

PIXE AND XRF ANALYSES OF COPPER ARTIFACTS FROM THE GUMELNIȚA AREA (ROMANIA)

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Abstract

The main aim of this research is to expand the knowledge of the early stages of copper metallurgy in the Chalcolithic within the Gumelnița communities through compositional analyses (PIXE, XRF) performed on a group of copper objects that originated from several sites belonging to Kodzhadermen–Gumelnița–Karanovo VI (KGK VI) communities in southeast Romania (Chitila–Fermă, Măriuța, Sultana–Malu Roșu, Sărulești, and Vidra). All analyses were performed at the Horia Hulubei National Institute for Research & Development in Physics and Nuclear Engineering (Romania), and the investigated items belong to the collections of the Lower Danube Museum in Călărași and the Bucharest Municipality Museum. The resulting data were used as a starting point of a discussion on the possible prehistoric copper sources used by prehistoric people to manufacture the analyzed artifacts.

Keywords: Northern Balkans – Copper Age – Gumelnița – copper artifacts – elemental analyses.

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Introduction: short outline of previous work

In the second half of the 5th millennium BCE, an important cultural synthesis occurred between the Eastern Balkans and the Carpathians. In Romania, it is labeled as Gumelnița (after the eponymous settlement site near Oltenița city), and in Bulgaria, as

Kodzhadermen–Karanovo VI and as Varna in the Black Sea coastal area. The so-called Kodzhadermen–Gumelnița–Karanovo VI (KGK VI) group occupied southeast Romania, the southern parts of the Republic of Moldova and Ukraine, east Bulgaria on both sides of the Balkan Range, and to the south extended to the Aegean (Lazar et al. 2018b).

First chemical analyses on Chalcolithic copper artifacts from Romania were performed by S. Junghans, E. Sangmeister, and M. Schröder in the 1960s, as part of a large-scale project within which more than 22,000 objects were sampled and analyzed. Ten artifacts from the Bucharest Municipality Museum were included in this project (Junghans et al. 1968, 238f).

Other archaeometric analyses were performed on copper artifacts from the tell sites of Luncavița (Micu & Belc 2005, 48) and Pietrele–Măgura Gorgana (Hansen et al. 2008, 70ff).

The first step in reconstructing the *chaîne opératoire* of southeast European copper mining in the fifth millennium BCE is the identification of the provenance of raw material sources exploited. Previous research demonstrated that several copper mines operated in the Chalcolithic. For example, the prehistoric exploitation of the Ai Bunar mine was confirmed by archaeological excavations in the 1970s (Černych 1978). Another possible source of ore that was identified by lead isotope analyses is the Majdanpek mine in eastern Serbia. Some authors have suggested that remains from Chalcolithic mining activities could have been destroyed by recent mining exploitation (Pernicka et al. 1993, 25).

It has been accepted that the copper used by the Gumelnița people probably derived from the same sources (e.g., Majdanpek, Ai Bunar), considering the extended social networks created by the KGK VI communities along the Danube, Northeastern Bulgaria and the Black Sea coast. This assertion is sustained by the lead isotope and chemical analyses performed on the copper objects from the tell site of Pietrele–Magura Gorgana, which led to the conclusion that ore deposits in Serbia (e.g., Majdanpek) and Bulgaria (e.g., Chelopech, Burgas-Strandzha, and Ai Bunar) could have been the sources of the raw copper used here (Hansen et al. 2008, 70ff).

These exchange networks were based on previously existing connections between the Mediterranean and Southeast and Central Europe like *Spondylus* sp. distribution routes (Lazăr et al. 2018a). The maximum network development in the KGK VI area coincided with the emergence of metallurgy in Southeast Europe (Lazăr et al. 2018b). This fact determined the wider distribution of similar morphological metal forms in the Southeastern Europe, in the KGK VI area.

The copper artifacts found at Chitila–Fermă, Măriuța, Sultana–Malu Roșu, Sărulești, and Vidra were first submitted to primary morphological analysis. The main morphological characteristics are briefly presented in this article.

We also focused on the archaeological context of the artifacts. The majority of them were discovered in settlements, except for an awl found at the cemetery of Măriuța and a bracelet found in a funerary context at the tell site of Chitila–Fermă.

Detailed information on the archaeological context was provided where it was available. Twelve items from Sultana–Malu Roșu and Măriuța were not published.

Furthermore, we submitted the investigated items to non-invasive analyses (PIXE and XRF) in order to determine whether objects with similar morphological characteristics with the artifacts found in Northeast Bulgaria share the same raw material sources. Our aim was to correlate the trace elements detected by the PIXE and XRF analysis with the available data on copper raw material sources exploited by the prehistoric communities in the Balkan area.

