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Case study

# The colours of Segesta. Searching for the traces of the lost pigments

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ABSTRACT

Many monuments and objects of the ancient civilizations were painted, but unfortunately the pigments are not still present and sometimes only small traces are evident. The analysis of the traces requires a multianalytical approach through the use of non-invasive techniques and only if necessary of a microsampling. Here, the study of the traces of colours found in some architectural elements and findings belonging to the Archeological Park of Segesta (Trapani, Italy) is reported. The traces are identified and characterised via several techniques such as Optical Microscopy, UV-Fluorescence Imaging, Fiber Optical Reflectance Spectroscopy (FORS), X-ray Fluorescence (XRF) and FT-IR Spectroscopy. Various pigments were identified, some of which are no longer clearly visible to the naked eye: hematite, umber, vegetable black and bone black. Despite the small amount of detectable pigment, the performed investigations allowed us to define part of the pictorial palette to imagine and relive the past in one place.


## 1. Introduction

Pigments have always played a role in human evolution and are a form of expression over time. Clearly, the availability of materials, as well as the function of each artefact in the social and cultural environment, determined the use and predilection of certain colours [1]. When pigments are applied to an object or a building, they interact with binder, substrate, environment, and so on, and as a whole evolve to become a part of it and its construction system [2,3]. Degradation processes due to lack of maintenance, abandonment and oblivion have caused their loss, leaving only traces, often not visible to the naked eye. In the archeological sites and museum, usually the attention of the visitors is restricted to the evidence and, without a guide, it is not easy to imagine how monuments or objects could be coloured and with which pigments. The searching of residual polychromy with the aid of scientific techniques in archeological monuments and objects is a recent topic. Even if it is well known that the ancient civilisations used polychromy, today only a few traces of their colours survive [1,4].

The numerous traces of color still visible on some important stone or marble buildings, including the Parthenon, the Erechtheum and the Theseion in Athens, prove the use of color of Greeks [1,5,6].

Several authors demonstrated the presence of traces of pigments in the Parthenon sculptures, on Campana reliefs from the Palatine Hill and Colosseum Valley in Rome and on the Frieze of the Siphnian Treasury [7–10]. Zink et al., showed the colours of Hermogenes' temple of Artemis [11].

Evidence of traces in objects saved at Morgantina (Italy) were recently founded [12–15] and the Project "*Morgantina a colori*" was finalised to their research [16,17]. The investigation showed the use of yellow and red ochres, manganese black and umber.

Recently, new data has emerged about the Temple B of Selinunte, around which a debate has developed on polychromy in Greek architecture and sculpture in the 19$^{th}$ century [18].

Although instrumental and technological progress of the last few decades has favoured the study of pigments and guaranteed the accuracy of results under certain measuring conditions, also in situ, pigments detection may be influenced by their quantity and their position on the surface of the objects, which can be for example concave or convex. This affects the capacity of colours to reflect, absorb or transmit the radiation, although effects due to physical characteristics such as particle size are also expected [19]. Especially in the searching of the traces, these aspects can affect the choice of the methodology and of the approach as well as the best technique to use for the investigation[20].

On the other hand, since the integrity of the traces is a key role and, quite often, the heritage objects are non-movable, the analysis of trace pigments necessarily requires in situ measurements with portable equipment. Thus, it is very important selecting the physico-chemical analytical techniques for a non-destructive char-

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acterization [21] to determine the real pigments present in any studied object [22]. Bracci et al., discussed about the methodology to investigate the traces highlighting the rules of the use of several non-invasive methods [23] and about a different methodological approach to identify the traces of color on statues excavated from the archeological site of Hierapolis of Phrygia (Turkey) [24]. The Ultraviolet Fluorescence and Visible Induced Luminescence were used to detect traces of organic materials and of Egyptian blue, respectively, demonstrating that the sampling is not always necessary.

Gasanova et al., to identify the traces of pigment on the limestone sculptures from Cyprus, discussed advantages and problems of combined and separate use of portable XRF and FORS spectrometers, raising the question of their complementarity and interchangeability for the purposes of pigments identification [25]. Both techniques have both advantages and disadvantages influencing their performance and which have to be considered. The combined methodology proved to be effective for the identification of general types of pigment compounds, enabling a preliminar characterization of polychromy. However, the results raised important questions and the need for direct evidence by FTIR or Raman Spectroscopy. Zink et al., identified, for the first time, the color remains on three marble fragments of the Artemis temple's exterior facade (Western Turkey), using the same methodological approach [11]. Traces of a black pigment, probably carbon black, red hematite and calcium-containing white were found. In some cases, however, the applied design departs from the traditional color. Consequently, the development of methodologies, allowing to the detection and interpretation of the traces of color remaining on the surfaces of archeological artefacts, is evolving and depends on the nature of the materials.

