

RECONSTRUCTING ANCIENT COPPER SMELTING
PRACTICES IN THE EASTERN PART OF THE
SREDNOGORIE METALLOGENIC ZONE (SE BULGARIA)
USING SLAG MINERALOGY AND CHEMISTRY

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Abstract

This study reconstructs the smelting conditions of ancient copper production in the eastern Srednogorie metallogenic zone (SE Bulgaria) based on the mineralogical and chemical composition of archaeological slags. Slag samples from three ore fields were investigated: Rosen (Propadnala Voda, Korucheshme and Rosen deposits, and Atiya metallurgical centre), Zidarovo (Krushevets archaeological site) and St. Iliya (Boyadzhik archaeological site). Mineralogical observations, bulk chemical analyses, SEM-EDS data and phase diagram evaluation were applied. The slags are dominated by iron-bearing phases (fayalite, magnetite/maghemite, wüstite, laihunite and kirschsteinite), with copper occurring mainly as metallic droplets and sulphide matte inclusions. Slags from Rosen ore field and Krushevets indicate smelting of sulphidic copper ores under moderately reducing conditions, whereas Ca-rich Boyadzhik slags lacking sulphides suggest smelting of copper ore from the oxidation zone of a copper deposit. The slag viscosity and melt characteristics varied significantly between metallurgical sites. Estimated smelting temperatures range from $\sim 1050\text{--}1100\text{ }^{\circ}\text{C}$ (Rosen ore field) to $\sim 1150\text{--}1200\text{ }^{\circ}\text{C}$ (Krushevets) and $\sim 1200\text{--}1300\text{ }^{\circ}\text{C}$ (Boyadzhik). These results reveal several metallurgical

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regimes in the eastern Srednogie region and provide new archaeomineralogical evidence for technological variability in ancient copper production. All studied slags contain critical and strategic elements. Their behaviour and distribution between the melt and the crystalline phases formed during cooling are directly governed by smelting conditions, a thorough understanding of which is essential for developing an appropriate methodology for their extraction.

Key words: archaeomineralogy, ancient copper slags, smelting conditions

Introduction. The eastern Srednogie metallogenic zone in SE Bulgaria represents an important centre of ancient copper production in the Balkans. Archaeological and mineralogical investigations have documented extensive mining and metallurgical activity, including ancient mines, slag accumulations, furnace remains, mining tools and ceramic materials [1–4]. The slags investigated in this study originate from copper ore processing in three ore fields of the eastern Srednogie zone: Rosen, Zidarovo, and St. Ilia. Evidence of ancient metallurgy in the Rosen ore field has been identified at the Propadnala Voda and Rosen deposits, Korucheshme deposit and metallurgical site, and the Atiya metallurgical centre [5, 6]. These sites were occupied during several periods, including possible prehistoric activity, the Classical Greek period (6th–5th century BC), the Roman period, and the Early Byzantine period [4]. At the Rosen ore field, archaeologists discovered pottery dated to the 6th to early 5th century BC (Late Archaic period) together with well-preserved in situ remains of smelting furnaces and slags [4]. Slags from the Zidarovo ore field were discovered near Krushevets village at the archaeological locality “Bakar Bokluk”, dated to the Late Iron Age and the Roman or Early Byzantine periods [4]. Metallurgical remains from the St. Ilia ore field occur near Boyadzhik village close to the Prokhorovo copper deposit and have been attributed to Antiquity or the Middle Ages [7].

Despite abundant archaeological evidence, the technological parameters of copper production in the eastern Srednogie region have not yet been sufficiently well defined. This study reconstructs ancient copper smelting practices in the eastern Srednogie metallogenic zone through mineralogical and chemical investigation of archaeological slags from the Rosen, Zidarovo, and St. Ilia ore fields. Particular attention is given to furnace temperature regimes, redox conditions and melt characteristics, which are essential parameters in archaeometallurgy [8–10], evaluated through mineralogical observations, chemical analyses and phase-diagram interpretation. Large accumulations of ancient slags, such as those from the metallurgical centre of Atiya, represent a significant potential source for the extraction of critical metals. The concentrations of trace elements in slags and their distribution among relics of the original charge and newly formed phases are directly governed by the initial composition of the charge and the prevailing smelting conditions. Determining these parameters is therefore crucial for developing effective strategies for the recovery of critical raw materials from slags and their potential reuse. Comparison of slags from the different ore fields allows the

identification of distinct metallurgical regimes and provides the first systematic reconstruction of furnace smelting conditions for ancient copper production in this part of southeastern Bulgaria.

