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CHARACTERIZATION OF ARCHAEOLOGICAL BRONZE OBJECTS FROM THE NATIONAL MUSEUM OF BOSNIA AND HERZEGOVINA (SARAJEVO)

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Abstract

The National Museum of Bosnia and Herzegovina represents one of the most important cultural center of Sarajevo. It has a large collection of archaeological objects including bronzes. The determination of the provenance of the raw material is an ongoing challenge and can provide useful information to archaeologists. The fulfilment of this task is related also to the determination of the major and trace elements of the alloy itself. In this work fifteen objects have been selected to perform elemental analysis. The aim was to widen the knowledge of the archaeometallurgy within the central Balkan area. The analyses have been carried out by Energy Dispersive X-ray Spectrometry (SEM-EDS) and Electron Micro Probe Analyser (EMPA).

***Keywords**: Bronzes; Archeological bronzes; Elemental analysis; SEM-EDS; EMPA*

Introduction

Bronze is the key material of the European Bronze Age, but important in the Iron Age as well, for this reason it represents one of the main topics within the archaeological and science-based research. Archaeometallurgical studies of bronzes are essentially aimed to the determination of the geological origin of copper tin and the other constituent metals, as well as their movement though the production chain. In the last decades many research projects have been addressed to the archaeometallurgy of Bronze Age Europe [1]. These investigations have been applied to objects, regional assemblages, and even more broadly the circulation of metals across time in Bronze Age Eurasia [2]. The fundamental question in provenancing Bronze Age metal objects to the specific ore deposits or regions of origin continues to be addressed by comparing the results from both trace element and lead isotope analyses of the metal objects and the potential ore sources [3-4]. The challenges and possibilities of scientific provenancing were recognized early on in trace element analyses by a range of research groups [5]. Those authors explained that, in their view, the identification of the geological source of the metal would not be possible due to the large number of analyses required to characterize all known copper deposits and smaller occurrences in Europe. Instead, since it was thought that the complexities induced by the smelting of ores and melting of metals would anyway make it

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difficult to relate metal objects to specific ore sources, the project sought to identify compositional groupings of metal objects to study their distribution in space and time [6].

Regarding the studies of such metal alloy in the central Balkan region, in particular in the current Bosnia and Hercegovina country, several decades [7-9] have passed before a research carried out by Gavranović and coworkers has been published [10]. They analyzed about 80 bronze objects coming from Doboj and Travnik regional museums (Bosnia and Herzegovina) by using electron microscopy equipped with Energy Dispersive X-ray Spectrometry (SEM-EDS) and X-ray fluorescence spectroscopy (XRF).

In this paper it has been analyzed some bronze archaeological objects coming from the National Museum of Bosnia and Herzegovina (Zemaljski Muzej Bosne i Hercegovine) in Sarajevo, one of the most important cultural center of Sarajevo. It was founded in 1888 and represents is the oldest western-style cultural and scientific institution in the country, beside archaeology, it includes several cultural areas such as art history, ethnology, geography, history and natural history. It has a large collection of archeological items from several excavations from all over the country. With the aim of widen the knowledge both of such collection in terms of elemental composition, and of archeometallurgy of the Central Balkans, fifteen bronze artefacts have been analyzed by SEM-EDS and by Electron Micro Probe Analyzer (EMPA) in order to characterize their composition in terms of major and trace chemical elements.

Materials and methods

Fifteen objects have been sampled (Table 1). From each object it has been collected a small fragment (1mm^3 as order of magnitude) of bronze after discarding the superficial layer in order to avoid the altered phases. Samples have been subjected to analyses in order to establish the elemental composition in terms of major and trace elements. In particular it has been used an - JEOL- JXA 8230 – electron microscope equipped with Electron Probe Micro Analyzer (EPMA) (used for trace elements) and a spectrometer EDS – JEOL EX-94310FaL1Q - Silicon drift type – (used for major elements). On each sample it has been carried out 6 measurements in terms of SEM and EMPA analysis.

