

Analytical Methods

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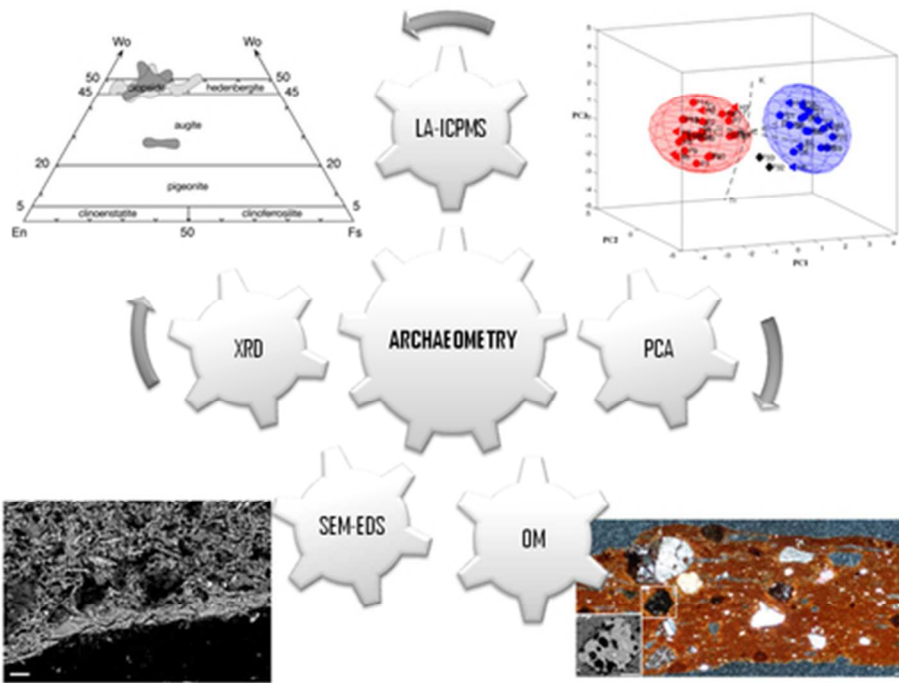


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Methodology of a combined approach: analytical techniques to identify technology and raw materials of thin walled pottery from Herculaneum and Pompeii

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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This study focuses on defining compositional and structural characteristics, identifying raw materials and production technology, and validating the archaeological hypothesis of a local production of thin-walled pottery (2nd cent. BC - 3th cent. AD) in the Vesuvian area. Samples investigated were analysed using OM, SEM-EDS, XRD and LA-ICPMS supported by a statistical multivariate treatment of the compositional data of the ceramic bodies. The results obtained show how an integrated approach of analytical techniques can provide replies to archaeological questions and also give a valuable insight into the exchange of raw materials and/or finished products between sites. The paper also discloses how a combined analytical methodology represents a positive step in answering the one question which remains unsolved concerning the entire ceramic production in the Vesuvian area: the provenance of the clayey raw materials used. Indeed, the massive pottery production in the Bay of Naples down the ages contrasts with the unavailability of the necessary clayey local resources.

Introduction

The scientific approach was previously considered to be of secondary importance in the study the ancient world. However, the adoption of this strategy can shed new light on our studies, leading us to reconsider earlier assumptions which were often grounded on weak evidence. Adopting a scientific approach also makes it possible to optimize restoration and conservation. The best methodological line of attack provides, as well as integrating morphological-stylistic and archaeometric research, an analytical instrumental synergy able to exploit the different techniques to the best of their key strengths and to overcome the limits relative to the preciousness and uniqueness of samples investigated.

A systematic archaeometric characterization enables us to provide compositional and structural information of bulk and surfaces (composition, microstructure, microstructural profile at various depths, different phases, inclusions and segregations), to recognize the manufacturing processes used in the production of ancient objects and to identify their differences and ateliers.

This is indispensable if we are to develop an accurate mapping of the circulation of these artefacts and their centres of production and attempt to provide an answer to the wider question concerning where the raw materials came from. Even if similar information can only be obtained through an integrated approach of analytical techniques, this kind of strategy has rarely been adopted in archaeometric studies.

Concerning the ceramic finds, the identification of the geographical sources of the raw materials used in production, supplies information about the objects' provenance,^{1,2} trade routes used and economic exchanges.

However, to trace the location of the clayey raw materials employed, it is necessary to take into account the complexity of the manufacturing process used (possible mixing of clays with different mineralogical and chemical characteristics, intentional addition of tempers of various types and origins (grog, sand, etc...), the inevitable changes in the minero-petrographic composition of the final paste, due to the whole process (firing, painting, glazing, etc...).

The average elemental composition of pastes is essential in order to determine the origin of the raw materials used. Unfortunately, even considering the simplest manufacturing process, which uses mere untreated clay, when pelitic sedimentary deposits are involved, the average elemental composition can show the same value for different mix. For example, a poor in clay and rich in coarse silt-sand deposit and a much more clayey and less rich in coarse silt-sand deposit could show the same average chemical composition, since they are formed by the same minerals in the same ratio. However, the fabric is completely different and the final paste will also show technological features which are entirely different.

There is also the question of accessory minerals, often indicators of different clayey sedimentary basins. Their presence, because of the limited amount, does not influence the average chemical composition, but their identification and

accurate composition allow us to recognize or to exclude the use of a given sedimentary deposit.

Only a synergy of all these results, obtained using different analytical techniques, will make it possible to assess the exact provenance of the raw materials used.

Indeed, the determination of the mineralogical composition of pastes from archaeological samples is also crucial in order to answer technological issues, such as the production processes of antique ceramics or changes in manufacturing techniques. In this respect, maximum heating temperature, duration of firing and kiln atmosphere are important factors which help in understanding the relevant transformations.

In this case, some phases of neo-formation, related to cooking temperatures, identifiable only with particular analytical techniques (because of their small quantity and their size often below the micrometer) play an important role.

The same reasons support the use of multi-techniques analyses for the coatings' characterization.

