Mineralogy and composition of historical Cu slags from the Rudawy Janowickie Mountains, southwestern Poland

Authors: Jakub KIERCZAK*, Anna PIETRANIK**

University of Wroclaw, Institute of Geological Sciences, ul Cybulskiego 30, 50-205 Wroclaw, Poland

* Corresponding author: jakub.kierczak@ing.uni.wroc.pl Tel. +48 (0) 713 759 296, Fax +48(0) 713 759 371

** Email address: anna.pietranik@ing.uni.wroc.pl
Abstract

Two types of slags produced during historical smelting of Cu ores occur in the Rudawy Janowickie Mountains, southwestern Poland. The prevailing massive slag has chemical composition dominated by FeO (up to 51 wt %), SiO$_2$ (up to 43 wt %) and Al$_2$O$_3$ (up to 12 wt %). It consists of silicate glass, olivine and hercynite. The second type porous slag is poorer in FeO (up to 28 wt %) and richer in SiO$_2$ (up to 70 wt %). It comprises two types of silicate glass, olivine, ferrosilite and SiO$_2$ group minerals (cristobalite and quartz). The morphology of olivine crystals, phase assemblages, phase chemistry and distribution of trace elements in slag phases vary from sample to sample, which is consistent with different cooling rates. Phase diagrams used in this study indicate that most of the slag samples have solidified under strong disequilibrium conditions caused by rapid cooling. Careful investigation of cooling conditions is essential to predict a susceptibility of slags to weathering and to reconstruct historical smelting conditions. For example, samples with longer cooling times are more resistant to weathering and they also should be used to reconstruct the temperature of slag formation.

Mineralogical and chemical study of Rudawy Janowickie slags and comparison with other historical slags in Europe indicates that: (i) temperature of slag formation was ca. 1200°C and overlaps with temperature ranges estimated for other historical slags, (ii) furnace charge was either self fluxing or silica was added as a flux, which is not so common for historical Cu slags but was observed for smelting of Pb and Ag ores in Czech Republic (iii) preliminary roasting of furnace charge was efficient similarly to other historical Cu-smelters (iv) the furnace atmosphere was reducing also similarly to other historical smelting processes.

**Keywords:** slag, mineralogy, disequilibrium, smelting, Cu ores, archaeometallurgy,
1. Introduction

Several sites of historical Cu-mining and smelting were important in Lower Silesia (southwestern Poland): Miedzianka, Ciechanowice and Janowice Wielkie (Fig. 1).

Miedzianka was the largest center for mining and smelting of metals such as Cu, As and Ag in Silesia (Dziekoński 1972). Mining and smelting near Miedzianka peaked in 16th century and produced voluminous slag as a by-product. Slags were deposited in the nearby area of the Rudawy Janowickie Mountains and presently form unconfined heaps covered by forest. Slag particles are also transported by streams and are distributed within soils and streambeds. Such long-term deposition of slags may pose an environmental risk. The extent to which slags interact with the surrounding environment is controlled by their texture and primary mineral composition. This study involves the detailed textural, mineralogical and chemical characterization of the slags. We focus on primary structure and minerals, which may vary widely in historical slags depending on the charge composition, smelting conditions and cooling time (Bachmann 1982; Maldonado & Rehren 2009; Heimann et al. 2010). We show that the slags in the Rudawy Janowickie are characterized by different cooling rates of the melt, and we describe how these different rates affect slag properties (e.g., phase composition and metal distribution). Such a study provides valuable information about slag waste which can be used as a basis for further environmental research. We also reconstruct some information on historical smelting process applied during the reworking of Cu ores in Poland. We compare our data with those available for other historical European smelting sites in order to create a database, which may be useful for future environmental studies dealing with stability of slags.
2. Geological settings of the study area

The Rudawy Janowickie area (RJ) is a mountain range in the Sudetes of southwestern Poland (Fig. 1). The western part of RJ is composed of Variscan granitoids (ca. 300 – 350 Ma old), and the eastern part is composed of Proterozoic and Paleozoic metasedimentary and metaigneous rocks: mylonitized gneisses, amphibolites, greenschists, quartzofeldspathic schists, chlorite schists and phyllites (Winchester et al. 1995). The hydrothermal solutions related to the Variscan granitoids intruded into the surrounding metamorphic rocks, forming polymetallic (Cu, As and Ag) mineralization. The ore in RJ forms veinlets along in fracture planes within amphibolites, greenschists, chlorite and mica schists. The ore minerals are mainly chalcopyrite with minor bornite and pyrite (Dziekoński 1972).

