MINERALOGICAL STUDY OF ARCHAEOLOGICAL COPPER SLAGS FOUND IN THE AREA OF THE BOYADZHIK VILLAGE, YAMBOL REGION, SOUTHEAST BULGARIA

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ABSTRACT. In this paper, we present the results from a phase-chemical and structural study of metallurgical slags, found in an archaeological site near the village of Boyadzhik, Yambol region. The studied samples are mainly composed of SiO_2 (37.22 – 37.45%), Fe_2O_3 (36.26 – 36.71%), CaO (11.11 – 11.66%) and Al_2O_3 (6.03 – 6.15). The dominant phase is fayalite, followed by magnetite and maghemite, augite, and augite-type pyroxene closest to esseneite. These minerals were observed microscopically in transmitted and reflected light and were established by XRD study and SEM CDD-EDS microanalyses. The copper in the studied slags goes up to 2.46 % indicating low process efficiency of copper extraction from the raw material. The copper was presented by metallic droplets as well as copper-oxide and copper-iron-oxide phases. No relics of sulfide minerals and sulfur-containing phases were found in the analyzed samples. The mineral composition of the studied samples, as well as their structural and phase characteristics, allow us to define these materials as by-products (slags) from copper containing oxidic ore smelting.

Keywords: Archaeological copper slags, SEM CDD-EDS, XRD, old copper mining, SE Bulgaria

МИНЕРАЛОЖКО ИЗСЛЕДВАНЕ НА АРХЕОЛОГИЧЕСКИ МЕДНИ ШЛАКИ, НАМЕРЕНИ КРАЙ СЕЛО БОЯДЖИК, ЯМБОЛСКО, ЮГОИЗТОЧНА БЪЛГАРИЯ

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РЕЗЮМЕ. В статията са представени резултати от фазово-химични и структурни характеристики на металургични шлаки, открити в археологически обект край с. Бояджик, Ямболско. Химичният състав на изследваните образци е представен главно от SiO_2 (37.22 – 37.45%), Fe_2O_3 (36.26 – 36.71%), CaO (11.11 – 11.66%) and Al_2O_3 (6.03 – 6.15). Фаялитът е доминираща кристална фаза. Освен него в образците са определени магнетит и магхемит, авгит и пироксен от авгитов тип, най-близък до есенеит. Тези минерали са установени микроскопски в преминаваща и в отразена светлина, и са доказани с рентгенофазов анализ и SEM CDD-EDS микроанализи. Съдържанието на мед в шлаките е до 2,46 %, което свидетелства за ниска ефективност на медодобивния процес. Медта в образците е под формата на метални капки, медно-оксидни и медно-желязооксидни фази. В анализираните образци не са установени сулфидни минерали и сяросъдържащи фази. Минералният състав на изследваните образци, както и техните структурни и фазови характеристики ни позволиха да определим тези материали като отпадни продукти (шлаки), получени от топене на медсъдържаща оксидна руда.

Ключови думи: археологически медни шлаки, SEM CDD-EDS, XRD, древен добив на мед, ЮИ България

Introduction

The studied metallurgical by-products were found at an archaeological site near Boyadzhik village. The archeological site of the slag finding falls into arable plowed fields (Fig. 1). It is located about 4 km northeast of the Prohorovo porphyry-copper deposit with three phased ore formation processes – skarn, hydrothermal and supergene (Bogdanov, 1987; Bogdanov & Bogdanova, 1984). Many other smaller copper mineralizations outcrop in this area also. The slags, object of this study, based on their external characteristics, was conditionally referred by the archaeologists to Antiquity or the Middle Ages (Leshtakov & Dimitrov, 2016; Leshtakov et al, 2018). A ceramic fragment with traces of strong temperature impact was found in the same archeological site also. It was identified as a part of an ore-smelting furnace and was dated to the Chalcolithic (Leshtakov et al, 2018).

The aim of this study is to present data about phase-chemical and structural characteristics of the archaeological slags found in the region of Boyadzhik village. These data will provide information about the ore raw material mined in this region in the past and about the type of metal extracted.

Fig. 1. The archeological site of slag finding and its location on the map marked with number 1

The obtained data will enrich our knowledge about the mineral composition and phase-structural characteristics of the old metallurgical by-products. This study is a part of a complex investigation on the archeological slags from Burgas and Yambol ore regions (Stavrakeva & Tzankova, 2016a, 2016 b; Tzankova et al., 2016).