Archaeological material and its context

The analyzed artifacts were uncovered at tell or flat sites as well as at cemeteries in the Mostiștea valley in the counties of Călărași (e.g., Măriuța, Sultana–Malu Roșu, and Sărulești) and Ilfov (e.g., Vidra and Chitila–Fermă) (fig. 1; table 1).

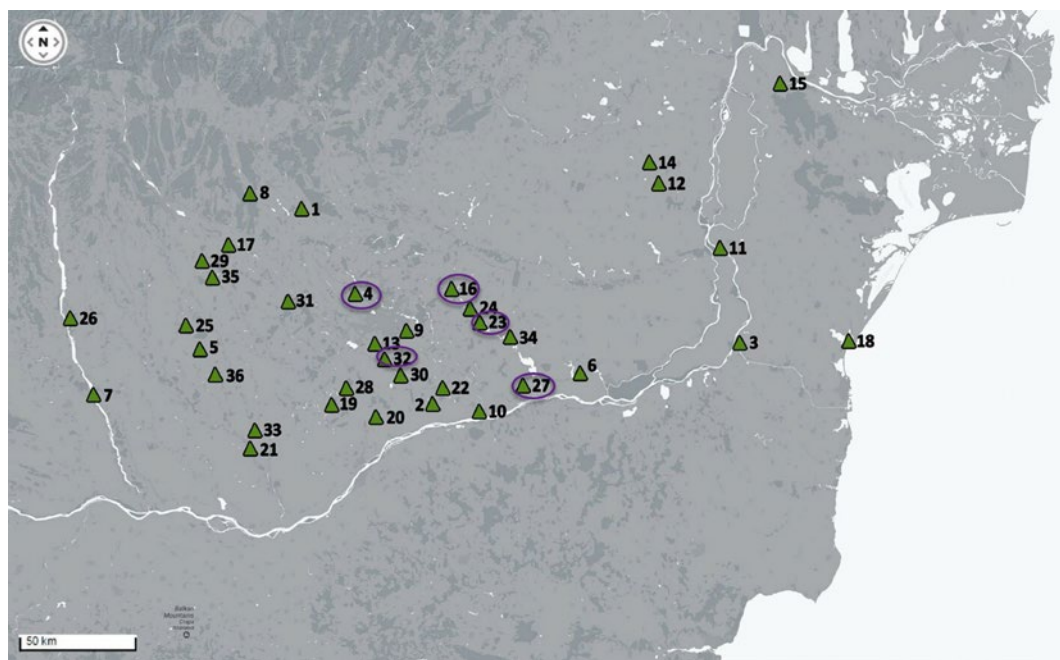


Figure 1. Map showing the distribution of copper artifacts in the Gumelnița area. The sites of origin of the artifacts analyzed in the paper are shown in purple ellipses. (1) Bușani-La Pod; (2) Căscioarele-Ostrovel; (3) Cernavodă; (4) Chitila; (5) Ciolăneștii din Deal; (6) Cunești; (7) Drăgonești-Olt; (8) Geangoiești; (9) Glina; (10) Gumelnița; (11) Hârșova; (12) Însurăței; (13) Jilava; (14) Lișcoteanca; (15) Luncavița; (16) Măriuța; (17) Morteni; (18) Năvodari; (19) Petru Rareș; (20) Pietrele; (21) Poroschia; (22) Radovanu; (23) Sărulești; (24) Șeinoiu; (25) Siliștea-Gumești; (26) Slatina; (27) Sultana-Malu Roșu; (28) Tangâru; (29) Teiu; (30) Vărăști; (31) Vânătorii Mici; (32) Vidra; (33) Vitănești; (34) Vlădiceasca; (35) Ziduri; (36) Gărăgău.

