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Analysis of the Colors of the Antique Portrait Terracotta Found in the Kerch Bay

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Abstract

The article is devoted to various studies of the antique terracotta performed as a man's bearded head, which was found in the Kerch bay during underwater excavations. It was successfully attempted to reconstruct the initial coloring of the terracotta and to set the palette composition of the ancient painters using the complex of analytical techniques such as optical and scanning electron microscopy, energy dispersive X-ray microanalysis, X-ray diffraction and infrared spectroscopy. As a result of the research the polychromic character of the decor was established and the composition of the pigments was determined. Sandarac and the manganese iron compounds were used as a dark brown pigment for the hair, beard and mustache coloring of the ceramic sculpture. The red ocher and gypsum were used for the lip coloring. It is supposed that the terracotta was used as a decoration element of a ship.

Keywords: Antiquity; Terracotta; Kerch bay; Pigment; Resin; Sandarac; SEM; FTIR; XRD; Synchrotron

Abbreviations: SEM: Scanning Electron Microscopy; FTIR: Fourier Transform Infrared Spectroscopy; XRD: X-ray Diffraction

Introduction

In 2017 during underwater archaeological excavations of cultural heritage object. The "Ak-Burun bay" in the waters of the Kerch bay a large piece of portrait terracotta was found at the depth of 0.7 m under the sea bottom. The "Ak-Burun bay" is an accumulation of the damaged cultural layer with the area of more than 75 000 m^2, which deposited in the harbor of the ancient Greek Panti capaeum city during VI cent. BC – XI cent. AD and displaced to Ak-Burun cape during dredging in 1970s. The displaced cultural layer predominantly consists of large pieces and whole ceramic vessels imported from various ancient Greek centers of the Mediterranean and Asia Minor.

The terracotta sculpture of a man's head established in the proportions of an adult human (Figure 1). The clay composition and a high amount of pyroxenes testify its similarity to the product of Sinope.

The way of the terracotta application was the key point of the study. It could be used as an architectural element of a public building, as a sculpture or a part of a ship decoration. Preliminary it could be supposed that it unites characters of two or three Art directions. The upper part of the face is performed in archaic traditions, which is confirmed by the presence of sharp transitions and large eyes. However, the lower part of the face is performed mostly in the eastern traditions, probably Persian. It is visually confirmed by the shape of the nose, lips and beard. Presumably, the sculpture was created in an unknown studio of Asia Minor, which imitated the approaches of well-known workshops or conveyed the portrait likeness of some famous person.

Materials and Methods

Before the transfer of the find to the museum during the initial sediment removal several micro samples from the surface of the sculpture were selected and preserved such as two samples from the inner part including an exfoliated piece (S1) (Figure 1, Area 1) and a fragment of the dark gray stuck piece (S2) (Figure 1, Area 2), two pieces of the dark brown substance from the mustache (S3) (Figure 1, Area 3) and from the nostrils (S4) (Figure 1, Area 4), a red brown fragment from the upper lip (S5) (Figure 1, Area 5) as well as a sample from a pit in the beard (S6) (Figure 1, Area 6). The selected samples were of a tiny size, no more than 1 mm. Thus, the sampling didn't cause any damage for the sculpture. The samples were delivered to the National Research Center 'Kurchatov Institute' for the further investigations.

The complex of the analytical techniques including optical and

Figure 1: The images of the ceramic sculpture in the three angles. The zoomed details in the left and right parts of the picture indicate the sampling sites (1-6).

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scanning electron microscopy (SEM) with the use of the energy dispersive X-ray microanalysis, Fourier transform infrared (FTIR) spectroscopy and synchrotron X-ray diffraction (XRD) was conducted.

The untreated samples were used for the XRD studies. After that they were polished to get micro sections for microscopic studies.

An optical stereomicroscope "Olympus SZX7" Leica DFC420C with the magnification of 8x-56x and the working distance up to 90 mm as well as a direct microscope Olympus BX51 with the optical system UIS2, which allows the magnification of 12,5x-2500x and the working distance up to 22 mm, were used for the microscopic studies.

