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Archaeometallurgical Characterization of Two Lombard Early Medieval Bloomery Slags from Ponte di Val Gabbia I Site (Northern Italy)

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Abstract: An archaeometallurgical characterization of two iron smelting tap slags recovered from the early medieval site of Ponte di Val Gabbia I (Brescia, northern Italy) was performed. The main goal was to infer from the slags the working conditions of the ancient bloomery furnace in terms of temperature and oxygen chemical potential. The petrology of both slags was investigated by light optical microscopy and scanning electron microscopy, while their chemical compositions were measured via scanning electron microscopy coupled with X-ray dispersive spectroscopy. High-resolution Raman micro-spectrometry was used to confirm the identification of the mineralogical phases. The software Rhyolite-MELTS was used to compute the liquidus temperatures of the two slags, which were found to be 1120 °C and 1146 °C. These temperatures approximate the working temperature of the bloomery furnace. A thermodynamic-based approach was adopted to estimate the redox conditions of the reducing atmosphere of the smelting furnace, revealing that the two slags formed in different redox environments. Specifically, the resulting oxygen chemical potentials were −382.61 kJ/mol and −243.80 kJ/mol at the liquidus temperatures of 1120 °C and 1146 °C, respectively.

Keywords: archaeometallurgy; Lombards; thermodynamics; bloomery slag; micro-Raman investigation



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1. Introduction

The physico-chemical analysis of ancient smelting by-products, i.e., pyrometallurgical slags, plays a crucial role in the smelting process reconstruction providing for the scarcity of historical written sources [1,2]. In particular, the chemical and mineralogical characterization of slags is a powerful tool for estimating key parameters of ancient iron and steel-making technology, such as temperature, oxygen fugacity of the reducing atmosphere, slag viscosity, and cooling rate. These parameters are intimately related to the efficiency of the reduction process and can give insight into the evolution of ancient technology [3,4]. It is worth mentioning that in Europe, starting from the first millennium BC until the 13th century AD, iron was exclusively produced by a one-step solid-state process (i.e., performed below the iron melting temperature at ~1200 °C) called the “direct” method [5]. The reduction of iron ores was carried out inside the “bloomery” furnace by the chemical reaction between iron ore and carbon monoxide gas (namely, the reducing agent) which is generated during charcoal combustion [6]. The iron ores charged in the bloomery hearth were generally a mixture of iron compounds and siliceous gangue, incorporating many oxides such as CaO, MgO, Al₂O₃, MnO, and P₂O₅. The slag formation was promoted by the chemical interaction between iron oxides and gangue constituents. During the smelting process, the fluid slag incorporates and shields from reoxidation the reduced iron particles which coalesce together, consolidating at the bottom of the furnace into a spongy iron mass, named “bloom” [5]. In recent years, archaeometallurgists have adopted many approaches to extract the above-mentioned technological information from ancient pyrometallurgical slags. Namely, the smelting temperature is usually estimated by projecting the slag bulk chemical composition on chemistry and mineralogy-based phase

diagrams [7–9]. Moreover, geothermometers and software for thermodynamic modeling, such as Rhyolite–MELTS, have proven to be useful and promising tools for high-resolution slag crystallization temperature reconstruction [10–14]. On the other hand, the smelting redox conditions were often inferred from the assemblage of slag mineralogical phases, using as references the oxygen buffer curves (e.g., Quartz–Fayalite–Magnetite oxygen buffer) in the oxygen fugacity–temperature space [15,16]. However, because equilibrium is rarely attained, it was suggested that a reliable proxy for oxygen fugacity is the iron oxidation state in slags, which can be expressed as the ferric/ferrous ratio ($\text{Fe}^{3+}/\text{Fe}^{2+}$) [17,18]. This redox-sensitive ratio is usually measured by Mössbauer spectroscopy, XANES spectroscopy, and redox titration (i.e., “wet chemistry”) [19,20]. In crystalline slag samples, the quantification of iron-bearing phases, such as fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4), allows an approximate estimation of the bulk ferric/ferrous ratio. Considering this framework, the present study concerns an archaeometallurgical characterization of two tap slags retrieved in the early medieval site of Ponte di Val Gabbia I (Brescia, northern Italy), hereafter referred to as PVGI (Figure 1).

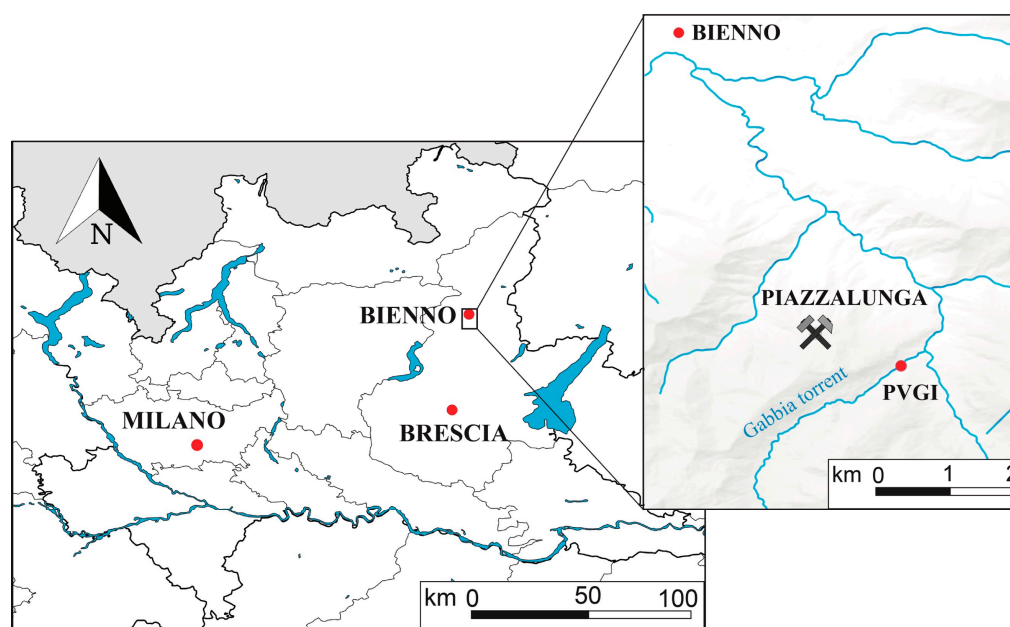


Figure 1. Geographical location of Ponte di Val Gabbia I archaeometallurgical context.

