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ISSUES OF THE USABILITY OF COPPER ORE (CHALCOPYRITE) FROM BĂLAN FOR USTENSILES PRODUCTION IN THE BRONZE AGE

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Abstract

Archaeological publications connect the raw material used for the production of copper and bronze artifacts discovered during the excavations carried on in Szeklerland to the use of the chalcopyrite from the Bălan copper ore deposit. So far, this assumption has not been confirmed by concrete evidence. Men of the Bronze Age can't possibly have had knowledge of the metallurgy of sulphide-type copper ores such as chalcopyrite. Applying investigations based on spectroscopy, the Bronze Age use of chalcopyrite from Bălan could be either confirmed or refuted, the new data throwing more light on the provenance of the bronze artifacts discovered in the Szeklerland.

Keywords: *copper ore from Bălan, chalcopyrite, ancient artifacts, copper ore composition, trace element content of copper ore and bronze, scientific methods in archaeology.*

1. Introduction

Archaeological investigations carried out on Szeklerland's territory has unearthed numerous Copper Age and Bronze Age dated artifacts, enriching the collections of the History museums and enabling historical periodization of the territory.

Among the unearthed artifacts, consisting mainly of abundant ceramic shards, metal relics (weapons, tools, jewels) of the local Copper and Bronze Ages can also be evidenced. These are typologically identified by archaeologists, however the historical periods could bear some specific local characteristics. There are relatively few sites which offer technology-related discoveries (smelters, smelting slag, casting moulds, pig) in the vicinity of the metallic or metal-related items, which would help describe the period in which they were made and/or used, and which would also help date the findings.

The use of scientific methods in the study of artifacts is not a novelty for archaeology. Information given by chemical analyses, microscopy, spectroscopy, radiocarbon dating and so forth all provide a supplementary support for the archaeologist in the interpretation of the research results acquired.

2. Beginnings of copper and bronze crafting in Szeklerland

The beginnings of copper crafting can be related to the geological occurrence of natural copper ore deposits. There are several theories regarding the independent appearance of copper smelting and processing in different regions. "Ore prospectors (miners) were required for the development of the metalworking, however it seems that Transylvanian copper and brass artifacts were made from locally smelted copper." [1] Presently Szeklerland's coppersmithing is considered part of the copper craft practiced in the Transylvanian Copper Age.

The primary raw material source used by Szeklerland's coppersmiths has not been elucidated yet, but the complex copper ore deposit lying near Sândominic (Csíkszentdomokos) and Bălan (Balánbánya) is not yet excluded. In the lack of exhaustive and detailed local archaeological excavations, the Szeklerland finds dating from the Copper Age are not able to offer a realistic general view of the local coppersmithing of that time, and in particular the Sândominic–Bălan ore deposit can't be positively identified as the raw material source for their fabrication. The problem can be solved at least partly analytical methods. E.g., the elemental composition of some artifact in question can be determined by spectroscopic investigation. The presence and/or the concentration of tellurium or some other specific trace element in the sample constitutes important information that could indicate the Bălan (or other) origin of the raw copper ore. Some copper ores like the chalcopyrite from the Bălan mining area reveal tellurium at spectroscopically measurable and characteristic level, so the concentration of tellurium could constitute a specific mark of the origin of the processed copper ore [2].

Thus, detection of the presence and determination of the concentration level of tellurium as well as of other trace elements is a valuable aid in the evaluation of the raw material provenance of the ancient Copper and/or Bronze Age metal artifacts. Of course, this relies on the existence of previous data on the elemental composition of the hypothetical raw copper ore, obtainable nowadays through routine metallographic analysis. Consequently, thoroughly applied science methods in archaeological research may open new perspectives on acquiring knowledge of the metalworking of the past centuries.

Figure 1. presents some of the ancient bronze vestiges from the collection of the Szekler National Museum in Sfântu Gheorghe (Sepsiszentgyörgy).

Figure 1. *Ancient bronze artifacts, property of the Szekler National Museum (Sfântu Gheorghe)*

Table 1. summarizes some of the most significant copper artifacts from the last centuries of the 4th millennium BC, discovered in Szeklerland archaeological sites.