Geological setting. The Rosen ore field is related to the Upper Cretaceous Rosen volcanic–plutonic complex and associated hydrothermal mineralization. More than 200 ore veins are known, about 40 of which were economically exploited until the mid-1990s. The ores are predominantly copper-bearing with variable contents of Mo, Fe, U, W, Co, and Au. Post-magmatic alterations include propylitic and quartz-sericite types up to secondary quartzites. The ore veins formed deposits in a NW–SE occurrence. The principal ore minerals are chalcopyrite, pyrite, magnetite, hematite and molybdenite, while gangue minerals include quartz, ankerite, ferrodolomite, calcite, chlorite and chalcedony [2]. The Zidarovo ore field is associated with the Upper Cretaceous Zidarovo volcanic–plutonic complex and quartz-sulphide veins formed during the final stage of magmatic activity and related hydrothermal processes [11]. Alteration ranges from propylitic to quartz-sericite types. Five hydrothermal zones are distinguished: Kanarata (including Yurta), Krushevets, Zidarovo, Izvor and Parlana Kokoshka–Tepeto. Mineralization occurs mainly as veins along fault zones and includes Cu, Pb–Zn and Au–Ag ores. Near Krushevets village, the main occurrences are Cu mineralization at Krushevets-1 and Au–Cu–Pb mineralization at Krushevets-2 [12, 13]. The St. Ilia ore field comprises Upper Cretaceous volcanic and plutonic rocks associated with the Prokhorovo porphyry-copper deposit and several hydrothermal and skarn occurrences. The deposit is related to the Prokhorovo intrusive body and is characterized by hornfels, calcic skarns, potassium-silicate and quartz-sericite alterations. The main ore minerals are chalcopyrite and pyrite with subordinate molybdenite, bornite, tennantite, native gold and electrum. The Boyadzhik-1 and Boyadzhik-2 occurrences are related to the St. Ilia pluton and formed at contacts with Triassic carbonate rocks, where Mg- and Ca-rich skarns host magnetite-dominated ore bodies with minor hematite, pyrite and chalcopyrite [14].

Materials and methods. Preliminary optical investigations of polished sections and thin sections were carried out using Meiji MT9200 and MT9430 optical microscopes in both transmitted and reflected light. The bulk chemical composition of the slag samples was determined by ICP-OES method using an Agilent Technologies 720-ICP-OES system. The chemical composition of the mineral phases was analyzed using a JEOL JSM-6010 Plus/LA InTouchScope™ scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (SDD-EDS) with a resolution of 128 eV. SEM-EDS microanalyses were performed on highly polished flat specimens coated with graphite at an accelerating voltage of 20 kV. The analyses were conducted using a standard set for microanalysis (SPI – 53 minerals). The estimation of the smelting characteristics of the slags (minimum temperature) was performed using the Slag Atlas method [15].

Results and discussion. *Initial composition of the charge in the furnaces.* The mineralogical and chemical composition of the studied copper slags from the eastern Srednogorie metallogenic zone reflects both ore characteristics and smelting conditions. Although the slags share mineralogical features typical of early copper metallurgy, compositional differences indicate variations in ore composition and technological practices. Slags from the Rosen ore field are dominated by iron-bearing phases such as fayalite, laihunite, magnetite/maghemite, wüstite, and kirschsteinite, and contain numerous copper droplets and copper-sulphide aggregates, indicating incomplete metal separation and persistence of sulphide phases during smelting [5, 6]. Krushevets slags display a more diverse silicate assemblage including fayalite and Mg-rich fayalite (olivine), kirschsteinite, laihunite and augite-type pyroxenes, with magnetite/maghemite as the main iron oxides. Copper occurs as metallic droplets with relic sulphides such as bornite and chalcopyrite, suggesting smelting of sulphide ores with incomplete oxidation [16]. Boyadzhik slags are mineralogically simpler, dominated by fayalite and augite-type pyroxenes with magnetite/maghemite as the principal iron oxides. Copper occurs mainly as metallic droplets, while sulphide relics are absent and copper oxide and copper-iron oxide phases are present [17].

