Mineralogical study of archaeological copper slags found in the area of Krushevets Village, SE Bulgaria

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Abstract. In this article, we present the results of our study on archaeological slags found near the village of Krushevets, Southeast Bulgaria. Chemical analyses of the slags show a high Fe_2O_3 (40.11–54.57%) and SiO_2 (29.32–42.28%) content, increased CaO content (3.01–6.51%), as well as very low quantity of SO_3 (from 0.20% to 0.52%) and P_2O_5 (between 0.23% and 0.30%). The unbound residual copper in the samples is in an amount of 0.41% to 1.07%. The main phases composition of the slags are as follows: fayalite-type silicate phases with impurities, kirschsteinite and laihunite; pyroxenes of the augite-type and amorphous hosted glass; iron-oxide phases (magnetite and maghemite); and copper-containing phases (drops of unbound copper, relicts of ore minerals such as bornite, chalcopyrite), as well as newly formed phases, such as chalcocite, and copper-containing spherical aggregates. The studied samples are a by-product of copper extraction metallurgical activity. The raw material used was of copper-sulfide type with impurities of manganese-, calcium-, magnesium- and aluminium-containing minerals.

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INTRODUCTION

The formation of copper ore deposits in the Burgas ore region is closely connected to four Late Cretaceous volcano-plutonic centers – Rosen, Varli Bryag, Zidarovo and Bakadzik. They were grouped in the four ore fields of the same names (Fig. 1). Three subformation types were subdivided among them: vein copper-molybdenum (Rosen), vein copper (Varli Bryag) and vein copper-polymetallic (Zidarovo and Bakadzik) (Bogdanov, 1987).

This paper presents the results of study on by-products from metallurgical activity, found in the Zidarovo ore field. It is located south of the Varli Bryag and west of the Rosen ore fields (Fig. 1). The copper-gold-polymetallic mineralizations in the Zidarovo ore field are of hydrothermal origin. The copper ore deposits named Kanarata and Yurta are of the greatest industrial importance (Bogdanov, 1987).

The studied slags were found in a locality named Bakarbokluk (copper trash in Bulgarian), situated southwest of the village of Krushevets, Sozopol Municipality. Georgiev (1987, pp. 38–39) and Mihaylov (2010) mentioned the presence of old mine excavations in the area. During the recent research there (Leshtakov *et al.*, 2015), ceramic fragments were found and, in addition, slags were also collected. The ceramic fragments date the studied metal mining activity back to the Hellenistic and Late Antiquity (Leshtakov *et al.*, 2015). Our field study did not lead to the finding of ore mineralization near the slag. The closest mineralization is Karaissak (unpublished study of Kalin Ruskov) with chalcopyrite, malachite, azurite and limonite, which is located about 1300 m to the west-southwest of the village of Varshilo (Hristov *et al.*, 1953) and is attached to the contact zone around the Harmanski (Varshilski) Pluton.

Fig. 1. Outcrop and subcrop occurrences of Upper Cretaceous rocks in Bulgaria (after Dabovski, 2009) and locations of copper ore fields in the Burgas ore region: 1) Rosen; 2) Varly Bryag; 3) Zidarovo; 4) Bakadzhik (according to Bogdanov, 1987, and Milev *et al.*, 1996).

The purpose of this study is to obtain data about the chemical and mineralogical peculiarities of the slags from Krushevet. These data will clarify the type of metal extracted and also the characteristics of the ore used. This research is a part of a complex study on archaeological slags from the Burgas and Yambol ore regions (Stavrakeva and Tzankova, 2016a, 2016 b; Tzankova *et al.*, 2016).

MATERIALS AND METHODOLOGY

Materials

The object of this study is more than 70 slag samples with a dark grey, almost black colour on a freshly broken surface. A common feature of the studied slags is the presence of a number of different secondary phases resulting from weathering. We observed secondary phases of dark green to yellow green, pink, rusty, red and white colours on the slag surfaces, occurring as coatings or stains. Some of them fill slag pores. The secondary phases are usually represented by carbonates with green color, orange-red iron oxides and hydroxides (Fig. 2). According to specimen colour and number of pores,

we divided the analysed samples into three groups: 1a, 2 and 3a. Each of the groups 1a and 3a were subdivided into two subgroups:

1) group 1a (1a¹ and 1a²) – grey, almost black slag, with visible crystal prismatic phases on a freshly broken surface, non-magnetic. The pores are up to 5 mm in size, visible only on the specimens' surfaces (Fig. 2a). Samples from group 1a² contain a greater number of crystal phases visible to the naked eye than the slags from group 1a¹;

2) group 2 – slags are grey-green, non-magnetic, heavy and compact, with microscopic pores (Fig. 2b);

3) group 3a (3a¹ and 3a²) – these slags are grey to reddish, with magnetic properties. The samples from group 3a¹ (Fig. 2c) are coarse-grained and relatively dense. They contain fewer pores than samples from group 3a² (Fig. 2d). The size of the pores is usually about 1–2 mm, rarely up to 8–9 mm. The smaller amount of pores in the samples from group 3a¹ indicates their slower cooling.

Methodology

The powdered and homogenized in an agate mortar slag samples were prepared for Powder X-ray dif-

Fig. 2. Macroscopic photographs of the slags selected for this study: *a*) sample from group 1a with crystalline prismatic phases on its surface, 8.5×3.5×3.5 cm; *b*) sample from group 2 with grey-green colour, 8×7×3 cm; *c*) sample from group 3a¹ with very little pore content, 7×5×1.5 cm; *d*) sample from group 3a² with weathering crust of orange-red iron oxides, 5×3.5×2.5 cm.

fraction 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 CuK α radiation, 2 θ 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 and 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, Bulgaria). The content ratio of basic oxides (CaO and MgO) to acidic oxides (SiO₂ and Al₂O₃) was used for assessment of the basicity of slag (B). 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 of the slags

