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ARCHAEOMETRIC STUDY OF THE HELLENISTIC METALLURGY IN SICILY: MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF IRON SLAGS FROM PUNIC PANORMOS (PALERMO, ITALY)

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ABSTRACT

Archaeological excavations carried out in the town of Palermo revealed important traces of metallurgical activity related to the Punic Panormos. Five samples of iron slags, recovered during the digging, were characterized by micro-structural, mineralogical and chemical investigations as well as by environmental scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray powder diffraction and X-ray fluorescence. The studied remains are spongy, rust colored, with a plano-convex shape and their textural and mineralogical features suggest they are metallurgical slags produced during smithing process. Wüstite, magnetite, fayalite, kirschsteinite, hedembergite, cristobalite and quartz are the main identified mineral phases, while goethite, lepidocrocite and calcite occur as minor secondary phases. The iron slags show heterogeneous structures such as hammering clues, layering in wustite crystals and presence of calcium-rich minerals which are consistent with a broad variation of the forging temperature due to the use of different smithing techniques. This assumption is confirmed by the different crystallization temperatures of the detected mineral phases. Skeletal and dendritic shapes are indicative of rapid cooling and, possibly, quenching. The chemical composition is dominated by iron, silicon and calcium and it is almost constant for all the samples suggesting that they were produced with similar raw materials and technology. The high Ca content suggests the use of carbonate-bearing rocks, widely outcropping over the Palermo territory, probably exploited as fluxing ores for the metallurgical process. The multidisciplinary approach adopted in this study provided new data for a better understanding of the metallurgical techniques evolution in the Sicilian territory in ancient times. Since the studied iron slags represent the unique traces so far known of metallurgical activity in the ancient Palermo town, our results open interesting perspectives for future study of metallurgy in ancient Sicily.

KEYWORDS: Hellenistic metallurgy, iron slags, SEM-EDX, XRPD, XRF, Punic Panormos

1. INTRODUCTION

Studying the use of metals and the evolution of metallurgical techniques is fundamental to better understand history and traditions of ancient societies from the antique Mediterranean world. Slags are the most visible evidences of iron making (smelting) and working (smithing). Their presence indicates that one or both of these metallurgical activities may have occurred over or close by the site. In this work, we focus our attention on the metallurgy of the Sicilian Punic Panormos in the first half of the 3th century BC, performing the study of some recovered iron slags.

As sea traders, the Phoenicians settled in many Mediterranean islands and coasts as far away as Spain, and during this enterprise they founded in Sicily the colonies of Mothia (Mozia), Solus (Solunto) and Panormos (Palermo) (8th – 7th century BC) (Anello, 1998; Spatafora, 2012). The latter was established on the narrow plain made of calcarenitic rocks (Palermo calcarenites) sited between the Papireto and the Kemonia rivers (Spatafora, 2017). The town of Palermo was an important harbor and was surrounded by imposing fortification walls; the settlement developed along a main E-W oriented road still in existence and today known as Corso Vittorio Emanuele. Piazza Bologni, located along this road axis, has been recently interested by a significant archeological intervention, carried out by the Soprintendenza BB.CC.AA. of Palermo (Fig. 1B). The intervention brought to light archaeological findings ranging from the 6th century BC to 13th century DC (Aleo Nero et al., 2012; Aleo Nero et al., 2014; Aleo Nero and Chiovaro, 2016; Aleo Nero and Chiovaro, 2017), confirming the urban centrality of this area, occupied continuously from antiquity to the present day. In the northernmost sector of the investigated trench, archaeological indicators relating to metallurgical activity were found, in a context dating from the late 4th and the first half of the 3th century BC. In a well-preserved layer, 30-40 cm thick, made up of intense red earth (somewhere blackened by the contact with high temperatures), numerous ceramic fragments with traces of combustion, big lumps of raw earth and many iron slag scoria have been discovered (Fig. 1C).

On the basis of the black painted pottery and amphorae found in the excavation, overall of Punic type (Aleo Nero et al., in press), the important archaeological context was dated to the Hellenistic age, probably preceding by fifty years the first Punic War (264-241 BC) (Aleo Nero and Chiovaro, 2017), which resulted in the conquest of Sicily by the Romans.

Figure 1. A) Map of the ancient Palermo city; B) Piazza Bologni, the dig trench in the western area of the square; C) Accumulation of iron slags.

Since little is still known about the organization of iron production in ancient period overall (Georgakopoulou 2014, p. 78) and in Sicily especially (Ingoglia et al., 2007, Ingoglia et al., 2010) and particularly during the Hellenistic period in this area of the Mediterranean basin (Pompianu, 2010; Kaufman, 2014; Fourmont and Tisseyre, 2018), this paper is intended to further our knowledge on this class of remains, and thus to enhance the information in the field of metallurgy. The archaeometric results are particularly important, on the archaeological point of view, because they constitute an initial piece for interpreting these important findings, the first provided at Panormos in a context of Hellenistic age. To reach these goals, textural, mineralogical and chemical characterizations of iron slags were carried out by a multidisciplinary analytical approach, including Energy-dispersive Environmental Scanning Electron Microscopy (ESEM-EDX), X-Ray Powder Diffraction (XRPD) and X-Ray Fluorescence (XRF). Given the great interest of the archaeological context and of the discovery, an effort was made to understand the pyro-metallurgical processes, in particular regarding the temperature undergone by the metal, also taking into account available evidence. Moreover, a geological map of the Palermo territory with the locations of the possible mining areas for the extraction of the raw materials was compiled and is here reported.

