Non-destructive method for the identification of ceramic production by portable X-rays Fluorescence (pXRF).

A case study of amphorae manufacture in central Italy

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ABSTRACT

Portable X-rays Fluorescence (pXRF) represents one of the most effective tools for in situ, non-destructive elemental analysis, which has a valuable application in the study of ceramic production. However, whilst the qualitative assessment of the composition of artefacts is reliable, the quantitative analysis can be biased by some limitations, due to instrumental features or materials properties. The analysis of ceramic materials is particularly challenging due to the lack of representative calibrations and standards, as well as the low density and poor homogeneity of samples. In this contribution, a method is proposed to fingerprint a ceramic production through pXRF analysis. At the site of Montelabate (Perugia) in central Italy four kilns were excavated revealing a production of amphorae. This site was therefore selected as a suitable case study for fingerprinting a ceramic production. After qualitative analysis, representative calibration standards were created based on different commercial clays and feldspars. These can help overcoming the well-known matrix effect, both physical and chemical, and may offer a representative and reproducible standard to be used in different laboratories.

Alongside the precise assessment of composition, the possibility to fingerprint a production was also assessed using a different method, based on the intensity ratio between selected elements. The relevant elements were chosen based on their correlation and non-correlation. Correlated elements were attributed to the raw clay used for ceramic production

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and non-correlated elements were attributed to the specific fabric recipe. Accordingly, some benchmarks to identify the clays and fabric used in the site of Montelabate were identified. Amphorae found at other ancient commercial sites in the area of Rome were therefore also compared with these benchmarks in order to assess their provenience.

Keywords: X-rays Fluorescence; Ceramic analysis; Fingerprinting a production; Amphorae analysis; Montelabate; Central Italy manufacture.

1 - INTRODUCTION

X-rays Fluorescence (XRF) is an analytical technique widely applied in archaeology for decades and the development of portable instruments allowed increasingly fast applications to analyse the elemental composition of archaeological material (Schackley 2011, Frahm and Doonam, 2013, Shugar and Mass 2014).

XRF is a non-destructive procedure which offers information on the chemical composition of samples, relying on its bulk elemental composition and not specifically sensitive to the surface. The use of a portable device, as in this case, additionally permits fast analyses in the field, requiring only a quick and standard setup to collect data. Therefore it can be conveniently adopted for routine analysis to correlate pottery productions and to confirm, or exclude, identifications based primarily on macroscopic observations.

The successful application of XRF analysis on ceramic elements and the results of the collected data has been widely debated (Hunt and Speakman, 2015; Speakman et al., 2011). Central to the debate is that ceramics have a lower density than metals and therefore scatter more effectively radiation, which may limit to some extent the sensitivity of the analysis. Typically, the lower detection limit for XRF is tens of ppm, but it requires longer spectra collection time and the absence of any interfering element. Some limitations are also intrinsically correlated to the type of analysis, which suffers of the so-called “matrix effect”. Instances in which it is necessary to obtain highly accurate quantitative analysis at low concentrations of critical light elements may require vacuum analysis as the surrounding air absorbs the lower energy X-rays generated by the excitation of low-Z elements. Therefore, it is often misleading to look at quantitative results of the order of few ppms: this is not a very sensitive analytical tool, as also noted by (Hunt and Speakman, 2015, 637).

A further critical point is based on the variable total intensity of spectra collected over different samples with identical composition, depending on scattering and on possible fluctuating intensity of the source, which often make quantitative analysis with absolute values unreliable. Indeed, the intensity of the whole spectrum seems to sometimes vary. The data should be compared (and in each case normalised) with repeated measurements of a standard or calibration sample, to check reproducibility.

Additionally, XRF incident radiation has limited penetration so that elements that are more abundant on the surface are predominantly detected, which may be significantly different from the bulk composition of a sample. This is particularly relevant when it is impossible to obtain a homogeneous sample through grinding or melting. It should also be noted that when using factory calibration through commercial algorithms, relative errors around 50% may be even achieved, while custom standardisation typically induces a relative error of less than 10%.

As previously noted, there has been extensive discussion of the error sources during quantitative XRF analysis of ceramics which have been reviewed by Speakman and Shackley 2013 and by Conrey et al., 2014, specifically focused on the archaeological application of this analytical method. These contributions also suggest procedures and calibration methods to avoid severely misleading results. It is clear from these studies that the use of commercial or automatic calibration software, as well as that of raw intensity data, must be carefully avoided. Furthermore, factory calibrations for ceramics and obsidian, the materials most intensively studied in this field, do not exist. Factory-installed calibrations are not adequate for quantification of elements in non-metallic archaeological materials (Speakman et al., 2011). A more positive stance on the application of pXRF on ceramics has been provided by (Attaelmanan and Mouton, 2014). The conclusion is that some of the limitations, amongst which are those described above, can be overcome by combining different analytical tools. It is apparent that the correct set up of an analysis protocol for data collection and interpretation can resolve most of the issues above described.

This paper presents an analytical method based on pXRF for the identification of ceramic fabrics and provenance identification. The results presented here are part of the FABRICS project, established between the McDonald Institute for Archaeological Research at Cambridge University and the Department of Chemistry of the Universitá degli Studi di Milano, which aims to develop an integrated methodology to fingerprint ceramics production. The techniques employed include portable X-ray fluorescence (pXRF) and Fourier Transform

Infrared Spectroscopy (FT-IR) for compositional data, while structural data are collected by X-Ray Diffraction (XRD) and Near-Infrared spectroscopy (NIRS).

This study aims to establish a standard non-destructive methodology to fingerprint pottery by pXRF, allowing the scientific classification of artefacts, using as a case study the unique discovery of four pottery kilns excavated in 2012 in central Italy at Montelabate (Perugia, Italy), in the framework of the Montelabate Project (under the direction of Simon Stoddart and Caroline Malone). The workshop, in use from the 1st century AD to the late 4th –early 5th century AD producing amphorae then later courseware, offers the perfect model for the study of the technique of production.

2 – THE CASE STUDY

2.1. Ceramic production

One of the earliest human skills was in crafting a range of clay objects. It is fundamental to understand the development of the technical processes of manufacture in antiquity as it can be seen as a foundation of the modern industrial process. Traditionally, archaeology classifies the development of technology on the basis of the evolution of objects and the identification of similar fabrics is performed on the basis of the colour of clay and its composition, however such observations can be misleading. Colour may vary due to organic impurities, leading to a brown or black clay colour, or to transition metal ions. Iron in variable amounts and/or oxidation leads to brown, red or yellow, whereas manganese usually leads to grey/green colour, which is also typical of partially reduced iron (ferrous compounds).

The composition and oxidation state of some elements in the final ceramic may vary depending on the thermal treatment in different sections. For instance, if a brown colour is imparted by carbon residue, firing may eliminate them from the surface, but less effectively from the inner part of the object, and this may be evidenced in a freshly broken section. Similarly, a light red/brown colour is due to ferric oxide (*i.e.* oxidised iron ions), whereas firing under reducing conditions, with limited air feed, may turn the surface greyish, leaving the section with the original red/brown colour.

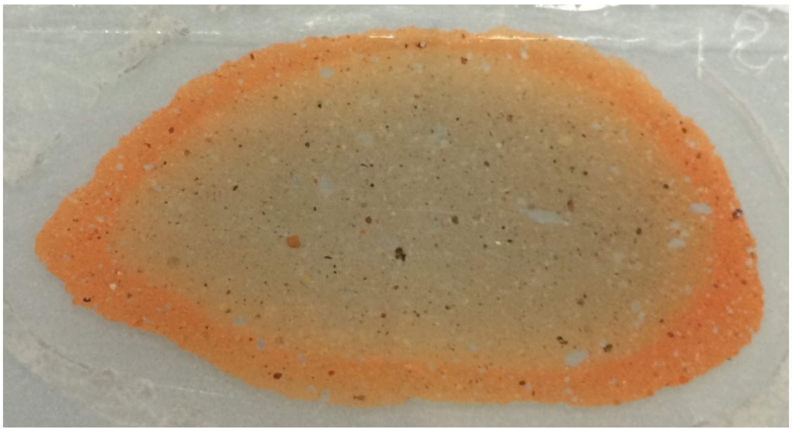

Fig. 1: Example of an object's section with different colours.

Temper is often added to impart specific properties. Calcium oxide can be added as a fluxing agent, usually obtained through the decomposition of limestone and other carbonates. The same function may be exerted by feldspars, which are stable in the temperature range of firing between 700°C and 900°C. Non plastic materials, typically coarser than the clay, are used to avoid excessive shrinkage during drying and firing. This is particularly important when fine grains are used for the clay, which make the escape of water harder from inner layers after the surface has dried. Coarser particles leave space for water to diffuse more effectively towards the surface. Different rocks may be used, such as basalts, ardesites, volcanic ash, glass or tuff. Sedimentary material may also be included, such as sandstone, limestone and dolomite, or diatomaceous earth.

