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Non-invasive characterization of the pigment's *palette* used on the painted tomb slabs at Paestum archaeological site

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Abstract. A scientific interdisciplinary team promoted an integrated archaeometric study of selected frescoed tombs within a project funded by Archaeological Museum of Paestum (Capaccio, Salerno, southern Italy). By using a multi-disciplinary approach, a comparative study of the pigments used on the representative painted slab tombs was carried out with the aim of identifying specific markers and unveiling the new features of the executive techniques. The investigated tombs, displayed at the museum or stored in the deposits, come from Hellenistic and Lucan necropolis. The preliminary investigation here discussed involved several non-destructive analytical techniques (IRR, UV fluorescence, VIL, FORS, ER-FTIR, Raman and XRF). This multi-analytical research was applied on the pictorial surface of the following frescoed tombs: the well-known Tomb of the Diver from Tempa del Prete necropolis; the Tomb of the Palmettes from Arcioni necropolis; the tombs T314 and T210 from Gaudio necropolis; the tombs T6, T23, T21, T76, T20, T11, T12 from Andriuolo necropolis and the tombs T109 and T110 from Santa Venera necropolis, were investigated. The archaeometric results shed light on



some markers of a local artisanal tradition developed in the Greek colony of Paestum around 500-475 BC.

1. From archaeological background to archaeometric research

The archaeological excavations carried out at the site of Paestum in Campania, province of Salerno (Italy), since the early nineteenth century led to the discovery of several tombs painted on the internal side of the walls [1–3].

The tombs were usually box-shaped, with four slabs of local travertine forming the walls, closed by a double sloping roof or by a single horizontal slab. Among the approximately one thousand burials, about eighty were painted and of these fourteen were chamber tombs. Although the ratio between painted tombs and the total number of burials is different over time, the former constitutes no more than 9-10% of the findings. The funerary paintings, therefore, can be considered as an indicator of social distinction and probably the choice of images is representative of the ideals of the hegemonic classes [2,3]. Besides that, also the choice of the raw materials could represent an important indicator for solving archaeological questions about the external or local artisanal tradition, as recently suggested by new hypothesis followed the discovery of the Tomb of the Palmettes and its similarity to the Tomb of the Diver. To understanding this open question a new archaeometric research has been started by Italian Association of Archaeometry (AIAR), in a concretely multidisciplinary way thanks to the manifold skills own of the AIAR researchers coming from different fields of study applied to Cultural Heritage. The research activities, carried out in collaboration with the archaeological Park of Paestum, were aimed to make a comparative analysis of raw materials and executive techniques used in the painted tombstones artworks belonging to the different chronological phases at the Paestum site and, then, to verify a possible local artisanal tradition at the Greek city in 500-475 BC.

To date other previous scientific studies have been focused on the identification of the used pigments for the pictorial representations on a considerable number of painted tombs [4-6]. H. Brecolouaki [4] analysed different samples of pigments and plasters taken from some tombs, to carry out a scientific study on colours, binders and materials used in Paestum, and in Italy in general, in the pre-roman period. Afterwards, pigments present in pictorial layers of frescoed tombs dated between the end of the VI century BC and the first half of the IV century BC (red, yellow, orange, pink, blue, green, black, grey and brown) have been also analysed [6]. X-ray fluorescence and Raman analyses confirmed that the artists' palette is quite limited and coherent with the contemporary funerary art in the Mediterranean basin. Red and yellow ochres prevail on other pigments, whereas the use of Egyptian blue and of a red ochre enriched in manganese is interesting and deeper studies on these materials could be useful to better clarify the commercial background of Paestum during the IV century BC. Most of the colour hues were obtained by mixing pigments whereas calcite was added to obtain lighter shades. The authors underline that the choice between one mixture or another could depend both on the availability of raw materials and on stylistic preferences of each workshop.

Starting to the available archaeological and archaeometric information, the new AIAR research activity has been in particular focused on the characterization of pigments and organic materials, pictorial binders; the petrographic study for the analysis of the stratigraphic structure and typology of mortars; the quali-quantitative characterization of the mineralogical phases. The following scientific methodologies are involved in the entire research project: *i*) Infrared reflectography (IRR); *ii*) UV Fluorescence imaging, *iii*) Visible-induced infrared luminescence (VIL); *iv*) X-Ray Fluorescence analysis (XRF); *v*) External Reflection (ER-) and Attenuated Total Reflection (ATR-) Fourier Transform Infrared Spectroscopy (ER-FTIR and ATR-FTIR); *vi*) Raman Spectroscopy (RS); *vii*) Polarised Light Microscopy (PLM); *viii*) Electron Microprobe Analysis coupled with Energy Dispersive Spectroscopy (EMPA-EDS); *ix*) Thermogravimetry and Differential Scanning Calorimetry coupled with Fourier Transform Infrared Spectroscopy for Evolved Gas Analyses (TG/DSC with FTIR-EGA); *x*) radiocarbon dating of mortars.