The most widespread techniques employed in the elemental analysis of ceramic bodies are Neutron Activation Analysis (NAA), X-ray Fluorescence Spectroscopy (XRF) and Inductively Coupled Plasma Mass Spectrometry (ICPMS), with the latter being the most popular thanks to its excellent detection limit for the entire periodic table and to the great availability of instrumentation.³⁻⁶

ICPMS, however, requires the breaking of a small part of the vessel down into its composing elements, often with a mixture of hydrofluoric, nitric and hydrochloric acids, and measuring the abundance of a selection of the composing elements by mass spectrometry.⁷ It is hyphenated to different instrumental facilities, and of them all, Laser Ablation (LA) appears to be the most successful.⁸⁻¹⁰ LA-ICPMS offers a great sampling alternative for solids: despite having a lower sensitivity compared to wet ICPMS, the key features are its simple and straightforward experimental implementation, speed of analysis, its almost non-destructive nature (some nanograms of material are ablated with each laser pulse) as well as the absence of sample preparation. In recent years these characteristics have attracted the interest of many scientists including archaeologists, art historians and conservators. As the fabric of pottery is a heterogeneous mix of clay, mineral inclusions and fillers, the chemical composition data obtained by using LA-ICPMS greatly depend on the sampling location. Nevertheless, this criticism can be overcome if numerous multiple samples (lines or points) of the same object are analyzed and appropriately averaged.

The prevalent techniques for the technological study of ceramics are: polarized-light Optical Microscopy (OM), Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometry (EDS) and X-ray Powder Diffraction (XRD).

OM provides information on the structure and texture of the ceramic body, with a particular contribution coming from non-plastic inclusions components: information about the outcrop supplies can be revealed by the presence of specific minerals or lithic fragments such as the rounded wind quartz grains from sedimentary rocks (i.e. the numidian flysch in Southern Italy), or the strongly stressed quartz from metamorphites, or the embayed quartz phenocrysts from acid volcanites, or the porphyric fragment of a volcanic groundmass, etc.

SEM is a powerful technique for characterizing archaeological materials. The possibility to obtain images by analysis of secondary and backscattered electrons and to achieve microanalysis when the microscope is coupled with EDS and WDS devices is extremely valuable for a morphological-

structural investigation, to evaluate the conservation state, to identify the mineralogical accessory phases present in the ceramic body, the sintering grade, the structure and thickness of coatings (glazes and engobes). XRD gives information on the mineralogical phases - in particular the neo-formation phases (only recognizable using this method), formed during the firing process and therefore on the firing process (temperatures reached and firing time).

Our research is devoted to the characterization of a fine tableware class -thin walled pottery- recovered from Pompeii and Herculaneum (Fig. 1), and hypothesized, on the basis of archaeological studies, as being of local production. We aimed, therefore, to identify the technological production and assess the provenance of pottery and raw materials.



Fig. 1 Image of some samples analysed. Scale bar =3 cm.

The case of ceramics from Pompeii and Herculaneum, characterized by a rich documentary basis but also by limited archaeometric data,¹¹⁻¹² is particularly intriguing in provenance study.

Indeed, thanks to the position of both sites at the foot of Vesuvius and to the geological characteristics of the surrounding area, useful answers concerning provenance can be obtained by petrographic, mineralogical and chemical analyses of non-plastic materials in their bodies especially, because of compositional markers such as volcanic products and/or the diffusion of deposits. Indeed, in some works,¹³⁻²⁰ the connection in minero-petrographic composition between some pottery typologies and their respective volcanic production areas are reported.

Nevertheless, the correlation between a common volcanic temper and a precise production area can be considered as ambiguous in sources such as Somma-Vesuvius, Campi Flegrei and Ischia where there are common characteristics in composition and outcrops. Moreover, excluding the volcanic non-plastic fraction, the provenance of the clayey raw materials required to supply the massive pottery production of the entire ceramic production in the Bay of Naples down the ages is unclear considering the unavailability of these resources in the area.

Archaeological framework

"Thin-walled pottery" refers to a class of fine tableware used to contain or pour liquids, characterized by the extreme thinness of the walls -0.5-4 mm-. They were essentially drinking vases, e.g. drinking pots, glasses, jugs, cups, goblets, small urns and very rarely featured closed shapes.²¹⁻²⁹ For a long time confused with productions of common use, thin-walled pottery is now recognized as one of the most important chronological indicators of the Imperial

age, from Augustus to the Flavian Dynasty.³⁰⁻³²

A peculiarity of this production was the attempt to imitate metal prototypes, not only in shapes and decorations but also in the hardness of the body and the thinness of the wall.³²

The most frequent motifs were: rows of dots, oblique spines arranged in a random fashion on the ceramic body, twisted elements, pearls, festoons, pine cone slivers, lunettes, running animals, ferns, plant shoots and waterleaves, while rarer motifs were made with stamp decorations.²⁹ Surfaces were decorated using wheel throwing, hand-engraving, sandblasting (sand was sprayed onto the pot while still fresh, both outside and inside. The excess sand could then be removed with a brush.). The Barbotine technique was also used, although to a lesser extent. This ceramic class appeared in Italy during the 2nd cent. BC, in an area between northern Lazio and southern Tuscany^{26,29,32} and its diffusion persisted in the Mediterranean area until the 3rd cent. AD.²⁶ Shapes and decorative motifs remained unvaried until the middle of the 1st cent. BC. From this period up to the Augustan age, the homogeneity of manufacture ended: different production centers which were both distant and independent of each other appeared around Italy, only few of which (where the furnaces were found) can be located with certainty.

Important centers have been identified in Siracusa (Sicily),^{26,32} in Chiusi and Sutri (Central Italy),²⁷ in La Celsa (Rome)²⁸ and in Aquileia (Po Valley).²⁷ From the Augustan age, a profound change in the characteristics of the specimens took place: cups and goblets were preferred and for the first time the outer and inner walls of the vessels were coated. At the beginning of the 1st cent. AD, the production scenario was no longer exclusively italic: workshops appeared in the provinces, especially in Gaul and the Iberian Peninsula where, in addition to imitating the Italic imported products, they began to manufacture original items.^{26,32} From the second half of the 1st cent. AD production in Italy appears to be completely standardized, with two or three basic forms which revealed an extremely simple decoration. Rather poor products were made, generally without a coating, or a polishing of the surfaces. The crisis of this production was probably due to the increasingly massive use of metal and glass, materials considered to be more practical as liquid containers, as they preserved the organoleptic characteristics of wines.³³

The first systematic archaeological study concerning the thin-walled ceramic of Vesuvius area was carried out by A. Carandini,²⁵ who considered items stored in Pompeii (Museum storage and Antiquarium) and Naples (National Archaeological Museum). He provided data and ideas which were then expanded on, discussed and organized by A. Ricci, who proposed a summary framework of this ceramic class (see the different typologies in the samples' description, Table A supplementary data).²⁷

The idea which we embraced was the presence of a massive and highly standardized production, with a particular concentration of certain shapes and decorations, which led the two scholars to believe that the Vesuvian area was a manufacturing center.