Finally, surface finishing is carried out to remove irregularities. In some instances a suspension of clay in water is used for finishing, which may lead to some differences between the surface and the bulk compositions. Therefore, it can be seen that is crucial to identify the technical process of pottery production through the application of an integrated method of analysis[1].

[1] An interesting approach to determine pottery fabric technology has been developed by the Groningen Institute for Archaeology (GIA) Laboratory for Conservation and Material Studies. It undertakes the classification of fabrics through the optical analysis of the compositional characteristics in fresh breaks in the pottery and by the re-firing of selected material at 600°C, 800°C and 1050° in an oxidising kiln in order to establish the firing characteristics of the material (Attema et al., 2003). However, no specific analytical method was employed in this study.

2.2. The site

The site of Montelabate is situated in the Upper Tiber valley, 30 km from Perugia, in a valley characterised by a series of gentle hills 250-300m above sea level. The valley is overlooked by the Abbey of S. Maria di Valdipone, today owned by the Gaslini Foundation, in an area known for pottery production until the early 20th century.

Geologically, the valley is in the plain of the Umbrian basin delimited by lower hills to the east separating it from the valley of Gubbio which is composed of Mesozoic-Tertiary and Marly limestone (Malone and Stoddart, 1994, 17). The territory of Montelabate comprises the catchment of a series of small rivers running south west flowing into the River Tiber.

The production site, used as key-study in this study, for pottery manufacturing used the Plio-Pleistocene clay deposits which are derived from the ancient Tiber basin, as the area is characterised by a series of lithostratigraphic units and alternating alluvial sandy-clay layers, created by water courses running into the lake that later become the River Tiber, interbedded with calcareous and travertine gravels[2]. The pottery manufacture is located in walking distance to a rich clay deposit[3] and both the river connectivity by the Ventia, a tributary to the Tiber at a distance of 5km, and the densely forested hills surrounding the site (Umbria was rich in forests as attested by Cic. Div. 1. 94) were the ideal combination for the exploitation of local resources for production[4].

An initial field walking survey conducted in 2010 (Stoddart et al., 2012) revealed an interesting spatial patterning in the valley in the Roman period: rural settlements filled the area, distributed both in the lower sandstone foothills between 250 and 300m above sea level, on the Pliocene lacustrine sediments and on the terraces of the Tiber tributaries. The evidence of the agricultural exploitation and the production of wine in the area are documented by a complex kiln site, excavated in 2012, formed of three kilns and a workshop.

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[2] For the area of Montelabate and the Tiber Valley (Beneduce and Lapadula 1997, 318-319). For Gubbio Bertacchini 2008, see also (Donnini and Rosi Bonci, 2008, 2-3).

[3] The application of Near-Infrared Spectroscopy (NIRS) to identify the composition and microstructure of a clay-based object has given the following results: Paligorskite, Leucite, Feldspar. The XRD results on the structure of iron oxide clay revealed the presence of Quartz, Muscovite, Anortite

[4] Similarly as noted for the area of Mugnano in Teverina on the other bank of the Tiber, where the production included stamped bricks, tiles and mortaria, Gasperoni 2003, 37- 38.

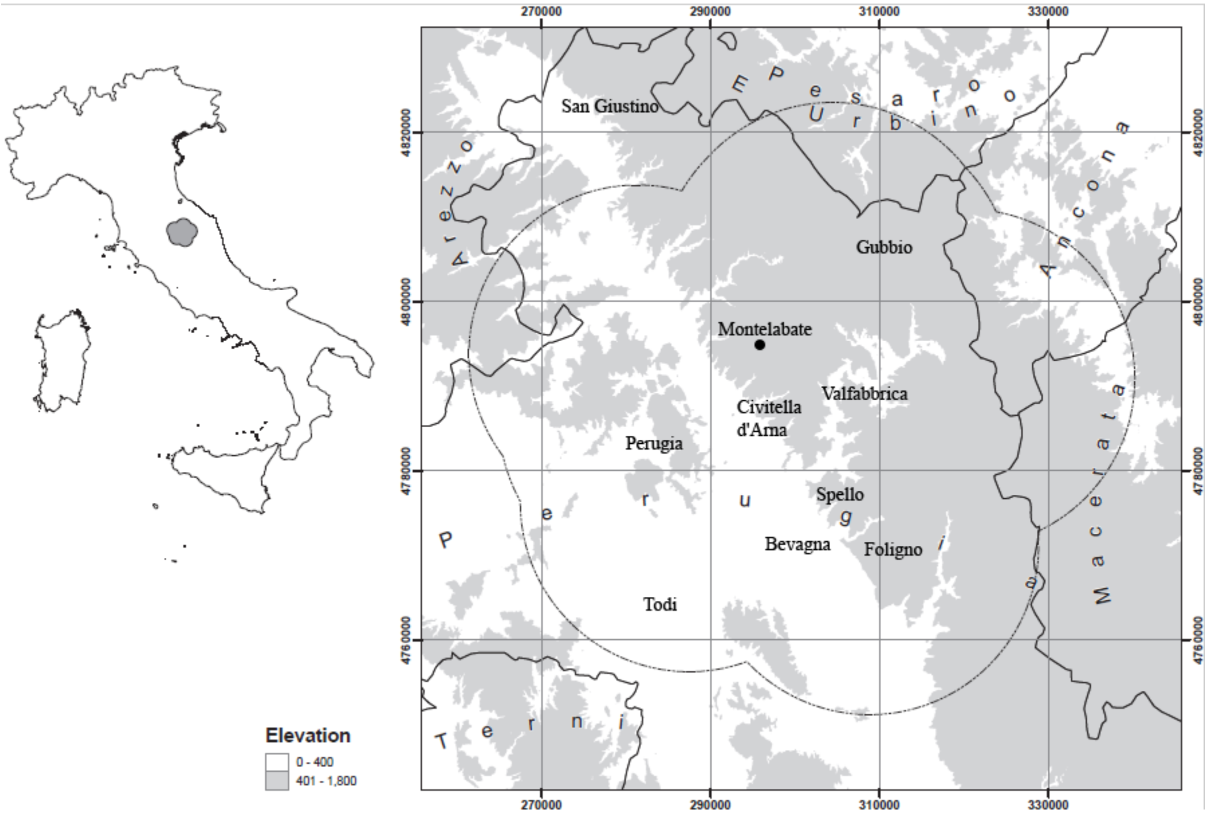


Fig. 2: Map of the site. The base map is courtesy of David Redhouse.

The excavation of the production centre at Montelabate concentrated on an area measuring 25m by 30m on the top of the small hill (Fig.2). The study of the surface material indicated six defined areas for excavation which subsequently revealed three kilns, three dumps of material and a separate structure, possibly a workshop. Two of the kilns, which had the longest period of use, were located at the summit of the hill and oriented North-South, probably in order to create an updraft favourable for the firing process (Fig.3, Kilns 1 and 2). A third kiln was located further down the hill (Fig.3, Kiln 3) had the same orientation but with an elongated combustion chamber, probably in order to increase the forced draught. The kilns were all rectangular in shape with a double updraft chamber (the Cuomo di Caprio II/b typology (Cuomo di Caprio, 2007, 523-525, fig. 169), consisting of a lower combustion chamber with a stoking hole or *praefurnium*[5].

[5] For the description of the single structures see Ceccarelli *forthcoming*

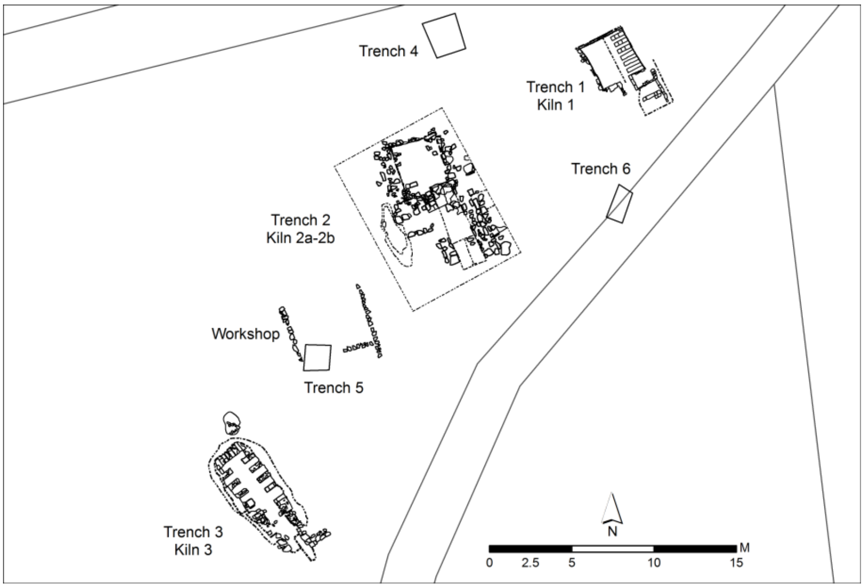


Fig. 3: Plan of the kilns identified during the excavation.

