From clay raw materials to ceramics: mineralogical and geochemical markers for assessing refinement technologies and provenance in north-western Tuscany (Italy)

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Abstract

Understanding the provenance and selection of ceramic raw materials is essential for reconstructing past technological practices and production networks. Twenty-four clay outcrops from geological formations and deposits located near documented production sites in north-western Tuscany (Italy) were sampled, refined into experimental briquettes, and fired. The samples were characterised using a multi-analytical approach that combined thin-section petrography to examine the compositional and textural features, X-ray diffraction (XRD) for mineralogical analysis, and X-ray fluorescence (XRF) for geochemical characterisation. This workflow was validated by comparing the results with existing literature on archaeological Middle Ages ceramics, resulting in an integrated reference catalogue of raw materials for ceramic production in north-western Tuscany.

Keywords

clay provenance; ceramic raw materials; Tuscany.

Introduction

Tracing the provenance of raw materials used in ceramic production is a fundamental objective of archaeometric research, as the movement of pottery from production centres to sites of recovery reflects human activities such as trade, exchange and migration (Quinn 2022). Minero-petrographic and geochemical analyses have become a key methodological tool for provenance studies, which are based on the theoretical assumption that natural clay deposits vary to an extent that exceeds, in some recognisable compositional and/or textural terms, the variability observed within a single deposit (Weigand *et al.* 1977; Hein and Kilikoglou 2020). However, while the characterisation of archaeological ceramics has been widely applied, robust provenance assessments require the availability of comparative reference datasets, including geological clay sources and kiln-related materials, in order to evaluate also the relationships among resource availability, exploitation strategies, and refinement practices at a regional scale.

Despite this methodological awareness, systematic datasets of raw materials exploited for ceramic production in Italy remain relatively limited (Barone *et al*. 2019; De Bonis *et al.* 2013; Gliozzo *et al*. 2014; Montana *et al.* 2011). In Tuscany, studies have been carried out on raw materials from the southern part of the region (Gliozzo *et al.* 2014), whereas the north-western sector remains comparatively underexplored. Indeed, existing research in this area is largely confined to specific archeological ceramics productions (e.g. Empoli tablewares or amphorae, Cantini *et al.* 2014; Menchelli *et al.* 2024) within restricted chronological and geographical contexts, and a comprehensive regional assessment of exploited clay resources is still lacking. Within this framework, this study aims to systematically characterise north-western Tuscany raw materials, in order to verify the reliability of minero-petrographic markers proposed in the literature for defining production areas (Menchelli *et al.* 2024). A total of 24 clayey sediments were sampled from geological outcrops near attested production centres and were subjected to minimal processing to preserve their natural mineralogical and geochemical variability and, thereby, to identify the original features of the raw material prior to their alteration by technological processes. The reference baseline for comparison with archaeological ceramics was established through petrographic, mineralogical and geochemical analyses of the sampled clay sediments.

Within a broader perspective, the findings of this research will contribute to the development of an Open Access database of the raw materials involved in north-western Tuscany ceramic productions, supporting the creation of shared and accessible scientific datasets. Such initiatives are increasingly central to the advancement of digital archaeology and to the reproducibility and comparability of archaeometric research (Anichini *et al.* 2013).

Geological and archaeological backgrounds

Geological context

The north-western Tuscany region is distinguished by its notable lithological diversity, reflecting the coexistence of the Ligurian and Tuscan Units alongside Miocene–Quaternary post-orogenic sedimentary successions (Conti *et al.* 2020).

The Ligurian Units primarily consist of ophiolites (gabbros, basalts, serpentinised peridotites), pelagic sediments, and turbidites, with major outcrops in the Livorno Hills. Smaller exposures also occur at Monte Ferrato (Monte Morello Unit), located east of Prato. The Tuscan Units include the Tuscan Metamorphic Units and the Tuscan Nappe. The former are characterised by acidic pre-Alpine metamorphites exposed in the Apuan Alps and Pisan Mountains, while the latter comprise claystones, siltstones, marls, micritic limestones and the micaceous sandstones of the Macigno Formation. From Miocene onwards, newly formed basins have been filled by lacustrine, marine, and fluvial deposits. In this scenario, the most widespread clay sediments include: (i) Varicoloured Clays (AVR), turbiditic deposits connected to the Ligurian Unit east of Prato; (ii) Blue-grey Clays (FAA), Plio-Pleistocene marine deposits; (iii) Villafranchian continental deposits (VILa), comprising siliciclastic conglomerates, sands, silts, and clays; (iv) Recent alluvial and coastal-lacustrine deposits (ALL).

This study covers the north-western part of Tuscany, including the Middle-Lower Arno River Valley, the Prato area, the Lower Serchio River Valley and the Livorno hinterland and surrounding hills.

Minero-petrographic markers in Roman and Medieval ceramics: state of art

The chronological framework adopted in this study spans from the 1st century BC to the Late Middle Ages. The lower limit corresponds to the establishment of *terra sigillata italica* production in Tuscany, particularly with the development of workshops in Pisa and in the *Ager Pisanus*. This phase also coincides with the peak of activity of *Portus Pisanus* (starting from the late 2nd century BC), reflecting a broader intensification of economic and productive dynamics in the region. From this period onward, the number of archaeologically attested production centres increases significantly, alongside the availability of archaeometric studies aimed at defining mineralogical and petrographic markers (Menchelli *et al.* 2001; Menchelli *et al.* 2024; Picchi *et al.* 2010). The Late Middle Ages provide an appropriate upper chronological limit, as this period witnesses a reorganisation of regional ceramic production. From the mid-14th century onwards, manufacture shifted towards specialised centres, accompanied by a strong growth in both scale and standardisation of ceramic production. These changes resulted in more industrialised structure (Boldrini *et al.* 1999). Late Medieval productions from Figline di Prato represent an effective endpoint for evaluating relationships among raw materials, ceramic fabric and production areas.

Archaeological and archaeometric research in north-western Tuscany has documented numerous ceramic workshops characterised by distinct petrographic and mineralogical signatures, reflecting the geological variability of the region. In the Middle Arno Valley, an important production district has been identified in the Vingone area (Florence). The activity of the workshop is primarily dated between 20 BC and AD 20, and archaeological evidence indicates an articulated production, including building materials, fine and coarse wares, and amphorae. Archaeometric analyses have enabled the identification of six distinct fabrics, the majority of which are proposed to be made with locally available raw materials and characterised by an iron-rich matrix, while the aplastic fraction is dominated by quartz and feldspars (De Marinis and Pallecchi 2006). Moving toward the Lower Arno

Valley, Empoli was a significant production centre between the 4th century AD until the first decades of 6th century AD. Here, red-slipped ware and transport amphorae (the so-called *Anfora di Empoli*) were widely manufactured; calcareous microfossils, including echinoid spines and coral fragments, are particularly characteristic of the amphorae. (Cantini *et al.* 2014; Menchelli *et al.* 2024). Within the same district, evidence of early medieval production (9th century AD) is then attested at San Genesio village, where the so-called *colature rosse* ware were produced, as evidenced by the presence of kilns and kiln-wastes. Ongoing petrographic studies indicate the use of highly refined pastes with a very fine aplastic fraction of quartz, plagioclase, K-feldspar, mica, metamorphic lithoclasts, rare microfossils, and scarce calcite (F. Cantini, personal communication, January 15, 2026; Principe *et al.* 2022). Another important manufacturing centre is Pisa, where the specialisation in *terra sigillata* production is evidenced by ateliers located in San Zeno, Santo Stefano and Galluppi streets (Menchelli *et al.* 2001; Menchelli *et al.* 2020). Most Pisan productions are characterised by an iron-rich matrix with siliciclastic and sedimentary rocks (sandstone, chert, and rare calcareous bioclasts), along a minor acidic metamorphic contribution (Menchelli *et al.* 2024).

In the Prato area, the main production district was situated in Figline di Prato, at the foot of Monte Ferrato. The site is well known for its Late Medieval ceramic production, the so-called *catini figlinesi* (Boldrini *et al.* 1999). Although no kiln structures have yet been archaeologically identified, production was likely already active in the earlier Medieval period, as supported by the analysis of excavated pottery dating to the 10th–13th centuries AD (San Salvatore di Vaiano and Palazzo Pretorio di Prato; Manganelli del Fà, Vannucci 1976; 1978). Petrographic analyses on cooking wares (such as *ollae* and *testi*) and *catini figlinesi* show a predominance of highly altered gabbros, ascribable to the Monte Ferrato area; according to Manganelli del Fà and Vannucci (1976), these were credibly mixed with approximately 30-40% of local Varicoloured Clays.

Along the Lower Serchio Valley, the Isola di Migliarino workshop is known for italic *terra sigillata* production between the 20 BC and the half of the 2nd century AD. Archaeometric analyses describe the fine ware fabrics with an alluvial clay matrix, while the spacers are characterised by an association of acidic metamorphites, sandstones, shales, and ophiolitic basalts added to the same clay (Menchelli *et al*. 2001; Menchelli *et al*. 2024; Menchelli and Vaggioli 1988). In the Livorno hinterland, several ateliers dating to the Roman period have been identified. At the Ca' Lo Spelli workshop (1st century BC), tablewares with calcareous, microfossil-rich matrices and coarse wares with iron-rich matrices and ophiolitic components have been documented (Menchelli *et al.* 2007; Picchi *et al.* 2010). Similar compositions are documented in the amphoraes from Casa Campacci and Vallimbuio workshops, dating from the 1st century BC to the 1st century AD (Thierrin-Michael *et al.* 2004). Moving southern in the Fine River Valley, the ceramics produced at the Poggio Fiori atelier (1st century BC-Late

Antiquity) are notable for their calcareous matrices containing ophiolitic and sedimentary fragments (Cherubini and Del Rio 1995; Menchelli *et al.* 2001). Another furnace has been identified at La Mazzanta, located in the coastline north of the Cecina River estuary and dating from the late 1st century BC to the 2nd - 3rd centuries AD. Kiln waste analyses indicate a production characterised by the use of locally sourced clays rich in iron and calcium carbonates, with inclusions of gabbro, quartz and chert (Cherubini and Del Rio 1995; Menchelli *et al.* 2007).

