SAPIENZA
UNIVERSITÀ DI ROMA

Faculty of Mathematical, Physical and Natural Sciences

DEPARTMENT OF EARTH SCIENCES

"Vito Volterra" Doctoral School

PhD in Earth Sciences - Curriculum in Environment and Cultural Heritage

40th cycle - a.y. 2024/2025

RESEARCH PROPOSAL

Archaeometric study of Etruscan metal and ceramic artefacts: reconstruction of the technological evolution

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Introduction and state-of-the-art

Scientific investigation of materials is important for understanding technological advancements in ancient populations. Ceramics and metals, most frequently encountered in archaeological contexts, represent *markers* of technical competence degree.

A multi-analytical approach is necessary for studying ceramic production technology. Thin-section petrography, enhanced by image analysis software, such as ImageJ, reveals raw material origins and pre-treatment practices, thanks to criteria outlined by Whitbread [1] and improved by Quinn [2]. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) offers higher magnification and spatially resolved chemical elemental data for microfossil identification and finishing layer (*i.e.*, slip, glazes, paints) analysis. X-ray powder diffraction (XRPD) determines *bulk* mineral composition, helping infer furnace conditions.

A multi-analytical approach is crucial for studying metallic artefact production and corrosion processes. Optical and SEM metallography of cross-sections identifies thermal and mechanical treatments, as described by Scott [3] and Oudbashi [4]. EDS analysis determines the chemical composition of alloys and inclusions (*i.e.*, slags or mineral ore residues). Electron microprobe analysis (EMPA) offers accurate quantitative elemental composition measurement.

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is a micro-destructive technique providing qualitative and semi-quantitative elemental and isotopic data [5]. Lead isotope analysis (LIA) is widely used for provenance studies, with well-established databases (*e.g.*, OXALID) offering comparative data for Mediterranean deposits [6]. Multivariate statistical methods, like PCA, help better identify correlations between artefacts.

In recent years, heritage science has adopted advanced techniques from various scientific fields to better understand ancient production methods and corrosion processes, minimizing artefact damage.

X-ray microtomography (XRM) enables non-invasive analysis of inner core microstructures [7]. XRM combined with XRF provides both microstructural and elemental analysis.

Nano-invasive electrochemical techniques, like Voltammetry of Immobilized particles (VIMP) and Electrochemical Impedance Spectroscopy (EIS), can be useful in identifying corrosion products on metals [8] and pigments on ceramic surfaces. They also show potential for distinguishing ceramics with different raw materials origins [9].

Secondary Ion Mass Spectrometry (SIMS), a micro-destructive technique like LA-ICP-MS, was recently applied to cultural heritage artefacts, proving valuable for provenance studies of Roman lead-glazed ceramics [10] and promising future applications.

Scientific investigation is crucial concerning Etruscan materials, given the scarcity of Etruscan written sources providing direct insights into their manufacturing techniques [11].

However, scientific literature on Etruscan ceramic and metal production is limited, primarily relying on non-invasive surface analysis techniques (p-XRF, μ-Raman and FT-IR-ATR) [12]. While these are essential for initial characterisation, they are insufficient to understand production techniques and corrosion mechanisms [13].

Conversely, the few comprehensive multi-analytical studies on Etruscan ceramics and metals often focus on secondary contexts and narrow periods [14]. The only exceptions, which provide a broader perspective, include the diachronic studies of Populonia's slags [15] and of Tarquinia's *bucchero ware* sherds [16].

The Etruscans were organised into independent city-states, each with political and economic autonomy. Therefore, diachronic studies using a multi-analytic approach, integrating surface and inner core analyses of the artefacts, are needed for other major Etruscan urban centres to fully reconstruct the development of technical practices of this population.

References

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General objective

The comprehensive reconstruction of the technological progress of the Etruscan civilisation.

Specific objectives

- The identification of microstructural variations in ceramics and metals of Vulci and Caere over time.
- The identification of compositional variations in ceramics and metals of Vulci and Caere over time.
- The identification of raw materials' origin variation over time by trace elements and isotopic analysis.
- Evaluation of the applicability of advanced techniques from other fields to heritage science research.

Future implications

- From an archaeological perspective, reconstructing the evolution of Etruscan manufacturing techniques can also provide insights into their economic-social history and help better understand cultural exchanges with other ancient populations.
- From a scientific perspective, validating novel, cutting-edge techniques to characterise archaeological ceramics and metals allows heritage science researchers to choose the most suitable techniques for specific projects, broadening the methodological repertoire available.

