Original Study

Anna M. Gueli, Antonio Delfino, Emanuele Nicastro, Stefania Pasquale*,
Giuseppe Politi, Antonella Privitera, Sofia Spampinato, Giuseppe Stella

Investigation by pXRF of Caltagirone Pottery Samples Produced in Laboratory

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Abstract: In the study of archaeological ceramics, it is important to have compositional data to identify their origin and source. The fabric also provides useful information on the production technology, especially with regard to the firing steps. The work presented here is connected to this field and focuses on the main parameters related to the terracotta artefacts preparation. Thus, one can consider the effects in terracotta characteristics of different raw materials and firing parameters, in particular for pottery of Caltagirone, which is one of most important centres of pottery production in Italy, active since the Neolithic. To this end, terracotta samples have been reproduced in a laboratory setting according to the ancient procedure of Caltagirone manufacture, starting from clay and degreaser extraction in local historical sites. The analysis was conducted using a portable X-Ray Fluorescence (pXRF) spectrometer for elemental characterization of sand degreaser and of clays during each step of the realization process and in different firing conditions. SEM-ED techniques were also employed to verify the method and results for some of the samples after firing process. Framing the technological context of manufacture production, known in the specific case, it is also possible to identify potential outcomes and limits in the study of potsherds using pXRF technology, in applying the methodology to historic artefacts.

Keywords: archaeology; pottery; pXRF; SEM-EDS; Caltagirone (Sicily)

1 Introduction

In Sicily, pottery production started in prehistoric times, continuing without significant pause through the Roman and medieval periods, and remaining active today. Such an extensive ceramic industry can be associated with the presence of rich, exploitable clay deposits, as well as the expertise developed by local craftsmen over the centuries. Historically, the most important production sites have been those at Caltagirone, Palermo, Sciacca, Trapani and Santo Stefano di Camastra. Systematic scientific studies of Sicilian pottery from these sites have been carried out with the aim to classify local production in terms of manufacturing techniques and raw materials. To this end, in recent years, research has focused on expanding the existing database characterizing pottery made from Sicilian clayey raw materials (Alaimo et al., 2004a, 2004b; Aquilia, Barone, Mazzoleni & Ingoglia, 2012).

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***Corresponding author: Stefania Pasquale,** Department of Physics and Astronomy, Catania University & INFN, S. Sofia 64, I-95123 Catania, Itay, E-mail: stefania.pasquale@ct.infn.it
Anna M. Gueli, Giuseppe Politi, Giuseppe Stella, Catania University & INFN, Catania, Italy
Antonio Delfino, Emanuele Nicastro, Art Institute "Luigi Sturzo", ex Matrice 153, 95041, Caltagirone (CT), Italy
Antonella Privitera, Sofia Spampinato, Catania University, Catania, Italy

Investigations of Sicilian pottery have also considered their circulation throughout the Mediterranean and the reconstruction of ancient commercial routes. With regards to this area of research, the distinction between autochthonous and imported pottery is important, but remains an open question (Alaimo, Giarrusso & Montana, 1998, 1999; Alaimo, Giarrusso, Iliopoulos & Montana, 2002).

In this framework, studies of Caltagirone pottery can contribute to a more thorough understanding of Sicilian production. In fact, Caltagirone was one of the region's most significant cultural and commercial sites, thanks to its central location between the southern and eastern coasts of Sicily. Pottery production in the area has proceeded without interruption from the Neolithic to the present day (Ragona, 1949, 1955, 1985; Leinghton, 1983; Maniscalco, 1999; Barilaro, et al., 2005). Several research projects have systematically analyzed Caltagirone ceramic production through full non-destructive characterization of both bulk and decorated coating (Barilaro, et al., 2005, 2007, 2008; Casaletto, Chiozzini, De Caro & Ingo, 2006; Crupi, et al., 2010).

The research presented here focuses on the compositional characteristics of the raw materials used in Caltagirone pottery. The challenge in undertaking such an investigation is connected with the geological position of the city. Caltagirone is situated on three calcareous, clayey hills, occupying the southern slopes of the Erean Mountains. The lithotypes that characterize the area include: the *gessoso-solfifera* series, which is mainly represented by gypsum deposits; the Trubi formation of the Late Pliocene age; the clayey marls formation of the Middle to Late Pliocene age; and the marly and silty clays formation of the Late Pleistocene age (Alaimo, et al., 2002; Di Grande & Giandinoto, 2002).

