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MINERALOGICAL AND PHYSICO-CHEMICAL DATA REGARDING THE BRONZES FROM SOME ARCHAEOLOGICAL SITES FROM ROMANIA

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Abstract. This study investigates bronze from archaeological sites from Arad area (RO), Șpălnaca archeological site (Alba County, RO) and Drajna de Jos (Prahova County, RO) and tries to make a link with geological sources of raw material. The samples referred to in this article are from two museums located in Romania. This study presents results of a quantitative analysis carried out with X-ray fluorescence (XRF) combined with optical observations made on the artifact's alloy. In addition, the analytical data from the "SAM" project - Germany, 1968 and previous isotopic analyses of stable lead isotope aided in this research also. Romania has no proven exploitable occurrences of tin and previous research has demonstrated that foreign material - tin (possibly from Erzgebirge-Germany) was used to manufacture the bronze alloy in the Bronze Age. The current study tries to establish that material from local sources has been added to the alloy. Our research showed that the Romanian archaeo-bronzes (bronzes found in archaeological sites) are considered complex tin bronzes with cadmium, lead, silicon, iron, nickel**,** arsenic, antimony, presenting a notable heterogeneity. Local sources of the copper could have been Apuseni Mountains, Banatitic area, Mehedinți Mountains, Leaota Mountains and East Făgăraș area. Beside Cu and Sn, the archaeo - bronzes from the Arad area contain Cd, Pb and Ni and rarely Cr, Si, As, Fe, Sb, Co, Al and those from Drajna archaeological site have Cd, Sb, Ni, As and Pb. For the first area the source may be considered Apuseni Mts. (Brusturi – Luncșoara, Băița Bihor and Highiș District) and for the second one Leaota Mts. and Eastern Făgărași Mts. (Nimaia – Bârsa Fierului Metallogenetic Sector).

Key words: archaeo-bronzes, South Apuseni, Banatitic area, South Carpathians, Mehedinți Mountains, Leaota Mountains, East Făgăraș area, complex tin bronze

1. INTRODUCTION

1.1. Today's notion of bronze

Regarding the bronzes from Romania there are two problems to consider – 1. the source of tin (a principal element in bronzes) and 2. the identification of peculiarities given by the trace elements. The issue of tin source has been approached in a previous article (Molofsky et al., 2014) and based on the common lead isotopic analyses resulted that a probable source for tin is the Erzgebirge area, Germany. For the ores in Romania, the tin content ranges between 0 - 40 ppm (rarely 100 ppm). As noticed, the tin content is insufficient to be considered utilizable local element for manufacturing of bronze. Today, the exploitable tin content must by at least 0.2%, this requirement is not satisfied by any of the Romanian tin occurrences (Neacșu & Popescu, 2009).

Current research will concentrate more on the bronze types defined by the main elements and associations of trace elements. For this purpose a chemical-physical, comparative study of the bronzes from Alba County (Șpălnaca), Arad area (Păuliș, Sântana, Felnac, Socodor, and Cicir) and Prahova County (Drajna de Jos) and the potential sources of raw material have been made.

Bronze is a special type of copper alloy that is defined by the system copper-M (where the M can be: Sn, Al, Mn, Ni, Si, Be, Cr, etc.; with the exception of Zn). The proportion of the „M" term gives the name of the alloy and is standardized (Buzatu & Moldovan, 2009).

Our study has as principal objective to investigate some archaeological artifacts establishing the participation degree of the local sources of raw material. This research will also determine what kind of alloy our ancestors have used.