The slags are now kept at the Ethnographic Museum of Iron in Bienna (Brescia, Northern Italy). The site of PVGI was dated to the Lombard Period (6th–7th centuries AD). It is situated near two other ancient metallurgical sites, i.e., Ponte di Val Gabbia II (PVGII) and Ponte di Val Gabbia III (PVGIII), which were operating during the Lombard Period (6th–7th centuries AD) and the Late Roman Imperial Period (5th–6th centuries AD), respectively [21]. The iron ore (manganese-rich hematite and goethite) reduced in these sites was exploited in the nearby mine of Piazzalunga [21]. Previous research works have pointed out the technological diversity of PVGI-II and PVGIII sites [21–23]. In particular, Cucini and Tizzoni [21] hypothesized that only the direct process was practiced in PVGI-II sites [21]. By contrast, the finding of a pig iron block and the archaeometallurgical investigation of a miner’s chisel indicated that in the PVGIII site iron was possibly produced by cast iron decarburization via the indirect iron-making method [22–24]. As a consequence, it was emphasized that the PVGIII context could backdate the transition from the direct to indirect process in Europe, which is usually dated to about the 13th century. At present, the driving factors of the technological differentiation of PVGI-II and PVGIII sites remain not completely understood, even if they are possibly linked to the local socio-economical changes that occurred in this region between Late Antiquity and the Early Medieval Period [21]. Against this background, the main goal of this study is to provide novel

information which can be useful for unraveling the iron-making technology evolution and differentiation in the complex archaeometallurgical context of Ponte di Val Gabbia.

2. Materials and Methods

2.1. Slags

Two tapped slags (hereafter referred to as slags A and B) retrieved in the early medieval ironworking site of PVGI were analyzed in this study (Figure 2). These smelting slags were withdrawn from the bloomery furnace through a tap hole positioned near its base and possibly collected in a small pool excavated in the ground in front of the hearth.



Figure 2. Photographic images of the two analyzed slags: (a,b) front and rear sides of slag A, and (c,d) front and rear sides of slag B.

2.2. Preliminary Description and Macro-Observations

Slags A and B were characterized by evaluating their outward appearance and external features such as surface morphology and colors. Both slags exhibit distinct flowing textures, especially on their front side (Figure 2a,c). In addition, slag A is characterized by a blistered surface with a higher porosity than slag B, which, in turn, appears more massive. On the rear side of both slags, some imprints of the ground substrate irregularities (possibly due to charcoal fragments and gravels) were observed (Figure 2b,d). Slag A is marked by a peculiar cylindrical shape with a hollow central channel. The formation mechanism of this tubular morphology probably relies on the multiple overlapping of slag waves flowing outside the furnace onto the sloping ground [21]. Both slags are characterized by dark grey-colored surfaces with reddish oxidation products (iron hydroxides) due to weathering. Moreover, slag A and B are magnetic, possibly due to the presence of iron particles and/or magnetite [1]. Considering their macroscopic features, both slags belong to type H according to the typological classification scheme suggested by Cucini and Tizzoni [21]. This slag class embraces most of the tap slags retrieved at the PVGI site that are primarily distinguished by their flowing texture and dense appearance with limited porosity, and occasionally exhibit a tubular shape [21].

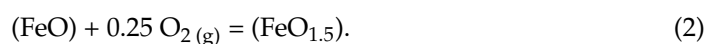
2.3. Experimental Methods

Two representative samples were taken from slag A and B, mounted in epoxy resin, and prepared following a standard metallographic procedure. The samples were ground with SiC paper (grade 1200) and polished with polycrystalline diamond suspensions (3 μm and 1 μm). The mineralogical and microtextural characterization of both slag samples was

performed by light optical (Leica DMI 5000M, Wetzlar, Germany) and scanning electron microscopy (LEO EVO 40 XVP, Carl Zeiss AG, Milan, Italy) in backscattering mode (BSE). The volume fraction of each mineralogical phase was quantified by the software ImageJ [25]. The bulk chemical composition of the slag samples and the chemistry of each mineralogical phase were analyzed with an energy-dispersive X-ray spectroscopy microprobe (Link Pentafet Oxford mod 7060, Oxford Instruments, Wiesbaden, Germany) integrated with the scanning electron microscope. All the chemical compositional data were expressed by the following stoichiometric oxides: Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO, TiO₂, MnO, FeO, BaO, and P₂O₅. To confirm the identification of the mineralogical phases, slag samples were investigated with a high-resolution Raman micro-spectrometer (Labram HR-800, Horiba Jobin-Yvon, Edison, NJ, USA) equipped with a He–Ne laser source ($\lambda = 632.8$ nm) operating at a power of 5 mW. The laser source was focused on a spot with a diameter of ~ 2 μ m, and the exiting light was collected using a 50 $\times$ microscope objective (Numerical Aperture: 0.5). All the Raman spectra were acquired with a 1 cm^{−1} resolution. The acquisition time was 30 s. Rhyolite–MELTS v.1.0.2 software package was used to compute the liquidus temperatures of the slags, starting from the slag bulk chemical composition [12,26].

2.4. Thermodynamic Modeling

The redox formation conditions of the analyzed slags were estimated in terms of oxygen chemical potential (μ_{O_2}) of the gas atmosphere in equilibrium with the liquid slag, as a function of the chemical activities of ferric and ferrous iron oxides (referred to as $a_{(\text{FeO}_{1.5})}$ and $a_{(\text{FeO})}$, respectively) and temperature (T, expressed in kelvin), at a fixed pressure of 1 bar (0.1 MPa). To this aim, the following chemical equilibria were considered (Equations (1) and (2)):



Equation (1) is suitable for describing the iron smelting slags coexisting with metallic iron in a strongly reducing environment, while Equation (2) permits to model the slags in more oxidizing conditions when the ferric iron content cannot be neglected. The standard Gibbs free energy changes (ΔG_1°) and the equilibrium constants (K_1) of Equation (1) were calculated from Barin's thermochemical data [27] (Equations (3) and (4)):

$$\Delta G_1^\circ = \Delta H_1^\circ - T\Delta S_1^\circ = 0.06T - 269.39 \text{ (kJ/mol)}, \quad (3)$$

$$K_1 = \exp(-\Delta G_1^\circ / RT) = a_{(\text{FeO})} / [a_{[\text{Fe}]} (p_{\text{O}_2})^{0.5}] = \exp[(269.39 - 0.06T)/RT]. \quad (4)$$

