

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

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12 Abstract

13 Two types of slags produced during historical smelting of Cu ores occur in the Rudawy Janowickie
14 Mountains, southwestern Poland. The prevailing massive slag has chemical composition dominated by
15 FeO (up to 51 wt %), SiO₂ (up to 43 wt %) and Al₂O₃ (up to 12 wt %). It consists of silicate glass,
16 olivine and hercynite. The second type porous slag is poorer in FeO (up to 28 wt %) and richer in
17 SiO₂ (up to 70 wt %). It comprises two types of silicate glass, olivine, ferrosilite and SiO₂ group
18 minerals (cristobalite and quartz). The morphology of olivine crystals, phase assemblages, phase
19 chemistry and distribution of trace elements in slag phases vary from sample to sample, which is
20 consistent with different cooling rates. Phase diagrams used in this study indicate that most of the slag
21 samples have solidified under strong disequilibrium conditions caused by rapid cooling. Careful
22 investigation of cooling conditions is essential to predict a susceptibility of slags to weathering and to
23 reconstruct historical smelting conditions. For example, samples with longer cooling times are more
24 resistant to weathering and they also should be used to reconstruct the temperature of slag formation.
25 Mineralogical and chemical study of Rudawy Janowickie slags and comparison with other historical
26 slags in Europe indicates that: (i) temperature of slag formation was ca. 1200°C and overlaps with
27 temperature ranges estimated for other historical slags, (ii) furnace charge was either self fluxing or
28 silica was added as a flux, which is not so common for historical Cu slags but was observed for
29 smelting of Pb and Ag ores in Czech Republic (iii) preliminary roasting of furnace charge was
30 efficient similarly to other historical Cu-smelters (iv) the furnace atmosphere was reducing also
31 similarly to other historical smelting processes.

32 **Keywords:** slag, mineralogy, disequilibrium, smelting, Cu ores, archaeometallurgy,

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34 1. Introduction

35 Several sites of historical Cu-mining and smelting were important in Lower Silesia
36 (southwestern Poland): Miedzianka, Ciechanowice and Janowice Wielkie (Fig. 1).
37 Miedzianka was the largest center for mining and smelting of metals such as Cu, As and Ag
38 in Silesia (Dziekoński 1972). Mining and smelting near Miedzianka peaked in 16th century
39 and produced voluminous slag as a by-product. Slags were deposited in the nearby area of the
40 Rudawy Janowickie Mountains and presently form unconfined heaps covered by forest. Slag
41 particles are also transported by streams and are distributed within soils and streambeds. Such
42 long-term deposition of slags may pose an environmental risk. The extent to which slags
43 interact with the surrounding environment is controlled by their texture and primary mineral
44 composition. This study involves the detailed textural, mineralogical and chemical
45 characterization of the slags. We focus on primary structure and minerals, which may vary
46 widely in historical slags depending on the charge composition, smelting conditions and
47 cooling time (Bachmann 1982; Maldonado & Rehren 2009; Heimann *et al.* 2010). We show
48 that the slags in the Rudawy Janowickie are characterized by different cooling rates of the
49 melt, and we describe how these different rates affect slag properties (e.g., phase composition
50 and metal distribution). Such a study provides valuable information about slag waste which
51 can be used as a basis for further environmental research. We also reconstruct some
52 information on historical smelting process applied during the reworking of Cu ores in Poland.
53 We compare our data with those available for other historical European smelting sites in order
54 to create a database, which may be useful for future environmental studies dealing with
55 stability of slags.

56 2. Geological settings of the study area

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

66 3. Mining and smelting history in the Rudawy Janowickie Mountains

67 The RJ was dominated by mining activity since medieval times. The exploitation of ores in
68 the area was focused in the vicinity of the towns Janowice Wielkie and Miedzianka (Fig. 1).
69 In the 14th century, Miedzianka was the largest center for mining and smelting of metals such
70 as Cu, As and Ag in Silesia (Dziekoński 1972). Historical sources describe mining activity in
71 Miedzianka as early as in 1310. Since then, exploitation recommenced several times before it
72 ceased entirely in 1925, leaving unattended mining pits and dumps. The ore was exploited
73 mainly in pit shafts and processed in smelters located close to Janowice Wielkie and
74 Miedzianka. The 16th century brought on the greatest prosperity of mining and smelting
75 activities in the area with, ca. 160 pit shafts being active near Miedzianka. Historical sources
76 from the 16th century described also reprocessing of the older slags covered by newly formed
77 secondary minerals (probably sulphates). The sulphates were an additional source of copper
78 and were obtained by the leaching method, characterized by low costs and relatively easy
79 application (Dziekoński 1972). At the end of the 16th century, the mining activities exhausted