Material and methods

The studied slag is dark gray with many pores inside. Their surface alteration has proceeded with the formation of secondary minerals such as green carbonates (mainly malachite), chrysocolla, iron oxides, and hydroxides. Two samples of the slag were analyzed (Fig. 2).

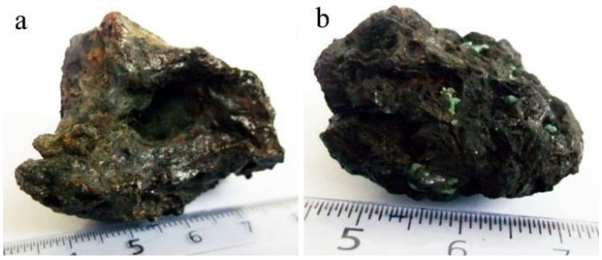

Fig. 2. Macroscopic photographs of the slags selected for this study: a) sample 1; b) sample 2

The powdered and homogenized in an agate mortar slag samples were prepared for Powder X-ray diffraction and subsequent ICP-OES analyses. XRD patterns for the selected samples were obtained using a Bruker D2 Phaser X-ray diffractometer (at 30 kV and 10 mA, with CuKα radiation, 2θ range from 4° to 70°, 0.2/0.5 s). The JCPDS PDF database (International Centre for Diffraction Data, 1997) was used for data interpretation. The bulk chemical composition of the slags was examined with inductively coupled plasma – optical emission spectrometry 720-ICP-OES, Agilent Technologies. The preliminary optical studies on the polished samples and thin sections were carried out using optical microscopes Meiji MT9200 and MT9430 in transmitted and reflected light mode. The microstructure of the samples and chemical composition of the slag phases were studied with JOEL JSM 6010 Plus/LA InTouchScope™ Scanning Electron Microscope (SEM) equipped with a silicon drift detector energy dispersive X-ray spectrometer (SDD-EDS) with a resolution of 128 eV. The device is equipped with a software platform that ensures accuracy and precision of measurements, and produces useful concentration values of the measured elements (Newbury & Ritchie, 2013). SEM CDD-EDS microanalyses were performed on highly polished flat specimens with graphite coating, 20 kV accelerating voltage. All analyses were conducted at the University of Mining and Geology „St. Ivan Rilski" – Sofia. The content ratio of basic oxides (CaO and MgO) to acidic oxides (SiO_2 and Al_2O_3) was used for assessment of the basicity of slag. The calculation of the valence of transitional elements in the composition of crystal phases is according to the methodology proposed by Stavrakeva (1990).

Results

Bulk composition

The analyzed samples contain SiO_2 (37.22 – 37.45 %), Fe_2O_3 (36.26 – 36.71 %), high levels of CaO (11.11 – 11.66%), and Al_2O_3 (6,03 – 6,15 %) . The copper is in the range of 1.73 to 2.46 %. In addition, the studied slags also contain minute amount of TiO_2, MgO, MnO, K_2O, P_2O_5, and very low SO_3 content (Table 1). The basicity value for both of the studied samples is smaller than one, and it referred slags to as acidic. The basicity for sample 1 is 0.31, and for sample 2 is 0.32. The basicity of the slag can affect its viscosity and melting temperature. Viscosity plays an important role in the area of mass transfer at chemical reactions in metallurgical processes (Schlesinger et. al., 2011.).

Table 1. *Bulk chemical composition of the studied slags – OES-ICP analyses*

Oxides/ mass%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5	SO_3	Cu	Σ
Samp. 1	37.45	0.40	6.15	36.71	11.11	2.26	0.29	0.67	<0.05	0.32	0.33	2.46	98.20
Samp. 2	37.22	0.38	6.03	36.26	11.66	2.16	0.31	0.74	<0.05	0.31	0.38	1.73	97.23

Mineralogy and phase composition

Powder XRD study

The dominant crystalline phase in the slag composition, as indicated by XRD analysis, is fayalite Fe_2SiO_4 (Fa) followed by magnetite $Fe^{2+}Fe^{3+}{}_2O_4$ (Mag), augite $Ca(Mg,Fe^{3+},Al)(Si,Al)_2O_6$ (Aug), and augite-type pyroxene closest to esseneite (Ess) (Fig. 3).