Raw material provenance from the Sândominic–Bălan chalcopyrite deposit of the above presented findings is, for the time being, only a supposition, as the finds of the archaeological prospections up to now have not been able to confirm prehistoric copper mining, nor copper smelting in the area. However, the archaeological exploration of the area is far from complete. So, although

Colin Renfrew has stated that there "is no doubt that the used raw copper was of local origin" [1], further archaeological research completed by science investigation methods is needed to clarify if this particular copper ore deposit was or wasn't the raw material source of the ancient coppersmiths in this specific case.

Table 1. *Significant Copper Age copper artifacts from Szeklerland.*

Copper Age		
Archaeological site	**Copper artifacts**	**Observations**
Ariuşd (Erősd), CV	Wire fragments, two-pointed thin prod, little copper wire made rings	From different excavation layers, in company of many ceramic shards
	Double bit axe	From the transition period between the Neolithic and the Bronze Era
Gheorgheni (Gyergyószentmiklós), HR	Single bit axe together with nine other items	Found on the Lázár counts property
Arcuș (Árkos), CV	Two axe heads	
Dumbrăvioara (Sáromberke), MS	Axe with handle hole spur	Similar findings also in Gălești (Nyárádgálfalva), Turia de Jos (Altorja), Covasna (Kovászna), Pădureni (Sepsibesenyő), Jimbor (Székelyzsombor).
Chinari (Várhegy), HR Albiş (Kézdialbis), CV Bodoc (Bodok), CV Cernat (Csernáton), CV Odorheiu Secuiesc (Székelyudvarhely), HR	Double bit axes	From the beginning of the Early Bronze Age
Dăneşti (Csíkdánfalva), HR	Axe	In private collection, with specially worked hole
Pădureni (Sepsibesenyő), CV	Hammer-axe	Unique specimen in the Szeklerland.

The first known ancient copper objects (ornaments, jewels, even tools) were made of native copper. [3] They were considered more valuable than the leather, bone, wooden made counterparts because of their color and shine. The first technology used for native copper processing was hammering; larger copper pieces were made by "laminating" sheets of copper together with this technique. Prehistoric coppersmiths discovered that the reddish metal can be easily shaped through hammering, although the procedure has a hardening effect, as the metal becomes brittle, and its further shaping becomes difficult. Later it was discovered that after a thermal treatment has been applied, the warmed up copper became softer and could be shaped again.

Centuries later, the craftmanship achieved by the coppersmiths culminated in the development of the metallic copper smelting from different copper bearing ores.

At an early stage the applied technology could have used only copper oxides and carbonates as raw materials, these being more easily reducible than the sulfide-type ores. [4]

The oxide- and carbonate-type copper ores (cuprite, Cu_2O, azurite, $2CuCO_3\cdot Cu(OH_2)$, malachite, $CuCO_3\cdot Cu(OH)_2$) are relatively easily reduced when heated with the fuel. During its combustion the charcoal assures the necessary heat as well as the reducing medium, thus the following chemical reactions take place at approx. 700ºC:

$$CuO + C = Cu + CO$$

$$CuO + CO = Cu + CO_2$$

However, as the melting point of copper is 1084ºC, these reactions can't produce metallic copper as the end product. This explains the role of pottery, one of the first ancient industries, in the appearance of coppersmithing. In that period temperature in a ceramics firing oven attained 600–700ºC which is the lowest limit for the smelting of copper. After introducing the use of bellows, these played an important part in metallurgical ore processing. Assuring a strong blast of supplementary air over the fuel, the temperature rises sufficiently to exceed the threshold value required in metal smelters.

The Bălan chalcopyrite ($CuFeS_2$) is sulfide-type ore, whose pyrotechnical processing with prehistorically methods is almost impossible. As in the case of oxide and carbonate type copper ores, the processing of chalcopyrite is also based on reduction processes. In a first step, the ignition feeding oxygen reacts with sulfur (commonly present in the reaction mixture) forming sulfur dioxide which leaves the smelter as one of the flue gas components. The remaining oxygen partly reacts with the iron sulfide of the chalcopyrite and in the presence of the quartzite sand added form the major slag component fayalite ($2FeO·SiO_2$):

$$2FeS + 3O_2 + SiO_2 = 2FeO·SiO_2 + SO_2$$

The slag formed is lighter than the copper-rich molten phase so it floats on the surface of the smelting mixture from where can be easily separated. Finally, the remained molten copper sulfide is reduced in two steps by the blown air. In the first step partially form the product copper oxide (Cu_2O):