80 the richest metal resources, and the exploitation was in decline until the end of the 17th
81 century. A more favorable period for industrial activities in RJ started at the beginning of the
82 18th century and lasted until the beginning of the 19th century. The ore mined at that time was
83 Cu-rich; the average copper content reached from 1.2 up to 3.8 wt.% Cu. After that, several
84 periods of increased mining activity occurred in 19th and 20th centuries, but did not yield a
85 significant amount of the ore e.g., in 1905 and 1906, the entire mine run was only 15 tonnes:
86 Dziekoński 1972).

87 The total metal production in the RJ area has been estimated at around 2000 t of copper,
88 800 kg of silver and 200 t of arsenic on the basis of historical data and the cubic capacity of
89 slag dumps located in RJ (Dziekoński 1972).

90 4. Sampling and analytical methods

91 4.1. Sampling.

92 The slag samples were collected south of Janowice Wielkie, in the vicinity of two streams: the
93 Janówka and the Smelter streams (50°52'26"N, 15°55'12"E; Fig. 1). These slags represent by-
94 products of smelting processes applied between 14 and 16th century (as known from historical
95 sources and reviewed in Dziekoński 1972). At this time the exploited ore was handpicked and
96 only the fragments rich in ore minerals were processed, while the remaining gangue was
97 discarded. Field observations of the waste rocks dumps, located in the vicinity of Miedzianka
98 (Fig. 1), revealed the presence of secondary phases issued from weathering of the ore. These
99 phases are mostly represented by iron oxyhydroxides (hematite, limonite) and copper
100 minerals such as chrysocolla and malachite. However, unweathered fragments of the ore
101 (composed of chalcopyrite) can still be found. Waste materials (including slags and mining
102 wastes) left over after metal processing were abandoned in the area of the Rudawy

103 Janowickie, without any control on their environmental impact. Neither waste rocks nor slags
104 were used in any way (e.g., road beds).

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

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

119 4.2. Mineralogical analyses.

120 Phase assemblages were identified using optical microscopy, scanning electron microscopy
121 (SEM) and X-ray powder diffraction. After petrographic observations, selected polished thin
122 sections were studied using a scanning electron microscope HITACHI S-4700 equipped with
123 EDX analysis system (in Laboratory of Field Emission Scanning Electron Microscopy and
124 Microanalysis at the Institute of Geological Sciences of the Jagiellonian University, Kraków).
125 X-ray powder-diffraction (XRD) patterns for selected samples were obtained from 4° to 90°

126 2 θ , at rate of 1.2° 2 θ min⁻¹ (SIEMENS D5005 diffractometer with CoK α radiation housed at
127 the Institute of Geological Sciences, University of Wrocław).

128 The phase compositions were established on two electron microprobes: a CAMECA SX100
129 (at the Štátny geologický ústav Dionýza Štúra in Bratislava) and a CAMECA SX50 (at the
130 Université de Paris Jussieu - CAMPARIS). Analytical conditions for both instruments were
131 15 kV accelerating voltage, 10 nA beam current, and counting time 10 s for all the elements.
132 The following set of standards was used: fayalite (Si, Fe), forsterite (Mg), Al₂O₃ (Al),
133 orthoclase (K), wollastonite (Ca), TiO₂ (Ti), rhodonite (Mn), GaAs (As), CuFeS₂ (Cu) and
134 willemite (Zn). The detection limits of As and Cu were ~ 500 ppm and of Zn was ~ 700 ppm.

135 4.3. Bulk chemical analyses.

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

143 5. Slag characteristics

144 5.1. Petrography and phase assemblages.