The archaeometric study of painted slabs has been preliminary based on a non-invasive approach, performed in-situ by portable equipment. More than 400 single spot measurements have been collected

by using different analytical techniques; areas were selected according to the results of imaging techniques, in an attempt to avoid the restored areas. To guarantee the significance of the new results, a preliminary mapping and analysis of the surfaces was carried out to localise the pictorial areas or preparation layers altered by past restorations and to know the conservative interventions that may have changed the original phase of the studied tombs. Moreover, for a deeper characterisation of painted slabs, micro-samplings of mortars were collected. In the present paper the authors report the preliminary data provided from the *in-situ* activities of the first step of the research project related to the characterization of pigments (Fig. 1). The results allowed to increase the current knowledge of the pictorial materials used for the painted tombs and available in the different period at the Paestum site.



Fig. 1 - Pictures of the *in situ* non-invasive diagnostic investigation carried out at the Archaeological Museum of Paestum.

2. Materials and Methods

A multidisciplinary analysis has been carried out on 13 painted tombs, dated between the end of the 6th century B.C. and the first half of the 4th century B.C.: Tomb of the Diver (from Tempa del Prete, end of VI century BC), the Tomb of Palmettes (Arcioni T. 781, end of VI century BC), Gaudo T. 314 and Gaudo T. 210 (V century BC); Andriuolo T. 76/1969, Santa Venera T. 109 and Santa Venera T. 110, Andriuolo T. 21, Andriuolo T. 23 (first quarter of IV century BC ca); Andriuolo T. 6, Andriuolo T. 11, Andriuolo T. 12, Andriuolo T. 20 (second quarter of IV century BC).

The techniques here described and the respectively instrumental parameters have been applied for each analysed painted slab keeping the same measurements protocol.

Multispectral imaging analysis was aimed to obtain a preliminary original and restoration pictorial materials mapping of painted surfaces, multispectral imaging analyses have been carried out by using a high-definition scientific CCD camera characterised by the following technical features: Spectral Sensitivity 0.8 - 1.1 micron; Spatial Resolution 3072×2048 pixel; Reflectogram gray levels: 12 bit/pixel; Large pixel 9×9µm; Full Well Capacity: 100 ke; Dark Current: 0.5 e-/pixel sec; Fill Factor: 100%; Peltier Cooled DT=40°. The acquisition system makes possible to quantify, store without ageing problems, form data bases and process: calibrate, correct for stray light, form thematic maps, compare, highlight details etc. etc. In detail, Calibrated UltraViolet fluorescence analysis, with specially filtered UV sources and multispectral acquisition technique, helps to identify the possible existence of inhomogeneity on the surface due to non-original materials, to assess the artwork conservation state and to reveal faded substances or other traces of possible interventions at later stages, guiding us to identify the original materials employed. InfraRed Reflectography survey allows the study of the deeper layers and in visualising, if existing, the presence or absence of an underdrawing carried out with carbonaceous matter and possibly the technique employed for it, such as tracing of the cardboard, dusting or using a grid.

For the Visible-induced infrared luminescence (VIL), two flashes Quantum T5D mounted with B+W 486 UV/IR blocking filter were used for irradiating with visible light the painted surfaces, in order to explore the peculiar characteristics of some pigments to be luminescent in the infrared region when excited with visible light. The infrared emission was collected with a modified (built-in filter for IR removed) Canon EOS 400D (10.1 Mpixel, CMOS sensor) with Canon lens EFS 28 mm fitted with B+W 093 IR830 infrared filter to cut all stray radiation from visible spectrum and thus collecting only infrared

luminescence emission. A white plate Spectralon® was used as reference. In this context, such a technique represented a useful tool for the identification and localization of Egyptian Blue pigment.

