

Metal finds from the Etruscan site of Spina (Ostellato - FE - Italy), 2023 field: preliminary results

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Abstract – Archaeological excavations at the Etruscan site of Spina in Ostellato (FE), performed during 2023, have revealed numerous metal finds. Using X-ray Fluorescence Microspectroscopy (XRF) and Scanning Electron Microscopy with an EDS microprobe (SEM-EDS), the samples were divided into two main macro-categories: artefacts and scoriae. These were further classified according to their chemical composition (iron, bronze, lead). This study in focuses on the artefacts, examining their chemical composition, to potentially trace the production techniques used and to better understand the socio-economic context in which these objects were made and used.

I. INTRODUCTION

Founded in the 6th century BC, the Etruscan city of Spina is one of the most significant examples of human presence in the Delta Region and a key reference point for archaeology in Northern Italy (fig. 1) [1].



Fig. 1. Map showing the major Etruscan centres, Etruria Padana and Etruria Campana.

Located on the right bank of a branch of the Po - identified as the ancient Eridano or Spinete and later known as the Padus Vetus - the settlement was strategically positioned approximately three kilometres from the mouth of the

river, in an area of the lagoon that was more stable and protected than the maritime coastline. The city was founded in response to the need for a commercial port for trade with Greece and other Mediterranean centres, as well as a river junction for trade with northern Europe. The necropolis, on the other hand, was located on sandy, Aeolic reliefs, which are now identified as the Trebba and Pega valleys [2].

According to Dionysius of Halicarnassus, the decline of the city of Spina was related to a long siege by barbarian populations, probably the Gauls, who had settled along the coastal strip by the middle of the 4th century BC. Despite losing connections with the hinterland, the city managed to maintain a certain vitality, perhaps thanks to the piracy carried out by its inhabitants. However, it was the progressive change to the landscape of the delta, characterised by silting and shifts in the rivers, that ultimately led to the city's abandonment. By the time of the Augustan Age, Spina had been reduced to a small village, as Pliny the Elder attests, referring to it as a town that had disappeared. In fact, its name no longer appears on the main coastal routes of the imperial era [3].

Today, the area of the Spina settlement is no longer near the sea, but inland, about 35 km from the coast.

The site was discovered in the 1920s during the reclamation of agricultural land in the Valle Trebba, following a report by Giuseppe Agnelli, a local history enthusiast. Excavations of the Valle Trebba necropolis occurred between 1922 and 1935, while those of the Valle Pega necropolis took place between 1954 and 1965. Both necropolises mainly contain individual inhumation or cremation tombs in pits. These tombs lack monumental apparatus but are accompanied by grave goods related to the deceased and the burial rite [4]. This first discovery led to a series of excavations and surveys that continue to this day. Various universities (including the University of Ferrara) are still conducting field research to uncover as much information as possible about this city of Etruscan Padania. In 2023, the archaeological excavation of the Spina site was carried out by the Consorzio Futuro in Ricerca (CFR) with the collaboration of the University of Ferrara (Department of Environment and Prevention

Sciences and the University Museum System), under the scientific direction of Dr. Caterina Cornelio Cassai and together of Professors Carmela Vaccaro and Ursula Thun Hohenstein (UNIFE).

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P/[34.61.07/7.34.3/2019] - Superintendence Ref. Dr. Carolina Ascari Raccagni).

P.ET.R.A. SocCoop, coordinated by Dr. Paolo Michelini support the archaeological excavation. The site investigation area is located northern of the precedent excavation of the SABAP BO (fig. 2).



Fig. 2. Area of the Spina site unearthed in 2023 (photo: CFR Archive).

II. MATERIALS AND METHODS

During the excavation, more than a hundred artefacts were found, including metal slag and fragments of nails, needles and fibulae (fig. 3).

