XRF ANALYSES PERFORMED ON THE ENEOLITHIC COPPER BRACELETS FROM THE CHIRNOGI – SUVITA IORGULESCU **NECROPOLIS**

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Keywords: copper, ornaments, Eneolithic, XRF measurements.

Cuvinte cheie: *cupru*, *podoabe*, *eneolitic*, *analize XRF*.

Abstract: The aim of this paper is to present a previously unpublished category of artefacts - the copper bracelets - identified in two burials from the Chirnogi - Suvita Iorgulescu necropolis. These copper adornments are part of the Gumelnița Civilization Museum Collection in Oltenita. Firstly, the artefacts were submitted to morphological and technological analyses. The bracelets were also analyzed through the ED-XRF method. It is also important to discuss the functions of the copper bracelets depending on the archaeological context.

Rezumat: Scopul lucrării noastre este de a prezenta o categorie inedită de artefacte, brățările din cupru identificate în două morminte din necropola de la Chirnogi-Suvița Iorgulescu. Podoabele din cupru fac parte din Colecția Muzeului Civilizației Gumelnița din Oltenița. Într-o primă etapă, piesele au fost studiate din punct de vedere morfologic și tehnologic. Brățările au fost apoi analizate prin metoda ED-XRF. De asemenea, au fost discutate funcțiile brățărilor din cupru, raportate la contextul arheologic.

Introduction

This article focuses on the Eneolithic copper bracelets found within the Chirnogi - Suvita Iorgulescu necropolis. Two spiral - shaped bracelets and a massive Durankulak type bracelet stand out within the artefacts attributed to the Eneolithic period of the necropolis.

This study aims to expand the research on the Eneolithic copper adornments identified in the Carpathian-Balkan area through morphological and typological methods. The artefacts were also submitted to XRF analysis; the results were then compared to those of XRF measurements obtained on the copper adornments from Vidra and Chitila-Fermă settlements, part of the Bucharest Municipality Museum's Archaeology Collection.

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Archaeological background

The Chirnogi - Şuviţa Iorgulescu necropolis (Călărași County) was located on the high terrace of the Danube (Pl. I), between Chirnogi and Căscioarele, 2 km west of the Chirnogi commune, on the east bank of the valley known by the locals as Şuviţa Iorgulescu¹.

The necropolis was identified in 1961 by Barbu Ionescu following agricultural work of planting vine. In 1989, during the construction of the Danube–Bucharest Channel, preventive archaeological excavations conducted by Done Şerbănescu took place in the area².

Chirnogi - *Şuviţa Iorgulescu* necropolis comprise burials belonging to several historical periods. Most of them (62), based on the present grave goods, were dated to the Gumelniţa culture, two to the northern Pontic population (EBA), and one to the Sarmatians. Twelve burials had no grave goods and thus could not be attributed to a certain period.

According to the anthropological data regarding the individuals attributed to the Gumelniţa culture, there were 36 males, 13 females and 13 undetermined. Most of the individuals were adults³. The dead were placed crouched on the left side, oriented ESE-WNW. The graves had irregular oval shapes, and reached depths varying between -0.90 m and 1.70 m ⁴.

Unfortunately, although two anthropological studies were published so far, complete archaeological data was not and thus a correlation between burials and grave goods cannot be established. Significant grave goods such as ornaments made of *Spondylus gaederopus, Dentalium* and copper, as well as vessels, stone and flint tools are known from this necropolis. In the absence of archaeological and anthropological data correlation, we are not able to make assumptions regarding the distribution of the adornments based on age and gender criteria.

The copper bracelets studied in this article are part of the Gumelniţa Civilization Museum Collection (Inv. No. 11962, 11963, 11964). The grave no. 68 included two double spiral-shaped copper bracelets (Plate II-III) and one copper bead. In grave no. 69, a significant grave goods were discovered such as a *Durankulak* type bracelet (Plate IV) and a *Spondylus* bracelet⁵.

The spiral-shaped forms were manufactured by cold hammering, possibly by wrapping the wire/bar around a cylindrical support; some of the ends were sharpened. Detailed microscopic images of the exterior surfaces of the bracelets showing the hammering technique and the sharpened ends were obtained using a HDM Pro Celestron #44308 digital microscope (Plate II-IV).