Precise studies of the morphology of the micro section surface as well as their chemical analysis were held using double beam scanning electron microscope Versa 3D at a high vacuum. The tool is equipped with the energy dispersive X-ray spectrometer that permits to obtain quantitative chemical composition data not only from a region of a material but also in the certain point with a nano scale space resolution and the energy resolution of 128 eV.

FTIR spectrometer Thermo Scientific Nicolet iS5 was used for the infrared spectroscopy studies. The scanning was held with the resolution of 4 cm^{-1} and the number of scans per each sample was 32.

The sample phase composition studies were conducted by XRD at the XSA beamline of Kurchatov synchrotron radiation source [1]. The monochromatic beam with the wavelength of 0.79 Å and the size of 400 × 400 μm^2 was used. The samples were placed in a cryoloop of 300 μm in size and rotated around the horizontal axis during the measurement, which made it possible to average the diffraction patterns according to the orientations of the sample. The exposure time was 3-5 minutes. Diffraction patterns were collected in transmissional mode by the 2D Rayonix SX165 detector, which was located perpendicular to the beam at a distance of 80 m. To calibrate the sample-detector distance we need a polycrystalline standard with a known position of the diffraction peaks; in this series of measurements, LaB_6 (NIST SRM 660a) powder was used. The two-dimensional diffraction patterns obtained on the detector were further integrated to the standard form of the dependence of the intensity on the scattering angle I (2θ) using Dionis software.

Results and Discussion

Firstly, microscopic studies were carried out in order to identify chemical composition and morphological structure of the samples. Figure 2 demonstrates optical images of the key samples and SEM images of their microsections. Energy dispersive X-ray analysis has shown that the material of S2 (Figure 1, Area 2) is lead. S2 could be a residual part of a mount placed in the inner part of the terracotta. Ancient Greeks and Romans often used lead for fixing sculptures, architectural details and stone blocks. Microphotographs (Figure 2) demonstrate that S3, S4 and S6 are of the same homogeneous structure with a smooth surface and roundish pores that might evidence heating of the materials in the past (Figure 2a, 2b and 2d). The morphology of S5 (Figure 2c) is different from the other samples, it consists of two red and white layers. SEM images of its surface demonstrate the needle structure.

Chemical analysis of the microsections (Table 1) has shown that S3 and S4 consist predominantly of oxygen and carbon (97%) that proves their organic origin. The composition of S6 with just 47% nonorganic fraction is close to those samples. S5 is predominantly consists of silicon (24.7%), calcium (20.3%) and iron (8.4%). These differences can be easily found on the 2d maps of the element distribution (Figures 3 and 4). S3, S4 and S6 were mostly organic, therefore they were studies by FTIR.

The spectra of the studied samples were predominantly similar (Figure 5). However, the spectrum of S6 demonstrates several differences such as the presence of the shoulder in the range of 3235 cm^{-1} as well as the lower absorbance at 1242 cm^{-1}.

Several characteristic absorbance bands can be seen for all studied samples (Figure 4). There are a wide band at 3365 cm^{-1}, which is due to the stretching vibrations of OH-groups, a weak peak at 3070 cm^{-1}, which is probably responsible for C-H vibrations of vinyl groups or aromatic rings, the peaks at 2930 and 2868 cm^{-1} due to the symmetric and asymmetric stretching vibrations of C-H bonds in methylene groups, the shoulder at 2955 cm^{-1}, which is responsible for the stretching oscillations of C-H bonds in methyl groups. The peaks at 1458 cm^{-1} and 1384 cm^{-1} can be referred to the deformation vibrations of C-H bonds [2,3]. The bands at 1606 cm^{-1}, 823 cm^{-1}, 756 cm^{-1} and 705 cm^{-1} are responsible for the aromatic ring vibrations. It should be noted that the absence of the peak at 720 cm^{-1} responsible for methylene chain rocking vibrations is due to the lack of the long linear carbon chains

