



## **Petrology of iron and copper slags from historical smelting activity in southern Tuscany**

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### **ABSTRACT**

In this paper we present a petrographic and chemical characterisation of slag samples from seventeen metallurgical smelting sites for iron and base metals in southern Tuscany and Elba Island, active during ancient, medieval and modern times. These new results, integrated with data available for some of the investigated sites, expand the information available for the investigated metallurgical sites and offer a new petrological viewpoint on the historical evolution of the smelting activity. The chemical composition of samples from different smelting sites can be used to derive information on the composition of charges (and fluxes) used in the furnaces, as well as to determine the physical conditions of slag formation. This study ultimately contributes to enlarge the dataset available on slag mineralogy thereby offering a solid base for the petrological analysis of the slag formation process in historical smelting sites.

**Keywords:** metallurgical slags; iron slag; copper slag; southern Tuscany; Elba Island; smelting.

### **INTRODUCTION**

The breakthrough of metallurgy constituted a turning point in human history that deeply influenced the economy and the socio-cultural structure of ancient societies. The first metal to be intentionally smelted was copper, eventually followed by the production of bronze and iron (Forbes, 1950; Giardino, 2010; Killick and Fenn, 2012). Although the knowledge of how to extract the metal from the ore improved across the centuries, the formation of a slag phase could not be avoided. Slags constitute by-products that must have specific characteristics in order to enhance the separation between the metal and the gangue (i.e. the undesirable material associated with the wanted metal in the ore) (Bachmann, 1982; Hauptmann, 2014). They represent the dominantly silicate part that is separated from the metal phase in the reducing ambient of the metallurgical furnace, constituted simply by a crucible or, later, by a bed of mineral and wood charcoal filling in a brick structure (Bayley and Rehren, 2007; Rehder, 2000). The matrix of the silicate slags often carries remains

of the original charges processed in the metallurgical furnace that did not completely react or separate from the silicate part. These charges were normally composed by the ore (oxides, sulfides, etc.), usually previously enriched and roasted, the gangue and flux agents favouring the extraction of the metal (Tylecote, 1992). Nowadays, slags are witnesses of ancient to relatively modern smelting processes and the only evidence through which physical-chemical parameters and overall efficiency of the smelting processes can be inferred (Bachmann, 1982; Rehder, 2000).

Owing to a peculiar geological setting, favourable to the formation of iron, copper and base metal ores, Tuscany represents the region in central Italy where mining and smelting activities historically developed. The smelting activity begun in southern Tuscany during the 4<sup>th</sup> millennium BCE (Artioli et al., 2017; Vigliotti et al., 2003; Zifferero, 2017) and continued throughout the modern age, alternating periods of intense extraction to decades or centuries of abandonment (Benedettini, 1983;

Corretti and Firmati, 2011). The metallurgical activity shut down in the late-20<sup>th</sup> century and left abundant remains of archaeological interest, along with slags heaps that, over the centuries, were abandoned in the environment surrounding the furnaces.

In this study, we examined the petrography and chemistry of slags from selected known and yet unexplored metallurgical sites, aiming at providing a petrological interpretation of the slag formation process.

### ORE EXPLOITATION IN TUSCANY

The smelting activity and the associated production of slags can be divided in three macro-groups: ancient (overall covering the Etruscan-Roman period), medieval (carried out from the 11<sup>th</sup> to 14<sup>th</sup> century) and modern (carried out during the 19<sup>th</sup> and 20<sup>th</sup> centuries). The Etruscan civilisation (9<sup>th</sup>-1<sup>st</sup> century BCE) discovered and exploited the skarn-sulfide deposits and the Cu-Pb-Zn-(Ag) ores associated to the Plio-Quaternary magmatism of southern Tuscany (Dini, 2003; Zifferero, 2017). The exploitation of the ore deposits continued during the Roman period, before being discontinued for approximately 600 years after the fall of the Roman Empire and intermittently resumed starting from the Middle Age (11<sup>th</sup> century) until the industrial age (late 19<sup>th</sup> century) (Benvenuti et al., 2014). In this last period, the advancement of the extraction techniques is testified by the fact that the formerly exploited ore deposits were processed again with modern plants and procedures (Carli, 2010; Pistolesi, 2006). The smelting activity was finally discontinued in the different metallurgical areas, while only minor mining activity continued in a few sites.

### Elba Island

Iron ores from Elba Island are very well known since ancient times and consist of hematite, in the area near Rio Marina, and, in the south-eastern part of the island, of magnetite ores (Benvenuti, 1996). The exploitation probably begun during 11<sup>th</sup>-10<sup>th</sup> century BCE and a wide dispersion of minerals from Elba starting from the 6<sup>th</sup>-5<sup>th</sup> centuries BCE is testified by the occurrence of artefacts made from Elba iron in locations bordering the Tyrrhenian Sea (Corretti, 2001). It is estimated that about 60 million tons of iron ore were extracted during a time span of almost three millennia (Tanelli et al., 2001). Due to the large requirement of firewood to run the furnaces, the iron ores from Elba Island were mostly transported and processed on the near coastal settlements. The smelting activity in Baratti and Poggetti Butelli (Follonica) can be in fact linked to the Elba metallurgical district, although it must be noted that also copper ores from Campiglia Marittima mines were processed in the same site during Etruscan and Roman periods (Benvenuti et al., 2000).

Nonetheless, the occurrence of some slags associated to waste material suggests that metal smelting was also done on site (Corretti, 1988; Corretti and Firmati, 2011) and recent studies based on modelling the different human activities confirm the possibility of smelting on the island (Becker et al., 2019, 2020).

### Campiglia Marittima

The Campiglia Marittima mines were first exploited during 4<sup>th</sup> millennium BCE, with the most ancient excavations in the Temperino Valley and in adjacent areas. The mineralisation is a sulfide ore associated to a skarn body (Vezzoni et al., 2016); the ores are mainly formed by copper and minor zinc and lead minerals (chalcopyrite, sphalerite and galena), but it seems that the Etruscan also used the cassiterite to extract tin and produce bronze items (Benedettini, 1983). The base metal were mined and processed to extract copper, although there is also evidence for smelting experiments aimed at extracting lead and silver from the Ag-rich galena (Mascaro et al., 1995). Additional studies and archaeological investigations were able to spot various mine entrances and smelting sites of pre-Industrial age in the whole Campiglia Marittima district, from Monte Valerio to Monte Rombolo and Rocca San Silvestro, and the nearby valleys (Valle di Capattoli, Val Fucinaia, Valle in Lungo, Valle del Temperino) (Cascone and Tinagli, 2016; Mascaro et al., 1995). In the modern era (20<sup>th</sup> century), the British society Etruscan Copper Estates Limited re-opened some old mines and built a vast metallurgical complex that, however, did not produced a significant amount of mineral, therefore the company declared bankruptcy in 1907 (Carli, 2010). Concerning the copper - and lead - slags of Campiglia Marittima smelting district, there are studies about two different sites: Rocca San Silvestro (Mascaro et al., 1995) and Capattoli Valley (Manasse et al., 2001).

### Massa Marittima

A relevant mining and smelting activity took place in the district of Massa Marittima, as also suggested by the toponym of the area "*Colline Metallifere*", literally translated as "metal-bearing hills". The mineralisation is mainly composed of pyrite ores and Cu-Pb-Zn-(Ag) sulfide ores. Although mainly present in sub-economic concentrations, the sulfide ores are represented, in the Niccioleta area, by lenses of limonite enclosing veins of galena, pyrite and chalcopyrite. Typically, this mineralisation is associated with pyrite bodies (Tanelli and Lattanzi, 1983) and was exploited by the Etruscan for the argentiferous galena and chalcopyrite near Accesa lake and Serrabottini mine, where a necropolis and many ancient shafts of Villanovan age (10<sup>th</sup>-8<sup>th</sup> century BCE) were found. During the Middle Age, Massa Marittima was

a very important mining and metallurgical area, as also testified by the publication of one of the European oldest collection of rules concerning mining (Rodolico, 1938). Near the medieval castle of Rocchette Pannocchieschi there is one of the few occurrences of polymetallic ores hosted near the contact between the limestones of the Tuscan domain and Ligurian units (Chiarantini et al., 2021). An archaeological investigation of this site indicated that only minor smelting activity was carried out inside the castle and that some buildings were probably used for storage of the mineral ores to be smelted elsewhere (Belli et al., 2003; Buracchi et al., 2015b). The slags in this site are the result of the smelting of sulfides, specifically chalcopyrite ( $\text{CuFeS}_2$ ) and galena ( $\text{PbS}$ ). During the 18<sup>th</sup> century, the mining activity started again on the Boccheggiano (Merse) and Fenice Capanne area. The Valpiana and Accesa metallurgical plants were renovated in order to process a larger amount of minerals. The blast furnaces, previously devoted to the iron smelting, were converted to extract mainly copper and to treat the results of the leaching and cementation (a chemical reaction through which a metal is removed from the solution and precipitated) of the ore from Fenice Massetana mine. Another target of the extraction process was the pyrite used to produce sulfuric acid. For this purpose, specific furnaces were built during the first years of 20<sup>th</sup> century. All the excavation and smelting activities terminated by

1910, except for the pyrite extraction that prompted the re-opening of some sections of the Boccheggiano mine starting in the 1950s (Dini, 2003). The intense mining and smelting activity deeply affected the territory, leaving a lot of waste material abandoned over the whole region (Benvenuti et al., 1999; Costagliola et al., 2008).

