СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО, год. 80, кн. 3, 2019, с. 256–258
REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY, vol. 80, part 3, 2019, p. 256–258

Национална конференция с международно участие „ГЕОНАУКИ 2019“
National Conference with international participation “GEOSCIENCES 2019”

Ancient pigments from the Early Hellenistic Documaci Tomb (4–3rd BC), near the Town of Mangalia, Romania: mineralogical and chemical characteristics

Древни пигменти от ранно-елинистичната гробница Докумаци (4–3 ВС), край град Мангалия, Румъния: минераложка и химична характеристика

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Keywords: color decoration, pigments, dark-blue, red, yellow, white.

The barrel-vaulted tomb Documaci on the area of Kallatis – an ancient colony of Herakleia Pontike, near the nowadays town of Mangalia, Southern Dobrudja, Romania, is an example of Early Hellenistic cultural influence in the North-Thracian territory on the Western Shores of the Black Sea (Ștefan, Sîrbu, 2016; Ștefan et al., 2017). The funerary chamber of the tomb is plastered and painted. The color decoration of the murals in the tomb is arranged in relief belts with incised vertical lines separating red and dark-blue colored panels (Fig. 1a). Right on them, white and yellow decoration is applied using a stencil. The decoration is elaborated in an illusionistic style typical of the Early Hellenistic murals (Ștefan, Sîrbu, 2016).

In the present work, wall paintings of the funerary chamber are studied in order to identify the materials used for the pigments, their origin, as well as to clarify the painting techniques.

Methods of study

The sequences of application of paints were studied in polished specimens and thin sections using a stereomicroscope and a light polarized microscope (Leitz-Orthoplan). Chemical and phase composition of materials were studied using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) on a ZEISS SEM EVO 25LS equipped with an EDAX Trident system at 20 kV acceleration voltage. Spectroscopic characteristics of the studied materials were obtained using Raman spectroscopy. Raman spectra of pigments were collected on a HORIBA Jobin Yvon Labram HR spectrometer equipped with an Olympus BH2 microscope using a backscattering geometry, a 633-nm line of He-Ne laser, an x50 objective, a grating of 600 g/mm, and a laser power on the surface of samples in the range 2–0.5 mW.

Characteristics of paints and materials for their preparation

Paint palette used for murals in the funeral chamber of Documaci tomb includes four colors: dark-blue, red, yellow and white (Fig. 1a). It was found that all paints used for color decoration represented a mixture of liquids lack lime binder and pigment.

Dark-blue paint or more accurately *dark-blue colored mortar* was applied in a layer about 1 mm thick on the relief belt of lime plaster and on the lower part of walls of the chamber (Fig. 1a, b). The study shows that the dark-blue coloring is attained by mixing of lime binder, calcite filler and charcoal as coloring material (Fig. 1b). As observed in SEM, the charcoal pigment preserves fibrous structural tissue of burned wood (Fig. 1c). Angular grains of calcites (0.1–0.5 mm) of finely ground marbles are added in the paint to increase its luster. The contact zone between the dark-blue paint and the underlying plaster is clear, without penetration of charcoal particles (Fig. 1b, d) into the plaster. This means that the paint/mortar was applied on the dry plaster (secco painting technique) (Piovesan et al., 2012).

Red paint in thin layer (0.1 mm) covers a part of dark-blue colored panels (Fig. 1a, d). The examination shows that the red paint is obtained by mixing of lime binder, red earth pigment and crushed cal-

cite as filler. The red earth pigment consists mainly of clay material and some amounts of hematite (α-Fe_2O_3). Besides these red pigments, particles of fine grinded charcoal and native gold are found in the paint. The clay material forms completely homogeneous mixtures with lime. Hematite is represented by grains 1–10 μm in size containing CuO (up to 0.3 wt%) and As_2O_5 (1.3 wt%) (Fig. 1d). The presence of hematite is confirmed by the obtained Raman spectra of the pigment – peaks at 227, 294, 411 and 612 cm^{-1} are typical for hematite (Fig. 1e). The peaks at 1087 and 712 cm^{-1} in Raman spectrum of hematite are related to calcite of the binding carbonate material. Chemical composition of paint is strongly dominated by $CaCO_3$ (78 wt%) with other important components (in wt%) SiO_2 (5.9), Al_2O_3 (2.2), Fe_2O_3 (11.6), CuO (0.3) and As_2O_5 (0.6).