This framework, derived from a critical review of the literature, provides the conceptual and empirical basis for the selection of the sampling areas and for interpreting mineralogical and petrographic comparisons with archaeological ceramic fabrics. It also supports a targeted investigation of the relationships among locally available geological resources, documented patterns of raw materials exploitation and clay preparation practices.

Methodology

Sampling campaign, clay refining, **briquettes** *preparation and firing*

Between spring 2023 and spring 2025, 24 clayey sediments were collected from outcrops and deposits along the Arno River and its tributaries, the Lower Serchio Valley, and the coastal portion and part of the hinterland between Livorno and Cecina (Figure 1). Sampling sites were selected by cross-referencing geological maps with information available in the literature regarding ceramic production centres (Table 1). In some areas, however, sampling was not possible due to extensive urbanisation, which limited direct access to potential clay deposits. This limitation was particularly significant in Pisa and, to a lesser degree, in Livorno.

Fieldwork was conducted using topographic maps of the area and GPS devices to record precise coordinates. The final selection of sampling points was refined through direct field observation, taking into account terrain morphology and accessibility conditions. Before collection, the superficial soil horizon was removed in order to minimise contamination from pedogenic processes and recent anthropogenic inputs. On-site, the collected material was preliminarily examined to exclude materials with excessive coarse or sandy fractions. Simple shaping tests were carried out to assess the plasticity of the sediment. A hand corer was employed to collect approximately 1kg of sediment, which was stored in labelled plastic bags for transport and further analysis.

The refining procedure followed the methodology outlined by Eramo (2020), avoiding intensive fractioning in order to preserve the natural textural, mineralogical and geochemical variability of the raw materials as they occur in primary and secondary geological contexts. The sediments were manually kneaded with water at a 2:1 ratio and left to settle for approximately two days to allow removal of floating organic matter. The suspensions were sieved through a 1 mm mesh. Sediments containing minimal or no coarse residue were processed using the whole material. Conversely, where coarse residue was abundant, it was crushed and added to the finer fraction, in a proportion not exceeding 25wt%, to three of the six *briquettes* (5×1×1cm). All experimental *briquettes* were air-dried under ambient conditions for one week.

This strategy enables a first-order characterisation of the sediments natural mineral phases, accessory components and bulk geochemical signatures, establishing a baseline reference to evaluate both the intrinsic suitability for ceramic production and the extent to which mild refinement may alter or preserve the original mineralogical markers derived from local geological sources. Indeed, it is recognised that the manufacture of specific ceramic classes often involved clay preparation techniques (such as levigation, settling, sieving or the selective removal of coarse inclusions) which may substantially modify the granulometric distribution and mineralogical assemblage of the starting material and, in some cases, affect the bulk geochemical composition through the preferential removal of mineral-rich fractions (Maritan *et al.* 2024). For this reason, establishing a reference framework based on minimally processed sediments represents a necessary analytical step: it constrains the original compositional spectrum of exploited clay sources, identifies primary mineralogical and geochemical markers available prior to technological manipulation, and assesses which components, particularly within the fine fraction, are likely to persist through refinement processes and remain detectable in kiln-fired ceramics.

Three *briquettes* from each sediment were fired respectively at 600, 800, and 950°C. The process was carried out in an oxidising atmosphere with a heating rate of 100°C/h, a 3h dwelling time and a cooling rate of 100°C/h, following established experimental protocols (Montana 2020 and reference therein). A detailed discussion of firing behaviour falls outside the scope of the present contribution and will be addressed in future works.

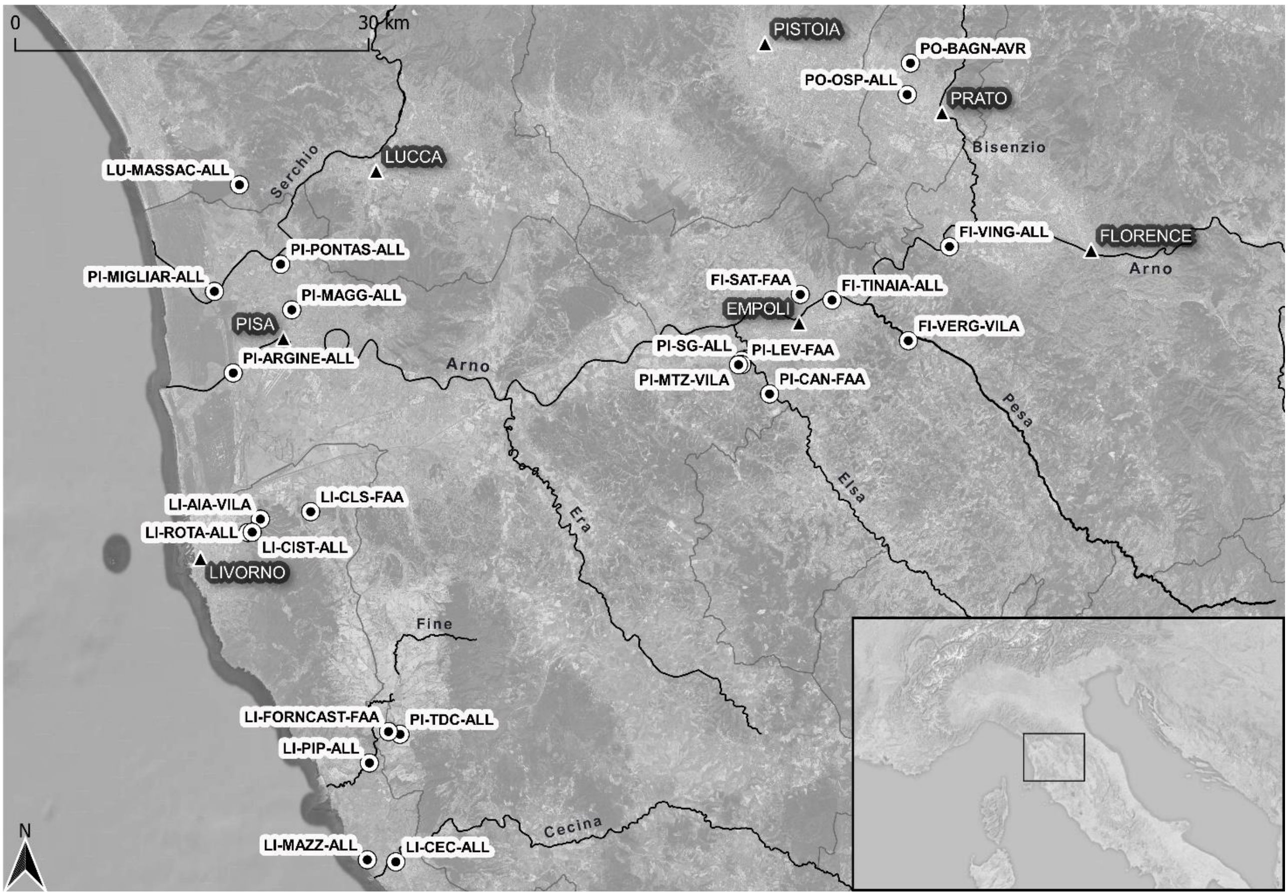
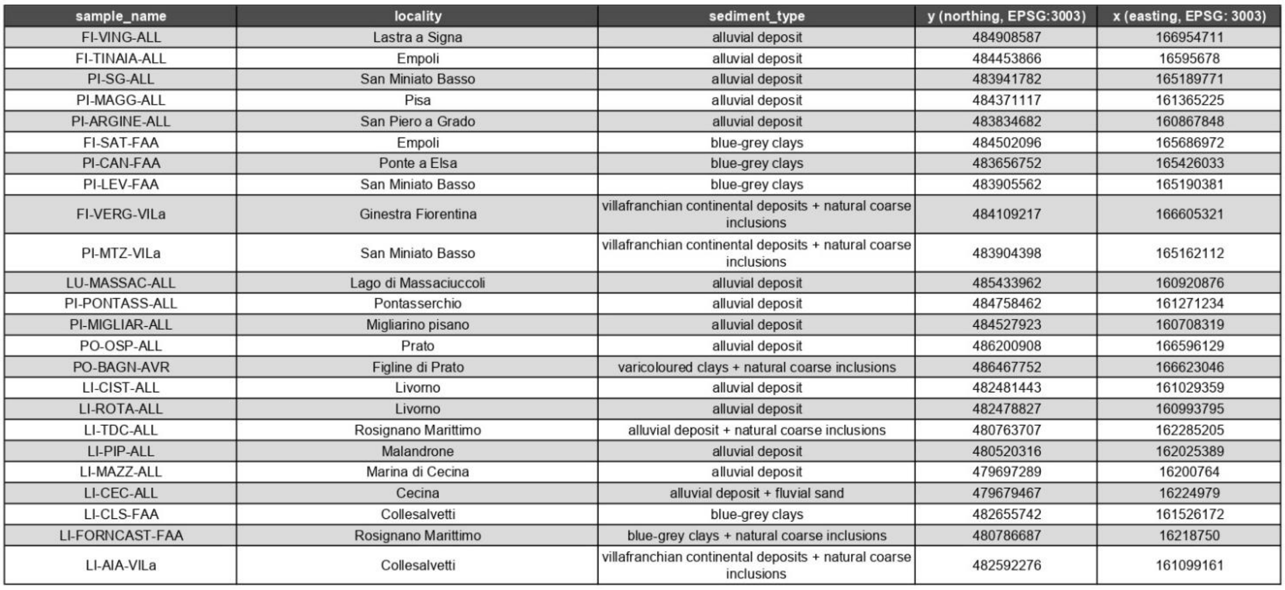


Figure 1: Sampling sites. The acronym for each sediment also refers to the type of the collected deposit. The darker lines indicate the main rivers of the region. Basemap © Google Maps, map compiled by the authors using QGIS.