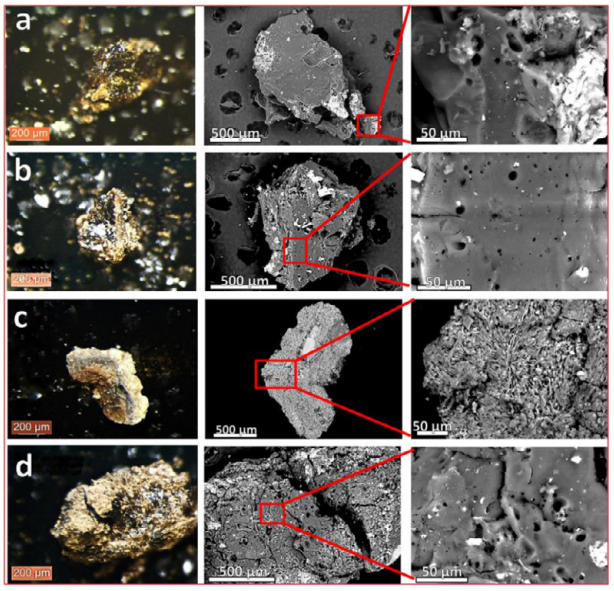

Figure 2: Optical images of the samples (on the left) and SEM images of their microsections (on the right): a) S3, b) S4, c) S5, d) S6.

Chemical element	Sample/Weight percentage					
	S2	S3	S4	S5	S6	Bottom sediments
C	-	85.2	78	-	-	-
O	-	13	18.2	33.4	53.4	31.8
Na	-	-	1.1	-	9.7	3.2
Mg	-	-	0.09	8.4	-	-
Al	-	0.16	0.08	3.4	2.50	13.2
Si	-	0.20	0.10	24.7	2.6	39
S	-	0.37	0.72	0.21	7.5	-
Cl	-	0.08	1.2	-	7.2	-
K	-	0.10	0.07	-	0.66	9
Pb	100	-	-	-	-	-
Ca	-	0.89	0.47	20.3	13.7	2.8
Ti	-	-	-	0.74	-	-
Mn	-	-	-	0.24	-	-
Fe	-	0.07	-	8.41	2.8	0.96

Table 1: Chemical analysis of the S2-S6 samples and the bottom sediments.

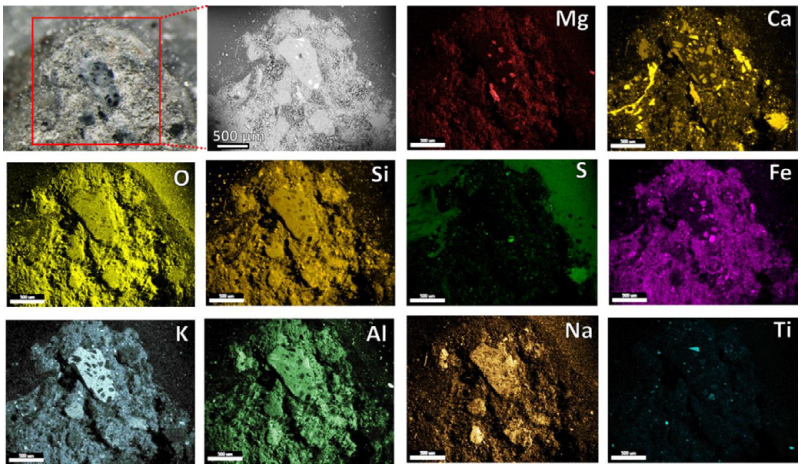

Figure 3: The map of the element distribution in the microsection surface of S3.