Traditionally, the hypothesis of a production center, in the absence of reliable indicators of production, is based on concentrations and homogeneity of the material found in different sites and a comparison with other classes of materials. Concerning thin-walled ceramic, productive indicators have rarely been found and archaeometrical investigations are sporadic. A production center in the Campanian area, and more specifically in the area around Vesuvius, of thin-walled ceramic has been hypothesized by many scholars,^{25,27,32} but reconsidered by others.³⁴ The only indication currently available to delimit the chronology of this production is the presence of these materials in Vesuvian contexts. Ricci,^{27,34} according to the characteristics of the findings in the

Campanian area, suggested three groups of pastes, with well-defined characteristics. However, recent investigations carried out in Herculaneum, showed a greater number of groups, which nevertheless do not include all the thin walled pottery findings.³⁵ The archaeological question is whether to confirm or reject, on the basis of unambiguous elements, the hypothesis of a Vesuvian manufacturing center of thin-walled pottery and, most of all, to identify possible differences between objects that could help distinguish between the different production processes and workshops.

Experimental

Samples

A collection of 48 samples of thin-walled pottery including the most representative shapes and decorations and coming from Casa di Bacco in Pompeii and from the archaeological storage of the Soprintendenza of Herculaneum, was analysed (Table A in supplementary data). The preservation state of the material restricted the sampling: it was primarily safeguarded the integrity of the artworks and their fragility. Moreover, considering the archaeological significance and value of the items, the sampling was performed by taking small flakes, along the border of the fragments, minimizing the visible impact (unfortunately, this condition imposed some limits on the type of selection for analysis owing to the small amount of samples available for investigation).

Techniques

The objects were examined by several complementary techniques: OM, SEM-EDS, XRD and LA-ICPMS.

Orthoscopic observations of the mineralogical textures were performed by means of optical microscope Axioscop 40 (Carl Zeiss) on polished thin sections; SEM investigations were carried out on the same thin sections, after graphite sputter-coating (30-nm thick) of the samples, using an EVO- 50XVP (LEO) system equipped with an Energy Dispersive X-Ray Spectrometer. Microanalyses were carried out with an Oxford-Link Ge ISIS Energy Dispersive Spectrometer equipped with a Super Atmosphere Thin Window. Quantitative results were obtained using the following operating conditions: 15 kV accelerating potential, 1nA probe current, about 2500 cps as average count rate on the whole spectrum and counting time 100 s. X-ray intensities were converted to wt% oxides by Z AF4/FLS quantitative analyses software support of Oxford-Link Analytical (UK). Analytical precision was 0.5% for concentrations > 15 wt%, 1% for concentrations of about 5 wt%, and < 20% for concentrations near the detection limit; the detection limit depends on the considered element, in any case never below 1000 ppm. Given the composition analyzed, the 1 σ precision corresponded to the following values: SiO₂ = 0.17-0.28 wt%; TiO₂ = 0.08-0.11 wt%; Al₂O₃ = 0.08-0.14 wt%; FeO = 0.05-0.21 wt%; MnO = 0.04-0.6 wt%; MgO = 0.08-0.15 wt%; CaO = 0.04-0.20 wt%; K₂O = 0.04-0.12 wt%; Na₂O = 0.04-0.06 wt%. Standards used for element calibrations are reported in Table Ba (in supplementary data). Furthermore, the accuracy of the analytical data was also checked using several standard minerals manufactured by Micro-Analysis Consultants Ltd. (U.K.) (Table Bb in supplementary data).

XRD analyses were performed with a Philips X'Pert Pro X-ray diffractometer in the following conditions: graphite-monocromated CuK α 1 radiation, X-ray tube power supply 40 kV and 40 mA,

divergence slit 1°, antiscatter slit 1/2°, programmable slit 0,2 mm, step size 0,02°2 θ , time for step 1 s, range 2-65°2 θ . In the semi-quantitative estimate of the results, it should be stressed that the small amount of sample available for X-ray diffraction analysis cannot be sufficiently representative for samples characterized by the presence of large crystals, not homogeneously distributed in the bulk ceramic.

LA-ICPMS (Thermo Electron X7 equipped with a Nd:YAG laser New Wave Research UP213AI 213 nm aperture imaged accessory) analyses were performed to investigate the elemental chemical composition of both the clayey matrices and clasts of the ceramic bodies.

As mentioned previously, when the material is homogenous, LA-ICPMS analysis does not need sample preparation, otherwise a procedure of homogenization is required, when the material is heterogeneous, to achieve accurate and reproducible results.

The samples investigated -showing a non-homogeneity by SEM-EDS analyses- required a particular care in LA-ICPMS experiments' scheme.

We handled the very reduced amount of sample available performing the examination on the polished cross-sections under microscope observation. The analyses of the matrix of the ceramic bodies were performed on lines -no less than 40 microns wide and 400 microns long- excluding volcanic minerals and rock fragments larger than 20 microns, and were replicated up to nine times.

The ICPMS was optimized for dry plasma conditions prior to each analytical session in continuous linear ablation mode on Nist SRM 610 by maximizing the signals for selected masses (Sr⁺ and Th⁺) and reducing oxide formation by minimizing the ThO⁺/Th⁺ ratio. He was flushed into the ablation cell to reduce the deposition of ablated aerosols and to improve signal intensities³⁶ and mixed with Ar before entering the plasma torch through a Y-shaped HDPE connector; this configuration allowed maintenance of stable and optimum excitation conditions.