sample_name	locality	sediment_type	y (northing, EPSG:3003)	x (easting, EPSG: 3003)
FI-VING-ALL	Lastra a Signa	alluvial deposit	484908587	166954711
FI-TINAIA-ALL	Empoli	alluvial deposit	484453866	16595678
PI-SG-ALL	San Miniato Basso	alluvial deposit	483941782	165189771
PI-MAGG-ALL	Pisa	alluvial deposit	484371117	161365225
PI-ARGINE-ALL	San Piero a Grado	alluvial deposit	483834682	160867848
FI-SAT-FAA	Empoli	blue-grey clays	484502096	165686972
PI-CAN-FAA	Ponte a Elsa	blue-grey clays	483656752	165426033
PI-LEV-FAA	San Miniato Basso	blue-grey clays	483905562	165190381
FI-VERG-VILa	Ginestra Fiorentina	villafranchian continental deposits + natural coarse inclusions	484109217	166605321
PI-MTZ-VILa	San Miniato Basso	villafranchian continental deposits + natural coarse inclusions	483904398	165162112
LU-MASSAC-ALL	Lago di Massaciuccoli	alluvial deposit	485433962	160920876
PI-PONTASS-ALL	Pontasserchio	alluvial deposit	484758462	161271234
PI-MIGLIAR-ALL	Migliarino pisano	alluvial deposit	484527923	160708319
PO-OSP-ALL	Prato	alluvial deposit	486200908	166596129
PO-BAGN-AVR	Figline di Prato	varicoloured clays + natural coarse inclusions	486467752	166623046
LI-CIST-ALL	Livorno	alluvial deposit	482481443	161029359
LI-ROTA-ALL	Livorno	alluvial deposit	482478827	160993795
LI-TDC-ALL	Rosignano Marittimo	alluvial deposit + natural coarse inclusions	480763707	162285205
LI-PIP-ALL	Malandrone	alluvial deposit	480520316	162025389
LI-MAZZ-ALL	Marina di Cecina	alluvial deposit	479697289	16200764
LI-CEC-ALL	Cecina	alluvial deposit + fluvial sand	479679467	16224979
LI-CLS-FAA	Collesalvetti	blue-grey clays	482655742	161526172
LI-FORNCAST-FAA	Rosignano Marittimo	blue-grey clays + natural coarse inclusions	480786687	16218750
LI-AIA-VILa	Collesalvetti	villafranchian continental deposits + natural coarse inclusions	482592276	161099161

Table 1: Sampling sites. The names of the sediment formations or deposits were obtained from the Geological Map of Italy (1:10,000).

Analytical methods

A multi-analytical approach was adopted to characterise the sediments from a petrographic, geochemical and mineralogical perspective. Sediment composition, matrix texture, and geological markers were analysed by optical microscopy. Thin sections analysis was carried out on *briquettes* fired at 600°C, as this temperature provides optimal conditions for studying mineralogical markers while minimising thermal alteration. Observations were conducted using a ZEISS Axioscope 5 microscope.

Bulk chemical characterisation of the raw *briquettes* was performed using X-ray fluorescence (XRF) spectroscopy to determine the elemental fingerprints. Three replicas of each sediment were analysed as 30mm diameter glass beads, prepared with $Li_2B_4O_7$ flux in an electric beader. Analysis was carried out using a ZSX Primus II WD-XRF (Rigaku Industrial Corporation), with a Rh source (4kW, 60mA) in a vacuum chamber. Background and mass absorption corrections were applied using 24 international geological standards for major/minor oxides (SiO_2, Al_2O_3, CaO, MgO, MnO, Fe_2O_3, Na_2O, K_2O, P_2O_5, TiO_2) and trace elements (V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Zr, Ba). Loss on ignition (LOI) was determined by heating 0.5g of each replicate to 950°C for 1.5h. Data analysis was performed using R Project for Statistical Computing. Principal Component Analysis (PCA) was conducted on the arithmetic mean of the three replicates after z-score standardization. Mineralogical composition of the sediments was assessed by X-ray powder diffraction (XRPD) to provide a qualitative overview and identify the presence of clay minerals. Measurements were carried out on powders derived from *briquettes* prepared exclusively from the sediments fine fraction. Analysis was conducted on a XRDynamic 500 diffractometer (Anton Paar), with Co-Kα radiation (40kV, 40mA) over the 3-60°/2θ range, step size 0.02°/2θ. Phase identification was performed using DIFFRAC.EVA software, with PDF-5 (2024) database.

Results and discussion

The integrated evaluation of petrographic, mineralogical and geochemical data provides a coherent framework for characterising the analysed clay sediments. This approach enables the identification of textural, compositional and mineralogical markers, as well as the relationships with local geological substrates and documented ceramic production contexts. The obtained results are presented according to geographical areas and geological contexts, allowing clearer recognition of the distinctive markers and compositional affinities within each group. The results of the XRPD and XRF analyses are presented in Tables 2 and 3, respectively.

Middle-Lower Arno River Valley

Alluvial deposits

The alluvial sediments sampled in the Arno River Valley display a moderately homogeneous, silty-clayey, iron-rich matrix composed of fine quartz, altered feldspars, mica, and calcareous fragments. Sub-angular to sub-rounded inclusions (200-500µm) of disaggregated quartzarenite, altered feldspar, quartzite, limestone, sparry calcite, and iron-rich ferruginous clots were identified in all studied sediments (Figure 2). XRPD semiquantitative analysis detected clay minerals and muscovite in high abundances, accounting for the elevated concentrations of SiO_2, Al_2O_3, K_2O, Na_2O and Rb measured by XRF. The elevated Cu concentrations are most likely attributable to environmental pollution. Calcium tenors are moderate (CaO, 3.1-4.9wt%). These features are indicative of the influence of the sedimentary and metamorphic parental rocks in the area, specifically, the Macigno Formation (Tuscan Nappe) and the Monte Morello Unit (Ligurian Units).

The Florentine deposits (FI-VING-ALL) are characterised by a preponderance of sedimentary and metamorphic material, exhibiting a distinctive aplastic fraction such as fine sparry calcite and micritic fossiliferous limestone. The Empoli sediments (FI-TINAIA-ALL) also contain micritic metamorphosed limestones, together with an enrichment in marine microfossils, chert, and a rare ophiolitic component. The latter is attributed to the sporadic presence of Ligurian-type lithofacies in the Macigno Formation (Falorni 2007), while the fossil content is related to the proximity of Plio-Pleistocenic marine sediments. The Lower Elsa River Valley deposits (PI-SG-ALL) differ slightly from the others, as they are distinguished by a heterogeneous matrix with abundant quartz inclusions, thereby accounting for the high SiO_2 content detected (70.5wt%). Quartzite, calcite, and limestone fragments up to 500 µm were identified; the latter two account for the abundance of calcite detected by XRPD. PCA highlights a distinct geochemistry for this sediment, due to its low iron content and a minimal elemental contribution associated with clay minerals (Figure 3). The sediments collected in the north-east of Pisa (PI-MAGG-ALL) are less silicic and comparatively enriched in aluminium and iron oxides. Petrographic analyses confirmed the absence of particular markers with the exception of sparry calcite dispersed in the fine and homogeneous paste. Finally, PI-ARGINE-ALL is readily distinguished by the presence of acidic metamorphites, reflecting the influence of the Pisan Mountains.

Blue-gray clays

The composition of the blue-grey clay sediments is closely linked to their geological formation. The analysed sediments are characterised by a homogeneous clayey matrix with a quartz-rich calcareous fabric, containing locally altered feldspars and calcareous fragments smaller than 50µm (Figure 2). The significance of the calcareous component is evidenced by the abundance of calcite identified by XRPD, while XRF analysis confirms CaO contents ranging from 5.1 to 8.8 wt%, together with elevated Sr concentrations. The abundance of clay minerals, along with muscovite and K-feldspar evidenced by XRPD is consistent with the elevated K_2O tenors in XRF measurements. The Empoli sediments (FI-SAT-FAA) are particularly enriched in marine microfossils and appear strongly influenced by the geology of the Middle Arno Valley, accounting for the presence of chert, quartzite, and micritic limestone and explaining their clustering with the alluvial deposits in the PCA (Figure 3). With regard to the sediments in the Lower Elsa River Valley area, PI-CAN-FAA is likely to be affected by the nearby Elsa River, which has contributed to its calcium enrichment and the occurrence of fine-grained sparry calcite and micritic limestone. The other sediment from the Lower Elsa River Valley (PI-LEV-FAA) exhibits reduced calcareous and micaceous contributions, favouring quartzite and minor metamorphic fragments attributable to occasional lithoclasts related to the Macigno Formation (Falorni 2007). Geochemical analyses recognised PI-LEV-FAA as enriched in silicon and depleted in iron.

Villafranchian deposits

The heterogeneous, iron-rich, silty matrix of the sampled Villafranchian deposits is characterised by an enrichment in fragments smaller than 100 µm of quartz, altered feldspars, and mica, similarly to what is observed in alluvial sediments of the same area. In contrast, only scarce sparry calcite fragments seem to be dispersed within the poorly fossiliferous matrix. The naturally occurring coarser fraction (<200-300µm) includes quartz, feldspars, quartzarenite, quartzite and iron-rich ferruginous clots (Figure 2). XRPD analysis of the *briquettes* confirmed a scarce presence of both clay minerals and calcite.

The sediments collected from the Pesa River Valley (FI-VERG-VILa) are weakly calcareous (CaO: 2.4wt%), although a notable carbonate contribution was reintroduced with the manual addition of the sediment coarser fraction: marly–quartz limestone, micritic limestone, and calcareous sandstone attributed to the Macigno Formation. Clay processing and analytical results indicate that these sediments are poorly suited for ceramic production due to their low clay content and the presence of marls, unless a thorough purification process is employed. In contrast, the deposits collected in the Lower Elsa River Valley (PI-MTZ-VILa) are moderately calcareous (CaO: 5.2wt%), likely due to their proximity to marine Plio-Pleistocenic deposits. Petrographic analyses also identified the presence of fine chert and quartzite, reflecting the geological context of the area.