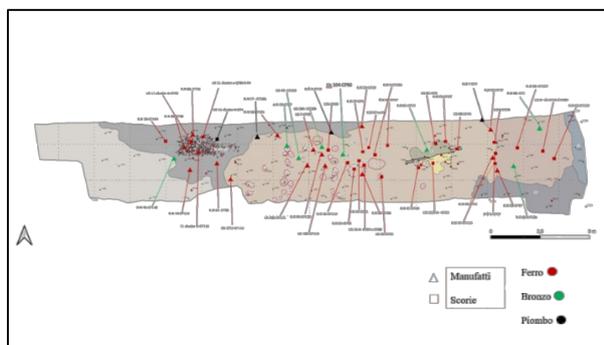


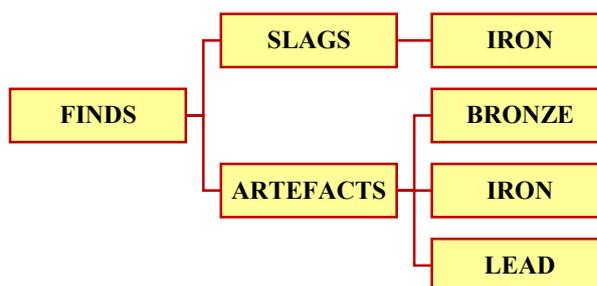
Fig. 3. Positioning of the concentration of metal finds (photo: CFR Archive).

Of these, only one sample was selected for study due to its representative nature and distinct chemical composition. Before proceeding with the analyses, a preliminary selection of the slag finds was conducted, based on size and weight criteria. At this stage, all the slag was measured and characterised using a digital caliper for size and a kitchen scale for weighing. This skimming proved essential to formulate initial hypotheses on the composition of the samples and to identify a representative group for analysis, chosen to include the greatest possible mineralogical variety.

The analytical process began with an archaeological approach, and then gradually evolved towards an archaeometry perspective, thanks to the application of non-invasive scientific techniques aimed at deepening our knowledge of the finds.

The aim of the present study was to examine the metallurgical finds, with a particular focus on their chemical composition.

Table 1. Subdivision of tested samples according to chemical composition.



Analyses were conducted using two main analytical techniques: the Scanning Electron Microscope with EDS microprobe (SEM-EDS) and X-Ray Fluorescence Spectroscopy (XRF).

SEM-EDS microanalyses were performed to determine the semi-quantitative elemental composition of slag and metal artefacts. Measurements were performed with a Zeiss EVO MA 15 scanning electron microscope (SEM) (Carl Zeiss, Oberkochen, Germany) equipped with a lanthanum hexaboride (LaB₆) source. The instrument was coupled with an X-Max 50N detector for energy dispersive X-ray spectroscopy (EDS) (Oxford Instruments, Abingdon, UK). Samples were analysed without any coating under variable pressure (VP) conditions of approximately 50-60Pa. Other operating conditions were as follows: working distance (WD) of about 8.5mm, acceleration voltage of 20kV, probe current of 200pA and cobalt as calibration standard. Data acquisition was performed with Aztec 3.1 software (Oxford Instruments, Abingdon, U.K.).

For the XRF technique, we used a portable XRF micro-analyser, ARTAX™ 200, from Bruker AXS

Microanalysis with a Mo target, and an SSD Peltier-cooled detector with a Be window and 1mm collimator was used at 30kV and 1500 μ A to analyse different colours on the potshards in air for 60s. The surface area under the deconvoluted K α 1 energy lines of Fe and Mn were used for comparison of energy counts of the elements.

The observation of the materials occurred in several stages: the first phase involved the photographic documentation of the findings, which was useful not only for an initial general observation, but also to preserve a reference image before the possible application of destructive analysis (fig. 4):

