Archaemineralogical study of plasters and paints from the Thracian tomb Maglizh (4th–3rd century BC), Bulgaria

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Abstract. Fragments of plasters and paints from the decoration of the chamber and the grave of the Thracian tomb Muglizh (4th–3rd century BC) were studied. It was established that the plasters are two or three-layered and consist of coarse plaster, pink colored plaster and white putty (stucco). The binder in all three layers is a lime prepared from organogenic limestone. Crushed materials from rocks and minerals were used as fillers in the coarse and pink plasters, and only white-colored minerals such as quartz, calcite, albite were used in the stucco. A mixture of red earth ocher and cinnabar was used as pigment in the red paint and pink plaster. For the black paint, a mixture of crushed charcoal and Egyptian blue was used. The binder in the red and black paints is lime. In pink paint, the binding material is gypsum, and the pigment is cinnabar.

Keywords: red earth ocher, cinnabar, charcoal, Egyptian blue, pigments, plasters, decoration, tomb.

Introduction

An integral part of the Thracian cultural and architectural heritage in the Kazanlak Valley are the numerous burial mounds, with monumental tombs, in which some of the richest burials in Thrace took place. The ancient Thracians believed in immortality and, according to their burial customs, built and decorated funerary monuments (Gergova, 2019). The decoration of the tombs reflects not only the funerary beliefs of the Thracians, but also the social and public status of the immortalized aristocrat. The main colors they used in the decoration of the tombs are: red, black, yellow and white, less often pink, orange, blue, gray, purple, etc.

In the present work, plasters and paints from the early Hellenistic tomb Maglizh (4th–3rd century BC) are studied with accent on their mineral and phase composition, sequences of application, technique applied and raw materials used.

General information about the Maglizh tomb

The Muglizh tomb mound is part of a large necropolis, located over an area on the southern slopes of Stara planina Mountains, near the town of Kazanlak. The tomb is located in the southern part of the mound. In ancient times, it functioned as a family mausoleum and was used for a long time for several burials. The tomb was uncovered in 1965 when started the construction of an industrial complex (today the “Arsenal” AD plant). It consists of an anteroom, two rectangular premises on both sides, a dromos, an antechamber and a funeral chamber. The funeral chamber and the antechamber are built of bricks, and the rest is built with split stones of different size, joined with mud mortar. On the walls of all the rooms of the tomb, a clay base was laid, then covered with plaster and stucco. The decoration of the burial chamber includes a plinth of orthostats in pink, white, red and black, a main wall painted in red and a frieze with a rhythmic alternation of black
amphorae and palmettes on a white background. The main colors used in the decoration of the tomb are red, black, white, pink, gray, red-brown and yellow (Getov, 1988).

**Material and methods**

A series of eight small selected mural fragments of white and pink plasters with white stucco and red, black and pink paints from the figural decoration in the chamber, the red wall of the tomb chamber and the grave (Fig. 1a–e) were studied in the Institute of Mineralogy and Crystallography (BAS). The materials were collected during a rescue archaeological research and were provided for investigation by the “Iskra” Historical Museum in the town of Kazanlak (Nekhrizov et al., 2017).

The sequences of application of mortars and paints were studied in polished thin sections using a binocular stereomicroscope (Carl Zeiss, Jena) and a light polarized microscope OM (Leitz-Orthoplan). Chemical and phase composition of fragments of materials were studied using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) on a ZEISS SEM EVO 25LS equipped with an EDAX Trident system at 20 kV acceleration voltage.

**Results**

**Plasters.** The plasters in the tomb are two- and three-layered (Fig. 1F–k), each consisting of binder and filler. The first layer represents a coarse plaster (layer 1, thickness 5–6 mm), which in some cases

![Fig. 1. a, c, d, b, e, fragments of the decoration, OM image: a, c, d, from grave; b, from figural decoration; e, from chamber; f, g, chronology of plasters, OM image: f, chamber: coarse plaster (layer 1), pink plaster (layer 2), red paint; g, grave: coarse plaster (layer 1), pink plaster (layer 2), white putty (layer 3); h, i, j, k, chronology of plasters, OM image: h, pink plaster (layer 2), red paint; i, detail from (h), pink plaster (layer 2), red paint with red ochre and cinnabar (HgS); j, k, coarse plaster (layer 1), pink plaster (layer 2); l, m, (grave) – pink paint, black paint, OM image; n, o, p, paints, SEM image: l, pink paint (cinnabar, gypsum); o, black paint (charcoal, Egyptian blue) on white lime putty; p, black paint (charcoal, Egyptian blue)]
is followed by a pink plaster (layer 2, thickness 1–2 mm). Fine white plaster (putty) (layer 3, thickness 0.2–0.7 mm) covers the coarse plaster (layer 1) and pink plaster (layer 2). The contacts between the plasters are sharp, which indicates that each new layer was applied after the previous one had dried.

**Plaster binder.** The binder is lime with similar chemical compositions in the three layers, indicating that the same source of raw material was used for its production. Contents of the main oxides are in the following ranges: CaO 71.1–83.6 wt%, MgO 6.6–12.4 wt%, SiO₂ 2.4–11.3 wt%, Al₂O₃ 0.5–6.0 wt%, Fe₂O₃ 0.2–2.0 wt%, Fe₃O₄ 0.5–5.1 wt% and P₂O₅ up to 2.2 wt%. The presence of phosphorus indicates that the raw material used was an organogenic limestone. The recalculated contents of CaO and MgO to that of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) give the following contents of the minerals: calcite 77.0–66.9 wt% and dolomite 23.0–34.1 wt%, which defines the raw material used as a dolomitic limestone.

