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

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

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The Documaci tomb of the Kallatis funerary areas is located near the nowadays town of Mangalia, Southern Dobrudja, Romania. Kallatis was known as an ancient colony of Herakleia Pontike settled on the Western shores of the Black Sea. The tomb is an example of Early Hellenistic cultural influence in the North-Thracian territory (Ștefan, Sîrbu, 2016; Ștefan et al., 2017). In the present work, the plasters of the funerary chamber and dromos of the Documaci tomb are studied in order to identify the materials used for the mortars, their origin, as well as to clarify the techniques of mortar application.

Material and methods

The sequences of application of mortars were studied in polished specimens and thin sections using a binocular stereomicroscope and a light polarized microscope (Leitz-Orthoplan) equipped with an Olympus C-5060 digital camera. Chemical and phase composition of manually picked fragments 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. EPMA study included energy dispersive spectroscopy (EDS) element analyses at selected points (point analyses) and selected areas (area analyses). Since the predominant part of the studied samples was composed of calcium carbonate (calcite), the content of CO_2 in them was determined by recalculation from the calcium content, and then the final analysis was normalized to 100%. Spectroscopic characteristics of the studied materials were obtained using Fourier-transformed infrared (FTIR) spectroscopy. FTIR spectra of plaster binder were collected at room temperature on a Bruker Tensor 37 spectrometer with 4 cm^{-1} resolution on standard KBr pallets in the spectral region 400–4000 cm^{-1}.

Results

Characteristics of plasters

Plasters consist of binding material such as lime, clay, gypsum and other ones, to which, filler material (sands, crushed building materials, etc.) is added to increase the strength of the final material. The mineralogical investigations of the plaster include finding the proportions between the binding and filler materials, chemical composition of the binding material, and mineral composition of the filler.

Plasters from dromos. The dromos plaster consists of three consequently rendered layers: the first two layers (layers 1 and 2) are coarse grained with thickness of 5–8 mm of each layer, and the third external layer is fine grained with thickness of about 1 mm (Fig. 1a). Layers 1 and 2 are composed of almost equal volumes (45–55%) of lime binder, beach sand and pieces of semi burned limestone as filler.

Chemical compositions of the binder in the three plaster layers are very similar and include mainly (in wt%) $CaCO_3$ (90.2–94.6), SiO_2 (2.8–5.3), Al_2O_3 (0.8–1.7), MgO (0.2–0.7), Fe_2O_3 (0.4–0.8) and in minor amounts (<0.5) Na_2O, P_2O_5, SO_3, MnO and Cl. The variation in lime compositions is due to variable content of clay materials in the original limestones. The sand consists mainly of mollusk shells (90%), quartz (5–10%), feldspars (2–5%) and sporadic grains of magnetite, limestone and epidote-chlorite-plagioclase aggregates. The principal difference between the two first layers is the particle size of the filler, which is 3–5 mm in the first layer and 0.5–1.0 mm, rarely to 3 mm, in the second layer. With the first plaster layer the ancient craftsmen smoothed the rough surface of the building limestone, using coarse-grained mortar.

Layer 3 represents a fine lime plaster with small quantities of calcite and crushed marble additives. The layer also contains sporadic plagioclase, rutile and quartz particles of 1–10 μm in size, derived from the original limestone used for lime production.

Plaster from funeral chamber. All walls of the funeral chamber are rendered by plaster layer 1, while the layer 2 covers locally the layer 1 in the form of relief belt about 20 cm wide nearly in the middle part of the wall. The layers 1 and 2 have nearly the same thickness of about 5–7 mm. In the upper part of the walls just above the relief belt, layer 1 is directly covered by white fine-grained layer 3a up to 1 mm thick (Fig. 1b). In the lower part of the chamber, layers 1 and 2 of the relief belt are covered by dark-blue painted fine-grained layer 3b.

The plaster layers 1 and 2 consist of lime binding material being about 40% of layer 1 and to 50% of layer 2, and of beach sand and pieces of semi-burned limestone filler. The particle size of the plaster filler of layers 1 and 2 is about 0.5–1.0 mm, rarely up to 3 mm. In layer 1, beach sands are used as filler, while in layer 2, crushed calcites are added to the beach sands (up to 1/3 of filler).

