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Identification of Bronze Artifacts from the Late Bronze Age from the Necropol of Baley Village to Lohbrügge near Hamburg

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Abstract
One of the great periods in human development after the Stone, New Stone and Copper Age was the Bronze Age. The name is associated with the discovery of the bronze alloy and the production of various objects from it. This period spans nearly two millennia (from the end of the 4th millennium BC to the 12th century BC) and is the time when, in addition to the making of the first bronze objects, the first major civilizations of the south and southeast – the Sumerian, Egyptian, Hittite, Minoan, Mycenaean and more. The territory of present-day Bulgaria does not remain isolated from the process of production and use of bronze objects, the apogee of this being the last period – the Late Bronze Age (the second half of the 2nd millennium BC). The article describes the applied non-destructive methods of element analysis of the artifacts through X-ray fluorescence analysis (XRF) and X-ray diffraction (XRD).

Keywords: radiography, defectoscopy, corrosion, Late Bronze Age, X-ray image

1. Introduction

The ancient metal products preserved to this day are those made of gold, silver, copper, bronze and iron. While precious metal objects arouse particular interest because of their exceptional jewelry and technological value, bronze objects prove to be a mystery that has greatly influenced the development of corrosion resistant technologies in the everyday life of mankind [1]. Only slight differences in the chemical composition of the alloy, composed of the two metals copper and tin, can change both the color of the object (from yellow-gold, at 6 to 18 wt.% Tin, to shiny silver at contents, above 18 wt.% Tin) and a number its mechanical properties such as malleability, hardness, etc. [2].
One of the great periods in human development after the Stone, New Stone and Copper Age was the Bronze Age. The name is associated with the discovery of the bronze alloy and the production of various objects from it. This period spans nearly two millennia (from the end of the 4th millennium BC to the 12th century BC) and is the time when, in addition to the making of the first bronze objects, the first major civilizations of the south and southeast – the Sumerian, Egyptian, Hittite, Minoan, Mycenaean and more. The territory of present-day Bulgaria does not remain isolated from the process of production and use of bronze objects, the apogee of this being the last period – the Late Bronze Age (the second half of the 2nd millennium BC).
One of the phenomena characterizing the Late Bronze Age in the Lower Danube basin is the distribution, production and deposition of bronze objects. The tradition of treading metal objects in the northern half of the Balkan Peninsula appears as early as the Early Bronze Age and continues into the Middle. In the second half of the 2nd millennium BC. On both sides of the Lower Danube, there is a change in this tradition, which is associated with a significant increase in both the number of collective finds and their volume and the nature of the objects they include in their composition. The deposition of dozens or hundreds of metal objects in one place, in some cases found in a ceramic vessel, has been widespread since the end of the

fourteenth century BC. The majority of these complexes include the tools of labor, mainly sickles and hollow bronze axes (Celts).
The geographical distribution of the collective findings shows that the majority of them are concentrated in the eastern part of the Lower Danube, the most numerous being in the territory of Central North, Northeastern Bulgaria, Eastern Muntenia and Dobrudja.
One of the intriguing topics in recent years in archeometric research is closely related to the origin of tin in ancient bronze artifacts in Europe [2, 3]. The tin has a lower melting point and retains the liquid state of the copper alloy longer, allowing controlled melting. The main source of tin was the cassiterite – tin oxide ($SnO2$) ore, with oxygen released during the smelting processes [3, 4]. Unlike copper, whose deposits are ubiquitous, with tin this is not the case. Even the scientific literature talks about a problem – the so-called "Tin Enigma". For Central European objects during the Bronze Age, tin was most likely extracted from the deposits in Erzgebirge (between Germany and the Czech Republic). Another source for Western Europe is the Cornell, England region [2, 4, 5]. Recently, tin deposits were discovered in Serbia, Ploničnik, which may be associated with the production of bronze objects in the Balkans since ancient times [6]. Tin-rich ores have also been found in areas around Turkey and Cyprus [2].

2. Location and Objects

Compared to some of the discoveries in larger collections, bronze objects found in settlements and necropolises are significantly smaller not only in Bulgaria but also in Europe. The Baley site, representing a settlement and a necropolis, provides a good basis for analyzing the character of these findings, originating from a clear archeological context and going beyond the widespread tradition of depositing metal objects over time. Precisely they can be associated with a specific object, including the population that used them and probably produced them. On the other hand, the localization of the site in northwestern Bulgaria provides a good basis for comparing these objects with those of the collective finds from central north and northeast Bulgaria, as well as with the lands north and west.