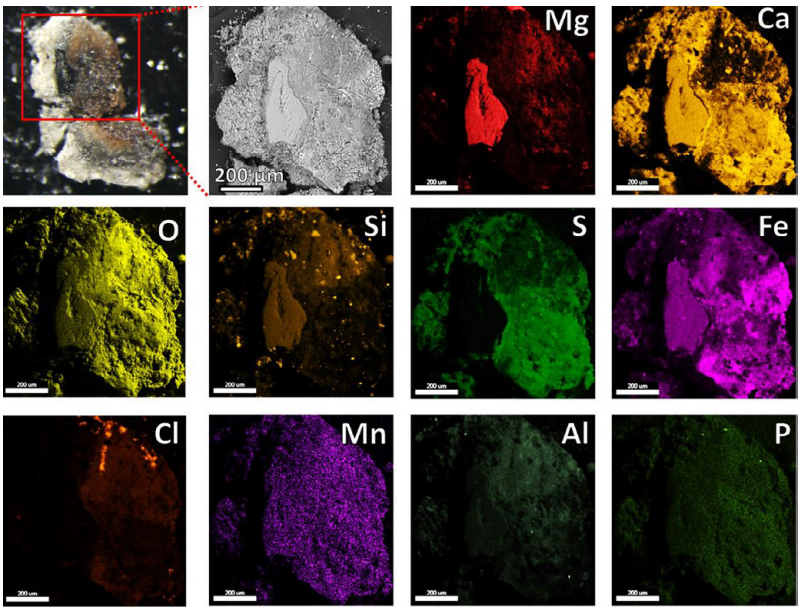

Figure 4: The map of the element distribution in the microsection surface of S5.

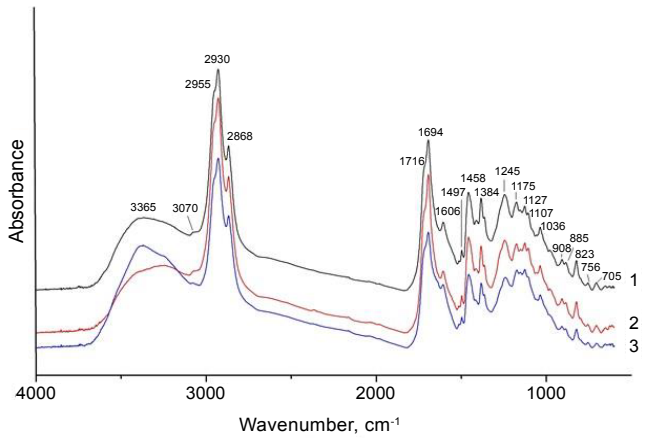

Figure 5: FTIR spectra of the samples: 1-S3, 2-S4, 3-S6.

in the samples, which always present in linear olefins and fatty acids. It is also an evidence that the samples do not include any amounts of vegetable oils [2].

The drastic peak at 1694 cm^{-1} is due to the stretching vibrations of C=O bonds, the peak at 1714 cm^{-1} is responsible for the presence of carbonyl groups, which can be found in a wide number of organic compounds. The wide band with a series of maxima in the area of 1250-1000 cm^{-1} is caused by the C-O and O-C=O bond vibrations.

Thus, spectra of S3, S4 and S6 samples evidence about the presence of terpenoids as the general substances of tree resins. In the same time, FTIR data can be divided to the peaks responsible for diterpenoid and triterpenoids compounds. The main absorbance band of C=O stretching vibrations for diterpenoid resins lay at lower than 1700 cm^{-1}, while the peak for the triterpenoids are at higher wavenumbers [3]. Thus, it is obvious that the studied samples consist mostly of diterpenoid resins.

According to the research [4] and to the position of the characteristic peaks in the present study the samples can be referred to tree resins such as sandarac. The general components of it are usually the diterpenoid acids such as pimaradiene and sandaracopimaric acids, which is in a fine agreement with the FTIR data. Coniferous trees extract such diterpenoid resins. Such trees from the Eastern Mediterranean are Cedrus Libani and Abies cilicica as well as Picea orientalis from the Asia Minor, larch and Pinus Pinea from Syria and Asia Minor. Sandarac can be extracted from the Cupressaceae coniferous trees as well, which are usual for mount regions in the north-west Africa, Spain and Malta. Usually sandarac is used as a paint varnish [5].

Similar fragments of a dark brown material were noticed in the pits and wrinkles of the hair of the sculpture during its thorough observation and the photogrammetric survey in the Kerch museum. A part of the analogous substance was found between the lips, that emphasized the mouth. The present analysis and the observation of the sculpture in the museum let us guess that the terracotta was intentionally coated with the resin. During graphical reconstruction after the contrast enhancement they appeared as an all-over coating (Figure 6). It should be taken into the account that the resins of coniferous trees are hydrophobic and non-water soluble that gave them a chance to preserve under the sea for ages. However, the dark brown material was not found on the cheeks, forehead and in the ears. We suppose that those parts were not covered with the resin.

Without a discussion of numerous examples of the ways of the ancient dye fabrication using the natural water-soluble gum [6] it is very important to list the facts of the applications of the natural hydrophobic resins similar to the studied fragments.