$$2Cu_2S + 3O_2 = 2SO_2 + 2Cu_2O$$

The remained Cu_2S reacts partly with the blown air and partly with the Cu_2O formed resulting i crude metallic copper (blister copper) as the end-product:

$$Cu_2S + O_2 = SO_2 + 2Cu$$

$$2Cu_2O + Cu_2S = SO_2 + 6Cu$$

In the same step, the remaining Cu_2O reacts with the firing coal, resulting also metallic Cu:

$$Cu_2O + C = CO + 2Cu$$

The iron contained by the ore remains in the slag as the iron melting point (1535 C°) is significantly higher than that of the copper. This explains the presence of iron oxide as one of the slag components in the case of the smelting of sulphide-type copper ores.

The question is, how did prehistoric craftsmen invent the retrieval of metallic copper from copper ores as early as 4500 BC?

Coppersmithing appeared in the Late Neolithic II sub period (4800−4500 BC), at the same time as painted ceramics. At that time, ceramics production (clay processing) already had a multi-millennial past and an elaborate technology. The potteries of the era used various types of ceramic firing kilns. Kilns with walls of rock slabs coated with a dense clay layer as thermal isolation could be the starting point for the production of crude metallic copper from copper ores.

People started to consciously seek the (mostly surface occurring) copper holding rocks, frequently containing native copper too, after realizing that melted metal is produced from the copper ore built in the firing kiln wall. When building the kilns, some copper containing rocks or copper ores could have been accidentally incorporated in the walls. Prehistoric men originally had no knowledge of the metal content of these ores, as they had no knowledge of the copper metal at all. However, by the repeated use of the kiln, that is, the repeated heating of the wall, pyrometallurgical (smelting) processes took place leading to the extraction of crude metallic copper (partial roasting, smelting, roasting, and reducing of the copper ore). The true beginning of coppersmithing took place when craftsmen were "hunting" rocks holding copper not only in the form of native copper. Following the identification of the rocks they had to extract the differently coloured lode (sometimes containing native copper as well) from the orebody using their stone tools. This must have been laborious work. The development and perfection of the whole process, from mining through smelting until being trained in the processing of the crude metallic copper obtained took up many centuries of prehistoric time, and the technology could spread worldwide only slowly.

Other observations lead to the making of the first open molds, i.e. the beginning of casting that can be considered real metalworking.

Observing the melt accidentally poured into (then solidified in) some ceramic pots, the ancient coppersmith discovered that the copper ores could be smelted in earthenware ceramic pots, and moreover, that the molten metal solidifies, taking the internal shape of the pot.

The next stage in metalworking was the development of closed molds which allowed the casting of complex-shaped end-products.

In some archaeological excavations carried out on Szeklerland sites, vestiges of open and closed casting molds were also unearthed (**Figures 2, 3**).

The real breakthrough marking the next era of metalworking was the practice of alloying. Around 2500 BC copper was melted combined with an additional lower melting point metal, forming a new metallic mixture, the bronze (brass) alloy. The great influence of this new metallic material on human civilization and culture started a new historical period, the Bronze Age.

As presented above, the start of prehistoric coppersmithing could be set in the Middle-East and in the South-Eastern European territory and can be dated to the Chalcolithic (Eneolithic) period of the Copper Age (4500–3500 BC). In this period the foundations of basic craftsmanship and knowledge of coppersmithing were laid down for the following millennia. The appearance and early development of this technology were accidental to some extent, but the continuation was logical and its evolution was a more and more conscious process.

Figure 2. *Closed mold from the collection of the Szekler National Museum, Sfântu Gheorghe.*

Figure 3. *Open mold and cast artifact from the Szekler National Museum, Sfântu Gheorghe.*

"The Bronze Age is the organic continuation of the Eneolithic and the Copper Age Period presented before, so its gradual evolution should have been followed step by step in Szeklerland too, like in the whole Transylvanian region." [5].

Some of the numerous artifacts unearthed during the archaeological excavations carried out on Szeklerland territory are presented in **Table 2**.

The multitude of the findings dating from 3500-3000 BC attest to the fact that bronze-working practices attained high levels; the discovery of vestiges of several ancient raw material and end product deposits in the area (Cernat, Bancu [3]) could certify that several Bronze Age foundries were run.