The kilns produced a type of flat-bottomed amphorae. It is labelled as the 'Spello' type after the name of the site where its production was identified for the first time. In the context of Ostia it is classified as Ostia III, 369-370 / II, 521 ((Panella, 1989, 143-146), Rizzo 2014, 130), while the examples from the Upper Tiber valley have been called 'Tiberine' and 'Altotiberine'[6]. The production of Montelabate revealed that there was little standardisation, as seven different types were identified with everted band rims (type 2.3-2.4 (Lapadula, 1997)), tapered rims (type 2.5 of (Lapadula, 1997)) and rounded rims (type 4.10 of (Lapadula, 1997)) with diameters between 7.5cm and 9 cm. (Ceccarelli, *forthcoming*) (Fig. 3).

[6] (Molina Vidal, 2008), 227-229.

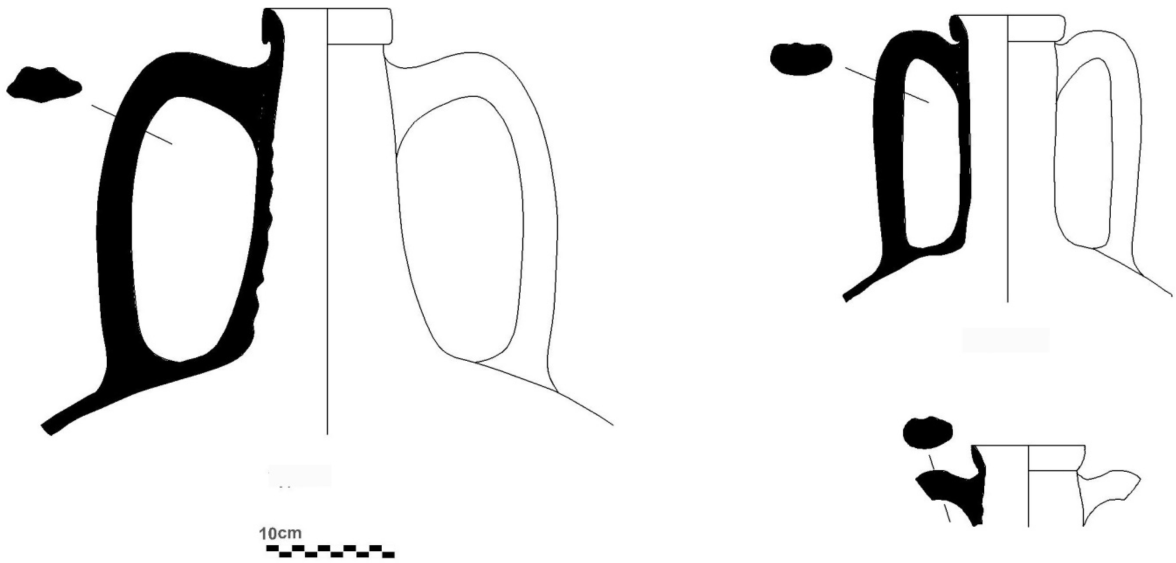


Fig. 4: Example of amphorae found at Montelabate.

These small wine amphorae, made from the Tiberian-Claudian period until the end of the 2nd century AD, were transported by river from the Upper Tiber valley to Rome and Ostia (see the recent analysis of Rizzo 2014). The local wine was the *Hirtiola,* as mentioned by Pliny (N.H. 14.37), that was exported from the Upper Tiber valley to Rome, the largest market, and Ostia. In Rome this type of amphorae represented the largest Italian production after the Dressel 2-4 from the Flavian period (see Ceccarelli *forthcoming*).
The kilns were also used to produce tiles and courseware, providing evidence for a local production system that continued in the late antique period, with production and consumption evidence until the 5th century AD.

3 – METHOD OF ANALYSIS

For the XRF analysis both kiln wastes and discarded failed products were selected: these artefacts were not suitable for the wine trade as they were either over-fired, under-fired or fractured amphorae[7]. The process of over-firing clay objects involved too higher temperature or too long a period of firing resulting in a ‘vitrification’ of the surfaces (ideal firing temperature was between 700 and 900°C). On the other hand the under-firing process

[7] Similarly, as discussed for the courseware production at Scoppieto (Peinado Espinosa, 2015).

produced a failed sintering, resulting in a soft porous surface. Another type of failed product were fractured ceramic vessels that did not withstand the thermal shock of cooling ((Cuomo di Caprio, 2007, p.499).

A selection of 38 samples were analysed representing the main diagnostic groups of amphorae, in addition to these groups are 12 samples of the same type of amphorae from other sites in order to compare different productions. As previously noted, the amphorae were distributed either by river and by land, therefore in order to test the method for a large distribution network amphorae from the river harbour at Ardea and an inland site, such as Segni, both in the area south of Rome were sampled. These sites which are distant from the workshop are useful to explore the distribution of vine and amphorae from Umbria. A programme of sampling fragments of amphorae discovered in the surrounding area with a 5km radius s currently on-going to determine the local distribution of the amphorae produced in the workshop of Montelabate.

The pXRF spectra were collected using a Bruker Tracer IIIDS instrument. The following settings have been used as the default choice: 40 keV and 10.70 μA. Each spectrum was collected for 30 seconds fixed time, following preliminary optimisation.

At the start of the process a reproducibility check was conducted by collecting at least three spectra at the same sample point. Depending on the sample geometry, by default each sample was analysed on one or more external surfaces and in one or more internal sections. Possible differences in section and external surface compositions may be ascribed to the production and firing process (e.g. external coating, combustion gas and ash, etc.).

The pXRF proprietary software was used for the peaks identification and to collect raw intensity data. A customise database was then developed to extract intensity from the raw spectra and to analyse them, as described below.

Quantitative data have been obtained by means of an innovative calibration. As described in the following section, for which commercial feldspars and clays with variable and certified composition as an internal standard for calibration were selected. Standardisation has been carried out by linear regression of net peak intensity for selected elements vs. composition (expressed as element or element oxide wt%) in each calibration sample.

4 – RESULTS AND DISCUSSION

4.1. The sampling method

The potters of Montelabate mainly used a source of natural clay deposits as most of the products were made of a non-calcareous iron clay matrix tempered with mica and quartz, as identified in some samples which were thin sectioned. A further element to take into account when sampling amphorae is the different formation methods: parts of the vessel, such as handles and necks were produced separately and added to the main vessel by wiping that may result in small differences in the matrix on the surface. Therefore, the sampling strategy involved analysing both surfaces and sections in order to detect variations. Samples were accurately prepared to avoid any chemical contamination, as suggested also in Hunt-Speakman (Hunt and Speakman, 2015, 627) and each fragment was sampled by six readings on average.

A critique that has been made of the use of pXRF on clays is the difficulty in determining compositional profiles for the lack of reproducibility and standard calibration. To test and overcome this potential problem, a study has been undertaken to test the performance of pXRF as for repeatability and reproducibility of the measurements.

The results illustrated in Fig. 5 show an example of spectra reproducibility, including seven different analyses repeated on the same object section, collected over the course of a two days period. Through an analysis of the overlapping curves, the incidence of the standard deviation was examined for each value with respect to the average of the population, as well as considering each single peak. An overall difference of ±3.5% was obtained for the peak intensity. Similar values were achieved when comparing peak area.