The Baley site is located on the eastern bank of the Timok River, about 2 km from its confluence with the Danube. It consists of a settlement and a necropolis. The village is situated at a low elevation – about 300 m from the river. The archaeological studies were carried out in the period 1970÷1989 under the guidance of R. Katincharov [7] and A. Yotsova [8]. Nearly twenty years of archaeological research have allowed the team to identify four major stages in the life of the settlement. In recent years, material analysis has allowed a team of archaeologists to subdivide the earliest stage into two separate sub-stages, as well as the latest stage. The dwellings surveyed show that they were constructed in the standard epoch with stakes driven into the ground, interwoven with rods and clay-coated. They have a rectangular, trapezoidal or apse shape, with one or two parts internally. In only one case is there an entrance hall. Many furnaces and dug-in structures were also studied – pits. With its several stages of habitation, the Baley settlement became one of the largest in the culture of inlaid ceramics, spread in the second half of the 2nd millennium BC in the western part of the Lower Danube basin [8].
In 2009, the necropolis was discovered. It is located at an elevation of about 450 m southeast of the village and is located in the eastern part of the modern village, as part of it falls within the limits of modern residential properties. So far, a total of 57 burial complexes and 4 structures, probably related to them, have been discovered.
Bronze objects are mostly found in the graves of the most recent stage. In only one case, several bronze objects emerge from the earliest stage, one of which is a preserved form. It is a 12 cm wide bronze pendant, which finds very good parallels among Halbmondförmige Blechanhänger crescent shaped pendants from Slovakia, Hungary and Northern Romania. The Baley instance

refers to the group of the unregistered. In the graves of the later group, especially those with rich inventory, other bronze objects were found – jewelry, parts of clothing and tools. Some of them were at the balefire, as a result of which they were deformed. Whole and well-preserved are a needle with the needle with ear, knife, knob and bracelet.

The graves and bronze objects studied provide information on the multifaceted cultural connections that are reflected in the archaeological materials from this necropolis. The latter are directly related to the interpretation and cultural affiliation of the individual structures. The ceramic materials of the earliest objects – those of the Middle Bronze Age, refer them to the cultural circle of Verbichoara-Vatina, which covers the territory of present-day Northwestern Bulgaria, Oltenia, Northern Serbia, Banat and reaches Hungary.

The graves, which are chronologically linked to the different stages of the life of the village, can culturally be associated with the arts of inlaid ceramics. Various variants of it are spread over a vast territory along the two banks of the Danube, which covers lands from Central Europe to the mouths of the Olt and Iskar rivers. At the same time, new cultural phenomena are reflected in the late graves, which lead to changes in the forms of vessels, the style of decoration and the funeral ritual itself. These influences are again linked to the lands of the north and northwest. All discovered bronze objects from the necropolis and the settlement confirm these interconnections between the north and the northwest.

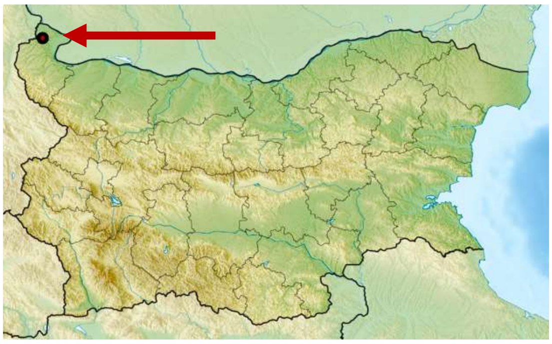

Fig. 1. Baley, Bregovo municipality

The present project involves the study of seven Baley necropolis objects (Fig. 1), which can be conditionally divided according to their purpose:

- jewelry and decorative items (button, bracelet, applique and pendant);
- tools and cutting tools (knife and needle);
- Shaped, scorched objects.

The purpose of the study is to determine the content of copper and tin elements and their distribution in the volume and surface of the artifacts. To this end, complementary analytical methods have been applied.

3. Research methodology

The methodology for the study of bronze products is based on three stages: determining the elemental composition, specifying the phase composition of the patina and clarifying the method of metal processing. The methods of element analysis include: X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), laser-induced spectroscopy (LIBS), photoelectron spectroscopy (XPS), energy-dispersive electron microscopy (EDX) and X-ray diffraction (EDX) methods. All of these methods are selected in such a way that information from different depths of the object can be obtained in a non-destructive manner (Figs. 2÷4).