3. Mining and smelting history in the Rudawy Janowickie Mountains

The RJ was dominated by mining activity since medieval times. The exploitation of ores in the area was focused in the vicinity of the towns Janowice Wielkie and Miedzianka (Fig. 1). In the 14th century, Miedzianka was the largest center for mining and smelting of metals such as Cu, As and Ag in Silesia (Dziekoński 1972). Historical sources describe mining activity in Miedzianka as early as in 1310. Since then, exploitation recommenced several times before it ceased entirely in 1925, leaving unattended mining pits and dumps. The ore was exploited mainly in pit shafts and processed in smelters located close to Janowice Wielkie and Miedzianka. The 16th century brought on the greatest prosperity of mining and smelting activities in the area with, ca. 160 pit shafts being active near Miedzianka. Historical sources from the 16th century described also reprocessing of the older slags covered by newly formed secondary minerals (probably sulphates). The sulphates were an additional source of copper and were obtained by the leaching method, characterized by low costs and relatively easy application (Dziekoński 1972). At the end of the 16th century, the mining activities exhausted
the richest metal resources, and the exploitation was in decline until the end of the 17th century. A more favorable period for industrial activities in RJ started at the beginning of the 18th century and lasted until the beginning of the 19th century. The ore mined at that time was Cu-rich; the average copper content reached from 1.2 up to 3.8 wt.% Cu. After that, several periods of increased mining activity occurred in 19th and 20th centuries, but did not yield a significant amount of the ore e.g., in 1905 and 1906, the entire mine run was only 15 tonnes: Dziekoński 1972).

The total metal production in the RJ area has been estimated at around 2000 t of copper, 800 kg of silver and 200 t of arsenic on the basis of historical data and the cubic capacity of slag dumps located in RJ (Dziekoński 1972).

4. Sampling and analytical methods

4.1. Sampling.

The slag samples were collected south of Janowice Wielkie, in the vicinity of two streams: the Janówka and the Smelter streams (50°52′26″N, 15°55′12″; Fig. 1). These slags represent by-products of smelting processes applied between 14 and 16th century (as known from historical sources and reviewed in Dziekoński 1972). At this time the exploited ore was handpicked and only the fragments rich in ore minerals were processed, while the remaining gangue was discarded. Field observations of the waste rocks dumps, located in the vicinity of Miedzianka (Fig. 1), revealed the presence of secondary phases issued from weathering of the ore. These phases are mostly represented by iron oxyhydroxides (hematite, limonite) and copper minerals such as chrysocolla and malachite. However, unweathered fragments of the ore (composed of chalcopyrite) can still be found. Waste materials (including slags and mining wastes) left over after metal processing were abandoned in the area of the Rudawy
Janowickie, without any control on their environmental impact. Neither waste rocks nor slags were used in any way (e.g., road beds).

The original historical distribution of slag dumps was most probably disturbed by downstream transport. At present, the slags occur within three types of environments: (1) at the surface, (2) in soils, and (3) in streambeds of the Janówka and Smelter streams. We collected a set of 25 slag samples from all three environments. The dominant type of slag, labeled massive slag, is black, has aphanitic, massive texture and occurs in all three environments (Fig. 2a). The second type, labeled porous slag, is highly porous and contains pieces of unmelted quartz gangue (Fig. 2b). It occurs only at the surface and within soils, but it is not present within streambeds. The fragments studied are isometric, with size ranging from a few to dozens of centimeters across, with the exception of slag fragments collected from streambeds, which are pebble-shaped. For the detailed study of chemical and phase composition of historical slags from the RJ, we selected 12 samples (Fig. 3).

We also collected 3 samples of waste rocks from the waste rock heaps located in the vicinity of Miedzianka (Fig. 1) in order to obtain some information about the nature and composition of the smelting charge.

4.2. Mineralogical analyses.

Phase assemblages were identified using optical microscopy, scanning electron microscopy (SEM) and X-ray powder diffraction. After petrographic observations, selected polished thin sections were studied using a scanning electron microscope HITACHI S-4700 equipped with EDX analysis system (in Laboratory of Field Emission Scanning Electron Microscopy and Microanalysis at the Institute of Geological Sciences of the Jagiellonian University, Kraków). X–ray powder-diffraction (XRD) patterns for selected samples were obtained from 4° to 90°
2θ, at rate of 1.2° 2θ min⁻¹ (SIEMENS D5005 diffractometer with CoKα radiation housed at the Institute of Geological Sciences, University of Wrocław). The phase compositions were established on two electron microprobes: a CAMECA SX100 (at the Štátny geologický ústav Dionýza Štúra in Bratislava) and a CAMECA SX50 (at the Université de Paris Jussieu - CAMPARIS). Analytical conditions for both instruments were 15 kV accelerating voltage, 10 nA beam current, and counting time 10 s for all the elements. The following set of standards was used: fayalite (Si, Fe), forsterite (Mg), Al₂O₃ (Al), orthoclase (K), wollastonite (Ca), TiO₂ (Ti), rhodonite (Mn), GaAs (As), CuFeS₂ (Cu) and willemite (Zn). The detection limits of As and Cu were ~ 500 ppm and of Zn was ~ 700 ppm.

4.3. Bulk chemical analyses.

Bulk chemical analyses were performed on pulverized slag samples in the ACME Analytical Laboratory (Vancouver, Canada) using ICP–ES for major elements and ICP–MS for trace elements. Total digestion of the material was carried out by melting the sample with LiBO₂/Li₂B₄O₇ and dissolving the residue with nitric acid. The analytical reproducibility (2σ), as estimated from eight analyses of standard DS7, ranges from 3 (Zn) to 16% (Cu) at 95% confidence limits. Analytical accuracy (2σ), as estimated from measurements of standard DS7 is from 3.5 (Zn) to 9% (As) at 95% confidence limits.