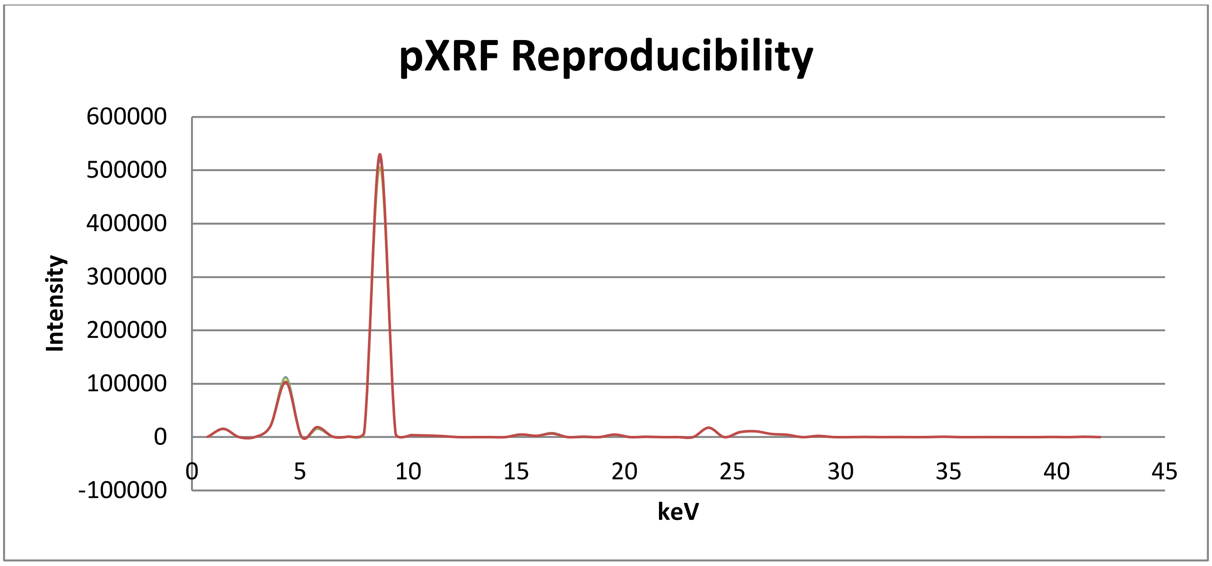
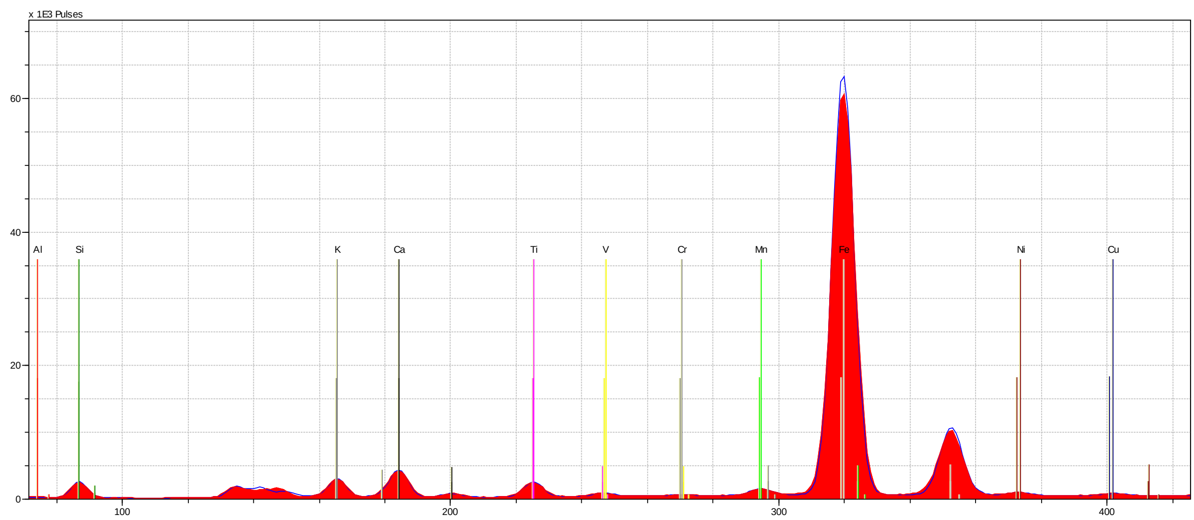


Fig. 5: Example of spectra reproducibility.

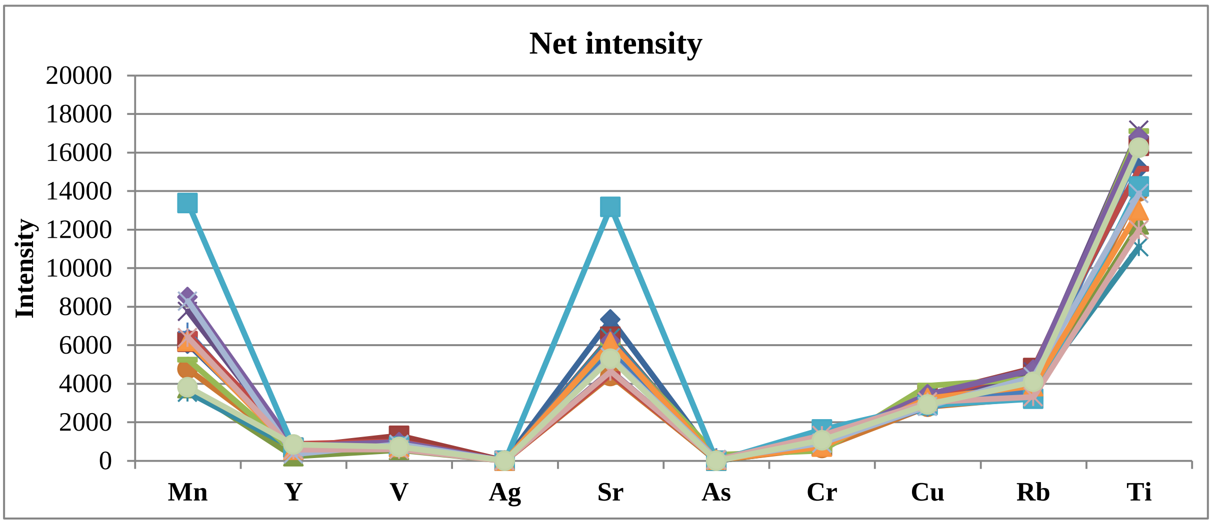
Through the extraction of the net intensity data, it can be noted that the most intense peaks are K, Ca and Fe (Fig.6*a*), which were also characterised by a broad variation of intensity, besides Si and Al which have low net intensity due to poor instrumental response to very light elements. In terms of the minor elements, Fig.6*b* shows that some are characterised by limited variations of peak intensity, others, such as Sr, Mn and Ti by a much broader gradient of concentration in the examined dataset.

Fig.6: Net peak intensity for some representative elements. *a*) Significant elements peaks (Kα peak); *b*) Net intensity of minor elements in different samples of the dataset.

a)



b)



In order to develop a robust method to fingerprint clay production, analysis was also compared the relative intensity of each element signal with respect to that of a reference peak. This procedure overcomes the possible variation of the overall intensity of the spectrum due to any instrumental or external reason. Abundant and scarce elements were considered separately in two distinct groups.

The representative samples of the dataset evidenced a marked variation of intensity ratio with respect to a reference element depending: a) on the selection of sections or external surfaces; b) on the provenience of the sample, as presented in paragraph 4.3.

4.2. Calibration

The aim of this work was to set up a fingerprinting method to assess the composition and origin of ceramic objects. This process could simply rely on peak intensities (absolute or relative). However, a quantitative analysis is proposed here to allow direct comparisons with literature, as far as it is consistent with the intrinsic limits of the technique for quantitative analysis. In order to conduct the analysis the study did not rely on automatized calibration algorithms provided with the instrument, due to the mentioned limitations of such calibration procedures. Furthermore, statistical methods, such as that proposed by (Goren et al., 2011) were not applied. Instead, several natural clay samples were identified, with a similar qualitative composition with respect to the collected ones. Different commercial samples of feldspars and clays were collected, with a variable composition certified by two different producers, to be used as standards. This procedure allowed the comparison of samples with the same matrix as the analytes, therefore limiting as much as possible the matrix effect limitations. A further advantage is that commercial samples represent a suitable comparison to check the reproducibility of the method in different laboratories.

The obtained calibrating curves were used to calculate the following composition (Table 1).

	Element (wt%)					
Sample	K	Al	Ca	Fe_2O_3	Si	Ti
A1	2.275	16.756	8.469	5.606	40.033	0.501
A2	2.535	17.311	9.934	5.566	27.276	0.489
A3	2.369	15.694	2.249	7.122	19.599	0.679
A4	2.425	18.235	3.186	7.709	21.926	0.646
A5	2.452	14.631	9.899	5.606	31.375	0.429
A6	2.250	14.470	9.615	4.914	30.191	0.427
A7	2.686	17.680	2.358	5.971	24.874	0.598
A8	1.543	14.400	1.206	5.568	20.202	0.528
A9	2.173	22.254	3.030	6.936	40.747	0.683
AT1	2.362	16.271	5.724	5.951	33.049	0.506
M1	1.979	17.195	2.063	8.109	25.978	0.816
M2	2.128	23.594	5.069	6.897	51.220	0.638
M3	2.035	16.964	2.225	7.758	35.794	0.739
M4	2.104	17.865	4.262	7.492	36.938	0.739
M5	0.479	9.272	0.966	2.237	0.000	0.203
M6	0.453	10.104	2.217	1.868	0.000	0.138
M7	2.692	19.321	4.529	8.247	33.449	0.756
M8	2.076	15.925	6.125	5.830	35.545	0.510
M9	1.713	15.139	1.266	5.048	6.829	0.433
M10	1.444	16.087	3.042	5.590	10.216	0.480
M11	1.918	16.294	5.347	5.688	36.108	0.518
M12	2.237	17.357	4.111	7.014	31.075	0.692
M13	2.074	15.948	4.747	6.449	38.381	0.591
M14	1.924	17.911	4.890	6.852	36.173	0.629
M15	1.272	14.031	2.847	5.215	13.366	0.497
M16	1.654	13.846	1.746	5.569	18.344	0.534
M17	1.783	16.410	7.917	5.196	25.642	0.456
M18	0.939	9.341	2.379	4.647	3.975	0.374
M19	2.329	17.311	1.277	7.555	32.453	0.682
M20	1.397	14.770	1.754	6.120	10.223	0.585
M21	2.169	16.433	3.883	7.358	31.458	0.608
M22	1.227	17.565	3.367	5.520	15.537	0.487