Figure 6: The version of the dye reconstruction of the terracotta.

Publication analysis evidences the wide-spreading of the centuries-old approaches to apply the diterpenoid resins as varnishes, coatings, adhesive layers, die binders, glue, incense and drugs [5]. The Ancient Egyptian tradition to use resins for ritual purposes and mummification is well known [7,8]. The resins were used in varnishes and glue for coating the Egyptian wooden sarcophagus since the Middle Kingdom. It is noticeable to emphasize the opinion of the investigators of the Ancient Egyptian technologies such as [9,10] about the resin application as a dye binding. It is well known that the resins become fluid at heating that makes them appropriate to be mixed with other components such as dye or filler.

Ancient Greeks and Romans used a technology for making varnishes based on the resins and vegetable oils. The later tradition to apply resins for the ritual purposes was known in antique Italy, France and Britain, which were under the Roman authority. Resin mixtures were identified in dyes found on the skin of buried people and on their clothes [11]. The authors of this book after the analysis of the Italic burials of 1-3 centuries A.D. concluded that application of pine and cedar resins had a sacral sense during the period of the Impair and they suppose earlier origin of the tradition. The resins as incense and cosmetics in the mixtures of vegetable oils were used in the Mediterranean and during the Hellenistic period. An untached tomb of 150/125–100 B.C. was found during recent excavations of the Etruscan necropolis in Chiusi. The alabaster with the mixture of resins and vegetable oils was found in the tomb. Using FTIR, gas chromatography and mass spectrometry it was identified that the resins were extracted from Anacardiaceae [12].

According to the published results on the series of archaeological finds studied by modern techniques it was established that the different types of resins used to be as the objects of the Mediterranean trade since the Bronze Age [13,14]. Antique authors reported about the initial application of the resins as a protective coating of bronze goods. The Greek author Pausanias wrote that the copper shields covered with the resin and taken away from the Lacedaemonians prisoned by the Athenians in the battle in 425 B.C. are preserved in Stoa Poikil on the Athenian Agora [15]. Probably the tradition was spread for the bronze and stone sculptures. The ancient Roman author Pliny related to I century A.D. wrote about in liquida pice sculptures in 'Historia Naturalis' emphasizing that the process of coating sculptures with the resin had been such an Ancient Roman tradition (before VII century B.C.) that found a lot of new ways of application in his time [16]. The bituminous was used with the same purpose, as a protective coating, as a decoration and to stick golden foil. Ancient authors reported that aromatic resins were used as incense that says about the sacral sense of some resins for rites.

It was concluded that the pigment in composition of the samples has a mineral nature because no other organic compounds except the resin have not been found in them. The phase composition data evidence that only resin samples include iron-manganese complex oxide from the group of spinel-mineral jacobsite and braunite manganese silicate. Filling the space between lips with the dark brown resin is an indirect argument that also proves the version about usage of iron-manganese dye in the mixture with the resin (Figure 1). Sandarac identified in the samples demonstrates light yellow color and darkens only in very long period, therefore a dark pigment must have been used there to highlight the lip line. Jacobsite and braunite could be used as the colors. However, it should be noted that elemental analysis did not identify

manganese at all and let us find just trace amounts of iron in S3, S4 and S6 (Table 1). In the same time, synchrotron diffraction identified iron-manganese compounds in those sample due to the integrity of the technique. Due to the difference in the techniques of the sample preparation for both methods it is most likely that the resin was used as the adhesive layer, while the dye was placed onto the top gradually getting the resistance.

S5 demonstrated high amount of gypsum (Table 2), which can be identified visually as a white layer (Figure 2c). The other compounds may be related to pollutions brought by the bottom sediments such as clay minerals, sand, sea salts and a shell fragment or to the components of colors such as clay fragments. However, the bottom sediments include hematite and magnetite, their particles could be caught to the bottom mixture from the other ceramic products, among those the sculpture was found.

As a result, it can be concluded that manganese and iron compound are performed as the dye attached to the resin that brings dark brown color to the samples. It is rather complicated to identify the initial coloring of the face because the dye could be easily eliminated from the smooth surface by the sea waves and sand.