5. Slag characteristics

5.1. Petrography and phase assemblages.

On the basis of mineralogical analyses, we divided the slags in three subtypes, each characterized by a different phase assemblage (Fig. 3). Massive slag comprises two subtypes, the first subtype consists of opaque silicate glass and olivine (phase assemblage 1; Fig. 3a), whereas the second subtype is characterized by presence of spinel, olivine and opaque silicate
Porous slag is classified as the third subtype and comprises pyroxene, olivine, cristobalite, two types of glass (opaque and translucent) and fragments of unmelted quartz gangue (phase assemblage 3; Fig. 3c).

Both types of slags contain numerous inclusions of sulfides (bornite, pyrrhotite) and metallic phases (metallic Cu and Pb) as well as secondary phases issued from slag weathering (e.g., malachite, brochantite). These phases are environmentally important as they concentrate metals and metalloids in slags. Furthermore, presence of secondary phases indicate that studied slags are not inert. However in this paper we focus on an analysis of volumetrically major components of the RJ slags (silicates, oxides and glass) with special attention on slag textures and formation conditions which determine slag stability during weathering.

Olivine occurs in all subtypes and is characterized by variable habits in different samples. It forms feather-like crystals up to 1 cm long (Fig. 4a), as well as large skeletal laths up to 1 cm long (Fig. 4b) or subhedral to euhedral crystals ranging in size from 10 to 100 µm (Figs. 4c, d). Spinel occurs only in the second phase assemblage and forms small (from 5 to 50 µm) euhedral crystals occurring as inclusions within olivine and as single grains in the glassy matrix (Fig. 4d). Pyroxene occurs only in the third phase assemblage and forms elongate, skeletal crystals of size ranging from 50 to 500 µm within the glassy matrix. It is also observed as small acicular crystals (up to 50 µm) located at a boundary between partially melted quartz crystals and translucent glass (Figs. 4e, f). The SiO₂ minerals are present as either fractured and partially melted grains ranging from 0.1 to 5 mm in diameter (Figs. 2b, 4e) or small (up to 50 µm long) euhedral crystals. The former represents fragments of unmelted gangue and the latter formed during crystallization of the slag melt. According to XRD analyses, the SiO₂ minerals correspond to cristobalite rather than quartz (Fig. 3c). Glass from the first and second assemblages (massive slag) is unvariably black under polarizing microscope (Figs. 4b, c), whereas in the third assemblage (porous slag) two types of glass
occur. The first type corresponds to black and opaque glass described in the first two
assemblages, the second type of the glass type is brownish and translucent and is located
within the grains of cristobalite and unmelted quartz (Figs. 4e, f).

5.2. Chemical composition of slag phases

The chemical composition of identified slag phases is included as supplementary material
(Table SM1). Below we give a general characteristic of all phases.

Glass

Chemical composition of glasses from each slag assemblage is dominated by SiO$_2$, Al$_2$O$_3$ and
FeO. These oxide components occur in different proportions but invariably constitute ca. 90
wt. %. The aluminum content in glass from the phase assemblage 2 reaches up to 28 wt%,
whereas it never exceeds 20 wt% of Al$_2$O$_3$ in the glass from the two other assemblages.
Translucent glass from the porous slag is silica rich (69-77 wt% of SiO$_2$) and contains smaller
amounts of FeO (6-15 wt%) and Al$_2$O$_3$ (5-9 wt%) than the black, opaque glass. The Zn
content in glass from the first and third assemblages is similar and generally ranges from 2000
to 4000 mg kg$^{-1}$. Glass from the second assemblage contains lower amounts of Zn than the
other glasses, but locally it contains up to 1% of Zn (Fig. 5).

Olivine

We analyzed olivine crystals only from the massive slag (phase assemblages 1 and 2). Olivine
is the most common crystalline phase in the slags. Its chemical composition is defined by
forsterite-fayalite solid solution (Mg$_2$SiO$_4$ – Fe$_2$SiO$_4$). Olivine from the phase assemblage 1
has a higher fayalite content than that from the second assemblage (Fig. 6). Olivine crystals
from both assemblages contains considerable amounts of Zn (up to 1 wt%; Fig. 6d), and the
Zn content in olivine from phase assemblage 2 is more variable than that in olivine from assemblage 1 (Fig. 6b, d).

Other phases

The chemical composition of pyroxene is close to ferrosilite – Fe$_2$Si$_2$O$_6$ (from 66 to 87 mol.% of ferrosilite). Also, the pyroxene contains up to 8340 mg kg$^{-1}$ of Zn.

The chemical composition of spinel is close to pure hercynite (FeAl$_2$O$_4$). The hercynite contains considerable amounts of Zn (up to 5.2 wt% of ZnO).