## MATERIAL AND METHODS

### Sample collection, selection and preparation

A total of 17 sites in the mining and smelting districts of Elba Island (Polverata, Sant'Andrea, San Giovanni, Valle della Nivera, two sites in Valle Litterno, Marmi, Gualdarone), Campiglia Marittima (Baratti, Schiumai, Rocca San Silvestro, Valle di Capattoli, Etruscan Copper Mines) and Massa Marittima (Poggetti Butelli, Rocchette Pannocchieschi, Marsiliana, Forni dell'Accesa) were inspected (Figure 1, Table 1). A preliminary selection of the slag samples, based on bulk chemistry, was performed on site using a Hand-held X-Ray Fluorescence Spectrometer (HH-XRF). The instrument used is a NITON XL3t GOLDD+ XRF spectrometer, equipped with a miniaturised tube with an Ag anode (6-50 kV, 0-200  $\mu\text{A}$  max) and fitted with an SDD detector. Statistically representative aliquots of each sample were ground to less than 20  $\mu\text{m}$  by jaw crusher and agate planetary mill. A total of 60 samples were selected and prepared in thin sections for observation under petrographic and scanning electron microscope (SEM).

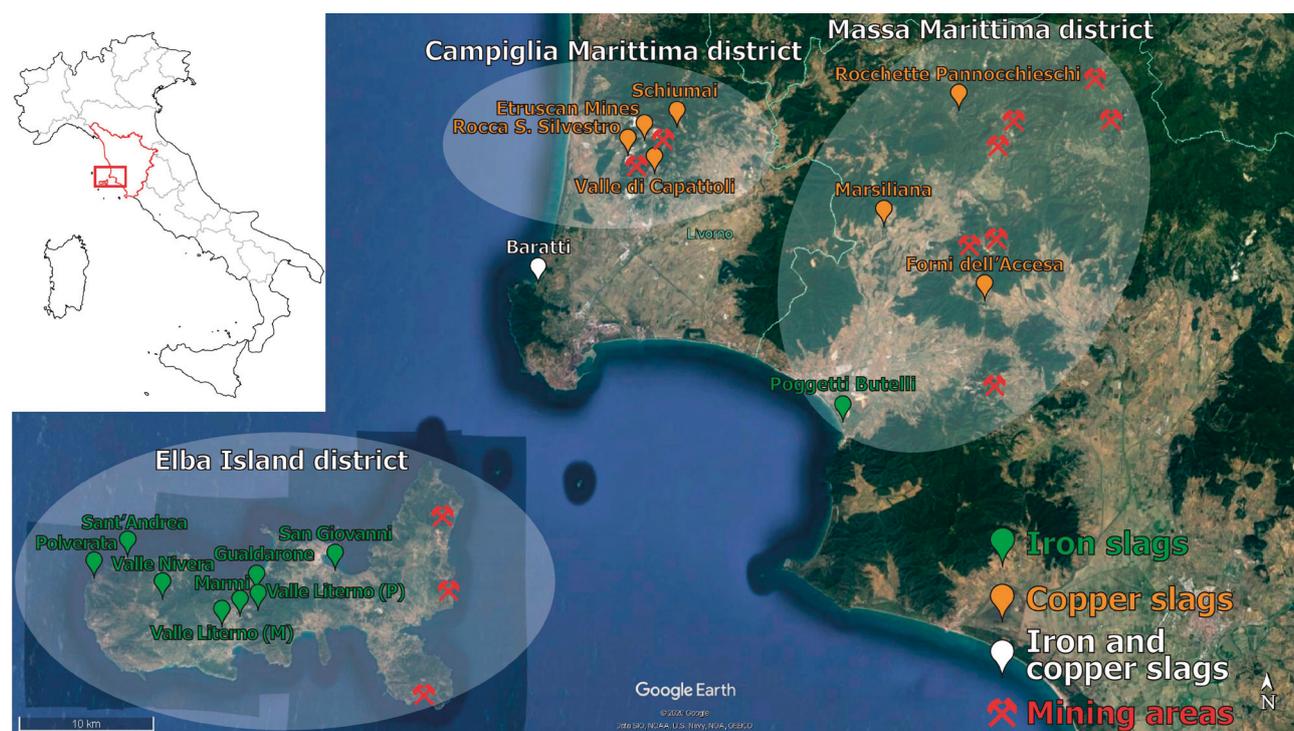


Figure 1. Satellite view of the sampling sites and the main mining areas of Southern Tuscany (© Google Earth 2020).

Table 1. Summary of the sampling sites.

Metallurgical district	Site	Latitude, longitude	Analyses (this work)	References
Campiglia Marittima	Etrusan Copper Mines	43.07920, 10.58806	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Muti, 2012
	Rocca San Silvestro	43.0866388, 10.6032111	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Mascaro et al., 1995
	Schiumai	43.10272, 10.62926	SEM, ICP-OES, ICP-MS, XRPD, EPMA	
	Valle di Capattoli	43.069775, 10.6167	SEM, ICP-OES, ICP-MS, XRPD	Manasse et al., 2001
	Baratti	42.988686, 10.505419	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Benvenuti et al., 2000
Massa Marittima	Marsiliana	43.02923, 10.82357	SEM, ICP-OES, ICP-MS, XRPD	Manasse et al., 2002; Costagliola et al., 2008
	Forni dell'Accesa	42.978610, 10.912456	SEM, ICP-OES, ICP-MS, XRPD, EPMA	
	Rocchette Pannocchieschi	43.10972222, 10.89166666	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Manasse et al., 2002
	Poggetti Butelli	42.8995389, 10.78677	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Costagliola et al., 2008
Elba Island	Sant'Andrea	42.808056, 10.14112	SEM, ICP-OES, ICP-MS	Corretti, 1988; Manzi et al., 2006
	Polverata	42.79334, 10.110278	SEM, ICP-OES, ICP-MS	Corretti, 1988; Manzi et al., 2006
	San Giovanni	42.801945, 10.32778	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Corretti, 1988
	Valle della Nivera	42.77741667, 10.18240833	SEM, ICP-OES, ICP-MS, XRPD, EPMA	Corretti, 1991; Manzi et al., 2006
	Valle Litterno (Portoferraio)	42.77532, 10.26116	SEM, ICP-OES, ICP-MS	Corretti, 1991; Manzi et al., 2006
	Valle Litterno (Marciana)	42.7744, 10.251167	SEM, ICP-OES, ICP-MS	Corretti, 1991; Manzi et al., 2006
	Gualdarone-Proccchio	42.786608, 10.256753	SEM, ICP-OES	Corretti, 1991; Manzi et al., 2006
	Marmi	42.77441389, 10.25014722	SEM, ICP-OES, ICP-MS	Corretti, 1991; Manzi et al., 2006

### Analytical methods

Backscattered electron (BSE) images and semi-quantitative chemical analyses were obtained using a FEI Quanta 450 FE-SEM installed at the Centre for Instrument Sharing of the University of Pisa (CISUP), equipped with a Bruker (Energy-dispersive system) QUANTAX XFlash Detector 6|10; high vacuum and 15-20 kV. Electron microprobe (EPM) analyses were performed on the same samples at Unitech COSPECT laboratory at the University of Milan (Italy) with a JEOL 8200 (EPMA-WDS), using 20 kV accelerating voltage, a beam diameter of 1 µm and a beam current of 5 nA. Aliquots of the 40 selected sample

powders were analysed for major and trace elements by Inductively coupled plasma optical emission spectrometry (ICP-OES) at Activation Laboratories LTD (Canada); to ensure the total dissolution of the sample, a lithium metaborate/tetraborate fusion was used, followed by the digestion of the resulting molten bead in a weak nitric acid solution. Additionally, 3 samples were investigated by infrared spectroscopy analyses for their sulphur content. Trace elements for 32 samples were analysed in the Department of Earth Sciences (University of Pisa), using an inductively coupled plasma mass spectrometry (ICP-MS). Sample digestion was performed using

consecutive additions of aqua regia, hydrofluoric acid and nitric acid. An external calibration with a blank solution and the geochemical reference material BE-N was used, in addition to two standard solutions: WSE and OKUM. Re and Rh were added as internal standard, to measure the instrumental drift and correct data for it.

