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Slag from Modern Copper Production Found in Bergwerk, Burgenland, Austria

Roland Haubner[1,a*] and Susanne Strobl[1,b]

[1]TU Wien, Institut für Chemische Technologien und Analytik,
Getreidemarkt 9/164-CT, A-1060 Vienna, Austria

[a*]roland.haubner@tuwien.ac.at, [b]susanne.strobl@tuwien.ac.at

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Abstract. The investigated slags from Bergwerk (Burgenland, Austria) are from the 17th century and a byproduct of a copper smelting process. These slags are typical plate slags but metallographic studies have shown that these slags are atypical compared to alpine slags. There is an elongated texture running across the slag but the typical fayalite dendrites are absent. Noticeable are high sulfur and Fe levels. SEM-EDX element mappings show that FeO and FeS coexist locally, suggesting that a eutectic FeO-FeS mixture exists. The melting point could have been lowered to 930 °C by the FeO-FeS eutectic. $CaSO_4$ was also detected in the slag. The glass phase, containing all the slag impurities, is located between the fayalite and the FeO-FeS mixture. The smelting process, in which these slags were formed, is currently unknown. It has been unproven as well, what advantages such a copper smelting process could have.

Introduction

Bergwerk is a small village in the district of Oberwart, Burgenland. Its Hungarian name was Öribanya. In the 17th century copper and iron were mined and smelted. During an archaeological excavation in 1985 K. Kaus collected the examined slags.

Along the Alps, especially in the Greywacke zone, there are many ore deposits that had been mined and smelted since the Bronze Age. Here are a few of numerous publications cited [1 - 3].

It should be mentioned that slags show differences in chemical composition and can have additionally a very inhomogeneous structure, especially if slags were not completely melted or the slags are mixed with sand during tapping. This should be taken into account when investigations and interpretations of process conditions were undertaken [4 - 6].

Agricola [7, 8] described several methods for medieval copper smelting, although it is difficult to relate slags to an individual process step.

The same can be said about the books dealing with the early metallurgy in Europe, written by Tylecote [9].

Experimental Procedure

The slag samples. All examined slags are typical plate slags. In Fig. 1 two of these slags are shown before cutting.

Metallography. The samples were sectioned with a cut-off machine and cold mounted in epoxy resin. Metallographic preparation started with a plane-grinding disc, followed by polishing with 9 – 1 µm diamond suspensions. The polished samples were investigated by a light optical microscope (LOM), a scanning electron microscope (SEM) and energy dispersive x-ray analyzer (EDX).

The elemental compositions of the slags were determined by X-ray fluorescence analyses (XRF).

Evaluation of the slag analysis. To compare chemical compositions of slags, the $FeO-SiO_2-CaO$ phase diagram was used. In previous work it had been shown that the Al_2O_3 and MgO contents should be included to CaO in the calculations to give realistic values for melting temperatures in the phase diagram [10 - 12].

Fig. 1 Plate slag from Bergwerk. Two of the examined samples.

Results and Discussions

Microstructure of the slags. Typical structural areas of the slags are compiled in Fig. 2. There would not be enough space to discuss all the slags individually.