2. EXPERIMENTAL

Five archaeo-metallurgical samples (labeled 701-38, 701-39, 701-40, 701-41, 701-42; Fig. 2) gathered from closed stratigraphic units excavated at Piazza Bologni, were kindly provided for this research by the Soprintendenza BB.CC.AA. of Palermo. A slice was cut from each slag (with the only exception of sample 701-41, due to its scarcity), to produce a sample for the micro-analytical investigation. The remaining material was cleaned in an ultrasonic bath, dried, crushed in a jaw crusher and powdered in an agate mill to produce the analytical specimens for XRPD and XRF analyses.

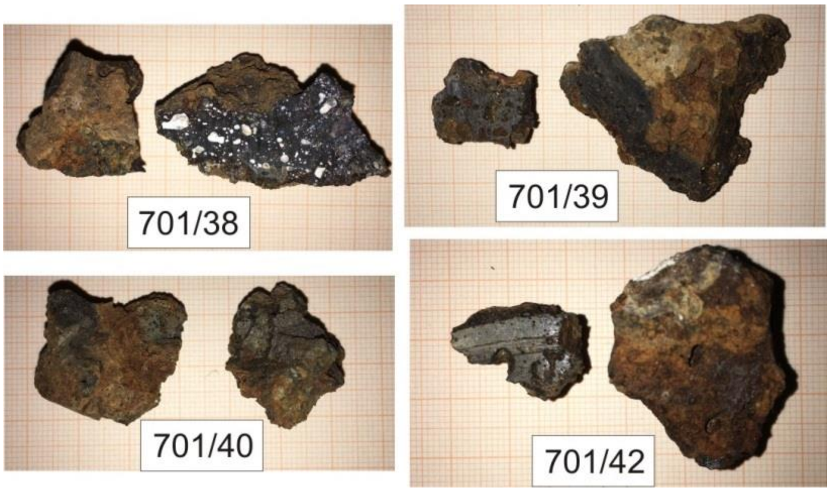

Figure 2. Studied iron slag samples characterized by the pseudo spherical shape, spongy appearance and rust color. Sample 701-38 shows the presence of vacuoles filled by secondary carbonate deposition.

The microstructure/texture as well as the chemical composition of selected areas of the polished samples were examined by using the backscattered electrons image mode (BSE), namely the ESEM coupled with X-ray energy-dispersive (EDX) apparatus. We used an ESEM-FEI Inspect-S electron microscope, coupled with Oxford INCA PentaFETx3 EDX spectrometer, a Si(Li) detector equipped by an ultrathin window ATW2, with a resolution of 137 eV at 5.9 keV (Mn Kα1). The spectral data were acquired in EDX conditions at a working distance of 10 mm, with an acceleration voltage of 20 kV, counting times of 60 seconds, count per second approximately 3000 (cps) with dead time below 30%. The results were processed by Oxford INCA software Energy. This software uses the XPP matrix correction scheme developed by Pouchou and Pichoir (1984, 1985).

The XRPD identification of the mineral phases was carried out using a BRUKER D8 ADVANCE diffractometer, with Cu Kα radiation on a Bragg-Brentano theta-theta goniometer, equipped with a Si(Li) solid-state detector, Sol-X. Acquisition conditions were 40 kV and 40 mA. Scans were obtained typically from 2 to 80 degrees 2θ, with step size of 0.02 degrees 2θ, with a count time of 3 seconds. Raw diffraction scans were stripped of Kα2 component, and background corrected with a digital filter. Observed peak positions were matched against the ICDD-JCPDS database.

XRF analyses provided major and trace element compositions using a wavelength dispersion XRF spectrometry Bruker S8 Tiger. The excitation source was a Rh tube at 4 kW for which power and the current intensity were set according to the analyzed element and their amounts, in order to avoid the detector saturation. The concentrations of the major and minor elements were evaluated using the GEO-QUANT M software package, an accurate tool for measuring 11 elements using more than 20 certified materials for calculating the calibration lines (Bruker

2015 a, b). The GEO-QUANT T software allowed the trace elements determination (Bruker 2015 a, b).

3. RESULTS

3.1 *SHAPE, TEXTURAL AND MINERALOGICAL FEATURE*

The studied iron-slags are spongy, rust colored, with a plano-convex shape. They are characterized by 2-5 cm thickness and 10-15 cm in diameter. Figure 3 and 4 show the slightly different textures revealed by ESEM analyses carried out on polished sections. Sample 701-38 shows a heterogeneous structure (Fig. 3A-B-C), with portions variously enriched in iron oxides, calcite and silica. Its texture is globular, with coexisting dendritic iron oxides and silica, and is variably enriched in calcite. Iron oxides are grouped in globular forms which are randomly diffused in the silica or calcite matrix and approaching hammer scale texture. Sample 701-39 is characterized by numerous iron oxide dendrites grown on a matrix of Ca-Fe silicate laths and glass, with areas with hammer scale texture (Fig. 3D-E-F).