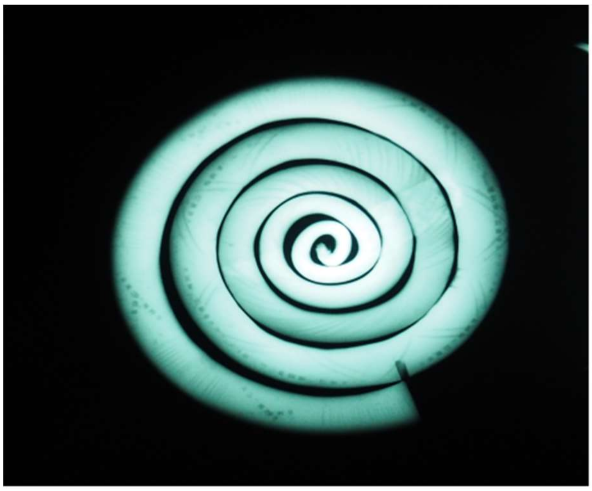

Fig. 2. Part of an artifact of unknown purpose [10]

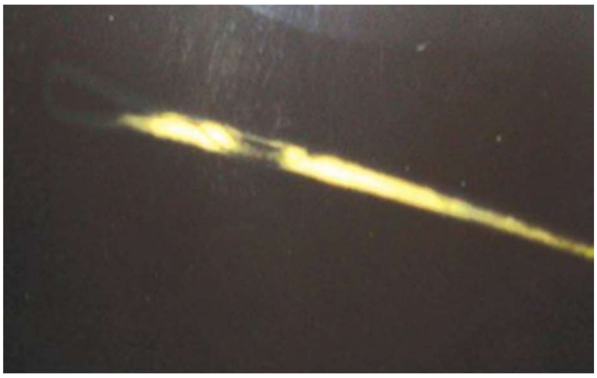

Fig. 3. Needle with ear

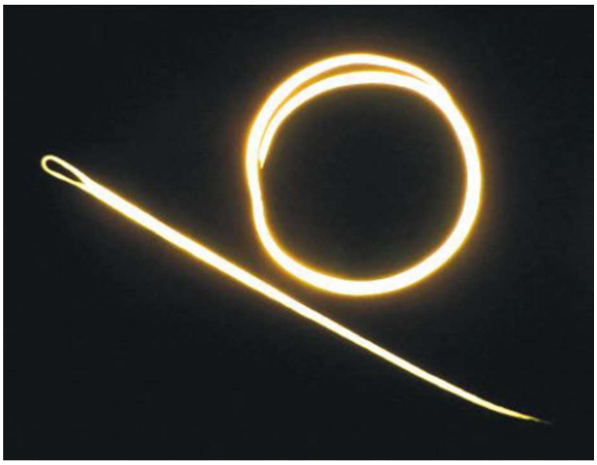

Fig. 4. Bracelet

It should be noted that the classical approach is by making a cross-section along the entire height of the object, but this implies its destruction. Therefore, in this project, we propose the original use of a combination of analytical and non-destructive methods so that the artifacts provided do not undergo any modification. Of all the analytical techniques, the most superficial is the XPS method, which provides information on the content of elements in a layer up to 5÷8

nanometers thick. In comparison, the XRF and XRD methods allow the material to be analyzed below the surface within a few tens to hundreds of micrometers (i.e. more than 15,000 times greater depth). Intermediate in depth of the analyzed layer is the EDX method, which covers an area a few micrometers below the surface of the object, i.e. about 1000 times deeper. Unlike the above-mentioned methods, the LIBS method allows a controlled study both directly on the surface and in depth, depending on the number of laser pulses applied at one point on the surface. In this case, the analysis was performed at a depth of about 120 micrometers.
All examinations with the X-ray diffraction method excluded (which is much more comprehensive and could not be limited to just a point of the subject) were performed in sections of the above-described objects cleaned by the millennium patina (Fig. 5). The patina is a corrosive product that forms on the surface of bronze articles and is of particular interest to archeometry scientists [5, 9]. The composition of the patina, as well as its thickness, are essential for determining the origin and migration of bronze articles, and this issue will be addressed in some way in this study. In the project, we used X-ray diffraction, which allows us to analyze objects where the patina cannot (or should not) be removed. The treatment of metals was monitored by radiographic testing.