The studied slags are mainly composed of SiO₂ (29.32–42.28%), Fe₂O₃ (40.11–54.57%), CaO (3.01–6.51%) and Al₂O₃ (7.01–9.03%) (Table 1). Slags with such type of composition are often referred to as fayalite slags, as fayalite often precipitates from these slags on cooling. The slag samples are relatively similar in their chemical composition. In addition, the studied slags also contain minute amount of TiO₂, MgO, MnO, K₂O, Na₂O, P₂O₅, SO₃ and Cu. The content ratio of basic oxides (CaO and MgO) to acidic oxides (SiO₂ and Al₂O₃) used for

Table 1
Chemical composition of the studied archaeological slags obtained from ICP-OES analyses, basicity of slag (B)

Oxides	Content, mass %			
	Sample 1a	Sample 2	Sample 3a ¹	Sample 3a ²
SiO ₂	37.79	42.28	29.32	39.72
TiO ₂	0.28	0.32	0.21	0.30
Al ₂ O ₃	9.03	7.17	7.77	7.01
Fe ₂ O ₃	41.34	40.11	54.57	41.58
CaO	5.98	5.56	3.01	6.51
MgO	2.45	2.12	2.17	2.19
MnO	1.05	0.25	0.72	0.15
K ₂ O	0.87	1.58	1.05	1.14
Na ₂ O	0.18	0.20	<0.05	0.44
P ₂ O ₅	0.27	0.30	0.23	0.26
SO ₃	0.32	0.46	0.20	0.56
Cu	0.74	0.45	1.07	0.41
Moisture	0.01	0.01	0.13	1.50
Σ	100.31	100.81	100.50	101.77
B	0.18	0.16	0.14	0.19

assessment of the basicity of slag is shown in Table 1. If the basicity value is greater than one, the slag is referred to as basic; slag with a basicity value small-

er than one is referred to as acidic. The basicity of all studied samples is less than 1, which determines the slags as acidic. When acidic oxides melt, they form polyions which give acidic slags high viscosities, making them difficult to handle, and increasing the amount of entrained copper or matte. Basic slags have low viscosities and high solubilities for acidic oxides. Up to a certain limit, adding basic oxides lowers the melting point of a slag (Schlesinger *et al.*, 2011).

Mineralogy and phase composition of slag sample 1a

Powder XRD analysis

This slag consists mainly of crystal phases from the olivine group, as indicated by XRD analysis. The dominant phase is fayalite Fe₂SiO₄ (Fig. 3, Fa). It is the most abundant phase composing this material, which was also confirmed by microscopic observations and elemental microanalyses. In addition to fayalite, magnesium fayalite (Fe,Mg)₂SiO₄ (olivine, Ol) and kirschsteinite CaFe²⁺SiO₄ (Kir) were detected in the sample, as well as augite-type pyroxene (Aug) (Fig. 3).

Fig. 3. XRD graph of sample 1a: fayalite (Fa); magnesium fayalite (olivine, Ol); kirschsteinite (Kir), augite (Aug).

Fig. 4. Microstructure of slag sample 1a¹: *a*) needle-like fayalite crystals, ×4, plane-polarized transmitted light; *b*, *c*) skeletal and elongated fayalite crystals, ×40, cross-polarized transmitted light; *d*) sub-radiating fayalite aggregates, ×10, plane-polarized transmitted light; *e*) sub-radiating fayalite aggregates, ×4, plane-polarized transmitted light; *f*) copper-sulfide aggregates, ×40, plane-polarized reflected light; *g*) copper-sulfide aggregates, ×40, plane-polarized reflected light; *h*) inhomogeneous copper-sulfide aggregates with relicts from the ore used, ×40, plane-polarized reflected light.

Light optical microscopy

Representative slag microstructure and phase assemblages, observed microscopically in transmitted and reflected light, are given in Figs 4, 5.

Sample 1a¹. Fayalite and silicate glass are the dominant silicate phases of the studied slag. Fayalite occurs as needle-like or prismatic skeletal crystals, indicating rapid crystallization (Fig. 4a–c). These crystals either are randomly distributed in the matrix or form sub-radiating aggregates (Fig. 4d, e). According to data from the XRD study, fayalite-type crystal phases are represented by fayalite Fe_2SiO_4 , magnesium fayalite and kirschsteinite $\text{CaFe}^{2+}\text{SiO}_4$ (Fig. 3). Fayalite crystals associate with elongated pyroxene crystals in the studied slags. The presence of augite-type pyroxene was also confirmed by the XRD and elemental microanalyses (Figs 3, 6b, c). The silicate matrix contains copper droplets and spherical inhomogeneous copper-sulfide aggregates. Most of them are scattered between the fayalite crystals (Fig. 4f–h). Microscopically, copper sulfide relics of the raw material used were observed in these aggregates (Fig. 4h).

Sample 1a². Microstructurally, this sample is analogous to sample 1a¹. Fayalite crystals are skeletal and prismatic. Most of them form sub-radiating to

parallel aggregates of prismatic crystals (Fig. 5a, b). Pyroxene crystals are small, needle-like, scattered among the fayalite ones.

Magnetite is in small amount. Under reflected light microscopy, it is light grey with brownish tinges and low reflectivity. Magnetite shows isotropic skeletal and dendritic forms, unevenly distributed in the volume of the sample, most often near sulfide inclusions. In this sample, in reflected light, there are many small copper droplets and copper-sulfide aggregates. Some of them have a distinct core and peripheral part (Fig. 5c, d).

Silicate phases

Silicate crystal phases in the studied sample are represented by fayalite, magnesium fayalite (olivine), laihunite, kirschsteinite and augite-type pyroxene. Variations in the chemical composition of the silicate crystal phases in samples 1a¹ and 1a², according to ten elemental microanalyses' (SEM CDD-EDS) data, are shown in Table 2. Fayalite, magnesium fayalite (olivine), kirschsteinite and pyroxene of augite type were detected by Powder XRD analysis with their characteristic set of d-spacings (Fig. 3).