145 On the basis of mineralogical analyses, we divided the slags in three subtypes, each
146 characterized by a different phase assemblage (Fig. 3). *Massive slag* comprises two subtypes,
147 the first subtype consists of opaque silicate glass and olivine (phase assemblage 1; Fig. 3a),
148 whereas the second subtype is characterized by presence of spinel, olivine and opaque silicate

149 glass (phase assemblage 2; Fig. 3b). *Porous slag* is classified as the third subtype and
150 comprises pyroxene, olivine, cristobalite, two types of glass (opaque and translucent) and
151 fragments of unmelted quartz gangue (phase assemblage 3; Fig. 3c).

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

159 Olivine occurs in all subtypes and is characterized by variable habits in different samples. It
160 forms feather-like crystals up to 1 cm long (Fig. 4a), as well as large skeletal laths up to 1 cm
161 long (Fig. 4b) or subhedral to euhedral crystals ranging in size from 10 to 100 μm (Figs. 4c,
162 d). Spinel occurs only in the second phase assemblage and forms small (from 5 to 50 μm)
163 euhedral crystals occurring as inclusions within olivine and as single grains in the glassy
164 matrix (Fig. 4d). Pyroxene occurs only in the third phase assemblage and forms elongate,
165 skeletal crystals of size ranging from 50 to 500 μm within the glassy matrix. It is also
166 observed as small acicular crystals (up to 50 μm) located at a boundary between partially
167 melted quartz crystals and translucent glass (Figs. 4e, f). The SiO_2 minerals are present as
168 either fractured and partially melted grains ranging from 0.1 to 5 mm in diameter (Figs. 2b,
169 4e) or small (up to 50 μm long) euhedral crystals. The former represents fragments of
170 unmelted gangue and the latter formed during crystallization of the slag melt. According to
171 XRD analyses, the SiO_2 minerals correspond to cristobalite rather than quartz (Fig. 3c). Glass
172 from the first and second assemblages (*massive slag*) is unvariably black under polarizing
173 microscope (Figs. 4b, c), whereas in the third assemblage (*porous slag*) two types of glass

174 occur. The first type corresponds to black and opaque glass described in the first two
175 assemblages, the second type of the glass type is brownish and translucent and is located
176 within the grains of cristobalite and unmelted quartz (Figs. 4e, f).

177 5.2. Chemical composition of slag phases

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

180 Glass

181 Chemical composition of glasses from each slag assemblage is dominated by SiO_2 , Al_2O_3 and
182 FeO . These oxide components occur in different proportions but invariably constitute ca. 90
183 wt. %. The aluminum content in glass from the phase assemblage 2 reaches up to 28 wt%,
184 whereas it never exceeds 20 wt% of Al_2O_3 in the glass from the two other assemblages.
185 Translucent glass from the porous slag is silica rich (69-77 wt% of SiO_2) and contains smaller
186 amounts of FeO (6-15 wt%) and Al_2O_3 (5-9 wt%) than the black, opaque glass. The Zn
187 content in glass from the first and third assemblages is similar and generally ranges from 2000
188 to 4000 mg kg^{-1} . Glass from the second assemblage contains lower amounts of Zn than the
189 other glasses, but locally it contains up to 1% of Zn (Fig. 5).

190 Olivine

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

196 Zn content in olivine from phase assemblage 2 is more variable than that in olivine from
197 assemblage 1 (Fig. 6b, d).

198 Other phases

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

201 The chemical composition of spinel is close to pure hercynite (FeAl_2O_4). The hercynite
202 contains considerable amounts of Zn (up to 5.2 wt% of ZnO).

203 5.3. Bulk composition of the slags

204 The chemical composition of *massive slag* is dominated by FeO (up to 51 wt. %), SiO_2 (up to
205 43 wt. %) and Al_2O_3 (up to 12 wt. %; Table 1). *Porous slag* is poorer in FeO (up to 28 wt. %)
206 and richer in SiO_2 (up to 70 wt. %) than *massive slag* (Table 1). Minor amounts of MgO (up
207 to 4 wt. %), K_2O (up to 4 wt. %) and CaO (up to 2 wt %) also occur in both types of slag
208 (Table 1). All slags show elevated concentrations of Cu (up to 1.34 wt %), Zn (up to 4906 mg
209 kg^{-1}), Pb (up to 268 mg kg^{-1}) and As (up to 131 mg kg^{-1} ; Table 1). In general, the *porous slag*
210 is slightly enriched in these metallic elements compared to *massive slag*. The sulfur content in
211 the slags does not exceed 1 wt. %, and its content is lower for *porous slag* than for *massive*
212 *slag* (Table 1).