All LA-ICPMS measurements were carried out using transient time-resolved acquisition operating in a peak jumping mode. Each experiment comprised at least two analyses of the external calibrator every ten-twelve unknowns to correct for the instrumental drift. We used the ablation yield correction factor (AYCF) approach for quantification. The detailed parameters used for quantification are reported in supplementary data and in previous papers.³⁷⁻³⁹

The calibration was performed using the standard reference materials "Silica brick" Standard reference material 199 (National Bureau of Standards), "Brick clay" Standard reference material 679 (National Bureau of Standards) and NIST 610 (National Institute of Standards and Technology, Gaithersburg, MD, USA) whereas NIST SRM 612 was used as quality control. The isotopes collected and used for PCA calculation and the operating conditions for LA-ICPMS analysis are summarized in Table C. Signal intensities over 105 cps were obtained for 88Sr when NIST SRM 610 was ablated with a 40 μ m spot at a repetition rate of 2 Hz and laser fluence of about 17 J cm⁻² in a He atmosphere. For a given instrument configuration, limits of detection (LOD) are a function of the amount of material ablated from the sample, counting time per element, and instrument sensitivity. The LOD, calculated using the 3 σ criterion for an actual laser beam equal to 55 μ m, ranged from 4 % for Si and 0.4 % for Ca to about 0.05 μ g g⁻¹ for heavier elements. Precision values, calculated as one relative standard deviation (RSD), ranged from 1-2 to 30-40%. Accuracy, expressed as the relative difference between the recorded and the reference values of NIST 612 standard reference materials, was better than 15% for all collected elements. The detection limits for the elements used for classification purposes have been reported (Table D supplementary data).

Finally, Principal Component Analysis (PCA) was carried out on standardized data (by subtracting the average value (per variable) and by dividing by standard deviation (per variable)) using the software package Minitab®.

Results and discussion

Ceramic bodies

The minero-petrographic characterization of the ceramic bodies of the investigated finds meant that they could be split into two groups (A and B) on the basis of their similar features, where each group included objects coming from both sites. Cluster A grouped objects (H8-H12, P18-P29, P34, P36) with a wall thickness which was lower than 2mm, characterized by a non-calcareous, fine textured and well sintered paste, with quartz, micas, feldspars and rare and small (<100 μ m) volcanic minerals and lithic fragments. Cluster B grouped objects (H1-H7, P1-P17, P30-P33, P35) with a thicker wall thickness (from 2 to 3 mm), characterized by a calcareous paste with a coarser texture and, most importantly, a strong presence of large and common volcanic minerals and lithic fragments (Fig. 2).

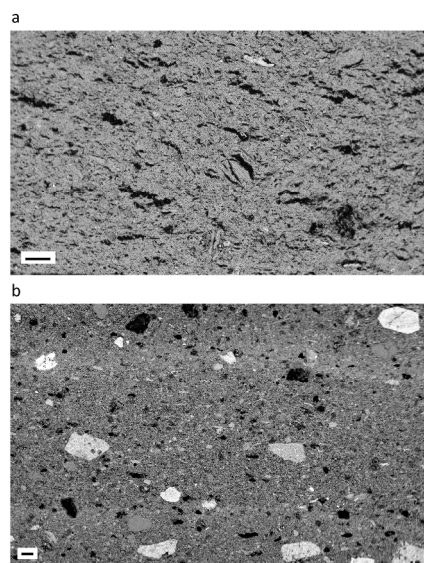


Fig. 2 Samples H11(a, cluster A) and P8 (b, cluster B): SEM images of the thin cross sections highlight the different fabric of samples belonging to unlike clusters. Scale bars = 100 μ m.

In particular, we identified sanidine, biotite and forsterite plus Ti-andradite (melanite garnet), pyroxenes (frequently green diopside), volcanoclastic and pumice fragments - which are considered markers of volcanic raw materials- (Fig. 3).

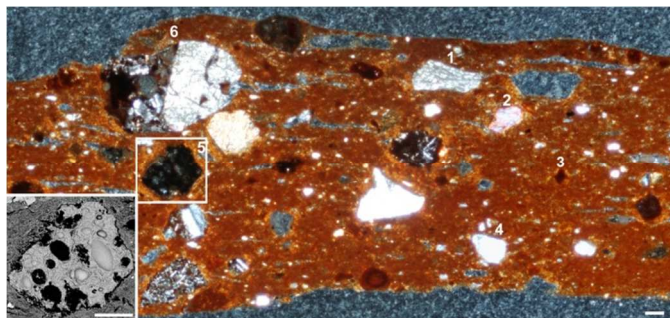


Fig. 3 Sample P12: OM (Nicol +) and SEM-BSE (inset) images of the cross thin section of the fabric show the coarse textured body and the volcanoclastic minerals and fragments (1: pyroxene, 2: olivine, 3: garnet, 4: sanidine, 5: pumice, 6 volcanic lithic fragment of pyroxene+anorthoclase+apatite). Scale bars = 50 μ m.

Diffraction data (Table 1) show a perfect correspondence with the data obtained from microscopy investigations on the thin cross sections, identifying inside the group of samples with mega crystals of pyroxenes and feldspars, a greater quantity of the same phases, with a higher presence of plagioclases in the feldspars.

The presence, in some samples, of neo-formed phase gehlenite suggests that the ceramic bodies of these samples of cluster B reached a temperature of about 950 °C during the firing process, which was maintained for a period sufficient to the completion of the reaction between clayey minerals and calcite.⁴⁰

Table 1 X-Ray Diffraction of pastes.

Sample	Micas	Qtz	Kfs	Pl	Px	Gh	Hem
H2	tr	xxxxx	xxx	x	xx	x	tr
H3	x	xxxxx	xxx	x	xx	/	tr
H5	x	xxxx	xxxx	xx	xxxxx	xx	tr
H8	/	xxxxx	xx	tr	/	/	tr
H9	/	xxxxx	xx	tr	tr	/	xx
H12	tr	xxxxx	xxx	x	/	/	tr
P2	x	xxxxx	xxx	xx	tr	tr	tr
P3	tr	xxxxx	xxx	xx	xxx	/	tr
P7	x	xxxxx	xxxx	xx	xxx	/	tr
P8	tr	xxxxx	xxx	xx	xxx	/	tr
P11	tr	xxxxx	xx	x	xx	/	tr
P15	tr	xxxxx	xxx	x	xxx	x	tr
P16	xx	xxxx	xx	tr	xx	x	tr
P27	tr	xxxxx	xx	tr	tr	/	/
P28	/	xxxxx	xxx	tr	tr	/	x
P31	tr	xxxxx	xxx	xx	xx	/	/
P33	x	xxxxx	xxxx	x	x	/	tr
P36	/	xxxxx	xx	tr	tr	/	/

Table key: tr = traces; x-xxxxx = relative abundance - number of (x) is in relation to mineralogical phase abundance (xxxxx > xxxx > xxx > xx > x). Mineral abbreviations: Qtz = quartz; Kfs = K-feldspars; Pl = plagioclase; Px = pyroxene; Gh = gehlenite; Hem = hematite.