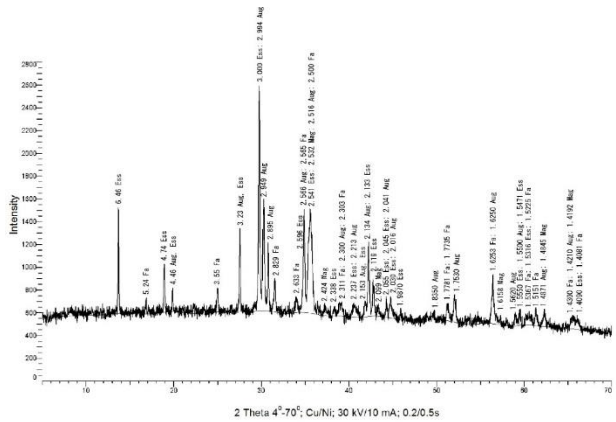

Fig. 3. XRD graph of the slag: fayalite (Fa); augite (Aug); esseneite (Ess); magnetite (Mag).

Light optical microscopy

Representative slag microstructure and phase assemblages, observed microscopically in transmitted and reflected light, are given in Figs 4, 5. The material is even-grained (Fig. 4a, b). Fayalite is the dominant crystal phase. It occurs as needle-like or prismatic skeletal crystals, indicating rapid crystallization (Fig. 4a-c; Fig. 5a-e). These individuals are either randomly distributed in the glass matrix or form sub-radiating aggregates. Fayalite is followed by magnetite/maghemite with white color in reflected light (Fig. 4d-f; Fig. 5f-h). Magnetite/maghemite shows isometric not fully formed skeletal crystals or dendritic aggregates also. They are situated separately in the hosted glass matrix or are arranged one after the other in one direction. The copper droplets are irregular in their shape. They are inhomogeneous. In the larger ones, two phases with different color and reflectivity were observed (Fig. 4a, c; Fig. 5e, f). Microscopically, no relics of sulfide minerals were detected in these droplets.

According to their chemical composition, the minerals and phases found in the slags were grouped as follows: silicate phases, iron oxide phases, copper droplets and hosted glass mass.

Silicate phases

The crystalline silicate phases are mainly presented by the crystals from fayalite group Fe_2SiO_4 and pyroxene group $Ca(Mg,Fe^{3+},Al)(Si,Al)_2O_6$. Their chemical compositions according to the conducted elemental microanalyses (SEM CDD-EDS) data, are shown in Table 2. Fayalite and augite-type pyroxene were detected by Powder XRD analysis with their characteristic set of d-spacings (Fig. 3). Pyroxene crystals are small and needle-shaped (Fig. 6c), while the fayalite crystals are well-developed elongated prismatic ones (Fig. 6e).

Table 2. *Chemical composition of fayalite (Fa) and pyroxene (Py), SEM CDD-EDS microanalyses*

Oxides	Content, mass. %			
	An. field 5-4 (Fig. 6e)		An. field 5-2 (Fig. 6c)	
	Point 1 (Fa)	Point 2 (Fa)	Point 1 (Py)	Point 2 (Py)
SiO_2	30.27	31.20	41.68	40.61
FeO	61.87	63.28	42.41	40.60
MgO	4.93	–	–	–
CaO	2.93	3.24	7.49	6.63
Al_2O_3	–	2.28	8.42	9.68
K_2O	3.02	–	–	2.48