X-Ray powder diffraction (XRPD) was performed using a Bruker D2 Phaser diffractometer (30 kV, 10 mA) operating in Bragg-Brentano geometry ( $\theta$ - $\theta$  scan mode) and equipped with a 1-dimensional Lynxeye detector. Ni-filtered Cu K $\alpha$  radiation was used. Data were collected in the scan range 4–65° in  $2\theta$ , with scan step of 0.02° and counting times of 0.1 s/step. Data were processed through the software Diffrac.Eva (Bruker AXS).

## RESULTS

### Petrographic features and mineral chemistry

The slag samples collected in the different metallurgical sites present a high petrographic variability (Table 2). Textures range from glassy or weakly vitrophyric to highly porphyritic, with most of the samples having a porphyricity index (PI) around 50–60 vol%. The principal phases observed are represented mostly by silicates (dominantly olivine and clinopyroxene), oxides and minor metal droplets (Figures 2, 3). The groundmass is commonly glassy, although some samples present microcrystals. In general, iron slags are composed of a single silicate phase (Fe-olivine), iron oxides and glass, while copper/lead slags are characterized by multiple silicate phases (Ca-Fe-olivine and Fe-pyroxene), in addition to iron oxides and sulfides. Moreover, iron slags are more vesicular with respect to copper ones, with average porosity being 11 and 5 vol%, respectively (estimated using jPOR on thin section images).

#### Elba district

The ancient and medieval iron slags from Elba Island are highly vesiculated with a spongy texture and are characterised by a superficial weathering (Figure S1). Macroscopically, there are no differences between the slags attributed to Roman period and those obtained during the medieval metallurgical activity. The slags can be found as both relatively small fragments and large pieces. The mineral assemblage of both ancient (Polverata, Sant'Andrea, San Giovanni) and medieval (Valle della Nivera, Valle Litterno, Marmi, Gualdarone) slags is characterized in large part by skeletal olivine (fayalite) and dendritic wüstite and magnetite (Figure 2 a,b). The iron oxides are widespread in all samples, but they are rather variable in size and thickness. Specifically, it can be noticed that the oxides chains are not composed of a single oxide, but they are formed by irregular wüstite in dendritic magnetite crystals (Figure S1d), while an

opposite pattern has been observed in medieval sample. Olivine is present as skeletal crystals in all the samples, showing a composition of nearly pure fayalite, both in ancient and medieval samples (Figure 3b). Droplets of metallic iron occur in variable abundance (never exceeding 5 vol%). Interstitial silicate glass is ubiquitous, commonly in amount around 10 vol%. EPMA analyses indicate lower FeO and SiO<sub>2</sub> concentration in the glass compared to bulk composition (Table S1; Figure S4), while Al<sub>2</sub>O<sub>3</sub> and CaO have higher concentration.

#### Campiglia Marittima district

Smelting of copper ores presumably from the nearby mines of Campiglia Marittima (Chiarantini et al., 2018), as mentioned above, occurred at Baratti (Crew, 1991) and is generally attributed to Etruscan-age metalworking, preceding the Roman iron smelting (Chiarantini et al., 2009). The samples of ancient copper slags usually exhibit an external weathering coating due to the interaction with marine aerosol, but they show a characteristic lustre in freshly cut sections (Figure S2a). Under the microscope, they display a porphyritic texture with large skeletal crystals of olivine, showing a variable enrichment in Ca (Figure 3a), and dendritic to skeletal iron oxides (Table S4). The groundmass is composed of clinopyroxene (hedenbergite, Figure 3b) and, in minor amount, by silicate glass. Throughout the section, droplets of copper sulfides (covellite, chalcocite) and residues of metallic copper can also be found (Table S3), pointing out an incomplete separation of the metal from the silicate slag.

The copper slags sampled in the other sites of the Campiglia Marittima mining district are highly porphyritic with a mineral assemblage characterized by olivine (fayalite and kirschsteinite) and clinopyroxene (hedenbergite) as main mineral phases; sulfides (galena, pyrrhotite, and wurtzite) and magnetite are accessory minerals. Olivine shows a variable enrichment in Ca ranging from nearly pure fayalite in modern slag samples, towards the kirschsteinite end-member in the medieval samples (Figure 3a, Table S2). Due to the complete partitioning of Ca in the M2 site, there is a limited miscibility between the fayalite-kirschsteinite solid solution end members (Mukhopadhyay and Lindsley, 1983). Analyses on clinopyroxene show an enrichment in CaO and Al<sub>2</sub>O<sub>3</sub> and project towards the wollastonite end member (Figure 3b, Table S2). Compared to medieval slags, modern slags generally are richer in hedenbergite and poorer in kirschsteinite. Bornite is the most abundant sulfide, especially in modern slags; pyrrhotite also commonly occurs and is slightly enriched in Fe. Other minor occurrences of chalcopyrite, galena and wurtzite have also been observed.

Medieval copper slags from Rocca San Silvestro site

Table 2 - Pyrometallurgical phases of some selected representative samples. Results from the combination of XRPD, SEM-EDS and EPMA-WDS data. Legend: CM: Campiglia Marittima district; MM: Massa Marittima district; \*\*\*: abundant (10-60%); \*\*: present (1-10%); \*: minor/occasional (<1%).

		Silicates			Oxides-hydroxides			Sulphides					Notes					
		Fayalite	Kirschsteinite	Hedenbergite	Wollastonite	Wüstite	Magnetite	Azurite	Wurtzite	Galena	Pyrrhote	Covellite	Chalcocite	Chalcocpyrite	Bornite	Glass	Metals/alloys	
		Fe <sub>2</sub> SiO <sub>4</sub>	CaFe <sub>2</sub> SiO <sub>4</sub>	CaFe <sub>2</sub> +Si <sub>2</sub> O <sub>6</sub>	CaSiO <sub>3</sub>	FeO	Fe <sup>2+</sup> Fe <sup>3+</sup> O <sub>4</sub>	Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	(Zn,Fe)S	Pbs	Fe <sup>x</sup> S	CuS	Cu <sub>2</sub> S	CuFeS <sub>2</sub>	Cu <sub>5</sub> FeS <sub>4</sub>		(Cu, Fe, ...)	
Fe slags	Ancient	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	subhedral-euhedral fayalite and dendritic iron oxides
		Poggetti Butelli (TS_PB3)																elongated, skeletal crystals of fayalite and dendritic iron oxides
		San Giovanni (TS_SG1)																skeletal fayalite and dendritic iron oxides
	Medieval	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	skeletal fayalite and dendritic oxides with minor hedenbergite and copper sulfides
Cu/Pb slags	Ancient (Baratti)	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	various silicate phases, dendritic iron oxides and droplets of sulfides
		Baratti (BB_03)																large skeletal fayalite and interstitial hedenbergite with droplets of copper sulfides
	Medieval (CM)	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	dendritic iron oxides and metal alloys with small crystals of kirschsteinite
		Schiunai (RS_05)																skeletal crystals of hedenbergite with minor fayalite and sulfides
		Rocca S. Silvestro (A 2000)																droplets of sulfides in a glassy groundmass
	Medieval (MM)	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	hedenbergite with interstitial sulfides and glass
		Rocchette Pannoecchieschi (RPS)																
	Modern (CM)	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	
		Etruscan Mines (MR.234.03.B1)																
	Modern (MM)	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	
		Forni dell'Accessa (RA_02)																
		Forni dell'Accessa (RA_03)																