Samples 701-40 and 701-42 show similar layering in the crystal habit of wüstite. Sample 701-40 is characterized by a spinifex texture with skeletal elongated fayalite crystals, in a pyroxene glassy matrix containing wustite crystals from dendritic to skeletal aspects (Fig. 4A-B-C). Sample 701-42 is heterogeneous (Fig. 4D-E-F) and contains skeletal or irregular dendritic shaped iron oxides. In an external part of the sample, rounded prills of metallic iron are grown in the wustite-rich area. The sample is characterized by large feather-shaped laths of silicates, dominant in the glass matrix and cross cut by dendritic wustite. There are vacuole and veins filled by secondary calcite.

ESEM-EDX data relative to the silicate mineral phases evidenced the presence of pyroxene and olivine. Concerning the analysed pyroxene crystals and glass, a prevalent hedembergite composition, characterized by different amount of Ca was detected. Pyroxene from sample 701-42 is the most depleted in CaO.

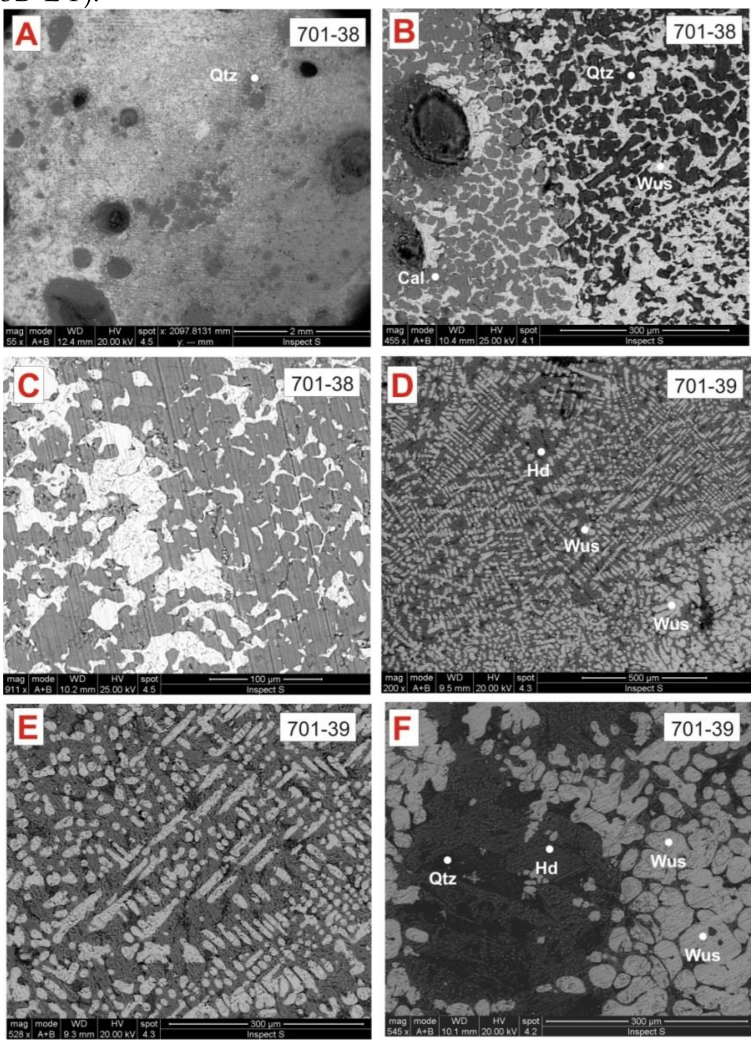

Figure 3. ESEM-EDX images showing textural features of slag samples 701-38 and 701-39. Qtz: Quartz; Cal: Calcite; Wus: Wustite; Hd: Hedembergite