5.3. Bulk composition of the slags

The chemical composition of massive slag is dominated by FeO (up to 51 wt. %), SiO$_2$ (up to 43 wt. %) and Al$_2$O$_3$ (up to 12 wt. %; Table 1). Porous slag is poorer in FeO (up to 28 wt. %) and richer in SiO$_2$ (up to 70 wt. %) than massive slag (Table 1). Minor amounts of MgO (up to 4 wt. %), K$_2$O (up to 4 wt. %) and CaO (up to 2 wt %) also occur in both types of slag (Table 1). All slags show elevated concentrations of Cu (up to 1.34 wt %), Zn (up to 4906 mg kg$^{-1}$), Pb (up to 268 mg kg$^{-1}$) and As (up to 131 mg kg$^{-1}$; Table 1). In general, the porous slag is slightly enriched in these metallic elements compared to massive slag. The sulfur content in the slags does not exceed 1 wt. %, and its content is lower for porous slag than for massive slag (Table 1).

The viscosity index ($v.i.$) was calculated using the method proposed by Bachmann (1982) and frequently used for historical slags. This method is based on the ratio of “basic” (CaO, FeO, MgO, MnO, K$_2$O, Na$_2$O) to “acidic” (SiO$_2$, Al$_2$O$_3$) oxides. Massive slag yields higher values of the viscosity index, ranging from 0.9 to 1.5, than porous slag, which has a viscosity index lower than 0.6 (Table 1).
6. Discussion

6.1. Modern and historical slags

Pyrometallurgical slags are by-products of base-metal smelting and steelmaking processes, but they found wide spectrum of applications. Slags produced during the last century were used in road construction (Xue et al. 2006), as cement additives (Shi & Qian 2000) or as adsorbents in on-site wastewaters treatment systems (Drizo et al. 2002). Numerous studies present detailed physicochemical and mineralogical characteristic of these modern anthropogenic materials (Proctor et al. 2000; Acosta et al. 2001; Waligora et al. 2010) in order to find the best application for the particular material. On the other hand, the pyrometallurgical slags originating from base-metal smelting often concentrate considerable amounts of metals and metalloids (Ettler et al. 2001; Lottermoser 2002; Puziewicz et al. 2007; Piatak & Seal 2010; Vitkova et al. 2010) and, once in place, they may undergo potentially harmful interactions with surrounding soils, sediments and waters (Sobanska et al. 2000; Ettler et al. 2004; 2005; Seignez et al. 2006; Bril et al. 2008). Primary texture, phase composition and distribution of metals between different phases in slags provide information on the possible future behavior of the slags. In this aspect studying historical smelting sites is particularly important because it gives one the possibility (i) to observe the long-term behavior of slag-environment interactions (ii) to study interactions between historical slags and old mortars and cements, reported to contain slag particles (Bartz & Filar 2010), and (iii) to predict the environmental consequences related with present storage and present applications of slags. Below we discuss these features of the RJ slags, which may affect their long-term behavior.
6.2. Cooling and crystallization of slags: How far from equilibrium?

Historical slags were often air-cooled and the cooling rates could vary depending on the amount of the deposited slag. Numerous experiments on rocks showed that such different cooling regimes affect not only crystal morphology and glass to crystal ratio (e.g., Conte et al. 2006), but may also affect partition coefficients between different phases and glass, and thus, the distribution of elements (Morgan & London 2003; Lofgren et al. 2006; Mollo et al. 2011). For example, Morgan and London (2003) and Lofgren et al. (2006) showed experimentally that partition coefficients for trace elements increase under conditions far from equilibrium.

Disequilibrium conditions generally apply to slags, which usually crystallize under much stronger disequilibrium conditions than rocks. We show that the properties of the RJ slags were also affected by disequilibrium crystallization.

Olivine morphology: The most striking feature of the slags is the morphology of the olivine crystals varying from slightly to strongly skeletal to dentritic. This feature was observed in many other slag samples worldwide (Parsons et al. 2001; Manasse & Mellini 2002a; Piatak et al. 2004; Ettler et al. 2009). In general, slags containing fayalite and spinel (Phase Assemblage II, Fig. 3) are characterized by less strongly skeletal olivine than the slags containing fayalite only (Phase Assemblage I, Fig. 3). The variable morphology of olivine crystals in slag samples is consistent with different cooling paths for different samples, from almost instant quenching to a period of several hours before complete crystallization (Fig. 4, Ettler et al., 2009).

