Università degli Studi di Padova

Padua Research Archive - Institutional Repository

The Misérègne slag deposit (Valle d'Aosta, Western Alps, Italy): insights into (pre-)Roman copper metallurgy.

Original Citation:

Availability:

This version is available at: 11577/3260763 since: 2020-01-09T14:30:27Z

Publisher:

Andy Howard

Published version:

DOI: 10.1016/j.jasrep.2018.02.030

Terms of use:

Open Access

This article is made available under terms and conditions applicable to Open Access Guidelines, as described at <http://www.unipd.it/download/file/fid/55401> (Italian only)

(Article begins on next page)

This is a post-peer-review, pre-copyedit version of an article published in Journal of Archaeological Science: Reports. The final authenticated version is available online at: <https://doi.org/10.1016/j.jasrep.2018.02.030>

The Misérègne slag deposit (Valle d'Aosta, Western Alps, Italy): insights into (pre-)Roman copper metallurgy

Luca Toffolo (1), Anna Addis (1), Silvana Martin (1), Paolo Nimis (1), Mauro Rottoli (2), Gaston Godard (3)

(1) Geosciences Department, University of Padua, via G. Gradenigo 6, 35131 Padua, Italy

(2) ARCO Cooperativa di Ricerche Archeobiologiche, via Crispi 12, 22100 Como, Italy

(3) Institut de Physique du Globe de Paris, Université Paris-Diderot, UMR 7154 CNRS, F-75252 Paris Cedex 05, France

ABSTRACT

The Misérègne hamlet (Fénis village, Valle d'Aosta region, Italy) rises on a huge metallurgical slag deposit, whose origin has so far been unknown. Here we provide the first detailed textural, mineralogical and chemical characterization of the slags and the results of radiocarbon dating of charcoal fragments contained therein. Three types of slags are found, i.e., coarse, massive and flat, which are composed of olivine, spinel and pyroxene crystals in a glassy matrix rich in anorthite $\pm$ magnetite/ulvöspinel crystallites. All the slags contain matte droplets, which show a Cu-enrichment from the coarse and the massive slags (intermediate solid solution, $\sim\text{CuFeS}_2$, or bornite solid solution, $\sim\text{Cu}_5\text{FeS}_4$ + abundant pyrrhotite solid solution, $\sim\text{Fe}_{1-x}\text{S}$) to the flat slags (bornite only). Olivine morphology indicates slow cooling for the massive slags (mostly euhedral crystals), rapid cooling for the coarse slags (dendritic crystals) and slow cooling followed by quenching, consistent with tapping, for the flat slags (euhedral-dendritic transitional crystals). Bulk slag compositions and olivine-spinel

geothermometry suggest that the coarse and massive slags are genetically related ($T = 880\text{--}1090\text{ }^{\circ}\text{C}$ and $T = 860\text{--}1140\text{ }^{\circ}\text{C}$ for coarse and massive slags, respectively), while the flat slags are distinct higher-temperature melts ($T = 1020\text{--}1415\text{ }^{\circ}\text{C}$). The data suggest a multiple-step smelting process, by which an impure chalcopyrite ore, was first smelted to produce relatively Cu-poor matte and coarse and massive slags; the matte was then reprocessed at higher temperature to produce more copper metal and flat slags. Based on radiocarbon dating, the Misérègne slags date back to the II-I century BCE and thus constitute the earliest known record of metallurgical activity in the north-western Italian Alps.

37

1. INTRODUCTION

39

The Valle d'Aosta region (Western Alps, north-eastern Italy) has been an important mining and metallurgical center until the second half of the XX century, as testified by numerous mines and metallurgical sites (Castello, 1981; Nicco, 1987). Written records for metallurgical activity in the region are very scarce before the XIX century (Nicco, 1987), even though the presence of a medieval activity was demonstrated by dating of charcoal in slags from the Servette copper mine (Tumiati et al., 2005). In this work, we present new radiocarbon dating from the Misérègne slag deposit (Fénis), yielding the first evidence of (Pre-)Roman metallurgical activity in the region, whose existence had previously been only hypothetical (Robilant, 1786, 1788). We also characterize the Misérègne slags following an established petrologic approach (Bachmann, 1982; Sáez et al., 2003; Tumiati et al., 2005; Addis et al., 2016), in combination with geothermometric techniques (olivine-spinel geothermometry), in order to obtain technological information and precise estimates of furnace working temperatures.

52

1.1. The Misérègne site

54

Misérègne is the easternmost hamlet of the Fénis village and is located on the apex of the alluvial fan of the Clavalité torrent, in the valley floor of the southern Valle d'Aosta (Fig. 1a). This portion of the valley is literally cluttered with mines and prospects (Fig. 2) where iron and iron-copper ores were exploited. The Fe ores are composed of dominant magnetite and are hosted in serpentinites (e.g., Lac Gelé, Ponton, Ussel mines); the Fe-Cu ores typically consist of pyrite and chalcopyrite in variable proportions, together with accessory magnetite, sphalerite, pyrrhotite and bornite. They are found as massive, semi-massive and disseminated concentrations hosted in chlorite schists (chlorite + minor garnet, quartz, talc, chloritoid and sodic amphibole), talc schists (talc + minor glaucophane, garnet, chloritoid, clinozoisite/epidote, paragonite, talc), glaucophanites (glaucophane + minor garnet, chloritoid, clinozoisite/epidote, paragonite, talc) and quartzites (quartz + minor garnet) (Castello 1981; Martin et al., 2008). All these lithologies belong to the same geological unit, i.e., the ophiolitic Piemonte Zone (Martin et al. 2004 and ref. therein).

Misérègne rises on a huge metallurgical slag deposit, which is called *Ferrùn* (i.e., slag; Gerbore, 2000) by the inhabitants. The site was referred to with the same name in a document dating to 1332 (Di Gangi, 1999), but no mention of the origin of the deposit was made. The slag deposit is composed of two parts (Fig. 1a): the first is an exposed slag heap (N 45°44'02", E 7°30'31"), 4200 m²-area and 6 m thick (at least); the other is a buried deposit (N 45°43'59" E 7°30'33"), which underlies the village and whose extension is hardly computable because of the urbanization of the area. The former is probably a dump produced in recent times, in which slags and modern inert waste are mixed together. The latter was fortuitously exposed in 2011 during the excavation for the foundations of a house and seems to be pristine.

76

77 2. MATERIAL, INSTRUMENTATION AND METHODOLOGIES

78

Seventeen slag specimens were sampled from the buried slag deposit (see Supplementary material). Six of them, i.e., two specimens representative for each slag type (see details below), were analyzed.

81 The samples were prepared in thin (30- μm thick) polished sections and studied with an optical
82 microscope under transmitted and reflected polarized light and with a scanning electron microscope
83 (SEM). We used a Nikon Eclipse ME 600 optical microscope and a CamScan MX 2500 SEM
84 (Geosciences Department, University of Padua, Italy) equipped with a LaB_6 crystal and an energy-
85 dispersive spectrometer (EDS), working at 20-kV accelerating voltage and 40 nA current.