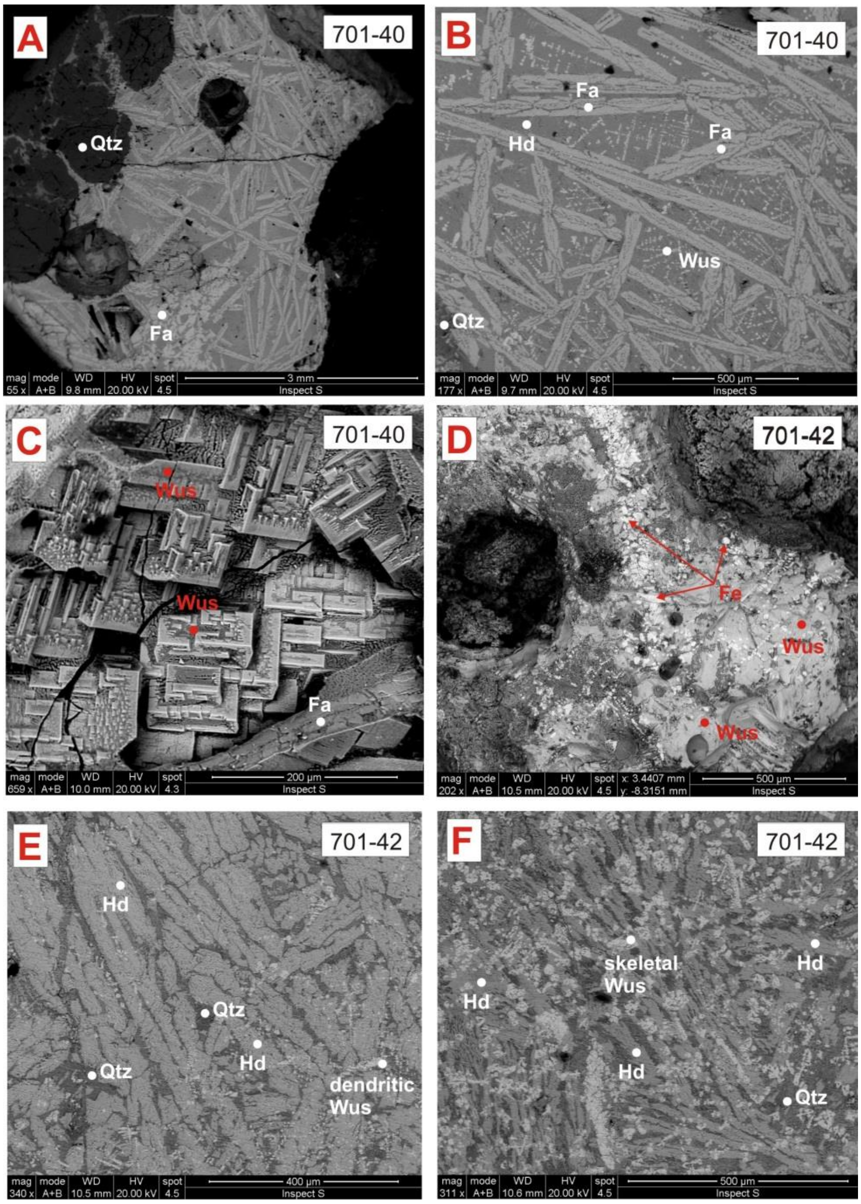

Figure 4. ESEM-EDX images showing textural features of slag samples 701-40 and 701-42. Qtz: Quartz; Fa: Fayalite; Wus: Wustite; Hd: Hedembergite

XRPD qualitative analyses, carried out to identify the main mineral phases, were performed using EVA software. The observed diffraction patterns (Fig. 5) were matched against the ICDD JCPDS database. The most abundant phases in the majority of the analysed samples are wustite (FeO) and hedembergite [$CaFe(Si_2O_6)$], followed by calcite (CaO), fayalite ($Fe^{2+}2SiO4$) and kirschsteinite ($CaFe^{2+}SiO_4$) and magnetite (Fe_3O_4). In addition, quartz occurs in all the samples, whereas maghemite (γ-Fe_2O_3), goethite [$Fe^{+3}O(OH)$] and lepidocrocite [γ-$FeO(OH)$] were identified in some samples. Cristobalite was found only in sample 701-40.