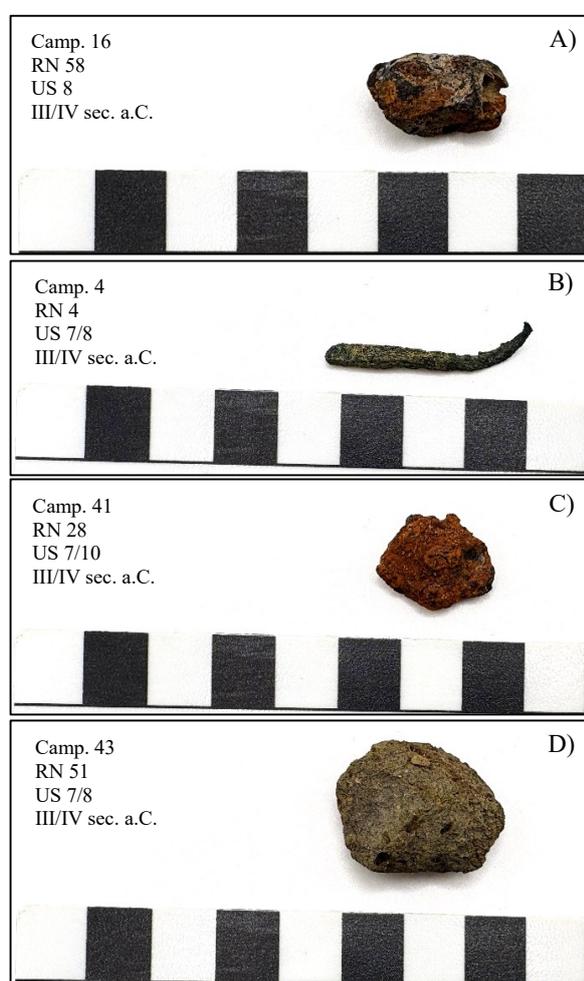


Fig. 4. Macroscopic photos of: A) lead slag; B) bronze needle fragment; C) small iron object; D) lead ingot fragment. Scale in cm.

III. RESULTS AND DISCUSSIONS

The detailed observation of the artefacts under a stereomicroscope (fig. 5) allowed for a more accurate assessment of their state of preservation. The visual examination revealed surface corrosion, inclusions, and mineral deposits, providing useful information for interpreting post-depositional alterations and identifying manufacturing techniques [5]. This procedure was carried out at the laboratories of the University of Ferrara, using an Optika sz6745tr stereomicroscope (total magnification 90x) equipped with a Moticam 2500 5.0m pixel webcam and Motic Images Plus 2.0 ml software.

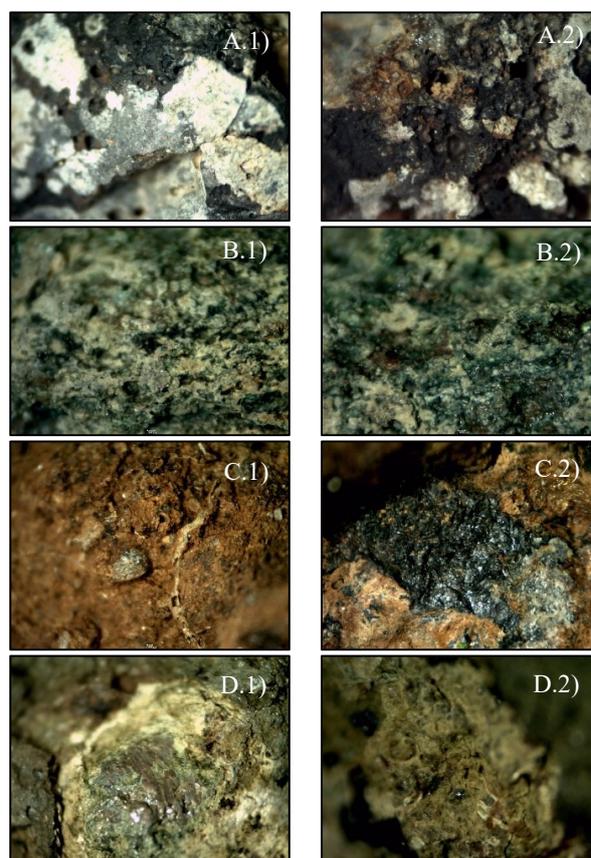
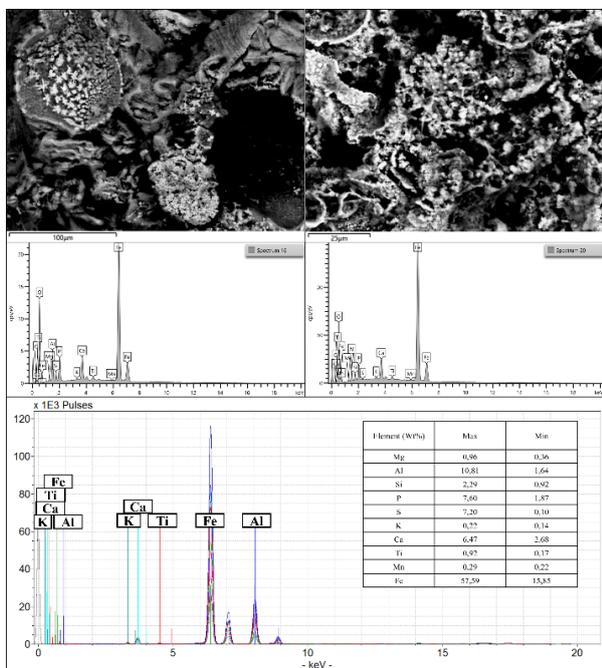


