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Non-destructive structural studies of coins from the Uzundara Fortress using X-ray diffraction and neutron tomography

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The copper Heliocles coin and two silver Demetrius coins dated to the II century BC from the archaeological works of the Uzundara fortress of the Greco-Bactrian Kingdom were studied using non-destructive structural diagnostics methods. The phase analysis of the coins was performed using the X-ray diffraction method. Also, the spatial distribution of the internal components of the coins was investigated by neutron imaging methods. It has been established that the dominant phase of the Heliocles coin is copper, however, a small volume of patina was found. It is mainly represented by tenorite CuO phase. The neutron tomography method indicates a deep penetration of tenorite into the thickness of the coin, and its volume fraction can reach 10% of the total volume. Two Demetrius coins consist entirely of silver. The complex profile of coins due to the features of a coinage was reconstructed. The phase composition, the content of the composite phases and three-dimensional models of the studied coins were obtained.

Keywords: neutron tomography; X-ray diffraction; Heliocles coin; Demetrius coin; Greco-Bactrian Kingdom; Uzundara fortress

Introduction

In the last decade, a unique archaeological monument of the Uzundara fortress [1], which is the main node in the extensive fortification system for a protection of the northern borders of the agricultural oases of ancient Bactria [2, 3] on the territory of modern Uzbekistan has been studied in detail. The participants of the collaborative archaeological expedition (the Tokharistan archaeological expedition of the Institute of Art Studies of the Academy of Sciences of the Republic of Uzbekistan headed by Academician E.V. Rtveladze in collaboration with Central Asian archaeological expedition of the Institute of Archeology of the Russian Academy of Sciences) obtained unique historical materials of the Hellenistic period of the III–II centuries BC, which reveal new facts about the location of the northern border of Bactria in ancient times along the spurs of the Baysun Mountains [4]. These large-scale archaeological studies allowed archaeologists to obtain a rich collection of weapons from the military garrisons of Bactria, various ceramic materials, utensils and household items. A particular interest is the numismatic complex, which is unique in quality and variety [5]. The well-preserved coins of the Uzundara fortress are represented by the posthumous issues of coins of Alexander the Great, the Seleucid kings Antiochus I and Antiochus II and the leader of the Greco-Bactrian kingdom from Diodotus to Eucratides [5]. They represent the largest of the known material sources about the cultural and trade relations of Bactria, about its place in the system of monetary circulation of the Hellenistic period [6–8].

Currently, active experimental research is being conducted on the coins discovered during excavations using both traditional research methods and modern methods of non-destructive structural diagnostics [9–13]. Such structural methods include the X-ray diffraction method [14, 15], which makes it possible to obtain information about the phase composition of the investigated object, and the neutron imaging methods, which allows to obtain the spatial distribution of phase components in the volume of the studied coins [13, 14, 16–18]. The neutron tomography method, due to the features of the neutron beam interaction while passing through the elements of the investigated object with different chemical compositions, thickness and density, makes it possible to obtain detailed information about the internal structure of metal coins [16, 19] with a spatial resolution at the micron level [20], as well as to obtain a virtual three-dimensional model of the coin for further analysis. The complex of the above-mentioned experimental methods of structural diagnostics makes it possible to reveal internal defects or cracks, identify the corrosion spread, and investigate the phase composition in copper [13] and silver [21, 22] numismatic objects.

Our work presents the results of such structural studies of two silver Demetrius coins and the copper Heliocles coin of the archeological excavations of the Uzundara fortress.

Materials and Methods

Photo of the front and back sides of the investigated coins are shown in Figure 1. On the front side of the silver coins of Demetrius I, who ruled Bactria at 200–185 BC, there is a profile of the king in an elephant helmet. The reverse of the coin depicts the Hercules crowning himself and the worn inscription "ΒΑΣΙΛΕΩΣ ΔΗΜΗΤΡΙΟΥ" – "Demetrius King" (Figure 1 a) [5, 6]. The thickness of this silver coin is about 1 mm, the diameter is 11.3–11.5 mm, and the weight is 0.67 g. The second silver coin is similar to the first coin (Figure 1 b). The mass of the second silver coin is 0.56 g, the size of the coin circle is 10.3 $\times$ 10.5 mm, and the thickness of the middle part of the coin is $\approx$1 mm.