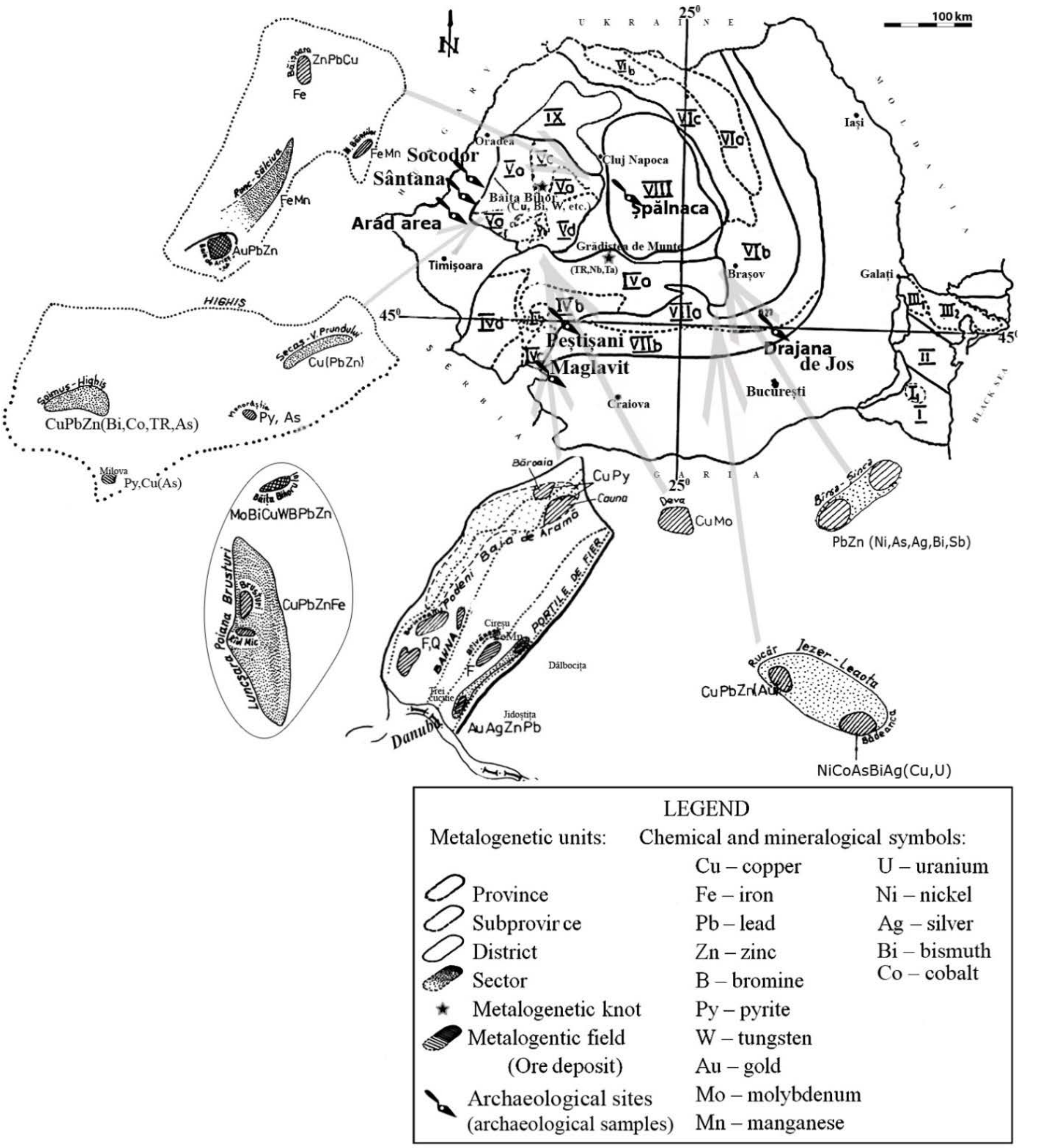


Figure 1: Metallogenetic units of Romania (after Popescu, 1986, with additions). Out of contours are evidenced the metallogenetic units considered as possible sources for the raw material: I. South Dobrogea province, I.1. District with phosphorites and glauconite, II. Central Dobrogea province, III, North Dobrogea province, III.1. Măcin district, III.2. Tulcea district, Carpathians Realm, IV. South Carpatians province, IV.a. Getic subprovince, IV.b. Danubian subprovince, IV.c. Mehedinţi subprovince, IV.d. Subprovince asociated of banatites, V. Apuseni Mountains province, V.a.North Apuseni province, V.b. Subprovince associated of mesozoic magmatism, V.c. Subprovince associated of banatite, V.d. Subprovince associated of Neogene volcanos, VI.East Carpatians province, VI.a.Crystalline-Mesozoic subprovince, VI.b.Flysch subprovince, VI.c. Subprovince associated to Neogene magmatism, VI.d. District of Maramureş basin, VII. Molasse province, VIIa. Subprovince with evaporates, VII.b. Subprovince with Ti-Zr placers, III. Transilvania Bassin province, IX. Gilău Mezeş-Preluca district).

1.2. Archaeo-bronzes in the world

One of the most well-known studies on archaeological object's composition from Europe (Romania included) is "SAM" (*"Studien zu den Anfkngen der Metallurgie"*, 1968) that used the trace elements to describe the distribution of 12 European metal groups in Bronze Age metal. Studies such as those carried out by Pernicka (1987, 1990) or Craddock and Meeks (1987) reassessed "SAM"'s interpretation, based on modern approach by applying thermodynamic principles. These studies indicated that the chemical composition help to create a better understanding for the archaeo - metallurgical processes (especially the presence of iron in copper alloys). Usually, this research is based on the main elements and no comprehensive study about the behavior of the trace elements have been carried out (Hauptmann 2007).

1.3. Archaeo-bronzes from Romania

In Romania there are only a few studies regarding the chemical composition and the internal structure of the archaeological bronze objects.

In recent years, Arheomet (2005-2008) and Romarheomet (2007-2010) were two big projects based on the study of archaeological metal objects (gold, silver, lead and bronze). These two projects were using only non-destructive methods of analyze - XRF, SR-XRF, PIXE and micro-PIXE. They also focused more on the gold objects and their provenience. Some archaeo-metallurgical studies of Bronze Age objects have been published presenting ED-XRF measurements at the surface of the objects and micro-PIXE on detached fragments. Bugoi et al. (2013) presented the principal elements identified in the bronze objects from the South Romania (Ocnița) and discussed the possible addition of arsenic for the improvement of the alloy.

Studies similar to this article were made by Kadar, 2007 and Macovei, 2011. There were the only ones in Romania with optical observations on the internal structure of the artifacts.

2. SAMPLES PRESENTATION

2.1. Archaeological samples

The chosen artifacts were from different archaeological sites: Alba County (Şpălnaca) and Arad area (Păuliș, Sântana, Felnac, Socodor, and Cicir). The samples are from 28 archaeological artifacts, which provided 37 probes (10 small fragments and 27 powder samples) from the Museum Complex of Arad; 28 samples from 16 sickles of Drajna - Prahova County archaeological

Table 1: Samples from archaeological artifacts

Sample No.	Object	Invent. No.	Weight (mg)	Location	Age
P1	Axe	FNI**	18	Păuliş	Early Bronze
P3	Sickle	16742	133	Sântana	Final Bronze
P7	Bracelet	New*	139	Sântana	Final Bronze
P12	Blade	New*	76	Sântana	Final Bronze
P13	Blade	New*	38	Sântana	Final Bronze
P16	Belt ornament (2 pieces)	New*	67	Sântana	Final Bronze
P17	"Ingot"	FNI**	84	Arad area	Middle Bronze
P19	"Solar disc"	FNI**	243	Cicir	Middle Bronze
P21	Chisel	FNI**	162	Socodor	Middle Bronze
P37	"Ingot"	12401	7902	Şpălnaca	Final Bronze
P39	Sickle (fragment)	15868	23	Drajna de Jos	Final Bronze
P41	Sickle (fragment)	15869	30	Drajna de Jos	Final Bronze
P42	Sickle (fragment)	15863	20	Drajna de Jos	Final Bronze
P44	Sickle (fragment)	15866	30	Drajna de Jos	Final Bronze
P45	Sickle	13332	79	Drajna de Jos	Final Bronze
P46	Sickle	13322	237	Drajna de Jos	Final Bronze
P48	Sickle	13317	28	Drajna de Jos	Final Bronze
P51 P52	Sickle	13325	35 and 25	Drajna de Jos	Final Bronze
P54	Sickle	13326	23	Drajna de Jos	Final Bronze
P55	Sickle	13272	470	Drajna de Jos	Final Bronze
P59	Sickle	13289	139	Drajna de Jos	Final Bronze
P61	Sickle	15861	134	Drajna de Jos	Final Bronze
P62	Sickle	13274	83	Drajna de Jos	Final Bronze
P65	Sickle	15870	1083	Drajna de Jos	Final Bronze

*Some of these artifacts did not had serial numbers because they were new (reported to the year of sampling - 2009) and therefore not registered

** no registry number (FNI)

deposit (12 dust samples and 16 small pieces) were taken from the National Museum of History, in Bucharest (Fig. 1). The weight of the dust samples ranged between 187 mg and 84 mg. The current study is based more on the solid samples that are presented in table 1.

2.2. Potential local sources for the raw material used to manufacture the archaeo-bronzes

Samples from the potential sources of raw material (probably used in the artifacts' manufacturing) are from the Collection of the Faculty of Geology and Geophysics. The provenance of those ores is in the Apuseni Mts. Province (Baia de Arieș, Deva, Băița Bihor) and the South Carpathians Province (Leota Masive and Eastern Fagaraș Mts., Fig. 1). Were chosen for comparison ores that could be exploited at that time.

In Western Romania (Metaliferi Mts., Zarand Mts. and Banat area) copper is very common and occurs in ores of different age and genetic affiliation as native copper, malachite, azurite, chalcocite, covellite and cuprite. These were very easy to identify by their specific color and they are most likely to be the principal source for the raw material in Bronze Age.

3. METHODS OF ANALYSE AND RESULTS

3.1. Optical observation on archaeological artifacts from Romania

On the compact samples from the archaeological material, microscopic investigation has been made. The polished sections have been observed with a Carl Zeiss Jena AMPLIVAL Microscope and the photos were taken with a Nikon Eclipse E-400, 40 W attached to a PANPHOT Microscope. These observations and their photos were made in the Department of Mineralogy, University of Bucharest, Faculty of Geology and Geophysics, Economic Geology & Metallogeny Laboratory. The microscopic study allows identifying the polyphase character of the sample.

