

# Microscopic and chemical characterization of metal slags found at the Porta Paola excavation in Ferrara

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**Abstract** –Microscopic and chemical characterization of some metal slags from iron processing were carried out at the Laboratories of the Department of Physics and Earth Sciences (University of Ferrara). Samples were collected in the archaeological excavation of Porta Paola and Via Bologna in the city of Ferrara in August 2003, following the exceptional discovery of a boat for goods transport which involved the surrounding stratigraphic study. The analysis of these findings allowed to understand their chemical and mineralogical origin.

conditions at a given site [5,6,7].

The microscopic and chemical investigation of historical metallurgical slags are good materials for providing information on former metal smelting methods [8]. The aim of this work was to characterize some metal slags, sampled during the excavation, through applied geochemical and mineralogical methods to understand the historical smelting technologies and to confirm that the city of Ferrara was culturally advanced also from the technological and metallurgical point of view during the Renaissance period in Italy.

## I. INTRODUCTION

The origins of the city of Ferrara date back to the 7<sup>th</sup> century, when the Byzantines defended themselves against the Lombard invasion from the north [1]. In this context, the *castrum* of Ferrara was built, a fortified nucleus near which the bishop's seat was moved in 657. Following numerous attacks from the Republic of Venice, the city of Ferrara increased the defense buildings with the city walls. From 1598, the city became the extreme northern border of the Papal States and it was therefore necessary to defend it further: the ancient southern doors were closed and replaced by the Porta Paola, built by the architect Aleotti to celebrate Pope Paul V Borghese. With the unification of Italy and the fall of the Papal States, in 1901 Porta Paola became a barrier with the duty offices [2].

The archaeological excavation was carried out following the discovery of a small boat used in the late Middle Ages to transport goods from the river to the city.

In medieval Europe, the development of countries and power centres was often connected with the sourcing and utilization of mineral resources. Slags, as waste materials, are considered to be indicators for historical smelting technology at numerous archaeological sites [3,4,5], moreover, geochemical and mineralogical investigations of slags are useful in understanding the smelting

## II. MATERIALS AND METHODS

The metal slags analyzed in this study were found during the excavation carried out in August 2003, meanwhile the redevelopment works of the area at Porta Paola (Fig. 1) and maintenance of the first part of via Bologna street in Ferrara (Emilia Romagna region, northeastern Italy).

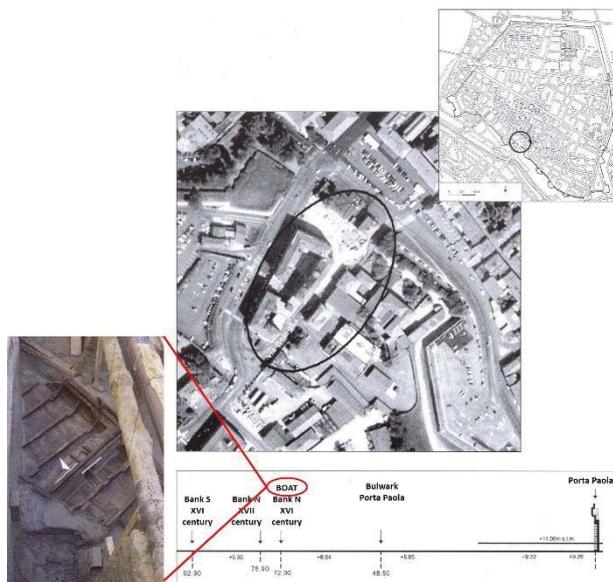


Fig. 1. Map of the sampling site. On the right top the castrum of Ferrara representing the actual city center and in black circle the sampling site at Porta Paola. On the left side a detail of the boat founded during the archaeological excavations.