ID	Type (inventory number)	Context	Height/thickness	Image / reference
1	awl (32909)	Măriuța 1988, S IV, sq. 1; -1.78 to -1.93 m	15.6 / 0.4 cm	fig. 3.1 / Şimon 2014
2	awl (32908)	Măriuța 1988, S IV, sq. 1; -1.78 to -1.93 m	6.8 / 0.2 cm	fig. 3.7 / Şimon 2014
3	wire (43246)	Măriuța 2001, S B, Sector 2, sq. E2; -0.86; SU 1005, domestic waste area	7.6 / 0.2 cm	fig. 3.6
4	awl (51488)	Măriuța necropolis 2005, grave 4, S 19, sq. C2; -1.57 m	12.5 cm	fig. 3.3 / Lazăr & Parnic 2007
5	pin with plate-shaped end (53181)	Măriuța 1989, S IV, sq. 11; -2.37 m	11.2 / 0.2 cm	fig. 3.5 / Şimon 2014
6	awl (54308)	Măriuța 2008, S C, Sector 2, sq. B6; SU 1208; domestic waste area	11.6 / 0.2 cm	fig. 3.2
7	chisel (54309)	Măriuța 2008, S C, Sector 1, sq. A3; SU 1204; debris SL 6	4,8 / 0.4 cm	fig. 3.10
8	awl (55565)	Măriuța 2010, S B, Sector 1, sq. B2; SU 1040; SL 8 floor	13.4 / 0.4 cm	fig. 3.4
9	awl with bone handle (45441)	Măriuța 2000, S B, Sector 1, sq. A3; SU 1002; -0.75; domestic waste area	4.1 / 0.2 cm	fig. 3.8, 11
10	awl (45441)	Măriuța 2000, S B, Sector 1, sq. A3; SU 1002; -0.75; domestic waste area	8.8 / 0.2 cm	fig. 3.9
11	awl	Sultana-Malu Roşu 1975, close to house 4	7.71 / 0.42 cm	Lazăr et al. 2018b
12	awl	Sultana-Malu Roşu 1975	9.59 / 0.42 cm	Lazăr et al. 2018b
13	awl	Sultana-Malu Roşu	5.08 / 0.21 cm	Lazăr et al. 2018b
14	awl	Sultana-Malu Roşu, house 1/1983, S XI, sq. 5, -1 m	14.55 / 0.26 cm	Lazăr et al. 2018b
15	awl	Sultana-Malu Roşu, house 1/1983, S XI, sq. 5, -1 m	5.20 / 0.40 cm	Lazăr et al. 2018b
16	awl	Sultana-Malu Roşu, house 1/1983	5.00 / 0.60 cm	Lazăr et al. 2018b
17	Chisel	Sultana-Malu Roşu 1983, S XIII, sq. 3, -0.90 m, ash layer	15.90 / 0.80 cm	Lazăr et al. 2018b
18	awl (nr. inv. 54434)	Sultana-Malu Roşu 2003, house 2	5.33 / 0.33 cm	fig. 2.3
19	awl (nr. inv. 54433)	Sultana-Malu Roşu 2003, house 2	6.20 / 0.32 cm	fig. 2.4
20	awl (nr. inv. 54432)	Sultana-Malu Roşu 2003, house 2	11.31 / 0.41 cm	fig. 2.2
21	hook (44013)	Sultana-Malu Roşu 2002, S II, sq. 2; -1.50 to -1.60 m	7.00 / 0.5 cm	fig. 2.6
22	awl (47104)	Sultana-Malu Roşu 2004, S Y, sq. D1; -1.58 m	7.7 / 0.2 cm	fig. 2.5
23	awl (47105)	Sultana-Malu Roşu 2004, S Y, sq. D1; -1.91 m	11 / 0.3 cm	fig. 2.1
24	awl (14384)	Vidra, Gumelnița layer	5.5 / 0.3 cm	Comşa 1978
25	awl (14386)	Chalcolithic, unknown provenance	7.1 / 0.4 cm	Darie & Georgescu 2017
26	awl (14387)	Vidra, Gumelnița layer	9.4 / 0.4 cm	Mareş 2002
27	awl (14389)	Vidra, Gumelnița layer	8.7 / 0.3 cm	Comşa 1978