86 The quantities of crystalline and amorphous phases of the bulk samples were estimated from X-ray
87 powder diffraction (XRPD) data. XRPD data were collected using a Bragg–Brentano θ – θ
88 diffractometer (PANalytical X’Pert PRO, Cu $K\alpha$ or Co $K\alpha$ radiation, 40 kV and 40 mA) equipped
89 with a PiXcel detector. Ten wt% ZnO was used as internal standard. Diffraction patterns were
90 interpreted using the X’Pert HighScore Plus 3.0 software by PANalytical, qualitatively reconstructing
91 mineral profiles of the compounds by comparison with the powder diffraction files from the
92 International Centre for Diffraction Data. Then, mineralogical quantitative phase analyses were
93 performed using the full-profile method (Rietveld, 1969). Refinements were accomplished with the
94 TOPAS software (v.4.1) by Bruker AXS.

95 Microchemical analyses (volume of $\sim 1\text{ }\mu\text{m}^3$) were performed at the Department of Earth Sciences of
96 the University of Milan (Italy), using a JEOL JXA-8200 electron probe micro-analyzer (EPMA)
97 equipped with five wavelength-dispersive spectrometers (WDS) and one EDS. Twelve elements were
98 analyzed by WDS spectrometry using these standards: olivine (Mg), omphacite (Na), galena (S),
99 rhodonite (Mn), K-feldspar (K), almandine garnet (Al, Fe), wollastonite (Si), anorthite (Ca), pure Cr,
100 nickeline (Ni), pure Cu, and ilmenite (Ti). Working conditions were a 15-kV accelerating voltage,
101 with a 5-nA beam current intensity, and counting times of 30 s for the peak and of 10 s for the
102 background. Detection limits were (in $\mu\text{g/g}$ or ppm): Al: ~ 180 ; Ca: ~ 150 ; $\sim\text{Cr}$: 260; Cu: 540; Fe: ~ 390 ;
103 K: ~ 120 ; Mg: ~ 180 ; Mn: ~ 360 ; Na: ~ 180 ; Ni: ~ 440 ; S: ~ 260 ; Si: ~ 200 ; Ti: ~ 330 .

104 Bulk chemical compositions were measured at the Geosciences Department of the University of Padua
105 by X-ray fluorescence (XRF) spectrometry, using a Philips PW2400 (XRF) wavelength-dispersive
106 sequential spectrometer equipped with a Rh tube. Reference standards were natural geological

107 samples (Govindaraju, 1994). The relative analytical precision is estimated to be within $\pm 0.6\%$ for
108 major and minor elements and within $\pm 3\%$ for trace elements. Samples were prepared as fine powder
109 ($<10\ \mu\text{m}$ grain size) using Retsch M0 mortar grinder and Retsch RS100 vibratory disk mill. Large
110 quantities of powder (about 100 g for each sample) have been prepared for the coarse slags, because
111 of their heterogeneity. The high Fe and S contents of the slags hindered the production of fused beads;
112 therefore, powder samples were pressed into 3 g pellets. The quantitative analyses were performed
113 using the SuperQ software package.

114 FeO was determined by potassium permanganate titration (permanganometry; see Appendix for the
115 details of the method).

116 Furnace working temperatures were estimated using an olivine-spinel geothermometer, which is based
117 on equilibrium Fe^{2+} -Mg partitioning between olivine and spinel (Irvine, 1965; Sack and Ghiorso,
118 1991). Among existing versions of this geothermometer, we have chosen that of Sack and Ghiorso
119 (1991) because is calibrated in the temperature range 400-1400°C, and thus ~~should~~ include the typical
120 working temperatures of ancient furnaces (Bachmann, 1982; Tylecote, 1992), and can be applied
121 down to atmospheric pressure ($\sim 0.1\ \text{MPa}$). To avoid possible disequilibrium issues, the olivine-spinel
122 geothermometer was generally applied on crystals in apparent textural equilibrium, i.e., small (10–20
123 μm in diameter) polyhedral hercynites included in euhedral olivines. In addition, we only chose
124 hercynites that were sitting near the Mg-rich (i.e., high-temperature) cores of the olivines, which are
125 supposed to represent “frozen” high-temperature assemblages. Olivine and spinel compositions were
126 measured by EPMA, focusing the electron beam a few microns away from the hercynite-olivine
127 crystal boundary in order to avoid mixed analyses. In the coarse slags, spinel inclusions in euhedral
128 olivines were too small to be analyzed without appreciable contamination by the host olivine.
129 Therefore, the analyses were performed on polyhedral hercynite included in the cores of big skeletal
130 olivine crystals, choosing only olivines free of glass inclusions near their cores.

131 Charcoal fragments contained in the slags were dated using the ^{14}C technique. We selected five slag
132 samples from different stratigraphic levels in the buried deposit, i.e., two coarse slags (FE-G10, FE-

133 G11) from the uppermost (0.4–1.0 m) level and two coarse and one massive slag (FE-G12, FE-G13,
134 FE-G3) from the lowermost (1–3 m) level (see details in Table 3). Whenever possible, we sampled
135 fragments derived from thin tree branches, which belonged to the youngest parts of the tree and whose
136 ages are thus, presumably, closer to that of the slag. Radiocarbon dating was performed at the Poznan
137 Radiocarbon Laboratories (Poznan, Poland) and at the CEDAD laboratories (Brindisi, Italy) of the
138 University of Salento (Lecce, Italy), using an accelerator mass spectrometer, following a standard
139 procedure [see instrumental and methodological details at
140 http://radiocarbon.pl/index.php?option=com_frontpage&Itemid=1 (Poznan) and in Calcagnile et al.,
141 2004, D’Elia et al., 2004 (CEDAD)].

142

143

144 3. RESULTS

145

146 3.1. The buried deposit of Misérègne and macroscopic features of the slags

147

148 As revealed by our survey in 2011, the buried slag deposit of Misérègne is a lenticular body with a
149 convex upper surface and a maximum observed thickness of 3.4 m, thinning northwards and
150 westwards and extending southwards beneath the village (Fig. 1a, b; Fig. 3). The base is flat and lies
151 on proximal alluvial fan sediments. In the studied section, the slag deposit is covered by soil and is
152 characterized by an open texture, with scarce sandy matrix. Its upper portion shows an E-dipping
153 cross-stratification. Based on the digital terrain model, we estimate the volume of the deposit to be >
154 60000 m³ (assuming an area of ~22000 m² and an average thickness of 3 m).

155 The slags are typically fragments with a mean size of 2–5 cm; 10–20 cm pieces are not frequent and
156 those measuring more than 20 cm are rare and tend to crumble easily. The slags are dark grey, with
157 brown coatings due to alteration to iron oxides/hydroxides (e.g. goethite, Fe³⁺O(OH)). Slags are
158 frequently stained by green-blue minerals, which probably consist of copper sulfates, carbonates and

159 silicates. Frequently, mm-to-cm-sized pieces of partly carbonized wood or charcoal protrude from
160 the surfaces of the slag or are included in them. Fragments of quartz and chlorite schist are other
161 common macroscopic inclusions.