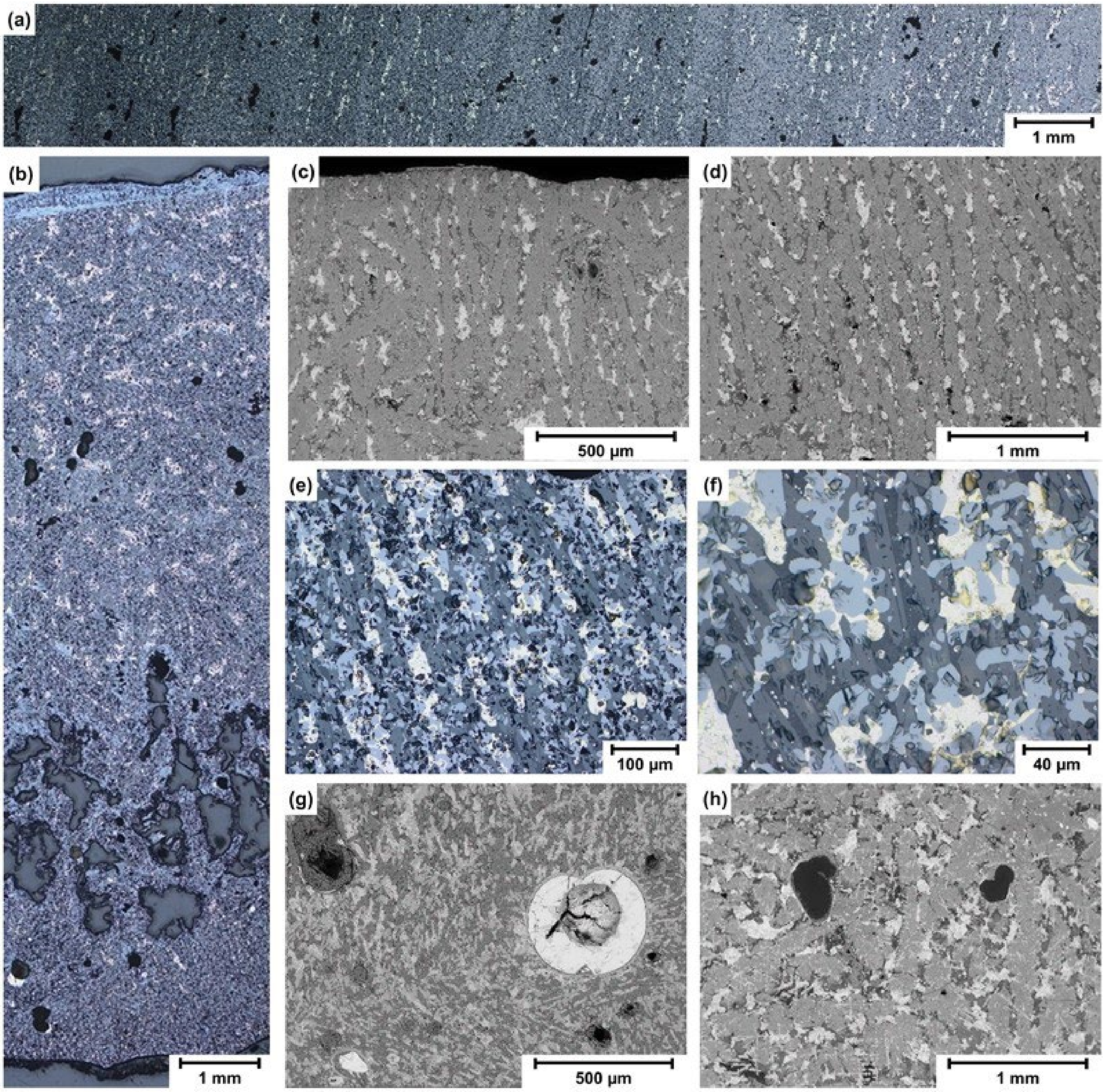

Fig. 2 Copper slag samples from Bergwerk. (a, b) cross sections in LOM, (c, d, g, h) slag microstructures in SEM, (e, f) details of the microstructure in LOM.

The first glance at the structure of the slags already shows that it is not a Bronze Age slag structure. The different phases are arranged in a line with a preferred orientation from the top to the bottom of the slag. In Fig. 2a you can see that this texture extends over the total sample area. In Fig. 2b you can see that the texture also extends over the whole thickness. A few elongated pores can be seen near the bottom of the slag in this figure. At higher magnifications the SEM and LOM images show a significant mix of differently colored phases (Fig. 2c - f). Occasionally, particles with an increased Cu content (Fig. 2g) or $CaSO_4$ inclusions (Fig. 2h) are visible.

Chemical composition of the slag. XRF measurements were carried out on the examined slags (Table 1). Noticeable is that these slags contain between 3.7 and 6 wt. % S. The Cu content varies between 1.7 and 0.4 wt. %.

SEM-EDX analyzes were performed to obtain more detailed information about the structure of the slag (Fig. 3). Spot analyzes were also calculated for entry in the FeO-SiO_2-CaO phase diagram. Area analyzes were carried out from the two image sections in (Fig. 3a, b) and entered into the phase diagram (Fig. 3c). It can be seen that both values are clearly in the range of wustite. In case of spot measurements, the values are in the area of the phase boundary wustite-olivine, or near the ternary eutectic olivine-wollastonite-SiO_2. Local measurements show, that besides olivine are mixed FeO and FeS areas (Fig. 3b).

SEM-EDX element mappings were performed for a better understanding the interrelationships between microstructure and element distribution (Fig. 4, 5).