213 The viscosity index (*v.i.*) was calculated using the method proposed by Bachmann (1982) and
214 frequently used for historical slags. This method is based on the ratio of “basic” (CaO, FeO,
215 MgO, MnO, K_2O , Na_2O) to “acidic” (SiO_2 , Al_2O_3) oxides. *Massive slag* yields higher values
216 of the viscosity index, ranging from 0.9 to 1.5, than *porous slag*, which has a viscosity index
217 lower than 0.6 (Table 1).

218 6. Discussion

219 6.1. Modern and historical slags

220 Pyrometallurgical slags are by-products of base-metal smelting and steelmaking processes,
221 but they found wide spectrum of applications. Slags produced during the last century were
222 used in road construction (Xue *et al.* 2006), as cement additives (Shi & Qian 2000) or as
223 adsorbents in on-site wastewaters treatment systems (Drizo *et al.* 2002). Numerous studies
224 present detailed physicochemical and mineralogical characteristic of these modern
225 anthropogenic materials (Proctor *et al.* 2000; Acosta *et al.* 2001; Waligora *et al.* 2010) in
226 order to find the best application for the particular material. On the other hand, the
227 pyrometallurgical slags originating from base-metal smelting often concentrate considerable
228 amounts of metals and metalloids (Ettler *et al.* 2001; Lottermoser 2002; Puziewicz *et al.*
229 2007; Piatak & Seal 2010; Vitkova *et al.* 2010) and, once in place, they may undergo
230 potentially harmful interactions with surrounding soils, sediments and waters (Sobanska *et al.*
231 2000; Ettler *et al.* 2004; 2005; Seignez *et al.* 2006; Bril *et al.* 2008). Primary texture, phase
232 composition and distribution of metals between different phases in slags provide information
233 on the possible future behavior of the slags. In this aspect studying historical smelting sites is
234 particularly important because it gives one the possibility (i) to observe the long-term
235 behavior of slag-environment interactions (ii) to study interactions between historical slags
236 and old mortars and cements, reported to contain slag particles (Bartz & Filar 2010), and (iii)
237 to predict the environmental consequences related with present storage and present
238 applications of slags. Below we discuss these features of the RJ slags, which may affect their
239 long-term behavior.

240 6.2. Cooling and crystallization of slags: How far from equilibrium?

241 Historical slags were often air-cooled and the cooling rates could vary depending on the
242 amount of the deposited slag. Numerous experiments on rocks showed that such different
243 cooling regimes affect not only crystal morphology and glass to crystal ratio (e.g., Conte *et al.*
244 2006), but may also affect partition coefficients between different phases and glass, and thus,
245 the distribution of elements (Morgan & London 2003; Lofgren *et al.* 2006; Mollo *et al.* 2011).
246 For example, Morgan and London (2003) and Lofgren *et al.* (2006) showed experimentally
247 that partition coefficients for trace elements increase under conditions far from equilibrium.
248 Disequilibrium conditions generally apply to slags, which usually crystallize under much
249 stronger disequilibrium conditions than rocks. We show that the properties of the RJ slags
250 were also affected by disequilibrium crystallization.

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

260 *Phase diagrams and temperature estimates:* Disequilibrium conditions during slag
261 crystallization can be well illustrated in phase diagrams. Such diagrams were constructed for
262 ceramic purposes (Osborn & Muan 1960), but are also widely used to estimate temperatures
263 of slag formation (Sáez *et al.* 2003; Tumiati *et al.* 2005; Ettler *et al.* 2009). However, the