The standard Gibbs free energy change (ΔG_2°) and the equilibrium constant (K_2) of Equation (2) were computed according to Ban-Ya [28] (Equations (5) and (6)):

$$\Delta G_2^\circ = \Delta H_2^\circ - T\Delta S_2^\circ = 0.05T - 126.82 \text{ (kJ/mol)}, \quad (5)$$

$$K_2 = \exp(-\Delta G_2^\circ / RT) = a_{(\text{FeO}_{1.5})} / [a_{(\text{FeO})} (p_{\text{O}_2})^{0.25}] = \exp[(126.82 - 0.05T)/RT]. \quad (6)$$

Rearranging Equation (4), the oxygen chemical potential can be expressed by Equation (7):

$$\mu_{\text{O}_2} (a_{(\text{FeO})}, T) = RT \ln p_{\text{O}_2} = 2RT \ln(a_{(\text{FeO})} / K_1) \text{ (kJ/mol)}. \quad (7)$$

According to Equation (6), the oxygen chemical potential can be expressed as follows (Equation (8)):

$$\mu_{\text{O}_2} (a_{(\text{FeO})} / a_{(\text{FeO}_{1.5})}, T) = RT \ln p_{\text{O}_2} = (RT/0.25) [\ln(a_{(\text{FeO})} / a_{(\text{FeO}_{1.5})}) + 126.82 - (0.05/R)] \text{ (kJ/mol)}. \quad (8)$$

The chemical activities of ferric and ferrous iron oxides in the slags were approximately estimated following the quadratic regular solution model proposed by Ban-Ya [28] (Equations (9) and (10)):

$$a_i = f_i x_i, \quad (9)$$

$$f_i = \exp\{[\sum_j \alpha_{ij}x_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk})x_jx_k]/(RT)\}, \quad (10)$$

where a_i , f_i , x_i , and α_{ij} are the chemical activity, activity coefficient, molar fraction of the i^{th} oxide, and the interaction energy between the i^{th} and j^{th} cations, respectively. The values of the interaction energies are shown in Table 1 [28].

Table 1. Interaction energies (α_{ij} , in J/mol) between the major cations of iron smelting slags (adapted from [28]).

j \ i							
	Fe ²⁺	Fe ³⁺	Mn ²⁺	Ca ²⁺	Mg ²⁺	Si ⁴⁺	Al ³⁺
Fe ²⁺	–	–18,660	+7110	–31,380	+33,470	–41,840	–41,000
Fe ³⁺	–18,660	–	–56,480	–95,810	–2930	+32,640	–161,080
Mn ²⁺	+7110	–56,480	–	–92,050	+61,920	–75,310	–83,680
Ca ²⁺	–31,380	–95,810	–92,050	–	–100,420	–133,890	–154,810
Mg ²⁺	+33,470	–2930	+61,920	–100,420	–	–66,940	–71,130
Si ⁴⁺	–41,840	+32,640	–75,310	–133,890	–66,940	–	–127,610
Al ³⁺	–41,000	–161,080	–83,680	–154,810	–71,130	–127,610	–

3. Results and Discussion

3.1. Petrological Study

The micro-textural features and the mineralogical phase assemblages of slags A and B were investigated by light optical microscopy and scanning electron microscopy in BSE mode. Slag A consists of elongated olivine with dendrites of wüstite and fine-scale intergrowths of leucite (KAlSi_2O_6) and second-generation olivine (Figure 3a,b). It was observed that small droplet-shaped particles ($\sim 0.5 \mu\text{m}$ up to $\sim 2 \mu\text{m}$ in size), which can be identified as wüstite micro-crystals, were exsolved from leucite anhedral grains forming cotectic intergrowths [29] (Figure 3c). Intergrowing olivine and leucite with exsolved wüstite were solidified from the residual liquid after the crystallization of the olivine primary phase. The leucite precipitation was driven by the potassium and aluminum enrichments in the residual melt, due to the incompatible behavior of these two elements with the olivine and wüstite crystals [2,30]. The crystallization sequence is: olivine I $\rightarrow$ wüstite I $\rightarrow$ (leucite + wüstite II) + olivine II. The volume fractions of each mineralogical phase were estimated by Image Analysis via ImageJ software analyzing micrographs ($500\times$ magnification) of five different zones. The resulting volume fractions of wüstite, olivine, and leucite were approximately 75%, 10%, and 15%, respectively.

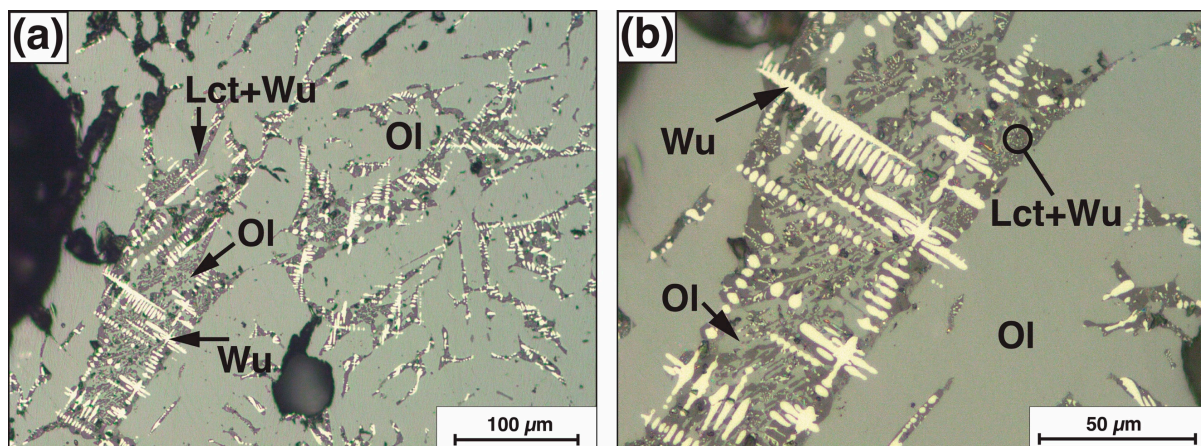


Figure 3. Cont.