ID	Type (inventory number)	Context	Height/thickness	Image / reference
28	awl (14391)	Vidra, Gumelnița layer	7.4 / 0.2 cm	Comșa 1978
29	awl (14392)	Chalcolithic, unknown provenance	10.3 cm	Comșa 1978
30	awl (14393)	Vidra, Gumelnița layer	9.2 / 0.2 cm	Comșa 1978
31	awl (14394)	Vidra, Gumelnița layer	13.4 / 0.4 cm	Comșa 1978
32	awl (14395)	Chalcolithic, unknown provenance	10 / 0.4 cm	Comșa 1978
33	awl (14396)	Vidra, Gumelnița layer	12 / 0.4 cm	Comșa 1978
34	awl (14398)	Vidra, Gumelnița layer		Comșa 1978
35	awl (14400)	Chalcolithic, unknown provenance	9.5 / 0.4 cm	Comșa 1978
36	awl (14401)	Vidra, Gumelnița layer	9.7 / 0.2 cm	Mareș 2002
37	awl with bone handle (14402)	Vidra, Gumelnița layer	5.4 cm	Comșa 1978
38	awl with bone handle (14404)	Vidra, Gumelnița layer	8.6 cm	Comșa 1978
39	awl with bone handle (14405)	Vidra, Gumelnița layer	8.7 cm	Comșa 1978
40	awl with bone handle (14406)	Vidra, Gumelnița layer	6.00 / 0.3 cm	Comșa 1978
41	awl with bone handle (16149)	Chalcolithic, unknown provenance	8.5 / 0.3 cm	Darie & Georgescu 2017
42	chisel (14382)	Vidra, Gumelnița layer	3.5 / 0.4 cm	Comșa 1978
43	chisel (14383)	Chalcolithic, unknown provenance	3.9 / 0.2 cm	Darie & Georgescu 2017
44	chisel (14390)	Chalcolithic, unknown provenance	6.1 / 0.5 cm	Comșa 1978
45	chisel (14397)	Chalcolithic, unknown provenance	7.2 / 0.5 cm	Darie & Georgescu 2017
46	double volute pin (14408)	Vidra, Gumelnița layer	3.2 / 1.5 cm	Comșa 1978
47	double volute pin (14409)	Vidra, Gumelnița layer	6.5 / 0.2 cm	Comșa 1978
48	double volute pin (14410)	Sărulești, Gumelnița layer	12.76 / 3.18 cm	Comșa 1978
49	double volute pin (14411)	Sărulești, Gumelnița layer	13 / 2.4 cm	Comșa 1978
50	double volute pin (14413)	Vidra, Gumelnița layer	5.2 / 2.1 cm	Darie & Georgescu 2017
51	Vidra type axe (14415)	Vidra, Gumelnița layer	17.2 cm	Vulpe 1975
52	hook (14451)	Vidra, Gumelnița layer	6.3 / 0.4 cm	Comșa 1978
53	miniature axe (15589)	Vidra, Gumelnița layer	8.2 / 1.4 cm	Darie & Georgescu 2017
54	bracelet with overlapping ends (173031)	Chitila-Fermă tell	6.4 / 1.4 cm	Boroneanț 1992

Table 1. List of the artifacts included in the study.

Firstly, we focused on the copper artifacts found at the tell site of Vidra. Most of them are awls (18), five still with their bone handles (Darie & Georgescu 2017).

The items from the tell site of Sultana–Malu Roșu included mostly tools (11 awls, a chisel and a hook; Lazăr et al. 2018b) (fig. 2). The copper awls from Măriuța (fig. 3.1-4, 7-9) are typologically comparable to those from Sultana–Malu Roșu and Vidra. We also studied a chisel (fig. 3.10) and a piece of copper wire (fig. 3.6). The artifacts were recovered from a domestic waste area or were associated with houses and are therefore related to everyday activities, except for an awl found in grave 4 of the Măriuța necropolis (fig. 3.3; Lazăr & Parnic 2007).

One spectacular artifact is the Vidra type hammer-axe from the eponymous tell site. It is exquisitely made and has a pentagonal outline, an oval shaft-hole and a wide semicircular blade (Vulpe 1975).