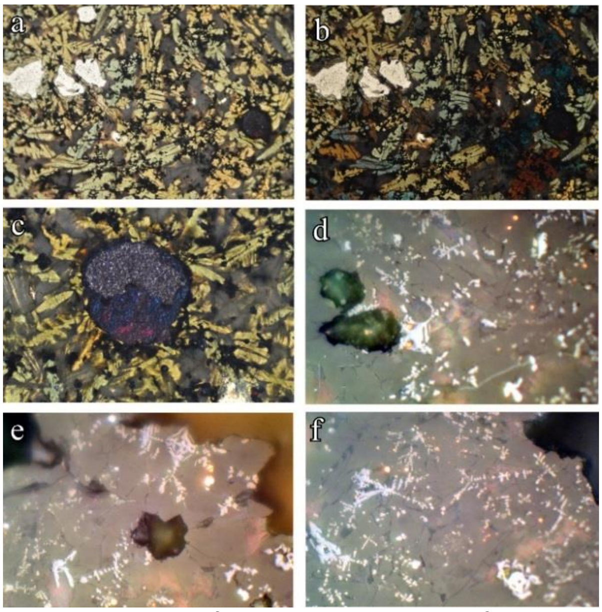

Fig. 4. Microstructure of slag samples: a) elongated fayalite crystals, x10, plane-polarized, transm. light; b) fayalite, x10, cross-polarized, transm. light; c) copper droplet and fayalite, x20, plane-polarized, transm. light; d) magnetite/maghemite crystals and copper droplets, x40, plane-polarized, refl. light; e) isometric and skeletal magnetite/maghemite crystals, x40, plane-polarized, refl. light; f) magnetite/maghemite crystals and copper droplets, x40, plane-polarized, refl. light.

Crystal-chemical formulas of the fayalite individuals in the analyzed field 5-4 (Fig. 6e):

– Point 1: $Fe_{1,76}\,Mg_{0,22}\,Ca_{0,10}\,Si_{1,03}\,O_4$ – fayalite;

– Point 2: $Fe_{1,87}\,Ca_{0,12}\,Al_{0.09}\,Si_{1,11}\,O_4$ – fayalite.

Crystal-chemical formulas of pyroxene crystals in the analyzed field 5-2 (Fig. 6c):

– Point 1: $(Fe_{0.77}\,Ca_{0,17}\,Al_{0.06})_{1.00}\,(Si_{0,92}\,Al_{0.15})_{1.07}\,O_3$ – pyroxene;

– Point 2: $(Fe_{0,73}Ca_{0,15}Al_{0.02}K_{0.06})_{1.00}(Si_{0,88}Al_{0.19})_{1.07}O_3$ –pyroxene.

Fayalite composition indicates that calcium-, magnesium- and aluminum-containing minerals were included in the ore used. These chemical elements are inserted in the fayalite crystals as impurities.

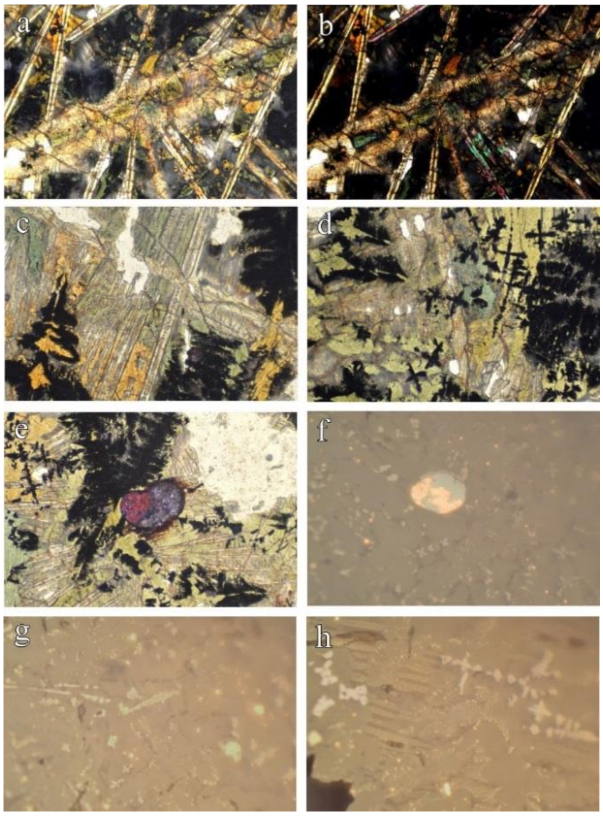

Fig. 5. Microstructure of slag samples: a) fayalite, x10, plane-polarized, transm. light; b) fayalite, x10, cross-polarized, transm. light; c) aggregate of fayalite crystals, x20, plane-polarized, transm. light; d) fayalite, plane-polarized, transm. light; e) fayalite, copper droplet, x20, plane-polarized, transm. light; f) copper droplet, magnetite/maghemite, x40, plane-polarized, refl. light; g) magnetite/maghemite, copper droplets, x40, plane-polarized, refl. light; h) magnetite/ maghemite, copper droplets, x40, plane-polarized, refl. light.

Iron oxide phases

Microscopically in reflected light magnetite/maghemite crystals were observed in the slag (Fig. 4d-f; Fig. 5f-h). Their chemical composition is shown in Table 3. The XRD study confirmed the presence of magnetite in the samples (Fig. 3).