162 Based on their morphology and on a qualitative estimate of porosity, we grouped the slags into three
163 categories, as suggested by Addis et al. (2016):

- 164 - *Coarse* slags (samples FE-G10, FE-G11, FE-G12), which have a lumpy and angular
165 morphology and exhibit the highest degree of porosity (Fig. 4a). Charcoal fragments can be
166 abundant both on the surface or as inclusions. Coarse slags can trap on their surfaces sand- to
167 gravel-sized quartz grains and lithic fragments (chlorite schist and talc schist).
- 168 - *Massive* slags (samples FE-G3, FE-C1), which have smooth or broken surfaces and very low
169 porosity (Fig. 4b). They are dense, and hard to crush and resemble an aphanitic volcanic rock
170 (e.g., a basalt). Charcoal fragments are rare and superficial.
- 171 - *Flat* slags (samples FE-P5, FE-P6), which have a maximum thickness of ca. 2 centimeters and
172 a low porosity (Fig. 4c, d). They have two main surfaces: one irregular, typically including
173 sand-sized rock fragments, and the other smooth or corrugated with “ropes” that indicate the
174 sense of the flow. Charcoal pieces are uncommon and superficial.

175 In addition, large (up to ~30 cm) composite slag blocks occur, which show a lumpy upper surface
176 and a lower surface composed of welded angular fragments (up to a few centimeters) of all major
177 slag types.

178

179 3.2. Microscopic description

180

181 All the slags are composed ~~by~~ of a dominant silicate fraction, i.e., the slag *stricto sensu*, comprising
182 variable proportions of crystals and glass, and ~~by~~ of a mixture of sulfides, i.e., the matte.

183

184 3.2.1. The silicate slag

185 In all the slags, the most abundant and largest crystals are those of olivine [forsterite (Fo: Mg_2SiO_4)-
186 fayalite (Fa: Fe_2SiO_4) solid solution] and spinel-group minerals [solid solutions of hercynite
187 (FeAl_2O_4), spinel (MgAl_2O_4), magnetite (Fe_3O_4), and ulvöspinel (Fe_2TiO_4), endmembers]. The
188 compositions of slag minerals are reported in Supplementary material.

189 Olivine. It always shows a concentric compositional zoning, which reflects the progressive rimward
190 increase in fayalite (Fe_2SiO_4) component. Olivine crystals in the three classes of slags have different
191 compositions and morphologies. In the *coarse* slags (Fig 5a), olivine (Fo_{52-34} ; ~29–34 wt%; Table 1)
192 mainly forms dendritic crystals, which surround a few large (up to 1.5 mm) skeletal olivine grains;
193 polyhedral (i.e., euhedral) olivines are rare and are usually found as aggregates of small (up to 50
194 μm) crystals. In the *massive* slags (Fig 5b), most of the olivine crystals (Fo_{53-18} ; ~35–45 wt%; Table
195 1) are large (100–200 μm) and polyhedral, but some of them are transitional to the skeletal type.
196 Dendritic crystals are infrequent, but they can be locally abundant. In the *flat* slags (Fig 5c), olivine
197 (Fo_{56-21} ; ~47–60 wt%; Table 1) mostly forms chain-like dendritic crystals near the smoother surface
198 and little (≤ 100 μm) polyhedral crystals that progressively become more abundant towards the more
199 irregular surface; some crystals exhibit polyhedral to dendritic transitional shapes.

200 Spinel-group minerals. They are mainly represented by a spinel-hercynite solid solution, in which the
201 hercynitic component is predominant. In all slag types (Fig 5a, b, c), hercynite crystals are always
202 polyhedral, with dimensions ranging from a few μm to 100 μm , and are frequently included in olivine.
203 Hercynite inclusions are unzoned, but crystals that are dispersed in the matrix may exhibit a thin (< 3
204 μm) Fe-enriched rim. The late generation minerals consist of skeletal crystals either of ulvöspinel
205 (actually a $\text{Fe}^{2+}_2\text{TiO}_4\text{-Fe}^{2+}\text{Al}_2\text{O}_4$ solid solution, with prevailing Ti-bearing endmember) in the massive
206 slags, or of Ti-bearing magnetite in the flat slags. In the flat slags, moreover, the smooth or corrugated
207 surface is lined by a thin (~10 μm) layer of skeletal magnetite crystals.

208 Orothopyroxenes. A Mg-Al-rich ferrosilite ($\text{Fe}_{0.97}\text{Mg}_{0.80}\text{Al}_{0.37}\text{Ti}_{0.03}\text{Si}_{1.79}\text{O}_6$) was found in the coarse
209 slags, forming long (up to several 100 μm) skeletal to dendritic crystals around quartz and talc relicts.
210 In the other slag types, ferrosilite has been identified only by XRPD.

211 Matrix. In all slag types, the groundmass surrounding olivine and hercynite crystals is a mixture of
212 crystallites and of Si-Al-Fe-Ca-Ti glass. The highest proportion of glass is observed in the coarse
213 slags (~49–51 wt%; Table 1), while in the massive and flat slags the groundmasses are crystallite-
214 rich. Based on XRPD data, the crystallites are probably composed of hedenbergite and anorthite
215 ($\text{CaAl}_2\text{Si}_2\text{O}_8$) minor ilmenite (FeTiO_3) and abundant magnetite/ulvöspinel were also observed in the
216 massive slags and in the flat slags, respectively.

217 Relict phases. Millimetric aggregates of anhedral and rounded Fe-oxides associated with metallic
218 copper patches (<50 μm) $\pm$ metallic iron are found in both coarse and massive slags (Fig 5d). Coronae
219 of tiny polyhedral crystals of hercynite occur around the aggregates, suggesting a reaction with the
220 molten slag. Relicts of quartz (SiO_2) and talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] have also been observed in all slag
221 types, although they are more abundant in coarse and massive slags. In the coarse slags, mm to cm-
222 sized domains with sharp boundaries are frequently found, in which the slag texture appears to be
223 different from the prevailing one: we interpret these domains as fragments of resmelted slags.

224 Alteration phases. Fractures, bubbles and charcoal pores are often filled with iron oxyhydroxides
225 [e.g., goethite, $\text{FeO}(\text{OH})$] and carbonates (calcite, CaCO_3 , identified by XRPD), derived from the
226 weathering of sulfides in the slags (Fig. 5d) and the percolation of carbonate enriched meteoric fluids.