Fayalite is the dominant silicate phase in all slags, confirming their typical fayalitic character formed during smelting of iron-rich ores. However, the presence of Mg-rich fayalite, kirschsteinite and laihunite in Rosen and Krushevets slags indicates variability in slag composition related to differences in ore chemistry and smelting conditions. Bulk chemical analyses (ICP-OES) show Fe_2O_3 contents of 36–66 wt% and SiO_2 of 20–42 wt% (Table 1), while Al_2O_3 contents of 4–7 wt% suggest contributions from clay-rich materials. Slag glass compositions confirm Fe and Si as the main melt components [5, 6, 16, 17].

Copper concentrations in the investigated slags reach up to approximately 4.4 wt.% Cu, indicating significant metal losses compared with most modern industrial copper slags. Some samples contain copper concentrations comparable to or even exceeding grades considered economically viable for reprocessing metallurgical waste. Modern economic cut-off grades for copper in primary ores typically range from 0.2 to 1 wt.% Cu [18, 19]. Copper-bearing mining and metallurgical wastes are often suitable for economic reprocessing at lower grades because the material has already been extracted, and modern technologies enable metal recovery from resources previously considered uneconomic.

The presence of sulphide relics in Rosen and Krushevets slags, unlike their absence in Boyadzhik slags, indicates differences in oxidation conditions and possibly ore type. The coexistence of fayalitic silicates and sulphide phases suggests partial oxidation of iron sulphides. The released iron entered the silicate melt as FeO and formed fayalite, whereas copper-rich sulphides remained preserved as matte inclusions.

T a b l e 1

Representative bulk chemical compositions of the studied slags

Oxides wt %	Propadnala Voda deposit	Korucheshme metall. centre and deposit	Rossen deposit	Atiya metall. centre	Krushevets	Boyadzhik
SiO ₂	36.58	20.57	28.74	31.49	42.28	37.45
TiO ₂	0.27	0.23	0.10	0.27	0.32	0.40
Al ₂ O ₃	6.39	4.62	3.93	4.62	7.17	6.15
Fe ₂ O ₃	46.41	66.07	58.40	53.96	40.11	36.71
CaO	1.42	3.17	1.18	2.15	5.56	11.11
MgO	0.45	1.11	0.80	1.29	2.12	2.26
MnO	0.05	0.20	0.05	0.50	0.25	0.29
Na ₂ O	0.20	0.24	0.13	0.31	0.20	< 0.05
K ₂ O	1.31	1.01	0.77	0.91	1.58	0.67
P ₂ O ₅	1.08	0.38	0.22	0.33	0.30	0.32
SO ₃	0.60	0.79	0.65	0.74	0.46	0.33
Cu	4.37	0.92	1.38	1.97	0.45	2.46
Moisture	1.06	0.18	0.56	1.37	0.01	1.70
Σ	100.19	99.49	100.91	99.91	100.81	99.90

This indicates partial desulphurisation of sulphidic ores under moderate oxygen potential, consistent with FeO–SiO₂–S phase-system interpretations described in the Slag Atlas [15]. Boyadzhik slags differ by higher Ca contents, lower relative Fe (Table 1), absence of sulphide matte and elevated Ca in slag glass ~11–14 wt% [17], suggesting a different melt chemistry and smelting regime, possibly involving Ca-rich ore components or added fluxes.