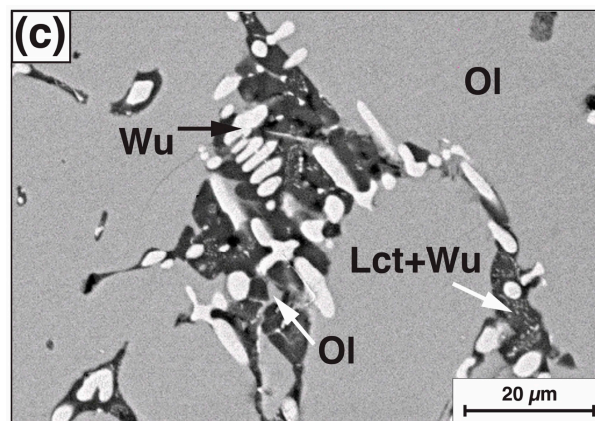


Figure 3. Microstructural features of slag A. (a,b) Light optical micrographs (200× and 500× magnifications, respectively). (c) Scanning electron micrograph in BSE mode (approximately 1000× magnification). Ol: Olivine, Wu: Wüstite, Lct: Leucite (abbreviations after [31]).

Slag B is characterized by chain and skeletal-shaped olivine laths with magnetite and/or wüstite sub-micrometer exsolutions embedded in a vitreous interstitial phase, which corresponds to the residual melt (Figure 4a). The outer zone of the slag section is marked by a layer that is mainly constituted by magnetite and/or wüstite (Figure 4b). The magnetite/wüstite skin at the slag external border has a thickness of ~25 μm and can be originated by oxidation during the slag cooling outside the smelting furnace [32]. Crystals with cruciform habit intergrowing with skeletal spinifex olivine were observed (Figure 4c). The peculiar shape of these crystals suggests that they probably consist of magnetite [33–35]. In addition, the presence of magnetite is consistent with the magnetism of slag B. It is worth noting that the presence of magnetite in bloomery slags is rather unusual, indicating a redox formation condition of slag B more oxidizing than those usually reported for the direct iron smelting process [36]. The mineralogical phase morphology is compatible with a high degree of undercooling [16,37]. The sequence of crystallization is: olivine → wüstite + magnetite → glass. The volume percentages of olivine, wüstite/magnetite, and glass estimated by analyzing micrographs (500× magnification) of five different zones with ImageJ were 73%, 6%, and 21%, respectively.

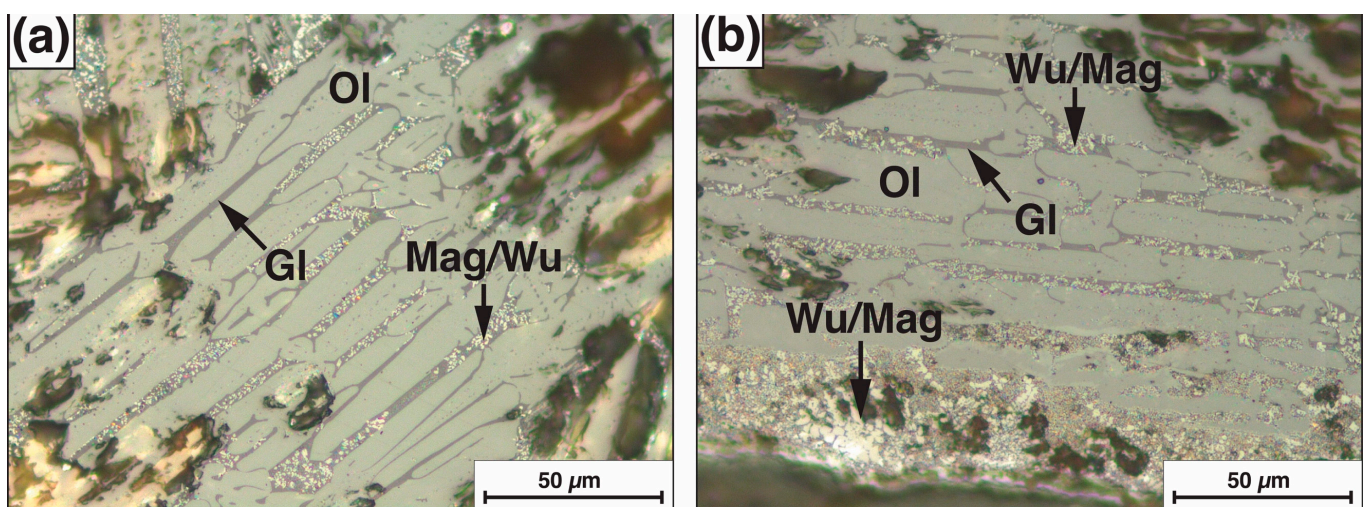


Figure 4. Cont.

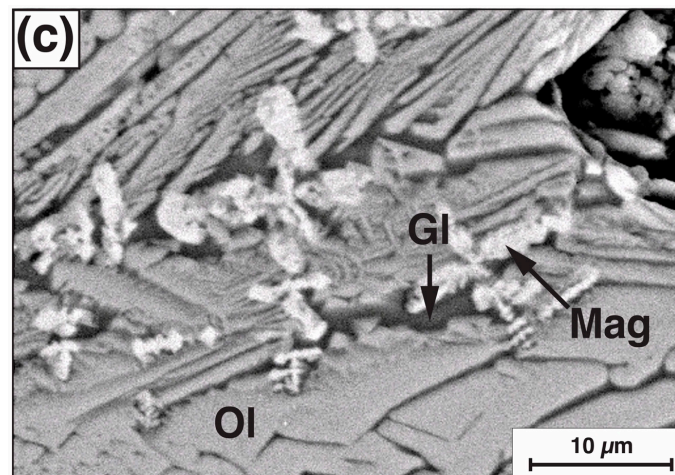


Figure 4. Microstructural features of slag B. (a,b) Light optical micrographs (500× magnification). (c) Scanning electron micrograph in BSE mode (approximately 2000× magnification). Ol: Olivine, Wu: Wüstite, Mag: Magnetite, Gl: Glass (abbreviations after [31]).

3.2. SEM/EDS Analyses

The bulk chemistry and average chemical composition of each mineralogical phase of slags A and B were obtained via SEM/EDS analysis (Table 2). The Fe-rich olivine phase of both slag A and B is characterized by a high manganese oxide content (up to 10.42 wt% and 8.36 wt%, respectively). The olivine phases of slag A and B are solid solutions of fayalite (Fa: Fe_2SiO_4) and tephroite (Tep: Mn_2SiO_4) end-members. Their composition can be expressed as $\text{Fa}_{84-87}\text{Tep}_{13-16}$ and $\text{Fa}_{87-90}\text{Tep}_{10-13}$, respectively. A significant quantity of manganese oxide (up to 3.42 wt%) was also detected in the wüstite phase of slag A. The high amount of manganese oxide was probably derived from the manganiferous gangue associated with iron ore which was exploited at the Piazzalunga mine [21,38]. The iron oxide detected in the leucite phase (KAlSi_2O_6) is due to the presence of wüstite micro-crystals in the areas analyzed by SEM/EDS. The interstitial glass phase of slag B is highly enriched in Al_2O_3 (up to 15.76 wt%), K_2O (up to 7.05 wt%), and CaO (up to 5.02 wt%), and depleted in MnO and FeO compared to olivine. In addition, the glass phase of slag B incorporates small amounts of Na_2O (up to 1.80 wt%), TiO_2 (up to 1.32 wt%), and BaO (up to 2.42 wt%).