The copper coin is an imitation of the Heliocles coins. The prototype for them was the silver coin of one of the last Greek kings of Bactria Heliocles I (c. 140–130 BC). The issue of these coins was due to the conquest of the territories of Sogd and Bactria by nomads in the 2nd century BC, this event led to a number of changes, including regular minting and the issue of so-called "barbarian imitations" here. Seleucid and Greco-Bactrian silver coins became the objects of imitation. For nomads, the idea of using metal coins for exchange was alien, in connection with this, many errors were noticed in the manufacture of coins. Errors and deviations observed in relation to the original prototype coins gradually accumulated from one generation of imitations to another, as a result of which the images on the surface of the coins lost their original meaning over time. In addition, the inscriptions on the surface of the coins became illegible or some of them disappeared altogether. The process was not limited to the loss of the original appearance of the surface of the coins, in parallel with this process, with each generation of imitation groups, the composition of the metal in them worsened and the weight of the coins decreased.

It is to such issues that the copper coin, minted in imitation of the silver Heliocles coins, belongs also. The profile on the obverse of the copper coin is a disproportionate. The distorted profile image of the king head in a diadem shifted to the right. On the coin reverse, a distorted image of a standing figure of Zeus with a lightning beam in his right hand and a wand in his left is presented. The image on the sides and below are distorted Greek letters that go back to the legend on the prototype coins: "ΒΑΣΙΛΕΩΣ ΔΙΚΑΙΟΥ ΗΛΙΟΚΛΕΟΥΣ". It is "King Heliocles the Just" [5, 6]. The size of the coin circle is 28.0 $\times$ 29.1 mm due to its slightly irregular shape. The thickness of this coin ranges from 1.4–3.7 mm, and its weight is 13.98 g.

The phase analysis of the coins was performed by an EMPYREAN PANanalytical X-ray diffractometer (Malvern, Worcestershire, United Kingdom), with a wavelength of X-ray radiation λ=1.54 Å. The obtained results were analyzed using the FullProf program [23] according to the Rietveld method [24].

The internal structure and spatial distribution of phases in the volume of coins were studied by neutron tomography method at the neutron imaging experimental facility [25] on the 5th horizontal channel of the WWR-SM nuclear reactor (INP AS RUz, Tashkent, Republic of Uzbekistan). A complete set of neutron radiographic images has been registered by the detector system based