The clays used in the Caltagirone area are thus of the Quaternary Period (Pleistocene) and blue-grey in colour, or belonging to the Mid-Early Pliocene with a more intense blue hue, finer, and more plastic and malleable (Wezel, 1964). The two kinds of clays were, for this reason, used in distinct types of terracotta production, the first (Pleistocene clays) for rougher material and the second (Pliocene clays) for finer ceramics (Ragona, 1991).

The earliest clay sourcing site for the region has been identified in the upper part of the San Giorgio mountain in the northwest of Caltagirone (Figure 1). The clay sediment found there was formed during the Pleistocene, in a marine environment. A second site has been identified nearby in the *Lazzaretto* area where the man-made Conadomini furnace (Figure 1) was active with clay dated to the Mid-Early Pliocene, (Ragona, 1949, 1985; Alaimo, et al., 2002).

The goal of the present work is the chemical characterisation of clays used for Caltagirone pottery and the study of pottery production processes in order to assess any variations in terracotta composition attributable to raw materials or firing parameters. With this aim, terracotta samples were made using ancient methods typical of Caltagirone ceramics, with clays taken from the above-mentioned sites of Monte San Giorgio quarry and the San Lazzaretto area. Even for sand, used as degreaser, the Caltagirone traditional manufacturing process was followed, sampling raw material from quartz-sandstones outcrop at Monte Stagno (Figure 1)—namely the Della Gatta site (Wezel, 1966) near Mirabella Imbaccari, San Michele di Ganzaria, and San Cono.

This research project stems from a collaboration between the Dipartimento di Fisica e Astronomia dell'Università degli Studi di Catania and the Istituto d'Arte per la Ceramica "Luigi Sturzo" of Caltagirone, the latter having a significant role in the preparation of terracotta samples. The aim is to study multiple aspects connected to clay manufacturing and firing, by using different analytical methodologies. The results presented in this article are then part of a wider research study.

The chemical characterization of samples was performed by portable X-Ray Fluorescence (pXRF), which in recent years has become more commonly used for the study of archaeological ceramics (Forster, Grave, Vickery & Kealhofer, 2011; Hunt & Speakman, 2015; Tykot, 2016). A major advantage of pXRF is that instruments can be transported to study objects in situ, thereby permitting multi-element analyses of archaeological materials in non-traditional laboratory environments. However, archaeological applications of pXRF are still today an object of discussion (Liritzis, & Zacharias, 2010; Tykot, et al., 2013), principally because of a perceived lack of analytic rigour (Shackley, 2010, 2012; Grave, Attenbrow, Sutherland, Pogson & Forster, 2012; Speakman & Shackley, 2013; Frahm & Doonan, 2013).