Some statements can be argued from the measurements:

- A mixture of oxides and sulfides is present.
- Copper is associated with the sulfide phase.
- Iron exists as oxide (FeO), sulfide (FeS) and silicate (olivine).
- A network of silicates (SiO_x) is interrupted by oxides and sulfides.
- Al, Ca, K, Na are next to each other.
- Mg is associated with Fe_2SiO_4 (olivine).

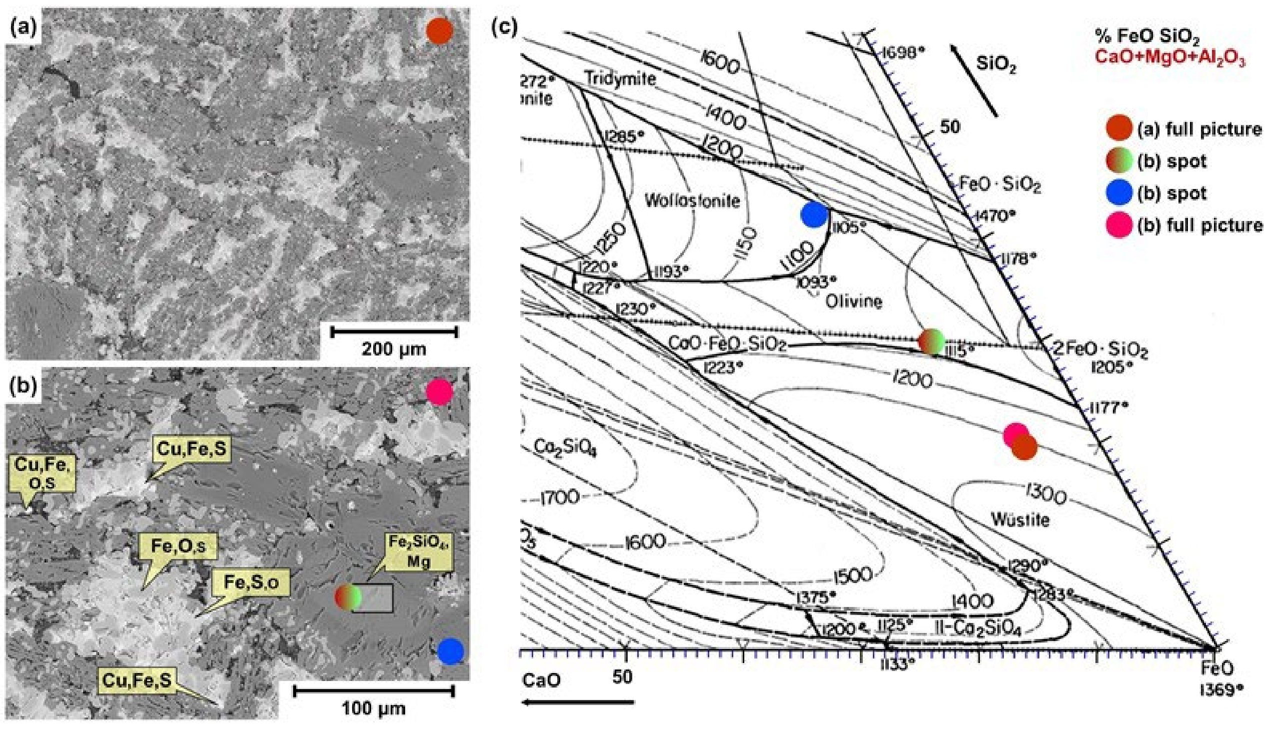

Fig. 3 SEM-EDX analyzes. (a, b) SEM images with marked points or areas where EDX was performed, (c) FeO-SiO_2-CaO phase diagram with the compositions calculated from the EDX analyses.

Table 1 Results of the XRF measurements of the investigated slags

wt. %	Bergwerk 1	Bergwerk 2	Bergwerk 3	Bergwerk 4
Fe	69.11	64.31	66.98	58.68
Cu	**1.73**	**1.09**	**0.90**	**0.41**
Si	13.29	17.57	17.14	20.4
S	**5.97**	**5.58**	**4.08**	**3.69**
Ca	2.84	2.62	2.62	4.9
K	1.93	2.11	1.83	3.39
Al	3.04	3.54	3.93	4.82
Mg	0.64	1.77	1.16	1.22
Na	0.87	0.61	0.59	1.29
Zn	n.n.	0.21	0.07	0.27
Ti	0.58	0.53	0.70	0.81
Mn	n.n.	0.06	n.n.	0.07
P	n.n.	n.n.	n.n.	0.05