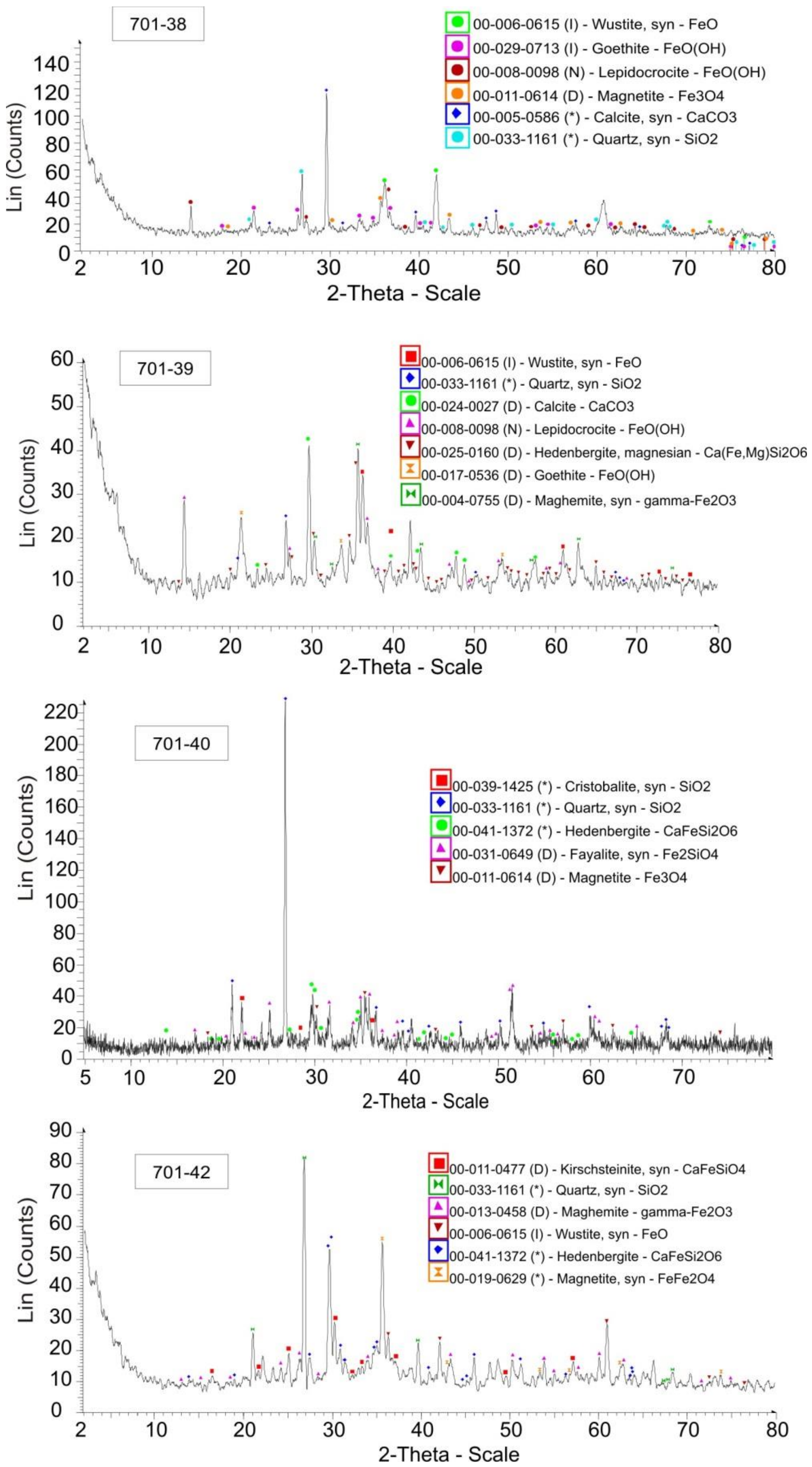

Figure 5. XRPD patterns of the studied samples.

3.2 *X-RAY FLUORESCENCE DATA*

Data of major and trace element compositions of the investigated samples are listed in Table 1. The data are consistent with the results of the above-mentioned mineralogical analyses. The main components are Fe_2O_3, SiO_2 and CaO, with minor amounts of Al_2O_3, MgO and P_2O_5 and values below 1 wt % of P_2O_5 , MnO, TiO_2, Na_2O and SO_3.

Fe_2O_3 ranges from 46.22 to 68.76 wt %, SiO_2 from 13.31 to 25.61 wt % and CaO from 9.22 to 19.38 wt %. Sample 701-40 shows the lowest Fe_2O_3 content (37.99 wt %) and the highest value of SiO_2 (46.12 wt %). MgO contents are very low (about 0.53 to 1.53 wt %) as well as K_2O (from 0.36 % to 1.13 %) and P_2O_5 (from 0.87 % to 2.26 %). Among the trace elements, the following relevant contents were detected for Ba (106-171 ppm), Sr (92-180 ppm), Zr (34-133 ppm), As (59-271 ppm), Cu (156-604 ppm) and Ni (55-107 ppm). On the contrary, other trace elements, such as V, Cr, Zn, Rb, Nb, Mo, Ce, Pb, occur in very low amounts.

Table 1 – XRF major and trace elements data of the analysed samples

		Samples									
Major oxides %											
	analitic range (%)	**701/38**	*std**	**701/39**	*std**	**701/40**	*std**	**701/41**	*std**	**701/42**	*std**
Fe_2O_3	0.01 – 70	60.77	0.08	66.21	0.09	35.54	0.09	66.46	0.07	43.6	0.09
CaO	0.02 – 100	15.56	0.33	14.97	0.36	49.24	0.36	14.9	0.3	27.34	0.25
SiO_2	0.04 – 100	15.71	0.42	12.59	0.28	9.84	0.28	12.42	0.54	20.69	0.39
Al_2O_3	0.04 – 90	2.7	1.1	2.37	1.12	3.3	1.12	2.41	1.44	3.06	1.22
P_2O_5	0.01 – 20	2.63	1.44	1.37	2.03	0.9	2.03	1.34	1.59	1.43	1.55
MgO	0.02 – 100	1.69	0.6	0.92	2.73	0.55	2.73	0.93	2.17	1.81	1.45
K_2O	0.05 – 15	0.41	0.2	0.73	1.11	0.99	1.11	0.7	1.26	1.18	0.98
SO_3	0.05 – 55	0.12	3.55	0.28	6.21	0.61	6.21	0.28	3.69	0.79	3.45
TiO_2	0.01 – 8	0.18	2.2	0.15	2.5	0.07	2.5	0.16	3.6	0.18	2.91
MnO	0.01 – 0.80	0.13	0.9	0.12	0.8	0.23	0.8	0.12	1.31	0.21	0.78
Na_2O	0.02 – 11	0.12	4.2	0.13	6.52	0.28	6.52	0.12	13.7	0.57	4.39
Trace Elements											
ppm	L.O.D.*		*std**		*std**		*std**		*std**		*std**
V	1.4	26	2.8	40	2.94	27	3.41	39	3.04	36	2.89
Cr	3.3	28	3.2	31	8.42	78	3.15	22	10.9	117	2.68
Ni	1.5	107	1.95	72	2.47	55	2.42	81	2.19	88	1.74
Cu	4.7	193	0.8	418	0.96	156	1.5	418	0.96	604	0.62
Zn	3.8	26	4.7	38	4.54	23	5.19	38	4.65	27	4.86
As	2.9	155	1.1	271	0.9	59	2.96	269	0.91	155	1.26
Rb	0.9	20	1.3	24	3.2	30	2.03	25	3.14	43	1.58
Sr	0.9	148	0.55	123	0.71	92	0.72	124	0.7	180	0.44
Zr	4.9	41	1.2	34	1.48	124	0.48	37	1.42	133	0.45
Nb	0.6	5	7.95	4	10.3	5	6.97	3	11.1	6	6.24
Mo	1	9	15.9	9	20.6	4	18.8	10	16.9	7	19.8
Ba	5	106	2.1	115	2.58	129	1.99	115	2.61	171	1.68
Ce	4	10	10.2	20	10.3	16	12.5	13	11.7	16	12.2
Pb	1.5	20	2.3	34	2.98	33	2.21	35	2.94	26	3.04