However, any investigation of traces is a challenge and the approach used in different case-studies needs to be documented. For this reason, some examples of investigation of traces of pigments are reported here.

All artefacts are saved at Archaeological Park of Segesta (Trapani, Italy) and come from a sacred area of the Elymian Segesta, the sanctuary of Contrada Mango. In detail, we searched the traces of pigments of 1) N. 4 architectural fragments of *sima* with eaves in the form of a lion protome of a Doric Temple [26]; 2) N.1 architectural fragment of *geison* of the same temple; 3) a Greek stone *statuette* of Athlete [27]. In our knowledge, no conservative treatments have been performed in the past on the investigated objects.

From the archeological point of view, the finding of the traces of pigments is important because it may provide data on the true aspect of architectures and objects with their chromatic combinations found in this sacred area and contributes to enrich our knowledge about polychromy in the temples and sculptures of Greek age.

The Sanctuary of Contrada Mango stands on a plateau on the south-eastern slopes of Monte Barbaro. The area was investigated between 1950 and 1960 by the Superintendence. The excavations brought to light a monumental wall of *temenos* inside which remains of architectural elements have allowed to identify a large Greek Doric temple dated around 450 BC. [28,29]. The Temple and the statuette, as well as other finds, testify to the intense cultural contacts that Segesta had with the Greek environment.

A different approach and several techniques were used for each artefact. In general, first, the pigment traces were discovered in a **non-invasive way** and **in situ** inspecting the objects via a portable optical microscope. UV Fluorescence imaging, X-ray Fluorescence Spectroscopy (XRF) and Fiber Optic Reflectance Spectroscopy (FORS) were thus used to identify the nature of the pigments. When the collected data were not considered of high quality, Fourier Transform-Infrared Spectroscopy (FT-IR), applied on collected samples, were used. Details on each instrument are reported in paragraph 3.

## 2. Research aim

The goal of the paper is to show a non invasive, multianalytical approach, mainly applied in situ, for the investigation of traces of pigments in archeological findings.

## 3. Methods

*Macrophotos* were acquired with a DigiMicro Profi USB 5.0 MPixel portable digital optical microscope and a magnification of 30x.

*UV Fluorescence.* The photos were taken with a Nikon D3100 camera equipped with a NIKKOR 18–55 mm 1: 3.5–5.6 G lens and lighting the artefacts with a UV-A Wood lamp (centered at 365 nm, power 400 Watt) equipped with a 52 mm long pass filter at 395 nm.

*FORS spectra* were acquired in situ through a UV–VIS–NIR Ocean Optics portable fiber-optic spectrometer. The instrument used is equipped with a DH mini light source, a detector operating in the spectral range 350 – 1100 nm (USB 2000 + XR1) and a reflection bifurcated probe, in which seven illumination fibres are installed around a central reading fiber, providing illumination and detection of diffused light from the same direction.

*XRF spectra* were acquired in situ through a portable Tracer III SD Bruker AXS spectrometer equipped with Rhodium Target X-Ray tube operating at 11 µA and 40 kV. The detector is a silicon drift X-Flash SDD with Peltier cooling system and 3–4 mm diameter spot. The instrument allows to detect elements with an atomic number $> 11$. For each measurement the acquisition time was fixed at 30 s in order to get a proper signal to noise ratio. Vacuum was not applied at the head of the instrument and no filters were used. Spectra were acquired with S1PXRF® Software, while their analysis was performed using ARTAX® software in order to assign each peak and estimate the peaks area performing a semiquantitative comparison of the spectra. The S1PXRF® software rules the data acquisition. Ar, Ni, Pd and Rh signals, due to the atmosphere and instrumental components, respectively, are also present in all spectra. Calcium sum peaks are also present in some spectra. These peaks are fake peaks and appear in the XRF spectrum at twice the energy of the XRF calcium emission lines $K\alpha 1$ (3,69 keV) and $K\beta 1$ (4,01 keV).

*FT-IR spectra* were acquired through a VERTEX 70 V Bruker spectrophotometer equipped with a Platinum ATR unit with diamond crystal ($\eta = 2.4$) operating in the spectral range between 4000 and 400 $cm^{-1}$, a spectral resolution of 2 $cm^{-1}$, and 120 scans. Spectra were acquired at a pressure of 2 hPa. In all spectra a baseline correction of scattering was made. Data analysis was performed using the OPUS 7.5® software.