² Bălteanu, Cantemir 1991, p. 3.

¹ Serbănescu 2008.

³ Bălteanu, Cantemir 1991, p. 11-16.

⁴ Bălteanu, Cantemir 1991 p. 3; Lazăr et alii 2012, p. 125.

⁵ Mărgărit, Dimache 2019, p. 398-413.

Catalogue of the copper bracelets from Chirnogi - *Şuvița Iorgulescu* necropolis

Object form I. N. 11962

- 1. Name/ Type: Spiral bracelet (Plate II)
- 2. Place of discovery: Chirnogi Şuvița Iorgulescu necropolis, 1989.
- 3. Archaeological context: Grave M68.
- 4. *Measurements*: diameter of bracelet = 6.8 cm, diameter of copper rod = 0.5 cm.
- 5. *Material*: The object was made of copper.
- 6. *Description*: Spiral bracelet made of copper rod, with circular cross-section. The artefact was manufactured using the cold hammering technique. The object presents two sharpened ends. The surface of the artefact is green in color due to corrosion.
 - 7. Dating: Eneolithic, the second half of the fifth millennium BC.
 - 8. Bibliography: Unpublished.

Object form I. N. 11963

- 1. Name/ Type: Spiral bracelet (Plate III)
- 2. Place of discovery: Chirnogi Şuvița Iorgulescu necropolis, 1989.
- 3. Archaeological context: Grave M68.
- 4. *Measurements*: diameter of bracelet = 7.5 cm, diameter of rod = 0.4 cm.
- 5. *Material*: The object was made of copper.
- 6. *Description*: Spiral bracelet made of copper wire, with circular cross-section. The artefact was manufactured by the hammering technique. The object presents two sharpened ends. The surface of the artefact is green in color due to corrosion.
 - 7. *Dating*: Eneolithic, the second half of the fifth millennium BC.
 - 8. Bibliography: Unpublished.

Object form I. N. 11964

- 1. Name/ Type: Durankulak type bracelet (Plate IV)
- 2. Place of discovery: Chirnogi Şuvița Iorgulescu necropolis, 1989.
- 3. Archaeological context: Grave M69, associated artefacts: one Spondylus bracelet.
- 4. Measurements: diameter of bracelet= 8 cm, thickness of bar = 0.5 cm, width = 1.8 cm
 - 5. Material: The object was made of copper.
- 6. *Description*: Durankulak type bracelet made of copper bar, with rectangular cross-section. The artefact was manufactured using the cold hammering technique. The object presents two overlapping ends. The surface of the artefact is green in color due to the corrosion.
 - 7. Dating: Eneolithic, the second half of the fifth millennium BC.
 - 8. Bibliography: Unpublished.

The XRF Method

The Energy Dispersive X-Ray Fluorescence (ED-XRF) analysis was performed using a handheld Skyray Instruments Genius spectrometer. Fitted with a silver anode

tube, the apparatus has excellent resolution within the domain concerning transitional metals (from Scandium to Zirconium), approximatively 140 eV.

The Genius spectrometer uses a Silicon Drift Detector (SDD) oriented backwards at an angle of approximatively 45° with respect to the incident silver X-ray beam, to record characteristic X-rays emitted by the analyzed sample.

The spot on the sample, as declared by the manufacturer, is ca. 5 mm. Multiple points were analyzed on each sample in order to ensure the sample was homogeneous. Each characteristic spectra was recorded for 60s. A tension of 38 kV was applied on the anode tube to generate the incident beam, resulting in an approximate 30 mA target current. The table of results contains the medium values obtained for each point analyzed and their specific errors.

The copper bracelets from Chirnogi – *Şuviţa Iorgulescu* necropolis are copper based finds (between 96-99%) with minor elements such as antimony, nickel, tin, lead, iron and zinc. The content of antimony ranges between 0.01-0.66%; the nickel value between 0.04-0.44%; the tin between 0.04-0.72%; while lead ranges between 0.04-0.11% (Plate V).

Discussion

The prehistoric metal adornments could have an aesthetic role and could have been used in the ornamentation of the human body. This hypothesis is supported by the funerary archaeological discoveries from the Neo-Eneolithic Carpathian-Balkan area, where archaeologists can reconstruct the placement of the artefacts on the body: arms, hands, neck, and chest.