Chemical investigations X-Ray Fluorescence analysis (XRF) were performed by using a portable spectrometer consisting of a miniature X-ray tube system, which includes the X-ray tube (max voltage of 40 kV, max current of 0.2 mA, target Rh, collimator 1 or 2 mm), the power supply, the control electronics and the USB communication for remote control; a Silicon Drift Detector (SDD) with a 125 to 140 eV FWHM @ 5.9 keV Mn K α line Energy Resolution (depends on peaking time and temperature); 1 keV to 40 keV Detection range of energy; max rate of counts to 5.6×10^5 cps; software for acquiring and processing the XRF spectra. Primary beam and detector axis form an angle of 0 and 40 degrees respectively with the perpendicular to the sample surface. Tube voltage 35 kV, current 80 μ A, acquisition time of 60 s, no filter was applied between the X-Ray tube and the sample, distance between sample and detector around 1 cm are the measurement parameters adopted for this study. The setup parameters were selected to have a good spectral signal and to optimize the signal to noise ratio.

Moreover, single spot analyses for each pigment were performed using Fibre Optics Reflectance Spectroscopy (FORS), a spectroscopic technique which analyses the light reflected from a surface illuminated with visible light. FORS measurements were carried out in the spectral range 400-800 nm by using a tungsten lamp (20W) as source and the grating Ocean Optics (model HR2000) as detector. Optical fibre bundles were used both to drive the light on the surface under analysis and to collect the reflected radiation. The measuring head geometry was 45°/0°/45°. The probe, in contact with the surface, was a homemade fibre holder, which, at the same time, guarantees a soft contact and permits to fix the best distance from the surface. This allow to maximize the signal and to maintain the measuring area shielded from undesired external light. The analysed area was 2 mm² and each acquired spectrum was the average of 30 scans. As a reference, a Spectralon® plate (WS-1S-L Labsphere certified standard) was used. Spectra were compared with reference ones available in ISPC-CNR reference database to identify pure pigments or mixture.

BRAVO Handheld Raman Spectrometer by Duo LASER was used to collect Raman spectra of the tombs *in situ*. BRAVO uses a patented technology (SSE™, Sequentially Shifted Excitation, patent number US8570507B1) to mitigate fluorescence phenomena and it is equipped with two excitation lasers with wavelengths (DuoLaser™) centered at 785 and 853 nm. The spectra have been collected in the 300–3200 cm⁻¹ range with integration times no longer than 60 s.

Finally, to obtain the Fourier Transform Infrared Spectroscopy (FTIR) spectra, the surfaces of painted slabs have been analysed by using at room temperature by means of a Bruker Optics Alpha-R portable spectrometer with an External Reflectance (ER) module for contactless and non-destructive analyses, covering a circular area of about 3 mm of diameter. The instrument is equipped with a ROCKSOLID™ interferometer and a ZnSe/KBr beam splitter with a DTGS detector. The spectra were collected in a spectral range between 4000 and 400 cm⁻¹, with a resolution of 4 cm⁻¹ and 128 scans for each run (up to 2 minutes). Bruker Opus 7.2 software was used for data acquisition and processing. The spectra were treated by baseline correction (Rubberband method), smoothing (Savitzky-Golay algorithm) and log-transformation (log (1/R)).

3. Results

Integrated and multi-analytical approach provided significant results for the identification and clustering of pigment palettes typical of different periods. Below, for each pigment hue (green, blue, red, yellow, white and black), the results obtained from the whole set of analytical techniques used for *in-situ* measurements are reported.

Thanks to the integrated non-invasive analyses on the green pictorial layers, two main typologies of mixture of pigments have been observed, mainly discriminated on the basis of their compositional features. The first type of green pigment was found in the Tomb of the Palmettes, in the tomb T210 and in the Tomb of the Diver. Green paint used for decorating the former tombs is characterised by the presence of iron along with calcium. ER-FTIR also evidenced the presence of peaks in the spectral range

between 3700 and 3500 cm^{-1} (OH stretching vibration) as well as the broad band between 1200 and 900 cm^{-1} (Si-O-Si stretching vibration) attributable to the presence of silicates [7]. The second typology of green pigments was observed on the tombs T21 and T110, in correspondence of decorations depicting the leaves. They are characterized by the presence of copper along with calcium and iron. Compositional features, as well as the high absorption of visible light and luminesce in the near-infrared region, suggests the presence of Egyptian Blue pigment, likely mixed with another colour for obtaining the green shades. The addition of the Egyptian blue to iron-rich earths to have brighter colour was a common practice, also in a later period among the Roman mural painters [8]. Moreover, a mixture of Egyptian blue with black pigments (carbon- and/or iron-based pigments) and iron-rich earths was already detected during previous analyses on painted slabs from Paestum [5] whereas the use of green earths was here observed for the first time (Fig. 2).