Table 2. Bulk chemistry and average chemical composition (wt%) of each mineralogical phase measured by SEM/EDS (n = number of analyses, b.d.l. = below detection limit).

Phase	Bulk	Olivine	Wüstite	Leucite	Bulk	Olivine	Glass	Magnetite/Wüstite
slag n=	A 1	A 6	A 6	A 6	B 1	B 5	B 5	B 2
Na_2O	0.17	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.97	b.d.l.
MgO	0.08	0.16	b.d.l.	b.d.l.	0.12	0.08	b.d.l.	b.d.l.
Al_2O_3	4.05	0.11	0.56	21.70	3.39	1.46	12.52	4.14
SiO_2	36.31	34.60	2.71	52.06	34.03	34.53	49.15	9.68
K_2O	1.60	b.d.l.	0.38	14.49	2.21	0.49	5.43	0.64
CaO	0.97	b.d.l.	0.15	b.d.l.	0.01	0.18	3.49	b.d.l.
TiO_2	0.07	b.d.l.	0.13	0.84	0.14	b.d.l.	0.54	b.d.l.
MnO	5.96	9.65	3.15	0.34	7.60	7.57	2.17	2.30
FeO	50.47	55.48	92.93	9.86	52.38	55.64	24.79	83.26
BaO	0.11	b.d.l.	b.d.l.	0.71	0.27	b.d.l.	0.95	b.d.l.

3.3. Micro-Raman Spectroscopy

The micro-Raman spectroscopy analysis of slag A verified the olivine phase identification and enhanced its characterization. In the Raman spectrum shown in Figure 5a, the

peaks positioned at 234, 281, 380, 807 (κ_2), and 834 (κ_1) cm^{-1} can be attributed to olivine, according to the published literature [39]. The two intense lines κ_1 and κ_2 are usually considered the main Raman features of olivine group members corresponding to Si–O asymmetric and symmetric stretching bands, respectively [39]. As reported by Mouri et al. [39], the parameter ω ($= \kappa_1 - \kappa_2$) is influenced by the olivine chemical composition. The ω value of the analyzed olivine phase is equal to 27 cm^{-1} . This result is compatible with fayalite-terephroite solid solutions in accordance with the olivine chemical composition measured by SEM/EDS [39]. The micro-Raman investigation did not succeed in the identification and proper characterization of the wüstite phase of slag A. In fact, the lines at 215, 273, and 385 cm^{-1} match with hematite (Figure 5b) [40]. However, these bands are probably due to the laser-induced oxidation of wüstite to hematite [40–42]. On the other hand, the Raman peak at 585 cm^{-1} can be assigned to wüstite or hematite (Figure 5b) [42,43]. The presence of leucite in slag A was proven by the Raman peak located at 495 cm^{-1} (Figure 5c) [44–46]. Regarding slag B, the olivine identification was confirmed by the Raman peaks at 234, 282, 808 (κ_2), and 833 (κ_1) cm^{-1} (Figure 6a). The parameter ω ($= \kappa_1 - \kappa_2$) is equal to 25 cm^{-1} and is consistent with the ω value computed for the olivine phase of slag A. The Raman spectrum of the cruciform crystals intergrowing with skeletal olivine is reported in Figure 6b. The peak at 667 cm^{-1} can be assigned to magnetite, based on the published literature [32]. However, it cannot be excluded that magnetite was generated through laser-induced oxidation of wüstite. Therefore, this result should be treated with caution. The doublet at 815 and 838 cm^{-1} is due to the presence of olivine in the analyzed area (Figure 6b). The oxidation effect caused by the laser prevented a proper characterization of the outer iron oxide skin of slag B. In fact, the hematite peaks at 212, 275, and 387 cm^{-1} are probably due to the oxidation of wüstite and/or magnetite [40–42] (Figure 6c). In addition, the interpretation of the peak positioned at 595 cm^{-1} is rather controversial because it can be attributed to both wüstite and hematite (Figure 6c) [40,47]. The micro-Raman investigation of the interstitial glass phase of slag B was not feasible due to the weak intensity of its Raman spectrum which was covered by the adjacent olivine signal.

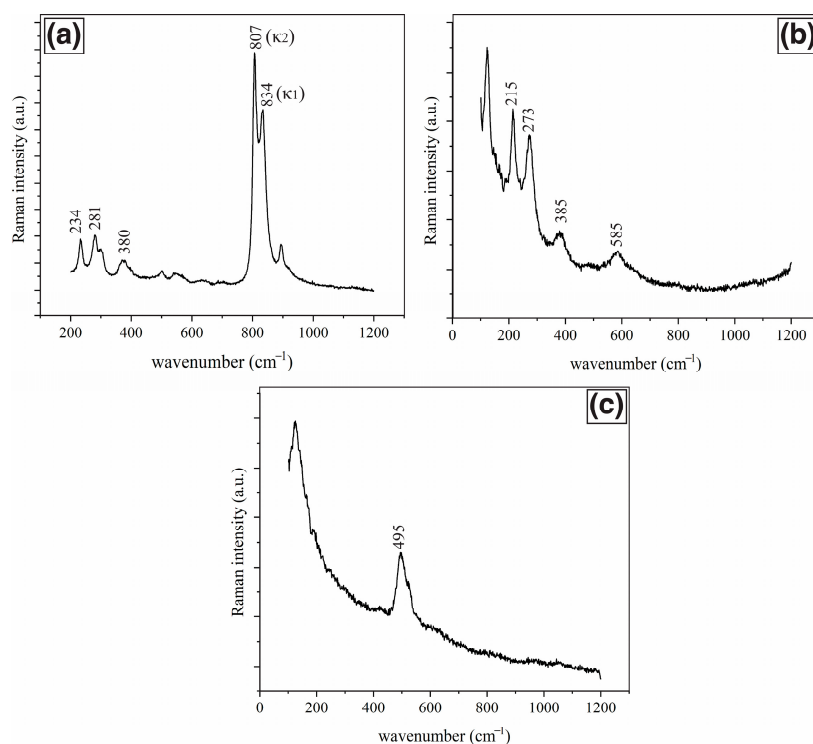


Figure 5. Raman spectra of the mineralogical phases detected in slag A. (a) Raman spectrum of olivine. (b) Raman spectrum of hematite (the presence of hematite is probably due to the laser-induced oxidation of wüstite). (c) Raman spectrum of leucite.