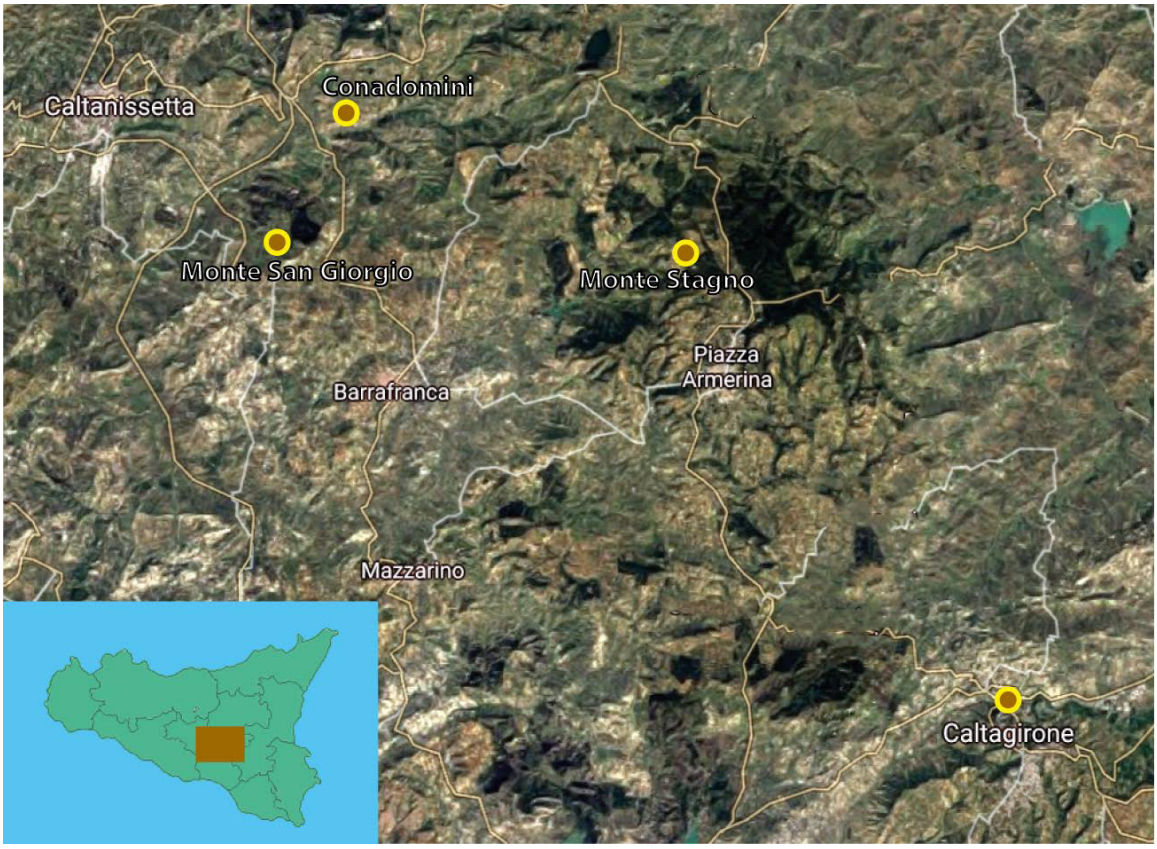

Figure 1. Geographical location of the sampling sites for the clays and quartz sand degreaser.

The present work contributes to this debate regarding pXRF through the study of Caltagirone pottery raw materials. Recently, similar studies undertaking chemical analysis of pottery have been performed using samples derived from Italian archaeological sites (Barone, et al., 2011; Donais, Wojtas, Desmond, Duncan & George, 2012; Bonizzoni, Galli, Gondola & Martini, 2013; Ceccarelli, Rossetti, Primavesi & Stoddart, 2016).

Concerning the effect of pottery firing conditions on bulk elemental compositions, there are many examples of studies that have used XRF, as well as other techniques (Cogswell, Neff & Glascock, 1996; Perlman & Asaro, 1969; Poole & Finch, 1972; Attas, Yaffe & Fossey, 1977; Kilikoglou, Maniatis & Grimanis, 1988; Storey, 1988; Maritan, et al., 2006; Bonizzoni, et al., 2013). In some studies considering the effect of changes in firing temperature on microstructure and physical properties of clay, XRF has been used for bulk chemical analyses (Cultrone, Rodriguez-Navarro, Sebastian, Cazalla, & De La Torre, 2001; Eramo, Laviano, Muntoni, & Volpe, 2004; Kurama, Kara, & Kurama, 2006; Johari, Said, Hisham, Bakar & Ahmad, 2010).

In order to explore colour and surface morphology of the pottery, most of the samples were also studied using SEM and spectrophotometric analysis. The main results of these investigations will be presented elsewhere; however, some information obtained via SEM-ED analysis will be referenced in this work.

2 Materials and Methods

2.1 The Samples

As noted above, the samples were prepared using raw materials obtained from historic quarries in the Caltagirone area, with the production process closely modelled upon presumed traditional techniques (Alaimo, et al., 1974; Fabbri, Fiori & Ravaglioli, 1989; Cuomo di Caprio, 2007).

Different samples with various fabrics (including both clays and degreaser) were made, and these samples were then prepared under varying firing conditions.

For clays, raw materials were collected from two quarries fallen into disuse—those at Mt. San Giorgio (SGA sample) and at Lazzaretto (CDB sample) on the northern side of Caltagirone. The quartz-arenite sand used as degreaser was sourced from the Della Gatta site at Mt. Stagno—whose name derives from the tin ("Stagno") content of this sand.

The research work, from extraction at the quarry to the firing steps, was divided into several phases following traditional processes.

After clay collection, the first phase consists of the barbotine preparation after a clay sedimentation of 1-2 weeks. Afterwards, the barbotine was sieved to remove organic substances or any other impurities.