The silicate phases in samples 1a¹ and 1a² are fayalite (Fa), laihunite (La), pyroxene (Py) and slag glass (Glass). Their representative chemical com-

Fig. 5. Microstructure of slag sample 1a²: a) prismatic crystals and sub-radiating fayalite aggregates, $\times 4$, plane-polarized transmitted light; b) parallel aggregates of prismatic fayalite crystals, $\times 10$, plane-polarized transmitted light; c) copper droplets and copper-sulfide aggregates, $\times 20$, plane-polarized reflected light; d) copper-sulfide aggregates and prismatic skeletal fayalite crystals, $\times 20$, plane-polarized reflected light.

Table 2

Variations in the chemical composition of the silicate crystal phases in samples 1a¹ and 1a² according to data from elemental microanalyses (SEM CDD-EDS)

Oxides	Content, mass %	
	Sample 1a ¹ (calculated from 4 points)	Sample 1a ² (calculated from 6 points)
FeO	59.29–62.77	47.56–60.94
MgO	4.38–4.74	2.10–6.53
CaO	0.66–1.45	0.64–4.25
MnO	1.82–2.14	1.45–2.10
Al ₂ O ₃	0–1.50	0.83–5.72
K ₂ O	–	0–0.79

positions are shown in Table 3. The major crystal phase in the studied materials is fayalite (Fig. 7a, b). The chemical composition of the silicate crystalline individuals in the analysed field 1a²-2 (Fig. 7c) with a shape of parallel skeletal forms are chemically close to transient between fayalite (Fe₂SiO₄) and laihunite (Fe_{1.6}SiO₄). These phases include impurities of magnesium, calcium, manganese, some aluminium and potassium, which were introduced from the slag glass during faster crystallization.

The silicate phases presented in Table 3 have the following crystal chemical formulas:

In the analysed field 1a¹-1 (Fig. 6a):

– Point 1: (Fe_{1.72}Mg_{0.23}Mn_{0.05}Ca_{0.02})_{2.02}Si_{0.99}O₄ – fayalite;

– Point 2: (Fe_{1.73}Mg_{0.21}Mn_{0.06}Ca_{0.02})_{2.02}Si_{0.99}O₄ – fayalite;

In the analysed field 1a¹-2 (Fig. 6b):

– Point 8: (Fe_{1.06}Ca_{0.52}Mg_{0.06}Mn_{0.05}K_{0.02}Na_{0.02}Al_{0.20})_{1.93}(Si_{1.84}Al_{0.16})_{2.00}O₆ – pyroxene;

In the analysed field 1a¹-3 (Fig. 6c):

– Point 1: (Fe_{0.85}Ca_{0.53}Mg_{0.05}Mn_{0.03}K_{0.05}Na_{0.04}Al_{0.40})_{1.95}(Si_{1.92}Al_{0.08})_{2.00}O₆ – pyroxene;

In the analysed field 1a¹-5 (Fig. 6e):

– Point 1: (Fe_{1.10}Ca_{0.18}K_{0.03}Al_{0.14})_{1.45}(Si_{0.83}Al_{0.14}Ti_{0.03})_{1.00}O₄ – laihunite with impurities;

– Point 2: (Fe_{1.25}Ca_{0.12}Mg_{0.02}Mn_{0.01}Na_{0.03}K_{0.03}Al_{0.12})_{1.58}(Si_{0.83}Al_{0.15}Ti_{0.02})_{1.00}O₄ – laihunite with impurities;

In the analysed field 1a¹-6 (Fig. 6f):

– Point 7: (Fe_{1.71}Mg_{0.22}Ca_{0.02}Mn_{0.05})_{2.00}Si_{0.97}O₄ – fayalite;

– Point 8: slag glass with impurities of polishing material – Cr₂O₃ and WO₃;

In the analysed field 1a²-1 (Fig. 7b):

– Point 1: (Fe_{1.61}Mg_{0.29}Mn_{0.05}Ca_{0.02})_{1.97}Si_{0.95}O₄ – fayalite;

– Point 2: (Fe_{1.60}Mg_{0.31}Mn_{0.05}Ca_{0.02})_{1.98}Si_{0.96}O₄ – fayalite.

Iron-oxide phases

These phases are mainly isometric, incompletely formed magnetite crystals, which, during their rapid crystallization, absorbed part of the melt. For this reason, their composition does not correspond to exact stoichiometry and contains impurities from the silicate glass phase. Sulfide inclusions can perform the

Table 3

Chemical composition of silicate phases in samples 1a¹ and 1a² according to data from elemental microanalyses (SEM CDD-EDS)

Oxides	Content, mass %									
	Sample 1a ¹								Sample 1a ²	
	An. field 1a ¹ -1 (Fig. 6a)		An. field 1a ¹ -2 (Fig. 6b)	An. field 1a ¹ -3 (Fig. 6c)	An. field 1a ¹ -5 (Fig. 6e)		An. field 1a ¹ -6 (Fig. 6f)		An. field 1a ² -1 (Fig. 7b)	
	Point 1 (Fa)	Point 2 (Fa)	Point 8 (Py)	Point 1 (Py)	Point 1 (La)	Point 2 (La)	Point 7 (Fa)	Point 8 (Glass)	Point 1 (Fa)	Point 2 (Fa)
SiO ₂	30.05	30.02	45.43	48.26	31.82	30.10	29.98	39.52	30.30	30.40
FeO	62.47	62.70	31.32	25.60	50.20	53.88	62.77	25.82	60.94	60.49
MgO	4.74	4.38	1.58	0.83	–	0.39	4.54	2.83	6.10	6.53
MnO	2.07	2.14	1.33	0.99	0.59	1.96	1.96	–	2.02	1.91
CaO	0.66	0.77	11.97	12.33	6.39	4.18	0.76	12.72	0.64	0.67
Al ₂ O ₃	–	–	7.64	10.28	9.42	8.38	–	8.45	–	–
TiO ₂	–	–	–	–	1.33	1.16	–	–	–	–
Na ₂ O	–	–	0.30	–	–	0.49	–	–	–	–
K ₂ O	–	–	0.44	1.14	0.84	0.83	–	–	–	–
Cr ₂ O ₃	–	–	–	–	–	–	–	1.62	–	–
WO ₃	–	–	–	–	–	–	–	9.04	–	–

Abbreviations: fayalite (Fa), laihunite (La), pyroxene (Py), slag glass (Glass).

role of crystallization centres, around which magnetite grows (Mihailova, 2009). This is a possible explanation for the presence of copper content in these phases.