Table 1. Summary of analyzed objects

Provenance	**Museum ID**	**Description**	
Veliki Mosunj Bronze Age	31210	Decorative object	
	31226	Anklet	
	3199	Big buckle	
	31221	Sword	

Provenance	Museum ID	Description	
Paklenica U Tesnju Bronze Age	27159	Axe	
	27157	Axe	
Glasinac Iron Age	5408	Shin guard	
	5410	Bowl	
	5457	Button (decoration)	
Glasinac Ilijak Iron Age	5539	Shin guard	
	5485	Bracelet	
Sipovo	SIPOVO	Sword	
Donji Vakuf	49984	Sword	
Donja Dolina	31186	Sword	
	30093	Sword	

Results and discussion

In Table 2 in has been reported results about all elements measured in samples. In Figure 1 it has been summarized the results of elemental analysis only in terms of major elements carried out with SEM measurements. For all objects copper represents the main metal of the alloy, which is always above 80 % wt. The amount of tin ranges from about 5 % wt, up to about

15 % wt. The addition of tin to copper reduces the melting point of the alloy and improve the mechanical properties.

Table 2. Summary of all elemental analysis carried out on samples

		Major Elements (%wt) EDS						Trace Elements (%wt) EMPA - WDS													
	ID	Cu	σCu	Sn	σSn	Pb	σPb	As	σAs	S	σS	Sb	σSb	Zn	σZn	Ag	σAg	Fe	σFe	Ni	σNi
VELIKI MOSUNJ BRONZE AGE	31210	83.6	1.9	9.4	0.3	7.0	1.9	0.144	0.026	0.103	0.123	0.392	0.062	0.000	0.000	0.110	0.020	0.124	0.076	0.129	0.008
	31226	90.1	3.1	6.0	1.0	3.9	2.2	0.109	0.015	0.123	0.063	0.518	0.070	0.011	0.019	0.101	0.009	0.066	0.061	0.133	0.005
	3199	91.6	2.4	7.3	0.5	1.1	1.8	0.176	0.011	0.000	0.000	0.699	0.034	0.000	0.000	0.164	0.040	0.012	0.011	0.214	0.009
	31221	88.2	2.7	10.6	2.6	1.2	0.2	0.122	0.075	0.025	0.019	0.470	0.199	0.005	0.009	0.098	0.101	0.073	0.101	0.113	0.046
PAKLENICA BRONZE AGE	27159	91.7	1.2	6.4	0.8	1.9	0.4	0.185	0.161	0.022	0.005	0.562	0.560	0.000	0.000	0.021	0.022	0.014	0.019	0.052	0.073
	27157	79.9	7.6	16.6	4.3	3.5	3.1	0.051	0.055	0.056	0.092	0.174	0.018	0.000	0.000	0.048	0.042	0.024	0.021	0.108	0.014
GLASINAC IRON AGE	5408	91.6	1.1	6.9	0.3	1.5	0.5	0.000	0.001	0.004	0.004	0.009	0.010	0.066	0.058	0.003	0.005	0.315	0.428	0.001	0.002
	5410	85.5	0.8	14.4	1.3	0.0	-	0.057	0.004	0.015	0.023	0.000	0.000	0.220	0.046	0.017	0.017	0.149	0.047	0.015	0.016
	5457	83.9	2.5	12.4	1.4	3.7	0.3	0.245	0.046	0.028	0.044	0.463	0.021	0.036	0.062	0.177	0.012	0.021	0.037	0.170	0.014
GLASINAC ILIJAK IRON AGE	5539	90.9	1.2	9.1	1.1	0	-	0.122	0.022	0.003	0.003	0.289	0.093	0.029	0.050	0.055	0.015	0.041	0.004	0.102	0.014
	5485	88.1	1.7	9.1	0.2	2.8	0.0	0.234	0.275	0.019	0.016	0.317	0.108	0.072	0.075	0.039	0.038	0.061	0.014	0.078	0.019
SIPOVO	SIPOVO	86.9	1.6	8.7	1.0	4.4	0.7	0.259	0.100	0.000	0.000	0.356	0.543	0.030	0.006	0.059	0.009	0.020	0.010	0.070	0.030
DONJI VAKUF	49984	89.5	2.2	5.1	1.2	5.4	0.8	0.326	0.185	0.222	0.384	0.679	0.516	0.277	0.316	0.066	0.050	0.036	0.012	0.058	0.015
DONJA DOLINA	31186	83.2	1.3	15.1	1.1	1.7	0.5	0.093	0.050	0.018	0.020	0.256	0.077	0.006	0.011	0.081	0.029	0.038	0.019	0.129	0.017
	30093	83.5	1.7	14.1	1.1	2.5	0.8	0.066	0.009	0.614	0.719	0.186	0.095	0.037	0.065	0.004	0.008	0.020	0.009	0.064	0.006