Archaeologists divided the site of Porta Paola into five historical periods [9] in order to better chronologically locate the various layers of soil and the relative finds. The stratigraphic units studies allowed to identify the ancient fortification structures relating to Porta Paola, the exact position of the riverbed of the southern branch of the Po river and the urban and environmental evolution of that area from 1400 to today [10]. Archaeological investigations founded a wooden structure boat at 72.90 meters south from the Porta Paola. Stratigraphic investigations have identified, at a depth of 90 cm, a uniform 17<sup>th</sup> century level (US 100), 25 cm thick, consisting of fragments of bricks, ceramics, lime, ferrous residues, which seems to identify a road surface. This layer was above the artificial contribution layers consisting of sandy silt, covering a very consistent peat filling layer which contained organic material and ceramic fragments from between the mid-16<sup>th</sup> century and the beginning of the 17<sup>th</sup> century. The underlying layers with a silty matrix were identified even before the boat. They were arranged in oblique layer in a southerly direction at a distance of 65 meters from Porta Paola, right next to the boat. The inclined position of the boat suggests that it was fixed to the bank of a canal. The layers just above the boat containing silt and plant materials were brought in by the currents to completely cover it. The boat belongs to the type of minor commercial boat, the first ever found in Emilia Romagna, used in this case for people and goods transportation from the Great River to the southern of the city. The boat was 9 meters long, flat-bottomed, made with poplar wood planks and by oak wood pegs [11]. Analyzed

metallic samples consist of iron slags produced by the extraction of pure iron processes. Examples of the samples analyzed was shown in figure 2. Fig. 2a shown a concave-shaped slag from iron processing with surfaces rich in irregular cavities, which seem to have been produced by air bubbles and flows of molten material. There are coal inclusions in the compact slag. The sample has a red-brown color, attributable to oxidized material. Also figure 2b represented an irregularly shaped slag from iron processing rich in cavities, but in this sample three distinct phases were observed: a part of earthy greyish nature, another of red-brown oxidized material and finally a translucent glassy nature with the characteristic blue-green conchoidal fractures. These materials probably come from furnaces of shallow depth (usually less than 30–40 cm) dug in the ground, in which the iron-rich minerals were arranged together with the coal generally of oak or pine. The combustion of coal gave rise to the processes of melting, carburizing and reduction of iron oxides which led to the scorification and enrichment in iron by unmixing of the silicate phase rich in iron called bloom, from the poor iron silica which corresponds to the slag. The pre-processed products were subsequently purified through the beating or shaping process carried out in special furnaces made with refractory materials. The purification required heating and beating cycles with a temperature above 1200°C in order to separate the silica slag still present [12].

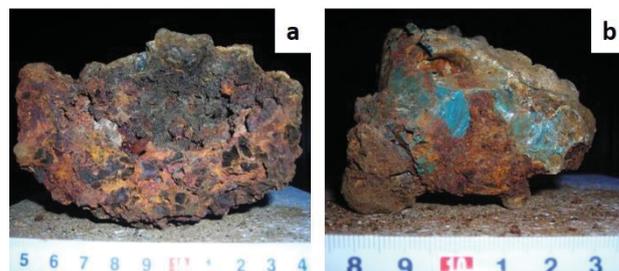


Fig. 2. Photo imaging of two samples collected and represented by a) concave-shaped slag from iron processing with surfaces rich in irregular cavities; b) irregularly shaped slag from iron processing rich in cavities with three distinct phases.

Preliminary observation of the samples was carried out using a reflection optical microscope (Leica IM 1000), and through a stereo transmitted light microscope, both equipped with a digital camera (Leica DFC 420 camera) managed by software for image acquisition. After that, the samples were ground until a powder with a particle size less than 2 µm was obtained. The powders obtained were dried in an oven at 110° C and the L.O.I. (loss on ignition) of each sample were calculated. The powders were prepared by pressing the tablets on boric acid support for XRF analysis. The compositional characterization of the collected samples was determined by X-ray fluorescence (XRF) analysis, carried out at the Department of Physics and Earth Sciences, University of Ferrara with a

wavelength dispersion spectrometer ARL Advant-XP (Thermo Fisher Scientific, Waltham, Massachusetts, USA) [13]. This technique allowed the determination of the major elements, expressed as a percentage by oxide weight ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ) and of the following trace elements reported in ppm (parts per million): Ba, Ce, Co, Cr, La, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Cu, Ga, Nd, S, Sc. The accuracy of the instrument, estimated on the basis of the results obtained on international standards of geological samples, and the precision, expressed as standard deviation of replicated analyses, were between 2% and 5% for the major elements and between 5% and 10% for trace elements. The detection limit (0.01% for major oxides) was estimated to be close to ppm for most trace elements, except for S for which 50 ppm was considered [14]. The processing of the acquired intensities and the correction of the matrix effect was performed according to the model proposed by Lachance and Trail [15]. The qualitative data obtained were expressed as single element weight.