The second step in this phase was only completed for half the sample of each clay type, while the remaining half was left untouched. Thus, four different mixtures were produced for this study:

- Mt. San Giorgio clay, not sieved, identified by the code SGA1;
- Mt. San Giorgio clay, sieved, identified by the code SGA2;
- Lazzaretto clay, not sieved, identified by the code CDB1;
- Lazzaretto clay, sieved, identified by the code CDB2.

After eliminating the excess water remaining from the mixing phase, the clay dough was kneaded, beat, and adjusted for plasticity before being left into water for about 10 days.

In order to increase sample variability, quartz sand was added in different proportions to half of the mixtures indicated above:

- Clay SGA1 + 10% (wet weight) sand → sample SGA3;
- Clay SGA2 + 10% (wet weight) sand → sample SGA4;
- Clay CDB1 + 30% (wet weight) sand → sample CDB3;
- Clay CDB2 + 30% (wet weight) sand → sample CDB4.

Samples of 2 cm for each side were produced and identified by alphanumeric codes according to the series and to firing conditions.

Firing took place in an electric oven. It was carried out by experimental firings with different heat treatments for the maximum temperature, from room temperature up to the maximum temperature, for maintenance of the maximum temperature rates.

The first selected temperature was 400°C. From here, investigations proceeded with a series of intermediate firings, with steps of 100 °C, up to the achievement of high temperatures (1100°–1200 °C). A total number of 15 firing conditions were obtained for each series, giving a total number of 128 samples to be examined.

Results in this paper concern only a subset of the samples, focusing on those fired at 400°C for 16 hours (code 2) and at 900°C for 22 hours (code 12)—the former chosen to simulate a rudimentary technology and the latter to represent a standard temperature used in terracotta production.

The analysis of 12 samples, illustrated in Table 1, is discussed below.

2.2 pXRF

The instrument used in the course of these investigations is the ASSIGN Lithos 3000, shown in Figure 2, a portable X-ray fluorescence spectrometer ideal for *in situ* analysis without sample preparation.

This type of instrument is routinely used in analysis of several archaeomaterial types—for example, pottery (Bonizzoni, Galli & Milazzo, 2010), bronzes (Bonizzoni, Galli & Poldi, 2008), wood (Franceschi, Cascone & Nole, 2008) and paintings (Bonizzoni, Galli, Poldi & Milazzo, 2007).

The X-ray source is equipped with a conventional Molybdenum tube, operating at a maximum acceleration voltage of 30 kV and a maximum current of 0.5 mA. The detection system includes an energy dispersive detector that is 600 μm thick, with 7 mm^2 of active area and a resolution of 160 eV at 5,9 keV. The pointing system relies upon a laser interferometer, which measures the distance between instrument and sample. This system allows the positioning of the firing point within a ±15 μm margin.

Table 1. *Monte San Giorgio* (SGA) and *Lazzaretto* (CDB) samples without firing and at different firing temperatures.

	***Monte San Giorgio* series**		
SGA1			
SGA4			
	***Lazzaretto* series**		
CDB1			
CDB4			
	Code 0 Without firing	Code 2 Slow firing 400° C	Code 12 Firing 900° C

Figure 2. Picture of the X-ray spectrometer ASSIGN Lithos 3000.

2.3 SEM-EDS

The Scanning Electron Microscope (SEM) used for sample investigation is a FEI Quanta 400 FEG (Field-Emission-Gun). It enables imaging in three modalities: high vacuum, low vacuum, and E-SEM (Environment-SEM) mode. It is designed to provide the maximum amount of data (imaging and microanalysis) for any samples and it does not require sample preparation.

Microanalysis was performed with an Energy Dispersive (EDS) detector, associated with the SEM.

3 Results and Discussion

3.1 ED-XRF Analysis

The results of X-ray fluorescence studies on quartz sand and on some samples of the SGA1, SGA4, CDB1, and CDB4 series are reported, using additional codes 0 (without firing), 2 (firing at 400° C) and 12 (firing at 900° C). All measurements were captured with an X-ray tube setting of 25 kV and 100 μA, for an acquisition time of 1500 sec for sand samples and 1200 sec for pottery. The X-ray peak intensities, reported in the following tables, are normalized according to measurement time. Sampling depth of the XRF technique in a portable configuration is not easy to control. Thus, the information obtained from the analysis comes not only from the surface but also potentially from the underlying layers. Penetration depth depends strictly on the elemental composition of the surface—heavy elements will tend to limit penetration, while light elements will allow greater penetration.