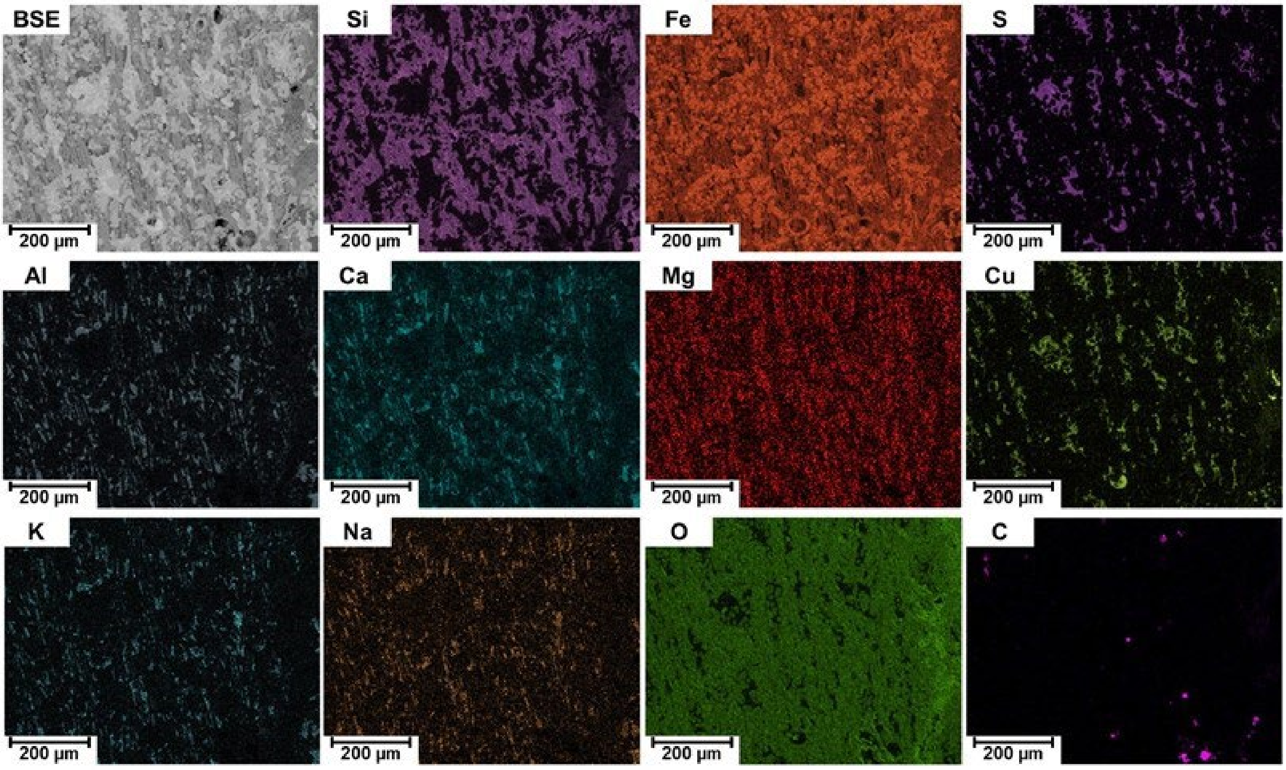

Fig. 4 SEM-EDX element mapping of a typical slag region.

The regions consisting of FeO and FeS suggest that they were formed from the FeO-FeS eutectic. It is characterized by a low melting point of 930 °C [13 - 15]. Since the melting point of the FeO-FeS eutectic is well below the lowest melting temperature in the FeO-SiO_2-CaO phase diagram (1093 °C), this would mean that these conditions were chosen intentionally to be able to work at lower temperatures or to get a more fluid slag.

It is already known from the Bronze Age slag that Mg is preferentially incorporated into the fayalite [10].

The other elements (Al, Ca, K, Na) and SiO_2 form the so-called glass phase. Due to the complex composition its melting range is unknown.

Regarding the presence of $CaSO_4$ (Fig. 2f - h) in the slag, it could had been added during production, or it could have been formed by weathering during storage.