Similarly to the dromos plaster, beach sand used as filler in the plaster of the funeral chamber consists of fragments of mollusk fauna (mussels and rarely of periwinkles) and sporadic quartz and plagioclase.

For fine-grained layer 3a, crushed calcite crystals are added in initial lime mortar. By adding crashed calcite, more white color is attained by layers 2 and 3a. For fine-grained dark-blue layer 3b, besides crushed calcite, grinded charcoal is added as pigment in primary lime mortar (Fig. 1c).

Chemical compositions of the binder in the three plaster layers are very similar and include mainly (in wt%) $CaCO_3$ (92.5–96.4), SiO_2 (2.1–4.7, Al_2O_3 (0.7–1.3), MgO (0.3–0.6), Fe_2O_3 (0.4–0.6), CuO (n.d.–0.3) and in minor amounts (<0.3) Na_2O, SO_3, MnO, TiO_2 and Cl. The presence of copper and lack of phosphorus seem to be an indicative property of the binding material inherited from the initial raw material. It is noteworthy that in a mussel shell of the filler, the presence of CuO ~0.3 wt% is also found.

IR study of binding material in layers of dromos and camera shows very similar spectroscopy characteristics (Fig. 1d). The most intensive peaks at 1440, 875 and 713 cm^{-1} in the IR spectra of binder correspond to the absorption bands of $(CO_3)^{2-}$ carbonate group of calcite. Peaks at 1797 and 2520 cm^{-1} corresponding to combination modes are also common for calcite and aragonite. The group of peaks in the range 2875–2980 cm^{-1} probably indicates the presence of organic carbon. The maximum of the