Important series of artefacts appeared in the Durankulak necropolis, where various typological categories are known (e.g. opened, closed or spiral – shaped, and the Durankulak type bracelets). The Durankulak type bracelets (TA 3, typ Durankulak⁶) were defined as massive disc-shaped bracelets, perpendicular to the arm. The crosssections of the bracelets were rectangular to trapezoidal or triangular. The artefacts can present overlapping ends. The *Durankulak* bracelets, which stand out within the grave goods, were found in five graves from Durankulak necropolis (Grave no. 183, 245, 253, 279, 660)⁷. A similar artefact was found in grave no. 69 from Chirnogi – Suvita *Iorgulescu* necropolis, being an important discovery within the Romanian region. Also, associations between bracelets are frequent. Different shaped bracelets could have been placed on the wrists of the deceased. For example, grave no. 253 (cenotaph) included a Durankulak type bracelet in association with a bracelet with overlapping ends, next to ceramic vessels, chalcedony bead and one antler axe⁸. Grave no. 660, belonging to a Juvens, presented grave goods such as a Spondylus bracelet on the left upper arm, a disc-shaped Durankulak bracelet with overlapping ends on the left wrist, a Spondylus bracelet around the right forearm associated with a copper bracelet with overlapping

⁶ Todorova 2002, p. 145, Abb. 167.

⁷ Todorova, Vajsov 2001, p. 79, Todorova 2002, p. 38, 41, 43, 64.

⁸ Todorova 2002, p. 41, Tabl. 24.

ends on the right wrist. A necklace made of *Spondylus* and malachite, a *Spondylus* headband, as well as ceramic vessels were also part of the funerary inventory⁹.

Copper bracelets appeared in Hamangia and Kodžadermen-Gumelniţa-Karanovo VI funerary area: at Agigea¹⁰ (one spiral-shaped and one closed bracelet), Durankulak (various types), Varna I and Varna II (spiral-shaped)¹¹. Copper bracelets were also found in KGK VI domestic areas: at Căscioarele - *Ostrovel*¹² (bracelets fragments), Geangoiești¹³ (one opened bracelet and one fragmented), Chitila-Fermă¹⁴ (one bracelet with overlapping ends in an *intra-muros* grave); Goljamo Delčevo *tell*¹⁵ (one opened bracelet and one bracelet with overlapping ends), Sălcuța – Slatina – Strehăreț settlement¹⁶ (one bracelet with overlapping ends).

The results of the ED-XRF analyses performed on the copper bracelets from Chirnogi – *Şuviţa Iorgulescu* were compared to the analyses¹⁷ performed with the same XRF equipment on the copper adornments from Chitila-*Fermă* and Vidra settlements. Therefore, it can be observed that all the items were manufactured using native copper with low values of minor elements. The ornaments from Chitila-*Fermă* and Vidra settlements present high values of copper, ranging between 99.35 – 99.69%, small values of antimony, nickel, tin, lead, zinc were detected (Plate VI). By comparing the chemical composition of the bracelets, we can observe the similarities between the *Durankulak* type bracelet and the bracelet with overlapping ends from Chitila-*Fermă* settlement. Based on scientific studies, various raw material sources such as Ai Bunar, Medni Rid, Majdanpek were exploited since prehistory and we can assume that the studied adornments were manufactured using raw material derived from one of these areas.

Conclusions

The present study discusses the Eneolithic copper bracelets from Chirnogi – *Şuviţa Iorgulescu* necropolis, currently part of the Gumelniţa Civilization Museum Collection. The article is part of the research conducted on the Eneolithic adornments from the Carpathian-Balkan area. Due to the incomplete archaeological information, published in short reports, the correlation between the skeletons and the funerary inventories could not be made. Despite this, the copper bracelets identified at this site distinguish this necropolis from others, with analogies in the Carpatho-Balkan area (Căscioarele, Chitila-Fermă, Durankulak, Geangoiești, Goljamo Delcevo, Varna I and Varna II).