The main smelting conditions at the furnaces. *Temperature.* The liquidus temperatures of the slags were estimated on the basis of their overall chemical composition and position in the relevant phase diagrams, using the phase relationships and isotherms presented in the ‘Slag Atlas’. Their mineralogical characteristics were assessed separately [15]. Slags from the Rosen ore field plot in the FeO–SiO₂ dominated region near the fayalite stability field and the 1000–1100 °C isotherms (Fig. 1a), indicate relatively low liquidus temperatures of approximately 1050–1100 °C. Chalcopyrite may have contributed to fayalite formation at temperatures below the fayalite liquidus [10]. Krushevets slags contain higher silica and lower relative Fe contents and plot toward the silica-rich fields of the FeO–SiO₂ system. Although SiO₂ generally lowers liquidus temperatures in iron-rich systems by promoting fayalite formation [8, 9], the higher silica contents shift the bulk composition away from the FeO–SiO₂ eutectic, resulting in higher liquidus temperatures. These compositions indicate smelting temperatures of about 1150–1200 °C and possibly up to ~ 1300 °C. Boyadzhik slags represent

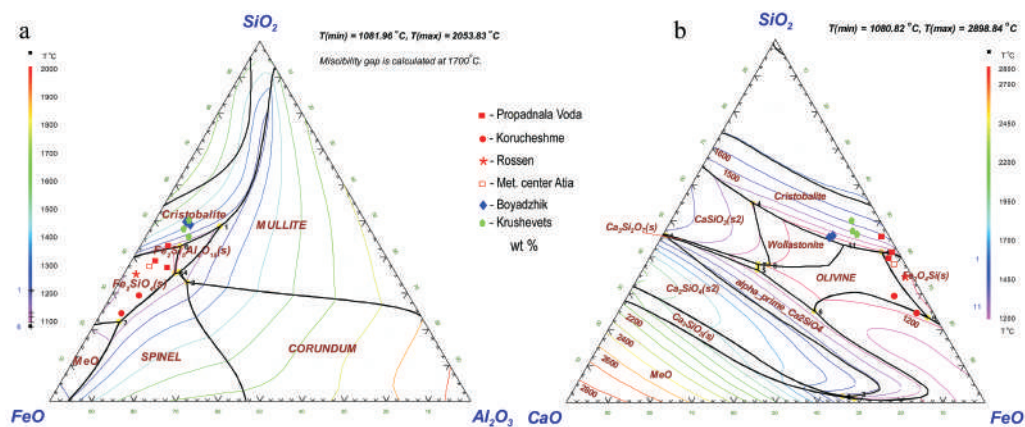


Fig. 1. Estimation of minimum formation temperatures based on the plotting of bulk major-element compositions in the ternary phase diagrams, indicating the stability fields of different phases under thermodynamic equilibrium: a) FeO–Al₂O₃–SiO₂, b) CaO–FeO–SiO₂

the highest-temperature regime. Their elevated CaO contents modify phase relations in the silicate system and increase melting temperatures [20]. Together with relatively high SiO₂ and lower FeO contents, these compositions suggest smelting temperatures between approximately 1200 and 1300 °C [20] (Fig. 1a, b). Experimental and archaeological data show that charcoal-fired furnaces could reach temperatures of about 1200–1300 °C, allowing complete melting of slag and metal and enabling efficient smelting [9, 21]. The positioning of slags from Krushevets and Boyadzhik within the cristobalite primary phase field (Fig. 1a, b) indicates silica enrichment relative to other oxides. However, this does not necessarily mean that cristobalite is formed, as archaeological slags rarely reach a state of equilibrium and often solidify into a glassy state. Such positioning, therefore, reflects bulk melt chemistry rather than mineralogical outcome. The silica enrichment observed in these slags most likely reflects quartz-rich gangue, incomplete assimilation of silica, and the partitioning of Fe into sulphides and oxides.

Furnace atmosphere. The mineral assemblages in the slags provide important evidence for the redox conditions during smelting. Early metallurgical furnaces rarely maintained constant redox conditions; instead, the smelting atmosphere fluctuated depending on air supply, fuel distribution and furnace operation. The coexistence of fayalite and magnetite in the studied slags may reflect local variations in oxygen potential during smelting and cooling. Fayalite represents the dominant Fe-bearing silicate phase, whereas magnetite is stable at relatively higher oxygen availability [22]. However, since fayalite–magnetite assemblages are characteristic of both ancient and modern copper slags, their occurrence alone cannot be taken as unequivocal evidence for alternating reducing and oxidizing furnace conditions. Nevertheless, it suggests that the smelting environment was not perfectly homogeneous and may have experienced localized fluctuations in redox conditions.