The first set of measurements come from the quartz-*arenite* sand characterization.

The investigations were made at four different points on the sample's surface. The semi-quantitative information about chemical composition deduced from the Kα peak intensities of each element identified in the four X-ray fluorescence spectra are reported in table 2; however, standard statistical errors must be considered.

Table 2. K_α peak intensities of different elements identified in the four measurement points of the quartz sand. Standard statistical errors have to be considered.

Elements	Energy Kα (keV)	Intensity			
		Point 1	Point 2	Point 3	Point 4
Si	1,740	30	45	67	30
S	2,309	17	14	18	16
K	3,314	257	187	183	216
Ca	3,692	102	93	155	150
Ti	4,512	303	176	176	200
Cr	5,415	59	68	59	77
Mn	5,900	89	133	104	122
Fe	6,405	525	931	1482	1315
Cu	8,046	145	103	103	116
Zn	8,637	-	-	-	122
Sr	14,165	-	127	134	-

The four points present essentially the same behaviour with some difference in the concentration of certain elements, probably due to some local heterogeneities. The sand from the Della Gatta site was known to contain small quantities of tin (Sn). According to oral tradition, the sand collected in this area was also used for the production of an opaque, glassy coating composed of tin dioxide. The Sn Kα peak is typically found at 25.27 keV, but the measurement was set at 25 eV and it has not been possible to fully detect it. The instrument used had some limitations at this peak. Difficulties were also encountered in the identification of peaks relating to Lα (3.414 keV) and Lβ (3.929 keV) emissions of Sn, as is shown in Figure 3, due to the simultaneous presence of calcium and potassium, whose energies fall in the range of Sn peaks. This case of ambiguity in identification due to the peak overlap can be considered a pXRF limit.

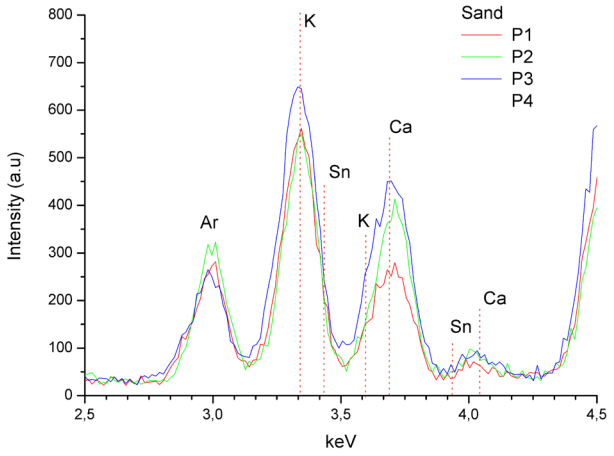

Figure 3. Zoom of XRF spectrum in the energy region of Sn L_α and L_β emissions for the four measurement points of quartz sand. Argon peak is related to atmosphere.

After the sand, a specific analysis was performed with Mt. San Giorgio, SGA1_0, and Lazzaretto, CDB1_0, clay samples that have not been subjected to sieving or had degreaser added. The two fluorescence spectra present a very good match as shown in Figure 4. The semi-quantitative results regarding element concentration are presented in the first two columns of table 3.