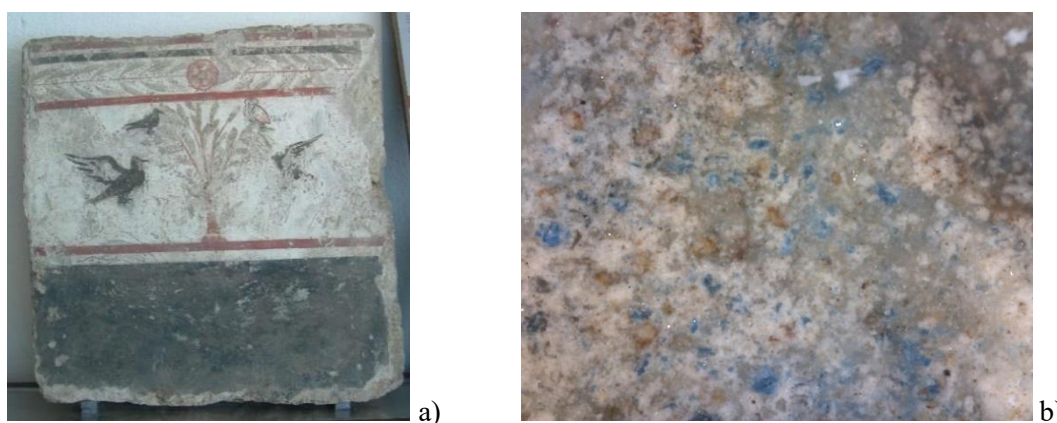


Fig. 2 – Use of Egyptian blue in green pictorial layers: a) Tomb 21 from Andriuolo (first quarter of IV century BC ca); b) the detail of green layers in correspondence with the leaves of the upper frame of T21, acquired with digital microscope (50 \times magnification), show the presence of the heterogeneous blue pigment grains added pictorial in mixture.

The light blue layers were investigated in the painted slabs belonging to the Tomb of the Diver and T6. XRF generally detected on the blue paints the presence of copper, along with calcium and lower amounts of aluminium, silicon, iron and strontium. The presence of copper suggested the use of Egyptian blue as the main component of blue pictorial layers, a synthetic pigment constituted of cuprorivaite blue crystals [$\text{CaCuSi}_4\text{O}_{10}$ or $\text{CaOCuO}(\text{SiO}_2)_4$ - calcium copper tetrasilicate] and obtained by the mixture of silica sand, lime, compounds of copper (or copper mineral fragments) and a fluxing (soda or plant ash). This pigment seems to be used on tombs belonging to different periods (Tomb of the Diver – at the end of VI century BC, and Andriuolo tomb T6 - second quarter of IV century BC), as confirmed and VIL images (Fig. 3), which, immediately identified the Egyptian Blue presence [9-10], and by FORS spectra.



Fig. 3 - VIL image of the detail painted on north slab of Tomb of the Diver (a) and comparison with the corresponding visible image (b).

In figure 4 the reference FORS spectrum of Egyptian blue is compared with the spectra of two blue areas on the Diver's slabs (TCF_02 and TFS_07). The same spectral features are observable in all the spectra. These absorptions are related to electronic transitions attributable to Cu^{2+} ions, responsible of the photoluminescence of the cuprorivaite.