3.1.1. The mineralogy of "ingots"

The principal phase of the "ingots" (Șpălnaca – P37, Arad – P17 and P10) is copper rich and the observed anisotropy is weaker than the one of the principal phase from the artifacts (the lack of tin may be the reason).

The internal dendrites and isometric grains (dark grey, iron-rich) are larger than those found in the manufactured artifacts and the material presents no traces of further mechanical or thermal work (the grains are not oriented and the isometric ones/grains present undistorted round or hexagonal shapes) (Fig. 2.g). They contain also sulfur and nickel and the aspect in reflected light is similar with the Fe_2O_3 oxide (maghemite). This can be a temperature indicator. Another temperature indicator is the relicts of pyrite discovered in the ingots (Macovei & Popescu, 2011) - thermal decomposition of pyrite into FeS (iron (II) sulfide) and elemental sulfur starts at 550 °C.

Third phase consist in iron dendrites, sometimes very large, associated with the iron oxides with skeletal forms (Fig. 2.e).

In/Inside the Șpălnaca "ingot" (P37) crystals of garnet, pyrite and magnetite have been identified as relicts. The external alteration is composed by cuprite, malachite, tenorite and some amorphous mineral/s; secondary marcasite has been identified (Fig. 2.e). The relicts are fewer and smaller in the Arad "ingot" sample (P17) - only pyrite grains. In the sample taken from the Sântana "ingot", relicts could not be seen.

3.1.2. The mineralogy of the artifacts

Under the optical microscope, the archaeo-bronze artifacts showed an internal structure composed by two or three phases depending on the object (see Table 2). The alloy presents fine scratches (especially on the principal phase) as a proof that the material has a low resistance to mechanical actions.

The principal phase is copper rich and relatively homogenous. It has a weak anisotropy because of the tin presence (if there was only copper, the anisotropy should not be present).

The second and the third phase from different dendrites or isometric shapes disseminated in the first phase (See Fig. 2.b) – one light gray, slightly anisotropic (tinny phase) and one dark grey, isotropic (iron oxide).

The dark-gray phase is occasionally disseminated in the principal mass without any orientation and sometimes it is orientated due to manufacturing degree of the object (Fig. 2.a).

Very interesting images were the margins of the samples where the patina can be observed (mostly malachite and cuprite, rarely tenorite) (see Fig. 2.hII). Sometimes the alteration can clearly outline the alloy grains (Fig. 2.hI). The relation between the material and the alteration is intimate (this is why mechanical or chemical cleaning of the objects is not recommended).

Usually, the color of the patina (and its composition) depends more on the environment and not on the elemental content of the object (Robbiola & Portier, 2006). The higher the damage of the object (cracks) the higher is the alteration (the contact surface with the environment is larger) (Fig. 2.d).

Native copper occurred in two objects (see Fig. 2.d). This is further proof of incipient metallurgy (the alloy is neither well melted nor mixed). Relicts of pyrite and copper also can be identified (Fig. 2.c).

Table 2. Alloy phases number, spatial distribution and the presence of relicts in polished sections from archaeological artifacts fragments: P1-P65 (for annotation see table 1)

Sam - ple No.	Object, Location	Alloy pha -ses	Orien- tation yes/not seen	Relicts
P1	axe, Păuliş	2	not	not seen
P3	sickle, Sântana	3	not	not seen
P7	bracelet, Sântana	2	yes	not seen
P10	“ingot”, Sântana	>3	not	not seen
P12	blade, Sântana	3	yes	**bronze(?)**
P13	blade, Sântana	2	yes	not seen
P16	belt ornament, Sântana	2	yes	not seen
P17	“ingot”, Arad area	>3	not	**sulphide, pyrite**
P19	“solar disc”, Cicir (Păuliş)	2	yes	not seen
P21	chisel, Socodor	2	not	not seen
P37	“ingot”, Şpălnaca	>3	not	**magnetite, garnet,pyrite, sulphide**
P39	sickle, Drajna de Jos	2	yes	**magnetite**
P41	sickle, Drajna de Jos	3	yes	**magnetite, silicate,copper**
P42	sickle, Drajna de Jos	3	yes	not seen
P44	sickle, Drajna de Jos	2	yes	not seen
P45	sickle, Drajna de Jos	3	not	not seen
P46 P47*	sickle, Drajna de Jos	3	not	**copper**
P48*	sickle, Drajna de Jos	2	not	not seen
P51 P52*	sickle, Drajna de Jos	2, 2	yes, yes	not seen
P54	sickle, Drajna de Jos	3	not	silicate
P55	sickle, Drajna de Jos	3	not	not seen
P59	sickle, Drajna de Jos	2	yes	**pyrite**
P61	sickle, Drajna de Jos	2	yes	not seen
P62	sickle, Drajna de Jos	2	yes	not seen
P65	sickle, Drajna de Jos	3	not	**sulphide (?)**

*the samples 46-47-48, P51-P52 are from the same object

3.1.3. The mineralogy of the samples from the potential sources of copper and minor elements – ore deposits

Regarding the source ore deposits mineralogy the most important for the raw material is the Băița Bihor ore deposit. The sample presents a complex mineralization: chalcopyrite, chalcocite, covellite, bismuthinite and Cu-Bi sulphosalts, galena, sphalerite, scheelite, etc. The Deva ore sample comprise chalcopyrite and some crystals of bornite included in covellite, big crystals of bornite substituted by chalcochite and covellite.

The mineralization from Baia de Arieş is characterized by the chalcopyrite disseminated in sphalerite (with parallel bends of chalcopyrite), small veins of tetrahedrite and chalcopyrite outspread in the gangue minerals. The analyzed sample presents a massive mineralization of galena with sphalerite, pyrite and inclusions of chalcopyrite.

In the ore deposit of Baia de Aramă 2 kinds of mineralization have been identified: a massive cupriferous mineralization consisting of chalcopyrite with pyrite, sphalerite inclusions and one disseminated mineralization (included in the host rock or as inclusions in sphalerite along with other ore minerals as anatase, pyrite, etc).

The ore deposits from Nimaia – Bârsa Fierului Metallogenetic Field are mainly composed of sphalerite and galena along with: nikolite, gersdorffite, ullmanite, tetrahedrite, chalcopyrite, native silver and millerite. As secondary minerals goethite is mentioned (Lupulescu, 1992).

Concerning the Iezer – Leoata Metallogenetic Sector two types of mineralisation can be identified: one with predominate cobalt minerals (safflorite, skutterudite, native bismuth, native silver, pyrite, chalcopyrite, tetrahedrite) and the gangue is composed of siderite, calcite and silica (Petrulian, 1934). The other mineralization is with predominate nickeliferous minerals (maucherite, niccolite, gersdorffite, millerite + pyrite and carbonate - ankerite) (Popescu, 1968).