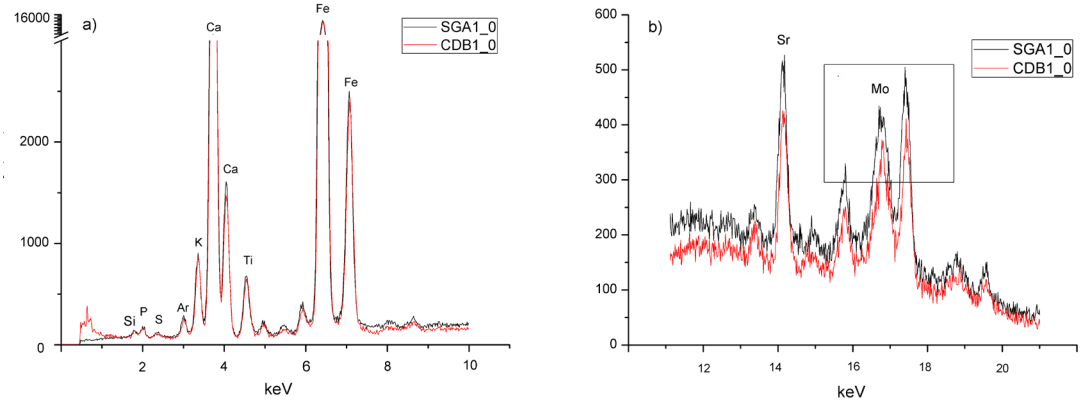

Figure 4. Comparison between the X-ray Fluorescence spectra of selected clays, not purified nor sieved: SGA1_0 and CDB1_0, in the energy regions 1-10 keV (a) and 10-20 keV (b). The three peaks in the high energy region come, in order of decreasing energy, from Rayleigh diffusion, Compton scattering and escape peak of anode Mo.

Table 3. K_α peak intensities of the two clays (SGA and CDB) before (label 1) and after purification (label 4).

Elements	Energy Kα (keV)	Intensity			
		SGA1_0	CDB1_0	SGA4_0	CDB4_0
Si	1,740	113	114	103	124
P	2,010	153	142	149	179
S	2,309	115	112	92	92
K	3,314	745	634	559	705
Ca	3,692	8480	7263	6941	7673
Ti	4,512	669	550	531	739
Cr	5,415	185	116	137	189
Mn	5,900	356	321	319	398
Fe	6,405	13054	13002	11006	13386
Cu	8,046	241	176	217	216
Zn	8,637	262	225	198	302
Sr	14,165	460	424	159	471

The two clays, despite originating in different geological periods, have the same chemical nature with the same concentrations of major and minor elements.

The result is plausible because the two quarries are located a short distance from one another. Their eventual differentiation would require the application of methodologies that better identify trace elements.

A further step of the study is the evaluation of chemical composition according to the XRF spectra after clay purification and the addition of degreaser. In the last two columns of table 3, the concentrations of different elements are reported for the clay samples with sieving and degreaser addition SGA4_0 and CDB4_0.

As shown by the comparison of element concentration presented in table 3, there are essentially no differences between the untreated samples (SGA1_0, CDB1_0) and those purified or treated with quartz sand degreaser (SGA4_0, CDB4_0). It is possible that in the sieving operation of purification, part of the sand present as a natural degreaser component was eliminated. Moreover, the added degreaser does not contain any chemical-element markers.

Finally, the possible effects of different firing conditions on the chemical composition can be considered by comparing XRF spectra on samples from the same series like SGA4_0/2/12 and CDB4_0/2/12, relative to samples not subject to firing, those fired at 400° C, and those fired at 900° C. An example is presented in figure 5 for SGA4_0 and SGA4_12, while all semi-quantitative results, for the SGA4_2/12 and CDB4_2/12, are summarized in table 4.

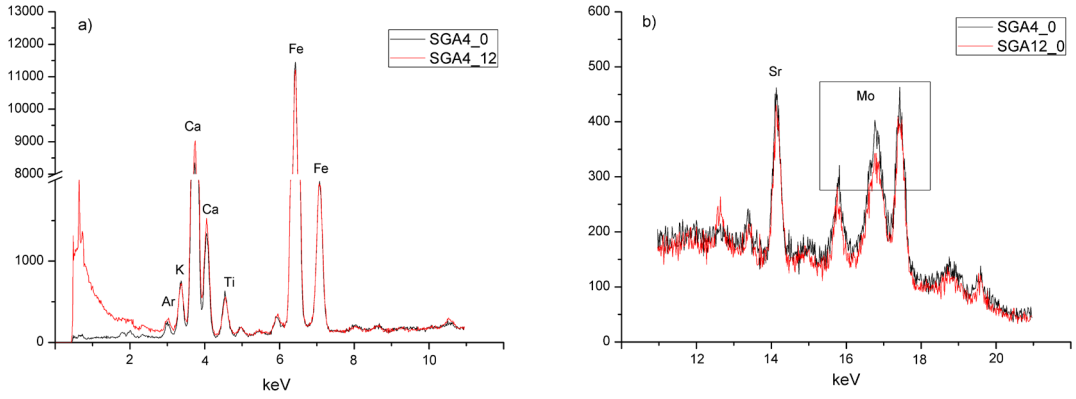

Figure 5. Comparison between the X-ray Fluorescence spectra of clays without firing and with firing at 900° C, SGA4_0 and SGA4_12. The three peaks in the high energy region come, in order of decreasing energy, from Rayleigh diffusion, Compton scattering and escape peak of anode Mo.