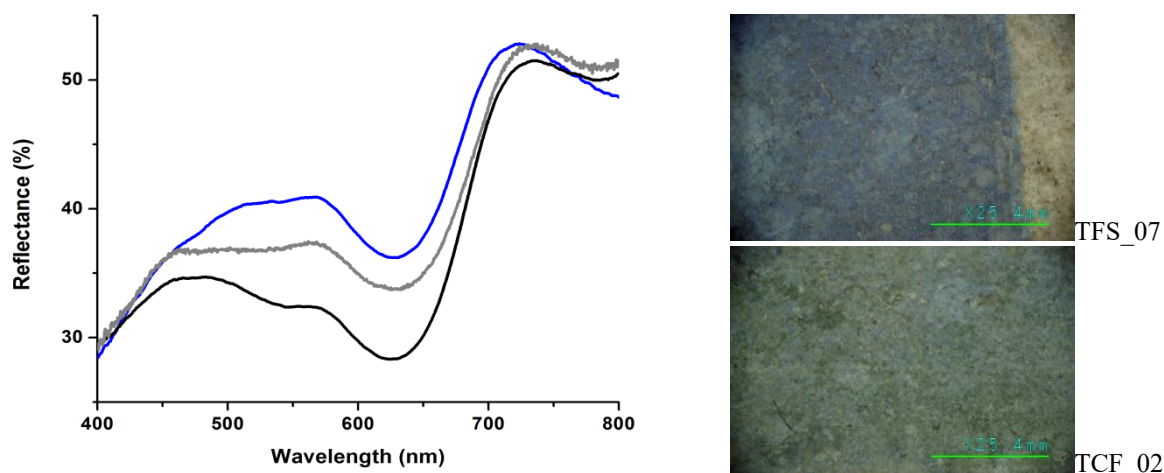


Fig. 4 – FORS spectrum of a reference Egyptian blue mock-up paint (black line) compared with the spectra of two blue areas from two different slab of Diver's tomb (TCF_02 - grey line, TFS_07 – blue line) along with images of the measured areas acquired with digital microscope.

The dark and light shades red layers have different compositional characteristics that permitted to distinguish three different typologies (Fig. 5). Red paints observed in Palmettes, T6, T11, T12, T20, T21, T76, T109 and T110 tombs are characterised by the presence of iron, and low counts of aluminium, silicon, potassium, manganese and sulphur, as highlighted by XRF. FORS positively identified iron-based pigments in almost all the tombs whereas Raman spectra acquired on Palmettes, T12, T20, T21, T76, T110 red and pink layers showed the bands at ca. 410, 498 and 612 cm^{-1} imputable to hematite pigment (Fe_2O_3) according to literature [11].

Moreover, ER-FTIR spectra at the acquisition points T12, T21 and T110 identified the silicate signals between 1200 and 1000 cm^{-1} , and with weak bands in the region between 600 and 400 cm^{-1} attributable to silicates and iron oxides, respectively [11]. All these evidences, therefore, suggested the use of red ochre, a natural red earth containing iron oxides/hydroxides and silicates.

A second compositional group was constituted by red pigment of the tombs T76 and T210; here, red hues show, along with iron and calcium, the presence of arsenic that suggests the use of different red pigments. Although FORS, ER-FTIR and Raman did not show significant spectral evidence, the compositional characteristics could be indicative of a mixture of pigments, likely constituted by a Fe-rich based pigment (e.g. red ochre) and an arsenic-based pigment, used on red layers both in lighter and darker shades. Finally, in addition to iron and arsenic, the Tomb of the Diver, the Tomb of the Palmettes and the tomb 314, the presence of lead has been detected in the red hues.

Also, for yellow paints different compositions were found. In particular, yellow decorations in the Tomb of the Diver and in tomb T6 contain arsenic along with calcium. Although the use of arsenic-based pigment could be invoked, the correct identification of this yellow pigment requires further analytical investigations.