Table 3. *Chemical composition of magnetite (Mag) and maghemite (Mgh), SEM CDD-EDS microanalyses*

El.	Content, mass. %						
	An. field 5-1 (Fig. 6a)		A. f. 5-2 (Fig.6c)	An. field 5-3 (Fig. 6d)		An. field 5-5 (Fig. 6f)	
	Point 1 (Mag)	Point 2 (Mag)	Point 4 (Mag)	Point 1 (Mag)	Point 6 (Mag)	Point 1 (Mag)	Point 2 (Mgh)
Fe	68.40	68.77	72.49	72.92	68.26	72.18	69.87
Ti	1.39	1.23	–	–	2.66	–	–
Al	2.14	2.02	–	–	1.59	–	–
O	28.07	27.96	27.51	27.08	27.49	27.82	30.13

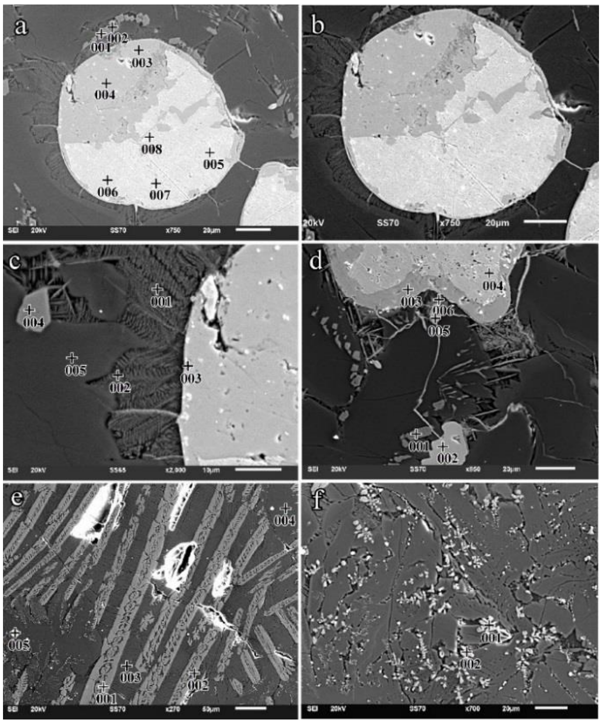

Fig. 6. Scanning electron microscope images of the phases identified in slag samples: a) analyzed field 5-1 with points: 1 and 2 (magnetite), from 3 to 6 (copper oxide phase, cuprite), 7 and 8 (copper); b) analyzed field 5-1 close-up; c) analyzed field 5-2 with points: 1 and 2 (pyroxene), 3 (copper iron oxide phase), 4 (magnetite), 5 (slag glass); d) analyzed field 5-3 with points: 1 (magnetite), 2 (copper iron oxide phase), 3 (copper oxide phase, cuprite), 4 (copper), 5 (copper iron oxide phase), 6 (magnetite); e) analyzed field 5-4 with points: 1 and 2 (fayalite), 3 and 4 (slag glass), 5 (copper iron oxide phase); f) analyzed field 5-5 with points: 1 (magnetite) and 2 (maghemite).

The crystal-chemical formulas of the iron oxide phases presented in Table 3 are as follows:

In analyzed field 5-1 (Fig. 6a):

– Point 1: $Fe^{+2}_{1.00}$ $(Fe^{+3}_{1.72}Ti_{0.06}Al_{0.18})_{2.05}$ O_4 – magnetite;

– Point 2: $Fe^{+2}_{1.00}$ $(Fe^{+3}_{1.81}Ti_{0.05}Al_{0.17})_{2.03}$ O_4 – magnetite.

In analyzed field 5-2 (Fig. 6c):

– Point 4: $Fe^{+2}_{1.00}$ $Fe^{+3}_{2.05}$ O_4 – magnetite.

In analyzed field 5-3 (Fig. 6d):

– Point 1: $Fe^{+2}_{1.00}$ $Fe^{+3}_{2.08}$ O_4 – magnetite;

– Point 6: $Fe^{+2}_{1.00}$ $(Fe^{+3}_{1.84}Ti_{0.12}Al_{0.13})_{2.09}$ O_4 – magnetite.

In analyzed field 5-5 (Fig. 6f):

– Point 1: $Fe^{+2}_{1.00}$ $Fe^{+3}_{1.97}$ O_4 – magnetite;

– Point 2: $Fe^{+3}_{1.995}$ O_3 – maghemite.