Phase diagrams and temperature estimates: Disequilibrium conditions during slag crystallization can be well illustrated in phase diagrams. Such diagrams were constructed for ceramic purposes (Osborn & Muan 1960), but are also widely used to estimate temperatures of slag formation (Sáez et al. 2003; Tumiati et al. 2005; Ettler et al. 2009). However, the
Phase diagrams generally yield temperatures of 1400°C or more, exceeding those expected in metallurgical furnaces (Ettler et al. 2009; Maldonado & Rehren 2009); this is also the case for the RJ slags (Fig. 7a). Two primary factors may affect results obtained from the phase diagrams: (i) the diagrams were constructed for ternary systems, and slags often contain additional components such as Cu, Zn, Pb and other elements in amounts exceeding 10 wt. %; (ii) some of the initial furnace charge remains unmelted after smelting and, therefore, composition of the bulk slag does not equal the melt composition. None of the factors apply to the RJ slags, as the major components SiO$_2$, Al$_2$O$_3$ and FeO sum up to 90-98 wt % and unmelted material was not detected in massive slag. Figure 7 shows that most of the glass compositions plot in quartz stability field, but quartz was not detected in XRD (Fig. 3). The reason for the disequilibrium glass composition is preferential crystallization of olivine or olivine and spinel and the lack of quartz crystallization (Fig. 7). Three different patterns are observed in phase diagrams:

(i) All the massive slags containing fayalite only are characterized by linear trends in SiO$_2$, Al$_2$O$_3$, FeO diagrams and the lines join fayalite, bulk slag and glass composition (Figs. 7 b, c), which is consistent with the trends being controlled by disequilibrium crystallization of fayalite. If this is the case, all the temperatures estimated for glass crystallization are meaningless.

(ii) Massive slags containing olivine and spinel show two types of trends in a single phase diagram, one similar to that described in (i), consistent with disequilibrium crystallization of olivine, and the second one semi-parallel to the quartz-mullite cotectic line, consistent with disequilibrium crystallization of spinel and olivine (Fig. 7d). Temperatures of slag crystallization estimated from such trends are again meaningless. On the other hand, a slightly different trend is observed for slag JK0102 containing fayalite and spinel (Fig. 7e); the glass and slag composition do not plot on a linear trend, but rather some glass composition seem to
plot close to co-ectic lines between fayalite, spinel, sekaninaite (iron cordierite) and quartz.

Such glass composition may suggest that the crystallization of the JK0102 slag occurred close to equilibrium, which is also consistent with the least skeletal shapes of olivine crystals in this sample (Fig. 4d). Temperature estimates for this sample are more reliable than for the samples showing strong disequilibrium and are ca. 1200°C.

(iii) Porous slags also show two trends in the phase diagram (Fig. 7f), the first one controlled by disequilibrium crystallization of orthopyroxene, the major Fe-rich mineral in porous slags and the second one observed for silica-rich glass enclosed in cristobalite and pyroxene domains (Fig. 4f). A stability field of pyroxene in the SiO$_2$-Al$_2$O$_3$-FeO diagram does not exist at 1 atmosphere, but it does appear if the orthopyroxene is Mg-Fe solid solutions (Maldonado & Rehren 2009), as is the case in the RJ slags. The glass enclosed in the cristobalite and pyroxene domains (Fig. 4f) seems to be a mixture between: (a) the glass formed at the eutectic point for pure SiO$_2$-Al$_2$O$_3$ composition; such a glass would have been formed after melting of gangue material, which for RJ slags was quartz veins with small amounts of micas, and (b) the slag glass similar to that in massive slags, but richer in silica. The main implication for porous slags, coming from the glasses composition, is that temperatures recorded in this type of slag must have been higher than those recorded in massive slags, first to dissolve more silica-rich material in the slag glass, second to stabilize cristobalite, and third to melt gangue material along the SiO$_2$-Al$_2$O$_3$ join. The temperature required to stabilize cristobalite is 1470°C in the pure silica system, and the temperature to melt SiO$_2$-Al$_2$O$_3$ material is ca. 1600°C. However, presence of other fluxing elements as Ca, Na, K could have decreased the temperature by approximately 100-200°C.
The main implication from the phase diagrams presented in Fig. 7 is that it is important to identify slags that crystallized close to equilibrium as only those may give reliable temperature estimates in phase diagrams.

6.3. Which parameters are affected by disequilibrium crystallization?

Massive slags in RJ include two types of samples; those which crystallized under strong undercooling conditions and those, which recorded more moderate cooling. The latter are not typical in modern slags but give us opportunity to study effects of varying undercooling in slag samples. Generally, slowly cooled slags have potential to record changing temperature conditions; phases composition should thus be more variable compared to the composition of phases in strongly undercooled slags. Such a difference is observed in the fayalite content in olivine, which is varied from low to high values in slowly cooled slags and show a narrow span of high values for strongly undercooled slags (Fig. 6). Also, for strongly undercooled slags, the $\text{Fe}/(\text{Fe}+\text{Mg})$ value in bulk slag is similar to the $\text{Fe}/(\text{Fe}+\text{Mg})$ value in olivine, whereas olivine from slowly cooled slags has lower $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio than that in the bulk slag. Similarity between $\text{Fe}/(\text{Fe}+\text{Mg})$ value in the bulk composition and the solid-solution phase is probably induced by almost instantaneous drop of temperature below the solidus. Zinc in olivine from slowly cooled slags is also more variable and has both higher and lower values than the olivine from strongly undercooled slags, even for slags with similar Zn content in bulk composition (Fig. 6 b,d). On the other hand, glass in slowly cooled slags is poorer in Zn that the glass in strongly undercooled slags with similar bulk Zn contents (Fig. 5). The lower values in glass in slowly cooled slags are probably caused by crystallization of spinel, which has high Zn contents and can impoverish the melt in Zn.