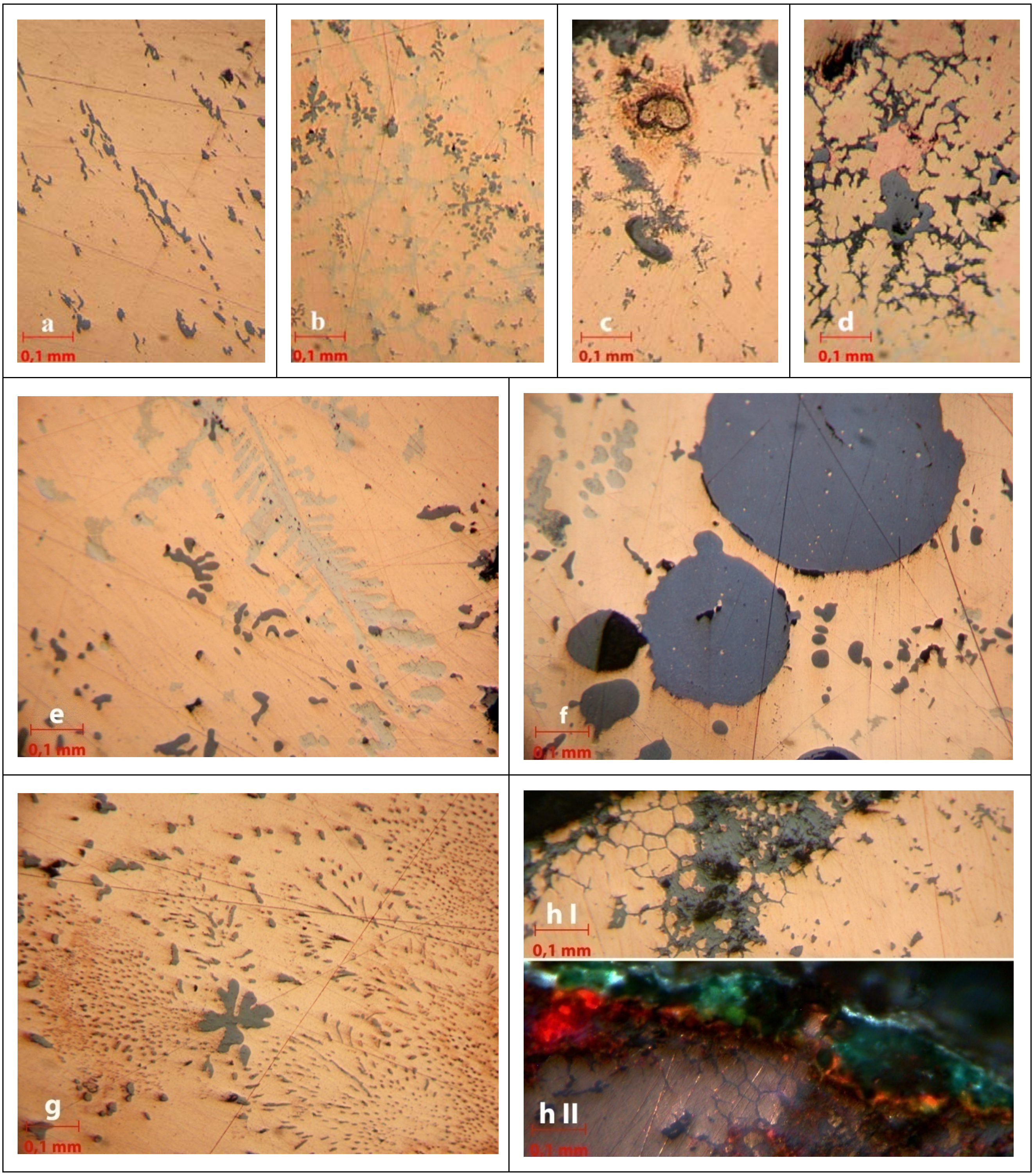


Figure 2: Microscopic images (reflected light) of the archaeo-bronzes sample from Arad area and Drajna de Jos: a. oriented skeletal crystals of phase I in bronze alloy - bracelet, Sântana (P7), b. three-phase bronze alloy with skeletal dendrites - more tin rich bronze phase (light grey), in centre secondary formed cuprite along a crack - sickle, Drajna de Jos (P55) c. relict of pyrite in sickle from Drajna de Jos (P51), d. relict of copper (in centre), marcasite (upper left corner) and secondary cuprite (gray) in sickle from Drajna de Jos (P46), e. iron oxide (dark-grey) and iron slightly alloyed (light-grey) - "ingot", Șpălnaca (P37) f. large "droplets" of copper sulphide and small "skeletal" grains of iron oxide - Șpălnaca "ingot" (P37); g. dendritic forms of iron oxide in "ingot"- Arad area (P17); h I. N// image on the edge of the sample from bracelet, Sântana (P7); II. N+, same area as h.I slightly turned to right – malachite (green), cuprite (reddish), rims of amorphous minerals.

3.2. Physico-chemical data regarding the archaeo-bronzes from Romania

In the current study, the samples were observed and analyzed with an analytical microscope XGT-7000 (Horiba). Compact samples have been chosen specifically for the purpose of X-ray mapping, which will provide more information. Before and after polishing analysis was performed. It is interesting to mention, the differences were not notable between the two situations.

The Analytical Microscope XGT-7000 has an analyzer spot of 100 μm. The precision of detection is 0.01% (100 ppm) when are no interferences. Usually the error (3sigma) for the lanthanides and actinides identification is sizeable, usually more than the mass percent. A problem was the mass determination for those elements adding overlaid peaks and were identified only by the L energetic line; those data were kept in the interpretation only when the error was small and their presence was over 0.1%. One of these overlaying situations, with high errors is the zinc. Its presence has to be determined by other means of analysis. The program used for the interpretation was XGT-7000 Suite version 1.43 (license rights: Oxford Instruments Analytical and HORIBA). The acquisition was made in the same conditions for all other samples (acquisition time: 100 [s] process time 5, XGT Dia. 100 [μm], X-ray tube vol. 30.00 [kV], current 0.224 [mA], no X-ray Filter was used, X-ray path was trough vacuum (whole), Quant. Corr. Standardless).

Every result shown in tables 4 and 5 is a mean of the values obtained in more than one point of analysis or is given by a surface analysis. The mean value has been calculated after eliminating the abnormal values.

The elemental distribution mapping made with Analytical Microscope Horiba XGT-7000 once again, prove that the material is very heterogeneous (acquisition time: 263 [s], process time 5, XGT Dia. 10 [μm], X-ray tube vol. 30.00 [kV], current 1.000 [mA], no X-ray Filter was used, X-ray path was trough vacuum(whole), Quant. Corr. Standard. The analyses are presented as mass percentage of the identified elements (the results can be seen in Table 3). That means that all the punctual-made analyses are unique and we can find significant variation of composition in the same object especially regarding those elements that tend to concentrate (compare the samples P51 and P52, that are from the same object, sickle from Drajna de Jos - see Table 5), (Fig. 3). The element’s distribution maps are showing that some elements tend to locally concentrate (Cd, Cr, Fe, Mn, Si) and some are dispersed in the whole probe (Pb, As, Sb, Ni, Al) (Fig 3).