264 phase diagrams generally yield temperatures of 1400°C or more, exceeding those expected in
265 metallurgical furnaces (Ettler *et al.* 2009; Maldonado & Rehren 2009); this is also the case for
266 the RJ slags (Fig. 7a). Two primary factors may affect results obtained from the phase
267 diagrams: (i) the diagrams were constructed for ternary systems, and slags often contain
268 additional components such as Cu, Zn, Pb and other elements in amounts exceeding 10 wt. %;
269 (ii) some of the initial furnace charge remains unmelted after smelting and, therefore,
270 composition of the bulk slag does not equal the melt composition. None of the factors apply to
271 the RJ slags, as the major components SiO₂, Al₂O₃ and FeO sum up to 90-98 wt % and
272 unmelted material was not detected in *massive slag*. Figure 7 shows that most of the glass
273 compositions plot in quartz stability field, but quartz was not detected in XRD (Fig. 3). The
274 reason for the disequilibrium glass composition is preferential crystallization of olivine or
275 olivine and spinel and the lack of quartz crystallization (Fig. 7). Three different patterns are
276 observed in phase diagrams:

277 (i) All the massive slags containing fayalite only are characterized by linear trends in SiO₂,
278 Al₂O₃, FeO diagrams and the lines join fayalite, bulk slag and glass composition (Figs. 7 b, c),
279 which is consistent with the trends being controlled by disequilibrium crystallization of
280 fayalite. If this is the case, all the temperatures estimated for glass crystallization are
281 meaningless.

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

289 plot close to cotectic lines between fayalite, spinel, sekaninaite (iron cordierite) and quartz.
290 Such glass composition may suggest that the crystallization of the JK0102 slag occurred close
291 to equilibrium, which is also consistent with the least skeletal shapes of olivine crystals in this
292 sample (Fig. 4d). Temperature estimates for this sample are more reliable than for the samples
293 showing strong disequilibrium and are ca. 1200°C.

294 (iii) Porous slags also show two trends in the phase diagram (Fig. 7f), the first one controlled
295 by disequilibrium crystallization of orthopyroxene, the major Fe-rich mineral in porous slags
296 and the second one observed for silica-rich glass enclosed in cristobalite and pyroxene
297 domains (Fig. 4f). A stability field of pyroxene in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ diagram does not exist
298 at 1 atmosphere, but it does appear if the orthopyroxene is Mg-Fe solid solutions (Maldonado
299 & Rehren 2009), as is the case in the RJ slags. The glass enclosed in the cristobalite and
300 pyroxene domains (Fig. 4f) seems to be a mixture between: (a) the glass formed at the eutectic
301 point for pure $\text{SiO}_2\text{-Al}_2\text{O}_3$ composition; such a glass would have been formed after melting of
302 gangue material, which for RJ slags was quartz veins with small amounts of micas, and (b)
303 the slag glass similar to that in massive slags, but richer in silica. The main implication for
304 porous slags, coming from the glasses composition, is that temperatures recorded in this type
305 of slag must have been higher than those recorded in massive slags, first to dissolve more
306 silica-rich material in the slag glass, second to stabilize cristobalite, and third to melt gangue
307 material along the $\text{SiO}_2\text{-Al}_2\text{O}_3$ join. The temperature required to stabilize cristobalite is
308 1470°C in the pure silica system, and the temperature to melt $\text{SiO}_2\text{-Al}_2\text{O}_3$ material is ca.
309 1600°C. However, presence of other fluxing elements as Ca, Na, K could have decreased the
310 temperature by approximately 100-200°C.

311 The main implication from the phase diagrams presented in Fig. 7 is that it is important to
312 identify slags that crystallized close to equilibrium as only those may give reliable
313 temperature estimates in phase diagrams.

314 6.3. Which parameters are affected by disequilibrium crystallization?

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

333 Strong disequilibrium conditions may also affect the distribution of elements between
334 different phases, as was shown experimentally (Morgan & London 2003; Lofgren *et al.*

335 2006). We were able to measure Zn contents in both glass and olivine and to calculate
336 partition coefficients for both slowly cooled and strongly undercooled slags. Figure 8 shows
337 that the calculated partition-coefficients between olivine and melt vary from 0.2 to 8; the
338 range is similar to that reported for basaltic rocks (0.8 – 3.4, GERM database). In general Zn
339 is only slightly compatible, and its partition coefficient should not be strongly affected by
340 conditions far from equilibrium (Morgan and London, 2003). Figure 8 shows, however, that
341 slowly cooled slags seem to have slightly lower partition-coefficients than strongly
342 undercooled slags, which is consistent with experimental data showing that partition
343 coefficients may increase in disequilibrium conditions (Morgan & London 2003, Lofgren *et*
344 *al.* 2006, Mollo *et al.* 2011).