Copper and residual sulfide phases in copper-containing aggregates

Copper-containing phases in samples 1a¹ and 1a² are chalcocite, pure copper droplets and aggregates

with copper-iron-sulfide composition. Microscopically, in reflected light, the aggregates were observed with a close to spherical shape. The chemical composition of the studied copper-containing phases is presented in Table 4. Studies on the copper (Cu) and sulfur (S) distribution in the copper-sulfide aggregates show that sulfur is fully concentrated in their periphery (Fig. 7g, h; Table 4).

Fig. 6. Scanning electron microscope images of the phases identified in sample 1a¹ and CDD-EDS mapping of analysed points: a) analysed field 1a¹-1 with points: 1 (fayalite), 2 (fayalite), 3 (aggregate – chalcocite), 4 (slag glass) and 5 (slag glass); b) analysed field 1a¹-2 with points: 1 (digenite), 2 (chalcocite), 3 (chalcocite), 4 (chalcocite), 5 (copper-iron-sulfide aggregate), 6 (magnetite), 7 (fayalite), 8 (pyroxene), 9 (slag glass) and 10 (slag glass); c) analysed field 1a¹-3 with points: 1 (pyroxene), 2 (pyroxene) and 3 (solid solution between fayalite and laihunite); d) analysed field 1a¹-4 with points: 1, 2, 3 (copper-containing aggregates); e) analysed field 1a¹-5 with points: 1 (laihunite) and 2 (laihunite); f) analysed field 1a¹-6 with points: 1, 2, 3, 4, 5, 6 (copper-containing aggregates), 7 (fayalite) and 8 (slag glass).

Fig. 7. Scanning electron microscope images of the phases identified in sample 1a² and CDD-EDS mapping of analysed points: a) overview with huge fayalite crystals; b) analysed field 1a²-1 with points: 1 (fayalite), 2 (fayalite) and 3 (fayalite); c) analysed field 1a²-2 with points 1, 2, 3; d) analysed field 1a²-4 with points: 1, 2 and 3 (copper-sulfide aggregate); e) analysed field 1a²-5 with points: 1 (chalcocite), 2 (chalcocite) and 3 (aggregate – copper with iron); f) analysed field 1a²-6 with points: 1 (copper), 2 (aggregate – copper with iron) and 3 (aggregate – copper with sulfur); g) distribution of copper (Cu) in a copper-sulfide aggregate – the concentration is higher in its central part; h) distribution of sulfur (S) in a copper-sulfide aggregate – it is concentrated in the periphery of the aggregate.

Table 4

Chemical composition of copper-containing phases and aggregates in samples 1a¹ and 1a² according to data from elemental microanalyses (SEM CDD-EDS)

Chemical element	Content, mass %										
	Sample 1a ¹				Sample 1a ²						
	Analysed field 1a ¹ -2 (Fig. 6b)				Analysed field 1a ² -4 (Fig. 7d)			Analysed field 1a ² -5 (Fig. 7e)		Analysed field 1a ² -6 (Fig. 7f)	
	Point 2	Point 3	Point 4	Point 5	Point 3	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3
Cu	78.43	78.81	78.30	65.86	77.52	80.32	80.51	98.68	99.15	98.94	80.46
Fe	1.44	1.29	1.67	8.82	2.47	—	—	1.32	0.85	1.06	—
S	20.14	19.89	20.03	25.32	20.01	19.68	19.49	—	—	—	19.54

In the analysed field 1a¹-2 (Fig. 6b) the following phases were calculated:

- Point 2: Cu_{1.96}Fe_{0.04}S – chalcocite;
- Point 3: Cu_{2.00}Fe_{0.03}S – chalcocite;
- Point 4: Cu_{1.97}Fe_{0.04}S – chalcocite;
- Point 5: Cu_{1.31}Fe_{0.20}S – copper-iron-sulfide aggregate;

In the analysed field 1a²-4 (Fig. 7d):

- Point 3: copper-iron-sulfide aggregate;

In the analysed field 1a²-5 (Fig. 7e):

- Point 1: chalcocite;
- Point 2: chalcocite;
- Point 3: copper-iron aggregate;

In the analysed field 1a²-6 (Fig. 7f):

- Point 1: copper;
- Point 2: copper-iron aggregate;
- Point 3: copper-sulfide aggregate.

Mineralogy and phase composition of slag sample 2

Powder XRD analysis

The XRD study of sample 2 (Fig. 8) shows the following phases in the slag composition: fayalite Fe₂SiO₄, augite Ca(Mg,Fe³⁺,Al)(Si,Al)₂O₆ (Aug) and laihunite-1M Fe_{1.6}SiO₄ (La).

Fig. 8. XRD graph of sample 2: fayalite (Fa), augite (Aug) and laihunite-1M (La).

Light optical microscopy

This slag sample differs significantly from samples 1a¹ and 1a² in having more parallel skeletal forms of defective crystals and copper-sulfide aggregates (Fig. 9a). The predominant crystal phase is fayalite with prismatic skeletal crystals and subradial aggregates (Fig. 9b–d). Some of the prismatic crystals are pyroxene-type, which matches the results from the XRD study of the sample (Fig. 8). This slag contains more ore relics, such as bornite, chalcopyrite and copper-containing aggregates, in comparison with other studied samples. The copper metal droplets and copper-sulfide spherical aggregates with high reflectivity were observed as included in the slag glass matrix, as well as between the prismatic crystalline phases (Fig. 9a). Some of them contain numerous small yellow-pink microspheres of copper sulfides (chalcopyrite?).

Silicate phases

The crystal silicate phases in this sample (mainly fayalite and pyroxene) are parallel skeletal forms

of defective crystals. Their composition differs from the exact stoichiometry because of the included impurities from the slag melt. The variations in chemical compositions of these phases are given in Table 5.

