SEM study of ancient Thracian pigments from Bulgaria: the cases from the Sboryanovo National Reserve

СЕМ изследване на древни тракийски пигменти от България: примери от Национален резерват „Сборяново“

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Introduction

The present study aims to elucidate the chemical and mineral composition of pigments used in decoration of the altar (eschara) from the embedded in ground tomb from the tumulus 21 (VI-III B.C.) in the eastern necropolis of the Sboryanovo National Reserve (Gergova, 2008), near the village of Sveshtari, municipality of Isperih. The eschara is the first find of painted and well preserved altar in the elite necropolis of the Getae in the Sboryanovo area. Similar escharae had been found in many places of ancient Thrace as well as far away in the north – on the lands of today's Poland, Denmark, Southern England – the fact that can serve as argument for the Thracian faiths influence on the Northern European peoples. The eschara has the form of short truncated pyramid with incised geometric ornaments colored in red and dark-blue and is situated on the white floor. The substrate below the pigmented layer of both, the aschara and the floor, is beige-yellowish, fine-grained, porous, weakly cemented material. Its mineral composition (quartz, feldspars, calcite, dolomite, mica, monmorillonite, chlorite, manganese gels, coals, etc.) and grain sizes (0.001–0.05 mm) define it as clayey loess (Fig. 1a). According to Filipov (1994) the local rocks of the area "Sboryanovo" are represented by Quaternary loess and Lower Cretaceous limestone.

For the present study, samples containing white pigment from the tomb floor and red and dark-blue pigments from the eschara were provided by the Center for Restoration of Art Work (Sofia, Bulgaria).

Material and methods

Small pieces (0.1–0.05 mm) of the pigmented materials were carefully extracted from the samples using binocular optical microscope, then mounted on specimen stubs and coated with carbon. Morphology, chemical and phase composition of the pigments were studied using ZEISS EVO 25LS scanning electron microscope (SEM) equipped with an EDAX Trident analytical system at 20 kV acceleration voltage (Institute of Mineralogy and Crystallography, BAS).

Results and discussion

White pigment. SEM and electron probe examination of the white pigment reveal that the pigment is composite material consisting of white lime binder and white filling material (30–40 vol.%). The lime is presented by micrometer-sized (3–8 μm) *scalenohedral calcite* crystals (Fig. 1b), while filling material is a polyphase system including grains of *quartz, potassium feldspar* and *non-burned chalk*. The non-burned chalk includes pieces of organogenic fragments of *coccoliths* (Fig. 1b). In the X-ray spectra of the lime binder, besides the X-ray lines of Ca were identified weak peaks of Si and Al, related to terrigenic constituents of the used raw lime stuff.

Red pigment. The red pigment is spread in a layer with width about 0.1–0.5 mm. It is found that the pigment is mainly composed of red iron oxide – hematite (Fig. 1c). Besides iron and oxygen, traces of arsenic were detected in the chemical composition of the hematite which is indication that the initial raw material was taken from the oxidation zone of iron sulfide deposit.

Dark-blue pigment. The decoration in dark-blue is achieved via application of a mixture of *hydrated lime* as a binder and fine-grained (5–15 μm) *dark-colored minerals* as filling material (Fig. 2). The following dark-colored minerals are established during the present investigation: *rutile, ilmenite, magnetite, chrome-spinel, jacobsite, fromboidal pyrite, cerussite*