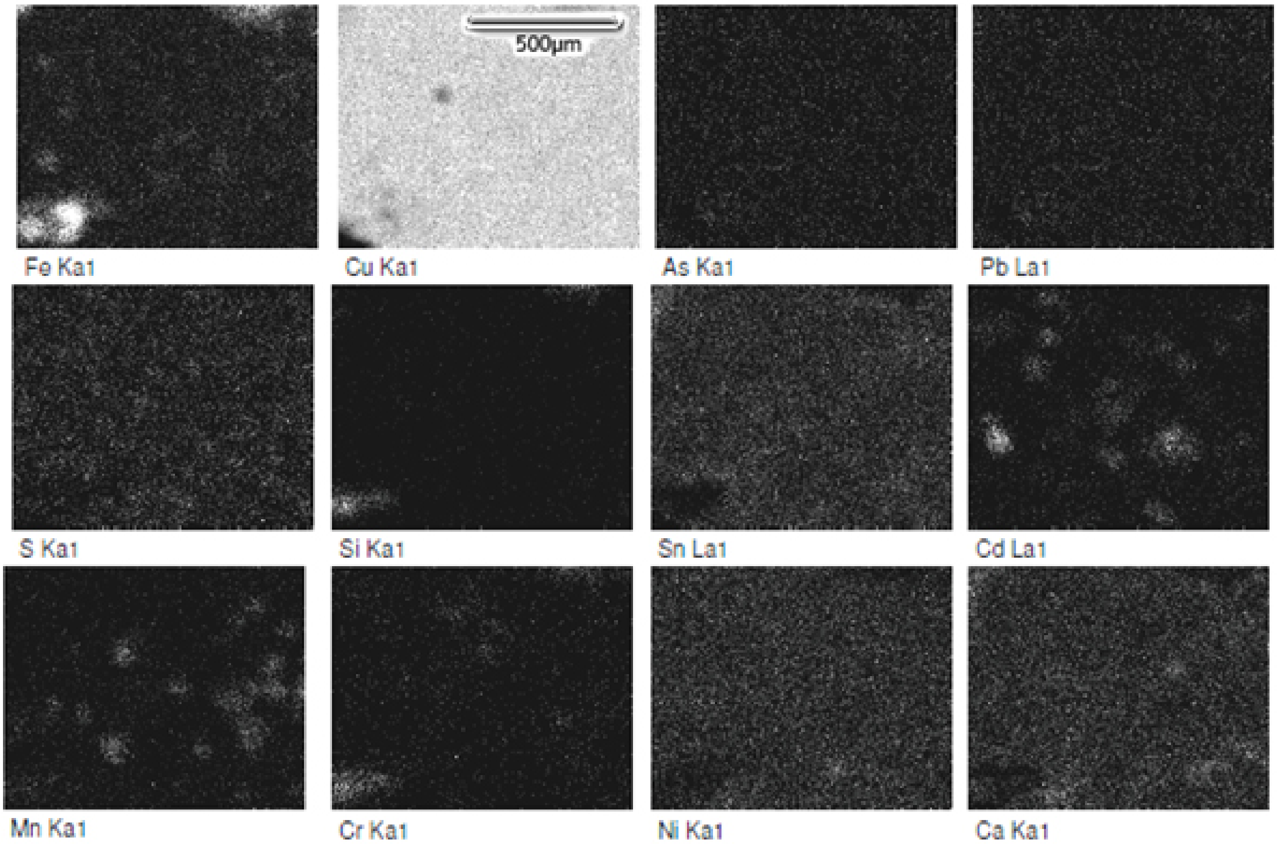


Figure 3: Elemental distribution mapping (Horibba XGT-7000) of sample from chisel, Socodor (P12)

They also suggested the presence of relicts from a garnet mineral (chromian grossular $Ca_3(Al,Cr^{3+})_2(SiO_4)_3$) (Fig. 3). These garnet relicts have been also confirmed by the microscopic observations (Table 2).

As a general physic-chemical observation, it is noticed that the **tin** content from the analyzed archaeological artifacts showed, in a majority of the cases less than 10 percent. It can also be noticed the differentiation between the two archaeological sites: as general presentation the artifacts from Arad area are distinguished by those from Drajna deposit by the lower tin concentration (Fig. 2).

The variation of **cadmium** percentage in the Arad area artifacts is between 3.3 % and 0.59%. Cadmium is a very chalcophile element and usually associates with sphalerite and it has a reversed rapport with manganese (Udubaşa et al., 1976). Cadmium content is higher in the Arad's samples than in those from Drajna de Jos; the dispersion suggests a provenance from several sources (the most important one is the Băița Bihor – Brusturi - Luncșoara area where the presence in sphalerite is notable: 0.61% for Băița Bihor and 1,032% for Brusturi ore deposit - Cheșu, 1983). It is important to mention the sample from Șpălnaca with 3.82% (a probabile source is Baia de Arieș with 0.493% cadmium in sphalerite - Cheșu, 1983). Cadmium is the first trace element in the analyzed artifacts appearing more often in Drajna de Jos samples; the values range between 2.2 % and 1.02% (see Tables 4 and 5, Fig. 4b). This proves a unitary source (Nimaia Metallogenetic Sector has a mean of 0.0355% cadmium in ore – Cheșu, 1983).

Lead is a trace element with a notable presence. In the modern metallurgy, there exists a category of lead bronzes; this is the reason for considering and very useful to separate a subtype of archaeo-bronze with lead.

In the samples from Arad area (Păuliș axe - P1 and Arad "ingot" - P17) the lead content is the same (0.5%) suggesting a common local source. The content of lead is higher in the samples from the Sântana and Socodor artifacts area than in the artifacts from Drajna de Jos with the exception for the sickle P42, that has a higher content of lead (3.78%) making from this sample a lead bronze one (Table 4, Fig. 4).

Nickel appears in the majority of the Arad's Museum samples (exceptions: axe, Păuliș - P1, and "Solar disc", Cicir - P19) and only on some sickles from Drajna. It has low values (0.14-0.66% for Arad area and 0.1-0.95% for the samples from Drajna de Jos).

In nature nickel forms sulfosalt minerals, occurring less often in the form of sulphides, sometimes associated with iron. In Romanian territory, often are found cobalt and nickel but with small concentrations (an average less than 100 ppm).

The presence of **arsenic** is notable in Drajna de Jos artifacts (0.19 – 0.75%) and presents a good correlation (0.78%) with nickel content suggesting a unitary source from the mineralization with nickel arsenides from Eastern Făgăraș area. In the Arad artifacts the variation of arsenic content (0.08 – 1.06%) suggests the provenance from multiple sources and presents a weaker correlation with nickel (0.43%).

Most authors consider that the arsenic in the archaeo-bronzes is not deliberately put there, so this can indicate a raw source with arsenic (Rovira & Montero, 1994). All of the archaeo - bronzes that have been analyzed contain a small amount of arsenic (between 0.04 – 2%) and that may be an important link to the local sources of naturally contain arsenic raw material.