*std = standard deviation; L.O.D. = Limit of detection

4. DISCUSSION

The combined minero-geochemical approach to the iron slags from the Punic Panormos, provided useful indication to define some activities carried out during metallurgical processes and also on the possible provenance of the used raw and fluxing ore materials. Distinguishing smithing slags from bloomer smelting slags is not simple. However, our results suggest that the studied slags can be associated to the last step of the metallurgical process related to smithing operations carried out by the blacksmith. Therefore, also on the base of literature data (Serneels and Perret, 2003), they can be classified as metallurgical waste, representing typical fused residual materials with plano-convex shape, low size and spongy appearance, frequently found in others archeological site in contexts of all ages (Soulignac and Serneels, 2014). Furthermore, the slag textures are similar to smithing slags from the Hellenistic to Byzantine city of Sagalassos (SW Turkey) recently studied by Eekelers et al. (2016). Those types of iron-slags - characterized by plano-convex shape, spongy appearance and rust colored - are also known by literature definitions as ‘‘smithing hearth”, “furnace bottoms’’ or ‘‘slag basins’’, and their presence is associated with iron-working sites (McDonnell, 1983; Allen 2006, 2008; Georgakopoulou, 2014).

4.1 TECHNOLOGICAL IMPLICATIONS FROM MINERALOGICAL AND TEXTURAL DATA

The bulk composition of the Panormos slags shows high Ca and Fe-Ca silicates concentration besides variable wustite and magnetite contents. All of those phases occur in skeletal or dendritic crystals inside the slags. Eekelers et al. (2016) interpreted the layering in wüstite textures as indicative of the use of different smithing techniques at different temperatures during smithing. Samples 701-40 and 701-42 can be defined as T-dependent slag, due to the presence of layering in wüstite crystals. In particular, sample 701-40 is indicative of rapid cooling (skeletal olivine) and possibly quenching (eutectic wustite and hedembergite in the glass), whereas sample 701-42 shows more standard dendritic shapes, still showing fast cooling, but without quenching (eutectic hedembergite, wustite and quartz) (Serneels, 1993; Bauvais, 2007; Eekelers et al., 2016). Those forms most likely occur when the metal is taken out of the hearth and cools immediately down to room temperature.

On the other hand, samples 701-38 and 701-39 are interpretable as mechanically worked slags. They are characterized by remarkably high wüstite content, compacted to crystals representing hammer scales, which are an indication for mechanical working of the material as suggested by Eekelers et al. (2016). By hammering the material, the outer oxidation layer is expelled, resulting in flat hammer scale (Crew, 1991). Hammer scales in the slag are hemispheric textures, consisting of iron oxides and metallic iron that are knocked off during hammering. This process must occur at elevated temperatures, since dendrites are formed (Eekelers et al., 2016).

From the mineralogical point of view, the studied iron slags are made up of a heterogeneous mixture of silicates (fayalite, kirschsteinite, hedembergite), iron oxides (wüstite, magnetite), amorphous material, alteration products (goethite, lepidocrocite) and calcite (Serneels, 1993). The predominant pyroxene, identified as hedembergite (Fig. 6), is segregated at estimated crystallization temperatures ranging from 700 to 900 °C, in contrast to the identified olivines which crystallization temperature is in the range of about 1100-1200 °C.

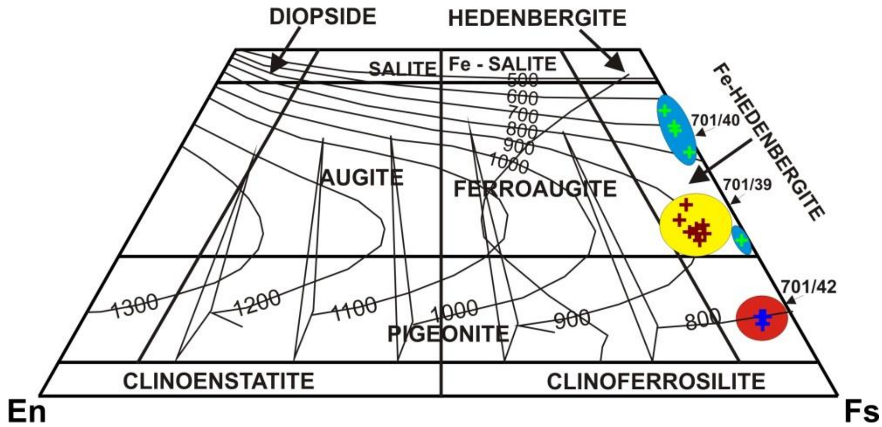

Figure 6. Pyroxene classification diagram.