Work plan

To achieve the research objective, the following will be carried out:

- **Task 0 - Literature review (months 1 – 36):** a comprehensive literature review will be undertaken to explore cutting-edge techniques for analysing ceramic and metal artefacts and to gain knowledge about Vulci and Caere (the archaeological contexts), the types of artefacts (e.g., figures 1-4) and the potential raw materials sources.
- **Task 1 – Sample selection and acquisition (months 1 – 12):** specific ceramic and metal artefacts from Vulci and Caere will be selected, according to archaeologists of the "Ancient Sciences" Department of Sapienza, to represent the full chronological sequence of Etruscan history. High-value artefacts will undergo non-invasive XRM analysis, while others will be sampled for sectional and XRPD analyses.
- **Task 2 - Surface material characterisation (months 4 – 14)**: non-invasive techniques, such as µRaman and XRF, will be used to characterise surface layers and to identify conservation treatments (e.g., acrylic resins). Additional nano-invasive techniques, VIMP and EIS, will be employed at the University of Valencia (Spain) to further investigate surface properties. The study will also explore the potential of VIMP and EIS to distinguish between ceramic classes and origins. The collected data will be processed and analysed.
- **Task 3 – Inner core material characterisation (months 6 – 24):**
    - **Task 3. a - Microstructure and chemical composition analysis**: the inner core microstructure of metal and ceramic artefacts will be investigated by section using OM and SEM. EDS technique,

coupled with SEM, or EMPA technique will be used to collect the elemental composition of the artefacts. XRM will be employed for non-invasive microstructural analysis on high-value artefacts. All of these techniques are useful for understanding production processes and corrosion mechanisms. The collected data will be processed and analysed.

  - **<u>Task 3. b - Mineralogical analysis of ceramics</u>**: additional micro-samples from some ceramic sherds will be powdered and analysed using XRPD to detect neo-phases and *bulk* mineralogical composition, useful to gain furnace conditions and potential provenance of raw materials. The acquired data will be processed and analysed.

- **<u>Task 4 - Trace elements and isotopic analysis</u> (18 – 26 months)**: LA-ICP-MS and SIMS will be used to determine trace elements and Pb and Cu isotopic signatures for provenance studies of the raw materials. SIMS data will be acquired at the University of Manitoba (Canada) to assess the potential of this technique for heritage science. The data will be processed and analysed.
- **<u>Task 5 - Data interpretation and chronological correlation</u> (25 – 30 months)**: analysed data, from both the surfaces and the inner core of the artefacts, will be interpreted and correlated with the chronological sequence of Etruscan history to assess the moments of changes in raw material sources and manufacturing techniques, in Vulci and Caere, throughout the 1st millennium BC.

Figure 1 - Etruscan red-figure kylix (*Vulci*)

Figure 2 - Iron plough digger (*Vulci*)

Figure 3 - Small bronze handle (*Vulci*)

Figure 4 – Blade tip (*Caere*)

<u>Milestones</u>

M1 (**month 14**) – completion of surface preliminary characterisation of artefacts.
M2 (**month 26**) – completion of analyses to identify production techniques and raw material origin.

<u>Dissemination</u>

Over the three-year program, I will disseminate the research data by submitting articles to high-impact scientific journals, with a focus on the field of cultural heritage. Additionally, I will present research results at international and national conferences (*e.g.*, TECHNART, EMAC, and others). The final year will be dedicated to the writing of the doctoral thesis.

Training Activities

During my first year of PhD study, I plan to attend the following institutional courses: Introduction to Matlab; Ricostruzioni paleoambientali nel record geologico e caratterizzazione degli ambienti attuali mediante l'utilizzo di foraminiferi; applicazioni GIS; creazione e uso dei database nelle Scienze della Terra; Spettroscopie Raman e FTIR nei progetti di dottorato di Scienze della Terra; Suggerimenti su come scrivere un lavoro scientifico, preparare una presentazione e scrivere un progetto di ricerca; Creazione e uso dei database nelle Scienze della Terra; i laboratori e le strumentazioni di ricerca del Dipartimento di Scienze della Terra; Introduzione al machine learning; ricostruzioni fotogrammetriche 3D per le Scienze della Terra ed i Beni Culturali. Other training activities I would like to attend are "*Scuola di Spettroscopia Infrarossa e Raman*" (2025) - Venaria Reale (Turin) and "*Elaborazione e gestione dei dati nel campo dei beni culturali*" – from the 2024/2025 PhD study plan of "National PhD in Heritage Science" (*the list could grow over time*).

Mobility abroad

I have planned to spend three months at the end of the first year at the University of València and at the Universitat Politècnica of València to learn and apply VIMP and EIS techniques under the supervision of professors Antonio and María Teresa Doménech-Carbó; at the end of the second year, another three months are scheduled at the University of Manitoba (Winnipeg, Canada) to collect isotopic and trace elements data by SIMS instrument under the guidance of Professor Mostafa Fayek.

Gantt chart