Chromium is a trace element more frequent in the samples from Arad area than Drajna de Jos samples (only three samples presents chromium). The percent variation ranges between 0.08 - 0.15% for Arad area and 0.03-0.07% for Drajna de Jos. It seems to correlate with silicon and iron. Chromium's presence is due to silicates and chromite spinels (Fig. 3).

Silicon is a trace element present in half of the samples. Its presence in modern bronzes is a positive fact by increasing their mechanical resistance and that is the reason why we take it in consideration in the analysis interpretation. The same as in the chromium's case there is a difference between Arad area (0.8-3.57%) and Drajna de Jos area (0.01-0.44%).

Calcium has a lower percent variation for the Arad area (0.26-0.46%) than Drajna de Jos (0.17-0.54%), and presents a negative correlation with silicon (Tables 4 and 5). In the "ingots", there is no calcium or silica.

Antimony is an element that appears very different in the two considered areas: it has significant contents (0.56 – 3.22%) for Drajna de Jos and it can only be found in one sample from Arad area (0.61% – sickle, Sântana, P3). The higher value (4.66%) is in the Șpălnaca "ingot".

The **manganese** presence is very discreet (between 0.02 – 0.06 % in four samples from Arad area and between 0.4 – 0.14 % in four samples from Drajna de Jos).

Cobalt appears only in two samples from Arad and two from Drajna de Jos, with very low values (0.03 - 0.07%). Cobalt is usually found as arsenide and sulfosalt minerals, forming also a small number of sulphides.

The artifact's **iron** content is lower for the Drajna de Jos (0.02 – 0.32%) than for Arad area (0.06 – 0.42%) and may be linked to the potential sources. The "ingot" (Șpălnaca - P37) is a special item with an unique pattern containing a high percentage of iron that manifests in the presence of native iron and iron oxides with skeletal morphology observed in the polished section (see Fig. 2.e and 2.f).

The presence of **sulphur** indicates that sulphides were involved for sure in the manufacturing process. In samples from the "ingot" Şpălnaca (P37), "ingot" from Arad area (P17) and Drajna sickle (P65) we have identified sulphide relicts. This may lead to the conclusion that not only the surface oxidation zones were exploited at that time but also deeper occurrences of copper ore.

Rare earth elements have been identified in a spot analysis in 5 samples: blade, Sântana P13 (Nd – 0,12%), "solar disk", Cicir P19 (Nd – 0,12%, Gd – 0,41%), chisel, Socodor P21 (Pr – 0,2%), sickle from Drajna de Jos P48 (Gd – 0,59%) and sickle from Drajna de Jos P55 (Pr -0,87%, Pd – 1,87%) (Macovei, 2011). A possible source for these elements is in the sulfides (especially the pyrite); in one of the analyzed geological sample from Baia de Arieș lutetium has been identified in a pyrite grain (Table 3).

Table 3: XRF analyze made with Analytical Microscope Horiba XGT-7000 on a pyrite from sample (SBAS_M) from Baia de Arieș ore deposit

Elem..	Line	Mass [%]	3sigma	Atomic [%]	Intensity [cps/mA]
16 S	K	49.43	0.34	63.44	3179.77
20 Ca	K	0.12	0.05	0.12	4.25
22 Ti	K	0.26	0.05	0.22	17.18
26 Fe	K	48.28	0.34	35.57	5069.96
30 Zn	K	0.26	0.04	0.16	19.15
33 As	K	0.31	0.04	0.17	24.39
71 Lu	L	1.35	0.17	0.32	22.95

As presented in table 2, three of the archaeo – bronzes ("ingots" from Șpălnaca and Arad area and one sickle from Drajna de Jos), showed the presence of the pyrite. Furthermore and thorough analyses on these relicts are needed in order to reveal the minor elements present in the pyrite crystals.

Table 4: XRF analyzes made with Analytical Microscope Horiba XGT-7000 on samples from Arad area (compact samples P1-P37)

Mass [%]	P1	P3	P7	P12	P13	P16	P17	P19	P21	P37
Cu	84.89	81.59	88.06	85.84	89.28	82.67	89.11	86.76	81.55	82.68
Sn	12.64	13.2	6	9.86	5.33	11.69	6.97	10.92	12.42	-
Al	-	-	-	0.33	-	-	-	-	-	-
Si	1.55	-	0.11	0.56	0.66	2.34	-	0.08	3.57	-
S	0.25	-	0.5	0.64	0.24	0.2	0.37	0.46	0.12	0.52
Ca	-	0.31	0.26	0.16	0.32	0.3	-	-	0.46	-
Cr	0.15	-	0.03	0.03	0.08	0.1	0.03	-	0.09	0.1
Mn	-	-	0.06	0.02	-	-	0.04	-	0.03	-
Fe	-	-	0.38	0.42	0.21	0.1	0.06	-	-	5.56
Ni	-	0.35	0.65	0.47	0.14	0.36	0.51	0.2	0.15	0.66
As	-	-	0.12	0.13	-	0.27	0.37	1.06	0.08	2
Cd	-	2.26	3.03	0.59	2.85	1.96	1.95	-	0.53	3.82
Pb	0.52	1.68	0.76	0.97	0.65	-	0.52	-	0.79	-
Sb	-	0.61	-	-	-	-	-	-	-	4.66
Co	-	-	0.03	-	-	-	0.07	-	-	-