M23	2.253	21.700	2.006	6.915	39.127	0.638
M24	1.826	17.403	5.066	5.409	30.094	0.486
M25	2.406	19.182	2.727	8.348	50.271	0.713
M26	1.979	20.684	3.202	7.447	28.160	0.683
M27	0.518	14.677	1.279	2.717	0.000	0.278
M28	1.832	13.823	6.215	4.593	18.030	0.433
M29	2.015	13.130	5.313	6.372	34.264	0.528
M30	1.881	15.902	4.582	6.287	26.901	0.541
M31	1.202	11.582	2.114	3.713	7.781	0.335
M32	2.036	14.262	3.442	6.664	29.160	0.580
M33	1.555	17.588	2.381	6.108	17.016	0.495
M34	1.805	15.925	3.101	6.494	22.305	0.573
M35	1.307	14.031	2.455	3.590	19.823	0.359
M36	1.793	20.291	3.321	6.970	38.345	0.662
M37	1.428	12.136	3.445	4.606	9.047	0.380
M38	2.143	18.628	2.935	6.410	37.598	0.687
S1	1.577	12.136	7.561	8.815	29.037	0.468
S2	1.412	13.638	5.811	8.130	17.222	0.437

4.3. Fingerprinting the Montelabate amphorae

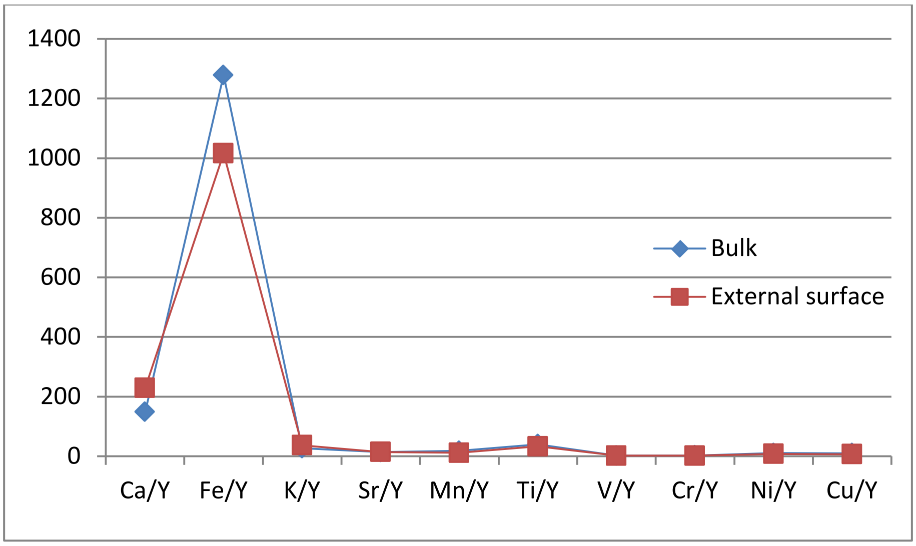
The net intensity of the XRF peaks of different elements was extracted for each sample which allowed the identification of the relative composition through the reported calibration curves. The following elements have been recognized in every sample: Al and Si are abundant in clay composition, but light elements are poorly detected unless operating under vacuum. Therefore, low intensity peaks are usually obtained, especially for Al. K and Ca were abundant elements, as expected, with intense peaks showing marked variability with provenience and surface analysed (external surface or internal section).

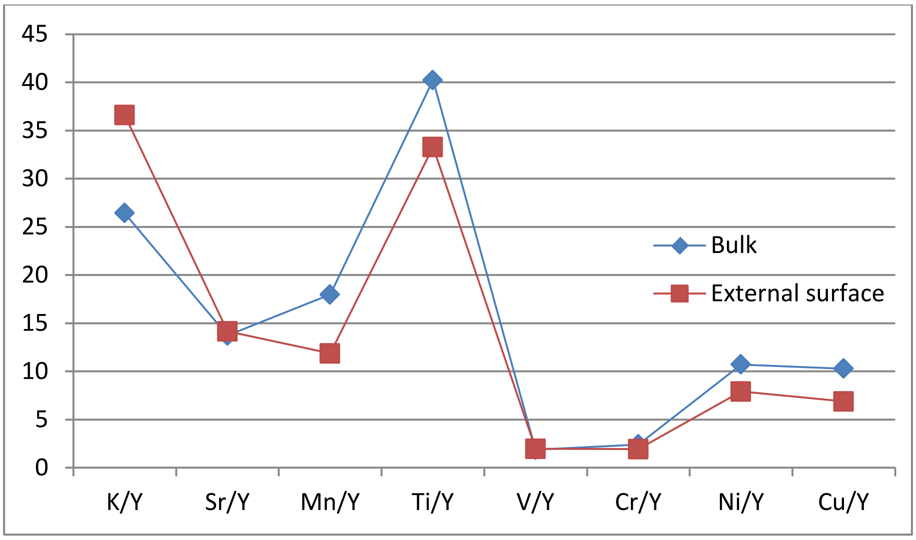
Ti, V, Cr and Mn were minor peaks usually correlated to Fe, in particular Ti, the attribution of the latter is relatively uncertain being very similar to the escape peak (ESC) of Fe. Mn showed some variability, also correlated with colour. Fe was the most intense peak, showing wide variations depending also in this case from provenience, type of clay and the analysed section. Ni, Cu and Zn were minor elements without any significant features for the purposes of fingerprinting. Rb, Sr, Y and Zr were regularly present. The former was not considered significant due to similarity with the sum peak of Fe. Furthermore, Y and Zr did not vary appreciably. By contrast Sr was very sensitive to the geographic provenience of the amphorae and or fabric.

The net intensities of each significant element's peak were extracted in order to compare them systematically to achieve fingerprinting of the Montelabate production. In the database, the raw dataset was recorded in terms of the object type, provenience and sampling date. The extracted data were automatically elaborated as intensity ratio between selected elements or ternary groups for multivariate analysis. In the database, the most significant elements identified for the fingerprint of the Montelabate production were selected in order to determine the elements ratio on the external surface and sections of the samples, i.e. K, Ca, Fe, Sr, Mn, Ti, V, Cr, Ni, Cu were factored by Y, Zr, Fe or Ca. The results were plotted using simple binary or ternary diagrams.

The section of every sample was richer in all the elements with the exception of K and Ca. The two latter elements were more abundant on the surface, possibly as a result of the firing process or due to the secondary deposition in the kiln in the dump of ash. To confirm this hypothesis, analysis was also made of some of the samples of ancient raw clay used as daub in the Etruscan settlement of Col di Marzo, excavated close to the area of the Roman kilns. The results reveal a perfect overlapping of the spectra confirming that the chosen elements were part of the raw clay for the amphorae production and not added as temper by the potter. Therefore, this method of elements internal ratio analysis has proved consistent to fingerprint any given ceramic production and the optimal results were achieved on sections.

Fig. 7: Example of representation of samples composition based on elements ratio. The composition is compared between the external surface and an internal section or bulk.





This method proved useful for clustering the different groups of amphorae (a similar approach was used on clay cuneiform tablets by (Goren et al., 2011)).

In order to understand which elements are correlated between each other, correlation matrixes were built, which can be exemplified by the following examples and graphics (Fig.8). The average peak intensity $I_{i,av}$ (or composition if rielaborated through the calibration curves) of every element has been calculated for a given set of objects, *e.g.* amphorae, section, Montelabate site by averaging out the single net intensities of that element's peak for every sample (I_i). ΔI_i has been calculated as:

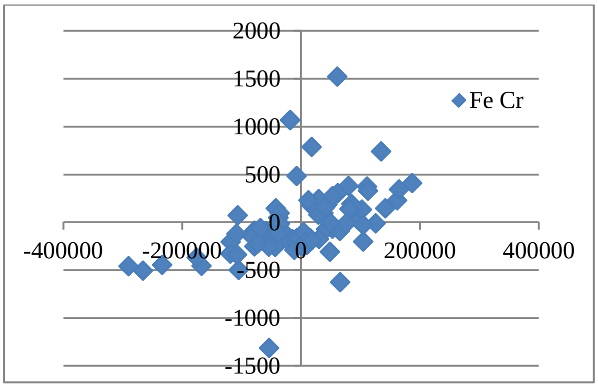
$$\Delta I_i = I_i - I_{i,av}$$

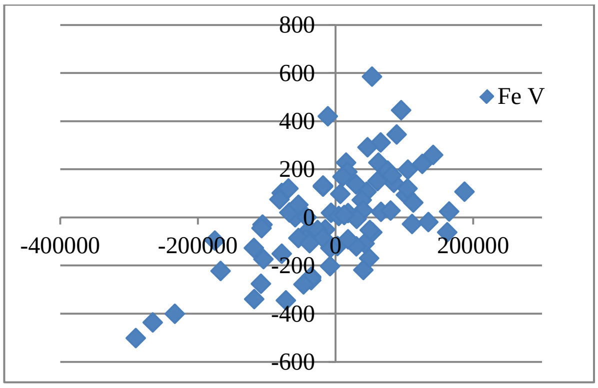
Correlation plots collect ΔI_i vs. ΔI_j valued for the selected object, i and j being two different elements. By focusing on section samples of Montelabate's amphorae, the following correlation plots require discussion.