One of them in particular, the kirschsteinite ($CaFe^{2+}SiO_4$), is not a natural mineral phase, typically found in metallurgical slags which formation requires reducing conditions and high temperature (Konev et al., 1970). All of those silicates are always characterized by skeletal shapes testifying fast cooling. The presence of calcium-rich minerals in the slag mineralogical compositions is interpreted as the result of a complex smithing process, whereby different temperature regimes were necessary. The quartz found in all samples can be the consequence of the flux addition (Blakelock et al. 2009) while the presence of cristobalite (701-40 sample) indicates the achievement of high temperatures during the metallurgical process. In the studied slags, the wüstite (FeO) is the most frequent oxides phase with minor amounts of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). These iron oxides are important indicators of the prevailing redox conditions in the furnace or in the hearth at the time of slag solidification, providing important constrains for process reconstruction and interpretation. A recent study explains the formation of iron oxides considering a process which includes the oxidation of Fe to $Fe_{1-x}O$ and its transformation to $Fe_{3-x}O_4$ that further transforms into Fe_2O_3, probably across a short-lived γ-Fe_2O_3 phase (maghemite) (Marciuš et al., 2012). Since wüstite is stable between 560 and 1370 °C (Kiessling and Lange 1978), this is consistent with the local presence of mildly reducing conditions. In contrast, goethite

(FeO(OH)), and lepidocrocite (γ-FeO(OH)) are typical weathering minerals (Bachmann, 1982; Kramar et al., 2015), and indicate wustite oxidation during burial (Kramar et al., 2015). From a geochemical point of view, the investigated slags are characterized by significantly high lime levels. Furthermore, it has been noticed, the relationship between the CaO content and the other characterizing major elements such as FeO and SiO_2, and the formation of the Ca-Fe silicates, as follow:

1. Fayalite occurs only in sample 701-40, characterized by the highest SiO_2 (46 %) and the lowest Fe_2O_3 (37.99 %) and CaO (9.22 %) contents;
2. Kirschsteinite olivine and hedembergite occur in sample 701-42, showing intermediate SiO_2 (25 %) and Fe_2O_3 (46 %) contents and the highest CaO (19 %) amount;
3. Hedembergite is the unique Ca-rich silicate phase present in all the other samples, which are characterized by the highest content of Fe_2O_3 (of about 59 ÷ 69 %), the lowest (~ 13 %) of SiO_2 and an intermediate of CaO (about 11 ÷ 14 %).

The observed heterogeneous structures and the variable estimated crystallization temperatures of the main identified mineral phases, suggest that the studied iron slags are the result of a variation in forging temperature and a consequence of smithing operations. Moreover, the indicators identified by archaeologists - such as intense red earth (somewhere blackened by the high temperature contacts), numerous ceramic fragments with traces of combustion and big lumps of raw earth - are the most diagnostic findings on an excavation associated with a smithing hearth.

4.2 *FLUX AND ORE SOURCE*

The Sicily region is not rich in metal resources, and little is known about the extent to which Punic influenced metallurgical trends on the island (Procelli 2008). A study (Triscari et al., 2005) of the metallurgical findings discovered in Sicily (and generally in Southern Italy) demonstrated that iron-ore or iron-bearing rocks, easily available over the territory (Benvenuti et al., 2010), could represent the exploited raw materials for the metallurgical processes. In this regard, Triscari et al. (2005) and Ingoglia et al. (2007), in a study of iron slags found in archaeological sites of the Messina Province (NE Sicily) and of Torre Galli (Calabria), demonstrated the use as raw materials of silicic lithologies, specifically some metamorphic rocks widely outcropping in the Calabria-Peloritani Arc.

Slags coming from the Gela archaeological excavation (Southern Sicily) studied by Ingoglia et al. (2010) contain high amounts of lime, suggesting the use of local outcropping carbonate lithology to extract the iron oxides. Furthermore, Giardino and Quercia (2008), in their study on metallurgical remains from the ancient Lecce (Apulia), highlighted the use of the local bauxite ore from deposits existing especially in the Salento area.

In the case of our samples, the most interesting aspect is represented by the high amounts of calcium that is present as lime and in the most abundant Ca-silicate phase as pyroxene. The results of formation of calcium oxides, highlighted by the CaO content (on average around 15%), which is much higher than that of slag material from other archaeological sites, allows to make some considerations. The presence of lime in the 701-38 and 701-39 samples slags and of Ca-rich pyroxene in the other samples, could be the results of several factors, including the addition of local lime-rich fluxe to achieve minimal temperature melting and facilitate the welding process (Eekelers et al., 2016). Fluxing is the process by which the silica is liquefied to melt off the iron bloom, and is often aided by calcareous materials such as lime or shells (Sim, 1998; Charlton et al., 2010).

In the Palermo territory, Ca-bearing lithologies widely outcrop and dominate the land on which the town of Palermo has developed. The use of Ca-bearing rocks as source of ore raw and flux materials is a plausible hypothesis. The occurrence within these lithologies of diffused oxidised portions enriched in iron and manganese is well documented (Catalano et al., 2013) as can be seen in Fig. 7A. The Ca-bearing lithologies mainly available in the area are limestones, arenaceous limestones and calcarenites, already used in historical time as building stones. Historical quarries used to extract those rocks have been mainly located close by the modern villages of Capaci, Carini and Bagheria. We have provided a geological map of the Palermo territory on which the potential mine areas exploited to extract the raw materials are reported (Fig. 7B).

