : Gypsum, carbon, calcite, magnetite, goethite
Salinas 34396	Cosmetics holder made with <i>Pecten lacobaeus</i> valves, T.138, 1953 excavations, Palermo	Red traces	Red pigments: Hematite, cinnabar  Other: Calcite, quartz, magnetite, lepidocrocite, goethite
Salinas 7317/7	<i>Alabastron</i> , Alabaster, Marsala, Capuchins necropolis, T.34	Bright red powder.	Red pigment: Hematite, cinnabar  Other: Gypsum, calcite, quartz, magnetite, TiO <sub>2</sub>
Salinas 1255	<i>Alabastron</i> , terracotta, Lilibeo necropolis	Pink powder	Red pigment: Hematite, cinnabar  Other: Calcite, magnetite, TiO <sub>2</sub>
Salinas 18180	<i>Alabastron</i> , polychrome glass	Red powder.	Red pigment: Hematite  Other: Magnetite, TiO <sub>2</sub> , quartz, silicates, Carbon, Calcite
Salinas 23443	Glass unguentary	Fine beige powder	Pink pigment: rhodochroite  Other: Calcite, carbon, orthoclase, analcime
Baglio 4235	<i>Alabastron</i> , glass, Lilibeo necropolis, 4th–3th cent. BC	Red-brown powder.	Red pigment: Hematite  Other: Magnetite, quartz, calcite, feldspar (amazonite), TiO <sub>2</sub>
Baglio 4268	Shaped-foot vase with shoe, uncertain origin, 3th	Red-brown powder	Red pigment: Hematite, cinnabar  Other: Calcite, carbon

	cent. BC		
Pepoli 1 98-1 e 2	Unguentarium, opaque glass	Pink-brown powder	Red pigment: Hematite, phoenicochroite, cinnabar  Other: Magnetite, lepidocrocite, calcite, TiO <sub>2</sub> , pyrolusite, apatite, carbon, cerussite, maghemite
Pepoli 6480-1	Globular unguentarium, Capuchins necropolis Lilibeo, 4th-3th cent. BC	Pink powder	Red pigment: Hematite, cinnabar  Other: Calcite

### Figure Captions:

Fig. 1. Archaeological origin sites of the examined Punic cosmetics.

Fig. 2. (a) Raman spectrum of sample 807 and crystalline hematite reference spectrum; (b) Raman spectrum of sample 7317/7 corresponding to cinnabar (peak at 1089 cm<sup>-1</sup>: trace of calcite); (c) Raman spectrum of sample 23443 and Rhodochrosite reference spectrum.

Fig. 3. Shell 34396 having traces of red color.

Fig. 4. From the top: sample 805 (red grain), crocoite reference, sample 805 (yellow grain), phoenicochroite reference.

Fig. 5. Infrared spectrum of N. 805 sample from Mozia: traces of degraded organic material suggest that it was a ready-to-use cosmetic.

Fig. 6. Micro-Raman spectrum of the mysterious organic red (sample 809) with (top) and without SERS colloid.

## **Supplementary material**

Tab. S1: Containers pictures of samples analyzed.

Fig. 1S Shell 34396 having traces of red color and microphotograph of the mixture.

Fig. 2S Image of the mysterious red point (sample 809).