227

228 3.2.2. *The matte*

229 The matte forms dispersed droplets and irregular patches in the silicate slag. The matte is composed
230 of anhedral and rounded, rarely dendritic, crystals. Three sulfide solid solutions were identified (Fig.
231 6): pyrrhotite (Po_{ss} , $\sim\text{Fe}_{1-x}\text{S}$), bornite (Bn_{ss} , $\sim\text{Cu}_5\text{FeS}_4$) and ‘intermediate solid solution’ (iss ,
232 $\sim\text{CuFeS}_2$). Frequently, Bn_{ss} and Po_{ss} form symplectitic intergrowths. The size, shape and composition
233 of the sulfides vary across the three types of slags. In the *coarse* slags, sulfides occur as irregular

234 patches, reaching 2–3 mm in size, or as droplets up to 1.3 mm in diameter (Fig 7a, b). Up to 10 μm -
235 sized sulfide droplets are disseminated throughout the slag. Common sulfide associations are Bn_{ss} +
236 Po_{ss} and Po_{ss} + *iss*. Relict chalcopyrite fragments are common (Fig 7c). In the *massive* slags, the
237 sulfides are less abundant (Fig 7d); they ~~and~~ occur as round or elliptical droplets with a diameter of
238 up to 1 cm and as smaller (10–30 μm) disseminated droplets. Sulfide associations and compositions
239 are the same as in the coarse slags. In the *flat* slags, the droplets have a diameter generally lower than
240 10 μm and rarely up to 230 μm (Fig 7e). They have a dominant Bn_{ss} composition and, therefore, a
241 higher mean Cu/Fe ratio than those in the other slag types. In all slag types, Bn_{ss} and *iss* are frequently
242 altered into microgranular digenite ($\sim\text{Cu}_9\text{S}_5$) + covellite (CuS), growing from fractures, grain
243 boundaries and the matte-slag interface (Fig. 7f).

244 Patches of metallic iron and copper were occasionally observed in the matte drops. Iron forms round
245 anhedral grains and is sometimes intergrown with sulfides. Copper is a late phase, which fills voids
246 (pores and fractures) and sometimes forms curls protruding from the matte towards the void space.

247

248 3.3. Slag bulk chemistry

249

250 The XRF bulk chemical compositions of the slags are reported in Table 1 and plotted in the SiO_2 -
251 FeO - Al_2O_3 ternary diagram of Levin et al. (1964; Fig. 8). This simplified chemical system can suitably
252 be adopted to describe the slags, since the sum of the three oxides makes up a great part of the slag
253 weight (~ 76 – 85%). The coarse and massive slags have very similar compositions, although the SiO_2
254 concentration in the coarse slag may have been overestimated by a few wt% units because of the
255 presence of unreacted quartz relicts. This notwithstanding, both slag types plot near the 1088°C
256 fayalite-hercynite-Fe-cordierite-melt peritectic point, which is only 5°C above the fayalite-Fe-
257 cordierite-tridymite-melt eutectic. The flat slags plot close to the fayalite-hercynite cotectic line, since
258 they contain more FeO and less SiO_2 . Moreover, the flat slags have lower contents of Cu (~ 0.6 – 0.9
259 wt%) than the coarse (~ 1.2 – 1.4 wt%) and massive (~ 1.0 – 1.3 wt%) slags.

260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285

3.4. Geothermometry

The temperature estimates obtained for the olivine-spinel crystal pairs are reported in Table 2. The coarse and massive slags yielded overlapping temperature ranges of 880–1090 °C and 860–1140 °C, respectively. The flat slags point to higher temperatures, falling in the range 1020–1415 °C. Since the expected uncertainty of the geothermometric estimates is not reported in Sack and Ghiorso (1991), the above absolute temperatures may not be very accurate, but should still be robust in relative terms. The presence of accessory cristobalite (identified by XRPD) in coarse slags is a proxy of high temperature conditions, however it cannot be used as geothermometer since it can occur metastably at much lower temperatures (> 900 °C; Mollah et al. 1999; Wahl et al., 1961) than ~~that~~ those predicted by thermodynamic models in a pure SiO₂ system ($T \geq 1470$ °C).

3.5. Radiocarbon dating

Charcoal fragments showed different degrees of carbonization and most of them were mineralized, i.e., impregnated and partly replaced, by Fe-oxyhydroxides and carbonates. Mineralization was a major hindrance for dating, because very mineralized charcoal fragments yielded not sufficient carbon quantities after acid-alkali-acid pretreatment. One exploratory analysis was made in 2006 on a coarse slag found on the surface of the reworked deposit (sample MO304 B) and yielded an age of 2120 ± 30 BP (before present, assumed as 1950 CE $\pm 1\sigma$), calibrated to 200-100 BCE (Fig. 9a). The mineralization issue was particularly severe for the slags in the buried deposit. For this deposit we could date only one composite sample made of the two subsamples FE-G12-C and FE-G12-D, which gave a virtually identical age of 2103 ± 35 BP, calibrated to 180-50 BCE (Fig. 9b).

286 4. DISCUSSION

287

288 4.1. The copper metallurgical process at Misérègne

289 4.1.1. The furnace charge

290 The Misérègne slags are clearly related to copper production, since we found evidence that
291 chalcopyrite was used in the furnace charge (relicts in coarse slags) and a Cu-Fe-sulfide phase, i.e.,
292 the matte, was produced and processed. This is not surprising, given the occurrence of chalcopyrite-
293 rich copper mines within a few km of the site, such as the Lovignanz mine along the Clavalité Valley
294 and the Servette mine in the Saint-Marcel Valley (pyrite-chalcopyrite ore hosted in chlorite schists,
295 talc schists and glaucophanites; Castello, 1981; Tumiatì et al., 2005; Fig. 2). In particular, matte
296 morphology (i.e., round patches or droplets), texture and composition suggest that the matte was
297 completely molten during the process and indicate different degrees of Cu-enrichment and
298 desulfurization. Starting from a charge of chalcopyrite with variable proportions of pyrite (consistent
299 with the mineralogy of local sulfide orebodies; Castello et al., 1981), the assemblages $iss + Po_{ss}$ and
300 $Bn_{ss} + Po_{ss}$, which are observed in the coarse and massive slags, would form upon cooling below
301 ~ 1000 °C of a molten sulfide phase (Barton and Skinner, 1979; Yund and Kullerød, 1966). This sulfide
302 phase would be variably desulfurized and Fe-depleted with respect to the starting material (~ 38 wt%
303 S in pyrrhotite vs. ~ 53 wt% S in pyrite; ~ 30 wt% Fe and ~ 35 wt% S in chalcopyrite and iss vs. ~ 11
304 wt% Fe and ~ 26 wt% S in bornite), with $Bn_{ss} + Po_{ss}$ representing a slightly more “mature” matte. All
305 the slags are SiO_2 -rich (> 25 wt%) and have high Al_2O_3 (9–13 wt%), MgO (4–8 wt%) and TiO_2 (1–2
306 wt %) contents. In particular, the $Al_2O_3:MgO:TiO_2$ ratios in the coarse ($\sim 7:3:1$), massive ($\sim 7-8:3-4:1$)
307 and flat slags ($\sim 9:4-5:1$) are very close to those in chlorite schists, talc schists and glaucophanites
308 from the same area ($\sim 7:4:1$ in chlorite schists; $\sim 7:5:1$ in talc schists, $\sim 9:6:1$ in glaucophanites; Martin
309 et al., 2008), which are the typical host-rocks of sulfide ores in Valle d’Aosta copper deposits (Castello
310 et al., 1981). This suggests the presence of high proportions of gangue minerals in the furnace charge,
311 such as talc (SiO_2 and MgO-rich) and quartz (both observed as relict phases in all the slag types),