Burials 68 and 69 are noteworthy for their funerary inventory made of materials such as copper or *Spondylus*, which emphasize the exchange of prestige goods between the Eneolithic communities. The microscopic analysis offered a detailed image of the

⁹ Todorova 2002, p. 64, Tabl. 114.

¹⁰ Slobozianu 1958, p. 737, Mareş 2002, pl. 56, 3.

¹¹ Todorova, Vajsov 2001, p. 80, Tafel 33, 426, 427.

¹² Bem 2000, p. 158, fig. 21, 1-3.

¹³ Ilie 2010, p. 81, pl. VII.

¹⁴ Boroneanţ 1992, p. 70, fig. 1/1.

¹⁵ Todorova, Vajsov 2001, Tafel 35, 451, Tafel 36, 466.

¹⁶ Stefan 2014, p. 202, pl. 19, 11.

¹⁷ Darie, Georgescu 2017, p. 56-77.

exterior surfaces of the bracelets and the ED-XRF analyses indicated the use of native copper in manufacturing the artefacts, similar to the objects identified in the Carpathian - Balkan area.

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Bibliography / Bibliografie

Bălteanu, Cantemir 1991: C. Bălteanu., P. Cantemir, *Contribuții la cunoașterea unor aspect paleodemografice la populația neolitică de la Chirnogi-Șuvița Iorgulescu*, Studii și Cercetări de Antropologie. 28, 1991, p. 3-7.

Bălteanu, Cantemir 1992: C. Bălteanu., P. Cantemir, *Considerații asupra populației neolitice de la Chirnogi-Șuvița Iorgulescu*, Studii și Cercetări de Antropologie. 29, p. 11-16.

Bem 2000: *Considerații privind o serie de tipuri de piese din aramă gumelnițene*, în Buletinul Muzeului Teohari Antonescu, 5-6, 2000, p. 155-179.

Boroneanț 1992: V. Boroneanț, *Tell-ul neolitic de la Chitila-București*, Materiale, a XVII-a sesiune anuală de rapoarte, Ploiești, 1992, p. 69-72.

Darie, Georgescu 2017: A. Darie, M. Georgescu, XRF analyses performed on the Eneolithic copper objects from the Bucharest Municipality Museum's archaeological collection, Revista de cercetări arheologice și numismatice III, 2017, p. 56-77.

Darie 2018: A. Darie, Podoabele din metal din aria KGK VI – Reconstruirea cadrului social. Context arheologic *versus tipologie*, Revista de cercetări arheologice și numismatice IV, 2018, p. 34-53.

Ilie 2010: A. Ilie, *Câteva date despre o posibilă producție metalurgică în tell-ul de la Geangoești*, Buletinul Muzeul Județean Teleorman 2, 2010, p. 79-99.

Lazăr et alii 2012: C. Lazăr, T. Ignat, M. Florea, C. Astaloș, V. Opriș, M. Voicu, The Catalogue of the Neolithic and Eneolithic Funerary Findings from Romania.

Mareș 2002: I. Mareș, *Metalurgia aramei în neo - eneoliticul României*, Suceava, Editura Bucovina Istorică, 2002.

Mărgărit, Dimache 2019: M. Mărgărit, M. Dimache, *Personal adornments from the Eneolithic necropolis of Chirnogi-Şuviţa Iorgulescu (Romania): a picture of prehistoric communities symbolism*, Documenta Praehistorica XLVI, 2019, p. 398-413.

Slobozianu 1959: Horia Slobozeanu, *Considerații asupra așezărilor antice din jurul lacurilor Techirghiol și Agigea*, Materiale V, 1959, p. 735-752.

Şerbănescu 2008: D. Şerbănescu, *Fişă de sit*. http://ran.cimec.ro/?descript=chirnogi-chirnogi-calarasi-necropola-eneolitica-de-la-chirnogi-suvita-iorgulescu-cod-sit-ran-101813.15 (Accessed at: 4.12.2019).

Ștefan 2014: C.E.Ștefan, *Așezări sălcuțene din stânga Oltului Inferior*, în C.E. Ștefan, M. Florea, S.C. Ailincăi, C. Micu (eds.) Studii privind preistoria sud-estului Europei. Volum dedicat memoriei lui Mihai Simon, Brăila, 2014, p. 169-212.