The chemical composition of a fayalite crystal from analysed field 2–5, point 2 (Fig. 10f) is the following: SiO₂ (31.82%), FeO (61.39%), CaO (1.68%), MgO (4.02%), Al₂O₃ (0.62%) and K₂O

Table 5
Variations in the chemical composition of the crystal silicate phases in sample 2 (from 6 analysed points) according to data from elemental microanalyses (SEM CDD-EDS)

Oxides	Mass %
SiO ₂	31.62–34.97
FeO	56.39–61.39
MgO	1.95–4.02
CaO	1.68–2.63
Al ₂ O ₃	0.62–2.49
K ₂ O	0–0.47

Fig. 9. Microstructure of slag sample 2, light microscopy: a) overview of slag sample 2 and copper-sulfide spherical aggregates, ×20, plane-polarized reflected light; b) prismatic fayalite crystals, ×4, plane-polarized transmitted light; c) radiating and sub-radiating aggregates of fayalite crystals, ×4, plane-polarized transmitted light; d) radiating and sub-radiating aggregates of fayalite crystals, ×10, plane-polarized transmitted light.

(0.47%), with calculated formula $(\text{Fe}_{1.65}\text{Mg}_{0.19}\text{Ca}_{0.06}\text{Al}_{0.02}\text{K}_{0.02})_{1.94}\text{Si}_{1.02}\text{O}_4$.

Copper and residual sulfide phases in copper-containing aggregates

In this sample, in reflected light, we observed copper-containing inhomogeneous inclusions (Fig. 9a) and many very small microspheres with a yellow-

pink colour. The latter are copper-iron sulfides with composition close to chalcopyrite. All six elemental microanalyses (SEM CDD-EDS) in studied fields 2-1 and 2-2 showed the presence of copper-iron sulfide inclusions in the sample. The results are listed below.

Table 6 presents the phase compositions of five elemental microanalyses in copper-containing aggregates from analysed field 2-2 (Fig. 10c). Ana-

Fig. 10. Scanning electron microscope images of the phases identified in sample 2 and CDD-EDS mapping of analysed points: a) overview; b) analysed field 2-1 with points: 1 (copper-containing aggregate), 2, 3 (slag glass), 4, 5 (fayalite crystals); c) analysed field 2-2 – copper-containing aggregates with points 1, 2, 3, 4 and 5; d) analysed field 2-3 with points 1, 2 (copper-containing aggregates), 3 (fayalite); e) microfield with a coarser-grained structure; f) analysed field 2-5 with point 2 being a fayalite crystal, points 5 and 6 – copper-containing aggregates, point 7 – slag glass.

Table 6

Chemical composition of copper-containing aggregates in sample 2, analysed field 2-2 (Fig. 10c) according to data from elemental microanalyses (SEM CDD-EDS)

Chemical elements	Content, mass %					
	Cu	Fe	S	Si	O	Cd
Point 1	65.30	10.26	24.44	—	—	—
Point 2	65.22	10.32	24.46	—	—	—
Point 3	96.11	2.41	—	—	1.48	—
Point 4	57.66	14.60	—	—	4.46	—
Point 5	22.97	32.17	22.90	7.76	11.93	2.26

lysed point 3 is a drop rich in copper. Points 1 and 2 are from an inhomogeneous inclusion with a composition of iron-copper sulfide close to bornite.

The chemical composition in points 1 and 2 in the analysed field 2-2 (Fig. 10c, Table 6) is very close to bornite (Cu_5FeS_4). For point 1, it is $\text{Cu}_{5.39}\text{Fe}_{0.096}\text{S}_4$. Results from the chemical study of point 3 show that it is almost pure copper with very low iron content and slightly oxidized. The melting process for sample 2 took place at lower temperatures and, therefore, some free copper and residual sulfide phases were registered.

Mineralogy and phase composition of slag sample 3a

Powder XRD analysis

The slags of samples 3a¹ and 3a² are mainly composed of silicate and iron oxide phases. For slag group 3a¹, XRD study registers fayalite Fe_2SiO_4 (Fa), magnesium fayalite (olivine, Ol) $(\text{Fe,Mg})_2\text{SiO}_4$, kirschsteinite $\text{CaFe}^{2+}\text{SiO}_4$ (Kir) and laihunite-1M $\text{Fe}_{1.6}\text{SiO}_4$ (La) (Fig. 11). X-ray study of sample 3a² indicates the presence of fayalite Fe_2SiO_4 (Fa), kirschsteinite

Fig. 11. XRD graph of sample 3a¹: fayalite (Fa), magnesium fayalite (olivine, Ol), kirschsteinite (Kir) and laihunite-1M (La).

$\text{CaFe}^{2+}\text{SiO}_4$ (Kir), augite $\text{Ca}(\text{Mg},\text{Fe}^{3+},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ (Aug) and magnetite $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ (Mag) (Fig. 12).

Light optical microscopy

Sample 3a¹. This sample is coarse-grained and contains fewer pores than sample 3a². Fayalite is the dominant crystalline phase, followed by magnetite/maghemite and copper-sulfide aggregates included in the slag glass matrix. Fayalite occurs as huge prismatic skeletal crystals (Fig. 13a, b) or shows textures with dendritic or irregular skeletal crystals indicating rapid crystallization (Fig. 13c). The X-ray diffraction pattern of sample 3a¹ revealed the presence of the fayalite, magnesium fayalite (olivine), kirschsteinite and laihunite phases (Fig. 11). This slag is rich in magnetite, observed as pale-grey crystals with brownish tinges in reflected light. Magnetite occurs either in skeletons or as dendritic aggregates (Fig. 13d). Grains of metallic copper and copper-sulfide aggregates show bright orangy red colour and higher reflectivity than the surrounding magnetite grains. The aggregates contain relics from bornite and covellite with yellow-pink and indigo blue colour in reflected light, respectively (Fig. 13d).

Sample 3a². The material is highly porous, with huge prismatic skeletal fayalite crystals (Fig. 13e).