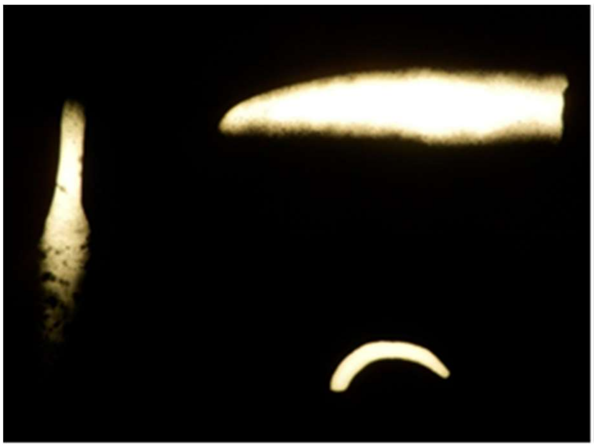

Fig. 5. Chisel, knife and fibula

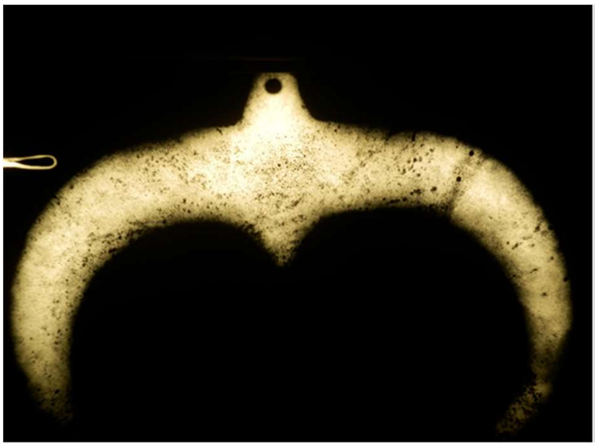

Fig. 6. Pendant

Last but not least, it is noted that the present project has attempted to create a protocol (a set of methods and their consistent use) to determine the composition of objects in a non-destructive manner. The obtained data allow the next stage to be compared with the results of similar groups of sites from other geographical places of Thracian heritage on the territory of Bulgaria and the region.
Radiographic analysis shows that Baley objects were obtained through the casting process.
Fig. 6 shows a radiograph of a crescent-shaped bronze pendant and an outgrowth in the middle, found in a tomb from the earliest stage. Black circular sections (up to 2 mm in size) of the image result from corrosion processes. The gray circular sections (they are spheres in volume) represent the pores / voids obtained during the casting process. They are drawn, often rounded, smooth-walled sheds located directly below the foundry bark perpendicular to the surface of the casting. Separate sheds can also come to the surface. The sheds are found individually or in groups. They are formed by the release of gases from the melt or the suction of gases upon spillage.
The ornaments of the later graves were also made by casting and forging (Fig. 7). The needle clearly distinguishes three stages of ear shaping after casting the original workpiece (wire): forging by drawing and folding to shape the ear.

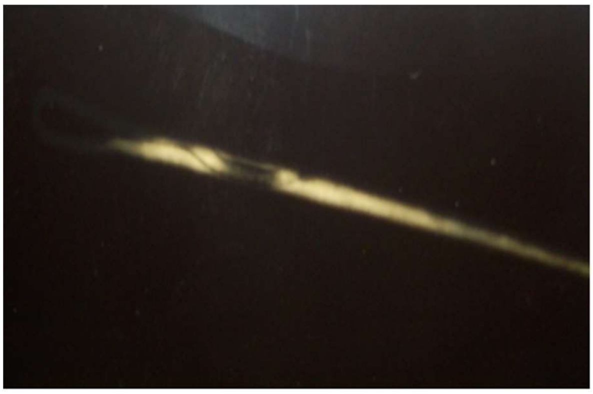

Fig. 7. Needle with ear (X-ray image)

Baley bronze products are subject to significant corrosion processes. To analyze the composition of corrosion products, we used the advantages of X-ray diffraction. The methodology used is of great practical importance in cases where the surface layer of corrosive products cannot or should not be removed. The corrosive product has a modified chemical composition (most often copper depleted) and if not cleaned, this circumstance would affect the final data from traditional chemical analyzes. However, the altered chemical composition of the surface does not affect the location of the diffraction peaks obtained from the crystal structure of the bronze alloy. Thus, although the location of the diffraction peak is a secondary marker, it is possible to determine the chemical composition if the elements present are known in advance. The same principle is used to analyze the carbon present in steel.