Strong disequilibrium conditions may also affect the distribution of elements between different phases, as was shown experimentally (Morgan & London 2003; Lofgren et al.)
We were able to measure Zn contents in both glass and olivine and to calculate partition coefficients for both slowly cooled and strongly undercooled slags. Figure 8 shows that the calculated partition coefficients between olivine and melt vary from 0.2 to 8; the range is similar to that reported for basaltic rocks (0.8 – 3.4, GERM database). In general Zn is only slightly compatible, and its partition coefficient should not be strongly affected by conditions far from equilibrium (Morgan and London, 2003). Figure 8 shows, however, that slowly cooled slags seem to have slightly lower partition coefficients than strongly undercooled slags, which is consistent with experimental data showing that partition coefficients may increase in disequilibrium conditions (Morgan & London 2003, Lofgren et al. 2006, Mollo et al. 2011).

Summarizing, differences in cooling rate seem to affect the general characteristic of slags such as:

(i) Mineral assemblages; more phases occur in slowly cooled slags,

(ii) Mineral shapes; skeletal and dendritic morphology develops in strongly undercooled slags,

(iii) Composition of phases; all phases are more chemically variable in slowly cooled slags, e.g. solid solution phases are zoned,

(iv) Composition of glasses; glass seems to be impoverished in Zn in slowly cooled slags, where more phases crystallized and acted as a sink for Zn. Such phases, e.g., spinel in massive slag, are usually more stable than glass in surface conditions, which can affect mobility of heavy metals in the slag heap during its deposition and weathering (Ettler et al. 2001; Kierczak et al. 2009).
Partition coefficients; partitioning for compatible elements seem to increase in strongly undercooled slags; however, we were able to measure the partition coefficients only for Zn.

6.4. Reconstruction of historical smelting conditions

Multidisciplinary studies of historical slags allow us to reconstruct former smelting techniques and to show how metallurgy evolved through human history. Numerous studies were aimed at an estimation of historical smelting conditions through a mineralogical and geochemical approach. Slags may record information about smelting technologies (e.g., smelting temperature, furnace temperature, smelting efficiency). Also the chemical composition of a slag gives valuable information about starting furnace charge (Manasse et al. 2001; Ettler et al. 2009). Many of historical smelting sites are located in Europe and dated from the third millennium BC (Sáez et al. 2003) through the Roman times (Alvarez-Valero et al. 2009) and Middle Ages (Chaudhuri & Newesely 1993; Manasse et al. 2001; Manasse & Mellini 2002b; Tumiati et al. 2005; Ettler et al. 2009) up to the 19th century (Manasse & Mellini 2002a). Most of these studies describe historical slags from western Europe. Except for two regions located in the Czech Republic (Manasse & Mellini 2002a; Ettler et al. 2009), there are no data about historical smelting slags from central and eastern Europe. Below, we apply the information gained from chemical and mineral composition of the RJ slags to reconstruct smelting conditions in RJ and compare it with other sites of historical smelting in Europe (Table 2).

Smelting temperature and efficiency of metal extraction.

As was shown in the section on Petrography and Phase Assemblages most of the smelting temperatures for RJ slags obtained from phase diagrams are meaningless. Reliable temperatures of ca. 1200°C are yielded only from phase diagrams for slags crystallizing in
close to equilibrium conditions. The smelting temperatures obtained for RJ slags overlap with temperatures estimated for other historical slags (Manasse & Mellini 2002b; Tumiati et al. 2005; Ettler et al. 2009). However, high-temperature phases, such as cristobalite (if it is pure), indicate that temperatures during smelting of RJ Cu ores could locally exceed 1300°C, which is not common for historical smelting furnaces. Viscosity indices calculated for RJ slags range from 0.88 to 1.55 for massive slag and from 0.16 to 0.55 for porous slag (Table 1). Lower viscosity indices are consistent with less effective separation of metal form silicate melt, and hence lower efficiency of metal extraction for porous slag. This lower efficiency is confirmed by Cu contents observed in RJ slags as massive slags are generally poorer in Cu (3000 – 7200 mg kg\(^{-1}\)) than porous slags (5900 – 13400 mg kg\(^{-1}\)). In comparison, historical slags from Italy yield higher values of v.i. (0.79-3.74; Manasse et al. (2001) and Manasse & Mellini (2002b)), indicating more effective smelting process, whereas medieval slags from Bohutin Czech Republic, have lower v.i. (average 1.03; Ettler et al., 2009) and represent less efficient segregation of metals from silicate melt than that recorded in RJ slags.