312 chlorite-group minerals, (Al_2O_3 and MgO -rich), ilmenite or rutile (TiO_2 -rich). Using such an “impure”
313 ore is advantageous because quartz and talc would provide the necessary SiO_2 for producing the slag.
314 Moreover, the addition of Al_2O_3 , contained in other gangue minerals, to a binary FeO - SiO_2 system
315 lowers the melting point of the silicate slag by $\sim 100^\circ\text{C}$ (see the ternary diagram in Fig. 8), resulting
316 both in an earlier onset of the slagging process and in saving of fuel. The nearly eutectic composition
317 of the coarse and massive slags suggests that a well-balanced mix of reactants was used in order to
318 maximize melting. Moreover, the concurrent addition of MgO and TiO_2 (and, to a lesser extent, CaO)
319 would increase the slag fluidity by decreasing the degree of polymerization of the melt (e.g., Best,
320 2002), thus favoring matte settling and separation from the silicate slag.

321

322 4.1.2. Furnace temperatures

323 The comparison between the compositions of the slags and those of experimental melts in the
324 simplified SiO_2 - Al_2O_3 - FeO system (Fig. 8) suggests melting temperatures $\sim 1080^\circ\text{C}$ for the coarse
325 and massive slags and 1200 – 1250°C for the flat slags. Temperature estimates based on olivine-spinel
326 geothermometry show relatively large variability, even when olivine-hercynite pairs from the same
327 slag sample are considered (Table 2). The interpretation of these estimates is not straightforward,
328 because olivine-hercynite pairs may have formed at any stage of the thermal history of the slag (initial
329 heating, steady-temperature stage and cooling) and could re-equilibrate upon cooling of the system
330 due to subsolidus Mg - Fe interdiffusion (e.g., Ozawa, 1984). Concerning the latter issue, although
331 olivine crystals are strongly zoned from Mg -rich cores to Fe -rich rims, they show no chemical zoning
332 around the hercynite inclusions, suggesting that subsolidus Fe - Mg diffusion was not significant.
333 Therefore, within-sample heterogeneity of geothermometric estimates suggests that the olivine-
334 hercynite pairs were formed over a range of temperatures. Statistically, the highest estimates should
335 be the closest to, and thus represent minimum estimates of, the actual furnace working temperatures.
336 The maximum temperature estimates obtained for the different slag types ($\sim 1100^\circ\text{C}$ for the coarse
337 and massive slags and $\sim 1400^\circ\text{C}$ for the flat slags) are reasonable and comparable to those estimated

338 with different methods by other authors for furnace working conditions in prehistoric to Roman sites
339 (1100–1400 °C; e.g., Pelton et al., 2015; Addis et al., 2016).

340

341 4.1.3. A multiple step process?

342 Considering the similar bulk and matte compositions and calculated temperatures, the coarse and
343 massive slags seem to be genetically related. This points to a common smelting process, in which raw
344 high-Fe-S sulfide ore (chalcopyrite + pyrite) was processed to obtain a matte enriched in Cu. However,
345 the massive and coarse slags show important differences concerning the degree of porosity (higher in
346 the coarse slags), the proportion of charcoal and unreacted material (higher in the coarse slags), and
347 olivine morphology. In particular, olivine morphology provides information about the cooling path of
348 the slags (Addis et al., 2016; Donaldson, 1976 and Faure et al., 2003, 2007): in the massive slags,
349 olivine crystals are polyhedral or skeletal, indicating a low degree of undercooling (ΔT , defined as the
350 difference between the temperature of the system liquidus and its actual temperature; Vernon, 2004),
351 which can be related to a steady-state crystallization followed by slow cooling (Faure et al., 2003); in
352 the coarse slags olivine is skeletal or dendritic, which indicates larger ΔT and faster cooling rates. The
353 coarse slags do not show flow structures and their high porosity suggests a higher viscosity compared
354 to the massive slags. Therefore, although they cooled relatively quickly, they are unlikely to have been
355 tapped from the furnace. One interpretation is that the coarse and massive slags were parts of the same
356 slag contained in the furnace: the former were in contact with the air, cooled more rapidly, trapped
357 ascending gas bubbles and included charcoal fragments that floated on the surface; the latter cooled
358 more slowly thanks to the insulating cap provided by the upper coarse layer. An alternative hypothesis
359 is that the massive slags were allowed to cool slowly in a relatively well-insulated furnace (with the
360 purpose of allowing the matte contained in the slag to settle); an earlier interruption of the same
361 process would have resulted in a partially reacted coarse slag (thus explaining their higher proportion
362 of unreacted material), which rapidly cooled when the furnace was torn down or raked off.

363 Compared to the massive and coarse slags, the flat slags are more Fe-rich and Cu-poor and contain
364 more Cu-rich matte droplets. Moreover, olivine morphology indicates an initial low ΔT (polyhedral
365 crystals) followed by a high ΔT stage, i.e., quenching (dendritic crystals). This observation, together
366 with the presence of flow structures, is compatible with slag tapping. Most likely, considering the
367 different matte and slag compositions, the flat slags are not a mere evolution of the other two slag
368 types, but rather the product of a distinct smelting process, in which the matte obtained from the first
369 smelting was re-processed to obtain metallic copper. Before the second smelting, the matte was
370 probably roasted in air (Tylecote, 1992), i.e., oxidized to remove most of the sulfur as SO_2 ; the
371 oxidation, however, was incomplete, since some matte is still found in the flat slags. Since the flat
372 slags have similar Al_2O_3 and TiO_2 contents to the other slag types, we suppose that a certain amount
373 of local rocks or earlier-stage slags was deliberately added to the charge as a flux for the second
374 smelting. The more Fe-rich composition of the resulting charge may have required higher
375 temperatures to achieve efficient melting (Fig. 8). The small average size of Misérègne coarse and
376 massive slags and their common angular shape may be related with matte/copper recovery by crushing
377 of the products of the first smelting.