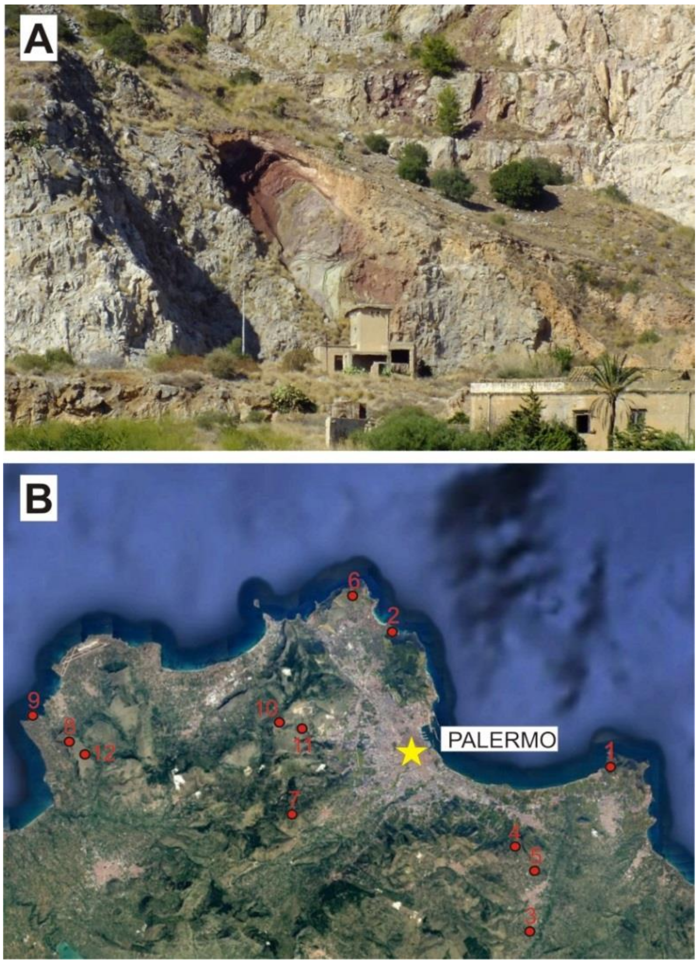

Figure 7. A) Example of oxidised portions in limestone outcropping near Bagheria (Crisanti and Caltavuturo Formations); B) Satellite map of the Palermo Mountains (modified from Google Earth), with ubication of the Piazza Bologni archeological site (yellow star) and of lithologies potentially used as ore raw materials. Localities and relative geological formations are reported in the legend as follow: 1) Capo Zafferano, Scillato Formation; 2) Addaura Loc., Palermo Calcarenites; 3) Loc. Casale, 4) C.da M. Nardo, 5) Loc. Rocca di Ciavole, Caltavuturo Formation; 6) M. Gallo, 7) M. Castellazzo, 8) M. Palmeto, 9) Capo Rama, Capo Rama Formation; 10-11) Cozzo s. Calogero, Cozzo di Lupo Formation; 12) M. Palmeto, Buccheri formation. B

A further assumption might be the use of calcarenite rocks, which represent the uppermost stratigraphic horizon lying on the deeper carbonate and terrigenous levels which consists of a coarse sandy material rich in limestone concretions. Their use could explain the considerable presence of silica in the slags. Taking into account this information, we might argue that during the metallurgical operation to obtain iron slags, no flux was used, since the processes could benefit of a self-fluxing ore material. In spite of all of those evidences, further investigations are needed to clarify the raw materials provenance and, in any case, we cannot exclude that the raw material was imported from other regions (Corretti and Benvenuti, 2001).

5. CONCLUSIONS

The important discovery of the iron slags at Panormos allows attesting that in the central area of the ancient city of Panormos, during the first half of the 3rd century B.C., production activities related to metallurgy took place. Since the real working area was not discovered, it is impossible to define in detail the spatial organization, the dimensions of the workshop and the kind of products that were forged. The traces of metallurgical activity found out in the urban area of the Panormos city and here sudied, represent an exceptional discovery, both for the quantities of metallic materials recovered and from the chronological point of view. This discovery is an "unicum" for the archaeology of Panormos and opens interesting perspectives for the understanding of this multi-layered city, characterized by an extraordinary continuity of life.

It is proposed that the iron slags found at Piazza Bologni site can be distinguished on the basis of textural, chemical and mineralogical parameters, and that the slag group is the product of a distinct metallurgical step related to the smithing phase. Analysis of slag samples from Panormos have highlighted the possibility that certain features of smithing slags can be closely linked to certain stages within the smithing process. The used ore materials, in terms of both ore and flux source, could be represented by the Ca-bearing rocks that widely outcrop in the Palermo Mountains. If Palermo calcarenites were used during the smelting process, the processes could benefit from the self-fluxing of used ore material.

In any case, more detailed field work, strictly linked to archaeometallurgical analyses, is needed to identify and to study the history of metallurgy in the ancient Palermo city.

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