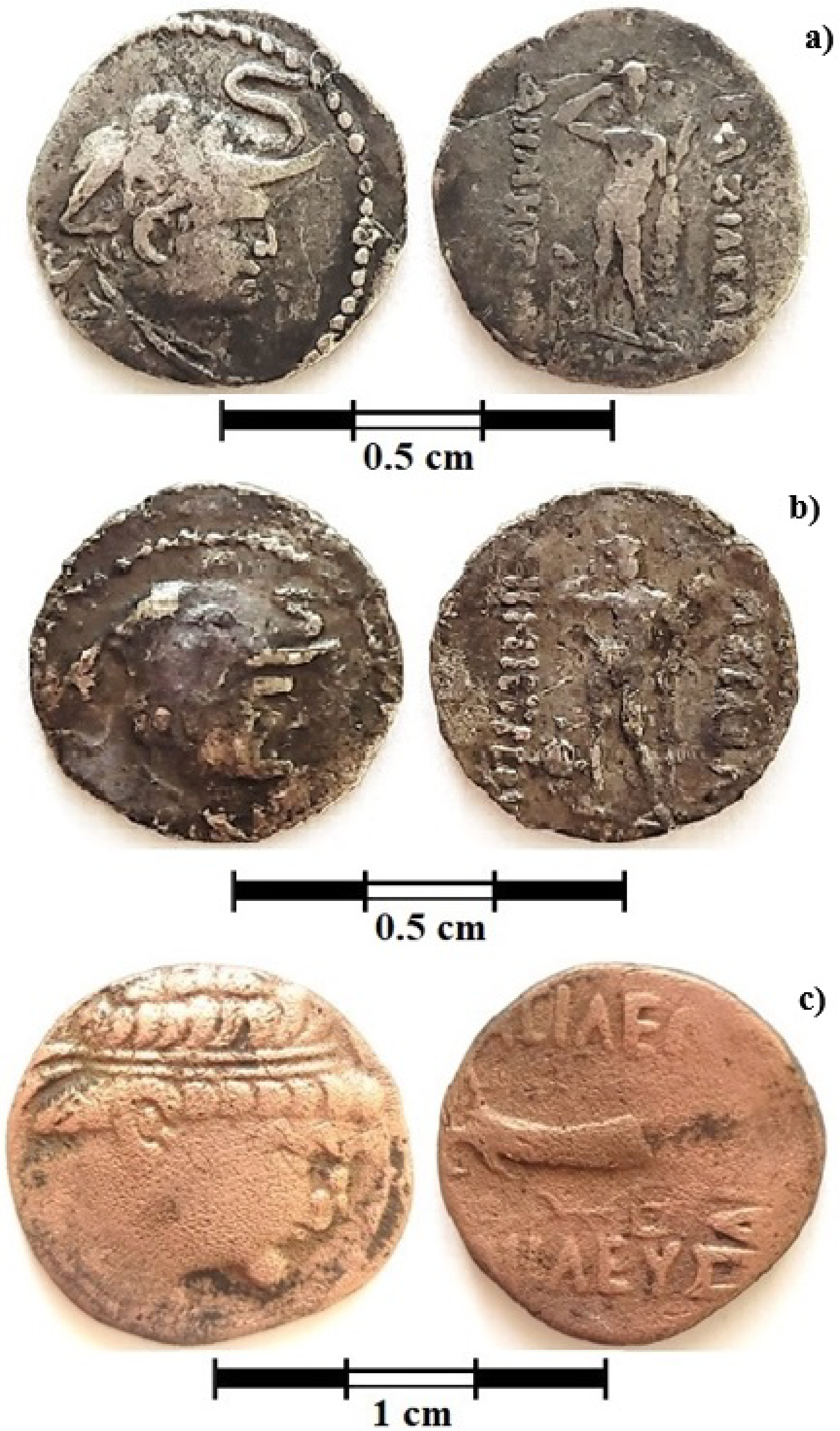

Figure 1. Photos of the obverse (front side) and reverse (back side) of the Demetrius silver coins (a, b) and Heliocles copper coin (c). Scale bars for each coin are shown.

on a $^{6}LiF/Zn(Cd)S:Ag$ scintillation screen and a high-sensitive ProLine PL-09000 CCD camera (Finger Lakes Instrumentation, USA). The attenuation of the neutrons passing through the test sample is described by the Bouguer-Beer-Lambert law [26]:

$$I = I_0 exp(-\Sigma d), \tag{1}$$

where I_0 and I are the intensities of the incident and transmitted neutron beams, respectively, Σ is the attenuation coefficient of neutrons, d is thickness of object. The tomographic experiments were carried out on a rotating goniometer designed for mounting samples, where the goniometer rotation step was chosen to be $0.45°$. To create a 3D model of the internal structure of the studied samples, 400 radiographic projections were recorded. It took 10 seconds to register each radiographic projection. These images were corrected for the background noise of the detector system and normalized to the incident neutron flux using the ImageJ program [27]. A three-dimensional reconstruction of the sample was performed using the SYRMEP Tomo Project program [28]. As a result of radiographic data processing, a set of three-dimensional volumetric distributions of the sample, consisting of voxels, was obtained. The size of one voxel is $61 \times 61 \times 61\ \mu m^3$. The reconstructed 3D models of the samples were visualized and analyzed using the VGStudio MAX software.

Results and discussion

X-ray diffraction

The phase composition of the coins was studied by the X-ray diffraction method. Figure 2 shows the obtained X-ray diffraction patterns of the investigated coins. The diffraction reflections for the obverse and reverse of the Heliocles copper coin (Figure 2 a) correspond to the cubic phase of copper with the space group $Fm\bar{3}m$. Usually, antique coins or items are made of tin bronze [29, 30], the copper unit cell parameter of which linearly depends on the tin concentration [31]. The average value of the copper unit cell parameter for various points of the Heliocles coin is a =3.621(1) Å. This value of the copper unit cell parameter is close to the pure copper parameter, which may indicate an insignificant tin content in the coin material. Calculations give a vanishingly low tin concentration of 0.5 at.% [31], which corresponds exclusively to the natural tin content in the ore material. The expected lead phase in the Heliocles coin not be detected by neutron diffraction methods, however, additional experiments using X-ray fluorescence analysis indicate a low lead content with a content of less 2 at.%.