Comparison with archeological ceramic productions

The comparison between the analytical results and recent petrographic studies of archaeological pottery reveals a close affinity between some of the clayey sediments sampled from Florence to Pisa and the fabrics of pottery excavated in the same area. Petrographic analyses of archaeological ceramics from the Florentine Vingone furnaces, as studied by De Marinis and Pallecchi (2006), demonstrate a strong correspondence with the locally sampled alluvial deposits (FI-VING-ALL). The archaeological ceramic fabrics are characterised by mono- and polycrystalline quartz, altered feldspars, iron-rich ferruginous clots, micritic limestone, and arenaceous rock fragments. Some of the fabrics reported traces of chert and pyroxene, which might be related to the close Empoli alluvial deposits (FI-TINAIA-ALL). However, the limited sampling coverage in the Middle Arno Valley may not fully capture the variability of trace mineral assemblages in the Florentine area. The typical enrichment in calcareous microfossils of Empoli amphorae (Cantini *et al.* 2014; Menchelli *et al.* 2024) is reflected not only in the local blue-grey clay sediments (FI-SAT-FAA), as expected, but also in the adjacent alluvial deposits (FI-TINAIA-ALL). Additionally, petrographic studies of Empoli red-slipped ware describe an iron-rich clay matrix with fine quartz and mica flakes, tempered with subangular quartz, feldspars, sandstone, chert, and calcareous bioclasts (Cantini *et al.* 2014). This composition finds comparison with Empoli alluvial deposits (FI-TINAIA-ALL). Ongoing petrographic analyses of the highly refined pastes of *colature rosse* wares from the San Genesio archaeological site indicate that their composition closely matches the fine fraction of the blue-grey clay sediments sampled in the Lower Elsa River Valley (PI-LEV-FAA). Within this ceramic class only one fabric differs, exhibiting a less refined paste with coarser sandstone and limestone fragments (F. Cantini, personal communication, January 15, 2026). The occurrence of limestone may represent a discriminating feature, suggesting that this ceramic could have been produced using a different raw material source, possibly related to the sampled alluvial deposits in the Lower Elsa River Valley (PI-SG-ALL).

Finally, Pisan ceramics described as iron-rich alluvial clays with fine inclusions of acidic metamorphic elements, sandstones, and shales (Menchelli *et al.* 2024) closely correspond to the composition of the sampled Pisan alluvial deposits (PI-ARGINE-ALL).

Low Serchio River Valley

Alluvial deposits

The alluvial deposits of the Serchio Valley were collected in the final stretch of the river course and include the lacustrine deposits from Lake Massaciuccoli. The sampled sediments are characterised by relatively homogeneous, silty, iron-rich, and weakly calcareous matrices. Fine fragments of quartz, plagioclase, K-feldspars, mica, and chert occur both within the matrix and as coarser inclusions (<200µm, with scarce fragments up to 400µm), together with iron-rich ferruginous clots, micaceous sandstones, quartzite, traces of schists, and micritic chert-bearing limestone. The fossil content is low

(Figure 2). From a mineralogical and geochemical perspective, the Serchio Valley sediments closely resemble those from the Arno Valley: XRPD analyses indicate an enrichment in clay minerals, muscovite, and feldspars; while PCA clusters these deposits together on the basis of elevated SiO_2, Al_2O_3, K_2O, Na_2O, Ba, and Rb concentrations (Figure 3).

Distinguishing features of the Lower Serchio Valley seem to include a reduced sedimentary contribution from the Macigno Formation, the acidic metamorphic input associated with the Pisan Mountains, and contributions from weathered, chert- and fossil-rich white limestones attributable to Maiolica-like outcrops in the Upper Serchio Valley, which also account for the enrichment in Fe and Mn oxides. The sediments collected near Lake Massaciuccoli (LU-MASSAC-ALL) are more fossiliferous and contain isolated rounded igneous fragments. This minor ophiolitic component is attributable to the Ligurian Unit outcrops in the Apuan Alps and the Garfagnana region. In contrast, the deposits sampled near Pontasserchio (PI-PONTASS-ALL) exhibit a fine fraction with a generic siliciclastic composition, without any of the distinctive markers observed in the other two Serchio Valley sediments (LU-MASSAC-ALL; PI-MIGLIAR-ALL).

Comparison with archeological ceramic productions

Petrographic and geochemical studies of ceramic workshops along the Serchio River broadly align with the characteristics of sediments sampled within this study. The spacers retrieved from the Isola di Migliarino workshop feature an alluvial clay with the addition of acidic metamorphic rocks, schists, sandstones and ophiolitic basalts as tempers (Menchelli *et al*. 2001; Menchelli *et al.* 2024; Menchelli and Vaggioli 1988). Similar metamorphic and sedimentary contributions are observed in the Lower Serchio River alluvial deposits (LU-MASSAC-ALL; PI-MIGILAR-ALL). However, the strong emphasis placed by Menchelli *et al*. (2024) on igneous inclusions as a key criterion for distinguishing Serchio from Arno Valley productions appears less evident in the sediments sampled here. Within the analysed dataset, scarce igneous fragments were identified in the fine fraction of only one sample (LU-MASSAC-ALL). In light of the limited and discontinuous occurrence of these components in the sampled sediments, the applicability of igneous inclusions as a robust discriminant marker at a regional scale should therefore be considered with caution.

Prato area

Alluvial deposits

The sediments collected from the Bisenzio River alluvial deposits in Prato (PO-OSP-ALL) are characterised by a silty-micaceous, non-calcareous matrix, with very fine-grained quartz, plagioclase and K-feldspars dispersed within the groundmass (<50μm). The coarser fraction (100-300μm, with rare instances up to 500μm) comprises mono- and polycrystalline quartz, altered feldspars, quartzarenite, siltstone, iron-rich ferruginous clots, acidic metamorphic lithoclasts, pyroxenes and rare altered gabbro (Figure 2). XRPD calcareous scarcity is confirmed by geochemical analysis (CaO, 1.01%wt). Despite the scarcity of calcareous components, the sampled alluvial sediment exhibits a robust correlation with both the Macigno and Monte Morello Formations. Specifically, the latter is evident in the coarser aplastic fraction of sub-angular altered feldspars and acidic metamorphites. The presence of ophiolitic clasts in the Monte Morello Units is responsible for the elevated Cr tenors and igneous fragments.

Varicoloured clays

The varicoloured clay sediments (PO-BAGN-AVR) are characterised by a heterogeneous, silty–clayey, non-calcareous, and iron-rich matrix. Natural fine inclusions (<100μm) of quartz, plagioclase, mica, and chert were observed, alongside iron-rich ferruginous clots containing small flakes of quartz and mica, likely derived from the weathering of Macigno rocks (Figure 2). The manual addition of the sediments coarse residue reintroduced angular fragments of micaceous sandstones, as well as traces of chert and altered gabbro (500–800μm). XRPD analyses reveal high concentrations of clay minerals and mica, while no K-feldspar or calcite patterns were observed. XRF analyses confirm a low calcium (CaO: 0.7wt%) and an enrichment in Al_2O_3, K_2O, and Rb, likely associated with muscovite and clay minerals. Furthermore, high concentrations of TiO_2, V, and Zn are detected. The Varicoloured Clays are part of the stratigraphic sequence of the Monte Morello Formation (Ligurian Units) and derive from the alteration of low to medium metamorphic grade, volcanic and sedimentary calcareous rocks. Notably, this particular clay type is distinguished by its absence of carbonate and marly components, which are commonly widespread in the area. Traces of serpentinized veins within the clay formation account for the Cr and Ni enrichments observed in the chemical analyses.

Comparison with archeological ceramic productions

The petrographic analyses of the ceramic production from the manufacturing centre of Figline di Prato primarily focus on the description of the medium- to coarse-grained temper (>2 mm). The inclusions consist of locally altered plagioclases, pyroxenes, micaceous sandstones, and iron-rich nodules (Manganelli del Fà and Vannucci, 1976). According to Manganelli del Fà and Vannucci (1978), Varicoloured Clays were suggested as raw material for cooking wares manufacture (*ollae* and *testi*), while alluvial clays were employed in the production of *catini figlinesi*. A comparison of the Figline di Prato varicoloured clay sediments sampled in this study (PO-BAGN-AVR) with the literature confirms this distinction, especially regarding the fine fraction of both sediments and archaeological ceramics. Similarly, the Prato alluvial deposits (PO-OSP-ALL) demonstrate close affinity with the fabrics of *catini figlinesi*, particularly due to the high quartz and K-feldspar content in the fine fraction. In both ceramic classes, however, raw materials appear to have been first depurated and then tempered with variable amounts of gabbroic sandy material (Manganelli del Fà and Vannucci 1978). XRPD data support this interpretation: the diffraction patterns of cooking wares are consistent with that of PO-BAGN-AVR, particularly in the absence of K-feldspar and calcite. In contrast, the XRPD results for *catini figlinesi* indicate a calcite-poor paste with higher quartz and K-feldspar contents and a lower contribution of plagioclase, in agreement with PO-OSP-ALL mineralogical composition. Notably, the plagioclase abundance reported in the archaeological ceramics is primarily attributed to the gabbroic temper rather than to the clay matrix itself.

Livorno Hills area

Alluvial deposits

The Livorno Hills alluvial deposits display a heterogeneous matrix with less than 30% sub-rounded inclusions (100-250μm), including iron-rich ferruginous clots, quartz, feldspars, micaceous sandstones, and igneous fragments (Figure 2). Gradual variations in calcareous, ferruginous, and ophiolitic components can be observed moving south along the coastal line.
In the Livorno hinterland (LI-CIST-ALL; LI-ROTA-ALL), fine fragments of quartz, plagioclase, K-feldspars, chert, rare sparry calcite, and minor pyroxene are dispersed within a silty, iron-rich matrix. The paste appearance is found to be more strongly influenced by the low abundance of Ca-rich elements (CaO: 0.5–4.8wt%) than by iron oxide concentrations (Fe_2O_3: 4.4–4.9wt%). The aplastic fraction is made of coarser subrounded feldspars, siltstones, metamorphites, altered olivines and scarce mafic fragments (<500μm). In the PCA biplot, these deposits are distinguished from the other Livorno Hills sediments due to their reduced calcareous and mafic contents (Figure 3). However, optical microscopy and XRPD reveal traces of igneous components.