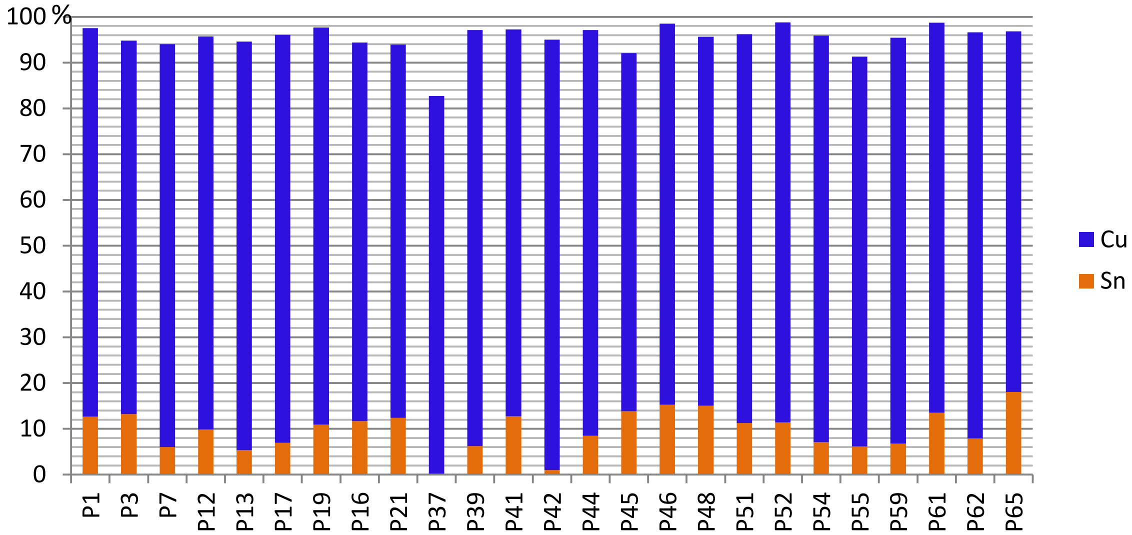
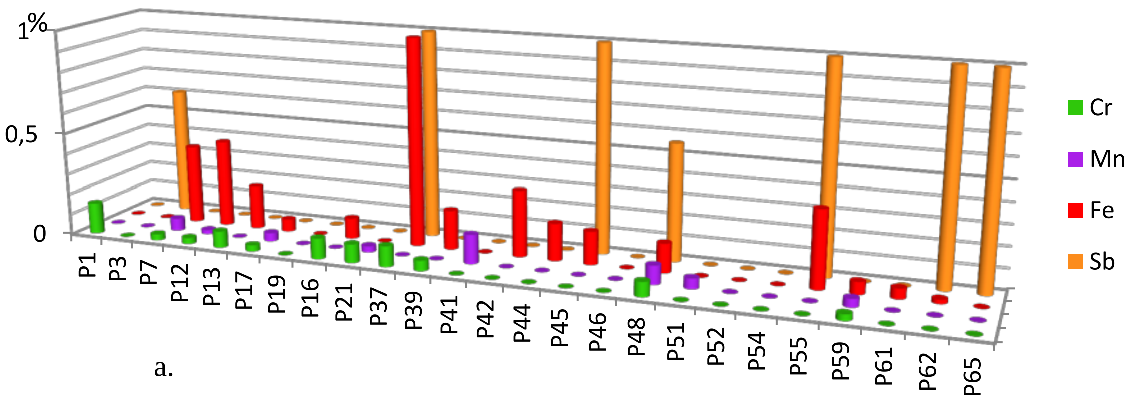
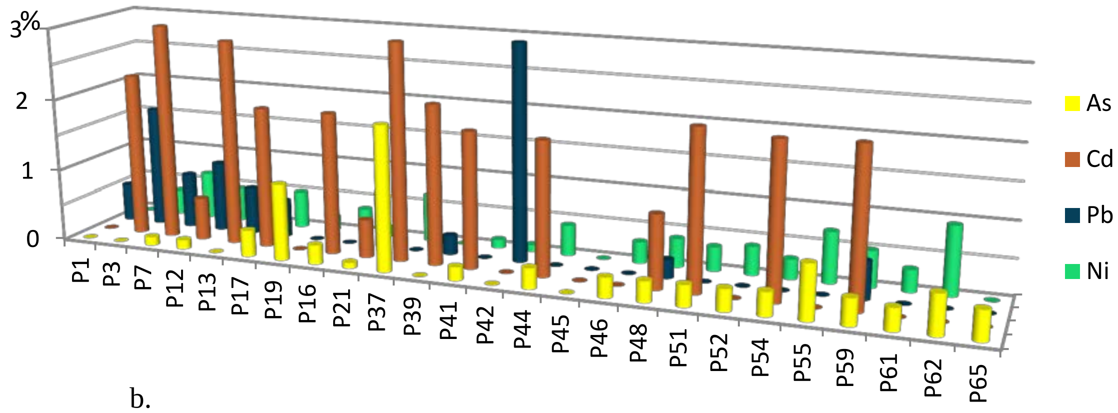


Figure 3: Diagram showing the variation of copper and tin content between the archaeological artifacts from Arad area, Sântana, Socodor and Drajna de Jos archaeological sites (as given in table 3 and 4, for annotations see table 1)



a.



b.

Figure 4: Diagrams showing the content of minor elements of the archaeological artifacts from Arad area Sântana, Socodor and Drajna de Jos archaeological sites (as given in table 3 and 4, for annotations see table 1):
a. The variation of chromium (Cr), manganese (Mn), iron (Fe) and antimony (Sb);
b. The variation of arsenic (As), cadmium (Cd), lead (Pb) and nickel (Ni)

Table 5: XRF analyzes made with Analytical Microscope Horiba XGT-7000 on samples from Drajna de Jos (compact samples P39-P65)

Mass[%]	P39	P41	P42	P44	P45	P46	P48	**P51***	**P52***	P54	P55	P59	P61	P62	P65
Cu	90.83	84.48	94	88.57	78.22	83.25	80.61	**84.93**	**87.36**	88.78	85.11	88.58	85.23	88.66	78.76
Sn	6.27	12.75	1	8.5	13.88	15.24	15.05	**11.28**	**11.44**	7.11	6.19	6.81	13.51	7.95	18.08
Si	0.01	-	-	-	-	0.35	0.44	**-**	**-**	0.25	-	0.12	-	-	0.38
S	-	0.44	0.42	0.18	0.27	0.22	0.14	**0.37**	**0.18**	0.73	0.92	0.37	0.17	0.2	0.15
Ca	0.17	-	0.29	-	0.35	0.36	0.29	**0.54**	**0.3**	0.4	-	0.38	0.41	0.49	0.5
Cr	0.05	-	-	-	-	-	0.07	**-**	**-**	-	-	0.03	-	-	-
Mn	-	0.14	-	-	-	-	0.09	**0.05**	**-**	-	-	0.04	-	-	-
Fe	0.19	-	0.32	0.18	0.16	-	0.14	**-**	**-**	-	0.37	0.06	0.05	0.02	-
Ni	-	0.12	0.1	0.43	-	0.3	0.4	**0.34**	**0.4**	0.28	0.71	0.51	0.31	0.95	-
As	-	0.19	-	0.29	-	0.28	0.29	**0.3**	**0.31**	0.33	0.75	0.37	0.31	0.55	0.41
Cd	2.2	1.88	0	1.85	-	-	1.02	**2.19**	**-**	2.12	-	2.15	-	-	-
Pb	0.27	0	3.78	-	-	-	0.26	**-**	**-**	-	-	0.52	-	-	-
Sb	-	-	-	-	2.5	-	0.56	**-**	**-**	-	3.22	-	-	1.17	1.73
Co	-	-	-	-	-	-	0.05	**-**	**-**	-	-	0.07	-	-	-

*the samples are from the same object

Analyses made by the IFIN-HH team, revealed that traces of **zinc** are present in many of the archaeo - bronzes from Arad's Museum (the percent ranges between 0 - 0.3%) and only in one sickle from the Drajna archaeological site (P44) (Macovei, 2011).

Traces of **silver** (under 0.01%) have also been identified in the most of the samples from the Arad Museum with the exception of an 0.03% Ag content for sickle from Sântana - P3, 0.03% for "ingot" from Arad - P12 and "ingot" from Șpălnaca - P37; there are also traces of silver in the sickles from Drajna (Macovei, 2011; Vasilescu et al., 2013).