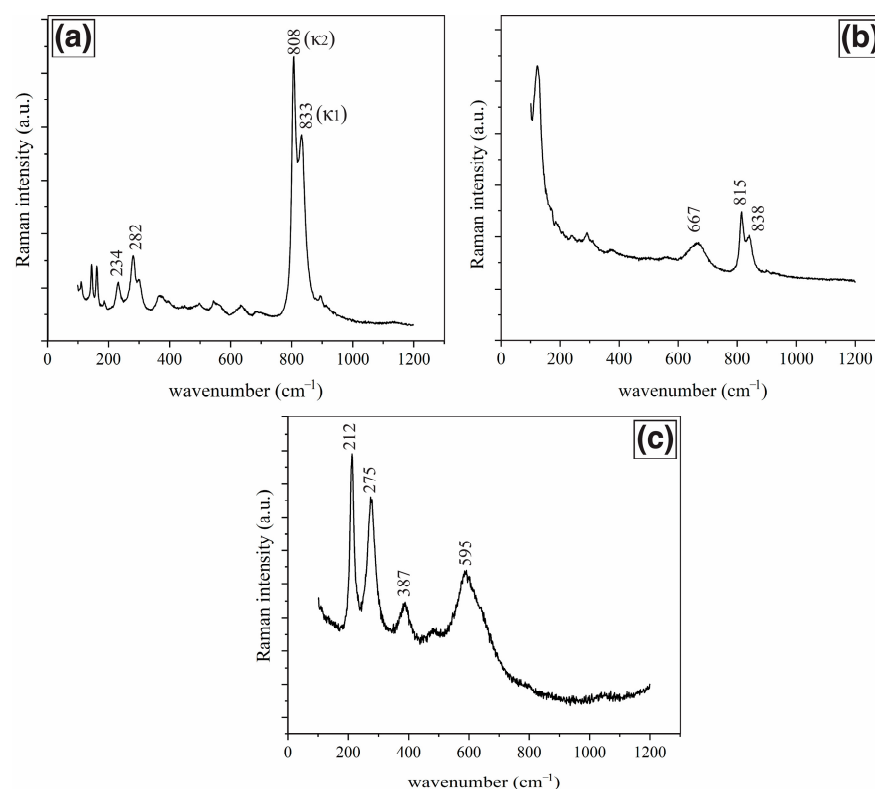


Figure 6. Raman spectra of the mineralogical phases detected in slag B. (a) Raman spectrum of olivine. (b) Raman spectrum of magnetite and olivine. (c) Raman spectrum of hematite (the presence of hematite is probably due to the laser-induced oxidation of wüstite and/or magnetite).

3.4. Smelting Temperature

To investigate the minimal temperature reached during the direct iron smelting process, the liquidus temperatures of both slags were evaluated by adopting two different strategies: phase diagram and Rhyolite-MELTS software. For this purpose, the FeO–SiO₂–MnO ternary system was selected as it encompasses 94 wt% and 93 wt% of the bulk chemical composition of slags A and B, respectively (Table 2). Minor oxides were included in the analysis based on their chemical compatibility with the three main compounds. In particular, basic oxides (CaO, MgO, Na₂O, K₂O, CuO, and BaO) were combined with FeO, while acid oxides (Al₂O₃ and P₂O₅) were added to SiO₂. In the ternary phase diagram reported in Figure 7, slags A falls into the fayalite–tephroite solid solution primary field with a liquidus temperature of ~1250 °C. On the other hand, slag B belongs to the tridymite primary field, exhibiting a crystallization temperature of ~1300 °C (Figure 7). For comparison, the bulk chemistry data of other bloomery slags from the PVGI, PVGII, and PVGIII sites, previously published by Cucini and Tizzoni [21] (Table 3), were plotted on the same ternary system (Figure 7). Table 3 includes both tap (T) and furnace (F) slags. In particular, tap slag class (T) includes the slags that flowed outside the furnace through a tap hole positioned at the bottom of the bloomery hearth. On the other hand, furnace slag type (F) refers to the slags that are retained inside the hearth and likely derived from the final charges of the furnace before the end of the process [21]. It is worth mentioning that furnace slags are usually highly porous, embedding charcoal fragments and eventually partially reduced ore [21]. The three slag groups greatly overlap each other in the phase diagram and are positioned in the fayalite–tephroite solid solution, manganese wüstite, and tridymite primary fields. The liquidus temperatures of PVGI, PVGII, and PVGIII slags vary approximately within the ranges 1200–1400 °C, 1200–1250 °C, and 1200–1350 °C. Remarkably, the liquidus temperatures of slags A and B exhibit a high degree of compatibility with those of the other previously analyzed bloomery slags from the PVGI site (Figure 7).

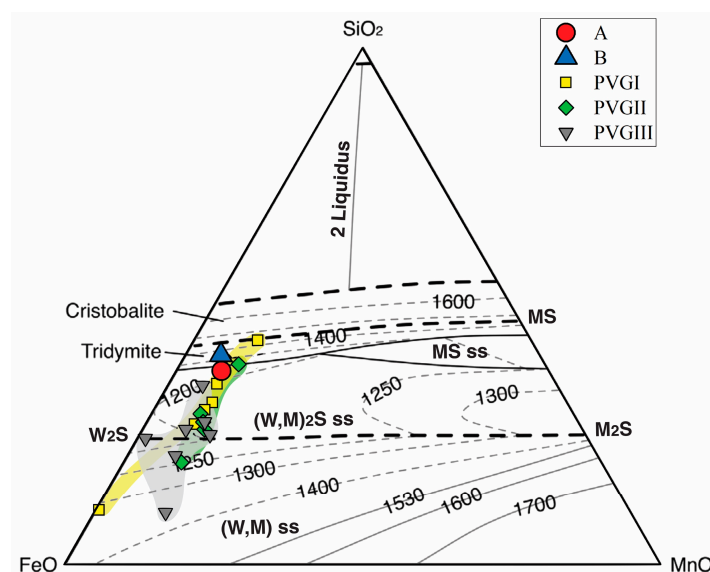


Figure 7. Projections of the bulk chemistry of slags A, B, and already studied iron smelting slags from PVGI, PVGII, and PVGIII sites (chemical data taken from [21]) in the FeO–SiO₂–MnO ternary system (readapted from [48]) in terms of (FeO + CaO + MgO + Na₂O + K₂O + CuO + BaO) – (SiO₂ + Al₂O₃ + P₂O₅) – MnO in equilibrium with metallic iron (W = FeO, M = MnO, S = SiO₂, and ss = solid solution).