**Smelting furnace atmosphere and roasting efficiency**

Historical sources (reviewed in Dziekoński, 1972) describe that the smelting process applied in Rudawy Janowickie consisted of: (1) pre-roasting in order to remove sulfur and (2) melting of the batch charge with the addition of flux (presumably silica) in order to separate molten metal liquid and silicate melt – slag. A slag may contain phases with variably oxidized iron, which may provide information about furnace atmosphere. Phases (e.g., magnetite) containing ferric iron indicate a large supply of oxygen during smelting, whereas ferrous-iron-rich phases such as olivine, pyroxene and hercynite, observed in RJ slags, indicate more reducing conditions. The furnace conditions recorded in the RJ slags are similar to other historical smelting furnaces, which also had a reducing atmosphere (Table 2). However, final steps of smelting process aiming to remove
residual iron and sulfur proceed under oxidizing conditions. This can lead to the formation of a porous slag through a phenomenon known as a slag foaming due to an excess of fine magnetite stabilizing sulfur dioxide bubbles. We therefore assume that the conditions during the final steps of smelting were oxidizing as evidenced by the presence of the porous slag. The sulfur content in slags gives information about efficiency of preliminary oxidation of sulfide ore. High residual sulfur contents were observed in historical slags from Italy (up to 8 wt%) indicating that the roasting of furnace charge was inefficient (Manasse & Mellini 2002b). In the RJ slags studied, the sulfur content is similar to values reported for medieval slags from Czech Republic (Ettler et al. 2009) and never exceeds 1 wt%. This finding shows that the roasting process, which was applied during first step of smelting of Cu ores in Rudawy Janowickie, was rather efficient compared to other historical sites (Table 2).

**Furnace charge composition and the type of flux**

It was pointed out in numerous slag studies (Manasse & Mellini 2002a; Sáez et al. 2003; Ettler et al. 2009) that bulk chemical composition of slags reflects the chemical composition of the furnace charge and indicates type of flux added during smelting process. However, in the case of the RJ slags the composition of analyzed waste rocks (gangue) seems to better reflect the composition of the smelting batch charge (Fig. 7a).

The RJ slags are poorer in Ca when compared to other studied slags. It can be explained by the composition of the rocks hosting mineral veins, which are rich in Si and poor in Ca and are represented by various metamorphic schists and gneisses. Also, it indicates that no Ca-rich material was added as a flux to the furnace charge, contrary to many other historical and modern examples (Manasse & Mellini 2002b; Sáez et al. 2003; Kierczak et al. 2009). The addition of silica-rich fluxes was also observed in historical smelting sites, as is evident from the high silica content in the slags (Manasse & Mellini 2002a; Ettler et al. 2009). The high silica content of the RJ slags (especially in porous slag) can be attributed to (i) gangue rich in
quartz and/or (ii) addition of the silica-rich material as a flux to the furnace charge. The latter might be consistent with the presence of considerable amounts of unmelted SiO_2-rich material in the porous slag. We therefore infer that the furnace charge was either self-fluxing or quartz-rich flux was applied during smelting of Cu ores in Rudawy Janowickie.

7. Conclusions

Historical slags in RJ comprise dominant massive slag and small amounts of porous slag. Currently, the slags are distributed in forests at the surface, in soils and in stream sediments. Therefore, it is important to characterize the slags from the environmental point of view, as they may strongly affect mobility of metals in the area. The historical slags are an interesting material also in other aspects. For example, the massive slag in RJ is characterized by various rates of cooling, and we examined how those rates affected slag mineralogy and the distribution of elements between different phases. As cooling rate gets slower in the RJ slags we observe that the morphology of crystals changes from acicular to euhedral, phase assemblages become more complex, the composition of phases becomes more variable and the partition coefficient decreases, at least for zinc, which is slightly compatible. In the case of RJ slags, the strongly undercooled slags seem to pose more risk to the environment because they has higher mineral to glass ratio and glass contain higher amounts of zinc, despite higher olivine-glass partition coefficient for this element.

Also, collecting data about historical slags allow us to reconstruct smelting conditions such as smelting efficiency, temperature and type of flux applied during the technological process. A database of historical slags at different sites and from different ages may be useful as a reference point for studies of both historical and modern slags, especially those that pose an environmental or construction problem. Historical slags offer possibility of long-term observations of slag-environment interactions and older slags were also already used in
historical mortars (Bartz & Filar 2010), which are of interest for their durability and preservation.

Acknowledgements

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8. References


Osborn, E. F. & Muan, A. (1960): Phase equilibrium diagrams in oxide systems. American Ceramic Society and E. Orton, Jr, Ceramic Foundation, Columbus, OH.


Geochemistry and tectonic environment of Ordovician meta-igneous rocks in the Rudawy Janowickie Complex, SW Poland. *J. Geol. Soc. London* **152**, 105-115


574
Figure captions:

Figure 1. Simplified map of the studied area indicating sampling locations.

Figure 2. Photographs of the representative samples of studied RJ slags (a) massive slag, (b) porous slag.

Figure 3. X-ray powder diffraction patterns of the RJ slags (a) phase assemblage 1, (b) phase assemblage 2, (c) phase assemblage 3.