## 4. Results

### 4.1. Fragments of sima of the Doric Temple of Contrada Mango with eaves in the form of a lion protome

The four fragments of *sima* (A, B, C e D; inv. SG 1701, 17.004, 17.002, 17.003 respectively [29]) are shown in Fig. 1a. The coloured points in the figure are the indication of the individuated traces and of the sampling.

The visual analysis of the *Gronde leonine* with the naked eyes did not allow to detect traces of pigments. The white area was evident to the eyes, while traces of red and black pigments were discovered only through an inspection carried out by using a portable

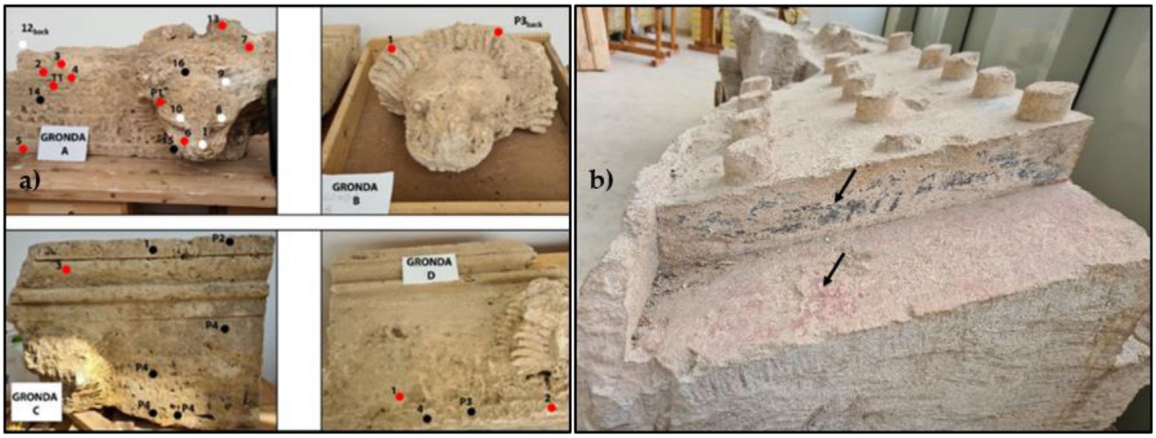


**Fig. 1.** Artefacts from the Doric Temple of Contrada Mango. a) (left) Fragments A, B, C e D. Red circles (●): traces of red or red-brown pigment. Black circles (●): traces of black pigment. White circles (**O**): traces of white area. The letter "P" indicates the area where the micro-samples were collected. b) (right) Pigmented areas of the geison fragment inv. SG 2021. The arrows (↑) indicate the sampling points.

digital optical microscope (Fig. 2). The UV photos, reported in Figure SI1 of Support Information, show the areas where traces of materials are still present. The blue-white fluorescence, mainly evident on the lion's head of the fragment A, is typical of calcareous concretions, carbonate substrate or a preparation layer [30,31]. The orange fluorescence can be attributed to several causes such as the presence of organic compounds extraneous to the substrate due to microorganisms growth [30,31]. Unfortunately, the color traces are very small to be well highlighted through UV fluorescence imaging.

The traces of red and black pigments, as well as of the white area, were found under the optical microscope and digitally photographed. For each fragment some macrographies of the representative traces are reported in Fig. 2 and the area is identified in Fig. 1a.

The first analysis of the traces was performed in situ using non-invasive techniques, the XRF and FORS. Due to the very small area to analyze, the optical fiber of FORS was placed using a suitable accessory placed at 90° angle with respect to the area to be analysed. This is the most suitable configuration, based on the expectation that different areas with small dimensions and appreciable surface roughness must be analysed. The use of this probe holder also allows one to assure a constant distance between the probe and the surface to be analysed, avoiding at the same time external light contributions. In detail, through FORS technique and the used configuration it was possible to provide immediate qualitative results without the need of transportation or sample removal, both of which require a special permission. Due to the heterogeneity of the surface, a multiple analysis of the same pigments in different areas was also performed. However, since of the irregularity of the surface, it was possible to acquire high quality spectra only in some areas which were more accessible. In addition, some of the area were covered by dirt, the presence of which compromised the XRF analysis due to the presence in the spectra of elements unrelated to the pigments and to the stone substrate, and caused a noisy signal in the FORS spectra. For these reasons, these data were considered preliminary giving only a hypothesis of the pigments, and four samples were thus collected from the red areas where they were easily detached, and from the black area which, being more adhered to the substrate, were detached by scalpel. FT-IR spectra were then also acquired.