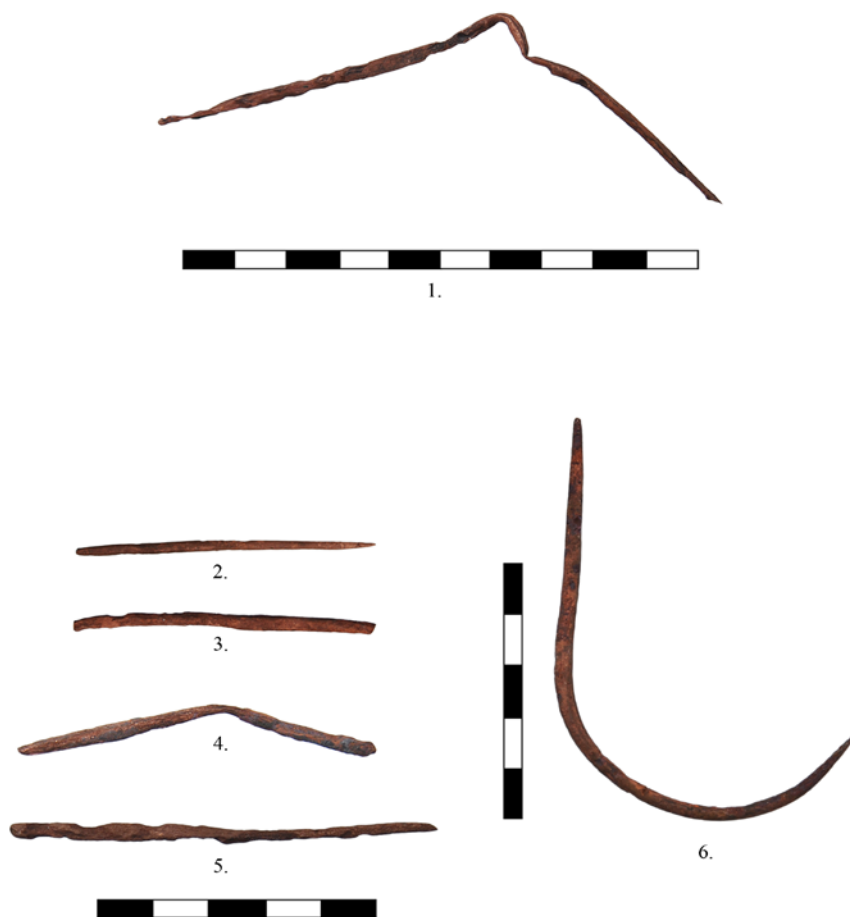


Figure 2. Copper tools (1–5) and a hook (6) from the tell site of Sultana–Malu Roșu.



Figure 3. Copper objects from the site of Măriuța: (1–4 and 7–9) awls; (5) pin with a plate-shaped end; (6) wire; (10) chisel; (11) bone handle.

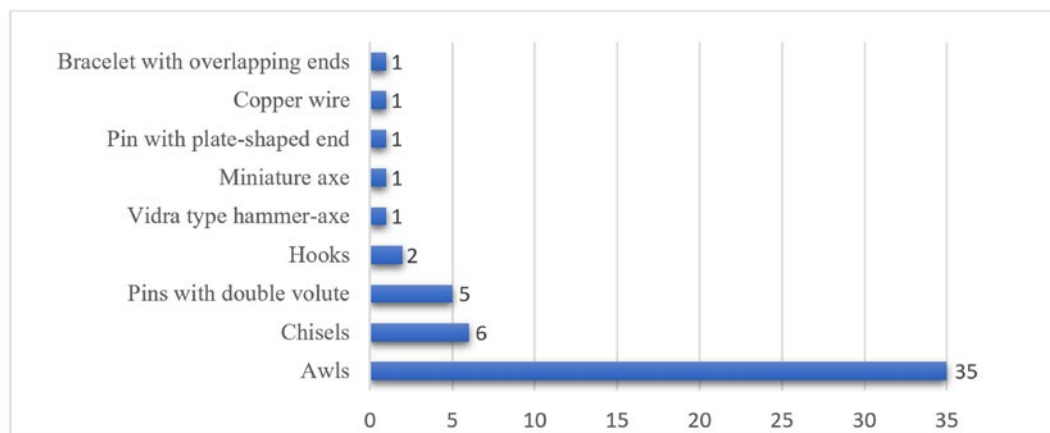


Figure 4. Types of copper artifacts included in this study.

In the copper ornaments category, we analyzed the double-volute pins from the Gumelnița cultural layers of Vidra and Sărulești (Darie & Georgescu 2017, 65), and one plate-shaped pin from Măriuța (fig. 3.5), as well as a bracelet with overlapping ends which was found near the skeleton in grave 2 at the tell site of Chitila–Fermă in 1982 (Boroneanț 1992, 70).

As is shown in figure 4, most of the examined artifacts are awls, which are a common typological category in the study area. The majority of them have a rectangular cross-section at the proximal end and a circular cross-section at the distal end; some of them are bent in distinct parts.

Methods

In order to identify trace elements that can be linked to raw material sources that were exploited in the Chalcolithic, we analyzed 35 copper items using PIXE and XRF methods.

Particle Induced X-ray Emission (PIXE)

For this analysis, a 3MV Tandetron™ particle accelerator at the Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH) was used to generate and deliver the proton beam onto the samples (Burducea et al. 2015). For this study, the AirBeam system was used in order to extract the proton beam ‘in-air’ and perform PIXE measurements in atmospheric pressure conditions. It has previously been used for various samples, with excellent results (cf. Opreș et al. 2022; Mirea et al. 2021).