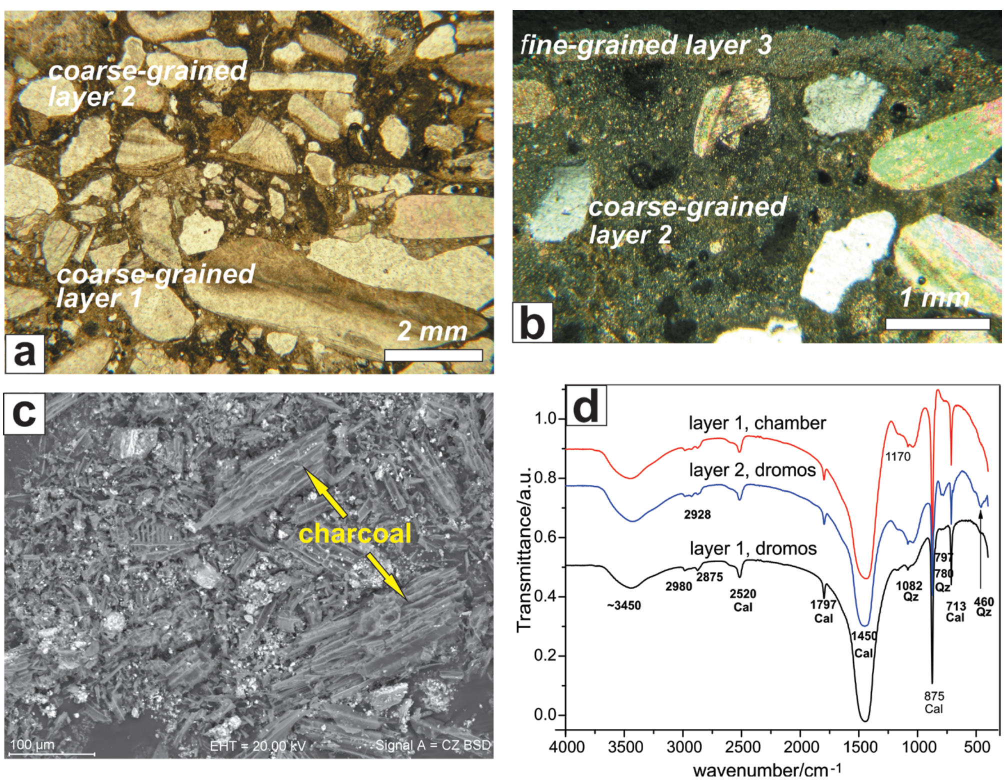

Fig. 1. *a*, cross-sections of the dromos plaster (layers 1 and 2). Filler is beach sands consisting of fragments of mollusk shells (transmitted light, plane-polarized light); *b*, cross-sections of the chamber plaster (layers 2 and fine-grained layer 3 (transmitted light, plane-polarized light); *c*, burnt wood (charcoal) with cellular structure from dark-blue colored plaster layer 3b. BSE image, SEM; *d*, IR spectra of binding material in plasters from dromos and funeral chamber.

main absorption band is shifted to higher wavenumbers compared to pure calcite, which may be due to the presence of aragonite of the mollusk shells. The 1080–1170 cm^{-1} absorption region related to Si-O stretching vibration is an indication of the presence of quartz. The presence of the mineral is also confirmed by the peak around 462 cm^{-1} (Si-O symmetrical bending vibration) and doublet at 780 and 795 cm^{-1} (Si-O symmetrical stretching).

Raw materials used for primary mortars

Principal constituents of the dromos and chamber plasters are lime as binder and beach sand as filler.

Lime. In the Southern Dobrudja region, Sarmatian organogenic limestones with thin layers of red clays are widespread (Popov, Kojumdjieva, 1987; Filipov, 1995; Ţenu, Davidescu, 2005;). The limestones are karstified and their cavities are colored in rusty-reddish by ferric iron oxides. In limestones, imprints of the shallow-sea fauna are well distinguished. The found pieces of semi-burnt limestones used for the production of lime for further use in the tomb show mollusk fauna typical for Sarmatian limestone. These mollusks are represented by mussel (Lamelibranchiata) and helix (Gastropoda) classes (Filipov, 1995). The composition of organogenic limestones, which are found 10–15 m from the tomb, shows the presence of copper 0.2–0.3 wt% CuO, which is close to those found in the plasters of the chamber.

The presence of CuO and similar mollusk fauna in the tomb plasters and in the adjacent limestones can serve as evidence of the production of lime from local raw materials. The chemical compositions of the lime used in the dromos and chamber plasters are close. The main difference is that the dromos lime contains phosphorus 0.1–0.5 wt% P_2O_5, while the lime in the chamber contains copper up to 0.3 wt% CuO. The slight differences in the chemical composition of the used lime can indicate that the raw materials for lime production are taken from different places (quarries) of the area.

Sand. Sand has been added to the plasters to increase its strength. The sand mainly consists of shells of mollusk fauna 85–90%, quartz 5–10%, plagioclase 2–5%, single grains magnetite, rutile, amphibole, biotite, barite, rock fragments of epidote-chlorite aggregates and pieces of limestone with fossilized shells of mollusks. According to Sotirov (2003), the composition of the modern beach sand in South Dobrudja is similar to that used for filler by the ancient craftsmen. The beach sand in region is formed by the destruction of Sarmatian limestones on the submarine slope of the Black Sea coast (Sotirov, 2003). The similarities found in the composition of the sand used in the plaster in the tomb and that of the beach sands indicate that the ancient craftsmen used the local source for the sand.

Conclusions

The plaster in the Documaci Tomb consists of 3 layers. The contact zones between the layers are not contaminated, which indicates that the layers were applied one after another without a long time interval, probably after the previous layer was hardened. The obtained characteristics of the plaster in the chambers and dromos, such as the chemical composition of the lime binder, the phase composition of the filler (sandy beach), the addition of crushed marble to the last layers to enhance the shine, indicate the use of the same techniques when applying the plaster to the chamber and the dromos. For preparation of primary mortars, local raw materials of Sarmatian organogenic limestone and coastal beach sand were used.

Built on the Black Sea coast, in Thracian territory, the Documaci tomb demonstrates both the features of Early Hellenism in its architectural style and the techniques for plastering and color painting used in Thracian tombs from neighboring territories. This means that the Documaci tomb reflects the local craftsman’s traditions and the influence of cultural interactions and communication of its time.

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