After thin section microscopic observations some minerals has been selected for Electronic Microprobe analysis (EMPA) using a CAMECA SX-50 at the CNR-IGG Institute of Padova with natural silicates and oxides as standards to provide quantitative analyses of the constituent phases.

### III. RESULTS

Samples have shown uneven color and consistency dimensions, with prevailing slags from 10 to 15 cm in diameter. They presented irregular shape, brittle on the outside and compact on the inside. They had earth gray colors on the outside, rust red and black on the inside, sometimes blue-green and translucent. The iron layers appear no homogenous due to the different melting rate between the external surface and the core. The internal areas, characterized by the presence of glassy iron-rich slag, have a compact and bullous appearance; the external parts were made of poor metal silicate material and not very compact, due to the lower degree of melting suffered. Included in the slags, the remains of coal or wood used for melting were observed.

Through the observation by reflected light microscope it was possible to identify four phases:

- Silica: partially crystallized with mineralogical phases of neo-formation and decomposition; characterized by stick-shaped and squat-shaped minerals, randomly arranged in a glass matrix (Fig. 3a);
- Metallic: compact and highly reflective, immersed in the silicate phase (Fig. 3b);
- Organic: plant-based, attributable to cell walls and vascular ducts of wood (Fig. 3c);
- Glassy: smooth and translucent with the presence of bubbles and characteristic fractures (Fig. 3d).

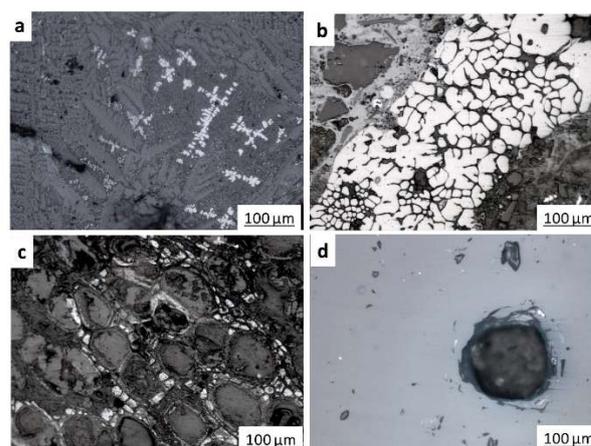


Fig. 3. Photo imaging at 200x magnification obtained by reflected light microscope: a) silica phase; b) metallic phase; c) organic phase; d) glassy phase.

Table 1 shows XRF data of major oxides expressed in weight oxide (%) in the analyzed samples. The XRF data show high values of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  confirming that slags are rich in iron bearing mineralogical phases, used for the extraction of the metal; silica came from mixing process between gangue and calcite used as flux. The heterogeneity of samples was confirmed ternary diagram of Fig. 4. These differences could come from mixing processes between silicate (gangue) phases, iron depleted, silicate melts (bloom), iron enriched, and probable use of carbonates as fluxes.

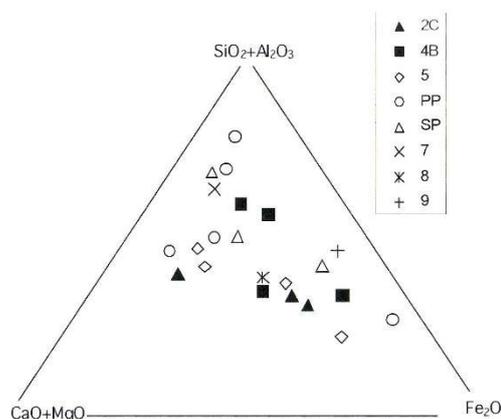


Fig. 4. Chemical composition of the slags plotted in the ternary diagram ( $\text{SiO}_2\% + \text{Al}_2\text{O}_3\%$ ) - ( $\text{CaO}\% + \text{MgO}\%$ ) - ( $\text{Fe}_2\text{O}_3\%$ ).

