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Composition of slag phases from an accidental find on the land of Gourkovo village, Balchik Municipality (NE Bulgaria). Preliminary data

Състав на фази от случайна находка на шлака в землището на с. Гурково, община Балчик (СИ България). Предварителни данни

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Introduction

Previous research (powder X-ray diffraction, optical microscopy, and SEM) revealed that the found slag fragments consisted mainly of crystalline fayalite and intersticial glass, and minor magnetite (Marinova, 2017). In places slag contains macroscopic to microscopic oval iron prills as well as minute troilite blebs a few microns across (Marinova, Tacheva, 2019). Here we present first data on the chemical composition of the already identified slag phases for further examination of the slag found and elucidation of the metallurgical activity which has produced it.

Material and methods

For this investigation, three slag fragments, found accidentally on the land of Gourkovo village, NE Bulgaria and provided by Georgi Dzhilyanov, were analyzed. The largest piece is 10×8×6 cm in size (Marinova, 2017). From each of them a polished section was prepared whose composition was determined by electron probe microanalysis (EPMA). Composition of the slag phases was obtained by energy dispersive X-ray spectrometry (EDS) using ZEISS SEM EVO 25 LS–EDAX Trident at acceleration voltage of 15 kV and beam current of 500 pA. Standardless software normalized the results to 100% for all the oxides or elements present in the spectra of the minerals/phases analyzed. The authors used the EDS analysis for quick preliminary semi-quantitative qualification of the slag material available. Further more precise wave dispersive analyses are planned for quantitative determinations.

Results

The main slag mineral fayalite (5 EDS analyses) contains traces of MgO (below 2 wt%), CaO (below 1 wt%), and Al_2O_3 (up to 0.5 wt%). Fayalitic component varies from 94 to 99% mol%, while forsteritic one – from 6 to 1 mol%.

Intersticial glass (6 analyses) is ferrous, calcareous and aluminous, and displays wide compositional variations: besides the major SiO_2 (38–41 wt%), FeO (16–27 wt%) and Al_2O_3 (14–19 wt%), it contains significant amounts of CaO (7–14 wt%) and K_2O (2–8 wt%) as well as traces of MgO and TiO_2 (both below 1 wt%), Na_2O (up to 1.6 wt%), P_2O_5 (below 3 wt%), SO_3 (up to 0.6 wt%), and in two analyses MnO (below 1 wt%).

Magnetite (7 EDS analyses) contains FeO from 30.8 to 31.8 wt% and Fe_2O_3 from 68.7 to 66.6 wt% as well as traces of Al_2O_3 (mostly <~1 wt%), SO_3 (below 1.5 wt%), and in some cases TiO_2 (below 0.6 wt%) and V_2O_3 (up to 0.2 wt%).

Iron prills (2 analyses) appear pure iron.

Troilite blebs (6 analyses) do not contain any trace element and display very narrow range of compositional variations. The content of Fe varies between 64 and 66 wt% while the one of S is in the range from 36 up to 34 wt%, respectively.

Discussion

As concluded by Marinova and Tacheva (2019) the lacking of copper prills found previously in ancient copper slags from SE Bulgaria (Stavrakeva, Tzankova, 2016) and elsewhere, and the presence of metallic iron prills found in our case mean that the studied slag appears an iron one.

The presence of fayalite and of Mg in the slag fayalite indicates smelting temperatures around 1200 °C which are common temperatures of the iron bloomery smelting (Miller, Killick, 2004; Török et al., 2012).

The stripped pattern displayed by one of the slag fragments investigated indicates flowing and fully molten state the slag has experienced. Unreacted submillimeter-sized angular quartz grains incorporated onto the outer surface of a slag fragment likely means that the slag was tapped from a furnace on the earth surface. The recognition of charcoal inclusions incorporated in the slag (Marinova, Tacheva, 2019) revealed the use of charcoal for ore reducer.

The significant amount of elemental iron in the slag studied means a respective significant loss of metal from the ore into the slag which is characteristics of the pre-industrial iron smelting.

The presence of magnetite instead of wustite, the latter being most common in ancient both iron and copper slags, means an incomplete reduction of iron oxides of the iron ore used (typical of primitive pre-industrial iron smelting as elucidated in numerous literature) and more oxidizing conditions than the usual ones (Miller, Killick, 2004) but the exact reason is unknown. Possible reasons are the lower charcoal-to-ore ratio or higher ventilation (i.e. higher air-to-ore ratio) both producing more oxidizing furnace atmosphere (Charlton et al., 2010).