In the Fine River Valley (LI-TDC-ALL; LI-PIP-ALL) highly calcareous, silty–clayey matrices contain fine quartz, plagioclases, K-feldspars, calcareous and ophiolitic fragments. Coarser inclusions of quartzite, micritic limestone, weathered olivine, rare basalts, pyroxenes, and volcanic glass are observed, collectively forming the complete ophiolitic assemblage. XRF analyses indicate slightly elevated iron oxide tenors (Fe_2O_3: 4.8-5.6wt%) and high calcium concentrations (CaO: 11.0 – 12.5wt%), the latter occurring both as dispersed within the matrix and as coarser inclusions.
Near the Cecina River estuary (LI-MAZZ-ALL; LI-CEC-ALL), calcium content decreases (CaO: 5.9–9.9wt%), whereas iron oxides continue to increase (Fe_2O_3: 5.3–6.4wt%). The silty–sandy

matrices appear iron-rich, exhibiting abundance of micas and rounded, altered olivine fragments. Chert occurs exclusively within the coastal deposits (LI-MAZZ-ALL), whereas LI-CEC-ALL contains quartzite, micritic limestone, sparry calcite, and traces of acidic metamorphic rocks. The fluvial sands that were manually added to LI-CEC-ALL are consistent with its natural inclusions. The XRPD patterns of both the Fine River Valley and Cecina River estuary alluvial sediments detected an abundance of calcite and clay minerals, along with the presence of serpentine. Geochemical data are strongly influenced by generally elevated CaO, MgO, and Sr contents, also resulting in higher loss-on-ignition (LOI) values. The enrichment in Cr, Ni, and Co is attributable to contributions from mafic and ultramafic rocks.

Livorno Hills alluvial sediments reflect the influence of Tuscan Nappe sandstones and the limestones, marls, and chalks of the Ligurian Units. The latter also contain ophiolitic veins, which are responsible for the mafic contributions. Sediments from the Livorno hinterland exhibit compositions that are intermediate between other Livorno Hills deposits and those from the Arno Valley, although with a limited calcareous contribution.

Blue-gray clays

Two blue-gray clay sediments were collected, one from the hinterland of Livorno (LI-CLS-FAA) and the other from the Fine River Valley (LI-FORNCAST-FAA). Both sediments display a homogeneous, clayey, and highly calcareous matrix containing fine fragments of quartz, calcite, pyroxene, minor feldspar and scarce mica (<50µm). Isolated sub-rounded inclusions reflect the composition of the fine fraction, with additional iron-rich ferruginous clots, micritic limestone, and quartzarenite (<100µm) (Figure 2). LI-CLS-FAA sediment is particularly fossiliferous and contains small fragments of chert and altered olivine.

In LI-FORNCAST-FAA, coarse angular igneous clasts (~1 mm) of basalt, gabbro, and serpentinite, originally occurring within the sediment, were intentionally crushed and reintroduced. XRPD analysis of the *briquettes* reveals abundant calcite and clay minerals, while serpentine phases were detected only in LI-FORNCAST-FAA. The PCA distribution is mainly influenced by elevated Ca and Sr contents (CaO: 14.0–18.8 wt%). The elemental contributions of mafic and ultramafic rocks are not particularly high in both the sediments (Figure 3). The Livorno blue-gray clays are closely linked to their geological formation, with both the fine and coarse aplastic fractions influenced by nearby ophiolitic outcrops of the Ligurian Units.

Villafranchian deposits

The VILa deposits (LI-AIA-VILa) collected from the hinterland of Livorno, appear to exhibit a mineralogical and geochemical composition quite analogous to that of the alluvial deposits from the corresponding area. The sampled sediments are characterised by a heterogeneous, silty, iron-rich and non-calcareous matrix. The natural aplastic fine fraction (<100µm) is composed of subrounded quartz, K-feldspars, plagioclase, and a scarce mafic contribution. The natural coarser fraction (<300µm) consists of quartz, feldspar, siltstone, sandstone, chert, iron-rich ferruginous clots, metamorphites and a minor mafic contribution (Figure 2). The altered feldspars, metamorphic and mafic rock fragments measuring around 500µm results from intentional reintroduction of the sediment coarse fraction. XRPD analysis confirms a scarce contribution of both calcite and clay minerals. The geochemical composition is comparable to that of alluvial sediments from the same area, although with reduced calcareous and igneous-related mineralogical assemblages. The arenaceous influence of the Tuscan Nappe is associated with an igneous contribution derived from the northern outcrops of the Ligurian Units in the Livorno Hills.

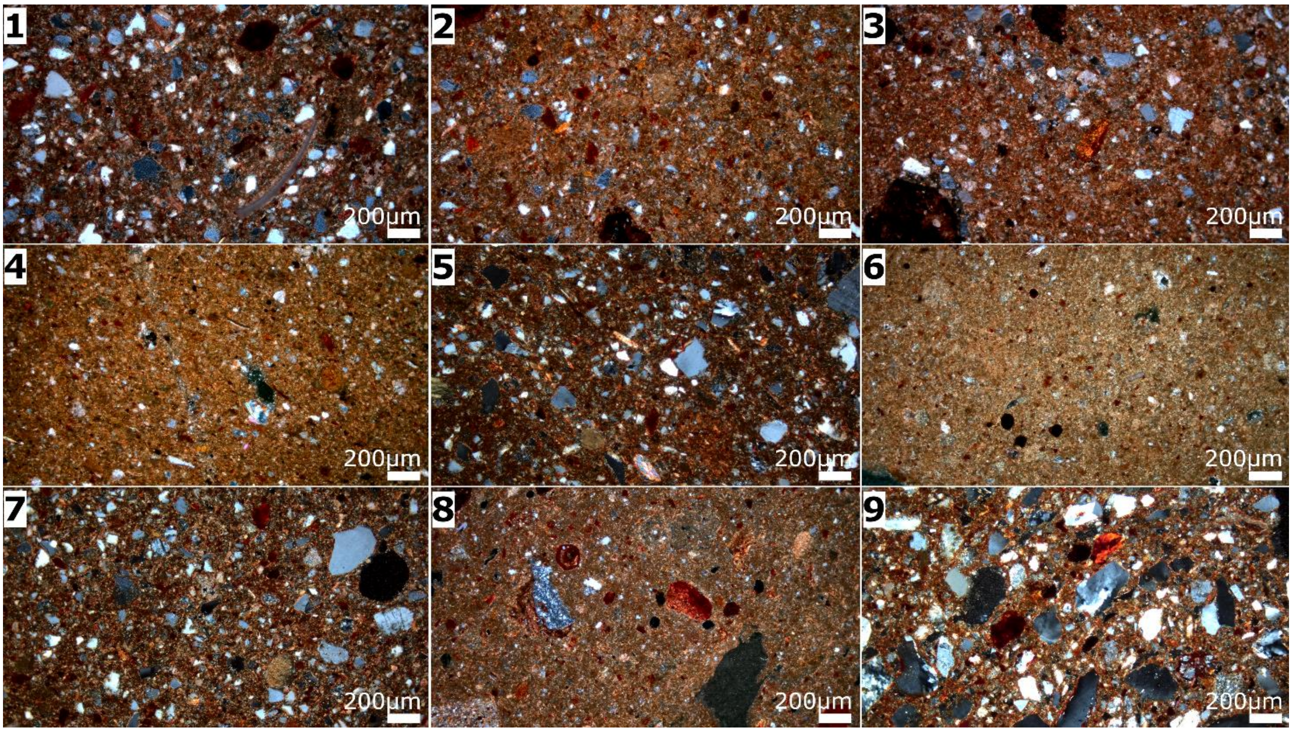


Figure 2: Photomicrographs in cross-polarized light of a selection of representative sediments. 1- Arno Valley alluvial deposits (FI-VING-ALL); 2- Arno Valley blue-gray clays (PI-CAN-FAA); 3- Arno Valley Villafranchian deposits (PI-MTZ-VILa); 4- Serchio Valley alluvial deposits (LU-MASSAC-ALL); 5- Prato alluvial deposits (PO-OSP-ALL); 6- Prato varicoloured clays (PO-BAGN-AVR); 7- Livorno Hills alluvial deposits (LI-PIP-ALL); 8- Livorno Hills blue-gray clays (LI-FORNCAST-FAA); 9- Livorno Hills Villafranchian deposits (LI-AIA-VILh).

