Phase and chemical composition of ancient pigments used in decoration of the Thracian tomb-temple Shushmanets, Shipka town, Bulgaria

Фазов и химичен състав на древни пигменти, използвани за декорация на тракийската гробница-храм Шушманец, гр. Шипка, България

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Introduction

The tomb-temple under the Shushmanets tumulus (IV–III century B.C.) near of Shipka town (Fig. 1a) is a part of vast necropolis of the Odrysian Kingdom in the Kazanlak valley and an example of architecture style typical for the South Thracian areas. It consists of a wide corridor, antechamber with a semi-cylindrical vault supported by Ionic column (Fig. 1b), and a circular main chamber (tholos) with vault pillared by Doric column. The entrance into the chamber was closed in ancient time with a two-leaved stone door decorated with incised symbolical solar disks. All premises (their walls, floors and ceilings), the columns and the door are built up of manually worked biotite granite and covered by two or one coat plasters recently studied by us in connection with the conservation-restoration work in the tomb (Tarassova et al., 2012). The present study is a prolongation of this work and aims at clarifying the phase and chemical composition of pigments used in decoration of light-blue frieze in the antechamber (Fig. 1c) and red tinted stone door (Fig. 1d) of the tomb. All samples for the present study were provided by the Center for Restoration of Art Work (Sofia, Bulgaria).

Materials 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 or gold for investigation.

Fig. 1. a, location of the Shushmanets tomb-temple on the map of Bulgaria; b, entrance of the tomb; c, antechamber; d, rock door of the tomb. Rings and numbers on figures indicate the places of sampling.
of their micro-morphology and chemical composition on a ZEISS EVO 25LS scanning electron microscope (SEM) equipped with an EDAX Trident analytical system. Secondary electrons (SE) and backscattered electrons (BSE) images and energy dispersive (EDX) electron probe microanalyses were obtained at 20 kV acceleration voltage. Petrographic analysis of thin sections of coloured plasters was completed on a Leitz Orthoplan-Pol optical microscope.

Results and discussion

Light-blue pigment of antechamber frieze

The light-blue pigmentation is not restricted to a thin upper layer but affects the whole coat of the plaster in the antechamber frieze. Such a distribution suggests that the pigmenting material have been added directly into primary mortar used for the coat. The mortar consists of lime as binder and grains of calcite, dolomite and limestone as aggregates. The only coloured material found in the plaster studied is ground charcoal (Fig. 2a). In combination with the prevailing white lime material i.e. calcite (Fig. 2b), the fragments of charcoal gives a bluish colouring effect to the plaster.

Red pigment of the stone door

The red pigment is found in the upper compact and intense red layer with a thickness of about 0.1 mm, as well as in the underlying coat of the plaster with light reddish to pink nuances (Fig. 2c). The plaster is mainly composed of lime binder and grains of calcite, dolomite and limestone. The red and reddish colour correlates with the content of FeO, which is up to 4.5 wt.% in the plaster layer, and up to 73 wt.% in the intense red layer. It suggests the presence of hematite (Fig. 2c), which is further confirmed by X-ray diffraction. Besides hematite, the upper red layer contains also calcite as lime binder material. Due to micrometric inclusions of magnetite within hematite, the whole material is fairly magnetic. This peculiarity of hematite supports the identification of Precambrian chlorite-sericite schists of the Berkovitsa unit with non-economic magnetite-hematite ore deposits (Kostov, 1949; Tsankov et al., 1995) cropping out in the neighbourhoods as source of the red pigment.

Conclusion

It is found that both artificial (charcoal – for blue tint) and natural (hematite – for red colour) pigments have been used in decoration of the Shushmanets tomb. The blue tint is achieved by mixing of lime and ground charcoal. Based on the mineralogical features of the hematite, it seems that mainly local raw materials extracted from the Precambrian chlorite-sericite schists of the Berkovitsa unit have been used for the red pigment. It is established that the pigments have been used mainly for colouring the initial mortars and only for the upper red layer on the stone door, a dye consisting of hematite and binding lime has been used.

References