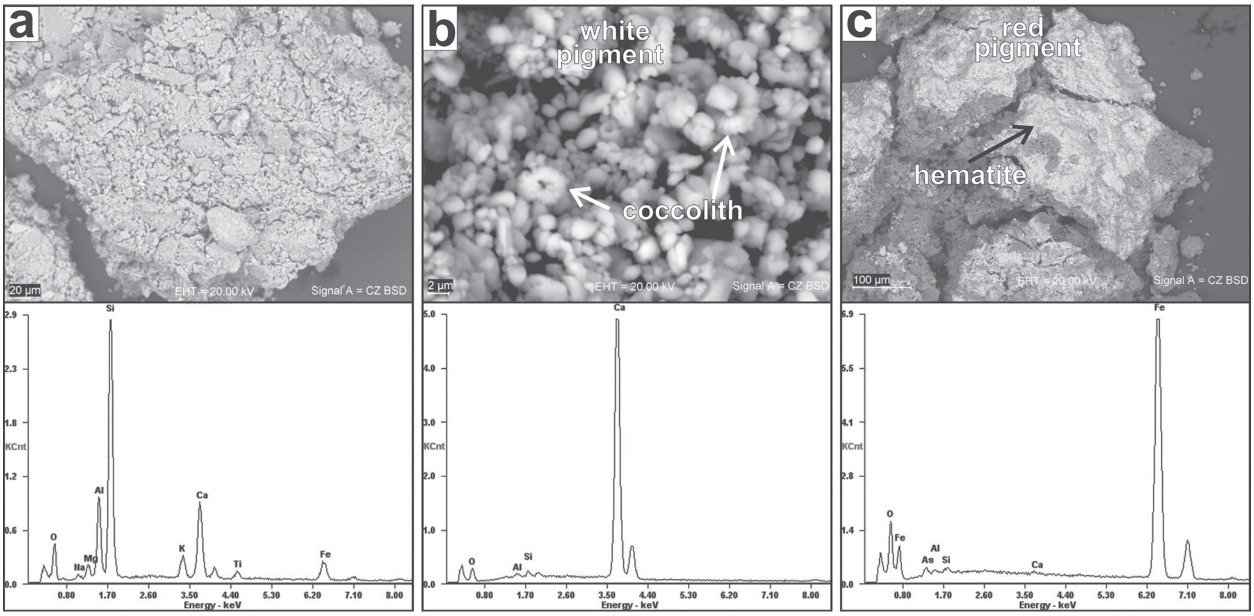

Fig. 1. SEM images and X-ray spectra of (*a*) substrate underlying pigments, (*b*) calcite and coccoliths of white pigment, and (*c*) hematite of red pigment

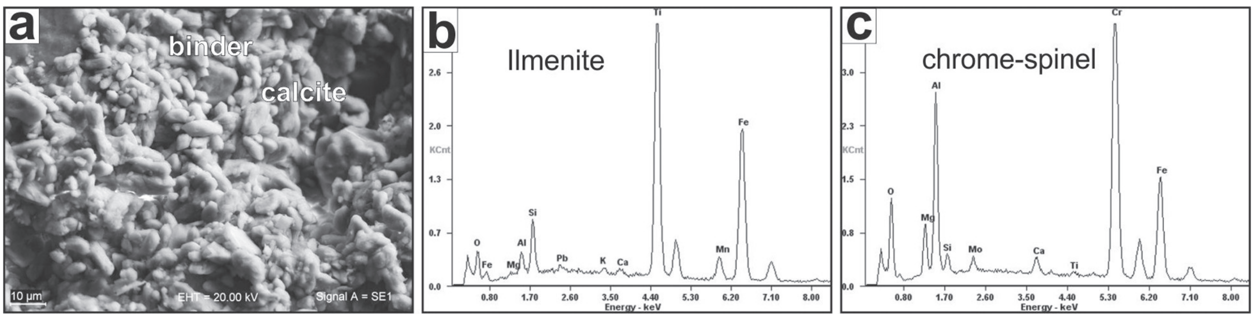

Fig. 2. (*a*) SEM image of binder in dark-blue pigment; (*b–c*) X-ray spectra of dark-colored minerals in the dark-blue pigment: ilmenite (b) and chrome-spinel (c)

and *manganese-oxide gels*. The major part of the identified minerals is representative for the heavy fractions of the river sediments in territories where basic and ultrabasic rocks are widespread. Cerussite is typical secondary supergene mineral formed after galena. Framboidal pyrite is found in coastal sediments, marsh soils, beach sands, coals.

Conclusions

The obtained results unequivocally demonstrate that extracted minimal quantities of pigmented materials from ancient artifacts are sufficient for identification and characterization of the coloring constituents. It is proved that the two pigments, white and dark-blue ones, are composite materials comprising a binding substance, presented by lime, and coloring mineral additives presented by quartz, potassium feldspar, organogenic limestones – for the white pigment, and by dark-colored minerals typical for the heavy fractions of the river sediments – for the dark-blue pigment. Hematite extracted from the oxidation zone of sulfide deposit is the only found coloring substance in the red pigment. The obtained data can serve as a basis for further investigation and correlation with pigments from other ancient object, indicating also possible provenance of the used raw material.

References

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