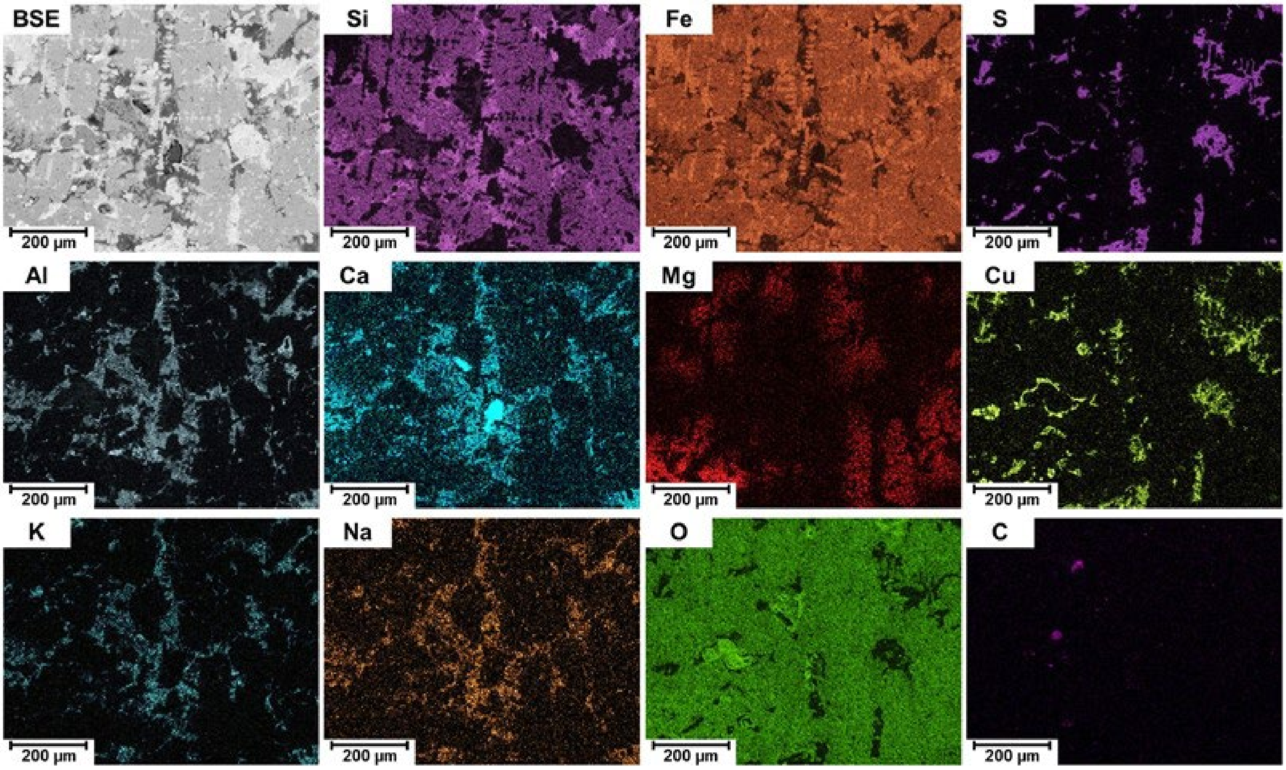

Fig. 5: SEM-EDX element mapping of a slightly different but again, typical slag region.

Considerations of the copper smelting process. Bronze Age copper smelting appears to be well understood in terms of smelting processes and the associated chemical reactions [4, 11, 16]. The investigated slags are generally very similar and can be classified as fayalite type. Differences are usually in the chemical composition, which affects the phase fractions.

Agricola [7, 8] described several methods for medieval copper smelting, whereby it is difficult to relate the slag to an individual process steps, because medieval, well-documented copper slags have not yet been examined.

The same can be said about the books, written by Tylecote, because in the numerous process descriptions there is none that could explain the formation of the slag from Bergwerk [9].

Summary

The copper slags from Bergwerk show an atypical morphology compared to Bronze Age alpine slags. A kind of elongated texture was observed, running from the top to the bottom of the slags.

The main difference to previously examined slags is the presence of areas with FeO and FeS mixtures, which were originated by a eutectic melt. This eutectic has a melting point of 930 °C.

The remaining fractions in the slags consist of fayalite (Fe_2SiO_4) and glass phase, which compositions correspond with that of conventional slags. Mg is preferentially incorporated into fayalite, whereas the other trace elements are in the glass phase.

Occasionally $CaSO_4$ inclusions were observed in the slags.

Copper is present as Cu_2S and is associated with the FeS.

When the analytical results are drawn in the FeO-SiO_2-CaO phase diagram, the concentrations of FeO are higher, because S (bonded in FeS) is not taken into account in the calculations.

The metallurgical process that led to the presented slags is unknown.

It has not yet been clarified whether this method of copper extraction has technological advantages.

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