The results show a clear correlation between the information obtained by both elemental and molecular spectroscopies.

The representative XRF spectrum of **red-brown pigments** shows that the main elements are iron (Fe) and calcium (Ca) (Fig. 3a-red). The significant presence of Fe suggests that the pigment is mainly composed of a red iron-based oxide pigment [32,33], responsible for its coloration, while Ca signal can be due to the substrate, the preparation or the binder. The small signals assigned to silicon (Si), aluminum (Al), potassium (K), titanium (Ti) and manganese (Mn), attributable to the presence of quartz, aluminosilicates, feldspars and oxides, are typical components of the stone, as can be seen from the comparison with the XRF spectrum of the stone substrate reported in Figure SI2 of Support Information. On the other hand, the stone is a calcareous rock [34].

It is interesting to note that the intensity of titanium Ka line in the spectra of red pigment is higher than the ones identified in the stone or other color ones. This could be explained taking into account that titanium presence can be associated with the terrigenous component of the sediments used as raw materials for the ochre, confirming that we are looking a pigmented area and providing an indication about the source of pigment even if a quantitative measurement should be necessary [35]. Generally, the characterization of a red pigment is complex [36] because an ochre is a natural earth containing silica and clay [37]. According to Gasanova et al. [25] the use of hematite is supported by low intensity of Al and Si lines whose presence would be typical for earths. The reflectance spectrum (Fig. 3b-red) is characterised by a typical double S-shape (black line). From the comparison with the reflectance curves of historical iron oxide-based pigments by Zecchi store collection [38], it is observed that the two inflection points at 573 and 690 nm and the characteristic slopes of the reflectance curve adapt to the **hematite ($\alpha$-$Fe_2O_3$)** (red line) [39], which presence is also confirmed by the bands at 536 cm$^{-1}$ and 470 cm$^{-1}$ in the IR spectra (Fig. 3c-red) [40]. However, the IR bands at 1432 cm$^{-1}$ and 874 cm$^{-1}$ are attributable to the functional group $CO_3^{2-}$ [41] of calcite ($CaCO_3$), which could be used as preparation layer while the bands at 1074, 798, 777 and 695 cm$^{-1}$ are attributable to the typical Si–O vibrations of quartz [41,42].

The representative XRF spectrum of **black pigments** shows that the main elements are calcium (Ca) and iron (Fe) (Fig. 3a-black), while phosphorus (P) and titanium (Ti) are present as minor elements. In this spectrum a strong contribution of calcium sum peaks is overlapping the iron K$\beta$1 signal deforming its shape. The IR spectrum (Fig. 3c-black) allows us to identify the presence of calcite by the bands at 1800, 1449, 875 and 712 cm$^{-1}$ [43]. A weak signal at 2513 cm$^{-1}$ is also observed, which some authors have associated with vibrations of $CO_3^{2-}$ in calcite and minerals of the calcite and dolomite groups [44]. In this case, considering how the collecting was made, the presence of calcite is justified by the calcareous nature of the stone substrate, being the calcite the main