The certain information can be obtained from S5, which was extracted from the pit in the lip corner of the sculpture. According to other scientific publications Ancient Greek artists used gypsum for attaching of a color layer or in order to eliminate defects from the surface such as pits. Feofrastus (IV century BC) wrote about the technique in his treatise 'About Stones' [17].

According to the phase analysis (Table 2) and optical microscopy the gypsum in S5 is used as a white underlayer (Figure 2c). The upper layer of S5 is red and includes 8.4% of iron by the chemical analysis data (Table 1). Such iron concentrations with the clay compounds (Table 2) can be identified as the red ocher suitable for the lip coloring.

Black pigment based on manganese compounds was applied even for picturing in the Paleolithic caves. During the Antiquity they were used for coloring sculptures, vessels and tomb walls. Archaeologists found numerous statuettes of Demetra (3-2 century BC) in Greek cemetery during 1995-1996 in ancient Dimitr city. It was found that manganese compounds were used as dark pigments for the polychrome painting [18]. The paper [19] reports that manganese compounds were used as a dye on the Greek product with polychrome decoration. Mineral black manganese oxide, pyrolusite, was also found by the Greek archaeologist Kakoulli in the dye of wall paintings of the Roman period from Cyprus [20].

Substance	Sample/content, %					
	S3	S4	S5	S6	Bottom sediment S7	Bottom sediment S8
Quartz (SiO_2)	50	20	19	25	17	20
Calcite ($CaCO_3$)	36	37	-	34	1	4
Halite (NaCl)	3	37	6	6	-	-
Albite ($Na[AlSi_3O_8]$)	6	-	10	30	7	54
Dolomite $CaCO_3$•$MgCO_3$	-	-	-	-	-	6
Magnetite ($FeO·Fe2O_3$)	-	-	-	-	-	9
Antatse (TiO_2)	2	2	-	2	-	-
Hematite (Fe_2O_3)	-	-	-	-	-	3
MgO_3	-	-	-	-	-	3
Jacobsite $[(Mn^{2+}),(Fe^{2+}),Mg][(Fe^{3+}),(Mn^{3+})]_2O_4$	3	2	-	2	-	-
Braunite $Mn_2O_3·MnSiO_3$.	-	2		1	-	-
Gypsum ($CaSO_4·2H_2O$)	-	-	27	-	-	-
Ackermanite $Ca_2Mg(Si_2O_7)$	-	-	27	-	-	-
Alunite $KAl_3(OH)_6(SO_4)_2$	-	-	11	-	-	-
Natrite $Na_2CO_3·10H_2O$	-		-	-	1	-
Aragonite Polymorph ($CaCO_3$)	-		-	-	74	-

Table 2: Phase composition of the samples S3-S6 and the bottom sediments identified by the means of synchrotron diffraction.

Manganese oxides are rather wide-spread black minerals, but manganese is usually performed by more complicated compounds, which often include iron. Iron in the ores changes their color bringing red tone if the mineral is used for coloring (Figure 6). It should be noted that today braunite found in the samples (Table 2) is used for manganese production. Jacobsite and braunite are mined in Israel, Italy and Turkey. Manganese can be found in soils of Siena and Umbria (Italy) [21].

Conclusions

As the main result of the comprehensive study it was found that the Antique ceramic sculpture of the man's bearded head found in the Kerch bay has sandarac coated hair, beard and mustache. The mineral iron-manganese dye of dark brown color was attached onto the resin. The lips were colored with red ocher attached onto the gypsum surface. The gap between lips was filled with the same substance as the hair. The face and eye color remain unknown due to its elimination during the stay on the seabed. Terracotta had lead fasteners in its inner part. The terracotta could be used for a ship decoration due to the way of resin using, which is rather seldom. Thus, Pliny reminded about the tradition to cover walls with the resins by the inhabitants of the Ancient Carthage in order to protect them from the wind, rain and sea evaporations. The resin is actually the best protective substance from permanent action of the sea salt and humidity for a vessel and the whole its rigging from marine ropes to a wooden trim. Therefore, such unusual way of decoration could be a natural tribute to maritime traditions. The usage of the heated resin could seriously enhance the adhesion and durability of the mineral pigment.

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