When plotting ΔI_{Fe} vs. ΔI_{Cr} (Fig. 8*a*) it is possible to observe that Fe and Cr increase at once. The same can be concluded for other elements, such as Fe with V, Y, Co (Fig. 8b-d), Cu, Ni (Fig. 8e,f), Ti (although very near to the *esc* peak of Fe, Fig. 8g), K (Fig. 8h).

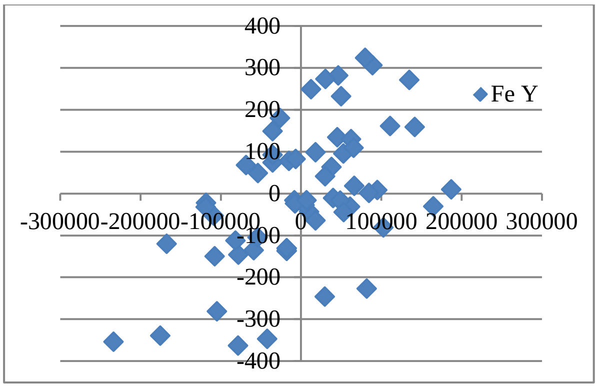
Fig. 8: Examples of correlation plots between Fe and other elements. ΔI_{Fe} reported on the x-axis in correlation with a) ΔI_{Cr}; b) ΔI_V; c) ΔI_Y; d) ΔI_{Co}; e) ΔI_{Cu}; f) ΔI_{Ni}; g) ΔI_{Ti}; h) ΔI_K.

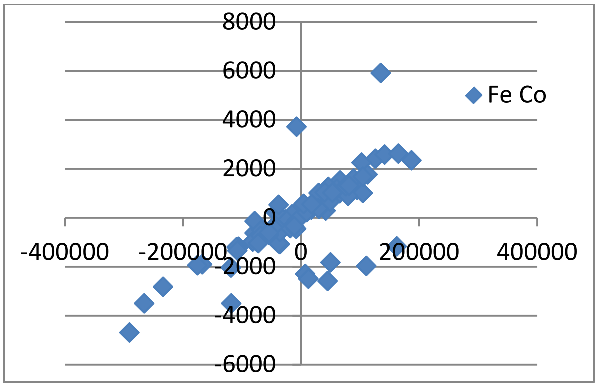
a) b)


Fe Cr
2000
1500
1000
500
0
-500
-1000
-1500
-400000
-200000
0
200000
400000

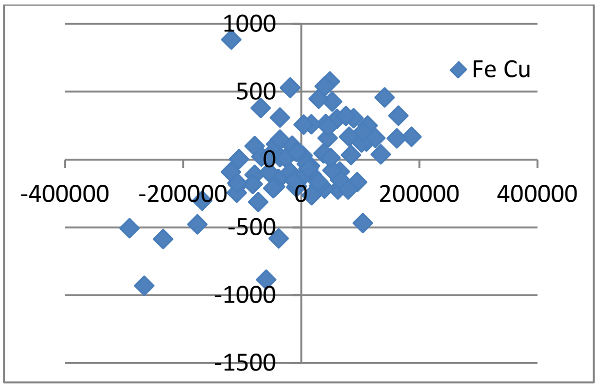

Fe V
800
600
400
200
0
-200
-400
-600
-400000
-200000
0
200000

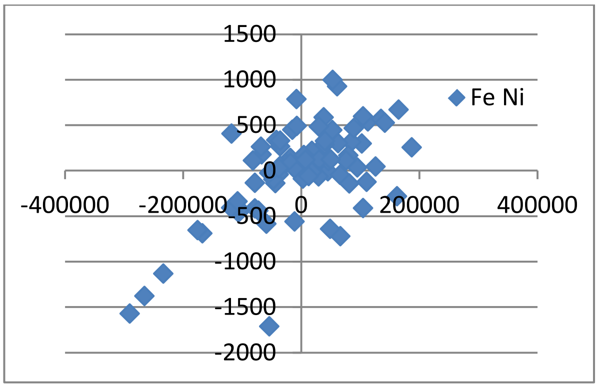
c) d)


Fe Y
400
300
200
100
0
-100
-200
-300
-400
-300000-200000-100000
0
100000 200000 300000

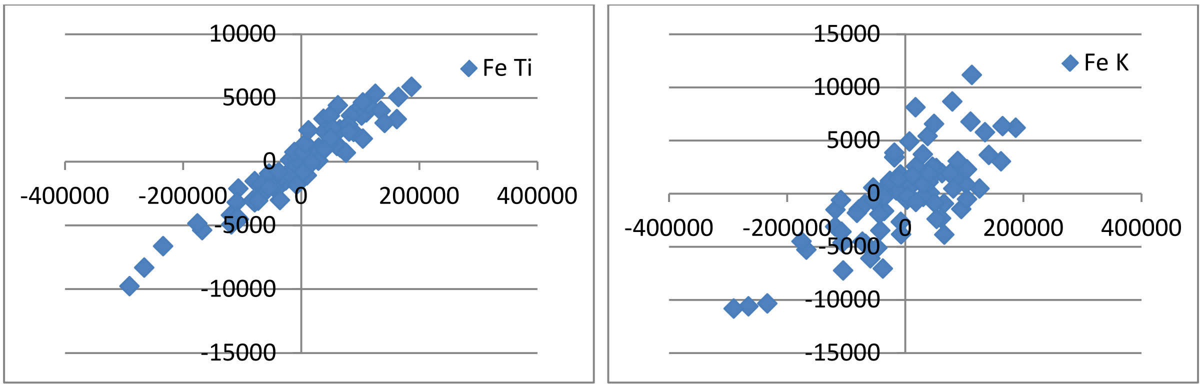

Fe Co
8000
6000
4000
2000
0
-2000
-4000
-6000
-400000
-200000
0
200000
400000

e) f)


Fe Cu
1000
500
0
-500
-1000
-1500
-400000
-200000
0
200000
400000


Fe Ni
1500
1000
500
0
-500
-1000
-1500
-2000
-400000
-200000
0
200000
400000

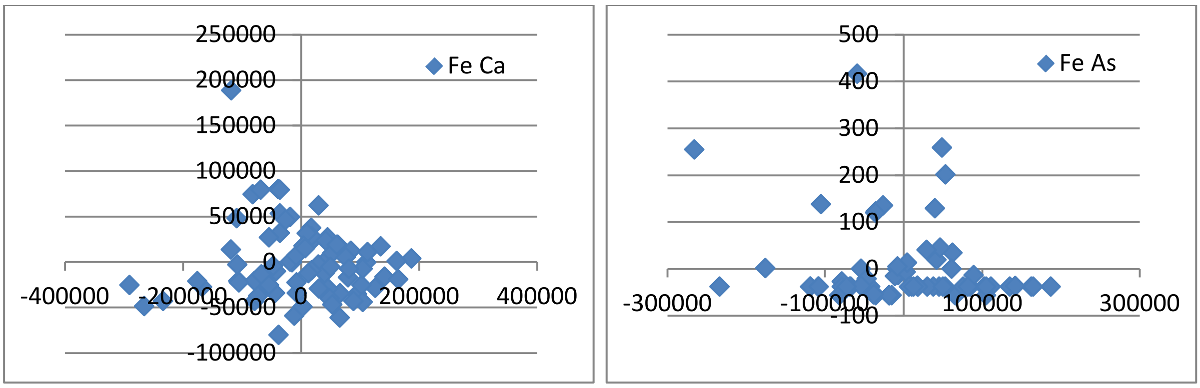
g) h)



Conversely, other elements do not seem correlated between each other. For instance, looking at ΔI_{Fe}, it seems rather independent from Ca (Fig. 9a), which is often reported as added to the fabric[8]. Additionally, Fe does not seem correlate to a signal at 10.5 keV circa, which may be indicative of the presence of As (line K) or Pb (line L) (Fig. 9b). The latter interpretation is supported here, since Pb could be pollution in the clay refinement. Accordingly, Mn and Fe or Cr are not correlated[9] (Fig. 9c,d).