Table 4. K_α peak intensities of the samples of the series SGA4 and CBD4 without firing (#_0), cooked at 400°C (#_2) and 900°C (#_12) temperatures.

Elements	Energy Kα (keV)	Intensity					
		SGA4_0	SGA4_2	SGA4_12	CDB4_0	CDB4_2	CDB4_12
Si	1,740	103	73	282	124	120	174
P	2,010	149	77	267	179	134	209
S	2,309	92	93	202	92	101	113
K	3,314	559	610	561	705	713	482
Ca	3,692	6941	8028	7291	7673	7265	6206
Ti	4,512	531	666	472	739	505	496
Cr	5,415	137	157	135	189	149	127
Mn	5,900	319	381	299	398	338	278
Fe	6,405	11006	13213	10583	13386	12970	10594
Cu	8,046	217	192	205	216	194	175
Zn	8,637	198	214	208	302	200	180
Sr	14,165	159	563	386	471	451	373

As expected, from this comparison one can deduce that no remarkable differences occur, or are at least observable, in the chemical composition of samples prepared in different firing conditions, at least for major and minor components.

The observed differences could be probably ascribed to sample heterogeneity as measurements was not performed at the same points for the different temperatures.

3.2 SEM-ED Analysis

A series of SEM analyses were performed on most of the sample with the aim of studying morphological differences related to manufacturing processes. These analyses also provided a set of SEM-ED measurements that can be seen as a qualitative investigation complementary to XRF results (Goldstein, 2003). With the XRF technique, it is difficult to identify any characteristic emissions up to about 1.5 keV due to the detector's low level of efficiency. The microanalysis, on the other hand, allows one to identify a broader range of low atomic number elements.

With respect to the portable technique, microanalysis has not produced a complete recording of fluorescence emission.

From the qualitative results of microanalysis, it was observed that some of the elements (P, Cr, Mn, Cu, Zn, Sr) found in XRF were present.

Their detection is probably due to the size of the investigated area and the depth from which the fluorescence signals are generated in the sample. The extreme focusing of the electron beam produces point analysis. The SEM source directs the electrons towards an extremely small surface area (order of μm^2) compared to the investigation area of about 3 mm^2 in the XRF technique. The SEM microprobe investigation depth is about 10 μm (therefore superficial), while with the XRF technique, the signals are deemed to arise from an infinite background, due to the high penetration power of X-rays. Thus, the electron microprobe is not entirely suitable for analysis of heterogeneous materials, since the information obtained from a single measurement cannot be extrapolated to the entire sample.

Therefore, for full characterization of the samples, various measurements at different locations should be performed, in order to obtain a mapping that unfortunately was not performed with these samples.

However, even with this kind of analysis, focused in the lower energy domain of X-ray emission and consequently on lighter element identification, no remarkable differences are evident in the chemical compositions of the two clays without firing and of the same clay series with different manufacturing processes.

4 Conclusions

The present research work was focused on the study of compositional characteristics of the raw materials used in Caltagirone pottery, as well as its technological production, in order to explore any variations in terracotta composition by changing raw materials and firing parameters. With this purpose terracotta samples were made following methods traditional of Caltagirone ceramics, by using clays and a degreaser sand extracted from local historical sites. Raw materials and samples were characterized with XRF analysis after firing, with a satisfactory result revealing the main chemical elements (Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Sr) present. Some elements characterizing the Caltagirone clay, such as Sn, have not been detected because of the impossibility of distinguishing XRF peaks from other elements. This mischaracterisation can be considered a limitation of this technique in this peculiar case, in addition to the general inability of the method to detect low atomic number elements. Some complementary results were obtained for some samples with another multi-elemental investigation technique, the SEM-ED, having a higher efficiency in the lower energy region of X-ray emission.

The two analyzed clays, even if coming from different geological periods, presented the same chemical nature, with the same concentrations of major and minor elements. Trace determination was not possible with the XRF spectrometer used here.

No remarkable differences, at least for major and minor components, were observed between results from XRF and SEM-ED techniques regarding the chemical composition among raw materials and terracotta samples prepared in different firing conditions.

The use of pXRF for pottery analysis, at least with this particular instrument, appears to be useful for the main chemical analysis, but it probably needs to be coupled to other techniques to provide a deeper look into the changes attributed to manufacturing processes.

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