The XRF data have shown sulfur content lower than instrument detection limit (Table 2). These data do not allow to hypothesize absence of sulphides in the raw materials, more likely to assume that the sulfur, present in the minerals used for the iron extraction, has been released in the form of sulfur dioxide during the melting process for the extraction of pure iron [16]. Major and trace elements

have shown low concentration in the transition elements (Table 2) probably due to extraction from minerals not enriched in Cu, Zn, Co, as can be for example the residual lateritic deposits associated with small deposits originated by karst dissolution of carbonates.

Table 1. XRF data of major oxides expressed in weight oxide (%) in the analyzed samples.

	7	8	9	2C	2CN	2CX	4BA	4BC
SiO <sub>2</sub>	44.98	26.25	36.94	24.12	20.90	22.99	41.27	22.87
TiO <sub>2</sub>	0.36	0.20	0.17	0.20	0.17	0.19	0.50	0.16
Al <sub>2</sub> O <sub>3</sub>	5.89	3.64	6.42	3.02	3.72	3.73	8.99	4.10
Fe <sub>2</sub> O <sub>3</sub>	9.32	26.56	43.67	11.08	38.04	33.81	24.11	43.17
MnO	0.11	0.14	0.09	0.18	0.17	0.14	0.17	0.14
MgO	1.64	0.91	0.98	1.32	0.70	0.65	2.21	0.60
CaO	18.74	20.38	6.80	29.40	16.83	18.27	13.56	10.09
Na <sub>2</sub> O	0.85	0.25	0.58	0.38	0.21	0.25	0.84	0.22
K <sub>2</sub> O	3.97	1.88	3.74	1.11	1.68	2.32	3.96	1.73
P <sub>2</sub> O <sub>5</sub>	2.96	2.69	0.62	4.59	3.57	4.06	2.28	2.85
LOI	11.18	17.09	0.00	24.59	14.02	13.59	2.12	14.08
Tot.	100	100	100	100	100	100	100	100

Table 2. XRF data of trace elements expressed in ppm (n.d. = not detected) in the analyzed samples.

	7	8	9	2C	2CN	2CX	4BA	4BC
Ba	222	208	216	160	167	142	311	166
Ce	n.d.	n.d.	223	n.d.	n.d.	n.d.	112	n.d.
Co	6.52	9.68	8.65	8.72	9.64	8.11	10.1	11.1
Cr	156	98.5	93.6	104	88.3	108	268	145
La	n.d.	n.d.	n.d.	2.51	n.d.	n.d.	n.d.	n.d.
Nb	3.84	1.36	n.d.	0.415	n.d.	n.d.	11.8	n.d.
Ni	19.1	8.42	n.d.	6.00	13.0	12.4	42.2	40.0
Pb	n.d.	0.590	25.6	684	n.d.	n.d.	5.45	7.37
Rb	64.5	20.4	51.9	20.3	20.6	26.7	85.1	25.4
Sr	413	585	379	346	327	312	444	224
Th	n.d.	n.d.	n.d.	5.52	n.d.	n.d.	n.d.	n.d.
V	23.8	21.5	23.6	22.8	23.2	20.0	54.9	27.3
Y	n.d.	n.d.	5.69	n.d.	n.d.	n.d.	5.09	n.d.
Zn	23.0	n.d.	n.d.	98.7	19.4	2.94	48.7	46.3
Zr	332	254	101	292	120	136	322	114
Cu	81.4	48.9	33.3	188	131	138	17.9	97.3
Ga	9.23	3.44	4.75	11.8	5.58	4.69	12.0	8.94
Nd	44.4	79.3	220	n.d.	92.6	76.9	126	125
S	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

EMPA analyzes of scoriaceous samples have shown

different mineralogical phases attributable to different formation conditions of the slags, such as chemical composition of the gangue and the type of cooling, and the extraction techniques of the pure metal. The most frequent minerals are Ca-Fe silicates, such as olivine, melilite (Fig. 6a) and kirschsteinite (Fig. 6b), and minerals with a high Fe content such as wustite - Fig. 6c. These Fe-rich mineralogical phases come from the raw materials used for the metal extraction. Less frequent minerals are feldspar (albite - Fig. 6d) and quartz (Fig. 6e) which probably derived from the additives introduced in the melting process as fluxes. Chemical composition of the olivine group varies between pure Fayalite Fe<sub>2</sub>SiO<sub>4</sub> and kirschsteinite CaFe<sup>2+</sup>SiO<sub>4</sub>. Through reflected light microscopy it was possible to observe that these phases are present both as oriented and parallel acicular crystals (fayalite - Fig. 6f) and as skeletal crystals or dendritic structures (kirschsteinite) immersed in a glass matrix (Fig. 6b). The morphology of these minerals indicates that the cooling of the silicate melt occurred quickly, blocking the complete crystallization process of the minerals present.