In "ingot" from Arad - P10 the identification of **bismuth** and **indium** could be an indication that the raw material originates in a polymetallic ore, possibly Băița Bihor. In the sickles from Drajna de Jos (P44, P46–62) and Sântana blade (P12) bismuth can also be found and sustain that the adjacent area, Leaota - can be the source for the raw material (Vasilescu et al., 2013).

3.3. The classification of archaeo - bronzes

The physicochemical analyses that we have made allowed the separation between several types of bronzes, differentiated by the minor elements associated with the principal ones (Cu, X – where X is the second metal as percentage of participation in the alloy, usually Sn). For the classification, only those minor elements that were present with more than 0.3% have been taken in account.

A first type is with **cadmium** as predominant minor element; actually, there are archaeo-bronzes in which Cd is by far the most important minor element. Other subtypes that have other minor elements associated with cadmium in significant quantities (over 0.3%) are those with Cd – Sb, Cd – Ni, Cd – Pb - Sb and Cd – Pb – Ni. The last subtype is the most common in the samples from Arad area, but is the same for the sickles from Drajna de Jos.

The second type of bronzes has the **lead** as principal minor element. In this case also may be separated a monotypic subtype of archaeo-bronzes for Drajna de Jos (the sickle P42 is composed in fact by a copper-lead alloy). Associated minor elements of second degree (Cd, Sb, Ni and As) have been revealed by analyses (Junghans, 1968).

In the third type of bronze **antimony** appears as the principal minor element. In this case, we deal also with a Sb monotypic bronze separated in the Drajna de Jos samples and other subtypes with Sb – Pb, Sb – Ni and Sb – As – Ni separated in the data extracted from Junghans et al. (1968).

In the same manner can be separated a fourth type of archaeo-bronzes with **arsenic**. They have a monotypic category found in our data but also in those from Junghans et al. (1968). In data from Peștișani and Pecica (Junghans et al.,1968) we can also separate two subtypes with As – Ni and As – Sb – Ni.

Samples from Arad area (Junghans, 1968) and Drajna de Jos presented also a category in which arsenic and nickel are participating in the same proportions and they form the fifth type.

We also took in consideration a sixth type of archaeo-bronzes with silicon (considering that in our-days bronzes there is a special type of silicon bronze) and separated two subtypes: Si – Pb and Si – Cd – Ni.

The last category includes only one sample, the "ingot" from Șpălnca. This is a Fe – Sb - Cd bronze where the tin it appears only as a minor element.

The majority of the analyzed archaeo-bronzes classifies as bronzes with tin and by having other elements (under 3%) they gain a greater refractory and corrosion resistance (Buzatu & Moldovan, 2009). As regarding the "ingots", they do not represent a common alloy for that time but they represent most likely the local material. The archaeological bronzes are sometimes very different from what we consider bronze to be, from metallurgical point of view. The composition is not a standard one and is not always the same and their internal structure is very heterogeneous.

4. CONCLUSIONS

Physico-chemical analyzes on bronze artifacts permit an attempt to correlate them with the potential sources of raw material based on the principle of the provenance from the closest occurrence. We have to mention that the metallurgical processes might affect the behavior of trace elements and thus change the original element pattern of the ore, but the elements will still be there with slightly changes in the proportions (Pernicka, 2014).

We must take into consideration that more recent exploitations have erased the ancient ones traces and the original contents of those occurrences may not be reconstituted even if their location would have been known. An example is the case of Deva ore deposit (0.5 to 1.5% Cu in the past, comparative with 0.3% today), and Highiș District (1-2% Cu before the Second World War) where the mining activity has stopped (Brana, 1958).

The archaeo - bronzes from the Arad area, beside Cu and Sn (principal elements), they have Cd, Pb and Ni (that appear in all the samples) and rarely Cr, Si, As, Fe, Sb, Co and Al. Regarding the first three trace elements (Cr, Si, As) they are clearly originating along with Cu from the closest ore deposits - from Apuseni Mts. (Brusturi – Luncșoara, Băița Bihor and Highiș District) (Fig. 1).

A separate commentary can be made related to the couples Cr - Si, Ni – As and Fe - As having a positive correlation in the samples. They have their source most likely in the nickeliferous arsenide, the silicates (the garnet whose presence have been mineralogical and physicochemical observed) (Fig. 3) and from arsenic - bearing pyrite that appears (pyrite also has been seen under the microscope) (Fig. 2c).

The samples from Sântana (P3, P7, P12, P13 and P16) are suggesting an origin from the banatitic ores area (Băița Bihor and Luncșoara - Poiana Brusturi, especialy if cadmium and lead are present in the archaeo - bronzes). Those from Arad area (P1, P17, P19 and P21) could suggest a Highiș District origin because of the arsenic, chromium, nickel and manganese presence also in the primary ore mineralisation.

The "ingot" from Șpălnaca correlates more with the ores from Baia de Arieș and those close by - Dealul Băieșilor and Băișoara, due to the notable content in Cd, Fe and Sb. Regarding the presence of antimnoy – the only possible source could be Baia de Arieș minerlisation that has antimonite in paragenesis.

The samples from the archaeological site Drajna chemically consist in a larger elemental variety. In this case, also we can observe the evident predominance of copper and tin, followed by Cd, Sb, Ni, As and Pb. This elemental grouping suggests an origin from the closer occurrences from Leaota Mts. and Eastern Făgăraș Mts. (Nimaia – Bârsa Fierului Metallogenetic Sector) (Fig 1). For this sources pleeds also the identification of REE and the Co. Regarding the correlation with the source is worth mentioning previously performed chemical analyses (Jugans et al, 1968) from which we have extracted the data regarding the bronze foundings from Sinaia (Prahova County) archaeological site: it can be observed the notable presence of Sb, As, Pb and traces of Ag and Ni. In the same way pleads the content of calcium whose source is more likely to be in the carbonate gangue from Nimaia and Leaota and also the positive correlation (0.71) between nickel - arsenic that suggests a common source in the nickel arsenide from primary ore; the Nimaia ore has a mean of 0.157% Ni (Cheșu, 1983).

Previous archaeological papers forespeak an ore in South Eastern Transylvania with As, Ag, Sn, Pb, Ni, Bi and Sb (Popovici, 1983). That one must be, as indicated by the chemical analyzes, the Nimaia ore, near Zărnești.

Regarding the southwestern part of Romania chemical data of archaeo - bronze came from the investigations made by the "SAM" project (Jugans, 1968). From 25 analyzed samples only four from Maglavit presents tin content that corresponds to tin bronze (Sn 4,8 – 10%) and one from Peștișani (Sn

3.1%). Minor elements have been detected: Pb (0.054 – 1.8%), As (0.11 – 1.6%) Sb (0.09 – 0.84%), Ag (0.01 – 0.36%), Ni (0.03 – 0.33%) and Bi (0.009 – 0.088%). We can appreciate that, accordingly with the principle of the provenance from the closest occurrence, the raw material came from Mehedinți Plateau (Baia de Aramă, for Cu and the Cireșu – Jidoștița area for As, Pb, Ni, Ag, Bi) (Popescu et al., 1988). These two metallogenetic areas are known to be exploited in the Prehistoric Ages.

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