Thus, a proton beam was generated, accelerated and transported to the IBA chamber. In high vacuum conditions, the energy was situated at 3 MeV. Through a thin silicon nitride window (Silson, UK), the proton beam was extracted in air and used to probe each sample. For this, the proton beam’s energy was calculated at approximately 2.835

MeV (SRIM simulations, starting from a 3 MeV beam inside the IBA chamber, in high vacuum conditions). The resulting characteristic X-ray spectra were recorded using a Silicon Drift (SDD, Amptek, USA) and analyzed with the Gupix software (Maxwell 1989).

Energy Dispersive X-Ray Fluorescence (ED-XRF)

The ED-XRF analyses were performed with a portable Bruker Tracer S1 Titan spectrometer which uses a Rhodium (Rh) anode tube to generate an X-ray beam to probe the samples. The generated beam has a maximum energy of 50 keV, but is usually limited at 40 keV. The beam passes through a collimator before probing the sample. The incident beam is characterized by a spot with 8 mm in diameter on the selected samples. A Silicon Drift Detector (SDD) positioned backwards at an angle of approximately 45° with respect to the Rh-anode tube, is used to record characteristic X-ray spectra. One point was analyzed on each sample; each point was exposed to the incident X-ray beam for 60 seconds. For this study, a work-mode dedicated to metal alloys was used. The point on each sample where the analysis was performed was chosen close to the point of the PIXE analysis due to the sample's nature. Each characteristic spectra was analyzed in order to identify composing elements and obtain their concentrations. The results obtained are expressed in parts-per-million (ppm).

Results and discussion

The results obtained are shown in tables 2 and 3. Considering the nature of the samples, a more invasive method to prepare the surfaces for analysis was unavailable. Due to this fact, the presence of a series of chemical elements that cannot be considered as part of the composing alloy can be noted: silicon, iron and aluminum. Their concentrations can be considered low, and their presence can be explained with the time the samples spent buried. The main composing element, copper, can be found in concentrations above 98% for all the pieces. The remaining elements are to be considered as trace elements and may be used to identify the provenance mine.

The results of the two analytical techniques indicate the same percentages for the elements identified. The composing elements, the elements characteristic for the soil where the samples were uncovered, and the trace elements were mostly identified by both techniques, and the calculated concentrations remained stable for each sample.

Following the procedures developed by E. Pernicka (1999 & 2014), we divided the samples analyzed using three trace elements: silver, cobalt and selenium. Following this, the bulk of the samples was divided, and two distinct groups were formed. One contains silver but neither cobalt nor selenium, and the other contains cobalt and selenium but not silver (fig. 5). Based on Pernicka 2014, cobalt is specific to the copper mine of Majdanpek whereas silver is specific to Ai Bunar. Considering the geographic location of the sites of origin of the artifacts, and the fact that these two mines were in use at the time the samples have been dated to, the provenance source of 13 of the analyzed samples containing cobalt might have been Majdanpek while the raw material for the other 23 might have come