Figure 4. Microphotographs (a, b, c, e) and BSE images (d, f) of the RJ slags showing: (a) feather-like olivine crystals from phase assemblage 1 – massive slag (crossed polars), (b) skeletal laths of olivine within black opaque glass (phase assemblage 1 – massive slag; parallel polars), (c) subhedral to euhedral olivine crystals within black opaque glass (parallel polars), (d) subhedral to euhedral olivine (Ol) and spinel (Spl) crystals (phase assemblage 2 – massive slag), (e) SiO₂ – group minerals and two types of glass: (TrGl) translucent and (OpGl) black opaque glass occurring within phase assemblage 3 – porous slag (parallel polars), (f) pyroxene crystals (Px) located between translucent glass (TrGl) and SiO₂ group minerals (cristobalite) crystals (phase assemblage 3 – porous slag).

Figure 5. Histograms showing Zn content in glass from (a) phase assemblage 1, (b) phase assemblage 2, (c) phase assemblage 3.

Figure 6. Histograms showing fayalite and Zn content in (a), (b) phase assemblage 1, (c), (d) phase assemblage 2 of the RJ slags.

Figure 7. FeO-Al₂O₃-SiO₂ ternary diagrams showing (a) chemical composition of the RJ slag and glasses from each phase assemblages (b-f) crystallization patterns for individual slag samples. Phase boundaries and isotherms (°C) are from Osborn and Muan (1960).
Figure 8. Fayalite content versus partition coefficients between olivine and melt (K_D Zn) and corresponding histograms showing distribution of K_D values in massive slags (open circles – phase assemblage 1, filled circles – phase assemblage 2).

Table captions:

Table 1. Bulk chemical analyses of the studied RJ slags.

Table 2. Comparison of different European historical smelting sites and smelting conditions obtained through mineralogical and petrological studies of the slags.
Table 1.

<table>
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<td>1.68</td>
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<td>#Fe, mol %</td>
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<td>86</td>
<td>91</td>
<td>96</td>
<td>88</td>
<td>89</td>
<td>91</td>
<td>86</td>
<td>92</td>
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<td>Cu, mg kg$^{-1}$</td>
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<td>3679</td>
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* total Fe expressed as FeO, v.i.: viscosity index calculated after Bachmann (1982), #Fe indicates Fe/(Mg+Fe) expressed in molar percent
Table 2.

<table>
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<tr>
<th>Site</th>
<th>Smelted ore</th>
<th>Age of slags</th>
<th>Estimated smelting conditions</th>
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</thead>
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<td></td>
<td></td>
<td></td>
<td>Estimated temperature</td>
</tr>
<tr>
<td>Rudawy Janowickie - this study</td>
<td>Cu-ores</td>
<td>XIV-XVI\textsuperscript{th} century</td>
<td>ca. 1200°C (locally 1300°C)</td>
</tr>
<tr>
<td>Campiglia Marittima (Italy)\textsuperscript{(1)}</td>
<td>Cu ores</td>
<td>XIII\textsuperscript{th} century</td>
<td>ca. 1100°C</td>
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<tr>
<td>Cabezo Juré (Spain)\textsuperscript{(2)}</td>
<td>Cu ores</td>
<td>1100°C</td>
<td>3000 years B.C.</td>
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<tr>
<td>São Domingos (Portugal)\textsuperscript{(3)}</td>
<td>Cu ores</td>
<td>Roman times 800 BC – 410 AD</td>
<td>1200-1400°C</td>
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<tr>
<td>Saint Marcel (Italy)\textsuperscript{(4)}</td>
<td>Cu-Fe ores</td>
<td>IX – X\textsuperscript{th} century</td>
<td>1100-1380°C</td>
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<tr>
<td>Massa Marittima (3 sites; Italy)\textsuperscript{(5)}</td>
<td>Marsiliana: Cu</td>
<td>XIII-XIV\textsuperscript{th} century</td>
<td>1150-1300°C</td>
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<td></td>
<td>Arialla: Ag/Pb</td>
<td>XIII-XIV\textsuperscript{th} century</td>
<td>1150-1250°C</td>
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<td>Rochette P.: Ag/Pb</td>
<td>XI-XII\textsuperscript{th} century</td>
<td>1200-1250°C</td>
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<td>Bohutín (Czech Republic)\textsuperscript{(6)}</td>
<td>Pb/Ag-ores</td>
<td>XIV century</td>
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<td>XVI-XVIII\textsuperscript{th} century</td>
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<td>Hartz Mountains (Germany)\textsuperscript{(8)}</td>
<td>Pb ores</td>
<td>XIII\textsuperscript{th} century</td>
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</table>

† - based on assumption that silicate melts are satisfactory fluid when v.i. > 1 (Bachman, 1982) high efficiency of metal extraction corresponds to v.i. > 1, while low efficiency of metal extraction corresponds to v.i. < 1.
‡ - low roasting efficiency corresponds to S_{total} > 1wt%, whereas high roasting efficiency corresponds to S_{total} < 1wt% in slags,
* - only slags from Sieber and Lauenthal were used for v.i. and average S_{total} calculations because bulk composition of slag from Langelsheim corresponds rather to matte than to silicate slag.