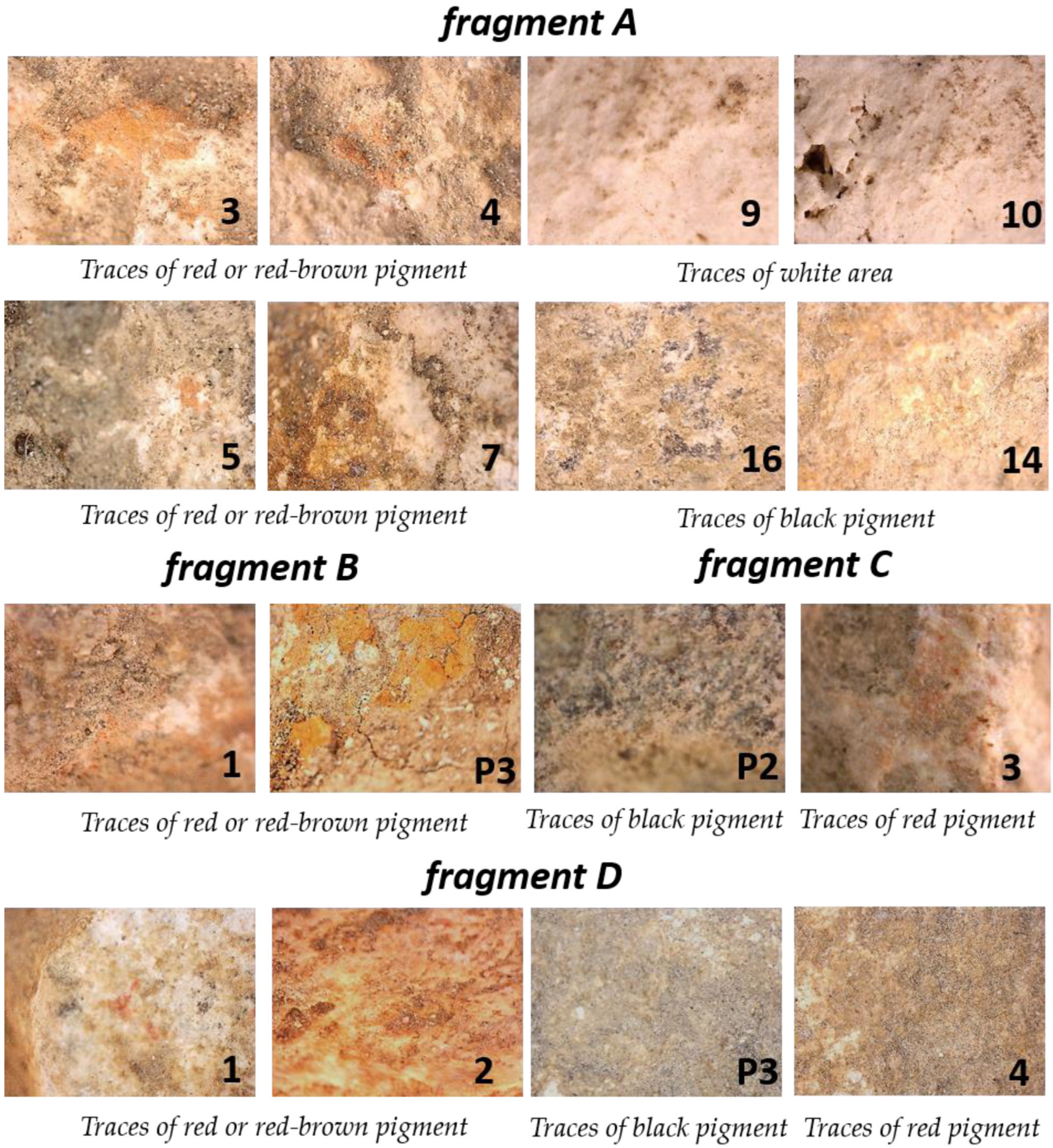


**Fig. 2.** Macrophotos of the traces observed in each fragment.

component of limestone (see Figure SI3 of Support Information). Intense absorption bands at 1005 and 1030 $cm^{-1}$ attributed to the stretching vibrations of Si–O bonds produced by the silicate minerals are also identified. Finally, in the lower spectral region the bands at 530 and 460 $cm^{-1}$ could be attributed to Si–O bending vibrations and Al–O vibrations of silicates [45]. There is no information regarding the presence of a black pigment. The reflectance spectrum (Fig. 3b-black) shows an approximately flat and linear curve typical of black pigments. The black pigments cannot be differentiated by FORS [46]. However, the presence of phosphorus in the XRF spectra of the traces, not present in the XRF spectrum of substrate, can be indicative of a black pigment of animal origin, probably **bone black** [47,48]. Unfortunately, the characteristic IR vibrations of the P-O-P bonds of phosphate from hydroxyapatite at 1256 $cm^{-1}$ and 800 $cm^{-1}$ are not visible due to the strong contribution of the absorption bands characteristic of calcite and silicate minerals, as observed by other authors [49–51].

### *4.2. Traces of pigments on geison fragment (inv. SG 2021)*

The pigmented areas of *geison* fragment are shown in Fig. 1b. The XRF and FORS spectra acquired in situ and the IR spectra of two collected samples are reported in Figure SI4.