XRF	Al	Si	P	S	Co	Fe	Ni	As	Ag	Pb	Cu	Area
14382	0.36	0.48	0.06	0	0	0	0	0	0.14	0.37	98.34	middle
14384	0.35	0.54	0	0	0.03	0.21	0.07	0	0	0	98.71	middle
14385	0.25	0.65	0	0	0.03	0.05	0.07	0	0	0	98.69	middle
14385	0.22	0.37	0.09	0.52	0.03	0.64	0.26	0.47	0	0	97.34	middle
14386	0.11	0.55	0.04	0.12	0	0.23	0.12	0	0.13	0	97.83	middle
14387	0.55	0.45	0.15	0.04	0	0.12	0.09	0	0.26	0	98.18	middle
14389	0.19	0.11	0.1	0.02	0	0.02	0	0	0.12	0	99.01	middle
14390	0.31	0.75	0.09	0	0	0.14	0.06	0	0.18	0	98.32	proximal
14392	0.57	0.48	0	0.01	0.03	0.04	0.05	0	0	0	97.37	middle
14394	0.63	0.24	0	0.03	0	0.06	0	0	0.1	0	98.79	middle
14397	0.36	0.49	0	0	0	0	0	0	0.19	0	98.93	middle
14398	0.54	0.57	0	0.02	0.03	0.06	0.1	0	0	0	98.29	middle
14401	0.14	0.77	0	0.04	0.02	0.04	0.31	0.16	0	0.11	96.64	middle
14408	0.12	0.04	0	0	0.04	0.07	0.09	0.08	0	0.09	99.42	middle
14408	0.19	0.56	0.05	0	0.03	0.24	0	0.27	0	0.12	98.07	volute
14410	0.52	0.37	0.09	0.02	0	0.06	0.07	0	0.11	0	98.49	double volutes area
14410	0.44	0.18	0.16	0.04	0.03	0.27	0	0	0	0	98.85	double volutes area
14411	0.22	0.08	0	0.04	0	0.21	0.12	0	0.1	0	98.67	double volutes area
14415	0	0.65	0	0	0	0.02	0.05	0	0.11	0.04	99.08	proximal
32908	0.05	0.58	0	0	0	0	0.05	0.07	0.15	0	98.52	middle
32909	0.43	0.63	0	0	0	0.06	0.14	0	0.14	0	97.74	proximal
43246	0.56	0.43	0	0	0.05	0.04	0	0	0.19	0	98.72	middle
44013	0.54	0.36	0	0	0.02	0.04	0.06	0	0	0	98.86	proximal
47104	0.69	0.59	0	0	0	0	0	0	0.17	0	98.24	flat end
47105	0.71	0.46	0	0.01	0	0.01	0.08	0	0.44	0	97.86	middle
51488	0.57	0.65	0	0	0.02	0.03	0	0	0	0	98.55	proximal
53181	0.55	0.41	0.15	0	0	0.04	0	0	0.16	0	98.42	proximal
54309	0.34	0.74	0	0	0.05	0.32	0	0	0.11	0	98.42	flat end
54432	0.47	0.53	0	0	0	0.02	0	0	0.18	0	98.73	proximal
54433	0.18	0.49	0	0	0	0.04	0.13	0.17	0.12	0	98.22	flat end
54434	0.41	0.34	0	0	0	0	0.09	0	0.23	0	98.41	middle
54434	0.58	0.74	0.04	0.01	0	0.04	0.11	0	0.32	0	97.46	middle
173031	0.43	0.76	0.04	0.02	0	0.06	0	0	0.06	0	98.57	superposed ends
45411_1	0.37	0.43	0.13	0	0	0.02	0	0	0.14	0	98.62	rectangular end
45411_2	0.51	0.58	0.07	0.01	0	0.06	0	0	0	0	98.44	flat end

Table 2. Results from XRF measurements.

PIXE	Al	Si	P	S	Co	Fe	Ni	As	Ag	Pb	Cu	Area
14382	0.14	0.15	0	0	0	0	0	0	0.18	0.31	99.13	middle
14384	0.18	0	0	0	0.04	0	0	0	0	0	99.12	middle
14385	0.12	0	0	0	0.03	0	0	0	0	0	99.09	middle
14385	0.12	0.13	0	0	0.03	0.27	0.02	0.21	0	0	98.21	middle
14386	0.09	0.14	0	0	0	0.27	0.01	0	0.19	0	98.28	middle
14387	0.11	0.12	0	0	0	0.23	0.03	0	0.42	0	98.93	middle
14389	0.11	0.11	0	0	0	0.03	0	0	0.19	0	98.43	middle
14390	0.18	0.21	0	0	0	0.09	0	0	0.23	0	98.99	proximal
14392	0.12	0.08	0	0	0.01	0.09	0.08	0	0	0.23	99.33	middle
14394	0.32	0.21	0	0	0	0.03	0	0	0.19	0	99.02	middle
14397	0.28	0.23	0	0	0	0	0	0	0.24	0	98.74	middle
14398	0.16	0.03	0	0	0.01	0.12	0.13	0	0	0.18	98.28	middle
14401	0.09	0.12	0	0	0.03	0.05	0	0	0	0.13	98.43	middle
14408	0.08	0.09	0	0	0.02	0.08	0	0	0	0.12	99.12	middle
14408	0.1	0.12	0	0	0.03	0.17	0	0.1	0	0.18	98.92	volute
14410	0.06	0.21	0	0	0	0.04	0.02	0	0.17	0.14	98.88	double volutes area
14410	0.21	0.09	0	0	0.01	0.29	0	0	0	0.22	99.13	double volutes area
14411	0.12	0.03	0	0	0	0.32	0.17	0	0.13	0.28	98.92	double volutes area
14415	0	0.23	0	0	0	0.21	0.07	0	0.19	0.08	99.12	proximal
32908	0	0.21	0	0	0	0.12	0.08	0	0.21	0	98.84	middle
32909	0	0	0	0	0	0.08	0	0	0.21	0	98.64	proximal
43246	0.31	0.28	0	0	0.03	0.07	0	0	0.27	0	99.03	middle
44013	0.21	0.19	0	0	0.02	0.03	0	0	0	0	99.32	proximal
47104	0.32	0.31	0	0	0	0	0	0	0.22	0	98.87	flat end
47105	0.23	0.19	0	0	0	0	0	0	0.63	0	98.74	middle
51488	0.14	0.15	0	0	0.03	0.06	0	0	0	0	99.21	proximal
53181	0.32	0.21	0.03	0	0	0	0	0	0.2	0	98.84	proximal
54309	0.21	0.23	0	0	0.03	0.21	0	0	0.19	0	99.08	flat end
54432	0.04	0.03	0	0	0	0	0	0	0.27	0	98.63	proximal
54433	0.17	0.39	0	0	0	0	0	0	0.22	0	98.93	flat end
54434	0.17	0.14	0	0	0	0	0	0	0.32	0	98.95	middle
54434	0.09	0.11	0.01	0	0	0	0	0	0.41	0	98.43	middle
173031	0.11	0.42	0	0	0	0.03	0	0	0.11	0.11	99.21	superposed ends
45411_1	0.21	0.21	0.08	0	0	0	0	0	0.18	0	98.72	rectangular end
45411_2	0.31	0.29	0.03	0	0	0.05	0	0	0	0	99.02	flat end