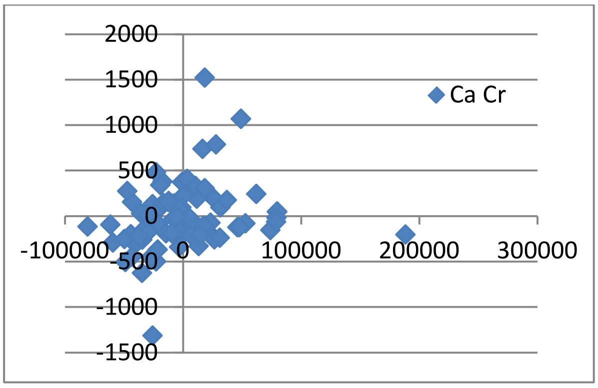
Fig. 9: Correlation plots between a) ΔI_{Fe} and ΔI_{Ca}; b) ΔI_{Fe} and $\Delta I_{As/Pb}$; c) ΔI_{Ca} and ΔI_{Cr}; d) ΔI_{Mn} and ΔI_{Cr}.

a) b)

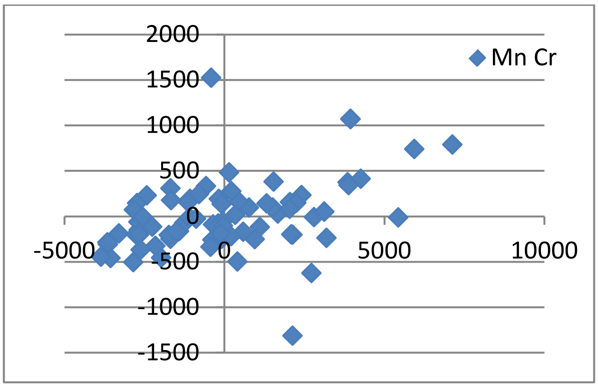


[8] For instance at Scoppieto in Umbria, for coarseware production it was employed a clay with high content of calcite (Calcium carbonate $CaCo_3$) with a percentage higher than 7-8% (Peinado Espinosa, 2015, 59).
[9] Although (Hunt and Speakman, 2015, 367), suggest that for Cr can only be performed a semi-quantitative analysis of archaeological ceramics, as the pXRF is not reliable for this element.

c)



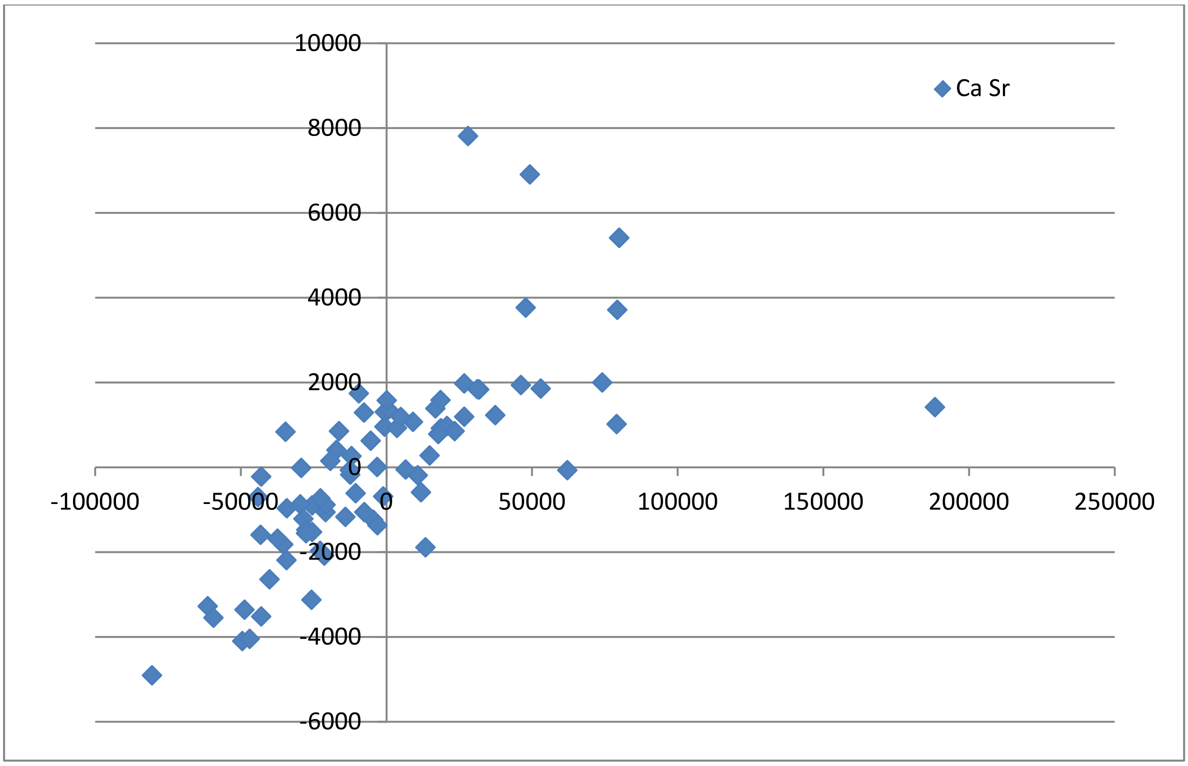
d)



Based on these considerations we have identified a set of elements, Fe/Y/K/Cr with a highly correlated concentration between each other in the Montelabate amphorae, which can represent the typical composition of the local clay used for production. Other elements, such as Ca and Pb, can be identified as typical of the Montelabate fabric. It is also possible to identify Sr as a minor element with an interesting variability. It did not seem correlated to the clay components, but predominantly to Ca (Fig. 10). Therefore, it can be interpreted as an alkali-earth impurity of the Ca-based additive used during manufacturing.

The future research will focus on sampling coarseware production as well as the raw clay at Montelabate. Concurrently, a representative selection of fragments have also been subject to petrographic analyses. The preliminary results of the study of the amphorae of Montelabate revealed a coarse grain texture characterised by oxide clay groundmass with a mineralogical composition consisting of angular and subangular quartz, crystallised volcanic rock, mica and feldspar.

Fig. 10: Correlation plot between ΔI_{Ca} and ΔI_{Sr}.



4.4. Comparison with amphorae from different sites.

In order to validate the results, the selected element intensity ratios based on amphorae provenience were clustered to fingerprint the production in the area of Montelabate of amphorae, found in different sites.

As discussed above, some elements were attributed to the natural clay, others such as Ca, Sr and Pb to manufacturing. By comparing the net intensity and intensity ratio between couples of elements, indicators of local production were searched. A first example was formed by Fe and Cr, which are attributed to the clay composition. Fig. 11 reports the Fe/Cr peak intensity ratio for amphorae found in different sites considering the sections (a) and external surfaces (b). It is evident that for the whole samples list from Montelabate, the values varied between ca. 250 and 750. Samples found in Ardea were partly included in the given intensity ratio, partly not (higher and lower values), whereas the samples found in Segni definitely did not match the intensity ratio range identified in the Montelabate site. The same method was applied to other significant intensity ratios, such as K/Cr (Fig. 12)

Fig. 11: Fe vs. Cr peak intensity ratio for amphorae found in different sites. Sections only .