This sample is probably from the more rapid cooling section of the molten material. Some fayalites have included in themselves ore mineral grains. The slag is full of isometric skeletal magnetite crystals and dendritic aggregates (Fig. 13e–g). Copper-sulfide aggregates are inhomogeneous, with an irregular shape. They also contain in their rims relics from ore minerals (Fig. 13h). The X-ray diffraction pattern of sample 3a² confirms the presence in the slag of fayalite, magnetite, kirschsteinite and augite (Fig. 12).

Silicate phases

Well-defined lamellar forms of fayalite were studied in points 1 and 2 of the analyzed field 3a¹-1 (Fig. 14a) and in field 3a²-1 (Fig. 15a). The results of these analyses are presented in Table 7.

The analysed fayalite individuals have the following crystal-chemical formulas:

In the analysed field 3a¹-1 (Fig. 14a):

– Point 1: $\text{Fe}_{1.76}\text{Mg}_{0.20}\text{Ca}_{0.04}\text{Si}_{1.00}\text{O}_4$;

– Point 2: $\text{Fe}_{1.72}\text{Mg}_{0.22}\text{Ca}_{0.01}\text{Si}_{1.00}\text{O}_4$;

In the analysed field 3a²-1 (Fig. 15a):

– Point 3: $\text{Fe}_{1.71}\text{Mg}_{0.29}\text{Ca}_{0.01}\text{Mn}_{0.03}\text{Al}_{0.01}\text{Si}_{0.97}\text{O}_4$;

– Point 4: $\text{Fe}_{1.81}\text{Mg}_{0.22}\text{Ca}_{0.01}\text{Mn}_{0.03}\text{Si}_{0.97}\text{O}_4$.

All compositions of the iron-silicate phases in samples 3a¹ and 3a² are very close to the stoichiom-

Fig. 12. XRD graph of sample 3a²: fayalite (Fa), kirschsteinite (Kir), augite (Aug) and magnetite (Mag).

Fig. 13. Microstructure of sample 3a, light microscopy: a) prismatic skeletal fayalite crystals, $\times 10$, plane-polarized transmitted light; b) prismatic skeletal fayalite crystals, $\times 10$, cross-polarized transmitted light; c) dendritic and irregular skeletal fayalite crystals, $\times 20$, plane-polarized transmitted light; d) magnetite and copper-sulfide aggregates, $\times 20$, plane-polarized reflected light; e) prismatic skeletal fayalite crystals, $\times 40$, plane-polarized reflected light; f) fayalite, magnetite and sulfide inclusions, $\times 20$, plane-polarized reflected light; g) dendritic magnetite aggregates, $\times 40$, plane-polarized reflected light; h) inhomogeneous copper-sulfide aggregate, $\times 40$, plane-polarized reflected light.

Fig. 14. Scanning electron microscope images of the phases identified in sample 3a¹ and CDD-EDS mapping of analysed points: a) analysed field 3a¹-1 with points: 1, 2 (fayalite), 3, 4 (copper-containing aggregates), 5, 6 (slag glass); b) analysed field 3a¹-2 with points 1, 2, 3 (iron-copper sulfide phases); c) relic of the raw material in the close-up; d) analysed field 3a¹-3 with points 1, 2, 3 (iron-copper sulfide phases) and 4 (magnetite/maghemite).

Table 7

Chemical composition of fayalite crystals in samples 3a¹ and 3a² according to data from elemental microanalyses (SEM CDD-EDS)

Oxides	Content, mass %			
	Sample 3a ¹		Sample 3a ²	
	Analysed field 3a ¹ -1 (Fig. 14a)		Analysed field 3a ² -1 (Fig. 15a)	
	Point 1 (Fa)	Point 2 (Fa)	Point 3 (Fa)	Point 4 (Fa)
SiO ₂	30.34	30.38	29.65	29.15
FeO	64.27	63.87	62.41	64.62
MgO	4.18	4.58	6.08	4.52
CaO	1.21	1.17	0.33	0.45
MnO	-	-	1.29	1.26

Abbreviation: fayalite (Fa).

etry of fayalite crystals and show the possibility of substitutions in it of magnesium, calcium, manganese and, in a small amount, aluminium.

Iron-oxide phases

The presence of magnetite/maghemite crystals in the studied slags was established microscopically in

reflected light and by XRD analyses (Figs 12, 13). Magnetite/maghemite was observed in isometric crystals and skeletal dendritic forms. Elemental microanalyses (SEM CDD-EDS) confirm these phases (Table 8).

The crystal-chemical formulas of the iron-oxide phases in sample 3a² are calculated and presented below.

Table 8
Chemical composition of iron-oxide phases in slag 3a² according to data from elemental microanalyses (SEM CDD-EDS)

Chemical elements	Content, mass %								
	Analysed field 3a ² -1 (Fig. 15a)		Analysed field 3a ² -2 (Fig. 15b)				Analysed field 3a ² -4 (Fig. 15d)		Analysed field 3a ² -6 (Fig. 15f)
	Point 1 (Mag)	Point 2 (Mag)	Point 1 (Mag)	Point 2 (Mag)	Point 3 (Mag)	Point 4 (Mag)	Point 4 (Mag)	Point 5 (Mag)	Point 4 (Mgh)
Fe	64.48	65.53	62.27	60.93	62.34	62.57	63.65	64.33	59.35
Ti	0.81	0.66	0.79	0.78	0.72	0.75	–	0.74	0.59
Al	4.71	4.12	6.39	7.17	5.93	6.01	4.85	4.67	4.20
Mg	0.53	0.50	–	0.30	0.26	0.36	–	–	–
Ca	–	–	–	–	–	–	–	–	0.77
K	–	–	–	–	–	–	–	–	0.36
Si	0.62	0.62	0.70	0.69	1.06	0.54	2.21	0.86	3.43
O	28.84	28.58	29.86	30.12	29.67	29.77	29.29	29.40	31.29

Abbreviations: magnetite (Mag), maghemite (Mgh).