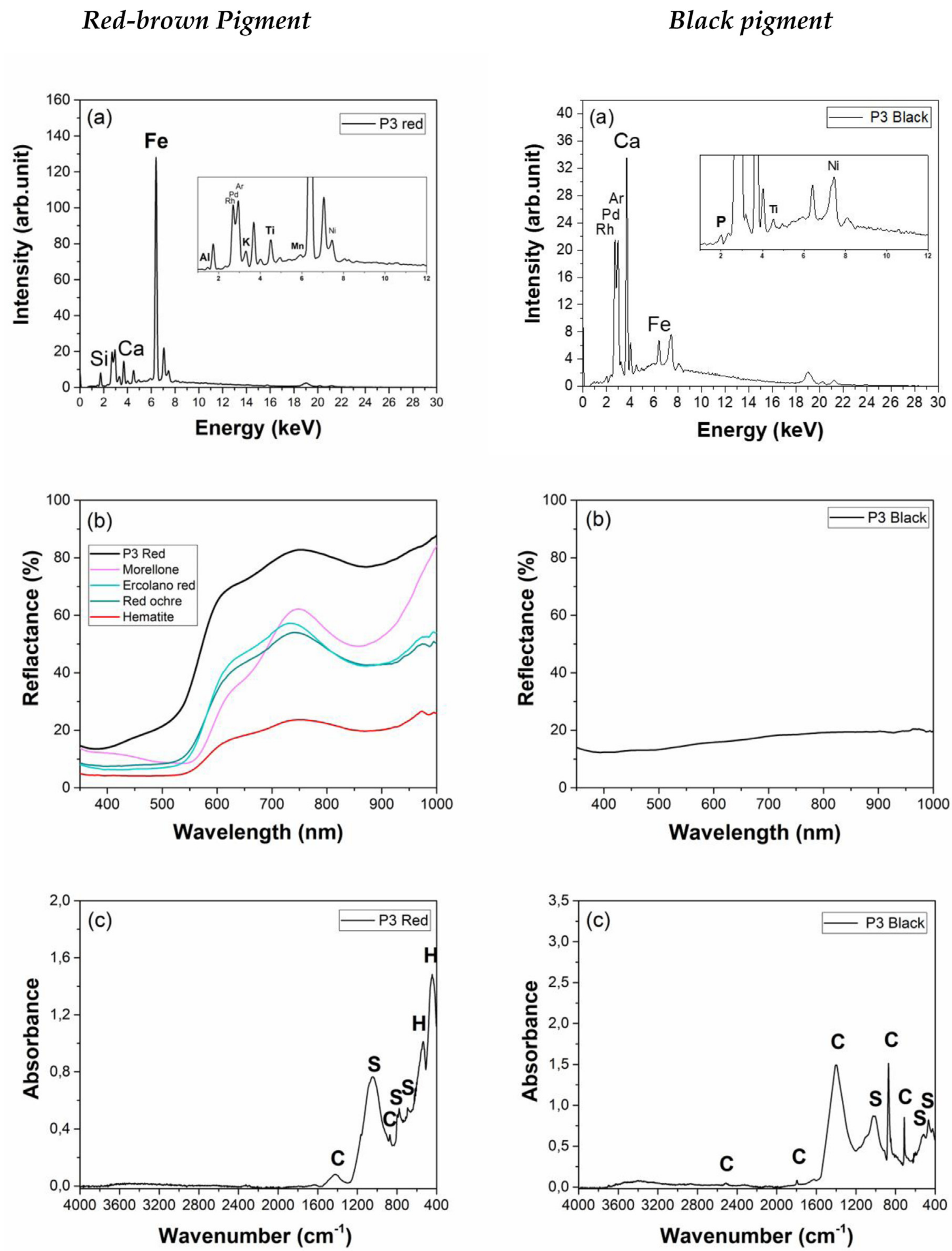


**Fig. 3.** (a) XRF, (b) Reflectance and (c) ATR-FTIR spectra of the samples collected from Fragment B, P3 Red (left) and Fragment D, P3 Black (right). Coloured lines are reference spectra. The letters C, H and S identify the peaks of calcite ($CaCO_3$), of Hematite ($Fe_2O_3$) and of silicate minerals, respectively.

The representative XRF spectrum of red pigments shows that the main elements are calcium (Ca), iron (Fe) and lead (Pb) (Figure SI4a-red) while titanium (Ti), present in trace, is a typical element of the stone (see Figure SI2 of Support Information). The anomalous presence of zinc (Zn) may simply be "environmental noise", meaning an element from the archeological context or impurities in the ochre [52].