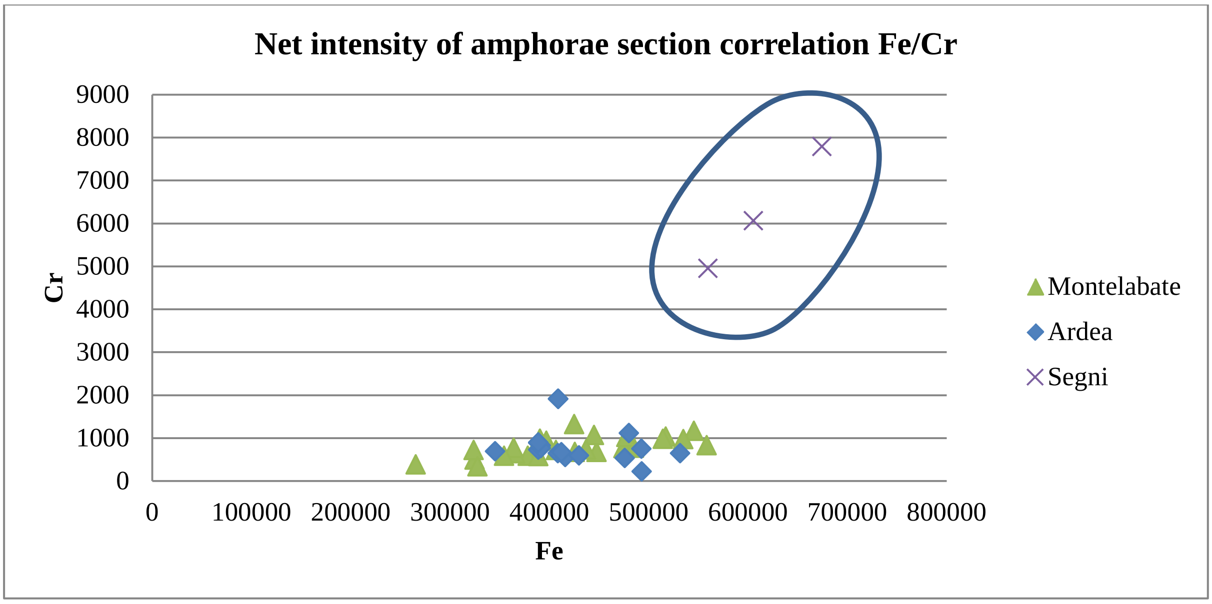
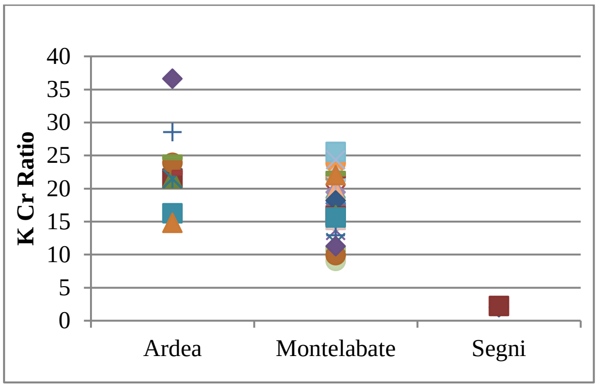
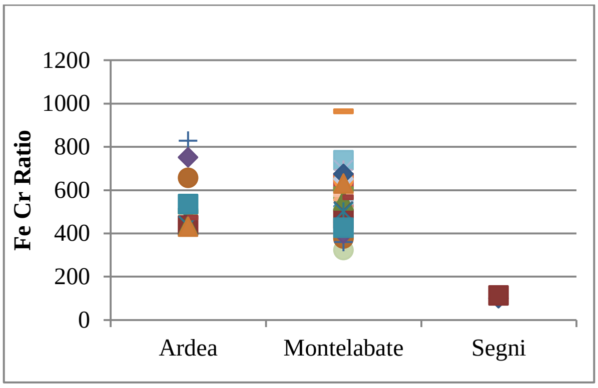


Fig. 12: Significant element intensity ratios clustered by site: a) K/Cr, section; b) Fe/Cr, section; c) Fe/Cr external surface; d) Ca/Cr, section; (e) Ca/Cr, external surface, f) Mn/Cr, section.

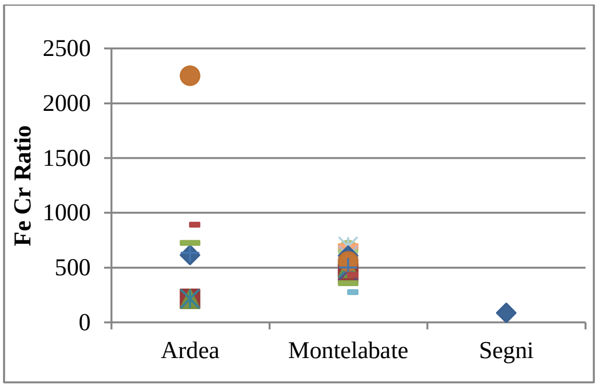
a)



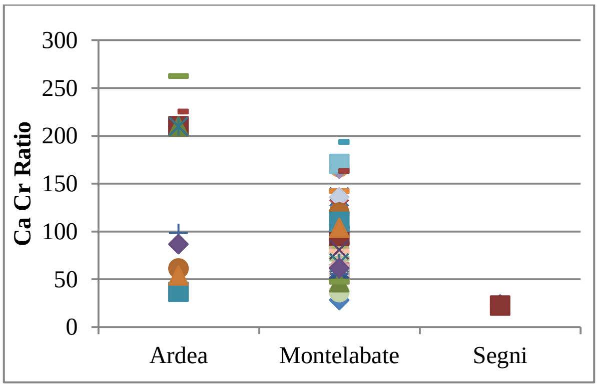
b)



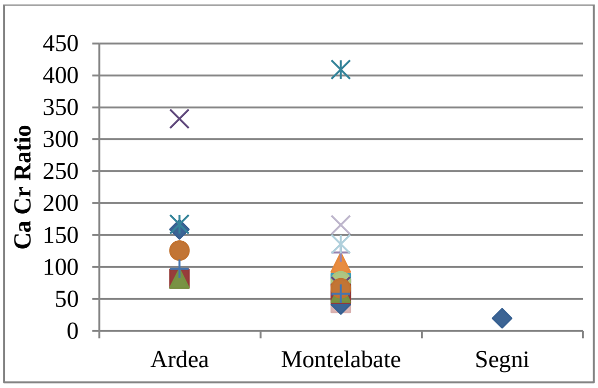
c)



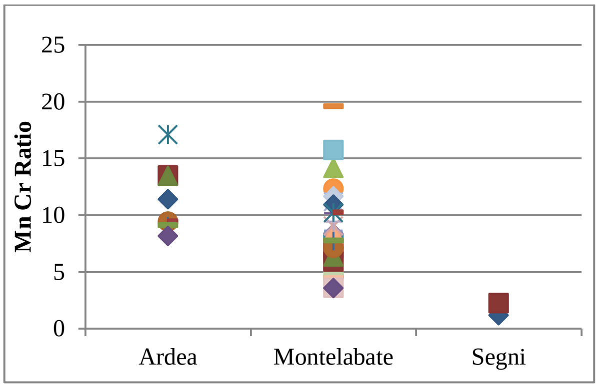
d)



e)



f)



Applying this method it is possible to identify a specific composition trend for the amphorae from Montelabate, characterised by clustered values of the intensity ratios of relevant elements. Some of them were typical of the clays used for ceramics production, other elements were added during manufacturing.

Therefore, by considering only the ratio between peak intensities it is possible to distinguish the main components which characterise the Montelabate production and to obtain a possible composition range which enables the distinction of amphorae produced in this site from other production areas. This represents a solid methodology as it is independent from the availability of the calibration standards, the spectra collection parameters and all those factors influencing the peak intensity of a single element.

5. CONCLUSION

The research presented in this paper aimed to develop an application of a non-destructive analytical method of clay analysis by portable X-ray fluorescence (pXRF). The innovative methodology proposed in this project to fingerprint any given ceramic production is based on the quantification of the internal ratio of the peaks area that when the values are constant indicate a similar composition.

This method is based firstly on the qualitative interpretation of the principal elements of each single spectrum and then, in a customised database, the intensity ratio of the elements is correlated to overcome the limits of each single reading. It allows identifying correlated peaks through a correlation matrix. Couples of elements that have significant variation are used as indicators of fabric nature, provenance and composition. For quantitative analysis, due to the lack of "off-the-shelf" calibration standards for ceramics, feldspars and clays with known composition were used to calculate the absolute amount of the components.

Applying this method has been possible to identify the local production of the Montelbate workshop, even if the amphorae fragments revealed many differences in the fabrics: some samples having a red fabric, hard when properly fired but generally the surfaces are soft and porous. The surface and breaks have the same colour and occasionally the grey core suggests an uneven firing temperature. Several examples have a hard grey vitrified surface. Other samples present a more refined reddish-yellow fabric. The surface is lighter in colour than in the breaks. Therefore, both morphologically and in colour of fabric the Montelabate amphorae differ greatly, however the chemical analyses have proved that they are produced with similar clay and temper.

The results have important archaeological implications because the kilns that have been excavated at Montelabate are the only certain site for the production of the flat bottomed wine amphora in the *Regio VI* (Umbria) and by assessing the technology of its production, it offers a model to study the ancient economy and the network of exchange, identified by a scientific method.

AKNOWLEGMENT

A special thanks to the McDonald Institute for Archaeological Research, University of Cambridge and Department of Chemistry, Università degli Studi di Milano for the use of the equipment and the laboratory.

We are really grateful to Dott. Francesco Di Mario and Dott. Alessandro Betori, Soprintendenza Archeologia del Lazio e dell'Etruria Meridionale for granting the permission to conduct the analysis on the sites of Ardea and Segni.

Fundamental is the support of Dott. Davide Maccaferri, Sibelco, Viale Dino Ferrari, 75/83, Maranello (MO), Italy, and of I.MA.F. SPA, Via Mulino Dionigi n. 2, Dorgola di Carpineti (RE), Italy, for providing their calibrated feldspars, sands and clays to test the instrument calibration.

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