What was the ancient metalworkers' craftsmanship, how large a technical knowledge could have been accumulated in the region to make Transylvanian bronze-working, including the Szeklerland, famous?

Prehistoric craftsmen knew the useful copper bearing ores. They knew how to build smelters and furnaces, knew how to make melting crucibles from clay and grog. They also knew how to produce charcoal and how to use charcoal as a furnace combustible, as well as how to realize combustion chambers with a blown air supply in order to raise the temperature of the melting process. They had knowledge of the properties of tin as well, as its role and importance in the mixture which deliberately resulted in the end product of a new metallic material, the bronze alloy. They learned the significance of the alloying component proportion, and out of necessity were able to prepare specific bronze alloy compositions for the different uses, to produce jewelry (fibulae, bracelets: arm-rings, arm-bands), everyday use articles (axes, knives, sickles), weapons (spears, swords, hatchets **Figure 4**).

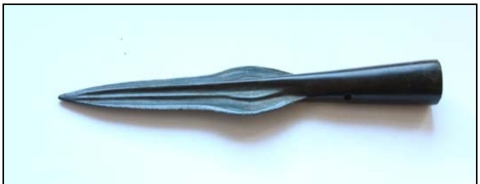

Figure 4. *Bronze spear-tip. The Szekler National Museum, Sfântu Gheorghe.*

It should be mentioned that according archaeologists, the unearthed casting tools (ceramic casting bowl or casting spoon fragment from Cernat; casting mold fragments) and the significant quantity of copper smelting slag, bear the marks of all the defining evolutionary stages of the Bronze Age, from its beginnings to its mergence in the early Iron Age. "The types of the tools denote the existence of Greek and other Balcanic connections." [3] In the early Iron Age stage B, indicating the final of the Bronze Age and beginning of the early Iron Age, the new metal iron appears side-by-side with bronze objects. The relatively large quantity of iron rods found near bronze-casting molds indicate that iron processing evolved together with the bronze-casting technique, although at least one millennium had to pass between the stage of the general use of bronze and that of iron-working. In this transitional period the heat treatment techniques applicable to iron alloys were unknown.

Coppersmithing in the Bronze Age attained its highest level with the invention and practice of lost-wax casting. This technique allowed precision casting of complex-shaped objects. The copy or the model of the object to be cast was formed in beeswax. The wax model was coated with a thick crust formed by plastering then drying it repeatedly with a slip constituted from cowblakes and clay mixture. The coated model - provided with a hole to pour in the molten alloy and several tiny holes to let out the evolved gases and the melted wax - was inserted in a sand bed. The wax model melted by the molten bronze ran out from the hard crust, the metal filling the emptied crust and, taking its shape, was left to solidify before being cleaned up from the broken crust.

Table 2. *Bronze artifacts unearthed on archaeological excavations carried out in the Szeklerland.*