378

379 4.1.4. Mining industry and copper metallurgy in the Valle d'Aosta during the Iron Age

380 Our dating constrains the metallurgical activity at the Misérègne site to the II-I century BCE. To the
381 best of our knowledge, this is the earliest archeometric evidence of copper metallurgy in the north-
382 western Italian Alps. Historical sources report that in the Iron Age the Salassi, a Celtic tribe settled in
383 an area roughly comprising the Valle d'Aosta and Canavese (a subalpine region the south-southeast
384 of the Valle d'Aosta), were renowned for extracting copper, silver and especially gold (Strabo,
385 *Geographia*, book IV, chapter 6, 7; Artom, 1935; Oberziner, 1900; Pipino, 2003; Brecciaroli and
386 Taborelli, 2011). In particular, the Salassi exploited gold placers, located in the Ivrea morainic
387 amphitheater at the mouth of the Valle d'Aosta (Pipino, 2003; Brecciaroli and Taborelli, 2011), by
388 diverting the Dora and Elvo river and using much of the water to wash the sediments, thus damaging

the downstream agricultural activities (Strabo, *Geographia*, IV, 6.7; Dio Cassius, *Historia romana*, fragment 245). The control of the water and of the mines and, in particular, the frequent raids that the Salassi made in the adjacent territories, were the pretext for the Romans to wage war on the Salassi (Artom, 1935). After a first defeat in 143 BCE, around 140 BCE the Romans seized the gold mines (“aurifodinae”) (Pipino, 2003; Brecciaroli and Taborrelli, 2011) and in 100 BCE they conquered the region enclosed in Ivrea morainic amphitheater and founded the Eporèdia (Ivrea town) colony (Bocca and Centini, 2005). However, in the I century BCE the Romans, which recognized the strategic position of the Valle d’Aosta as a gateway to the central Gaul (through the Little and Great St Bernard passes), repeatedly attacked the Salassi, until they definitively imposed their rule on the region by founding the military colony of *Augusta Praetoria* (Aosta town) in 25 BCE (Strabo, *Geographia*, IV, 6.7; Suetonius, *De Vita Caesarum*, Augustus, chapter XXI; Gruen, 2006). From the above documentation, it is uncertain whether copper production at Misérègne was carried out by the Salassi or if it was promoted by the arrival of Roman entrepreneurs. We are not aware of any historical source specifically referring to Iron Age copper mining and metallurgy in Valle d’Aosta region, if we exclude the information reported by Pliny the Elder in his *Naturalis Historia* (book XXXIV, chapter 2) about a good quality of copper coming for a short period from the territories of the Ceutrones, i.e., the region of Tarentaise (France; Hirt, 2010), adjoining the Valle d’Aosta to the west. The mining/metallurgical sites may have been overlooked by the Romans because of their “local” character or because they had already been abandoned by the I century CE; also, their importance may have been obscured by the much more productive ore deposits in Gaul and Spain (Nicolet, 2006). This notwithstanding, traces of Roman structures rising on a slag deposit near the Servette copper mine (Framarin, 2011), located 6 km south-east of Misérègne (Fig. 2), would confirm the presence of early metallurgical activities shortly prior to or during the Roman domination.

412

413 5. Conclusions

414

415 In this paper, we present the first direct evidence of early copper smelting in Valle d'Aosta region. At
416 the Misérègne metallurgical site, an impure chalcopyrite + pyrite ore, compatible with that occurring
417 in nearby mines, was smelted to produce copper and different types of slags. Coarse and massive slags
418 have similar compositions and sulfide associations. Their origin could be interpreted in two different
419 ways: (i) the two slag types were sitting at different levels within the furnace (the coarse slags were
420 the upper viscous portion that entrapped gas bubbles and less dense charcoal/wood, quartz and talc
421 fragments; the massive slags represented the molten slag that accumulated on the bottom of the
422 furnace); (ii) the massive slags are the end product of first smelting (they were allowed to cool slowly
423 in the furnace, probably to let the matte settle through the slag), while coarse slag represent the
424 outcome of an earlier and sudden interruption of the same process (possibly obtained by demolishing
425 the furnace). The flat slags show substantially different morphologies and chemical compositions,
426 suggesting that these slags were tapped during a separate and more advanced smelting process.
427 Minimum furnace working temperatures estimated by olivine-spinel geothermometry are consistent
428 with a multiple-step smelting process, involving a lower-temperature stage that produced the coarse
429 and massive slags, close to the eutectic conditions, and a subsequent higher-temperature (≥ 1400 °C)
430 stage that produced the flat slags.

431 Our radiometric data constrain the metallurgical activity to the II-I century BCE, i.e., shortly prior to
432 or during the Roman domination of the Valle d'Aosta, and to our knowledge are the first direct
433 archeometric evidence of copper-making in Valle d'Aosta region and in the north-western Italian
434 Alps.

435

436 ACKNOWLEDGMENTS

437 We would like to thank Andrea Risplendente (Earth Sciences Department, University of Milan) for
438 the technical assistance during the EPMA analyses and Dr. Federico Zorzi (Geosciences
439 Department, University of Padua) for performing XRPD analyses. We are also grateful to Prof.
440 Franco Gianotti (University of Turin) and Dr. Sandro Rossato (University of Padua) for their help in

441 the analysis and interpretation of geomorphological data. LT and SM acknowledge financial
442 resources made available by the project between the University of Padua and Fénis municipality,
443 named “Convenzione per la realizzazione dello studio dei siti minerari della Val Ponton, Val
444 Clavalité e di Fenis (Aosta)”. PN acknowledges financial support by Progetto di Ateneo 2013
445 CPDA138741 “Copper metallogenesis and provenancing in the Alpine realm” (University of
446 Padua).

447

448 APPENDIX

449 The procedure used for FeO determination is based on a modified version of the method described
450 by Pratt (1984): a known quantity of sample, previously is prepared into powder, is mixed in a Pt
451 crucible with 15 ml of an acidic mixture composed of one part of deionized H₂O, one part of
452 hydrofluoric acid (HF 40%) and one part of sulfuric acid (H₂SO₄ 95%). The crucible is then placed
453 on a preheated (180 °C) graphite plate for ca. 8 minutes. The content of the crucible is then poured
454 into a polyethylene beaker containing 300 ml of deionized H₂O, 5 ml of H₂SO₄ and 0.6 g of H₃BO₃,
455 and stirred. Titration is performed using a 0.1 N solution of potassium permanganate (KMnO₄).
456 During the titration the following reaction occurs:

458 The volume (in ml) of permanganate needed for the titration is used to calculate the percentage of
459 FeO in the sample according to this formula:

$$460 \quad \% \text{FeO} = [\text{used KMnO}_4 \text{ solution (ml)} \cdot 0.007185 \text{ (g/ml)} \cdot 100] / \text{sample weight (g)}$$

461 Where 0.007185 is the quantity (in g) of FeO equivalent to 1 ml of 0.1 N KMnO₄ solution.

462

Fig. 1. (a) Simplified geomorphological map of the Fénis area. Valle d'Aosta region is highlighted and the star indicates the studied area. In the inset, the Misérègne slag deposit is outlined and the asterisk indicates the section through the buried slag deposit shown in Fig. 3. (b) Profile through the Misérègne slag deposit as inferred from the digital terrain model. Vertical scale is exaggerated. Cartographic base from the website of Regione Autonoma Valle d'Aosta (<http://geonavsct.partout.it/pub/GeoCartoSCT/index.html>).