In order to assess the provenance of raw materials used to manufacture bodies, we performed the chemical quantitative analyses of the ceramic body separately on the matrix, and volcanic clasts of fragments (which form the non-plastic part of the body).

Moreover, we compared the compositional data of pyroxenes, obtained by SEM-EDS, in samples from all groups. Almost all pyroxenes (Fig. 4), fell near or inside the diopside field. In detail, as regards items from group B, the idea of a Campanian provenance is supported by both the presence of volcanic minerals and fragments previously mentioned and by pyroxenes which fell mainly in the diopside field or inside the zone of pyroxenes of the magmatic Campanian area (Pompeii, Campi Flegrei or Monte Somma).

Group A showed a different scenario, because although most part of pyroxenes also fell inside the diopside group, the absence of discriminating markers for the magmatic area (for instance melanite garnet or volcanoclastic fragments) linked to the occurrence of two pyroxenes in the augite field, which did not reflect the composition of pyroxenes of the Campanian volcanites,^{41,42} suggest a contribution of the component of detritic sedimentary rocks, most probably those of the Apennine mountain chain.

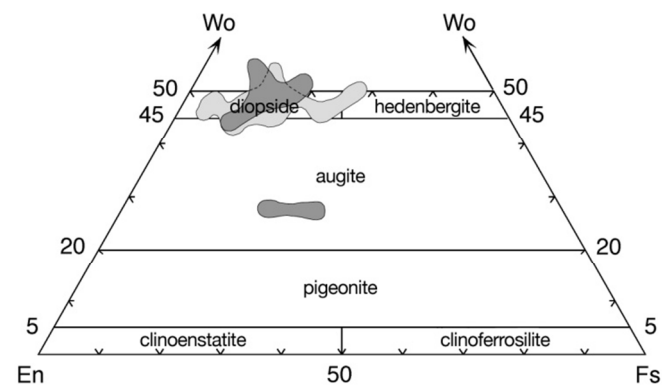


Fig. 4 Composition of pyroxenes^{7,41,42,43}. Group A pyroxenes (dark grey areas): H9, P22, P23, P25, P27, P36. Group B pyroxenes (light grey area): H7, P8, P9. (Wo=wollastonite, En=Enstatite, Fs=Ferrosilite).

Regarding the ceramic body, the two groups of ceramics differed especially in abundance and size of minerals and lithic fragments (more numerous and larger in group B compared to group A). These differences were highlighted by the presence of muscovite and the more frequent presence of feldspars (especially plagioclase) and olivine in group B. We only found pyroxenes with augitic composition in group A.

OM and SEM analyses also highlighted differences in the surfaces of the two groups. The absence of any coating characterized the surfaces of samples in cluster A and a comparison between the composition of ceramic bodies and their surfaces showed only a slight increasing in Al/Si and K/Ca atomic ratio from the ceramic body upward to the surface, in agreement with a superficial polishing process which caused a depletion of silica and calcium, consistent with the removal of more superficial coarse quartz and carbonate grains.⁴⁴

On the contrary, a red or black gloss -15-20 μ m thick- was highlighted on surfaces of items in cluster B. The glosses showed a more compact and sintered structure and a different composition, compared to the ceramic body (Fig. 5).

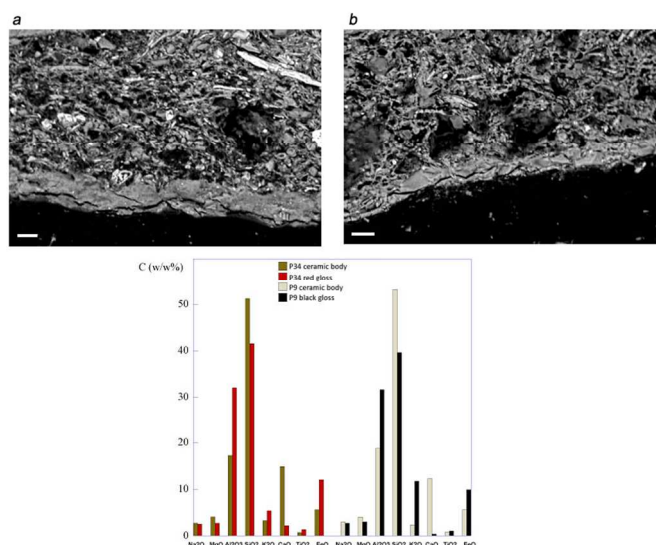


Fig. 5 Samples P34 and P9: SEM images of the cross thin sections show the presence of red (a, P34) and black (b, P9) gloss. Scale bars: 10 μm . The histogram highlights the compositional differences between red (left, P34) and black (right, P9) glosses considering element oxides reported in Table 2.

The red gloss was slightly different to the black gloss, in composition and microstructure. It had lower quantities of K, slightly higher amounts of Ca and Fe (Fig. 5 and Table 2) and a coarser textured structure with a slightly higher porosity. It is noteworthy the presence of S in all the glosses examined with an amount from the detection limit up to 0,3%, probably related to the sulfides and sulphates present, as accessory phases, in the clayey materials.

Table 2 Microprobe analysis of red and black glosses.

Samples	Gloss colour	% w/w							
		SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O
H7	black	41,0	0,9	31,6	9,8	2,9	1,6	3,1	9,2
P2	red	41,8	1,0	33,9	10,7	2,7	1,2	2,4	6,1
P3	black	38,5	0,9	29,2	10,8	2,8	1,1	2,3	14,4
P5	red	41,4	1,2	31,7	9,9	3,2	2,7	3,4	6,4
P9	black	39,6	1,1	31,6	9,9	3,0	0,4	2,7	11,7
P12	black	41,7	0,7	27,7	9,1	3,5	1,2	2,5	13,6
P16	red	48,3	1,3	29,1	12,0	2,2	2,0	2,0	2,7
P17	red	42,0	0,9	33,8	10,7	2,9	2,0	2,7	4,6

As extensively reported in literature,⁴⁵⁻⁴⁹ these glosses could be obtained in three different ways: selecting a particular clay, using the finer fraction, of a purified clay whose coarser part was used for the ceramic body, or using specific compounds to modify the composition of clay used to make the ceramic body. Our results (chemical and mineralogical compositions and structural characteristics) confirm the use of different raw materials for the body and for the gloss. Moreover, a comparison between data on black and red glosses suggests the use of two different, naturally K-

rich, illitic clays, characterized by slightly different chemical compositions and textural structures.