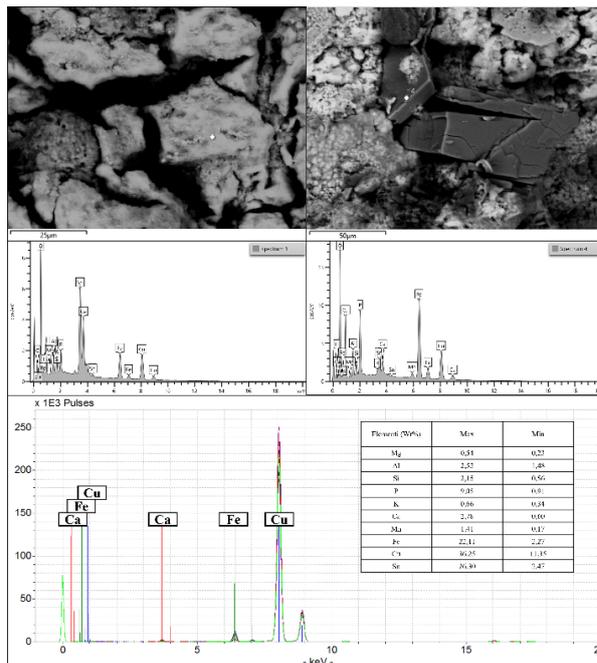
Fig. 5. Stereomicroscope images: A.1) lead slag, magnification: 2X; A.2) lead slag, magnification: 3X; B.1-B.2) bronze needle fragment, magnification: 3X; C.1) small iron object, magnification: 2X; C.2) small iron object, magnification: 3X; D.1) lead ingot fragment, magnification: 2X; D.2) lead ingot fragment, magnification: 4.5X.

The subsequent SEM-EDS and XRF analyses enabled the characterisation of the chemical composition of selected samples, highlighting the presence of distinct metallurgical categories among the finds [6]:

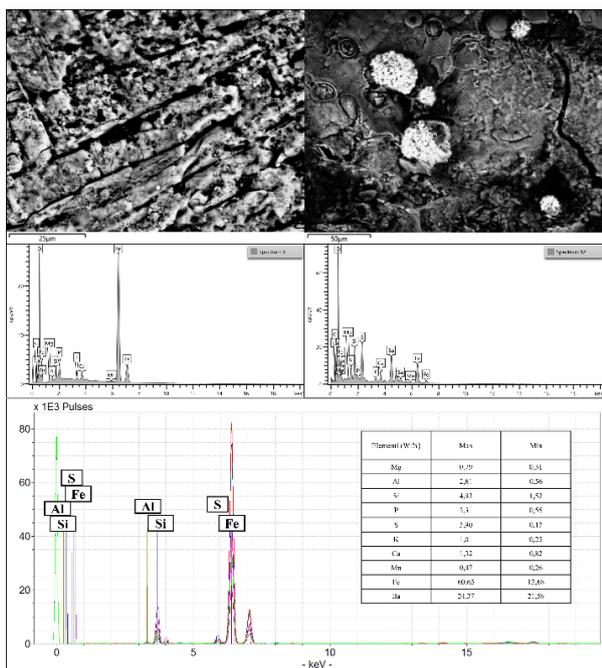
- The SEM-EDS spectrum of RN 58 sample is dominated by strong iron (Fe) peak, confirming its ferrous nature. Minor elements such as aluminium (Al), phosphorus (P), sulphur (S) and calcium (Ca) were also detected, which are commonly associated with smelting residues and flux inclusions [7]. The morphology and composition suggest that this slag is a by-product of ironworking activities, possibly related to forging or casting processes, as observed in other Etruscan and Italic contexts [8].