The weak diffraction reflections at $2\theta \approx 33°$ and $111°$ indicate the presence of an additional phase of corrosion or patina on the imitation of Heliocles coins. Analysis of the X-ray diffraction data indicates the CuO tenorite phase having a monoclinic structure with space group C2/c. The parameters of the crystal cell of this phase, calculated from the experimental data: a =4.671(3) Å, b =4.087(3) Å, c =5.270(3) Å, β = 95.16(5)°. The formation of tenorite may indicate the presence of the studied copper coin in dry sandy soils without long-term oxygen access [14], which, in principle, is typical for the sites of archaeological excavations of the Uzundara fortress. From the analysis of the X-ray diffraction data by the Rietveld method, the relative content of tenorite in the volume of the studied imitation of Heliocles coins was obtained. The calculated volume fraction of the tenorite was 1.7(1)%.

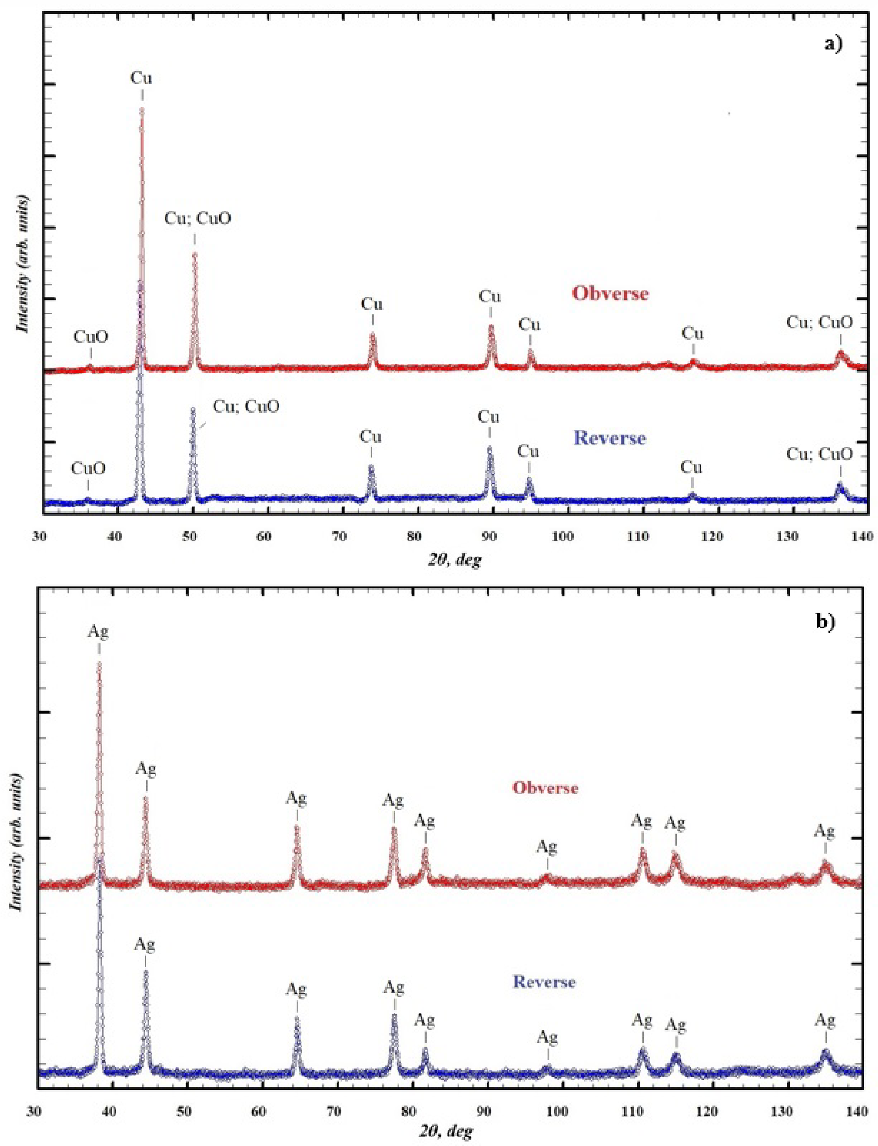

Figure 2. X-ray diffraction spectra of the obverse and reverse sides of the copper coin of Heliocles (a) and the silver coin of Demetrius (b). The figure shows the experimental data and the calculated profile obtained by the Rietveld method. The diffraction peaks in the obtained results correspond to the phases of copper, silver and tenorite. The Miller indices for cubic phases of copper and silver are indicated.