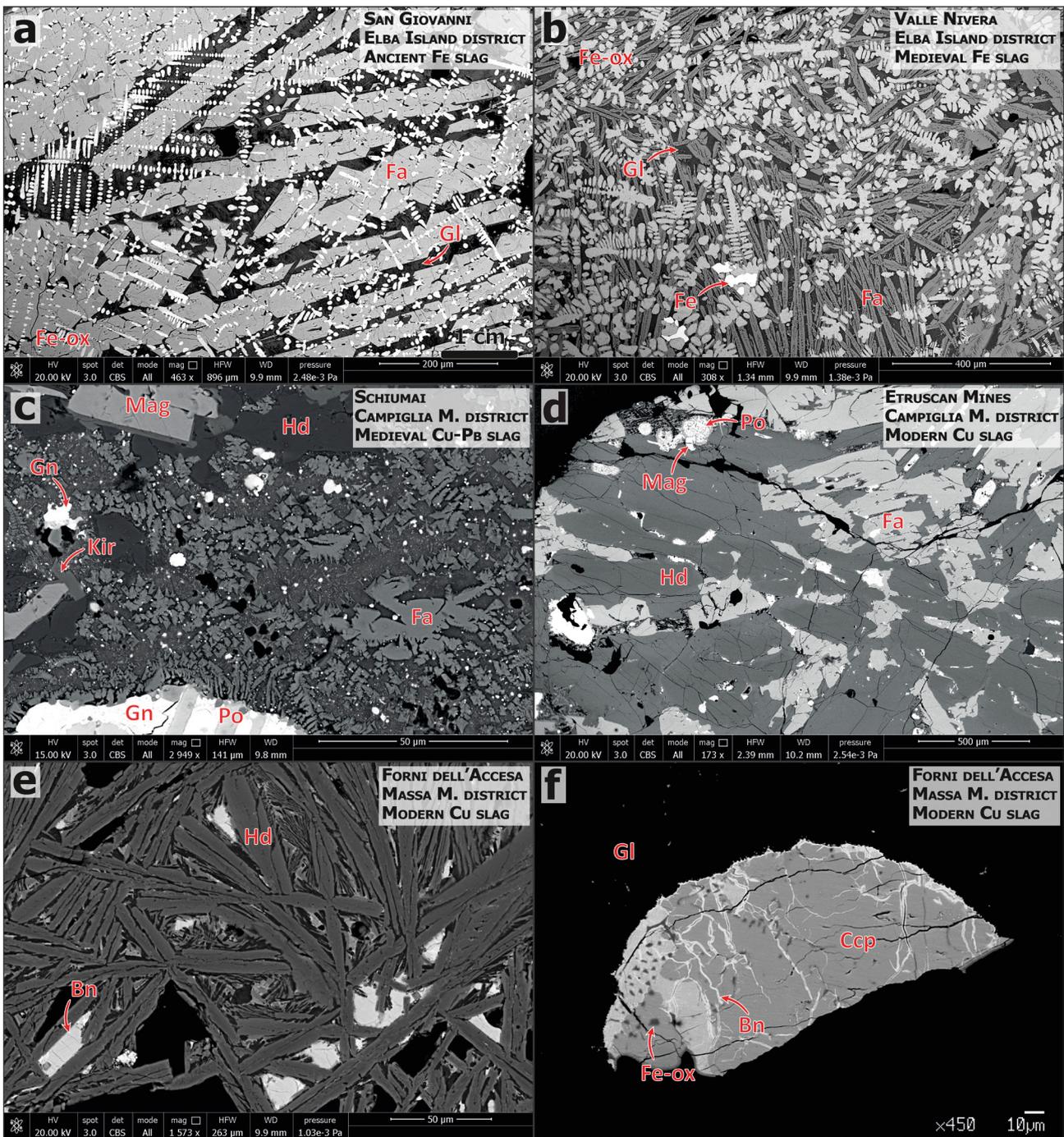


Figure 2. Backscattered electron images of: (a) an ancient Fe slag showing olivine crystalized after the Fe-oxides dendritic structures, in a glassy groundmass; (b) a medieval Fe slag similarly showing skeletal olivine, dendritic Fe-oxides and metallic Fe droplets in a glassy matrix; (c) a medieval Cu slag sample showing different silicate phases, magnetite and aggregates of sulfides; (d) large hedenbergite and fayalite skeletal crystals with droplets of Fe-oxides and sulfides in a modern Cu slag; (e) a modern crystalline Cu slag from Forni dell'Accesa site showing crystals of hedenbergite with interstitial bornite; (f) a modern glassy Cu slag from Forni dell'Accesa site showing a sulfide droplet amongst the glass, composed of chalcopyrite with veinlets of bornite and Fe-oxides. Legend: fayalite (Fa), kirschsteinite (Kir), hedenbergite (Hd), magnetite (Mag), galena (Gn), pyrrhotite (Po), bornite (Bn), glass (Gl).

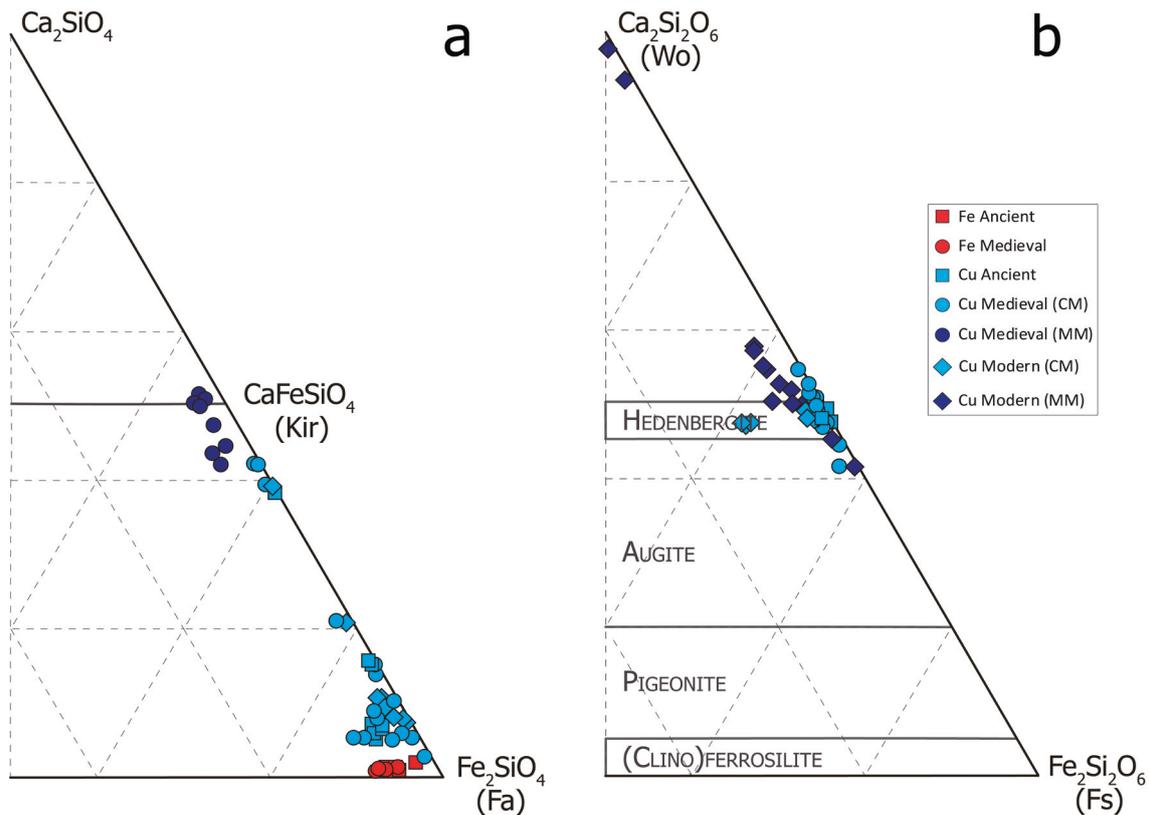


Figure 3. Classification diagrams for olivines (a) and pyroxenes (b) from electron microprobe analyses on selected slag samples. Legend: CM: Campiglia Marittima district; MM: Massa Marittima district.

(Figure S2b) are characterized by large and elongated skeletal crystals of fayalite, with interstitial hedenbergite and large patches of copper sulfides and iron oxides. The medieval copper-lead slags from Schiumai site (Figure S2c) show a comparable phase assemblage, although with different textures. These slags are characterised by skeletal to dendritic crystals of fayalite, small euhedral kirschsteinite and sulfides. Hedenbergite is also present as anhedral interstitial crystals. Sulfides are ubiquitous; they can be identified as droplets of various dimensions, or as aggregates of different sulfides. An example of galena with pyrrhotite stringers is reported in Figure 2c, but also galena droplets and wurtzite were observed.