Fig. 8 [10] shows how the experimental analysis of a crescent-shaped application is performed. The results show that the corrosion products have the same origin for all tested bronze articles. They contain the phases of cassiterite SnO_2, biotite K (Mg, Fe) $3AlSi_3O_{10}$ $(OH)_2$, spangolite Cu_6Al (SO_4) (OH) 12Cl $(H2O)_3$, malachite $Cu_2CO_3(OH)_2$, tenorite CuO, cuprite Cu_2O and calcium stann $CaSnO_3$.

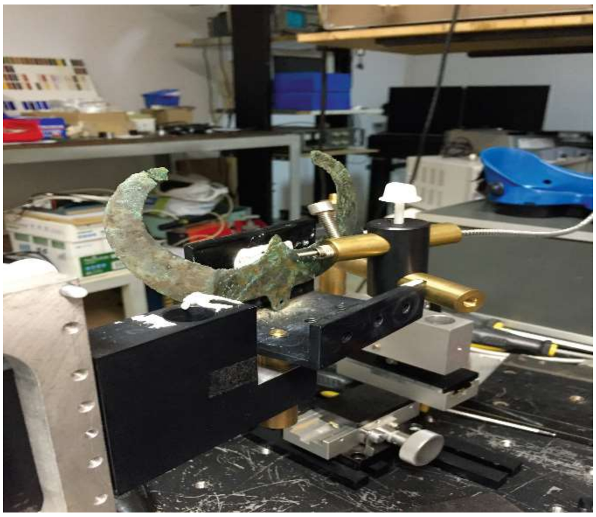

Fig. 8. Crescent shaped application in X-ray diffractometer chamber (Inv. № Baley 27-4 [10])

Fig. 9. Needle with an ear [11]

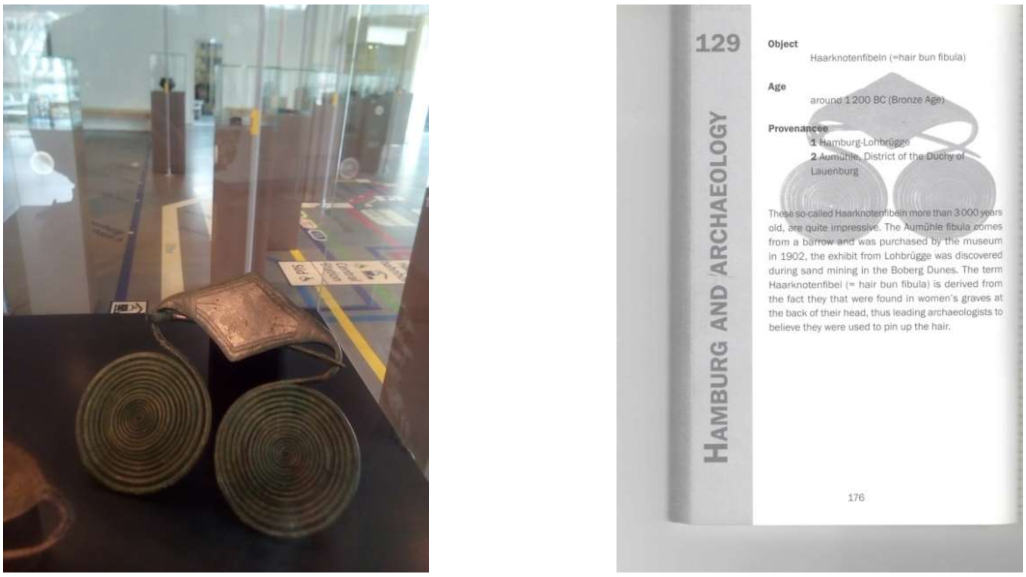

Fig. 10. Hair bun fibula in Hamburg Archaelogical Museum, found in Lohbrügge near Hamburg [11]

4. Conclusion

The interdisciplinary study sheds new light on the technological abilities of ancient masters from the second half of the second millennium BC in the western part of the Lower Danube basin. Despite the great distance from the Baley area near Vidin to Hamburg Germany (more than 2500 km), we find identical artifacts, which speaks of cultural and commercial ties during the Bronze Age. The needle with an ear (on the showcase at the bottom first) [11] of Fig. 9 is identical in size and shape of the ear to that of Baley of Fig. 7.

Part of an artifact of unknown purpose [10] on Figure 2 is a part of the exhibit from Hamburg Object hair bun fibula Fig.10 (A, B), dated around 1200 BC (Bronze Age) [11].

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