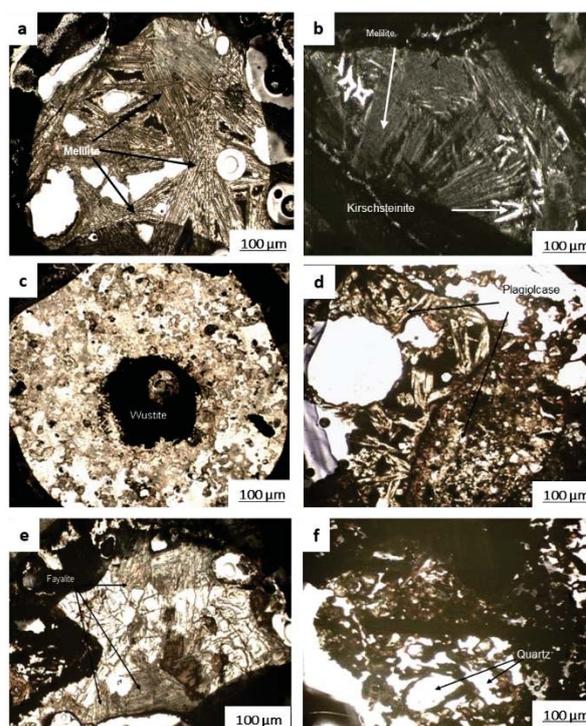


Fig. 6. Photo imaging at 50x magnification obtained by electronic microprobe: a) melilite crystals; b) kirschsteinite crystals; c) wustite crystal; d) plagioclase crystals; e) quartz; f) fayalite crystals.

Electron microprobe results were plotted in ternary diagrams. Fig. 7a shown the chemical composition data concerning olivine group varying between fayalite and kirschsteinite. These two different phase were present in the samples SP2A and 9 associated with fayalite and kirschsteinite respectively.

In the Fig. 7b shown the ternary diagram  $\text{SiO}_3$ - $\text{MgSiO}_3$ - $\text{FeSiO}_3$  the results obtained by electron microprobe on melilite were plotted. This high temperature ferro-calcium silicate phase was present in the samples SP2A and 9 associated with fayalite and kirschsteinite respectively, as already mentioned.

The values of feldspars, measured by electron microprobe, were plotted in the Or-Ab-An ternary diagram (Fig. 7c). The results obtained confirm that in the analyzed samples there were minerals belonging to the sodium term Albite ( $\text{NaAlSi}_3\text{O}_8$ ), mineralogical phase of the Plagioclase series. The presence of Plagioclases was found in the SP1A and SP3A slags.