In the analysed field 3a²-1 (Fig. 15a):

– Point 1: (Fe⁺²_{0.96}Mg_{0.04})_{1.00}(Fe⁺³_{1.60}Ti_{0.03}Al_{0.38}Si_{0.04})_{2.05}O₄ – magnetite;

– Point 2: (Fe⁺²_{0.95}Mg_{0.05})_{1.00}(Fe⁺³_{1.67}Ti_{0.03}Al_{0.34}Si_{0.05})_{2.09}O₄ – magnetite;

In the analysed field 3a²-2 (Fig. 15b):

– Point 1: Fe⁺²_{1.00}(Fe⁺³_{1.50}Ti_{0.04}Al_{0.53}Si_{0.05})_{2.12}O₄ – magnetite;

– Point 2: (Fe⁺²_{0.97}Mg_{0.03})_{1.00}(Fe⁺³_{1.26}Ti_{0.03}Al_{0.55}Si_{0.05})_{1.89}O₄ – magnetite;

– Point 3: (Fe⁺²_{0.98}Mg_{0.02})_{1.00}(Fe⁺³_{1.43}Ti_{0.03}Al_{0.47}Si_{0.08})_{2.01}O₄ – magnetite;

– Point 4: (Fe⁺²_{0.97}Mg_{0.03})_{1.00}(Fe⁺³_{1.43}Ti_{0.03}Al_{0.48}Si_{0.04})_{2.02}O₄ – magnetite.

In the analysed field 3a²-4 (Fig. 15d):

– Point 4: Fe⁺²_{1.00}(Fe⁺³_{1.49}Al_{0.39}Si_{0.17})_{2.05}O₄ – magnetite;

– Point 5: Fe⁺²_{1.00}(Fe⁺³_{1.51}Ti_{0.03}Al_{0.38}Si_{0.07})_{1.99}O₄ – magnetite;

In the analysed field 3a²-6 (Fig. 15f):

– Point 4: (Fe⁺²_{0.96}Ca_{0.04})_{1.00}(Fe⁺³_{1.21}Ti_{0.03}Al_{0.32}K_{0.02}Si_{0.25})_{1.83}O₄ – maghemite.

Copper and residual sulfide phases in copper-containing aggregates

Copper-containing aggregates are mainly copper-iron-sulfide inclusions. In reflected light, they are observed as spherical drops. In sample 3a¹ in the analysed field 3a¹-2 (Fig. 14b), relics of ore were found and, more precisely, sulfide minerals bornite and chalcopyrite with the composition given in Table 9. Point 4 in the analysed field 3a¹-1 (Fig. 14a, Table 9) is probably a residue of the used raw ore material with tennantite-type minerals.

Numerous sulfide inclusions and copper-containing aggregates were found in sample 3a². They are very clearly visible in analysed fields 3a²-3,

Table 9
Chemical composition of iron-copper sulfide phases in slag sample 3a¹ according to data from elemental microanalyses (SEM CDD-EDS)

Chemical elements	Content, mass %							
	Analysed field 3a ¹ -1 (Fig. 14a)		Analysed field 3a ¹ -2 (Fig. 14b)			Analysed field 3a ¹ -3 (Fig. 14d)		
	Point 3	Point 4	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3
Cu	54.32	21.44	62.76	65.07	71.00	55.30	64.53	64.99
Fe	18.03	33.07	13.56	16.36	9.86	15.71	10.04	9.73
S	27.64	17.62	23.68	–	19.14	21.19	24.30	24.12
As	–	10.22	–	18.57	–	7.81	1.13	1.17
Ca	–	1.61	–	–	–	–	–	–
Si	–	5.20	–	–	–	–	–	–
Al	–	1.66	–	–	–	–	–	–

3a²-4 and 3a²-6 (Fig. 15c, d, f). Analysed field 3a²-4 contains a copper-sulfide aggregate with clearly manifested zonation (Fig. 15d). Its periphery and the central parts are with different compositions, presented below. The results of the elemental mi-

croanalyses in fields 3a²-3 (Fig. 15c) and 3a²-4 (Fig. 15d) are presented in Table 10.

The results of the chemical study of copper-containing aggregates from the analysed field 3a²-6 (Fig. 15f) are presented in Table 11. They have a

Fig. 15. Scanning electron microscope images of the phases identified in sample 3a² and CDD-EDS mapping of analysed points: a) analysed field 3a²-1 with points: 1, 2 (magnetite), 3, 4 (fayalite), 5, 6 (slag glass); b) analysed field 3a²-2 with points 1, 2, 3 and 4 (magnetite); c) analysed field 3a²-3 with points 1, 2, 3 (copper-containing aggregates); d) analysed field 3a²-4 with points 1, 2, 3 (aggregates), 4 and 5 (magnetite); e) microstructure of the slag from sample 3a²; f) analysed field 3a²-6 with points 1, 2, 3 (aggregates) and 4 (maghemite).

Table 10

Chemical composition of copper-containing aggregates in slag sample 3a² according to data from elemental microanalyses (SEM CDD-EDS)

Chemical elements	Content, mass %					
	Analysed field 3a ² -3 (Fig. 15c)			Analysed field 3a ² -4 (Fig. 15d)		
	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3
Cu	79.47	80.66	97.12	80.90	87.78	93.96
Fe	3.62	2.70	–	2.34	2.23	1.70
S	16.29	16.63	–	16.76	16.63	–
O	–	–	2.98	–	9.99	4.34

chemical zonation and a very heterogeneous composition at different points. Some of these aggregates have high sulfur content in their periphery (Fig. 15f, Table 11 – point 1). The periphery of other aggregates consists of copper-iron oxide without sulfur, and with impurities of Si, Al and Ca (Fig. 15f, Table 11 – point 2). The central parts of the units are made of almost pure copper (Fig. 15f, Table 11 – point 3).

Slag glass

During the cooling of molten copper-containing raw materials, the main crystal phases in the slag crystallize from the melt. The residual mass is a multicomponent, optically isotropic, amorphous phase, referred to as slag glass. The chemical composition of the slag glass in all studied samples was analysed by spot analyses. The results are presented in Table 12.