Red earth pigment is the most widespread and easily available inorganic pigment from ancient times. Commonly, it is represented by hematite (α-Fe_2O_3) in different proportions with clays and sands. Red clays (kaolinite) with ferric iron oxides are found in Sarmatian limestones in the vicinity of the tomb (Filipov, 1995; Tarassova et al., 2019). It is noteworthy, that the red clay material contains CuO (0.2–0.3 wt%) and Fe_2O_3 (~10 wt%). This means that the clay with ferric iron oxide from the limestone adjacent to the tomb is a potential source of red natural pigment used for the tomb decoration.

White paint is applied on the dark-blue and red panels (Fig. 1a, d). The paint originally was represented only by lime solution with no other additives. The chemical composition of the paint obtained by EPMA, beside $CaCO_3$ (~92 wt%), shows the presence of (in wt%) SiO_2 (4.2), Al_2O_3 (1.7), As_2O_5 (1.0) and CuO (0.4).The material contains relatively low amounts of Fe_2O_3 (0.3 wt%). Raman spectra of the white pigment correspond to that of calcite with characteristic peaks at 282, 714 cm^{-1} and the most intense peak at 1087 cm^{-1} associated with symmetric stretching (ν_1) of CO_3 calcite groups (Fig. 1e). The presence of Cu and As in the composition of