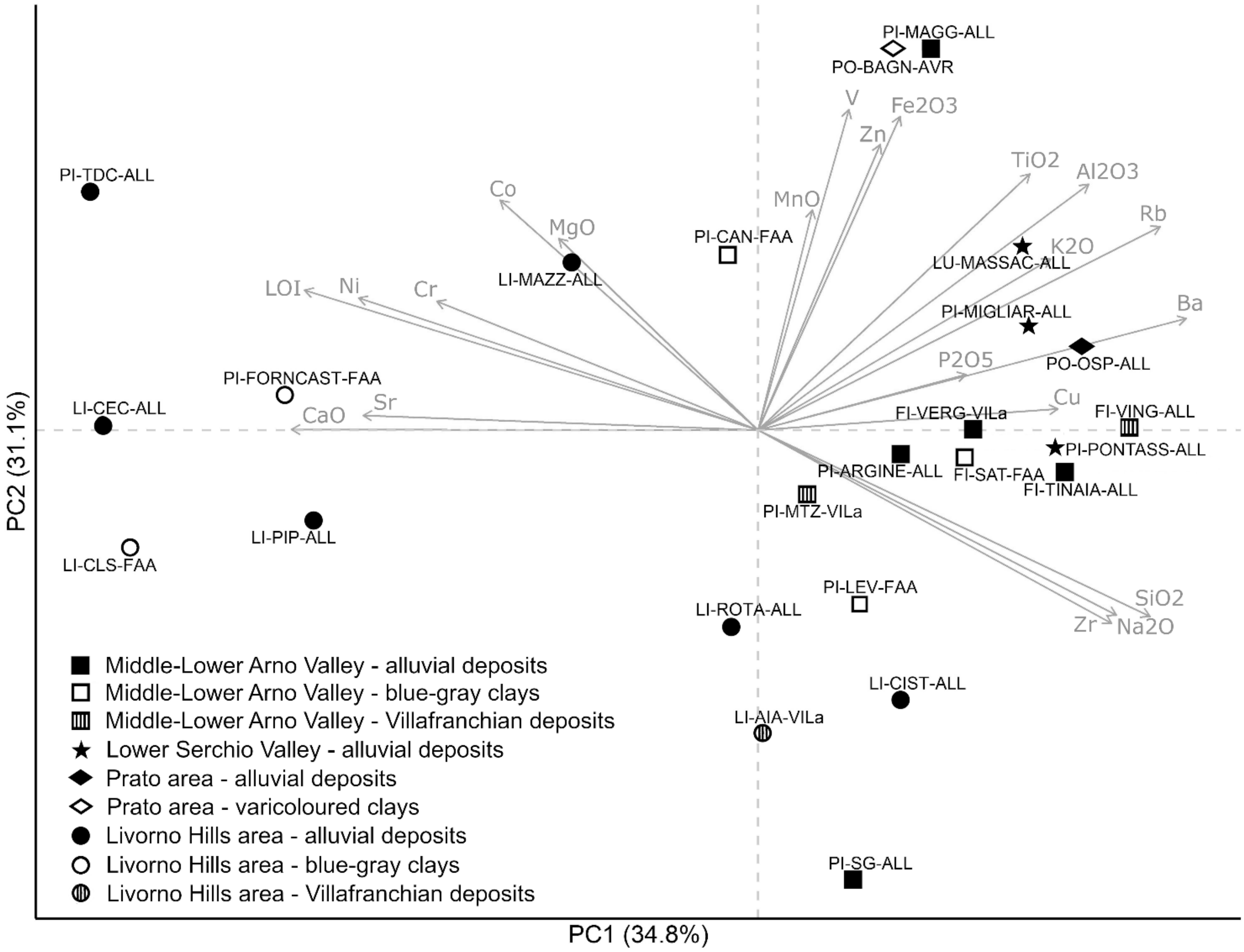
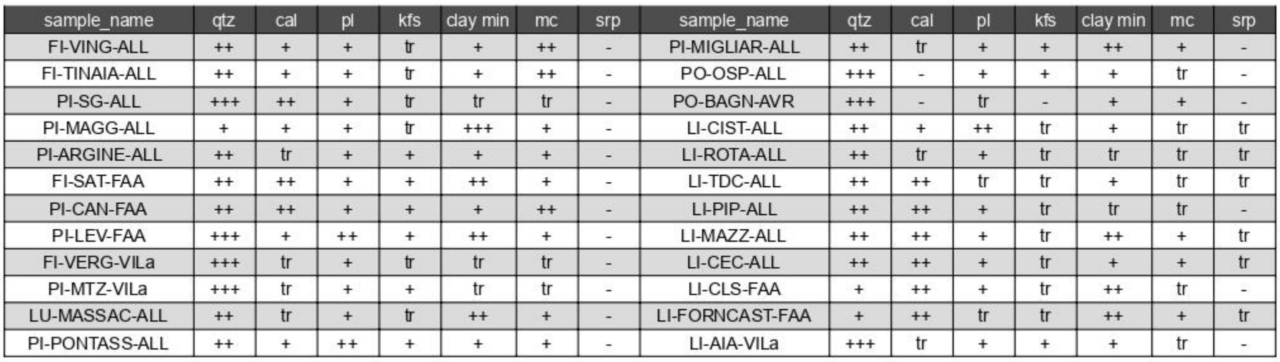


Figure 3: PCA biplot from the XRF mean results of the three sediment replicates (z-scored). The first two principal components account for 65.94% of the total variance.



sample_name	qtz	cal	pl	kfs	clay min	mc	srp	sample_name	qtz	cal	pl	kfs	clay min	mc	srp
FI-VING-ALL	++	+	+	tr	+	++	-	PI-MIGLIAR-ALL	++	tr	+	+	++	+	-
FI-TINAIA-ALL	++	+	+	tr	+	++	-	PO-OSP-ALL	+++	-	+	+	+	tr	-
PI-SG-ALL	+++	++	+	tr	tr	tr	-	PO-BAGN-AVR	+++	-	tr	-	+	+	-
PI-MAGG-ALL	+	+	+	tr	+++	+	-	LI-CIST-ALL	++	+	++	tr	+	tr	tr
PI-ARGINE-ALL	++	tr	+	+	+	+	-	LI-ROTA-ALL	++	tr	+	tr	tr	tr	tr
FI-SAT-FAA	++	++	+	+	++	+	-	LI-TDC-ALL	++	++	tr	tr	+	tr	tr
PI-CAN-FAA	++	++	+	+	+	++	-	LI-PIP-ALL	++	++	+	tr	tr	tr	-
PI-LEV-FAA	+++	+	++	+	++	+	-	LI-MAZZ-ALL	++	++	+	tr	++	+	tr
FI-VERG-VILa	+++	tr	+	tr	tr	tr	-	LI-CEC-ALL	++	++	+	tr	+	+	tr
PI-MTZ-VILa	+++	tr	+	+	tr	tr	-	LI-CLS-FAA	+	++	+	tr	++	tr	-
LU-MASSAC-ALL	++	tr	+	tr	++	+	-	LI-FORNCAST-FAA	+	++	tr	tr	++	+	tr
PI-PONTASS-ALL	++	+	++	+	+	+	-	LI-AIA-VILa	+++	tr	+	+	+	tr	-

Table 2: Bulk mineralogical composition of the sampled sediments. Mineral abbreviations: (qtz) quartz; (cal) calcite; (pl) plagioclase; (kfs) K-feldspar; (clay min) clay minerals; (mc) mica; (srp) serpentine. Semiquantitative estimates: (+++) very abundant; (++) abundant; (+) frequent; (tr) scarce.

sample_name	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI	V	Cr	Ni	Cu	Zn	Sr	Zr	Ba	Co	Rb
LOD	0,50	0,80	0,03	0,01	0,03	0,02	0,30	0,02	0,01	0,02	-	3	10	5	3	3	3	5	30	5	5
FI-VING-ALL	61,69	13,46	5,26	0,13	2,30	3,11	1,50	2,29	0,62	0,24	8,99	99	149	96	143	135	159	224	450	15	208
FI-TINAIA-ALL	61,01	13,25	5,13	0,13	2,21	3,73	1,46	2,20	0,63	0,21	9,61	98	148	94	107	109	164	226	454	12	209
PI-SG-ALL	70,51	10,17	3,07	0,07	1,15	3,77	1,68	1,81	0,46	0,13	7,02	59	112	61	67	56	171	253	330	11	167
PI-MAGG-ALL	50,38	16,87	6,60	0,14	3,22	3,63	0,53	2,53	0,80	0,13	13,70	158	209	151	56	128	182	136	469	36	257
PI-ARGINE-ALL	58,67	13,23	5,23	0,13	2,15	4,90	1,22	2,09	0,63	0,12	10,99	101	160	107	64	110	192	207	434	16	201
FI-SAT-FAA	57,37	13,29	5,42	0,09	2,30	5,14	1,09	2,36	0,61	0,16	11,43	110	151	103	143	102	176	222	343	13	215
PI-CAN-FAA	47,91	15,22	6,45	0,13	2,50	8,81	0,44	2,51	0,69	0,10	14,01	129	135	125	57	111	268	150	341	20	207
PI-LEV-FAA	60,96	12,12	4,56	0,09	1,75	5,75	1,23	2,19	0,52	0,13	10,10	87	133	89	102	95	201	210	331	12	190
FI-VERG-VILa	63,87	12,34	6,01	0,24	1,12	2,40	0,60	1,52	0,58	0,15	10,63	102	168	108	76	93	117	213	469	15	238
PI-MTZ-VILa	59,79	13,16	5,33	0,09	1,85	5,24	1,12	2,25	0,60	0,07	9,91	110	137	93	38	88	189	153	349	13	199
LU-MASSAC-ALL	56,23	15,34	6,41	0,15	3,40	3,36	1,25	2,52	0,72	0,15	9,91	126	182	119	68	110	166	164	457	19	239
PI-PONTASS-ALL	62,12	13,76	5,42	0,14	2,79	2,39	1,67	2,27	0,67	0,14	8,33	107	171	91	92	90	144	199	444	17	219
PI-MIGLIAR-ALL	57,52	14,51	5,94	0,15	3,30	3,17	1,44	2,52	0,68	0,20	10,01	115	179	111	74	102	149	167	451	16	223
PO-OSP-ALL	63,38	13,59	6,15	0,17	2,46	1,01	1,43	2,07	0,70	0,14	8,52	119	238	124	71	115	114	203	446	14	239
PO-BAGN-AVR	54,70	17,14	6,69	0,19	1,79	0,70	0,32	2,70	0,99	0,05	13,51	151	358	177	55	122	89	191	342	46	226
LI-CIST-ALL	68,64	12,93	4,85	0,03	1,36	0,52	1,50	2,03	0,61	0,00	7,29	100	188	76	27	67	115	228	345	7	164
LI-ROTA-ALL	63,52	10,63	4,45	0,12	2,18	4,84	1,10	1,69	0,58	0,08	10,19	88	252	159	44	91	166	274	336	20	176
LI-TDC-ALL	41,41	11,27	5,61	0,18	3,97	11,03	0,00	1,80	0,54	0,08	20,67	114	638	559	56	103	282	108	346	50	165
LI-PIP-ALL	49,41	9,85	4,78	0,14	1,98	12,50	0,67	1,51	0,52	0,10	16,68	88	309	232	46	94	225	155	243	26	153
LI-MAZZ-ALL	51,79	12,75	6,36	0,15	3,61	5,95	0,53	1,93	0,70	0,12	14,76	118	362	273	55	110	226	159	313	27	200
LI-CEC-ALL	49,02	9,43	5,27	0,13	5,36	9,87	0,84	1,32	0,53	0,07	16,41	90	584	391	52	93	288	138	228	35	132
LI-CLS-FAA	36,37	10,02	4,03	0,07	1,67	18,83	0,32	1,90	0,42	0,12	22,72	98	132	149	27	88	470	122	271	17	152
LI-FORNCAST-FAA	39,96	12,32	4,87	0,11	2,68	14,03	0,31	2,27	0,52	0,15	20,07	113	148	159	31	95	612	121	281	17	177
LI-AIA-VILa	73,04	10,55	4,24	0,12	1,11	1,76	1,14	1,87	0,53	0,00	5,54	79	204	118	36	64	110	206	300	19	156