471

472 **Fig 2.** Principal Fe and Cu mines and orebodies in the southern Valle d'Aosta region. Fe: magnetite
 473 ore. Cu: pyrite-chalcopyrite ore. Cartographic base from the website of Regione Autonoma Valle
 474 d'Aosta (<http://geonavsct.partout.it/pub/GeoCartoSCT/index.html>).

475

Fig. 3. Section of the Misérègne slag deposit. 1: soil (15-20 cm). 2: slag strata interlayered with sand beds (60 cm). 3: slag deposit, cross-stratified towards the upper surface (340 cm). 4: lenticular sand bed (20 cm). 5: matrix-supported chaotic coarse-grained deposit (sub-angular pebbles, cobbles and boulders) belonging to the alluvial fan of the Clavalité creek. Star indicates the position of the radiocarbon-dated sample.

a

1 cm

b

1 cm

c

1 cm

d

1 cm

483

484

485

486

Fig. 4. Representative slag samples from the Misérègne deposit. (a) coarse slag; (b) massive slag; (c) flat slag, plan view; (d) flat slag, profile.

Fig. 5. SEM-BSE images of microstructural features of the Misérègne slags. (a) Coarse slag, with zoned dendritic olivine (Ol) and euhedral hercynite (Hc). Hercynite is also included in olivine (arrow). Tiny white patches disseminated in the slag are sulfides (matte). (b) Massive slag, with zoned polyhedral olivine and hercynite. White patches are sulfides (Sulf) and Fe-oxides (Fe-ox). (c) Flat slag, with zoned polyhedral, dendritic and transitional (arrow) olivine and euhedral hercynite. (d) Radial section of a carbonized branch (*Fagus sylvatica*). Note that the pores are variably impregnated with Fe-oxyhydroxides (light grey portions).

Fig. 6. Sulfide compositions plotted on a Cu-Fe-S phase diagram at 1000°C (modified from Barton and Skinner, 1979). *Iss* is not stable at this temperature and its stability field at 700°C (Yund and Kullerud, 1966) is shown (dashed lines). “Ccp relict” refers to a fragment of slightly reacted chalcopyrite ore.

Fig. 7. Microphotographs under reflected polarized light of sulfides in coarse (a, b, c, f), massive (d) and flat (e) slags. (a) Po_{ss} (cream) + iss symplectite (yellow); light-grey areas within and around the symplectite are secondary Fe-oxyhydroxides. (b) Droplet composed by Bn_{ss} (purplish brown) and Po_{ss} (cream) associated with very minor iss (yellow patches around Po_{ss} grains). (c) Relict chalcopyrite fragment (at the center) (d) Round Bn_{ss} grains (pinkish brown) enveloped by Po_{ss} (cream), with interstitial Bn_{ss} - Po_{ss} symplectite. Dissected curls of metallic copper (bright pink) occur in an empty area. (e) Droplet of Cu-rich Bn_{ss} . (f) Extensive alteration of Bn_{ss} (at the center) into fine-grained covellite (dark blue) + digenite (greyish blue); alteration does not affect Po_{ss} (cream). In all the pictures Bn_{ss} shows exsolution lamellae of Cu-richer Bn_{ss} (more violet). Blue patches, mainly occurring along the fractures and rims of Bn_{ss} , are an alteration to covellite/digenite analogously to what is shown in (f).

Fig. 8. FeO-Al₂O₃-SiO₂ phase diagram at 1 atm (modified from Levin et al., 1964). Al₂O₃ and FeO were recalculated as recommended by Tumiati et al. (2005): Al₂O₃ = Al₂O₃ + TiO₂ + Cr₂O₃ and FeO = FeO + MgO + MnO + CaO (+ Na₂O + K₂O); all iron is considered to be FeO. Numbers refer to temperatures in °C. Mineral abbreviations: Crs = cristobalite; Crn = corundum; Fa = fayalite; Fe-Crd = Fe-cordierite; Hc = hercynite; Trd = tridymite; Wus = wüstite. All the fields indicated by mineral names are actually divariant surfaces where melt is also present.

523

524 **Fig. 9.** Radiocarbon dating of samples of: (a) Poz-15643 (= MO304 B) from the reworked deposit;
 525 (b) LTL13517A (= FE-G12-C/D) from the buried deposit. Plots have been prepared using OxCal
 526 software v4.3.2 (Bronk Ramsey, 2009, 2017).

527

528

529 REFERENCES

- 530 Addis, A., 2013. Late Bronze Age metallurgy in the Italian Eastern Alps: copper smelting slags and
531 mine exploitation, PhD Thesis, Geosciences Department, University of Padua, 222 pp.
532
- 533 Addis, A., Angelini, I., Nimis, P., Artioli, G., 2016. Late Bronze Age copper smelting slags from
534 Luserna (Trentino, Italy): interpretation of the metallurgical process. *Archaeometry* 58, 96-114.
535
- 536 Artom, E., 1935. L'industria dell'oro presso i Salassi. Società industriale grafica Fedetto & c.
537
- 538 Bachmann, H.G, 1982. The identification of slags from archaeological sites. Institute of Archaeology
539 Occasional Publications, 6, 36 pp.
540
- 541 Barton, P.B., Skinner, B.J., 1979. Sulfide mineral stabilities. In: Barnes, H.L. (Ed.), *Geochemistry of*
542 *Hydrothermal Ore Deposits*. Wiley, pp. 278-403.
543
- 544 Best, M.G., 2003 *Igneous and Metamorphic Petrology*, 2nd ed., Blackwell, Berlin, 758 pp.
545
- 546 Bocca, C., Centini, M., 2005. Sulle tacce dei Salassi. Origine, storia e genocidio di una cultura alpina.
547 Quaderni di cultura alpina. Priuli e Verlucca, 87 pp.
548
- 549 Brecciaroli Taborelli, L., 2011. Oro, pane e scrittura. Memorie di una comunità "inter Vercellas et
550 Eporediam" Edizioni Quasar, 533 pp.
551
- 552 Bronk Ramsey, C., 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51, 337-360.
553
- 554 Bronk Ramsey, C., 2017. OxCal software (version 4.3.2), <https://c14.arch.ox.ac.uk/oxcal.html>
555
- 556 Calcagnile, L., Quarta, G., D'Elia, M., Rizzo, A., Gott dang, A., Klein, M., Mous, D. J. W., 2004. A
557 new accelerator mass spectrometry facility in Lecce, Italy. *Nucl. Instrum. Meth. B* 223, 16-20.
558
- 559 Castello, P., 1981. Inventario delle mineralizzazioni a magnetite, ferro-rame e manganese del
560 complesso piemontese dei calcescisti con pietre verdi in Valle d'Aosta. *Ofioliti* 6, 5-46.
561

562 D'Elia, M., Calcagnile, L., Quarta, G., Sanapo, C., Laudisa, M., Toma, U., Rizzo, A., 2004. Sample
563 preparation and blank values at the AMS radiocarbon facility of the University of Lecce. Nucl.
564 Instrum. Meth. B 223, 278-283.