A tin amount higher than 15 % wt would improve the castability, but also increases the embrittlement due to the $\alpha + \delta$ eutectoid phase formation [11-12]. Lead was detected in variable amounts in almost all samples except in 5410 and 5539. The amount of lead found in the analysed object results to be definitely higher than the concentration found in object examined by Gavranović, in that case Pb content rarely exceed 2% wt. Lead (Pb) is a common additive to bronze, improving fluidity and castability, but it reduces the alloy's hardness and toughness [13-14]. Only 2 wt% Pb is needed to produce optimal fluidity, but more than 2 wt% Pb has been found in most Hellenistic and Roman bronze-cast artefacts [15]. The Pb was probably a cheap additive used for economic reasons, although Pb was seldom added in making bronze to be hammered, since it has a deleterious effect on the ductility of the alloy and tends to segregate upon solidification [15]. In such cases, any attempt to perform deformation by hammering will result in the propagation of cracks along the Cu/Pb interface. Late Bronze Age metallic objects from Atlantic Europe were made of leaded bronzes and contained more than 2 wt% Pb, whereas European regions around the Mediterranean Sea, such as Greece and Italy, were using mostly a binary Cu–Sn alloy [16].

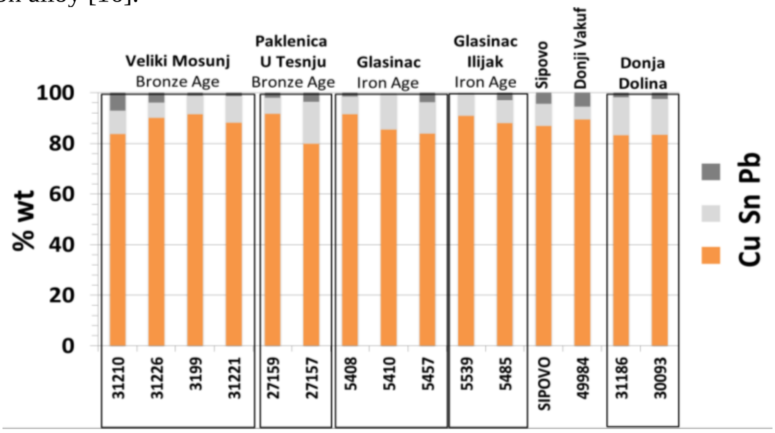

Fig. 1. Major element contents

The analysis of trace elements can be useful to establish the provenance of the raw materials with particular reference to the copper. The trace elements contained in copper should be characteristics of the ore deposit from where the material had been taken. Unfortunately three main issues have to be considered at this point. The first one is related to the inhomogeneity of trace elements within the same ore deposit. However, in some case the trace element pattern are constant, for example in the mining region of Mitteberg in Austria is characterized by a constant ratio of Ni and As and low amount of Sb. The second problem is related to the smelting process which can alter the concentrations of trace elements in copper. The third one raises by the fact that also the other components of the alloy (in our case tin and lead) have their own trace metals, although lead tends to be segregated into the copper/tin phase, trace elements can be mixed into the two phases. However, the analysis of trace elements can also be a chance to understand the similarity among the objects. In figure 2 it has been made a correlation chart among all samples in terms of concentration of each element. Paying attention to lead, it can be noted that it has a positive correlation with As and Sb, it is well known that these elements represent lead impurities.