However, the addition of wood ash as a deflocculant for the black slip's raw materials, may also contribute to the potassium enrichment. The different colours of the glosses were linked to the various chemical and structural compositions of the clays used: a different permeability to oxygen discriminates the colour of the surfaces produced, giving rise to different iron oxidation states during the last step of a three phases (oxidant-reducing-oxidant) firing cycle.⁵⁰

Generally, the gloss covered the external surface of the item. When gloss was also present on the inside it was usually of the same colour. Only in a few cases was the gloss black on the outside and red on the inside. A different permeability, most probably linked to a difference in thickness -about 5 μm for the internal red gloss and 10 μm for external black gloss- could also explain the different colour glosses observed internally and externally on these samples. We may suppose that thinner coatings did not remain black during the last oxidant firing step, because of the incomplete sintering process. Therefore, all data leads us to hypothesize the use of two different, local, raw materials, related to different technological processes for the production of these ceramics.

Indeed, the addition of volcanic sand as a temper to an imported clay (as reported in literature in the case of ceramics coming from the same area but characterized by a larger wall thickness)^{16,19,51,52} would not have been possible in this case, due to the extreme thinness of the walls of this class of pottery.

In order to obtain further confirmation of this hypothesis, we decided to carry out an elemental chemical analysis on the clayey matrix of samples. Samples P34 and P35 were excluded from LA-ICPMS due to the contamination on their ceramic bodies, related to restoration work which had not been documented, but highlighted by SEM-EDS analyses. The compositional data (Table 3) were processed with PCA, with the main aim of identifying groups of objects distinguishable on the basis of their compositional features.⁵³⁻⁵⁷

It is interesting to underline that S was present in a non-negligible amount in almost all ceramic bodies and the quantities of Mn were very different for the samples of the two groups – lower than the LOD for almost all samples in group B and about 800 ppm for the samples in group A-. Thus, even though Mn can be a strongly discriminating parameter for the sampling investigated, it was not possible to include it in the statistical treatment.

Table 3 Matrix composition of ceramic bodies and relevant standard deviation (σ) calculated considering all the performed scans.