Again, the significant presence of Fe suggests that the pigment is mainly composed of a based red iron oxide pigment [32,33], identified as ***Hematite*** (**$\alpha$-$Fe_2O_3$**) by FORS and IR spectroscopy. In fact, the reflectance spectrum (Fig. 4b-red) is characterised by the typical double S-shape and two inflection points at 573 and 690 nm [33], while the IR bands (Fig. 4c-red) at 531 and 471 $cm^{-1}$ are attributable to vibrations Fe – O [53]. The presence of

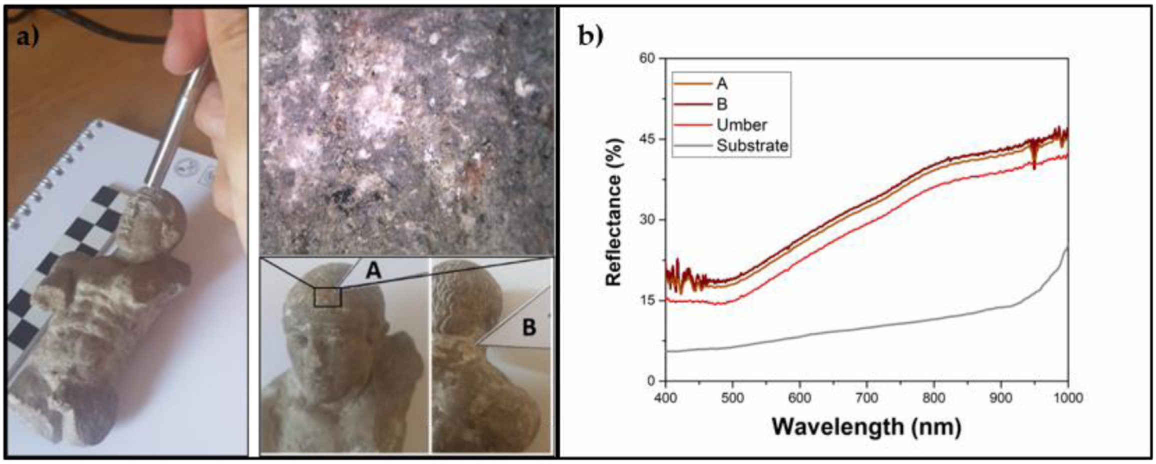


**Fig. 4. a)** (left) Photo of Athlete during the acquisition of FORS spectra; (right-up) macrophotos of the pigment traces and (right-down) photos of the analysed area, **b)** (right) Reflectance spectra. The red line is the reference spectrum of Umber.

Pb signals in the XRF spectra together with IR bands at 287 and 230 $cm^{-1}$ (Fig. 4c-red), attributed to vibrations Pb – O [41], suggests the use of **Minium** ($Pb_3O_4$), probably mixed with Hematite [27,28]. This finding is in agreement with results of Marketou et al. [54] and of Gasanova et al. [25] which demonstrated the presence of Pb lines in the traces of red pigment on the limestone sculptures from Cyprus. A mixture of iron red with red lead ($Pb_3O_4$) was detected also in samples from Thassos island [55] and Southern Kea island [56].

In the IR spectrum the characteristic bands of calcite at 1800, 1406, 876 and 712 $cm^{-1}$ are also present [57]. The representative XRF spectrum of black pigments shows the presence of calcium (Ca), titanium (Ti) and iron (Fe) (Figure SI4a-black). The presence of Ca is attributed to calcite ($CaCO_3$), as confirmed by IR spectra (Figure SI4c-black). The flat reflectance spectrum (Figure SI4b-black), typical of a black pigment, and the absence of characteristic peaks in the XRF and FT-IR spectra useful to identify a type of pigment, suggests the presence of an organic pigment of vegetable origin, probably **Carbon black** [39].

### *4.3.* Athlete

The statuette of *Athlete*, together with the analysed red area and the FORS spectra, is shown in Fig. 4. The figurine (9.4 cm high), comparable with sculptures of Cycladic production [27], comes from the same archeological context as the *sima* fragments (the contrada Mango sanctuary), and it is probably a votive offering. This is a find of great interest, datable to 460–450 BC, namely more or less contemporary to the Doric temple above mentioned; it is now devoid of the polychromy that was to complete it, barely perceptible and no longer visible in its entirety [27].