The contents of SiO_2, FeO_t, P_2O_5, and Na_2O of both fayalite and glass studied appear common for slags obtained in the iron bloomery smelting worldwide (which appears "solid state reduction of iron oxides into a spongy mass of iron called a bloom and the production of a ferrosilicate slag") (Charlton et al., 2010). Our EDS analyses display a peculiarity in the slag glass composition with higher amounts of Al_2O_3, CaO and K_2O compared to slags from iron bloomery smelting (Paynter, 2006; Charlton et al., 2010; Thiele, 2010; Török et al. 2012; Olovčić et al., 2014; Benvenuti et al., 2016; Lareina-Garcia et al., 2018). As it is well known, metallurgical slag obtains its chemical composition by contributions from ore, furnace lining, fuel (charcoal) and possibly flux. Commonly, the presence of SiO_2, Al_2O_3 and CaO are being ascribed to contribution from the furnace lining (mainly quartz-rich clay), while the one of P_2O_5, K_2O and Na_2O – from the charcoal (review in Paynter, 2006). Other results indicated that SiO_2, Al_2O_3, MgO, CaO, and P_2O_5 contributed in some extent to the slag from the ore (Pyanter, 2006; Thiele, 2010; Charlton et al., 2010) as well as CaO and MgO – partly from the charcoal (Crew, 2000; Charlton et al., 2010; Török et al. 2015; Benvenuti et al., 2016). Sulfur derives from the charcoal since biomass ash commonly contains S (Charlton et al., 2010; Benvenuti et al., 2016; Vassilev et al., 2017). Generally, charcoal contributes only to about 5 wt% to the slag composition (Crew, 2000). In our case, the considerably high amounts of Al_2O_3, CaO and K_2O in the slag glass indicate significant contribution from the furnace lining and/or ore and/or charcoal but this issue cannot be clarified without archaeological excavation to elucidate the smelting technology and for finding furnace remains.

The episodic presence of MnO in the slag glass, moreover in very low contents, and the amounts of Mn and P in the iron prills below the detection limit of EDS (~<0.05 wt%) mean that the use of bog ore is unlikely. Common bog ores have high Mn and/or P contents which significantly contribute to the iron slag: to several wt% MnO and to 1–2 wt% P_2O_5 (e.g. Paynter, 2006; Charlton et al., 2010; Török et al., 2015). On the other side, the presence of Ti and V traces in the slag magnetite indicates a possible magmatic origin of the ore used in the smelting (Kanurkov, 1988).

There are pusblished data, collected from NE Bulgaria about small-scale Roman and Medieval iron metallurgical activities around the towns of Rouse, Silistra, Shumen, Preslav and Dobrich using on-shore magnetite sands or limonitized pyrite concretions (from Cretaceous limestones) and charcoal for ore reducer (Georgiev, 1978). Further to the north, in Romania (to the east of Danube River), there are data about iron metallurgy since 10th CE BC and usage of local iron ores (Ailincai, 2016). In SE Bulgaria documented iron mining (of hematite and limonite) and iron smelting are known for the area of Sliven town, East Balkan Mountains (during Antiquity and Middle ages – Gospodinov, 2015); Vulche Pole village – Haskovo District, East Rhodopes Mountains from alluvial pieces (X–I century BC – Tsintsov et al., 2006), and for Apolonia Pontica (VI–V century BC), Strandzha and Sakar Mountains from magnetite sands (Orachev, 2018). Excavation is needed for elucidation the archaeological context and dating of the slag from the Gourkovo village. To reveal the ore provenance, sampling and analysing of different iron ore sources and comparison to the composition of the already identified slag phases are required.

Conclusions

1. The mineral and chemical compositions of the studied slag fragments, with the absence of copper prills and the presence of metallic iron prills indicate an origin from direct iron bloomery smelting activity.

2. The high loss of iron from the ore into the slag reveals low efficiency of smelting, characteristic of the pre-industrial iron bloomery smelting.

3. For elucidation the archaeological context and smelting technology, and the slag dating archaeological excavation is needed, while for ore provenance – sampling and analyzing of different iron ore sources and comparison to the chemical composition of slag phases already identified.

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