Bronze Age		
Archaeological site	**Bronze artifacts**	**Observations**
Sfântu Gheorghe (Sepsiszentgyörgy), CV	axe	
Belin (Bölön), CV	axe	sickle, axe fragments, disc, a vessel
Târgu Secuiesc (Kézdivásárhely), CV	several axes	a Hungarian type axe
Zagon (Zágon), CV	hammer	rare
Malnaş (Málnás), CV	sickle (Transylvanian type) knife	similar artifacts found at Dăneşti (Csíkdánfalva), HR.
Fotoş (Fotosmartonos), HR	dagger	similar findings at Zăbala (Zabola), CV; from the very end of the Transylvanian Bronze Age
Topliţa (Maroshéviz), HR	dagger blade fragment, saw, dagger	
Brăduţ (Bardóc), CV	dagger	the length of 305 mm corresponds to a shorter sword
Măgheruş (Magyaros), HR	sword	a similar sword of 920 mm length found at Covasna (Kovászna), CV
Brăduţ (Bardóc), CV Suseni (Marosfelfalu), MS Turia de Jos (Altorja), KCV)	sword	weapons of different types and shapes, axe, 25 gold plate rings, a kettle, a sickle
Dumbrăvioara (Sáromberke), MS	sword	with curved flat blade
Sântana Nirajului (Nyárádszentanna), MS	battle axe	similar findings at Dumbrăvioara (Sáromberke), MS
Band (Mezőbánd), MS Suseni (Marosfelfalu), MS	tip of spear, axes, bracelets, fibulae, belt fragments, sword fragments	Spear tips are frequent in Szeklerland treasures: at Zagon (Zágon), CV, 9 were found and several were found at Breţcu (Bereck), CV, and Porumbenii Mari (Nagygalambfalva), HG, too
Reci (Réty), CV	bracelet	twisted-wire type
Zagon (Zágon), CV	bracelet fragments	similar findings at Belin (Bölön), CV, Malnaş (Málnás), CV, and Dăneşti (Csíkdánfalva), HG.
Suseni (Marosfelfalu), MS	several bracelet	fragmented items too
Breţcu (Bereck), CV	axe, spear tips	
Dăneşti (Csikdánfalva), HR	15 axes, 10 sickles, 5 bracelets, 2 spear tips	The treasure is in the vicinity of remains of a foundry, the sickles are mostly of Transylvanian type.
Drăuşeni (Homoróddaróc), BV	30 axes, sword	The axes formed a regular ring around the sword.
Sângeorgiu de Pădure (Erdőszentgyörgy), MS	12 axes, chisel, a small cup, a small plate, cauldron, harness ornament	some pieces were rusted
Tălişoara (Olasztelek), MS	sickle fragment, bracelet, hook	part of a greater find
Sâncrăieni (Csikszentkirály), HR	cauldron, cup, pan, ring (IXth Century BC)	Among the first evidence of iron presence on the Szekler territory: the findings from Bancu (csíkbánkfalvi), HG, and Suseni (marosfelfalusi), MS, are slightly rusted

3. Conclusions

The provenance of the copper and the alloying component in case of the copper and bronze artifacts unearthed in the course of the Szeklerland performed excavations is not yet proven. The supposition that metallic copper could be obtained using native copper or chalcopyrite from the Bălan ore deposit requires further evidence, because if native copper was found in this area in the prehistoric era, why haven't geologists found it up to now?

Additionally, as we know, extraction of metallic copper from chalcopyrite requires a multiphase process, and this technology couldn't have been known around 3000-2500 BC. However it can't be excluded that a high copper content ore, which would have been easy to recognize by the naked eye, could have been enriched sufficiently through repeated heating and hammering so as to be transformed in to metallic copper. This also requires proof, which could be obtained by applying modern research methods.

Until the above problems are answered, it is a real possibility that raw metals (copper, tin, lead) were imported. This also might be proven by performing elemental analysis of the questionable copper and bronze artifacts found e.g. on the Cernat site, then comparing the experimental results with the elemental composition of the copper ore located near Bălan. To support a local provenance, all the archaeological findings should contain the same trace elements (Te, Ni, Au, Ag) at the same concentration level as the Bălan copper ore.

We can conclude that in order to clarify the problems raised by the prehistoric coppersmithing in Szeklerland, a complex chemical and spectroscopic characterization of the previously unearthed prehistoric smelters and slag remains is essential, although these are rather iron metallurgy related even in the Bălan area.

Today a great variety of analytical equipment, enabling the investigation of material structure, composition and properties is accessible for all scientists, and their (reasonable) use is mandatory for the archaeologist as well. Ancient artifacts will reveal their actual value and meanings only if the conditions of their production and use are also revealed.

References

[1] Renfrew C.: *A civilizáció előtt.* Osiris Kiadó, Budapest, 1995, 177–204.

[2] Kővári L.: *Erdélyország statisztikája*. *I.* Kolozsvár, 1847, 78–94.

[3] Székely Zs.: *Csernáton község régészeti monográfiája*. Státus Kiadó, Miercurea-Ciuc, 2007, 70–79.

[4] Dumitrescu I., Paştiu I.: *Metalurgia metalelor neferoase.* Editura Didactică şi Pedagogică, Bucureşti, 1969, 117–118. .

[5] Roska M.: *A Székelyföld őskora.* In: Emlékkönyv a Székely Nemzeti Múzeum 50 éves Jubileumára (ed. Csutak V.). Székely Nemzeti Múzeum Kiadása, Sepsiszentgyörgy, 1929, 258–326. http://mek.oszk.hu/17900/17988/pdf/17988_1.pdf