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

- 347 (i) Mineral assemblages; more phases occur in slowly cooled slags,
- 348 (ii) Mineral shapes; skeletal and dendritic morphology develops in strongly
349 undercooled slags,
- 350 (iii) Composition of phases; all phases are more chemically variable in slowly cooled
351 slags, e.g. solid solution phases are zoned,
- 352 (iv) Composition of glasses; glass seems to be impoverished in Zn in slowly cooled
353 slags, where more phases crystallized and acted as a sink for Zn. Such phases, e.g.,
354 spinel in *massive slag*, are usually more stable than glass in surface conditions,
355 which can affect mobility of heavy metals in the slag heap during its deposition
356 and weathering (Ettler *et al.* 2001; Kierczak *et al.* 2009).

357 (v) Partition coefficients; partitioning for compatible elements seem to increase in
358 strongly undercooled slags; however, we were able to measure the partition
359 coefficients only for Zn.

360 6.4. Reconstruction of historical smelting conditions

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

377 *Smelting temperature and efficiency of metal extraction.*

378 As was shown in the section on Petrography and Phase Assemblages most of the smelting
379 temperatures for RJ slags obtained from phase diagrams are meaningless. Reliable
380 temperatures of ca. 1200°C are yielded only from phase diagrams for slags crystallizing in

381 close to equilibrium conditions. The smelting temperatures obtained for RJ slags overlap with
382 temperatures estimated for other historical slags (Manasse & Mellini 2002b; Tumiati *et al.*
383 2005; Ettler *et al.* 2009). However, high-temperature phases, such as cristobalite (if it is pure),
384 indicate that temperatures during smelting of RJ Cu ores could locally exceed 1300°C, which
385 is not common for historical smelting furnaces. Viscosity indices calculated for RJ slags range
386 from 0.88 to 1.55 for *massive slag* and from 0.16 to 0.55 for *porous slag* (Table 1). Lower
387 viscosity indices are consistent with less effective separation of metal from silicate melt, and
388 hence lower efficiency of metal extraction for *porous slag*. This lower efficiency is
389 confirmed by Cu contents observed in RJ slags as *massive slags* are generally poorer in Cu
390 (3000 – 7200 mg kg⁻¹) than *porous slags* (5900 – 13400 mg kg⁻¹). In comparison, historical
391 slags from Italy yield higher values of *v.i.* (0.79-3.74; Manasse *et al.* (2001) and Manasse &
392 Mellini (2002b)), indicating more effective smelting process, whereas medieval slags from
393 Bohutin Czech Republic, have lower *v.i.* (average 1.03; Ettler *et al.*, 2009) and represent less
394 efficient segregation of metals from silicate melt than that recorded in RJ slags.

395 *Smelting furnace atmosphere and roasting efficiency*

396 Historical sources (reviewed in Dziekoński, 1972) describe that the smelting process applied
397 in Rudawy Janowickie consisted of: (1) pre-roasting in order to remove sulfur and (2) melting
398 of the batch charge with the addition of flux (presumably silica) in order to separate molten
399 metal liquid and silicate melt – slag.

400 A slag may contain phases with variably oxidized iron, which may provide information about
401 furnace atmosphere. Phases (e.g., magnetite) containing ferric iron indicate a large supply of
402 oxygen during smelting, whereas ferrous-iron-rich phases such as olivine, pyroxene and
403 hercynite, observed in RJ slags, indicate more reducing conditions. The furnace conditions
404 recorded in the RJ slags are similar to other historical smelting furnaces, which also had a
405 reducing atmosphere (Table 2). However, final steps of smelting process aiming to remove

406 residual iron and sulfur proceed under oxidizing conditions. This can lead to the formation of
407 a porous slag through a phenomenon known as a slag foaming due to an excess of fine
408 magnetite stabilizing sulfur dioxide bubbles. We therefore assume that the conditions during
409 the final steps of smelting were oxidizing as evidenced by the presence of the *porous slag*.