The traces of red pigment, located on the head and body, were identified by examining the statue under a digital optical microscope (Fig. 4a, right-up). Due to the small size of the traces (∼ 6 $mm^2$) respect to the larger size of the XRF equipment analysing spot (∼ 16 $mm^2$), the acquisition of XRF spectra was not considered suitable, because of the strong influence of the signals of other elements located in the surrounding of the traces. In addition, the sampling was not considered suitable because of the very few observed traces. Thus, in situ, it was possible to carry out only the FORS measurements whose spot size is about 5 $mm^2$. Furthermore, in order to achieve a better control on the analysed area and reduce the noise due to difficult probe-holder placements, the measurements were performed by using only a reflection probe in a dark environment. This approach provided a better quality of the spectra and can be considered a good solution for the in situ examination of traces on not flat surfaces. In this way it was possible to discriminate the FORS signal of the pigment from that deriving from the substrate (Fig. 4b, gray line) which does not exhibit any spectral characteristics. The reflectance curves of the red area show a typical S-shape characterised by a weak positive slope at the wavelengths between 550 and 800 nm. These spectral features are characteristic for **Umber** pigment, as comparable with the reference spectrum [39]. Umber is a general designation for a mineral substance containing between 5 and 20% manganese oxides and hydroxides and a larger percentage of iron oxides [58].

## 5. Considerations

In this paper, the investigation of the traces of pigments of some architectural elements and objects belonging to the Archeological Park of Segesta is reported. In light of the literature, this study can be considered an additional example of physical and chemical analyses useful to determine the real pigments where it highlights the importance of the use of several non invasive methods, as Bracci et al. claim [23]. The traces were mainly analysed through a non invasive approach by using a combination of several analytical techniques such as optical microscopy, UV-fluorescence, XRF and FORS spectroscopy, all non-invasive and applicable in situ. The FT-IR Spectroscopy, applied on collected samples, was used to confirm the hypothesis when the quality of the spectra was not good enough to have an unique answer. Among all used techniques, the FORS, by using an optical fiber, was the most adequate, centering the traces perfectly even in roughness area.

Since the traces of polychromy are often located in areas of deep depressions of the relief, they are hardly accessible with bulky analytical equipment. For example, some of these were easily accessible for acquiring FORS spectra, but not XRF spectra. The interchangeability of XRF and FORS techniques for the identification of general type of pigments is a valuable knowledge that should be considered, when choosing among analytical techniques in conditions of limited accessibility of analysed spots. Based on various studies, the methodology we have applied and the sequence of imaging, optical and chemical-physical investigations are therefore effective and indispensable for obtaining useful information in respect of the work of art.

In addition, the most important challenge was the data analysis. ***Hematite*** and ***Minium*** as red, ***Umber*** as dark red and ***Carbon black*** and ***Bone black*** as black pigments were identified (Table 1). Most of them are not visible with the naked eyes, so that the ob-

**Table 1**
Pigments identificated in the investigated findings.

| | red | black |
|---|---|---|
| *Fragments of sima of the Doric Temple of Contrada Mango* | Hematite ($\alpha$-$Fe_2O_3$) | Bone black ($Ca_3(PO_4)_2$ + $CaCO_3$ +*C*) |
| *geison fragment (inv. SG 2021)* | Hematite ($\alpha$-$Fe_2O_3$) Minium ($Pb_3O_4$) | Carbon black |
| *Athlete* | Umber ($Fe_2O_3$ (· $H_2O$) + $MnO_2$·(n $H_2O$)+ $Al_2O_3$) | |

tained information is a support for the archeological research. The presence of ***Carbon black*** and ***Bone black*** can be discussed in light of the position of the two different parts belonging to the same temple. They may have been applied by purpose with the idea to give a different shade of black. However, we cannot also exclude that it was only accidental because they had two different black pigments. As reported by other authors *"Nonetheless, it is hard to draw general conclusions about the function and "value" of the applied pigments on such a limited group of tiny wall painting fragments."* [4].

These findings are in agreement with the known architectural polychromy of the temple of Athena at Priene and of Apollo at Didyma and the Mausoleum at Belevi [11]. Unfortunately, we didn't find the presence of other pigments such as yellow ochre, green ochre or azurite, which could give a deeper idea of the used pigments as well as on the decoration. Probably they could also be present, but today we cannot observe even the traces.

The results of this study were also highlighted during the new exhibition of the Archeological Park of Segesta, showing some panels close to the artefacts, where a digital restoration was proposed by Prof. Limoncelli of the University of Palermo (Italy). In this way it can be considered an example of fruitful cooperation between chemists, archeologists and the public Institutions which has as its only common goal the safeguard of the Cultural Heritage.

## CRediT authorship contribution statement

**Veronica Ciaramitaro:** Data curation, Formal analysis. **Francesco Armetta:** Data curation, Formal analysis. **Monica de Cesare:** Investigation. **Maria Luisa Saladino:** Conceptualization, Methodology, Investigation, Writing – review & editing.

## Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2022.11.003.

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