The modern copper slags from the Etruscan Copper Mines site (Figure S2d) exhibit similar textural features compared to the medieval ones. The mineral assemblage is characterized by predominant large skeletal crystals of hedenbergite showing a characteristic chemical zoning and, in minor amount, large skeletal crystals of fayalitic olivine. The hedenbergite crystals result enriched in FeO and Al<sub>2</sub>O<sub>3</sub> towards the rim, whereas SiO<sub>2</sub> and MgO percentages are enriched in the core. Pyrrhotite is the main sulfide, often associated with magnetite and wurtzite

(Figure 2d).

The sulfides usually contain trace elements in significant amount, for instance Zn is always detected in all the sulfide phases with a concentration reaching up to 1 wt% in medieval slags from Schiumai site and 0.48 wt% in modern slags from Etruscan Copper Mines site. The presence of Ag in the copper sulfides from Rocca San Silvestro site can be observed, with an average of 0.12 wt%; also, a significant Ba concentration is detected in this site (0.11 wt% average) and in modern samples from Etruscan Copper Mines (0.14 wt% average in bornite). Tungsten is also detected in all samples from this district, with an average concentration from 0.11 to 0.19 wt% in bornite and galena phases. Magnetite, along with several other iron oxides, can have Fe replaced by a large range of cations that can fill both the octahedral and the tetrahedral positions. In these samples, the partial replacement of Fe<sup>3+</sup> by Al can be noticed (Table S4), with Al<sub>2</sub>O<sub>3</sub> concentration reaching up to an average of 5.63 wt% in the medieval samples from Schiumai site. The Al<sub>2</sub>O<sub>3</sub> content in magnetite seems to not be related to the metallurgical district, nor to the age of smelting, in fact the modern samples also present an average of 1.52 wt% of Al<sub>2</sub>O<sub>3</sub>.

*Massa Marittima district*

Medieval slags from Massa Marittima district are characterised by fayalite, kirschsteinite and hedenbergite as main silicate minerals in the medieval slags, whilst modern slags present fayalite and hedenbergite. Iron oxides, metallic grains and copper sulfides often occur in accessory amounts both in medieval and modern slags.

In the site of Poggetti Butelli, near Follonica, iron ores from Elba Island were smelted and processed during Roman times (Costagliola et al., 2008). The ancient iron slags from this site are very similar to the iron slags found in Elba Island. Macroscopically they are characterised by a vesicular weathered outer layer and by some glassy slag in fragments of various dimensions (e.g. Figure S3a). Microscopically they show subhedral-euhedral crystals of fayalite and pervasive dendritic iron oxides (wüstite) included in the olivine crystals as well as in the glassy matrix. Fayalite crystals invariably have skeletal texture, yet variable in size. Iron oxides are found either as small dendrites or long chains.

The copper slags of Massa Marittima district vary from highly porphyritic to glassy. Their mineral assemblage is characterised by hedenbergite (clinopyroxene often show a composition plotting slightly above the diopside-hedenbergite joint) and abundant kirschsteinite as main silicates (Figure 3).

The medieval copper slags from Massa Marittima district were sampled in the Marsiliana (Figure S3b) and Rocchette Pannocchieschi (Figure S3c) sites. They appear weathered on the surface, with many visible inclusions of residues from the charge. Once cut, they show the typical dark grey colour and lustre. The mineral assemblage of medieval copper slags from Rocchette Pannocchieschi, includes kirschsteinite, as the only silicate phase. The iron oxides (wüstite, magnetite) occur in pervasive dendritic structures, intertwined with metallic grains and sulfides. Throughout the section, the iron oxides can be found in both large, complex structures and smaller dendrites. Wüstite and magnetite are strictly associated and intermixed with pyrrhotite. Metallic Pb and intermetallic compounds were also detected as aggregates or as interstitial droplets. The medieval copper slags from Marsiliana site are described as having a similar mineral assemblage mainly represented by silicates (hedenbergite, fayalite and minor kirschsteinite) and sulfides (sphalerite, galena) (Manasse and Mellini, 2002).

The modern copper slags from Forni dell'Accesa site present a high variability, with both glassy and crystalline slags (Figure S3d). Flow textures are often visible, especially on the larger samples, and a weathered coating is present. Glassy samples very much resemble a natural obsidian, with a greenish colour blended to a darker shade in some portions. The mineral assemblage mainly includes

glass, sulfides and metallic droplets. Within the glass, flow and devitrification textures are observed, in addition to droplets of various dimensions, mainly composed of iron/copper sulfides, probably a matte residue from the smelting process (Figure 2f). The crystal-rich slags show a phase assemblage characterised by skeletal hedenbergite and minor wollastonite with presence of sulfides and glass among the phenocrysts (Figure 2e). Bornite is the main sulfide, along with minor chalcopyrite and pyrrhotite. A small amount of iron oxides is sometimes associated with the sulfides.

Compared to Campiglia Marittima district, chalcopyrite exhibits similar values of Zn in the modern samples (0.18 and 0.73 wt%). Ba reaches up to 0.19 wt% in the glassy modern sample from Forni dell'Accesa site, and also W is present in variable abundances in the modern samples from this site: the concentration is up to 0.21 wt% in bornite, but the average is 0.05 wt% in bornite and chalcopyrite, and 0.07 wt% in pyrrhotite. Electron microprobe analyses on glassy copper slags from modern site Forni dell'Accesa (Table S1) show a composition rather similar to the bulk composition analyses, although the glass is enriched in  $Al_2O_3$  and depleted in FeO. Moreover, the glass is slightly enriched in Zn and depleted in Cu (Figure S4b), compared to bulk chemistry, while other abundant trace elements enriched in the glass are W and Ba.

**Bulk chemistry**

The heterogeneity of the bulk chemical compositions of the slags is in general reflected by the different mineral assemblages, that in turn result from the type of ore and smelted metals (Table 2). The chemical composition of iron slags is more homogeneous across the sites and over the historical periods with respect to the copper and lead slags, that show a high variability of the bulk chemistry across the different metallurgical districts and a minor variability from ancient to modern period of production. All bulk composition of iron and copper slags are reported in Tables S5 and S6.

*Iron slags*

The ancient iron slags found both on Elba Island and Poggetti Butelli site can be subdivided into silica-rich and silica-poor groups (Figure 4a). The silica-rich group has high  $SiO_2$  content (62-77 wt%) and low FeO content (8-19 wt%), whereas the silica-poor one has  $SiO_2$  ranging from 17 to 26 wt% and FeO ranging from 59 to 70 wt%. The second most remarkable difference is observed for  $Al_2O_3$ , with the first group enriched in this component (up to 11.7 wt%) compared to the second group (4.3 wt%). The concentration of  $K_2O$  is similar in the two groups (up to 4 wt%). The composition of iron slags is similar to that of iron slags from other sites in Tuscany (Benvenuti et al.,