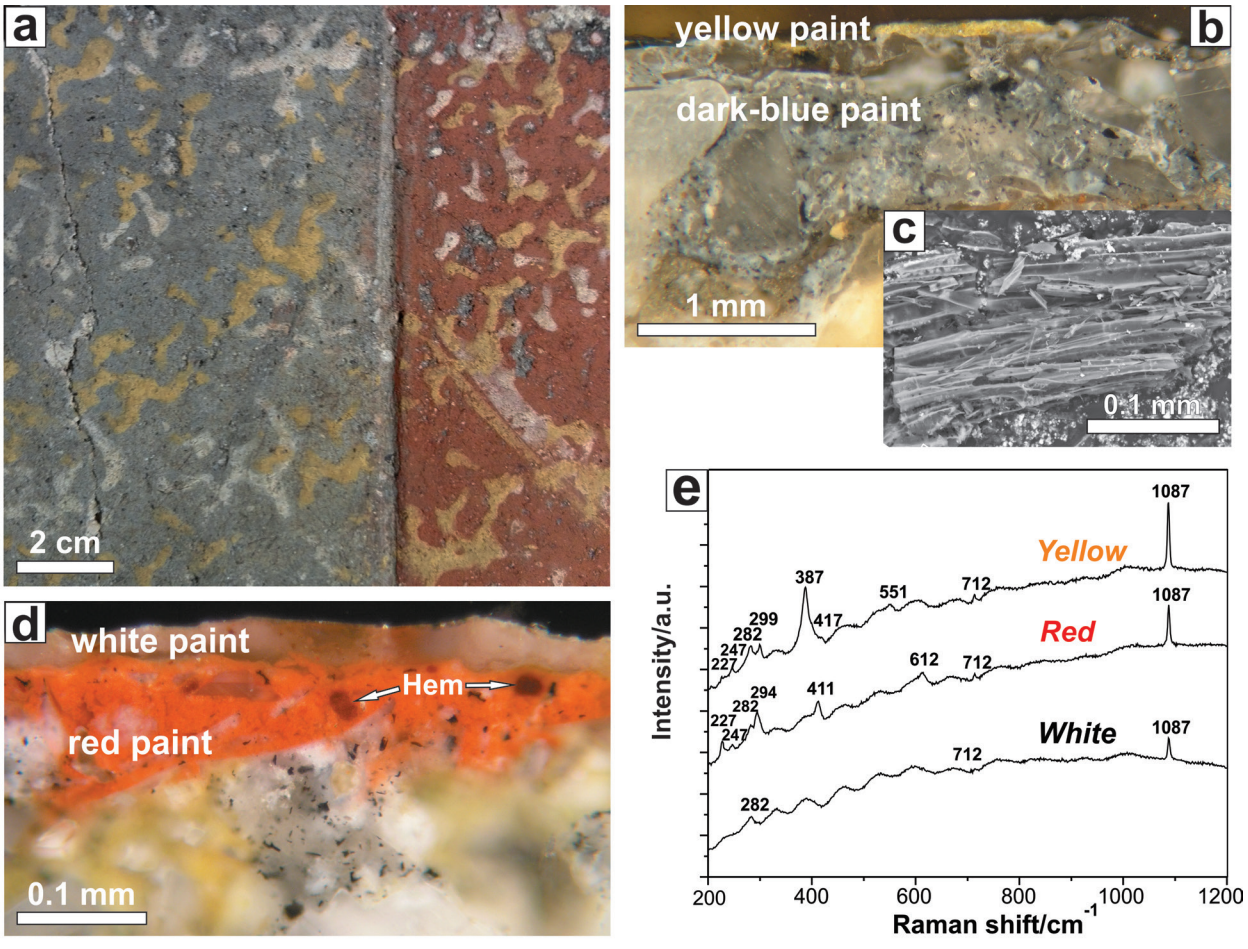

Fig. 1. *a*, color decoration of the funeral chamber; *b,* cross-sections of dark-blue and yellow paints of the decoration (stereomicroscope image); *c,* charcoal with preserved fibrous structural tissue f, burnt wood (BSE image, SEM); *d,* cross-sections of dark-blue, red and white paints (stereomicroscope image), Hem – hematite; *e,* Raman spectra of white, red and yellow paints

the white paint is indirect sign that, similarly to the tomb plasters (Tarassova et al., 2019), local limestones were used for production of lime for the white paint.

Yellow paint was the last one applied on dark-blue and red panels (Fig. 1a, b). The yellow paint comprises yellow earth pigment and lime as a binder. The yellow earth pigment is represented by mixture of clay material and goethite sporadically accompanied by hematite. Besides $CaCO_3$ (87 wt%), the yellow paint contains (in wt%) SiO_2 (4.5), Al_2O_3 (2.0), Fe_2O_3 (4.2), CuO (0.3). It is noteworthy that this paint does not contain As_2O_5 (according to EPMA), and the presence of Cu was not established as well in some analyzed areas of the paint. The studied goethite grains demonstrate similar geochemical behavior: none of the mineral analyses show the presence of As_2O_5, the content of CuO is very sporadic – from the levels below the detection limit of the method (~<0.1 wt%) to 0.5 wt%. The Raman spectrum of the yellow paint (Fig. 1e), besides the well pronounced and narrow peaks of calcite binder (at 1087, 282 and 712 cm^{-1}), shows the presence of an intense peak at 387 cm^{-1} and other peaks at 248, 299 и 550 cm^{-1}, typical of goethite α-FeOOH. Additional peaks at 294 and 410 cm^{-1} are indicative for small amounts of hematite.

Although we did not observe any distinct yellow material in the limestone adjacent to the tomb, the copper found (<0.1–0.5 wt% CuO) in the yellow paint and goethite from the tomb suggest that the raw material for the yellow paint was extracted from clay layers in Sarmatian limestone.

The adding of crushed calcite crystals in paints to increase their luster as well as the use of grinded wood charcoals as a pigment are widespread and accessible technologies broadly applied in the Thracian tombs at the time the Documaci tomb was built. Such a technological approach was used, for example in the Thracian tombs Shushmanets and Dolno Lukovo on the territory of nowadays Bulgaria (Tarassova et al., 2014; Nehrizov et al., 2017).

Conclusions

The color palette of Documaci tomb murals includes dark blue, red, yellow and white colors. Earth pigments as red ochre (hematite + clay) – for red paint and yellow ochre (goethite + clay) – for yellow paint, as well as wood charcoal – for dark-blue coloring and lime – for white paint were used. All these pigments have local origin – from Sarmatian limestone (lime) or from red clay layers of the same limestone (clay, hematite, goethite). It is found that secco technique was applied for wall painting. Built on the Black Sea coast, in Thracian territory, the Documaci tomb demonstrates both the features of Early Hellenism in its illusionistic style of decoration and the techniques for color painting used in Thracian tombs from neighboring territories.

Acknowledgement: The study was performed on a bilateral project „Investigation of pigments and plasters from cult objects (IV–III BC) in the Dobrudja region of Bulgaria and Romania“ between the Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences and the Institute of Archaeology, Romanian Academy.

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Tarassova, E., M. Tarassov, R. Titorenkova**.** 2019. Ancient plasters from the Early Hellenistic Documaci Tomb (4–3rd BC), near the Town of Mangalia, Romania: mineralogical and chemical characteristics. – *Rev. Bulg. Geol. Soc.*, 80, 3, 253–255.