Copper droplets

The chemical composition of the copper droplets is presented in Table 4.

Table 4. *Chemical composition of copper droplets, SEM CDD-EDS microanalyses*

El.	Content, mass. %											
	An. field 5-1 (Fig. 6a)						5-2 (F.6c)	An. field 5-3 (Fig. 6d)				5-4 (F.6e)
	P. 3	P. 4	P. 5	P. 6	P.7	P.8	P. 3	P. 2	P. 3	P.4	P. 5	P. 5
Cu	90.10	90.14	98.89	98.55	100	100	87.89	88.56	90.97	100	87.40	92.20
Fe	–	–	–	–	–	–	2.46	2.05	–	–	3.21	4.07
O	9.90	9.86	1.11	1.15	–	–	9.65	9.39	9.03	–	9.03	3.75

Many spherical droplets of unbound (free) copper, copper-oxide and copper-iron-oxide phases were established during the microscopic study of the slag samples in reflected light (Fig. 4d-f; Fig. 5f-h). The composition of the copper oxide phase corresponds to cuprite (Cu_2O) – $Cu_{2.28}O$. The copper iron oxide phase is a solid solution of Fe_2O_3 in cuprite. Its stoichiometry is close to $Cu_{2.29}Fe_{0.04}O$.

Slag glass

No sulfur content was recorded in the chemical composition of the hosted glass matrix in the studied slag samples (Table 5).

Table 5. *Chemical composition of the glass mass, SEM CDD-EDS microanalyses*

	Content, mass %		
Oxides	An. field 5-2 (Fig. 6c)	An. field 5-4 (Fig. 6e)	
	Point 5	Point 3	Point 4
SiO_2	46.84	43.18	44.29
Al_2O_3	2.35	7.57	5.48
FeO	32.66	27.94	28.43
CaO	15.60	20.34	18.31
MgO	2.56	0.97	3.49

Discussion

The chemical compositions of the slag glass and the copper-containing inclusions are very informative about the ore used for copper extraction. The following phases were established with complex methods of investigation: silicate phases – fayalite, pyroxenes of the augite-type and amorphous hosted glass; iron-oxide phases – magnetite and maghemite; copper-containing phases. Among the minerals found in ancient, as well as in modern, slags are fayalite, pyroxene, magnetite and maghemite (Ivanov *et al.*, 1967; Mihailova, 2009; Mihailova and Mehandrejiev, 2010; Stavrakeva and Stoytseva, 1966).

The performed analyses on the copper-containing inclusions in the slag show no sulfur in their composition (Table 4). This indicates that either the melting process was at a sufficiently high temperature to achieve an oxidizing atmosphere and complete desulfurization of the sulfide copper feedstock, or that the copper-containing ore used was not of sulfide minerals. The second assumption is supported by the higher amount of copper oxide phases in the slag. Slags from smelting oxidic ores differ from those of sulfide smelting slags with the lack of sulfide inclusions like matte, relics of primary ore particles, often in a state of decomposition (Bachmann, 1982).

The copper content in the studied slags goes up to 2.46 % (Table 1), indicating low process efficiency of the copper extraction from the raw material. The results from the chemical analyses of the copper droplets showed: pure copper in 3 points, copper oxide phase in 5 points, and copper-iron oxide phase in the other 4 analyzed points (Table 4).

The slag samples from the area of the Boyadzhik village, Yambol region, differ from the previously studied from us slags found in Burgas ore region (Stavrakeva and Tzankova, 2016a; Stavrakeva and Tzankova, 2016b; Tzankova *et al.*, 2016) in the lack of sulfur in the hosted glass matrix and sulfur-containing secondary or relics minerals. This leads to the assumption that the studied slags from both regions are products from different raw materials used and ore smelting methodology.

Conclusion

The microstructural characteristics of the studied slag samples, as well as their mineralogical composition, indicate that they are technogenic materials – by-products from metallurgical copper production. The absence of sulfur-containing inclusions in the copper droplets and the lack of sulfur content in the hosted glass matrix suggests that the raw material used was not of sulfide minerals. Probably the raw material used was mined from an oxidizing zone of copper deposit with malachite and azurite. This conclusion also explains the high content of CaO in the slag, which reaches up to 11,66 % (Table 1). Based on their chemical and mineralogical peculiarities, we assume that these samples are one of the oldest studied slags found in our lands.

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