Figure 2 b shows X-ray diffraction spectra from the obverse and reverse of one of the Demetrius coins. The diffraction data for the other silver coin are identical, and we did not consider it necessary to present these data in the context of our publication. As can be seen from the above diagram, only the cubic phase of silver was found on the example of Demetrius' coins. No additional diffraction reflexes from impurities or patina were detected. The X-ray fluorescence analysis provide a low lead content with a content of less 1 at.%.

Neutron tomography

To study the spatial distribution of phases in the volumes of the coins under study, neutron tomography experiments were carried out. The reconstructed three-dimensional models and those virtual slices of imitation of Heliocles coin and Demetrius silver coins are shown in Figure 3. The neutron data indicate a uniform distribution of silver in the coin material.

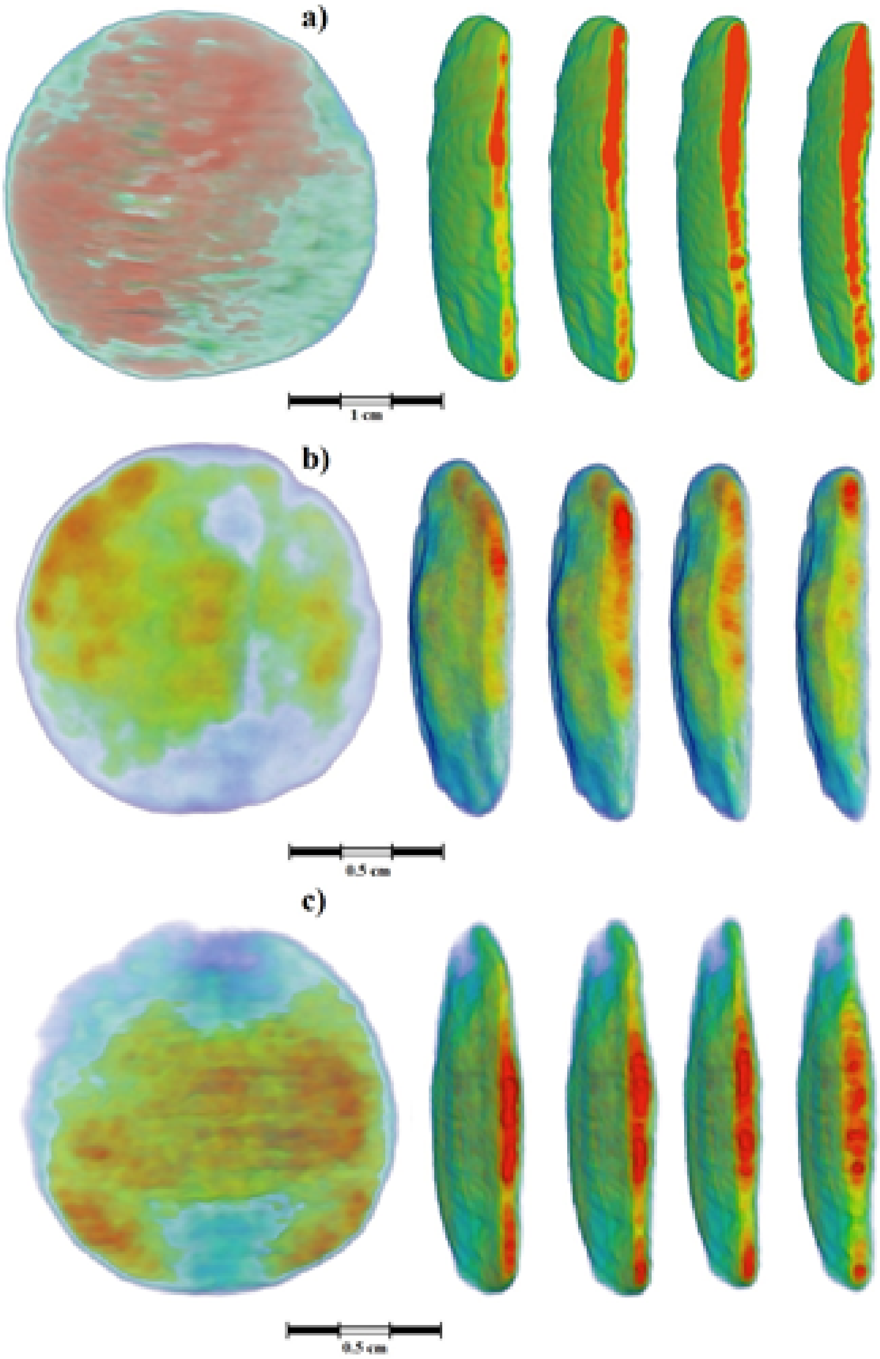

Figure 3. The 3D models after tomographic reconstruction and several longitudinal virtual slices of the 3D models of the Heliocles coin (a) and Demetrius silver coins (b, c). The red areas on the visual 3D models correspond to the maximum attenuation coefficient of the neutron beam. The green and blue regions are characterized by low neutron attenuation coefficient due to the spatial distribution of phases inside the coins. For silver coins, there are correspond to external contamination and variations in the thickness of the coin. The scale bars are shown.

At analysis the obtained 3D model of imitation of Heliocles coins it was clearly detected an uneven distribution of the neutron attenuation coefficient in the corresponding volume of the coin (Figure 3 a). A possible explanation for this may be a rather deep penetration of the patina into the volume of the coin [13, 14]. To estimate the relative volumes of the patina phase inside the coin, the segmentation procedure [13] of 3D neutron data was performed, as a result of which areas with a higher neutron attenuation coefficient were distinguished from the entire volume of the 3D model, which corresponds to volumetric regions with an increased patina content. It