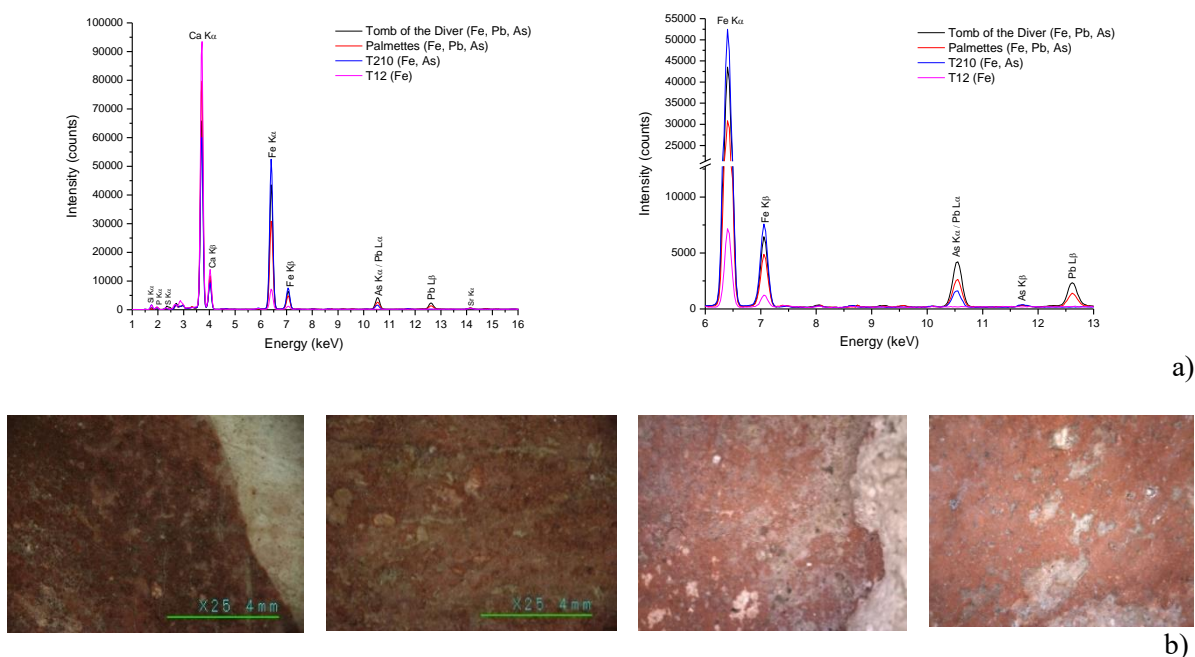


Fig. 5 – a) Representative XRF spectra of the three different typologies of red pigment mixtures identified on the analysed painted surfaces. b) Images of representative red pictorial layer measured areas acquired with digital microscope, from left: Tomb of the Diver, Tomb of Palmettes, T210, T12.

By contrast, the yellow layers analysed in the other tombs (Andriuolo T12 and T20 Tombs, second quarter of IV century BC) are instead made of iron-based pigments. XRF analyses showed the presence of iron along with calcium and FORS analyses suggest the use of a pigment based on iron hydroxides (yellow ochre). Moreover, the Raman spectra, showed the presence of a peak at 388 cm^{-1} , attributable to goethite. Its use for decorating other painted slabs in Paestum was also detected [6].

The calcite is the main mineral constituting the white layers of the whole set of analysed tombstones. XRF spectra reported the ubiquitous presence of calcium that Raman spectroscopy identified as calcium carbonate. Actually, Raman spectra collected on the white background layers of Palmettes tomb, T12, T76, T21, T110 and T20 showed the typical bands at 712 and 1086 cm^{-1} , typical of calcite (CaCO_3). ER-FTIR results also provided evidences in agreement with the presence of calcite in the white layers. The obtained results are supported by several studies carried out on the frescos of other coeval archaeological sites, which confirm the use of calcite as the most widespread white pigment [5,6] along with other carbonates.

Finally, the presence of weak Raman bands at 1596 cm^{-1} and 1320 cm^{-1} permitted the identification of carbon black pigment on black pictorial layer [12]. Different analytical evidences have been obtained, instead, for the superficial black layer that covers the original pictorial layer in the T109, T110, T20, T23 and T76 tombs. The XRF analysis has systematically verified a high count of manganese and iron. Raman analysis on T109 confirmed that this is a manganese-based black with characteristic bands at 366 , 480 , 628 and 1478 cm^{-1} in addition to those of calcite. Then the blackening of original pictorial layer could be caused by the manganese oxide precipitates initiated by the activity of manganese oxidizing microbes during the burial period [13]. Further investigation will be need to confirm this phenomenology of degradation.

4. Conclusions

In the present paper, preliminary results obtained with the multi-disciplinary project “Paestum Inside: the lights of the science” were presented. The project, carried out by Italian Association of Archaeometry (AIAR) in collaboration with the Archaeological Park of Paestum, aimed at studying decorated

tombstones preserved at the archaeological site of Paestum by means of a multi-analytical and interdisciplinary approach in order to define the executive techniques as well as the chronological evolution of technological skills of artisans. The project, articulated in a preliminary in-situ investigation by means of non-destructive analytical techniques, shed light on the decorative techniques and pigments adopted from the Hellenistic to Lucan period. Valuable information on the palette used for decorating the slabs was here presented. In order to better understand any similarities between the different necropolis of Paestum site and executive changes over time, further analyses on micro-samplings (e.g. PLM, EMPA-EDS, TG/DSC-FTIR (EGA), ATR-FTIR) are ongoing for investigating the manufacturing techniques used for pictorial layers and underlying plasters. The features of painted tombs, as well as those of other public edifices (e.g. temples), will also permit to deepen the knowledge on the production technology adopted from the end of the VI and the first half of the IV century BC in Paestum and also evaluate possible changings occurred during a time span of about two centuries.

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