410 The sulfur content in slags gives information about efficiency of preliminary oxidation of
411 sulfide ore. High residual sulfur contents were observed in historical slags from Italy (up to 8
412 wt%) indicating that the roasting of furnace charge was inefficient (Manasse & Mellini
413 2002b). In the RJ slags studied, the sulfur content is similar to values reported for medieval
414 slags from Czech Republic (Ettler *et al.* 2009) and never exceeds 1 wt%. This finding shows
415 that the roasting process, which was applied during first step of smelting of Cu ores in
416 Rudawy Janowickie, was rather efficient compared to other historical sites (Table 2).

417 *Furnace charge composition and the type of flux*

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

423 The RJ slags are poorer in Ca when compared to other studied slags. It can be explained by
424 the composition of the rocks hosting mineral veins, which are rich in Si and poor in Ca and
425 are represented by various metamorphic schists and gneisses. Also, it indicates that no Ca-rich
426 material was added as a flux to the furnace charge, contrary to many other historical and
427 modern examples (Manasse & Mellini 2002b; Sáez *et al.* 2003; Kierczak *et al.* 2009). The
428 addition of silica-rich fluxes was also observed in historical smelting sites, as is evident from
429 the high silica content in the slags (Manasse & Mellini 2002a; Ettler *et al.* 2009). The high
430 silica content of the RJ slags (especially in *porous slag*) can be attributed to (i) gangue rich in

431 quartz and/or (ii) addition of the silica-rich material as a flux to the furnace charge. The latter
432 might be consistent with the presence of considerable amounts of unmelted SiO₂-rich material
433 in the *porous slag*. We therefore infer that the furnace charge was either self-fluxing or
434 quartz-rich flux was applied during smelting of Cu ores in Rudawy Janowickie.

435 7. Conclusions

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

449 Also, collecting data about historical slags allow us to reconstruct smelting conditions such as
450 smelting efficiency, temperature and type of flux applied during the technological process. A
451 database of historical slags at different sites and from different ages may be useful as a
452 reference point for studies of both historical and modern slags, especially those that pose an
453 environmental or construction problem. Historical slags offer possibility of long-term
454 observations of slag-environment interactions and older slags were also already used in

455 historical mortars (Bartz & Filar 2010), which are of interest for their durability and
456 preservation.

457 Acknowledgements

458 We express our thanks to an anonymous reviewer, for his constructive comments, whose
459 enabled us to improve the earlier version of the manuscript. We would like to acknowledge
460 the associate editor Dr. Allen Pratt and the principal editor of the *Canadian Mineralogist* Prof.
461 Robert F. Martin for editorial work and helpful comments on an earlier version of the
462 manuscript. Thanks are extended to Prof. Jacek Puziewicz (University of Wrocław) for
463 support during fieldwork. The study was supported by Polish Ministry of Science and Higher
464 Education grant no. NN 307 05 1237 and by a Foundation for Polish Science *START*
465 scholarship.

466

467 8. References

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574

575 **Figure captions:**

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

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

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

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

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

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

594 **Figure 7.** FeO-Al₂O₃-SiO₂ ternary diagrams showing (a) chemical composition of the RJ slag
595 and glasses from each phase assemblages (b-f) crystallization patterns for individual slag
596 samples. Phase boundaries and isotherms (°C) are from Osborn and Muan (1960).

597 **Figure 8.** Fayalite content versus partition coefficients between olivine and melt (K_D^{Zn}) and
598 corresponding histograms showing distribution of K_D values in massive slags (open circles –
599 phase assemblage 1, filled circles – phase assemblage 2).

600 **Table captions:**

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

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

Table 1.

