

Preliminary mineralogical study of wall paintings from the Red Church (IV–XIV AD) near the town of Perushtitsa, Bulgaria

Предварителни минераложки изследвания на стенописи от Червената църква (IV–XIV AD) край гр. Перушица, България

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Introduction

The Late Antique/Early Mediaeval Christian basilica “Holy Mother of God” has been in operation during IV–XIV centuries AD. Today its remains rise near by the town of Perushitsa, at the northern foot of the Rhodopes Mts, and are known as the Red Church due to the Roman red bricks constructing the church. From the old and rich in ornament murals, quite little part is preserved to our days – fragments of 2 layers of wall painting which according to the expert’s opinion have been made between the VI and XI centuries. There is also an assumption that the first layer has been painted at the end of the V – beginning of the VI century, while the second layer – in the XI century. It is historically dated, that at the beginning of the VII century the church has been seriously damaged by the Avar inva-

sions, evidenced by traces of fire and destruction. The church has been rebuilt again in the XI century. In the present communication, the first data on the phase and chemical composition of the two saved original layers of wall painting of the Red Church are presented and compared.

Samples and methods

Samples from the Red Church (western part of the church, portico) for the present study were provided by the Center for restoration of art work (Sofia, Bulgaria). The fragments of murals are colored in blue, green, yellow and black – for the 1st (lower) layer, and in red, yellow and black – for the 2nd (upper) layer (Fig. 1). The samples are firstly examined on an optical micro-

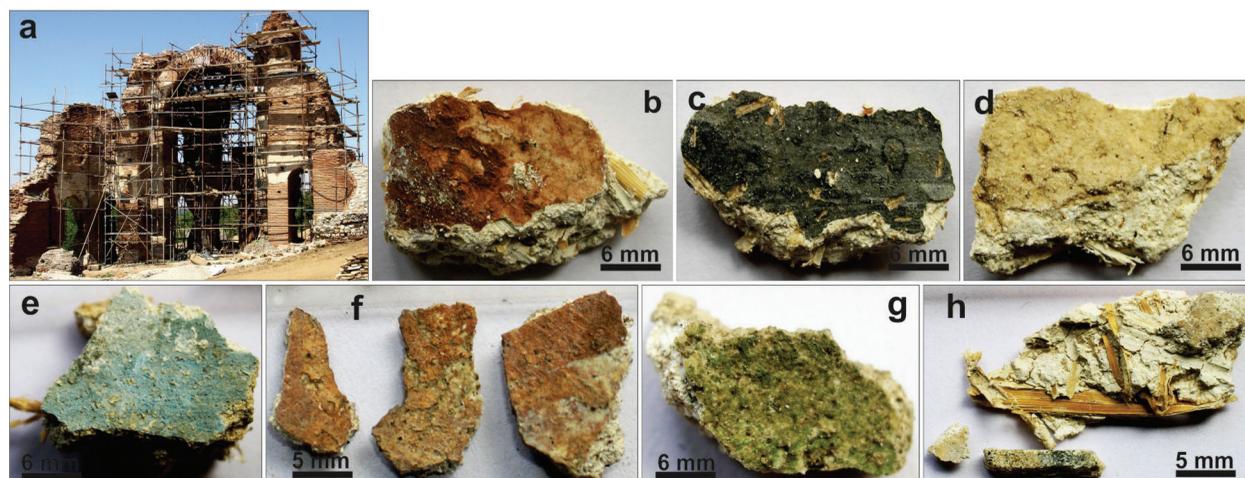


Fig. 1. *a*, the Red Church during the restoration in 2012. Images of the studied mural fragments: upper (second) layer: *b*, red, *c*, black, *d*, yellow; lower (first) layer: *e*, blue, *f*, red, *g*, green, *h*, black and yellow

scope for petrography analysis (Leitz Orthoplan Pol, transmitted light), then on a scanning electron microscope for morphology and chemical composition characterization (ZEISS SEM EVO 25LS with an EDAX Trident analytical system), X-Ray powder diffractometer (D2 Phaser BrukerAXS) and micro-Raman spectrometer (LabRAM HR Visible with an optical microscope and a 633 nm He-Ne laser) – for phase analysis.