Table 11

Chemical composition of copper-containing aggregates with zonal structure in slag sample 3a² according to data from elemental microanalyses (SEM CDD-EDS)

Chemical elements	Content, mass %		
	Analysed field 3a ² -6 (Fig. 15f)		
	Point 1	Point 2	Point 3
Cu	75.86	16.55	97.66
Fe	3.68	48.67	–
S	17.97	–	–
Ca	–	0.44	–
Al	–	4.31	–
Si	–	2.39	–
O	2.49	27.67	2.34

Table 12

Chemical composition of the slag glass in the studied samples from the area of the village of Krushevets according to data from elemental microanalyses (SEM CDD-EDS)

Oxides	Content, mass %										
	Analysed field 1a ¹ -1 (Fig. 6a)		Analysed field 1a ¹ -2 (Fig. 6b)		Analysed field 2-1 (Fig. 10b)		Analysed field 2-5 (Fig. 10f)	Analysed field 3a ¹ -1 (Fig. 14a)		Analysed field 3a ² -1 (Fig. 15a)	
	Point 4	Point 5	Point 9	Point 10	Point 2	Point 3	Point 7	Point 5	Point 6	Point 5	Point 6
	Point 4	Point 5	Point 9	Point 10	Point 2	Point 3	Point 7	Point 5	Point 6	Point 5	Point 6
SiO ₂	46.51	47.50	48.74	48.78	54.13	54.60	56.45	53.45	54.20	42.88	41.74
TiO ₂	0.59	0.58	—	0.64	—	—	—	—	—	—	—
Al ₂ O ₃	13.18	13.45	14.87	14.48	10.96	10.98	11.65	11.45	11.61	16.41	11.92
FeO	26.63	24.46	20.07	20.82	20.36	20.22	17.97	18.14	17.52	31.84	36.89
CaO	9.16	10.71	11.79	11.99	11.89	11.53	11.30	13.46	13.35	6.38	5.73
MgO	0.50	—	0.26	0.32	—	—	—	—	—	—	0.29
MnO	0.84	0.82	0.68	0.70	—	—	—	—	—	—	0.74
K ₂ O	1.87	1.57	1.58	1.55	2.66	2.68	2.61	2.13	2.18	2.48	2.23
Na ₂ O	0.72	0.91	0.61	0.72	—	—	—	1.36	1.14	—	0.44
CuO	—	—	0.93	—	—	—	—	—	—	—	—
SO ₃	—	—	0.43	—	—	—	—	—	—	—	—

DISCUSSION

The phase and chemical composition, as well as the microstructural characteristics of the studied samples from the area of the village of Krushevets, show that they are waste materials from sulfide smelting for copper extraction. Compared with slags from smelting oxidic ores, those from sulfide smelting are more abundant (Bachmann, 1982). The following phases were established with complex methods of investigation: silicate phases – fayalite-type with impurities, kirschsteinite and laihunite; pyroxenes of the augite-type and amorphous hosted glass; iron-oxide phases – magnetite and maghemite; copper-containing phases – bornite and chalcopyrite, chalcocite, copper-iron-sulfide and copper-sulfide aggregates, as well as drops of unbound pure copper. Among the minerals found in ancient, as well as in modern, slags are fayalite, kirschsteinite, pyroxene, magnetite and maghemite (Ivanov *et al.*, 1967; Mihailova and Mehandrejev, 2010; Stavrakeva and Stoytseva, 1966).

The copper content in the studied slags goes up to 1.07% (Table 1), indicating low process efficiency. It was presented in the form of either metallic droplets, non-stoichiometric copper oxides or sulfides, the latter being practically insoluble in the silicates. The presence of ore relics of sulfide minerals (bornite and chalcopyrite) and copper-containing aggregates (Tables 4, 6, 9–11) indicates that the heat treatment of the material did not reach the required temperature for complete melting of the ore used and complete extraction of copper.

The copper-containing ore raw materials used were probably of two main types. Samples 1a (1a¹ and 1a²), 2 and 3a² (Table 1) have approximately the same composition: SiO₂ (37.79–42.28%); Fe₂O₃ (40.11–41.58%); CaO (5.56–6.51%) and CuO (0.41–0.74%). In sample 3a¹, the content of SiO₂ is lower (29.32%) and Fe₂O₃ is higher (54.57%) compared to the other three samples. Sample 3a¹ also has a higher Cu content (1.07%).

The amount of slag glass phase in the samples depends on the chemical composition of the heat-treated materials and the thermal regime – maximum melting temperature and cooling rate of the melt. Thus, in the studied slags, it was found that the glass phase in sample 2 is in smaller amount compared to the other slag samples. It is likely that this slag was

obtained by heat treatment at lower temperatures, due to which more ore relics, such as bornite, chalcopyrite and copper-containing aggregates, were found in sample 2. Probably, the starting ore material in sample 2 was more difficult to melt than the other samples, judging by their chemical compositions. It was found that the composition of slag 2 has a higher content of SiO₂ (42.28%) (Table 1).

The ore used was included in host rocks containing quartz and potassium feldspar minerals. Proof of this is the constant presence of CaO in 10 of 11 analysed points (9.16–13.46%) with the exception of sample 3a²-1 (Table 12). This assumption is also supported by the presence of K₂O and Al₂O₃ in the slag glass. The composition of fayalite shows that the used ore raw material contained manganese-, calcium-, magnesium- and aluminium-containing minerals (Tables 2, 3, 7).

The slag samples from the area of the village of Krushevets are very similar in their characteristics to the previously studied slags found in the archaeological sites in the areas of Propadnala Voda, Koru Cheshme, Rosen and Atiya (Stavrakeva and Tzankova, 2016b; Tzankova *et al.*, 2016).

CONCLUSION

The archaeological metallurgical slags provide valuable information about the material culture, mining and metal extracting skills of the local population. The mineral composition of the slags, as well as their structural and phase characteristics, allow us to claim that, in the studied area, in the past there was copper metallurgical activity based on copper sulfide mining. The phase composition of the slags shows that the population of this region melted sulfide ore with different additive content. While the origin of the ore could not be determined, it may be related to the copper-sulfide ore deposits in the region.

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