565

566 Di Gangi, G., 1999. L'attività estrattiva e metallurgica nell'arco alpino occidentale tra medioevo ed
567 età moderna. La Valle d'Aosta: note e documenti, Att. Conv. Miniere fucine e metallurgia nel
568 Piemonte medievale e moderno, Rocca de' Baldi (CN), 12 dicembre 1999, 103-123.

569

570 Donaldson, C. H., 1976. An experimental investigation of olivine morphology. Contrib. Mineral. Petr.
571 57, 187-213.

572

573 Faure, F., Trolliard, G., Nicollet, C., Montel, J. M., 2003. A developmental model of olivine
574 morphology as a function of the cooling rate and the degree of undercooling. Contrib. Mineral. Petr.
575 145, 251-263.

576

577 Faure, F., Schiano, P., Trolliard, G., Nicollet, C., Soulestin, B., 2007. Textural evolution of polyhedral
578 olivine experiencing rapid cooling rates. Contrib. Mineral. Petr. 153, 405-416.

579

580 Gerbore, E.E., 2000. Miniere e forni di fusione, in: Fénis. Une communauté au fil de l'histoire.
581 Musumeci Editore, pp. 287-299.

582

583 Gruen, E.S., 2006. The expansion of the empire under Augustus. In: Bowman, A.K., Champlin, E.,
584 Lintott, A. (Eds.) The Cambridge ancient history, 2nd edition, Vol. X, The Augustan Empire, 43 B.C-
585 A.D. 69. Cambridge University Press, pp. 147-196.

586

587 Govindaraju, K., 1994. Compilation of working values and sample description for 383 geostandards.
588 Geostandard Newslett. 18, 1-158.

589

590 Hirt, A.M., 2010. Imperial mines and quarries in the Roman world: organizational aspects 27 BC-AD
591 235. Oxford University Press, 551 pp.

592

593 Irvine, T.N., 1965. Chromian spinel as a petrogenetic indicator: Part 1. Theory. Can. J. Earth. Sci. 2,
594 648-672.

595

596 Levin, E.M., Robbins, C.R., McMurdie, H.F., 1964. Phase diagrams for ceramists. The American
 597 Ceramic Society Inc., Columbus, Ohio, 601 pp.
 598
 599 Martin, S., Godard, G., Rebay, G., 2004. Walking on a palaeo ocean floor. The subducted Tethys in
 600 the Western Alps-An excursion guide. J. Virtual Explorer 16, 1-46.
 601
 602 Mollah, M.Y.A., Promreuk, S., Schennach, R., Cocke, D.L., Güler, R., 1999. Cristobalite formation
 603 from thermal treatment of Texas lignite fly ash. Fuel 78, 1277-1282.
 604
 605 Nicco, R., 1987. L'industrializzazione in Val d'Aosta - Studi e documenti, Quaderni dell'Istituto
 606 Storico della Resistenza in Valle d'Aosta, I, II, III, 89 pp.
 607
 608 Nicolet, C., 2006. Economy and society, 133-43 B.C. In: Crook, J. A., Lintott, A., Rawson, E. (Eds.),
 609 The Cambridge ancient history, 2nd edition, Vol. IX, The Last Age of the Roman Republic, 146-43
 610 B.C. Cambridge University Press, pp. 599-643.
 611
 612 Oberziner, G., 1900. Le guerre di Augusto contro i popoli alpine. Loescher, Rome, 239 pp.
 613
 614 Ozawa, K., 1984. Olivine-spinel geospeedometry: analysis of diffusion-controlled Mg-Fe²⁺ exchange.
 615 Geochim. Cosmochim. Ac. 48, 2597-2611.
 616
 617 Pipino, G., 2003. Oro, Miniere, Storia. Miscellanea di giacimentologia e storia mineraria italiana.
 618 Museo Storico Oro Italiano, 510 pp.
 619
 620 Pratt, J.H., 1984. On the determination of ferrous iron in silicates. Am. J. Sci., 284, 149-151.
 621
 622 Reimer, P.J., Bard E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk Ramsey, C., Buck, C.E.,
 623 Cheng, H., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Haflidason, H., Hajdas,
 624 I., Hatté, C., Heaton, T.J., Hoffmann, D.L., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B.,
 625 Manning, S.W., Niu, M., Reimer, R.W., Richards, D.A., Scott, E.M., Southon, J.R., Staff, R.A.,
 626 Turney, C.S.M, van der Plicht, J., 2013. IntCal13 and Marine13 radiocarbon age calibration curves
 627 0–50,000 years cal BP. Radiocarbon 55, 1869-1887.

628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660

Rietveld, H., 1969. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* 2, 65–71.

Robilant (Nicolis de), E.-B., 1786. *Essai géographique suivi d’une topographie souterraine, minéralogique & d’une docimasie des Etats de S. M. [Sa Majesté] en terre ferme*, Mémoires de l’Académie royale des Sciences, Turin, I, 191-304.

Robilant (Nicolis de), E.-B., 1788. *Description particulière du Duché d’Aoste, suivie d’un essai sur deux minières des Anciens Romains et d’un supplément à la théorie des montagnes et des mines*, Mémoires de l’Académie royale des Sciences, Turin, III, 254-274 + pl. vii-ix.

Sack, R.O., Ghiorso, M.S., 1991. Chromian spinels as petrogenetic indicators: thermodynamics and petrological applications. *Am. Mineral.* 76, 827-847.

Sáez, R., Nocete, F., Nieto, J. M., Capitán, M.Á., Rovira, S., 2003. The extractive metallurgy of copper from Cabezo Juré, Huelva, Spain: chemical and mineralogical study of slags dated to the third millenium BC. *Can. Mineral.* 41, 627-638.

Tumiati, S., Casartelli, P., Mambretti, A., Martin, S., 2005. The ancient mine of Servette (Saint-Marcel, Val d’Aosta, Western Italian Alps): a mineralogical, metallurgical and charcoal analysis of furnace slags, *Archaeometry* 47, 317-340.

Tylecote, R.F., 1992. *A history of metallurgy*, 2nd edition. Institute of Materials, London, 205 pp.

Vaughan, D.J., (Ed.), 2006. *Sulfide mineralogy and geochemistry* (Vol. 61). Mineralogical Society of America, 714 pp.

Vernon, R.H., 2004. *A practical guide to rock microstructure*. Cambridge University Press, 606 pp.

Wahl, F.M., Grim, R.E., Graf, R.B. 1961. Phase transformations in silica as examined by continuous X-ray diffraction. *Am. Mineral.* 46, 196-208.

661 Yund, A.R., Kullerud, G., 1966. Thermal stability of assemblages in the Cu-Fe-S system, J. Petrol. 7,
662 454-488.