Table 3. Bulk chemistry data (wt%) of bloomery slags recovered from PVGI, PVGII, and PVGIII sites (compositional data taken from [14]) and liquidus temperatures (°C) computed with the Rhyolite-MELTS software (T = tap slags; F = furnace slags).

Slag	Type	Site	MgO	Al ₂ O ₃	SiO ₂	CaO	MnO	FeO	P ₂ O ₅	MELTS Liquidus Temperature (°C)
B, 12	T	PVGI	0.63	0.01	31.37	0.03	9.22	58.57	0.17	1128
B, 6	T	PVGI	0.54	0.01	29.98	0.04	8.61	60.70	0.12	1144
A, 10	T	PVGI	0.68	0.01	43.41	0.15	10.76	44.92	0.06	1207
SP.	T	PVGI	0.45	2.06	32.96	1.30	8.14	55.04	0.05	1110
P, 5	T	PVGII	0.43	1.28	38.85	0.21	6.74	52.29	0.20	1180
P, 5	F	PVGII	0.40	1.32	27.93	0.26	8.25	61.53	0.32	1157
P, 6	F	PVGII	0.42	1.21	25.02	0.35	10.41	62.41	0.17	1181
U, 16	T	PVGII	0.42	2.78	36.05	0.46	9.86	50.32	0.11	1093
P, 6	T	PVGII	0.60	1.97	25.66	0.68	9.52	61.38	0.19	1167
L1, 25	T	PVGIII	0.99	3.57	24.09	2.08	9.73	58.86	0.68	–
A1, 3	F	PVGIII	2.65	4.19	19.59	11.71	9.13	52.73	0.00	1160
I1, 23	T	PVGIII	0.76	3.53	31.09	0.25	5.84	58.51	0.00	1167
E1, 11	T	PVGIII	1.93	3.20	23.16	6.14	7.38	57.30	0.89	1219
C1, 6	F	PVGIII	0.18	3.98	21.84	3.86	12.15	57.98	0.00	1171

It is important to note that the liquidus temperature estimated via phase diagrams should be only regarded as rough approximations due to the complex slag bulk chemistry. For this reason, the liquidus temperature was also assessed with Rhyolite-MELTS software to better address the complex slag chemical composition. Based on the petrological characterization of both slags, the Rhyolite-MELTS thermodynamic computations were performed at a constant pressure of 1 bar (0.1 MPa), constraining the oxygen fugacity at the Iron–Wüstite (IW) and Quartz–Fayalite–Magnetite (QFM) oxygen buffers for slag A and B, respectively. The resulting crystallization temperatures of slags A and B were 1120 °C and 1146 °C (Figure 8), respectively. In addition, the liquidus temperatures of other previously studied bloomery from the PVGI, PVGII, and PVGIII sites were calculated with Rhyolite-MELTS software at the Iron–Wüstite (IW) oxygen buffer, starting from the

compositional data reported in Table 3. The estimated liquidus temperatures were in the ranges 1110–1207 °C, 1057–1093 °C, and 1160–1219 °C for PVGI, PVGII, and PVGIII slags, respectively (Table 3 and Figure 8). Even in this case, the liquidus temperatures of slags A and B fall in the temperature range of the PVGI slag group. Moreover, the liquidus temperatures predicted with Rhyolite-MELTS software were observed to be significantly lower than those estimated by the ternary phase diagram.

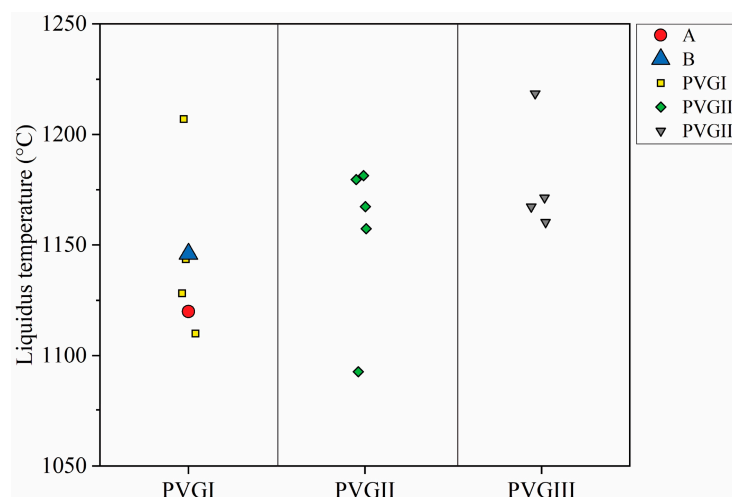


Figure 8. Liquidus temperatures estimated by the Rhyolite-MELTS software of slags A, B, and other already analyzed iron smelting slags from PVGI, PVGII, and PVGIII sites.

3.5. Redox Conditions

The redox formation conditions of slag A were estimated in terms of oxygen chemical potential by Equation (7), considering the bulk chemical composition reported in Table 2. The adoption of Equation (7), which is based on the equilibrium between ferrous iron in slag and pure metallic iron ($a_{[Fe]} = 1$), is justified by the petrological analysis results. In fact, the presence of coexisting olivine and wüstite in slag A clearly indicated the predominance of ferrous iron and suggested a strongly reducing atmosphere inside the bloomery furnace. The activity of ferrous iron oxide was computed by Ban-Ya's quadratic regular solution model [28,49] (Equations (9) and (10)) using the interaction energies between the major cations provided in Table 1. The oxygen chemical potential of slag A is located below the Quartz–Fayalite–Iron (QFI) buffer at -382.61 kJ/mol, considering the liquidus temperature of 1120 °C which was previously computed with the Rhyolite-MELTS software (Figure 9). On the other hand, the oxygen chemical potential of formation of slag B was estimated by Equation (8), starting from the bulk chemical composition reported in Table 2. In this case, the use of Equation (8) was considered appropriate due to the coexistence of olivine, magnetite, and glass phases in slag B. This mineralogical phase assemblage indicates a more oxidizing atmosphere within the bloomery furnace compared to slag A, resulting in a non-negligible ferrous/ferric iron oxide ratio. The bulk ferric/ferrous iron oxide ratio ($x_{FeO1.5}/x_{FeO}$) was approximately estimated as the average weighted on the phase volume fractions:

$$x_{FeO1.5}/x_{FeO} = 0.5 \text{ vol\% (magnetite + glass)}/100. \quad (11)$$

This formula relies on the assumption that the ferric/ferrous iron oxide ratio is equal to 0.5 in the stoichiometric magnetite and magnetite-saturated interstitial glass phases, and zero in the stoichiometric olivine phase. The value of the ferric/ferrous iron oxide ratio computed by Equation (11) is 0.16. The chemical activities of ferrous and ferric iron oxides were evaluated by Ban-Ya's quadratic regular solution model [28] (Equations (9) and (10)) using the interaction energies between the major cations provided in Table 1. The resulting formation energy of the oxygen chemical potential of slag B is positioned close to the Quartz–Fayalite–Magnetite (FMQ) buffer at -243.80 kJ/mol, considering a liquidus temperature of 1146 °C which was previously

computed with the Rhyolite-MELTS software (Figure 9). Notably, these redox conditions are more oxidizing than those usually observed in the bloomery smelting process [49].

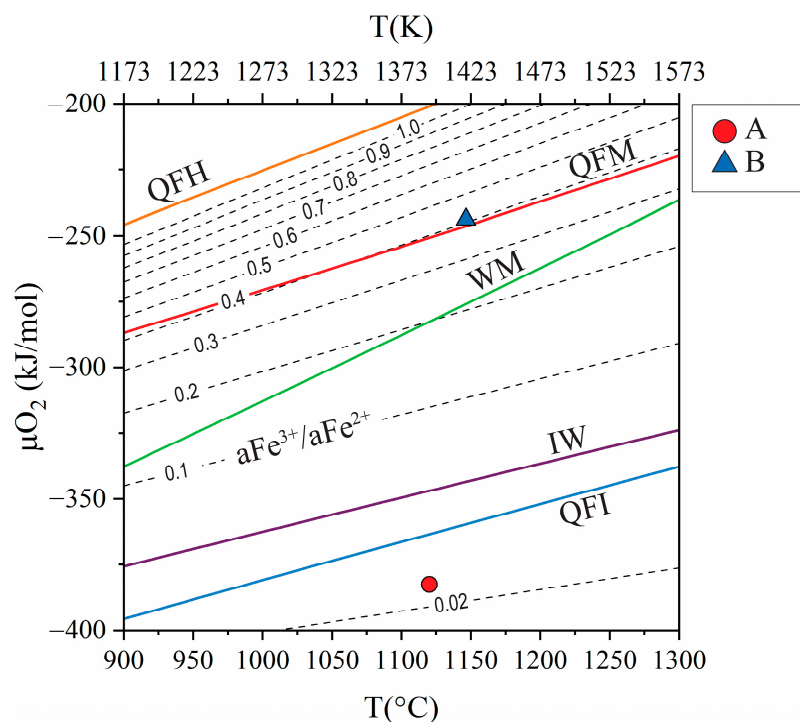


Figure 9. Redox formation conditions of slags A and B plotted in the oxygen chemical potential space at a fixed pressure of 1 bar (0.1 MPa). The oxygen buffer equilibria Quartz–Fayalite–Hematite (FHQ), data from [50], Quartz–Fayalite–Magnetite (FMQ), data from [51], Wüstite–Magnetite (WM), data from [52], Iron–Wüstite (IW), data from [53], and Quartz–Fayalite–Iron (QFI), data from [51] were included in the diagram as reference curves. The isopleths of the ferric–ferrous iron activities ratio ($a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}$) (dashed lines) were computed by Equation (8).

4. Conclusions

In this study, an archaeometallurgical characterization of two bloomery tap slags retrieved in the early medieval site of Ponte di Val Gabbia I (Brescia, northern Italy) was carried out. In this site, iron was produced via the direct ironmaking process. The main goal of the present research was to estimate the key parameters of the ancient direct iron-making process. The petrological features of both slags were investigated by light optical and scanning electron microscopy. It was found that slag A consists of olivine, wüstite, and leucite, whereas slag B is marked by olivine–wüstite–magnetite–glass phase assemblage. The morphology of the mineralogical phases of both slags indicated a high degree of undercooling. The slag bulk chemistry and the chemical composition of each mineralogical phase were measured by SEM/EDS. The identification of olivine and leucite was successfully confirmed by micro-Raman spectroscopy. This method was used in conjunction with the SEM/EDS results; through this combined approach, the identification of both minerals was confirmed with a high degree of accuracy. Conversely, wüstite and magnetite could not be properly recognized and characterized due to the laser-induced oxidation effect. To estimate the working temperature of the bloomery furnace, the liquidus temperatures of both slags were computed by projecting their bulk chemical compositions in the FeO–SiO₂–MnO ternary system and by the Rhyolite-MELTS software. As determined from the phase diagram, the liquidus temperatures for slags A and B were approximately estimated to be ~1250 °C and ~1300 °C, respectively. On the other hand, the slag crystallization temperature predicted with Rhyolite-MELTS was significantly lower, namely, 1120 °C and 1146 °C for slags A and B, respectively. Considering that Rhyolite-MELTS allowed to better address the complex slag chemistry, the later outputs were considered the better estimates of the smelting

temperature. Furthermore, both slags showed a liquidus temperature compatible with that of previously studied slags from Ponte di Val Gabbia I. According to the results of the petrological analysis, the redox formation conditions of both slags were computed in terms of the oxygen chemical potential of the gas atmosphere in equilibrium with the liquid slags. It was concluded that slags A and B were generated in significantly different redox conditions. In particular, slag A formed in strongly reducing conditions, whereas slag B tended to equilibrate with a more oxidizing environment. Specifically, based on the equilibria between ferrous and metallic iron, the oxygen chemical potential for slag A was -382.61 kJ/mol at the liquidus temperature of 1120 °C. Conversely, the predicted oxygen chemical potential for slag B was -243.80 kJ/mol at the liquidus temperature of 1146 °C, under equilibrium between ferrous and ferric iron in the liquid slag. These results can reflect a large variability in the redox conditions during the smelting process.

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