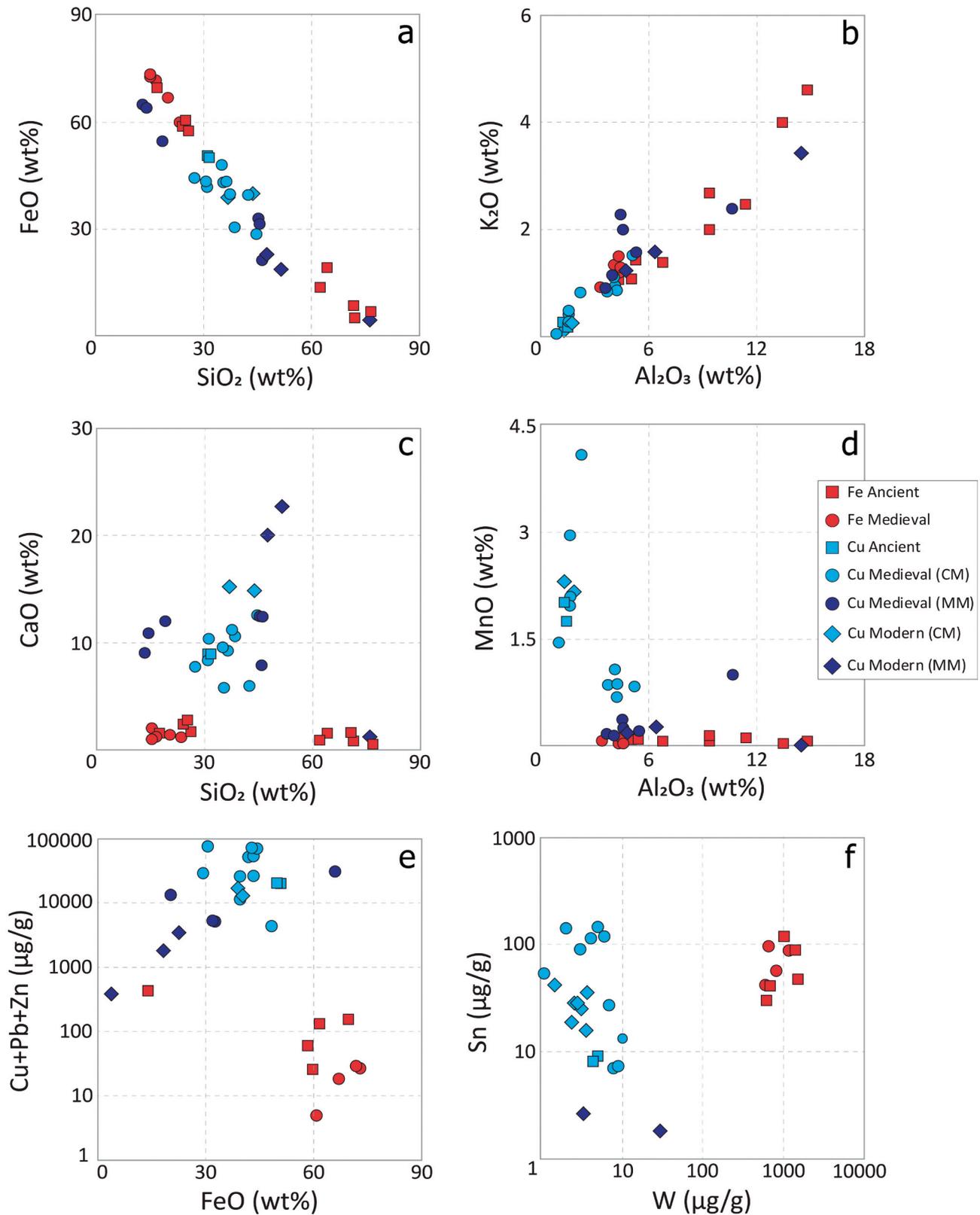


Figure 4. Bulk chemistry composition of major and trace elements determined by ICP-OES and ICP-MS analyses. Legend: CM: Campiglia Marittima district; MM: Massa Marittima district.

2000; Costagliola et al., 2008).

The medieval iron slags are homogeneous in composition and similar to the low-silica group of ancient slags. The SiO<sub>2</sub> ranges from 15 to 23 wt%, while FeO ranges from 60 to 73 wt%. They also have an average of 4.2 wt% Al<sub>2</sub>O<sub>3</sub>, and 1.3 wt% CaO and K<sub>2</sub>O.

The overall trace element content of both ancient and medieval iron slags is usually very low (Figure 4e), with the exception of Ba (up to 260 µg/g), Pb (up to 80 µg/g) and W (600-1400 µg/g). The high concentration of W is consistent with the significant enrichment in this element in the ores from Elba Island, compared to other iron ores from Tuscany and Europe (Benvenuti et al., 2013). The Sn concentration is comparable to the Sn concentration in copper slags, but W is indeed higher, so its concentration in the samples helps to easily distinguish copper/lead slags from iron slags (Figure 4f).

#### *Copper and lead slags*

The copper slags from Campiglia Marittima district are mainly composed of SiO<sub>2</sub> (30-40 wt%) and FeO (30-47 wt%), with variable amount of CaO (6-15 wt%). The CaO content increases from medieval (7-8 wt%) to modern slags (15 wt%), whereas other components (Al<sub>2</sub>O<sub>3</sub>, MgO and MnO) do not exceed 4 wt% (Figure 4).

The copper slags from Massa Marittima have slightly higher SiO<sub>2</sub> (45-50 wt%) and lower FeO (20-30 wt%) contents compared to slags from Campiglia Marittima district. They have a high CaO concentration (10-20 wt%), and Al<sub>2</sub>O<sub>3</sub> up to 7 wt%. MgO and MnO concentrations are less than 2 wt%. The lead slags from Rocchette Pannocchieschi site shows higher FeO (61 wt%) and lower SiO<sub>2</sub> content (15 wt%) compared to copper slags (Figure 4a). Concerning the transition from medieval to modern slags, there is a decrease in FeO concentration (30 and 20 wt% respectively) and an increase in CaO concentration (10.5 and 21 wt%) (Figure 4c).

Compared to iron slags, copper/lead slags exhibit remarkably high concentration of certain trace elements (Figure 4e). In the Campiglia Marittima district, the Cu concentration in medieval and modern slags varies from 2,000 to 3,000 µg/g while the Zn content is around 10,000-15,000 µg/g. The concentration of Pb is around 20,000 µg/g in medieval slags, whilst modern slags exhibit a much lower value of 150 µg/g. In the Massa Marittima district, a much larger variation in trace element content is observed from medieval to modern slags: Cu content decrease from 3,000 to 1,100 µg/g, and Zn from 6,200 to 1,400 µg/g. Similarly, the concentration of Pb is largely variable in medieval slags (1,200-18,500 µg/g) but decreases substantially in modern slags (below 100 µg/g). Among the other elements, it is to note the high concentration of Ba in medieval samples (1400-4800

µg/g) and the anomalous concentration of Sb in the Rocchette Pannocchieschi site (3,800 µg/g), the latter consistently with Manasse and Mellini (2002). Moreover, the modern copper slags from Forni dell'Accesa site (Massa Marittima district) have higher Sr concentration. The Sn content of slags from Campiglia Marittima district reaches up to 140 µg/g, whereas it is nearly absent in the bulk analyses of modern samples from Massa Marittima and it has not been detected in the medieval slags from the same district (Figure 4f).

## DISCUSSION

### **Petro-chemical differences among slags from different districts**

Iron and copper/lead slags from the different smelting sites display chemical and mineralogical differences: the first are characterized by fayalite and iron oxides as the main minerals, and the second by large skeletal crystals of fayalite and hedenbergite. As expected, considering the different ores used as starting material, the chemical and textural variability is more evident when iron or copper slags from different metallurgical districts are compared. Minor variability is also observed among smelting sites of the same district, most likely related to the different ores from which the metals were extracted and possibly, in some sites, to the addition of fluxes to improve the efficiency of the smelting process (Manasse et al., 2001; Manasse and Mellini, 2002; Mascaro et al., 1995). To a lesser extent, this can be ascribed to the extractive process itself, which partially improved during the centuries, and thus affected the temperature that was possible to reach or the cooling rate experienced by the slag during the extraction from the furnace.

Regarding the charges, it is likely that fluxes were obtained from materials occurring nearby the extraction and smelting sites, as it is unlikely that trading of fluxes was involved. In the case of the Elba district, the iron slags are characterized by high K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (Figure 4b), which suggests that quartz-feldspathic materials were present in the charge, probably intermixed with the ore as gangue material, or added as a flux to allow a more efficient extraction of iron from hematite. The provenance of this material was most likely from the nearby outcropping acidic intrusive complexes of Monte Capanne and laccolith porphyries (Farina et al., 2010; Rocchi et al., 2002) or from their erosional products found as readily available beach sands. In the Campiglia Marittima district, the high concentration of CaO (Figure 4c), and sometimes of Al<sub>2</sub>O<sub>3</sub>, suggests that copper ores were mixed with locally outcropping limestones and/or shales. The Massa Marittima district presents a more complex situation since it is possible to find slags deriving from the smelting of ores of several different mining areas. Some variation can be associated to the diverse age of

smelting, for instance concerning the CaO concentration, that is lower in medieval samples compared to modern ones. This could result from a different process that introduced in the furnace some CaO-rich flux derived from the nearby marl-limestone and sandstone mined to extract pyrite and chalcopyrite.