Sample	% w/w																			
	SiO ₂		Al ₂ O ₃		CaO		FeO		MgO		K ₂ O		TiO ₂		Cr ₂ O ₃		Rb ₂ O		SrO	
	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ
H1	54,4	0,3	13,3	0,2	19	1	5,4	0,3	3,1	0,2	2,0	0,3	0,42	0,04	0,014	0,003	0,006	0,001	0,065	0,006
H2	57	3	14	1	14	1	6,5	0,5	2,8	0,2	2,8	0,3	0,31	0,03	0,023	0,002	0,016	0,001	0,053	0,003
H3	60	3	14	1	11	1	6,0	0,5	2,9	0,3	3,7	0,2	0,31	0,03	0,012	0,001	0,024	0,003	0,049	0,005
H4	54	2	13,4	0,5	18	2	5,2	0,4	3,2	0,4	3,1	0,4	0,41	0,03	0,022	0,002	0,020	0,001	0,063	0,003
H5	62	2	10	1	14	1	6,0	0,2	3,3	0,1	2,4	0,2	0,41	0,05	0,019	0,002	0,015	0,001	0,052	0,005
H6	60	2	11	1	14	1	6,2	0,3	3,2	0,5	2,4	0,3	0,52	0,06	0,024	0,003	0,014	0,001	0,055	0,008
H7	57	2	13	1	15	1	6,3	0,6	3,1	0,3	2,3	0,2	0,41	0,01	0,022	0,002	0,014	0,003	0,056	0,004
H8	67	3	17	2	2,4	0,2	6,3	0,4	1,6	0,2	2,6	0,4	0,55	0,07	0,015	0,001	0,041	0,009	0,025	0,003
H9	68	4	19	2	1,4	0,1	5,6	0,3	1,4	0,0	2,9	0,3	0,31	0,05	0,011	0,002	0,034	0,007	0,016	0,003
H10	64	3	20	1	1,0	0,1	7,3	0,4	1,8	0,2	3,1	0,3	0,31	0,03	0,019	0,002	0,039	0,006	0,021	0,002
H11	63	2	21	1	2,7	0,2	5,3	0,2	1,6	0,1	3,0	0,4	0,41	0,06	0,011	0,002	0,025	0,004	0,043	0,004
H12	69	3	15	2	1,9	0,0	6,2	1,0	2,1	0,2	3,3	0,6	0,31	0,02	0,020	0,002	0,034	0,003	0,023	0,003
P1	55	1	15	1	17	1	5,5	0,6	2,7	0,2	1,6	0,3	0,41	0,04	0,013	0,003	0,009	0,001	0,061	0,007
P2	62	3	11	1	12,3	0,4	6,4	0,7	2,6	0,1	2,8	0,3	0,41	0,05	0,027	0,005	0,031	0,008	0,054	0,008
P3	61	1	13	1	13,0	0,3	5,9	0,3	2,9	0,2	2,4	0,2	0,42	0,08	0,021	0,002	0,022	0,002	0,056	0,006
P4	56	1	16	1	14,8	0,5	5,5	0,4	2,6	0,3	2,1	0,2	0,41	0,03	0,015	0,003	0,007	0,001	0,060	0,002
P5	56	2	14	1	16	1	5,3	0,4	2,7	0,1	3,1	0,3	0,41	0,04	0,018	0,001	0,018	0,001	0,073	0,007
P6	58	3	15	1	13	1	5,9	0,6	2,5	0,1	3,0	0,1	0,31	0,01	0,018	0,001	0,028	0,004	0,060	0,004
P7	58	5	11	2	18	1	6,1	0,4	1,9	0,2	1,5	0,2	0,22	0,02	0,014	0,003	0,026	0,003	0,05	0,01
P8	59	3	11	1	16,8	0,2	6,2	0,4	3,0	0,5	1,9	0,2	0,41	0,04	0,023	0,004	0,014	0,003	0,05	0,01
P9	60	2	12	1	13,4	0,5	6,7	0,7	2,6	0,2	2,6	0,2	0,52	0,07	0,025	0,003	0,015	0,004	0,056	0,006
P10	59	3	13	1	15	1	5,7	0,6	2,7	0,2	1,8	0,3	0,41	0,04	0,014	0,003	0,014	0,003	0,051	0,009
P11	60	2	13	1	14	2	5,6	0,4	2,6	0,3	1,7	0,2	0,31	0,03	0,022	0,004	0,006	0,001	0,058	0,004
P12	60	1	12	1	13,1	0,4	6,9	0,3	3,1	0,2	2,6	0,2	0,42	0,06	0,031	0,006	0,027	0,002	0,043	0,004
P13	59	3	13	1	14	2	5,6	0,5	3,4	0,3	2,4	0,2	0,34	0,02	0,025	0,005	0,020	0,003	0,064	0,003
P14	58	3	13,2	0,3	13,3	0,5	7,0	0,4	2,6	0,2	3,0	0,2	0,31	0,01	0,024	0,002	0,017	0,002	0,067	0,008
P15	58	4	9,8	0,1	18	1	6,1	0,6	2,4	0,4	2,5	0,4	0,41	0,03	0,023	0,003	0,012	0,001	0,048	0,006
P16	60	2	16	1	10	1	5,7	0,9	2,7	0,1	3,1	0,2	0,41	0,08	0,016	0,003	0,017	0,003	0,050	0,003
P17	61	2	16	1	9	1	5,1	0,6	2,7	0,2	2,9	0,2	0,31	0,03	0,023	0,005	0,020	0,005	0,055	0,004
P18	68	4	18	2	1,5	0,1	5,6	0,5	1,7	0,1	2,6	0,4	0,31	0,04	0,021	0,003	0,033	0,004	0,019	0,002
P19	67	2	19	1	2,1	0,1	5,3	0,6	1,4	0,1	2,8	0,5	0,32	0,02	0,012	0,002	0,030	0,006	0,020	0,001
P20	65	2	21	1	1,7	0,1	6,0	0,4	1,5	0,2	1,9	0,4	0,31	0,05	0,006	0,001	0,018	0,004	0,028	0,006
P21	65	1	18	1	1,8	0,1	7,0	0,7	1,9	0,2	3,7	0,6	0,41	0,03	0,021	0,002	0,036	0,007	0,029	0,004
P22	66	1	21	1	0,3	0,0	5,7	0,5	1,7	0,1	2,4	0,3	0,31	0,04	0,006	0,001	0,032	0,004	0,021	0,002
P23	66	1	19	1	0,7	0,1	6,9	0,7	1,4	0,1	3,3	0,1	0,42	0,05	0,022	0,003	0,068	0,007	0,015	0,002
P24	63	1	21	1	1,3	0,1	6,7	0,3	1,6	0,1	2,9	0,2	0,41	0,03	0,020	0,003	0,05	0,01	0,019	0,002
P25	67	3	19	1	1,0	0,1	6,4	0,6	1,8	0,1	2,9	0,1	0,41	0,06	0,017	0,002	0,048	0,008	0,016	0,003
P26	66	1	18	1	3,0	0,2	5,7	0,1	1,8	0,1	2,8	0,2	0,31	0,02	0,016	0,004	0,033	0,004	0,025	0,003
P27	64	2	20	1	1,2	0,1	6,9	0,2	1,8	0,1	2,9	0,2	0,31	0,03	0,018	0,002	0,047	0,005	0,022	0,002
P28	68	1	17	1	1,8	0,1	5,9	0,3	1,9	0,1	3,0	0,2	0,41	0,04	0,024	0,003	0,039	0,005	0,019	0,001
P29	65	2	21	1	1,6	0,2	5,9	1,0	1,3	0,0	3,0	0,6	0,41	0,05	0,007	0,002	0,035	0,005	0,023	0,004
P30	58	1	15	1	12,6	0,5	6,0	0,5	2,5	0,1	2,9	0,7	0,40	0,05	0,017	0,002	0,027	0,003	0,031	0,006
P31	69	2	14	1	4,8	0,2	5,3	0,7	1,8	0,1	2,8	0,6	0,21	0,01	0,013	0,003	0,016	0,004	0,015	0,004
P32	55	2	20	1	14,3	0,5	5,9	0,6	1,2	0,1	1,0	0,2	0,31	0,05	0,006	0,001	0,005	0,001	0,041	0,007
P33	65	1	15	1	6,5	0,3	6,3	0,6	2,3	0,3	2,8	0,4	0,52	0,07	0,015	0,001	0,031	0,006	0,024	0,002
P36	69	4	17	1	1,6	0,0	5,6	0,5	1,8	0,2	2,6	0,5	0,48	0,05	0,018	0,001	0,032	0,003	0,021	0,002

The results of the multivariate statistical treatment are shown in Fig. 6, illustrating the scores plotted on to the first three principal components subspace, which accounts for 80% of the total variance, and the loading plot of the different parameters.

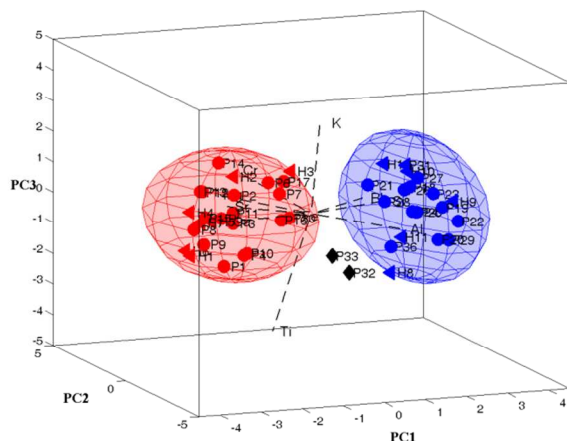


Fig. 6 Scores and loadings diagram for the first three principal components related to matrix Pompeii fragments (circles) and Herculaneum (triangles). The accounted variance is 80% of the total.

Two markedly distinct groups can be identified. The same figure shows 95% isoprobability ellipsoids, whose surfaces define the boundary of the clusters. Cluster A (blue ellipsoid) differs from B (red ellipsoid) principally along PC1, because of the loadings relative to Ca, Sr and Mg parameters. In particular, the scores of cluster B are characterized by negative values of PC1 due to higher amounts of Ca and Mg, while the scores of samples belonging to cluster A are spread along positive PC1 values due to their lower content. The widening of both clusters along PC3 is mainly due to the loadings of Fe, K and Ti. This result indicates that the matrices of the samples of the two groups were different and since the samples of the two clusters differed also in type, amount and size of minerals in the paste, the use of at least two different raw materials (different both in clay fraction and non-plastic inclusions), is further supported.