The occurrence of sulphide matte droplets trapped in the slag matrix in the Rosen ore field and Krushevets slags further supports this interpretation. These droplets represent incompletely oxidized sulphide phases derived from the original ore and indicate incomplete desulphurisation during smelting. In contrast, Boyadzhik slags lack sulphide phases and contain copper mainly as oxidised forms (Cu_2O and Cu–Fe oxides), suggesting the smelting of oxide-rich copper ores rather than sulphidic feedstock. Nevertheless, the presence of iron silicates indicates that smelting still occurred under predominantly reducing conditions. The coexistence of fayalite with magnetite and locally wüstite points to intermediate oxygen potentials during smelting.

Slag viscosity. It plays a key role in the efficiency of metal separation and is largely controlled by the FeO–SiO₂ ratio. Fayalitic slags generally exhibit relatively low viscosity, which facilitates the separation of metal droplets from the melt [9]. Accordingly, the fayalite-dominated slags from the Rosen ore field likely formed comparatively fluid melts that enabled partial separation of copper metal. Silica in slags may derive from gangue minerals in the ore, such as quartz or other silicate phases, or may have been intentionally added as a flux to regulate slag composition and viscosity. The higher silica contents observed in the Krushevets slags would increase melt viscosity [20], possibly explaining the relatively heterogeneous textures of these materials and the reduced mobility of metal droplets within the melt. In contrast, the Ca-rich slags from Boyadzhik likely developed modified melt structures due to the presence of CaO. Calcium acts as a network modifier in silicate melts and can reduce viscosity even at relatively high silica contents, thereby enhancing slag fluidity [20]. The elevated CaO contents observed in both bulk analyses and slag glass therefore likely played an important role in controlling melt behaviour during smelting. This Ca-rich composition may reflect the processing of copper ores associated with carbonate or calc-silicate gangue minerals.

Conclusions. The mineralogical and chemical investigation of archaeological slags from the eastern part of the Srednogorie metallogenic zone provides important insights into ancient copper smelting practices in the region. The studied materials are predominantly iron–silicate slags characterized by fayalite as the principal mineral phase. Their bulk compositions, dominated by Fe and Si, confirm a typical fayalitic slag type associated with the smelting of iron-rich copper ores. Mineralogical similarities between slags from the Rosen ore field and Krushevets indicate comparable smelting technologies based on sulphidic copper ores. Entrapped Cu–Fe–S sulphide droplets demonstrate incomplete desulphurisation and support smelting under predominantly reducing conditions. The associated fayalite–magnetite assemblages suggest local variations in oxygen potential during smelting and cooling. In contrast, Boyadzhik slags differ markedly in composition and mineralogy. The absence of sulphide matte suggest a distinct metallurgical regime related to the smelting of copper ore from the oxidation zone of

a copper deposit. Phase-diagram evaluation indicates smelting temperatures of $\sim 1050\text{--}1100^\circ\text{C}$ for Rosen ore field slags, $\sim 1150\text{--}1200^\circ\text{C}$ for Krushevets slags, and up to $\sim 1200\text{--}1300^\circ\text{C}$ for Boyadzhik slags. Differences in slag composition also reflect variations in melt characteristics and viscosity; melts with a high fayalite content are likely to be more fluid, whilst the calcium in the Boyadzhik slags acts as a modifier of the network structure. Overall, the results demonstrate the existence of several metallurgical regimes in the eastern Srednogorie region, reflecting adaptation of ancient smelting practices to different ore types and a well-developed understanding of metallurgical processes. This study provides the first integrated reconstruction of the main smelting conditions in ancient furnaces in the eastern Srednogorie metallogenic zone based on combined mineralogical and chemical analysis of archaeological slags.

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