Plasters

The plaster of the lower layer consist of two coats or sublayers (denoted as 1a and 1b), while the upper plaster is single-layered (denoted as 2). The coats 1a and 2 show distinct similarity. They consist of binding material (60–70 vol.%) and fillers. The binding material is composed of lime (main constituent) and gypsum (1–7%). The gypsum has been added to the mortar to accelerate solidification of the plaster (Kulev, 2012). A lot of plant residues (straw, hay, plant seeds), rock aggregates (crushed marble), pieces of minerals of about 1 mm (calcite crystals, half-burnt calcite, and in small quantities – quartz, feldspar, barite, apatite, muscovite, biotite, chlorite, epidote, amphibole, magnetite, specularite), and charcoal were established in the filler material. The coat 1b is with thickness of 2–5 mm. Typical for this coat is: absence of plant residues, the smaller size of mineral pieces <0.3 mm, lower content of the binding material (about 30 vol.%), although the binder is with the same phase and chemical composition as the binders of the coats 1a and 2.

Wall paintings

The painting techniques used for the layers 1 and 2 are the same: homogeneous mixtures (paints) of pigments, lime, gypsum, and water have been applied over the solidified plasters.

Pigments used in the wall paintings of the layer 1:

Blue pigment. Cuprorivaite ($\text{CaCuSi}_4\text{O}_{10}$) known also as Egyptian blue has been used for coloring in blue. The established cuprorivaite crystals are sky-blue with size 50–100 μm . Among its crystals, oxide of tin (cassiterite ?) was also found. The cuprorivaite is rarely occurred mineral, but its synthetic analogue has been effectively produced in the ancient Egypt and later in the Rome Empire (Kulev, 2012).

Green pigment. The green coloring optical effect has been achieved by mixing cuprorivaite and green minerals of the hydromica group, and mainly of glauconite $(\text{K,Na})(\text{Fe}^{3+},\text{Al,Mg})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$. Chlorite as well as tremolite-actinolite amphibole were also found.

Red pigment. Fine crystalline hematite aggregates containing phosphorus has been used for red coloring.

Yellow pigment. Hornesite $\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ was identified as yellow pigment. It is known as second-

ary arsenic minerals resulted from low-temperature oxidation of primary arsenic sulfide ores (Bowell et al., 2014). In the studied hornesite were found also traces of Cu.

Black pigment. Only carbon and small amounts of oxygen were registered by EDS analysis of the pigment. Raman spectrum of the material shows broad peaks at 1340 and 1590 cm^{-1} typical for charcoal.

Pigments used in the wall paintings of the layer 2:

Red pigment. Similarly to the layer 1, fine crystalline hematite aggregates containing phosphorus give red coloring in the used paint.

Yellow pigment. Mixture of greenockite (CdS) and iron hydroxide (limonite) has been used for yellow coloring. Among the greenockite crystals, galena (PbS) was found indicating rather natural origin of the pigment. It is known that in the Late Middle Ages, the synthetic greenockite has begun to be used in the paintings.

Black pigment. The black pigment is identical to that in the layer 1 being charcoal.

Conclusions

The obtained results show essential similarity of the two preserved original layers with wall paintings from the Red Church, namely in: (1) the techniques of preparation and applying of paints (pigments in lime-gypsum-water mixture) and the technology of mortar preparation for plasters (ratio of binding material and fillers, lime-gypsum binding material); (2) the usage of similar raw materials (half-burnt calcite crystals in the filler), black (charcoal) and red (fine crystalline hematite with phosphorus) pigments can be considered as indicative materials for this similarity. Some apparent differences (the presence of cuprorivaite, glauconite, hornesite in the layer 1, and greenockite – in the layer 2) are due to a small number of samples provided for the investigation. Fundamental similarities in the techniques and technologies of the plasters and murals making speak rather in favor of that the wall painting (layer 1 and 2) in the Red Church has been accomplished by one and the same craft studio after the reconstruction of the church in the XI century. The obtained result could be useful for the methodology of restoration activities on the object.

References

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