Todorova 2001: H. Todorova, I. Vajsov, *Der kupferzeitliche Schmuck Bulgariens*, Prähistorische Bronzefunde XX (6), 2001, Stuttgart.

Todorova 2002: H. Todorova, *Durankulak II. Die Prähistorischen Gräberfelder*. Teil I. Berlin, Deutsches Archäologisches Institut, 2002.

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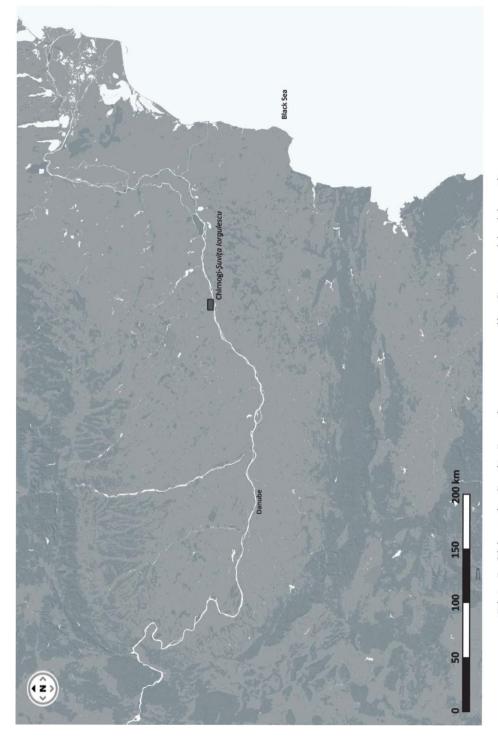


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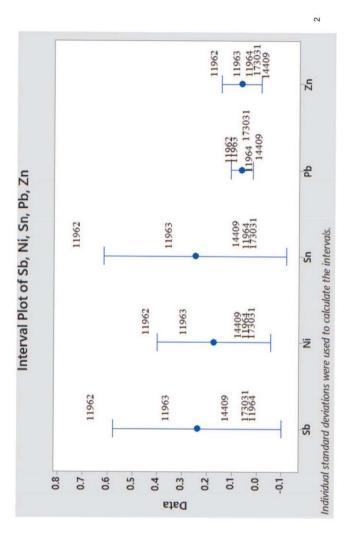


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Zn +/-	0.17	0.01	0.001
Zn(%)	0.17	80.0	0.03
Fe +/-	0.02	0.02	0.01
Fe(%)	1.53	1.88	0.00
Pb +/-	0.01	0.01	0.003
Pb(%)	0.11	60.0	0.04
-/+ uS	0.02	0.01	0.001
Sn(%)	0.72	0.35	0.04
Ni +/-	0.02	0.01	0.001
Ni(%)	0.44	0.29	0.04
-/+ qS	0.02	0.01	0.001
Sp(%)	99.0	0.36	0.01
-/+ n	0.2	0.17	0.12
Cu(%)	96.15	96.81	99.66
Inv. No.	11962	11963	11964
Nr. crt.	1	2	3



ED-XRF portable spectrometer, 38 kV, 30mA, used time 60s. 2. Diagram showing Plate V. 1. Results of the ED-XRF analyses performed on the copper bracelets, using an the interval plot of the minor chemical elements, realized using Minitab 17.1.0 version.

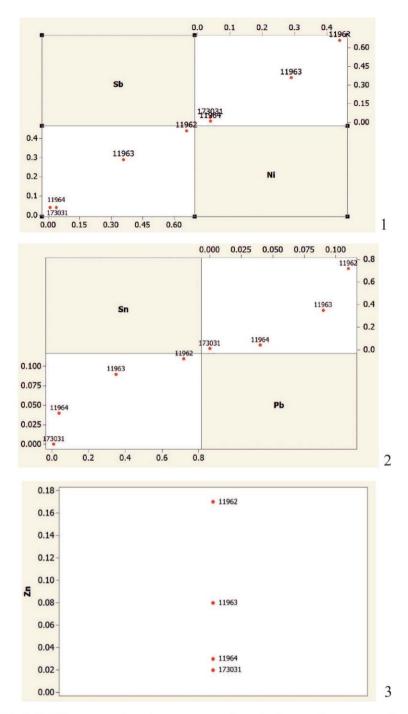


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