has been established that the entire volume of the 3D model of the coin consists of approximately 5986846 voxels, and the total volume of these voxels corresponds to 1293.15(3) mm^3. The calculated volumes of patina-rich areas consist of 623229 voxels or 134.61(1) mm^3 or 10.4% of the total coin volume. The division of the total volume of the coin into components of the copper phase and patina by neutron tomography is more of an estimate.

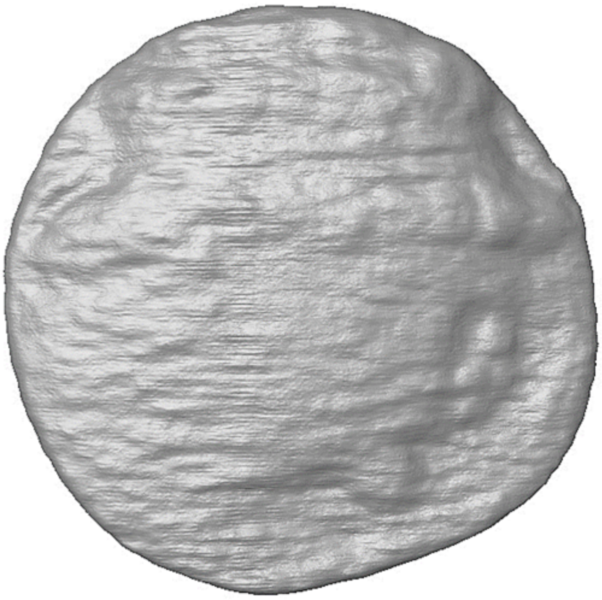

Figure 4. Reconstructed 3D model of the obverse profile of a copper imitation coin of Heliocles.

From the analysis of the 3D model of the coin, it is possible to reconstruct the coinage profile [13, 14] within the achievable spatial resolution of the neutron tomography method. Figure 4 shows the profile of the obverse of copper coin with an improved relief of the image coinage in the imitation of the Heliocles coin.

The reconstructed 3D models of the Demetrius silver coins are presented in Figure 3 b and Figure 3 c. In this case, the neutron data indicate a uniform distribution of the silver phase in the coin material. Although worth noting that there is a very weak neutron radiographic contrast between individual regions of the coin, but this is definitely caused by the complex profile of the coin, which corresponds to the features of coinage. However, by reason of the small average diameter and thickness of the Demetrius coins, it was not possible to restore the coinage profile.

Conclusion

The non-destructive structural studies of three coins from the archeological excavations of the Uzundara fortress were performed using neutron diffraction and tomography method. The phase composition, as well as the 3D data of the spatial distribution of inner components, were obtained for the copper Heliocles coin and two silver Demetrius coins. Small concentrations of tin and lead were detected in copper Heliocles coin. The ways of tenorite patina penetration into the thickness of the copper coin were determined. The uniform distribution of silver and vanishingly small concentrations of lead in both silver Demetrius coins were found.

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