Table 3: Bulk geochemical composition of the sampled sediments. Major oxides and LOI are expressed in wt%, whereas minor and trace elements are reported in ppm. Each value is the mean results for the three sediment replicas.

Comparison with archeological ceramic productions

The sediments sampled in the Livorno hinterland show a strong correlation with the local ceramic production attested in the literature. The petrographic description of the tablewares recovered from the Ca' lo Spelli workshop, particularly in terms of the Ca-rich, micaceous, and fossiliferous matrix containing quartz, feldspars, sandstone, chert, various calcareous fragments and a scarce basaltic contribution (Picchi *et al.* 2010), closely matches the composition of the Livorno hinterland blue-gray clay sediments (LI-CLS-FAA). The acidic metamorphic component described in some ceramic fabrics was not detected in the analysed sediment, supporting the hypothesis proposed in the literature that acidic metamorphites and sedimentary elements were intentionally added as temper. A comparable paste composition, though lacking the metamorphic component, was documented in the amphorae from Casa Campacci, where traces of serpentinite and basalt were reported. Furthermore, XRF analyses on Ca' lo Spelli amphorae show a clear correlation with LI-CLS-FAA, while Vallimbuio ones display lower concentrations of Ca, Sr, Cr, and Ni, similar to the sampled alluvial sediments from the Livorno hinterland (Thierrin-Michael *et al.* 2004). In contrast, the cooking wares recovered from the Ca' lo Spelli workshop display a different composition, with an iron-rich matrix and angular, coarse temper of ophiolitic, sedimentary, and metamorphic origin (Menchelli *et al.* 2007; Picchi *et al.* 2010). Direct comparison with the archaeological ceramic paste and the sampled iron-rich alluvial deposits from the Livorno hinterland (LI-CIST-ALL, LI-ROTA-ALL) remains limited, due to the limited petrographic descriptions of matrix and fine fraction characteristics available in the literature.

A clear correlation also emerges between the ceramics produced at the Poggio Fiori manufacturing centre (Menchelli *et al.* 2001) and the sampled blue-gray clays of the Fine River Valley (LI-FORNCAST-FAA). There is a strong correspondence in the calcareous matrix, the fine fossiliferous fraction containing small pyroxenes, and the coarser fraction composed of both sedimentary elements (limestone and sandstone) and the complete ophiolitic assemblage (serpentinite, gabbro, and basalt). The similarity in the coarse fractions suggests that archaeological ceramics were made with tempering materials naturally present as coarser components within the clay source itself. XRF analyses of Poggio Fiori amphorae confirm the use of a blue-grey clay comparable to LI-FORNCAST-FAA, particularly in Ni, Cr, and Sr concentrations (Thierrin-Michael *et al.* 2004). Cherubini and Del Rio (1995) also reported the use of iron-rich alluvial clays at Poggio Fiori, containing mica, quartz, serpentine, gabbro, and sedimentary rocks. However, only low abundances of mica and iron oxides were observed in the Fine River Valley alluvial deposits (LI-PIP-ALL; LI-TDC-ALL), although the latter exhibit a more consistent ophiolitic contribution.

Regarding the Cecina River area, a clear correspondence is observed between the iron-rich matrices of the sampled alluvial deposits (LI-MAZZ-ALL) and the kiln waste materials described by Cherubini and Del Rio (1995) and Menchelli *et al.* (2007). Both archaeological remains and sampled sediments show an aplastic fraction composed of calcareous fragments (limestone and minor sandstone), quartz, chert, and ophiolitic-related lithologies, with variable proportions and grain sizes. This evidence suggests the exploitation of alluvial deposits, possibly accompanied by variable tempering with ophiolitic material sourced from the nearby Livorno Hills. XRF analyses of amphorae manufactured in the La Mazzanta furnace demonstrate a strong geochemical correspondence with the Cecina River alluvial deposits (LI-MAZZ-ALL), particularly in trace elements such as Cr, Ni, Cu, Zn, Zr, Ba, Rb, and Y. Conversely, Sr and CaO concentrations are slightly lower in the geological sediments (Thierrin-Michael *et al.* 2004).

Conclusions

This study provides the first systematic and regionally integrated characterisation of clayey raw materials exploited for ceramic production in north-western Tuscany, establishing a geologically grounded reference framework for provenance studies. A baseline set of compositional markers was defined through the combined application of petrographic, mineralogical, and geochemical analyses to minimally processed clay sediments sampled near documented production centres, spanning from the Roman period to the Late Middle Ages. Placing these markers in dialogue with ceramic fabrics described in the literature, this study supports the existence of coherent provenance domains and allows a more refined distinction between manufacturing areas operating within the analysed contexts.

The integration of petrographic, mineralogical and geochemical data highlighted the existence of a hierarchical structure within the analytical framework. Petrography plays a central role, as it allows the identification of matrix texture as well as fine and coarse grained markers that directly reflect the local geological setting. When combined with diffraction analyses, these features can be linked to specific lithologies and depositional environments. XRPD analysis proved useful for detecting - when present - igneous contribute, and for confirming the presence/absence of discriminant phases (e.g., K-feldspars in Prato area). However, when used alone, it lacks sufficient discriminatory power to reliably distinguish between different clay sources. Conversely, geochemical data proved highly effective in differentiating macro-areas as well as specific clay types. Chemical signatures provide a robust tool for regional-scale investigations and offer an independent means of testing provenance hypotheses developed through petrographic observations.

However, when dealing with archaeological ceramics, clay refining and tempering practices may result in the partial modification of the original compositional signal. Refinement processes can remove or reduce diagnostic coarse components, thereby complicating provenance assessment. For this reason, particular attention in petrographic studies should be devoted to the fine fraction, which is more likely to survive refining processes and thus remains diagnostically relevant, particularly in highly purified wares.

By reviewing the main results, the main minero-petrographic differences between the alluvial clayey sediments of the Arno and Serchio Valleys are largely confined to the coarse fraction (>100μm). As a result, ceramic pastes derived from these sources may appear similar when extensively purified or levigated. Nonetheless, a distinctly calcareous and fossiliferous matrix may indicate an Empoli source, while lower carbonate content associated with a micaceous matrix and acidic metamorphic fragments may suggest a Pisan provenance. The Lower Arno Valley blue-grey clays are distinguished from alluvial deposits by a higher proportion of altered feldspars in the fine fraction, together with a generally calcareous and fossiliferous matrix.

In the Prato area, differences in aplastic composition are indicative of the nature of the sampled clay sources. The alluvial deposits display an iron-rich, micaceous, non-calcareous matrix with fine plagioclase, K-feldspar, and pyroxene. The varicoloured clay sediments exhibit a similar matrix but contain chert and pyroxene fragments and lack K-feldspar. These distinctions in the fine fraction indicate that, even after clay preparation, the two raw materials in question retain distinct mineralogical signatures.

The sediments of the Livorno Hills area are easily distinguishable from those of the Arno and Serchio

Valleys on account of their calcareous enrichment and a consistent ophiolitic contribution. These features, present in both the fine and coarse fractions, appear only minimally affected by refining processes and therefore serve as robust provenance markers. In the Livorno hinterland, the alluvial and Villafranchian deposits are moderately ferruginous and poorly calcareous, with pyroxene in fine fraction. In the alluvial deposits of the Fine River Valley, the iron-rich and highly calcareous matrix exhibits fragments of the full ophiolitic assemblage. In the Cecina River estuary, the alluvial deposits are moderately calcareous and iron-rich, with limited ophiolitic input. The degree of igneous contribution is distinctive among the blue-grey clays of the Livorno Hills, being more pronounced in the Fine River Valley than in the Livorno hinterland. This compositional gradient reflects changes in sediment supply and depositional conditions, allowing differentiation among distinct source areas within the Livorno sector.

Although petrographic analysis is fundamental to the assessment of provenance, it is not sufficient on its own for a comprehensive evaluation. The limitations of this technique can be mitigated through the implementation of XRF trace element analysis. Bulk geochemical data, while potentially influenced by refinement-related fractionation, remain reliable for evaluating compositional coherence and constraining provenance at a regional scale. This was demonstrated by the strong geochemical correspondence between archaeological ceramics from the Livorno area, subjected to varying degrees of purification, and the minimally refined sediments collected from the same region.