**Plaster filler.** Petrographic and SEM observations show that rock fragments and minerals (size up to 2 mm) such as quartz, chlorite, sericite, biotite, albite, mica, rutile, smectite, as well as plant residues were used as fillers in coarse plaster (layer 1) (Fig. 1h–k). The mineral composition of the fillers in the pink plaster (layer 2) is the same as that in the coarse plaster (layer 1), but their size is smaller (up to 1.2 mm). Finely ground (size ~ 0.05 mm) light-colored minerals, such as calcite, dolomite, quartz, albite, mica, were used as fillers in the fine white plaster (putty) (layer 3).

**Pigments in pink plaster.** The pink coloring of the plaster is achieved by adding a ground mix of two pigments: (i) red earth ocher composed of hematite, clay minerals, jarosite and schwertmannite and (ii) cinnabar (Fig. 1f).

**Paints.** Red, black and pink paints were studied (Fig. 11–p). They are applied in thin layers (about 0.02 mm) on the fine white putty (layer 3). The sequence of their application is different in different areas of the decoration (Getov, 1988). The phase and chemical composition of the paints shows that the technology of their preparation involves mixing an inorganic binding solution (lime for red and black, and gypsum for pink) with finely ground mineral fillers and pigments. The filler takes up to 10 % of the paint and is represented by crushed calcite, dolomite and quartz. All paints were applied on dry plaster (secco technique), which is evidenced by the absence of pigment particles penetrated into the white plaster (Fig. 1f, h, i).

**Pigments in red paint.** The red coloring was achieved by using a mixture of two pigments – red earth ocher and cinnabar (HgS) in different proportions (Fig. 1b, e–i). Red ocher predominates. It consists of iron oxides/hydroxides, mainly hematite (α-Fe₂O₃) (+jarosite and schwertmannite) in different proportions with clay minerals. In the red ocher, As (As₂O₃ to 2.7 wt%) and Cu (CuO up to 0.6 wt%) were established, which indicates that the raw material was extracted from the oxidation zone of Fe sulfide deposits. Mineral cinnabar is ca. 5–8% in the paint, and its particle size is about 10–20 µm (Fig. 1h, i).

**Pigments in black paint.** The black coloring was achieved by using a mixture of crushed charcoal and small amounts of Egyptian blue (cuprorivite CaCu₃Si₄O₁₀) (Fig. 11–p). Charcoal is of vegetable origin, which is evidenced by the absence of phosphorus in their chemical composition. Cuprorivite was probably added to the pigment mixture to increase the gloss of the paint.

**Pigments in pink paint.** Cinnabar is the only pigment found in pink paint (Fig. 1d, l, n).

**Concluding remarks**

The plasters in the Magliz tomb chamber are two-or three-layered and consist of rough plaster, pink-colored plaster and white putty (stucco). The binder in all three plasters is lime, for the preparation of which dolomitic organogenic limestone was used. Fillers in the coarse and pink plasters are fragments of crushed rock and minerals such as quartz, chlorite, sericite, biotite, albite, mica, rutile, calcite, dolomite, quartz, albite, mica, were used as fillers in the fine white plaster (putty) (layer 3).

A mixture of two pigments was used in the pink plaster and in the red paint: (1) a predominant red oche composed of hematite, clay material, jarosite and schwertmannite, and (2) cinnabar. Red oche is the most widespread and easily available inorganic pigment since ancient times. The established content of As and Cu in the oche indicates that it was extracted from the oxidation zone of sulfide iron ore deposits. The raw materials used usually reflect the geological features of the area in which they were mined. However, the obtained data are not sufficient to assume from which exact deposit the oche was mined. The pink paint from the grave differs from the other paints – the binder in it is gypsum, and only the mineral cinnabar is used as a pigment. Cinnabar was an expensive pigment in ancient times due to its bright red color and resistance to time and limited distribution in nature. Its use is often associated not so much with funeral and religious customs of the Thracians as with demonstrating the high social and economic status. On our lands, the mineral cinnabar is found only in small quantities in heavy fractions of river sediments from the area of
lead-zinc and polymetallic deposits in Kraishte and the Eastern Rhodopes. From such samples no cinnabar could be extracted for use, suggesting that the mineral used was not of a local origin.

For coloring in black, a pigment mixture of crushed charcoal and Egyptian blue (cuprorivaite) was used. The use of ground charcoal is a widespread practice applied in other Thracian tombs such as Shushmanets (Tarassova et al., 2014), Dolno Lukovo (Tarassova et al., 2020), Documaci (Tarassova et al., 2019). Egyptian blue is a very stable synthetical pigment of varying blue color and, like cinnabar, is not of a local origin.

The paints were applied to dry plasters using the secco technique. The color palette is controlled by the concentrations of pigments in the binder.

Acknowledgement: The research is funded by the General Academic Project of Bulgarian Academy of Sciences “Thracians – genesis and development of ethnicity, cultural identity, civilizational interactions and heritage of antiquity”, 2017.

References