Trace elements distribution in bulk slag samples readily distinguishes low base metals iron slags from high Cu-Zn-Pb copper slags (Figure 4e). In general, iron slags are poorer in trace elements, compared to copper slags, apart from the higher concentration of W in iron slags from Elba Island. Concerning the copper slags, all the samples from Campiglia Marittima mining district show higher Sn concentration relative to the samples from Massa Marittima district, which have a barely detectable Sn content. This difference between the two districts can be ascribed to the different chemical composition of the smelted charges, since in the area of Campiglia Marittima, especially in the Monte Valerio region, there is a known occurrence of cassiterite ( $\text{SnO}_2$ ) (Venerandi-Pirri and Zuffardi, 1982). In contrast, copper slags from Massa Marittima district present a higher content of Ba and Sr, compared to copper slags from Campiglia Marittima, likely derived from the feldspar-rich materials used as flux agent and/or from gangue minerals.

#### Physical conditions of slag formation

The temperature reached in the furnace during the smelting process can be inferred on the basis of the isotherms of ternary phase diagrams (Figure 5). All the iron slags plotted in the Anorthite- $\text{SiO}_2$ - $\text{FeO}_{\text{tot}}$  diagram (Figure 5a) fall in the fayalite primary phase field, near to the wüstite boundary, mostly between the isotherms 1100 °C and 1150 °C, with the exception of two samples that fall in the cristobalite field, presumably due to the presence of quartz-rich gangue/flux material resulting in a  $\text{SiO}_2$  enrichment. Roman and medieval copper slags from Campiglia Marittima plot near the thermal minimum of the Anorthite- $\text{SiO}_2$ - $\text{FeO}_{\text{tot}}$  diagram, indicating temperatures below 1150 °C. Medieval copper slags from Massa Marittima and modern slags from both districts plot in a region comprised between the isotherms 1100 °C and 1350 °C, suggesting higher temperatures reached during the smelting process and in accordance with previous temperature estimates from Mascaro et al. (1995) and from Manasse and Mellini (2002). The medieval copper slags from Rocchette Pannocchieschi, based on their different composition, are reported in the Anorthite-Wollastonite- $\text{FeO}_{\text{tot}}$  diagram, where they plot on the spinel-wüstite boundary and indicate temperatures between 1230 and 1270 °C (Figure 5b). The composition of modern copper slags from the Forni dell'Accesa site in Massa Marittima district record even higher temperatures,

between 1300 °C and 1350 °C, which testifies to the increased efficiency of modern furnaces with respect to ancient and medieval ones.

The ternary diagrams reported in Figure 5a and 5b reasonably approximate the chemical composition of the different slags, however, they do not fully describe the plagioclase-free phase assemblages observed in the slag samples. For this reason, the  $\text{SiO}_2$ -CaO-FeO ternary diagram is also considered (Figure 5c). All the iron slags plot near the boundary between fayalite and wüstite fields, in accordance with the observed mineral assemblage. The isotherms in these fields range from 1150 °C to 1250 °C, a temperature slightly higher to what observed in the An- $\text{SiO}_2$ - $\text{FeO}_{\text{tot}}$  diagram (Figure 5a). Three samples with significantly high  $\text{SiO}_2$  concentration represent an exception, probably related to the occurrence of some unmodified gangue or residues from the furnace materials affecting the bulk composition of the slag samples. Copper slags from Campiglia Marittima district, both medieval and modern ones, approximately fall in the olivine field, at temperatures of 1100-1200 °C in accordance with the An- $\text{SiO}_2$ - $\text{FeO}_{\text{tot}}$  diagram. Medieval copper slags from Rocchette Pannocchieschi plot near the wüstite compositional field corresponding to formation temperatures of 1250-1300 °C (Figure 5c), in accordance both with the An- $\text{Wo}$ - $\text{FeO}_{\text{tot}}$  diagram (Figure 5b) and with the high iron oxide content observed in the samples. Also, they have a high CaO content, therefore they plot in a different portion of the wüstite field with respect to the CaO-poor iron slags.

The reconstruction of the working conditions of the furnaces is a critical issue for archaeometallurgy that cannot be easily solved by means of ternary diagrams only, as the chemical components of the slag outnumber those represented in the diagram. In support of phase diagrams, we used the thermodynamic modelling software easyMelts to predict the liquidus temperature of the slag compositions (Table S7) (Kądziołka et al., 2020). For the medieval and modern copper slags from Campiglia Marittima district, easyMelts yields temperatures that are in agreement with those inferred from the An- $\text{SiO}_2$ -FeO ternary diagram. In contrast, for ancient copper slags from Baratti (Elba district) and for the medieval and modern copper slags from Massa Marittima the software yields liquidus temperature that are, respectively, overestimated and underestimated with respect to the temperatures expected from the An- $\text{SiO}_2$ -FeO ternary diagram (Table S8).

The different associations of silicate minerals (pyroxenes are found only in copper slags, whereas fayalite occurs in both iron and copper slags) result from the diverse composition of the silicate liquid that separated from the metal during the smelting process.

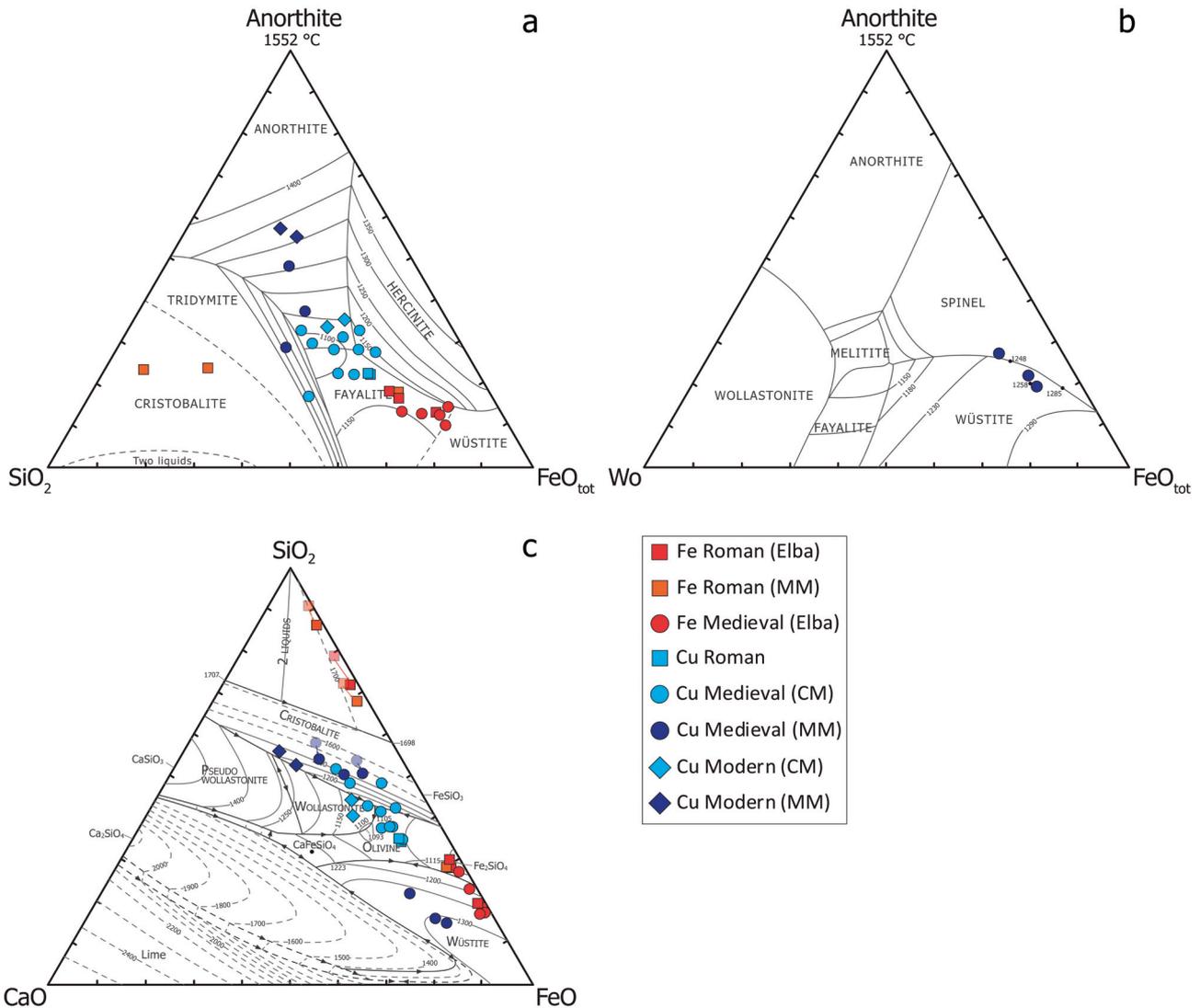


Figure 5. (a) Slag composition plotted in the ternary diagram An-SiO<sub>2</sub>-FeO, modified after Bachmann (1980) and Schairer (1942). (b) An-Wo-FeO ternary diagram for slags from Rocchette Pannocchieschi site after Bachmann (1980) and Schairer (1942). (c) Samples plotted on the SiO<sub>2</sub>-CaO-FeO ternary diagram modified after Allibert et al. (1995). Arrows show the re-calculated bulk chemistry after the removal of SiO<sub>2</sub> content derived from flux/gangue inclusions (sum of oxides recalculated to 100). Legend: CM: Campiglia Marittima district; MM: Massa Marittima district.