Future perspectives

The reference dataset presented here is currently being expanded through new sampling campaigns aimed at collecting additional clayey sediments, particularly in areas where some discrepancies have emerged between raw material compositions and archaeological ceramics reported in the literature (e.g. Serchio Valley; Lower Elsa Valley). At the same time, sampling processes will be extended also to those areas that are currently underrepresented in the dataset (e.g. Middle Arno Valley), in order to increase the number of reference collections and improve regional coverage. All geological, technological, and analytical data generated in this study are being organized within a relational database designed for long-term preservation and for comparative, provenance-oriented analyses of ceramic raw materials. Upon completion, the full dataset will be deposited in the MOD – Mappa Open Data Repository, the FAIR-compliant institutional repository for archaeological open research data at the University of Pisa (Anichini *et al.* 2013). The dataset is being organized into three interconnected levels: raw materials (sampling metadata), *briquettes* (clay processing choices and firing outcomes), and analytical results (OM, XRF, XRPD), all linked through unique identifiers to ensure complete traceability. In this way, the database functions as a dynamic reference framework for investigating proximity-based exploitation of geo-resources, technological choices in ceramic production, and the persistence of mineralogical and geochemical signals across different stages of the production sequence.

Acknowledgements

The authors would like to acknowledge Dr. Claudia Sciuto (Univ. of Pisa) for the assistance in the execution of sampling campaigns.

Author contributions

Irene Strufaldi, Sara Longo and Simona Raneri jointly conceived the study and defined its objectives. Irene Strufaldi was responsible for the archaeological and archaeometric background of the research and wrote the section *Minero-petrographic markers in Roman and Medieval ceramics: state of the art*.

Sara Longo was responsible for the geological, methodological and analytical components of the study and wrote the methodological sections of the manuscript.

Sara Longo and Irene Strufaldi collaborated on data interpretation and the writing of the *Results and discussion*.

Simona Raneri supervised the research, contributed to the interpretation of the analytical data, and critically revised the manuscript.

All authors approved the final version of the manuscript.

Bibliography

Anichini, F., Gattiglia, G., Gualandi, M. and Noti, V. 2013. MOD (MAPPA Open Data). Conservare, disseminare, collaborare: un archivio open data per l'archeologia italiana. In M. Serlorenzi (ed.) *ARCHEOFOSS: Free, Libre and Open Source Software e Open Format nei processi di ricerca archeologica. Atti del VII Workshop (Roma, 11–13 giugno 2012). Archeologia e Calcolatori*, Supplemento 4: 45–52.

Barone, G., Mazzoleni, P., Spagnolo, G. V. and Raneri, S. 2019. Artificial neural network for the provenance study of archaeological ceramics using clay sediment database. *Journal of Cultural Heritage* 38: 147-157. https://doi.org/10.1016/j.culher.2019.02.004.

Boldrini, E., Grassi, F. and Castillo, J. Q. 1999. Un contributo allo studio dell'introduzione di nuove tecniche ceramiche nella Toscana del medioevo: la ceramica foggiata a matrice. *Archeologia Medievale* XXVI: 395-409.

Cantini, F., Boschian, G., Gabriele, M. 2014. Empoli, a Late Antiquity pottery production centre in the Arno Valley (Florence, Tuscany, Italy). In N. Poulou-Papadimitriou, E. Nodarou, V. Kilikoglou (ed.) *LRCW 4 Late Roman Coarse Wares, Cooking Wares and Amphorae in the Mediterranean. Archaeology and archaeometry. The Mediterranean: a market without frontiers*: 203-212. Oxford: Archaeopress.

Cherubini, L., Del Rio, A. 1995. Le produzioni ceramiche delle basse valli del Fine e del Cecina, in G. Olcese (ed.) *Ceramica romana e archeometria: lo stato degli studi:* 217-223. Sesto Fiorentino: All'insegna del giglio.

Conti, P., Cornamusini, G., and Carmignani, L. 2020. An outline of the geology of the Northern Apennines (Italy), with geological map at 1:250,000 scale. *Italian Journal of Geosciences* 139(2): 149-194. https://doi.org/10.3301/IJG.2019.25.

De Bonis, A., Grifa, C., Cultrone, G., De Vita, P., Langella, A., and Morra, V. 2013. Raw materials for archaeological pottery from the Campania region of Italy: a petrophysical characterization. *Geoarchaeology* 28(5): 478-503. https://doi.org/10.1002/gea.21450.

De Marinis, G. and Pallecchi, P. 2006. *Caratterizzazione composizionale e tecnologica della produzione ceramica delle fornaci del Vingone*, in Shepherd, E. J., Capecchi, G., De Marinis, G., Mosca, F. and Patera, A. (eds.) 2006. *Le fornaci del Vingone a Scandicci. Un impianto produttivo di età romana nella valle dell'Arno*: 241- 243. Firenze: All'insegna del Giglio.

Eramo, G. 2020. Ceramic technology: how to recognize clay processing. *Archaeological and Anthropological Sciences* 12(8): 164-188. https://doi.org/10.1007/s12520-020-01132-z.

Falorni, P. 2007. Macigno, viewed 15 December 2025, https://www.isprambiente.gov.it/files/pubblicazioni/periodicitecnici/quaderni-sgi/quaderno7fasc7.

Gliozzo, E., Iacoviello, F., Foresi, L.M. 2014. Geosources for ceramic production: The clays from the Neogene–Quaternary Albegna Basin (southern Tuscany). *Applied clay science* 91: 105-116. https://doi.org/10.1016/j.clay.2014.01.012.

Hein, A. and Kilikoglou, V. 2020. Ceramic raw materials: how to recognize them and locate the supply basins. Chemistry. *Archaeological and Anthropological Sciences* 12: 180. https://doi.org/10.1007/s12520-020-01129-8.

Manganelli Del Fà, C., Vannucci, A. 1976. Studio mineralogico delle ceramiche di S. Salvatore a Vaiano e considerazioni sulle materie prime utilizzate. *Archeologia Medievale* 3: 139-165.

Manganelli Del Fà, C., Vannucci, A. 1978. Le caratteristiche petrografiche e tecnologiche della produzione ceramica pratese, in R. Francovich, S. Gelichi, D. Melloni and G. Vannini (eds.) *I saggi archeologici nel Palazzo Pretorio di Prato*: 297-322, Firenze.

Maritan, L., Filippou, V., Renson, V., Pasqual, D., Cattò, S., Koutovaki, E., Nodarou, E., Cantisani, E., Dikomitou, Eliadou M. and Zomeni, Z. 2024. Influence of clay processing on bulk chemistry signature in ancient pottery productions, in Congresso SGI-SIMP (Bari, 2-5 september 2024), Abstract Book: 212. https://www.socgeol.it/files/download/pubblicazioni/Abstract%20Book/Abstract%20Congresso%20SGI-SIMP%202024-4.pdf

Menchelli, S., Vaggioli, M. A. 1988. Ricerche archeologico-topografiche nell’ager “pisanus” settentrionale: il sito costiero di Isola di Migliarino. *Studi Classici e Orientali* 37: 495–520.

Menchelli, S., Capelli, C., Del Rio, A., Pasquinucci, M., Thirion-Merle, V. and Picon, M. 2001. Ateliers de céramiques sigillées de l’Étrurie septentrionale maritime: données archéologiques et archéométriques. *Rei Cretariae Romanae Fautorum Acta* 37: 89–105.

Menchelli, S., Cabella, R., Capelli, C., Pasquinucci, M., and Picchi, G. 2007. Anfore dell'Etruria Settentrionale costiera in età Romana: nuovi dati alla luce delle recenti indagini archeologiche ed archeometriche, in *Le fornaci e le anfore di Albinia. Primi dati su produzioni e scambi dalla costa tirrenica al mondo gallico* 1: 141-150. Officine Grafiche Litosei.

Menchelli, S., Baronti, T., Sangriso, P. 2020. Gli scavi in via Galluppi, in F. Cantini, F. Fabiani, M. L. Gualandi, C. Rizzitelli (eds.) *Le case di Pisa. Edilizia privata tra Età romana e Medioevo*: 57-64. Firenze: All’insegna del giglio.

Menchelli, S., Starnini, E., Cabella, R., Capelli, C., Piazza, M. 2024. Ceramic production and raw materials in the Tuscan-ligurian region: an archaeological and petrographic approach in a diachronic perspective. *ArcheoLogica Data* IV.2: 25-46.

Montana, G., Ontiveros, M.Á.C., Polito, A.M., Azzaro, E. 2011. Characterisation of clayey raw materials for ceramic manufacture in ancient Sicily. *Applied Clay Science*, 53(3): 476-488. https://doi.org/10.1016/j.clay.2010.09.005.

Montana, G. 2020. Ceramic raw materials: how to recognize them and locate the supply basins - mineralogy, petrography. *Archaeological and Anthropological Sciences* 12(8): 175-194. https://doi.org/10.1007/s12520-020-01130-1.

Picchi, G., Cabella, R., Capelli, C., Ducci, S., Menchelli, S., Pasquinucci, M. and Piazza, M. 2010. Attività manifatturiere nel retroterra di Portus Pisanus. *Rei Cretarieae Romanae Fautorum Acta* 41: 291-302. https://doi.org/10.32028/rcrf-acta-41-pp.291-302.

Principe, C., Goguitchaichvili, A., Devidze, M., La Felice, S., Cejudo, R., Morales, J. and Cantini, F. 2022. Archaeomagnetic Dating of Three Furnaces inside the Middle Age Settlement of San Genesio (San Miniato, Pisa, Italy). *Land* 11: 19-36. https://doi.org/10.3390/land11111936.

Quinn, P. S. 2022. *Thin section petrography, geochemistry & scanning electron microscopy of archaeological ceramics.* Oxford: Archaeopress.

Thierrin-Michael, G., Cherubini, L., del Rio, A., Menchelli, S. and Pasquinucci, M. 2004. Les amphores de l’Ager Pisanus et Volaterranus: productions et distribution vers le Nord à la lumière des analyses. *Actes Du Congrès de Vallauris, 20-23 mai 2004*: 237–245.

Weigand, P. C., Harbottle, G. and Sayre, E. V. 1977. Turquoise sources and source analysis: Mesoamerica and southwestern U.S.A., in T. K. Earle and J. E. Ericson (ed.) *Exchange systems in prehistory studies in Archaeology*: 15-34. New York: Academic Press