<i>Slag assemblage</i>	<i>1</i>	<i>2</i>	<i>1</i>	<i>1</i>	<i>3</i>	<i>2</i>	<i>1</i>	<i>3</i>	<i>1</i>
<i>Sample ID</i>	<i>JK0101</i>	<i>JK0102</i>	<i>JK0103</i>	<i>JK0106</i>	<i>JK0111</i>	<i>JK0113</i>	<i>JK0118</i>	<i>JK0122</i>	<i>JK0124</i>
SiO ₂ , wt%	43,30	33,34	41,61	31,88	54,81	38,38	35,91	70,72	38,87
TiO ₂	0,38	0,63	0,47	0,26	0,40	0,58	0,39	0,38	0,46
Al ₂ O ₃	7,46	11,91	6,58	3,84	6,85	9,27	6,73	11,43	6,44
FeO*	39,35	45,26	43,85	51,13	28,30	44,32	47,99	5,58	47,43
MnO	0,15	0,20	0,15	0,13	0,20	0,25	0,16	0,06	0,14
MgO	1,54	4,19	2,57	1,17	2,27	2,97	2,75	0,53	2,35
CaO	1,16	0,96	1,07	1,25	1,15	0,68	1,68	0,59	0,75
Na ₂ O	0,32	0,34	0,17	0,36	0,28	0,19	0,37	2,05	0,15
K ₂ O	1,98	1,68	1,63	1,25	1,78	1,27	1,92	4,37	1,30
P ₂ O ₅	0,15	0,12	0,12	0,12	0,16	0,15	0,11	0,07	0,10
S total	0,59	0,91	0,48	0,73	0,38	0,67	0,75	0,06	0,55
v.i.	0,88	1,16	1,03	1,55	0,55	1,04	1,29	0,16	1,15
#Fe, mol %	94	86	91	96	88	89	91	86	92
Cu, mg kg ⁻¹	7230	3030	4845	5372	13400	3679	7043	5922	5544
Pb	19	40	11	151	269	52	143	65	26
Zn	748	3419	1583	3791	2281	3611	3827	4906	4207
As	92	3	13	3	131	15	254	30	29

* total Fe expressed as FeO, v.i.: viscosity index calculated after Bachmann (1982), #Fe indicates Fe/(Mg+Fe) expressed in molar percent

Table 2.

Site	Smelted ore	Age of slags	Estimated smelting conditions				
			temperature	efficiency of metal extraction (average <i>v.i.</i>) [†]	type of flux	furnace atmosphere	roasting efficiency (average S_{total} in slags) [‡]
Rudawy Janowickie - this study	Cu-ores	XIV-XVI th century	ca. 1200°C (locally 1300°C)	<i>massive slag</i> : high (1.1) <i>porous slag</i> : low (0.4)	silica or self fluxing charge	reducing	high (0.6 wt%)
Campiglia Marittima (Italy) ⁽¹⁾	Cu ores	XIII th century	ca. 1100°C	high (1.6-2.3)	self fluxing charge	reducing	low (1.6-4.4 wt%)
Cabezo Juré (Spain) ⁽²⁾	Cu ores	3000 years B.C.	ca. 1200°C	low (0.7)	mafic rocks	no data	high (0.05-0.9 wt%)
São Domingos (Portugal) ⁽³⁾	Cu ores	Roman times 800 BC – 410 AD	1200-1400°C	high (1.1)	Fe-oxide rich	no data	high (1 wt%)
Saint Marcel (Italy) ⁽⁴⁾	Cu-Fe ores	IX – X th century	1100-1380°C	high (1.8)	Fe-rich rocks	reducing	high (0.8 wt%)
Massa Marittima (3 sites; Italy) ⁽⁵⁾	Marsiliana: Cu	XIII-XIV th century	1150-1300°C	high (1.2)	lime	reducing	low (3.0 wt%)
	Arialla: Ag/Pb	XIII-XIV th century	1150-1250°C	high (2.1)			low (2.2 wt%)
	Rochette P.: Ag/Pb	XI-XII th century	1200-1250°C	high (3.3)			low (3.3 wt%)
Bohutín (Czech Republic) ⁽⁶⁾	Pb/Ag-ores	XIV century	800-1200°C	low (0.6)	silica	no data	high (0.3 wt%)
Kutná Hora (Czech Republic) ⁽⁷⁾	Ag-ores	XVI-XVIII th century	1150-1300°C	high (1.2)	silica	no data	low (4.0 wt%)
Hartz Mountains (Germany) ⁽⁸⁾	Pb ores	XIII th century	1150-1400°C	low (0.8)*	Ba-rich	reducing	low (2.4 wt%)*

[†] - 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 Laenthal 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,

(1) Manasse and Mellini (2001), (2) Saez et al. (2003), (3) Alvarez-Valero et al. (2009), (4) Tumiati et al. (2005), (5) Manasse and Mellini (2002b), (6) Ettlér et al. (2009),

(7) Manasse et al. (2001), (8) Chaudhuri and Newesely (1993),