	Sn	Pb	As	S	Sb	Zn	Ag	Fe	Ni
Sn	1.00	-0.21	-0.45	0.16	-0.59	-0.13	-0.10	-0.15	0.05
Pb	-0.21	1.00	0.47	0.22	0.34	0.03	0.26	-0.13	0.15
As	-0.45	0.47	1.00	-0.09	0.72	0.28	0.39	-0.53	0.23
S	0.16	0.22	-0.09	1.00	-0.05	0.14	-0.28	-0.19	-0.15
Sb	-0.59	0.34	0.72	-0.05	1.00	-0.07	0.63	-0.57	0.58
Zn	-0.13	0.03	0.28	0.14	-0.07	1.00	-0.29	0.20	-0.52
Ag	-0.10	0.26	0.39	-0.28	0.63	-0.29	1.00	-0.36	0.91
Fe	-0.15	-0.13	-0.53	-0.19	-0.57	0.20	-0.36	1.00	-0.53
Ni	0.05	0.15	0.23	-0.15	0.58	-0.52	0.91	-0.53	1.00

Fig. 2. Correlation values among the element concentrations

Beside lead, the highest correlations are achieved by Ni/Sb and Ag/Ni, this could mean that although all issues listed before, the element ratios tend to be constant. In order to try to perform a discrimination among each group binary element charts have been proposed in figures 3 and 4. A certain linearity have been confirmed in both cases, unfortunately the samples generally seem not to be able to be grouped on the basis on their provenance, this would suggest that the object coming from the same archaeological sites have different "history" in terms of both provenance of raw materials and production technology.

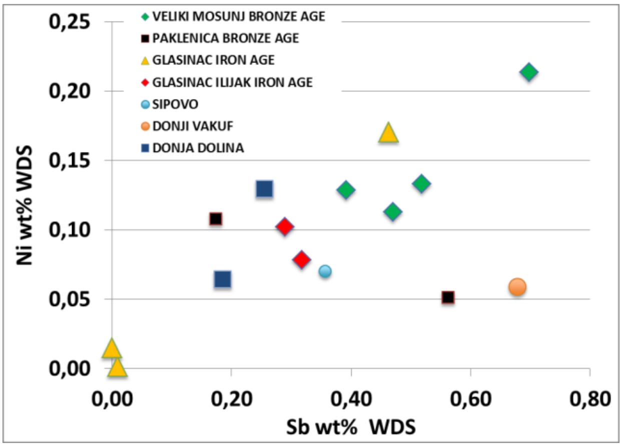

Fig. 3. Nickel-Antimony plot

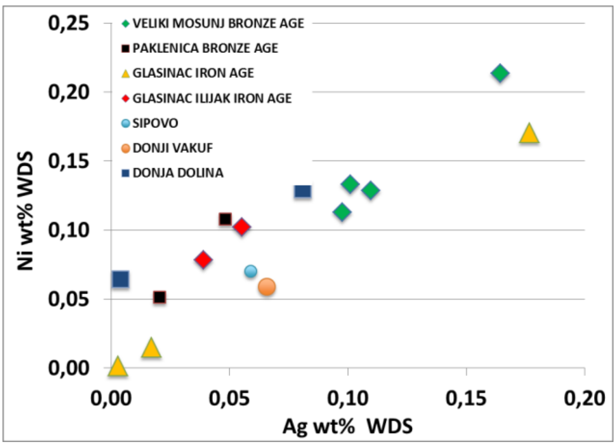

Fig. 4 Nickel-Antimony plot

Conclusions

Fifteen bronze archaeological items coming from The National Museum of Bosnia and Herzegovina objects have been selected to perform elemental analysis in terms of major and trace elements. Those objects come from different excavation sites. Such measurements have been carried out by Energy Dispersive X-ray Spectrometry (SEM-EDS) and Electron Micro Probe Analyser (EMPA). Results revealed that all objects are made of tin bronze with variable amount of lead. Trace elements suggested a low similarity among the objects from the same archaeological site, this aspect could be confirmed or disproved by enlarge the number of analysed samples.

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