- The spectrum of sample RN 4 displays high concentration of copper (Cu) and tin (Sn), indicating a typical bronze alloy. The presence of iron (Fe) could be attributed to post-depositional contamination, possibly due to soil interactions or corrosion products. The choice of Cu-Sn alloy reflects typical Etruscan metallurgical practices aimed at producing functional objects such as needles, pins, and small ornaments [9].



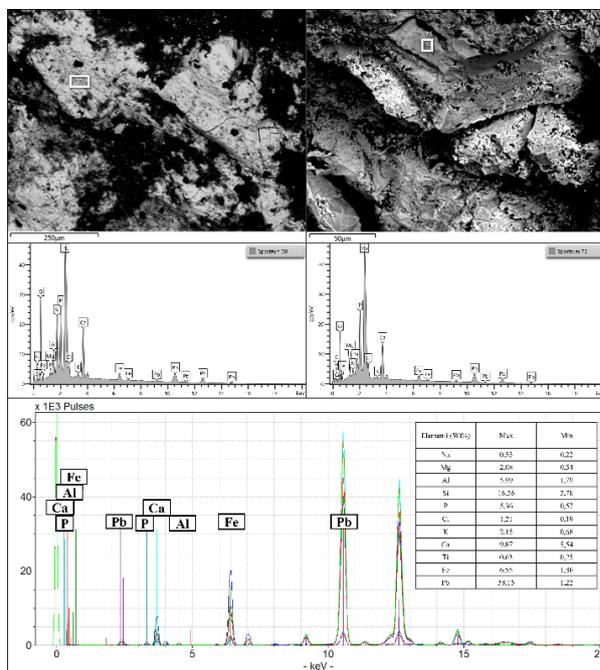
- The analysis confirms the artefact RN 28 is made of an iron alloy. Interestingly, SEM-EDS images revealed spherical structures on the surface, while the spectrum showed an unexpected enrichment in barium (Ba). This could result from diagenetic processes within the burial environment or contamination by local sediments, as also observed in the Po Delta region [10]. The detection of these features raises questions about the post-depositional history of the artefact and the burial context at Spina.



- The sample RN 51 exhibits dominant peaks from lead (Pb), with concentrations exceeding 40 wt.% confirming it as a lead-based artefact. Minor elements such as silicon (Si), calcium (Ca), aluminium (Al) and iron (Fe) were also detected, possibly as inclusions or surface contaminants. Lead objects were common in Etruscan contexts, often used for weights, small vessels, or decorative purposes. The high lead content suggests intentional alloying possibly reflecting either local production or imported raw materials [6]. These analytical results are summarised in Table 2, which provides an overview of the composition and key observation for each artefact.

Table 2.

Sample	Object Type	Main Composition	Minor Elements	Observations
RN58	Slag	Fe	Al, P, S, Ca	Typical ferrous slag; residue from smelting
RN4	Needle fragment	Cu + Sn (Bronze)	Fe	Post-depositional iron contamination; corrosion evidence
RN28	Iron object	Fe	Ba, Ca, Al	Spherical structures; possible diagenetic alteration
RN51	Lead fragment	Pb (>40 wt.%)	Si, Ca, Al, Fe	Typical lead artefact; likely for weights or small objects



IV. CONCLUSIONS

The preliminary analysis of metallurgical artefacts from the 2023 CFR-UNIFE excavation at Spina provided valuable insights into the composition of slag and metal objects. Iron was the dominant element in the slag, while bronze and lead were identified in artefacts, suggesting a diverse range of metallurgical activities at the site.

These findings support the hypothesis that Spina was an active centre for metalworking, with evidence of production both within and outside the urban area. The discovery of smelting tools, such as crucibles, and production scraps indicates a local craft industry supporting both functional and commercial needs.

A notable observation comes from the analysis of the iron artefact RN 28, where SEM-EDS revealed spherical surface structures and a high concentration of barium (Ba). This may result from diagenetic processes in the Po Delta's sedimentary environment, where the precipitation of barite (BaSO_4) under reducing conditions and the accumulation of iron and barium through flocculation processes are known phenomena. These findings raise important questions about the post-depositional history of artefacts at Spina and highlight the need for further mineralogical and isotopic studies.

Analysing alloys, impurities, and diagenetic alterations lays the groundwork for tracing raw material sources and understanding technological choices. Moreover, studying corrosion phenomena like oxidation, carbonate encrustations, and chlorides informs future conservation strategies.

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