In fact, we obtained the same distinction in two clusters – in separated ways – by using chemical and mineral-petrographic analyses, which excluded the addition of volcanic sand as a temper to the same clay.

Samples P32 and P33 are outliers in the clusters observed. These show intermediate values of Ca and Mn and were expected to belong to cluster B considering their morpho-mineralogical features. The only peculiarity highlighted is the absence of any pyroxenes in the cross thin section of sample P32. This characteristic would suggest the use of a different raw material to that employed in both A and B but, taking into account the low number of samples, we preferred not to draw conclusions.

We found indirect confirmation that the raw materials used could be local thanks to the investigation of a different ceramic class which however belongs to the same period and comes from the same sites, also considered by the archeologists to be of local production and showing the same types of volcanic clasts in the ceramic bodies as in the thin walled pottery here investigated.

The samples considered consist of objects – mostly lamps, but also *skyphoi*, cups, small *amphoras*, statuettes – extensively studied from an archaeological perspective,⁵⁸⁻⁶⁰ characterized by a monochrome, sometimes bichrome, green or yellow-ochre colored lead glazed

coating. The glaze is present on the external surface of the closed shapes and on both surfaces of the open ones. In this latter case, it is generally green on the external surface and red-yellow ochre on the internal surface.

Decorative motifs, made mostly in relief, with barbotine and by stamp include phytomorphic designs and individual characters' depictions, unconnected to each other on the body of the vase. The similarity of the minero-petrographic characteristics of their ceramic bodies to that of thin-walled justified the comparison, thus we extended the multivariate analysis to the paste matrices chemical data, obtained by LA-ICPMS using the same experimental conditions, of lead glazed pottery.

Glazed pottery samples are spread inside the same two clusters previously obtained, considering only thin walled pottery (Fig. 7) and again, the glazed finds containing larger and more numerous volcanic clasts are located in cluster B (Fig. 8). Therefore, this additional statistical treatment reinforces the idea of the use of very similar, local raw materials.

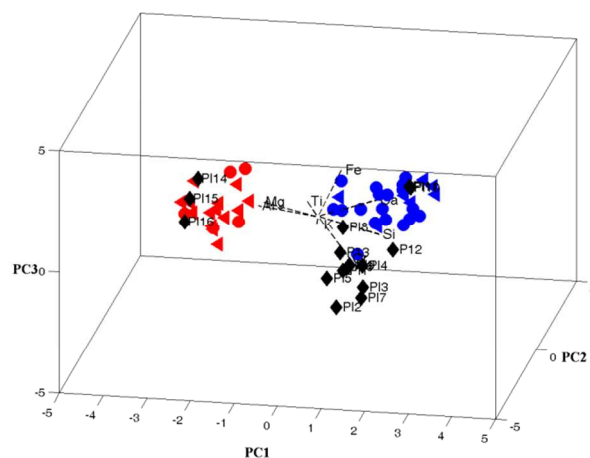


Fig. 7 Scores and loadings diagram for the first three principal components related to thin walled pottery matrix from Pompeii (circles) and Herculaneum fragments (triangles) and glazed pottery (diamonds). The accounted variance is 83% of the total one.

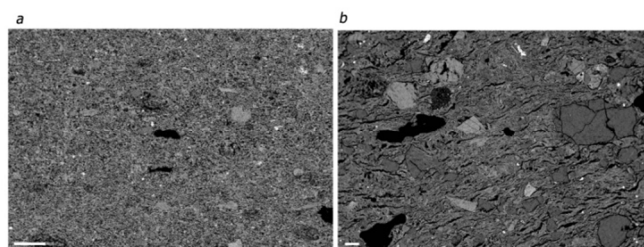


Fig. 8 Samples 19300 (a) and 6587B (b) of Roman glazed pottery (belonging to the same period) from Pompeii: SEM-BSE images of the thin cross sections show the different characteristics of the matrix and non-plastic parts of samples belonging to the two groups. Scale bars=100 μm .

Conclusions

The results obtained using a multi-technique approach on thin walled pottery from Herculaneum and Pompeii provided useful information about technological-productive aspects and the provenance of raw materials.

All the data collected support the hypothesis that raw materials used came from the Campanian region, even if scrap material coming from some kilns and/or objects of certain provenance were not found. The differences observed both in ceramic matrices and in volcanic minerals and fragments make it impossible to think that they were added as tempers to an imported clay (a statement also endorsed by the extreme thinness of the walls of this class of pottery). Moreover, the remarkable similarity in the chemical and mineralogical composition of raw materials used in the two sites, for two different classes of pottery - thin-walled and glazed - belonging to the same period, and both considered as a local production based on the typological-stylistic studies, supports this conclusion.

Results also highlight the use of at least two different, local, raw materials. The most attested hypothesis is the employment of Campanian alluvial clayey sediments with at least a component of sedimentary material, probably from the Apennine mountain chain, for one of the two raw materials. These alluvial deposits are still present and are not located far from the sites studied.⁶¹

The two different raw materials are associated with two different manufacturing productions. The first includes objects with a non-calcareous, fine-textured and well-sintered paste, no surface coating, few and small volcanic minerals and fragments. On the contrary, the second includes samples with a vitrified surface coating, a calcareous, coarser textured paste, with abundant and large volcanic minerals and fragments. It is not surprising that these coatings are related to calcareous ceramic bodies. Indeed, it is impossible to obtain a well-defined red or black surface using, for the body, local raw materials which are too rich in Ca and with a low ratio content of Fe/Ca.⁶² Moreover, the coefficient of thermal expansion of a clay rich in calcium is more similar to the glossy slip, reducing the possibility of having poor quality objects.⁴⁴ The results obtained, e.g. the presence of neo-formed phases (such as gehlenite) in the paste samples of cluster B, lead us to formulate a hypothesis regarding the firing temperature reached.⁶³

It should be emphasized that only the matching of data obtained thanks to a multi-technique strategy allowed us to reconstruct the entire technological cycle of this production, although limited to Herculaneum and Pompeii, from the recovery of raw materials (type and supply basin) to the manufacturing and firing process.

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