Independently from the composition of the silicate melt, the dendritic to skeletal texture observed for both pyroxene and olivine can be interpreted as an effect of the undercooling of the slag. Normally, at increasing degree of undercooling, crystal morphologies evolve from euhedral to skeletal and dendritic and more incompatible elements are increasingly incorporated in the mineral during the rapid growth (Masotta et al., 2020; Pontesilli et al., 2019; Shea and Hammer, 2013). In the case of copper slags, the dendritic-skeletal crystals of pyroxene display a variable enrichment in CaO, plotting above the Diopside-

Hedenbergite joint (Figure 3b), and a higher content of non-quadrilateral elements such as Al<sub>2</sub>O<sub>3</sub> (2.2-7.6 wt%) and Zn (2.0-3.0 wt%). Despite a roughly similar bulk composition, a slight enrichment in Al<sub>2</sub>O<sub>3</sub> is typically observed in clinopyroxene from ancient/medieval slags with respect to modern ones. This could be interpreted as due to conditions of higher undercooling for the ancient/medieval slags compared to modern ones. Similar to clinopyroxene, olivine crystals from copper slags display a variable enrichment in CaO, varying in composition from nearly pure fayalite (modern slags) to kirschsteinite

(medieval and partially ancient slags) (Figure 3a). Also in this case, the increase of an element like CaO, which is not easily accommodated in the crystal lattice of olivine, may testify to a high degree of undercooling (Mollo and Hammer, 2017). These differences can be attributed to different temperatures reached in ancient and modern furnace during the smelting process and to the consequently different thermal history of the slags. Specifically, the glassy nature of copper slags produced in modern furnaces (e.g. Forni dell'Accesa; Figure S3d) indicates that these slags were likely superheated when poured outside the furnaces after the smelting and quenched at a higher temperature than ancient-medieval slags.

Increasing viscosity affects the smelting process, reducing the possibility of separating the metal phase. Bachmann (1982) proposed an empirical method to measure a viscosity index (VI) based on the ratio between network modifiers and network formers cations

$$(VI = \frac{CaO + MgO + FeO + MnO + K_2O}{SiO_2 + Al_2O_3});$$

a high viscosity index corresponds to low viscosity, and therefore to a favourable condition of the segregation of the metal phase. The effect of viscosity on metal separation efficiency is observed in the trace element content, although the correlation is not always so straight, since it depends on many factors; for example, zinc is known to increase the slag viscosity (Mascaro et al., 1995), but it is not considered in the viscosity index, therefore the viscosity can be higher than the obtained result (Figure S5). Moreover, temperature should also be considered, as it has a positive effect in increasing the extraction efficiency by reducing the system viscosity.

Overall, the textural and chemical features of the slags indicate that the temperature achieved in the furnaces during the smelting process significantly increased from ancient to modern times, as expected from the increased knowledge of furnace buildings techniques and consequent increase of the efficiency of the smelting process.

### Efficiency of the metallurgical smelting process

The petro-chemical characteristics of the silicate slags can be directly related to the efficiency of the smelting process that separates the metal phase from the gangue through the reduction of the metals in the ore. The slags characterized by low melting temperature and low viscosity can be reasonably associated to a higher efficiency of metal extraction during smelting (owing to a lower metal concentration in the slag). However, none of these physical parameters can be univocally associated to the efficiency of the smelting process, as they largely depend on the amount and composition of

possible flux components added to the charge and to the presence of the gangue, here commonly made of limestone and/or quartz-feldspathic rocks. The most favourable conditions for smelting are obviously that of melting a pure ore (Bachmann, 1982), but the tentative addition of flux components was an important step to overcome the temperature limits of the furnaces and increase the efficiency of smelting, although not always successful. For example, if too much quartz is added in the charge, but the furnace can only reach 1200 °C, the process would probably result in a partially melted slag and some relicts of quartz would be found almost untouched within the slag itself. This would result in an increased viscosity of the slag and consequently less efficient separation of the metal from the gangue, which could possibly obstruct the furnace (Hauptmann, 2014). The occurrence of inclusions in ancient slags indicates that this problem was quite common because the process was not yet optimised. The charge composition was obviously different from site to site, principally because of the different provenance of the smelted ore and the type of fluxes added, normally related to the local availability of both components. Typical fluxes were iron/manganese oxides, limestone and quartz-feldspathic sands. In this regard, it is possible to observe that the slags with high concentration of SiO<sub>2</sub> from Massa Marittima were probably obtained from a charge containing quartz. Similarly, the high concentration of K<sub>2</sub>O in the samples from Elba Island (Figure 4b) could be related to the addition of the local feldspar-rich materials. The high concentration of CaO in modern samples from Massa Marittima (Figure 4c) is linked to the addition of lime used as fluxing agent. A general consideration about the efficiency of each metallurgical process can be done by determining the amount of metal found in the slags, with the more efficient process leaving less metal in the slag. However, it is not possible to find out the exact original grade of the ores used in the process producing the analysed slags, so the efficiency of the process is discussed taking into account only the residual metal identified in the slags, and by associating a high residual metal content to a low extraction efficiency. The ancient slags from Baratti have the highest concentration of copper (approximately 11,500 µg/g), while medieval slags from Campiglia Marittima have both high copper (1,100-61,000 µg/g) and lead (20,000-50,000 µg/g). Modern slags from Campiglia Marittima, that should have been obtained by a more efficient extraction process, still contain a remarkable concentration of copper from 2,000 to 3,000 µg/g, comparable to that of medieval samples from Rocca San Silvestro and Schiumai sites. Slags from Massa Marittima, however, seems different since they show a general minor abundance of base metals

(Figure 4e, Cu+Pb+Zn from 1,800 to 13,000  $\mu\text{g/g}$ ) and, in particular, the modern samples from Forni dell'Accesa have the lowest amount of copper (1,100  $\mu\text{g/g}$ ) and a quite low amount of lead (around 90  $\mu\text{g/g}$ ).

Concerning the iron slags, the occurrence of residues of metallic iron and the prevalence of wüstite with respect to magnetite suggest the achievement of strongly reducing conditions and thus a theoretically more efficient metallurgical process (Miller and Killick, 2004). Metallic iron has been mostly noticed in medieval iron slags from Elba Island, while the ancient iron slags seem to contain fewer and smaller iron droplets. However, magnetite and wüstite appear strictly associated and intermixed both in ancient and medieval slags, making it difficult to evaluate their relative abundances. The study of iron slag samples by XRPD identified the presence of both magnetite and wüstite, then the FE-SEM observation highlighted the presence of mainly magnetite with minor wüstite crystals in the ancient samples, and the opposite trend in the medieval samples. These observations suggest a higher efficiency of the metal extraction during the medieval period, compared to the former ancient smelting.

## CONCLUSIONS

The results of this study allow to expand the petrochemical dataset for ancient, medieval and modern slags from different metallurgical smelting sites in southern Tuscany and Elba Island, and overall provide a petrological interpretation of the metallurgical process. The petrographic and chemical variability of the slags is mostly related to the type of ore processed in the different metallurgical districts and, secondly, to the gangue associated to the different ores and potentially to the flux material added to the charge (normally derived from rocks outcropping nearby the smelting sites). It is also possible to notice a variability related to the historical age of the smelting that, for a given composition of the charge, could be related to the efficiency of metal extraction, interpreted as the lowest possible amount of metal retained by the slag phase during the smelting process. Although the smelting process was probably very variable due to the different knowledge and ability of the metallurgists, in general there seems to be a correlation with the temperature reached in the furnace, which, by increasing from ancient to modern times, improved the efficiency of the smelting process.

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