Table 3. Results from PIXE measurements.

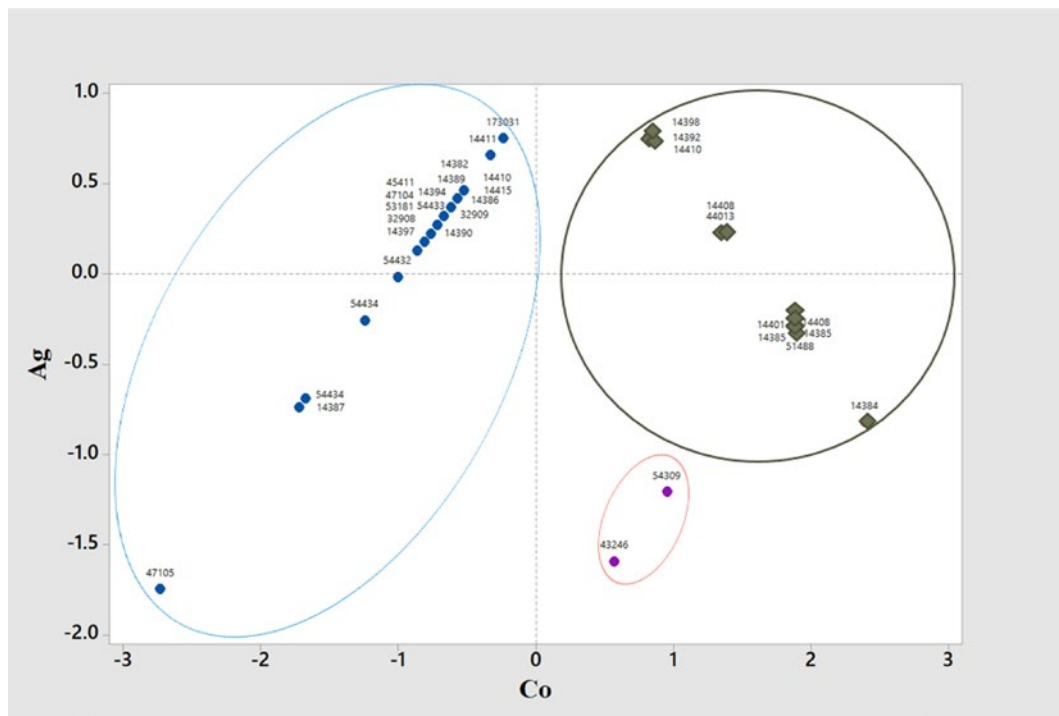


Figure 5. Diagram showing the variations of Ag and Co in the results of the PIXE analyses.

from Ai Bunar. Also, two samples were identified to have both cobalt and silver traces in their composition, and the possible explanation is the usage of re-cast metal.

Conclusions

This short investigation of a copper items assemblage offers new insights into the KGK VI metallurgy in Southeast Romania. We tried to correlate copper sources exploited by KGK VI people with the data resulting from compositional analyses (PIXE and XRF). Both techniques reveal copper as the main composing element (~98% and over) and trace elements such as cobalt and silver for all investigated items. Based on these results and on a comparison with Pernicka et al. 1999 & 2014, the copper sources used to manufacture the investigated artifacts could be at Majdanpek and Ai Bunar. However, the increasing presence of metal objects with similar morphological and compositional characteristics in the KGK VI communities, especially during the Gumelnița A2 phase, could be a strong indicator of the standardization of copper recipe production, but also a sign of growth of the interactions and communications between metal workshops and tell communities on both sides of the Danube.

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