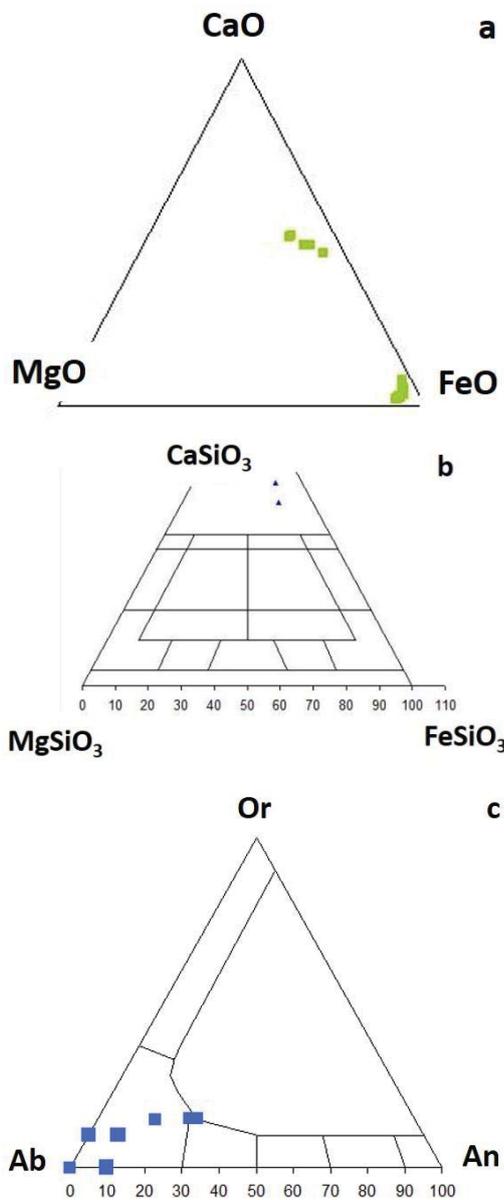


Fig. 7. Chemical composition of the slags plotted in the

ternary diagram: a)  $\text{CaO} - \text{MgO} - \text{FeO}$ ; b)  $\text{CaSiO}_3 - \text{MgSiO}_3 - \text{FeSiO}_3$ ; c)  $\text{Or} - \text{Ab} - \text{An}$ .

#### IV. DISCUSSIONS AND CONCLUSION

Microscopic and chemical analysis conducted on the iron processing slags have allowed to reconstruct the metallurgical process in terms of raw materials and technologies used and to provide indirect historical information regarding the technological level reached in the city of Ferrara during Renaissance period.

Microscopic and chemical characterization of the slags from Porta Paola in Ferrara, has made possible to trace the raw materials used, such as the minerals rich in iron, the melting additives and the fuel used, the temperatures reached in the furnace and the procedures through which pure metal was obtained.

First of all, the presence of slags allowed to confirm a direct metallurgical process, through which perfect metal was obtained, as pure as possible, through the process of scorification of the silica phases from those rich in iron. Direct process allowed to obtain slags of pure iron, but rich in scoriaceous inclusions that had to be eliminated by subjecting the bloom to annealing and beating. The preliminary phase of the indirect process was roasting of iron-rich minerals in order to eliminate water and sulfur in the raw materials. This operation has shown good efficiency, since, through XRF analysis, it has been found that the quantity of sulfur is lower than the limit of detection of the instrument. The next phase, corresponding to the melting and scorification process, began with the combustion of coal together with the roasted iron-rich minerals. Combustion, favored by the ventilation of the hearth, gave rise to the carburization and reduction process of iron oxides. The combustion of charcoal produced carbon dioxide ( $\text{CO}_2$ ) which lead to the formation of carbon monoxide ( $\text{CO}$ ) at a temperature of  $1000^\circ\text{C}$ . Carbon monoxide lead to reduction on iron oxides producing metallic iron. The iron obtained from this reaction coagulated in a spongy mass giving rise to the process of slagging, i.e. the mixing of the metal from the silicate phases of the original mineral.

The presence of melilite and kirshsteinite, high temperature phases with a melting point of  $1300^\circ\text{C}$ , confirms that this was probably the maximum temperature reached in the furnace. The achievement of such high temperatures was favored by good ventilation that allowed the introduction of oxygen favoring the combustion process. The oxygen increase lead to the presence of a reducing environment which lead to the formation of iron oxides, such as wustite and to silicates such as olivine and melilite [3,5,6,7,16]. Such efficient ventilation was obtained only through the use of hydraulic force, that is, through the application of the hydraulic wheel of a mill applied to the furnaces for the production of iron. This hypothesis cannot be excluded, given the presence in Ferrara, and in particular in the slag recovery area, of a

large-scale watercourse.

The high content of silica and calcium suggests that quartz and calcium carbonate were added as fluxes during the combustion process, in order to lower melting temperature of iron-rich minerals.

The scoriaceous materials collected during the excavation at the Porta Paola site were the result of an advanced metallurgical process, in line with the technologies for working metal in the late Medieval and Renaissance periods in Italy. Samples analyzed were produced in a historical period including an epoch of maximum splendor and without war under the Duchy of Borso and a war period against Venice with Hercules I and Alfonso I. This historical context, which alternates periods of wealth and political stability with periods of war, certainly favored the development of metallurgical art in Ferrara. The necessity of metal for the production of weapons, combined with the wealth of the lordship, probably favored an increase in the production and development of metallurgical techniques.

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