Università degli Studi di Napoli Federico II

Scuola Politecnica e delle Scienze di Base

Area didattica di Scienze Matematiche, Fisiche e Naturali

Dipartimento di Scienze della Terra, dell'Ambiente e delle

Risorse





DOTTORATO DI RICERCA IN SCIENZE DELLA TERRA, DELL'AMBIENTE E DELLE RISORSE – XXXV ciclo

Ceramic production in the *Ager Calenus* from the 3rd century BCE to the early imperial period

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Academic year 2022/2023

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Abstract

The ancient city of Cales is considered one of the most important production and distribution centers of fine-grained pottery, among the most renowned there is the black glazed ware, a class of fine pottery widely distributed in the central and western Mediterranean (3rd century to the middle of the 1st century BCE). In fact, for centuries the black glazed pottery has been considered the hallmark of Calenian production, thanks to the availability of raw materials close to the city. In such an important manufacturing center of ceramics it is not surprising that the workshops also produced common ware.

In this study, a total of 125 sherds belonging to different ceramic classes divided in two main groups, fine-grained pottery (black glazed pottery, Terra sigillata, fine common ware) and coarse-grained pottery (common cookware, thin-walled pottery, internal red slip ware, large container) recovered at the archaeological site of Cales were studied, along with production indicators.

A multi-faceted analytical approach via minero-petrographic techniques (PLM, XRPD, TG-DSC, FESEM, FESEM-EDS, XRF) was performed in order to discriminate the different Calenian productions in a chronological span between the 3rd century BCE to the early imperial period, in terms of: firing dynamics; provenance of the ceramics and provenance of the raw materials. The collected data allowed us to shed new light on the production activities of the Calenian workshops and document their remarkable continuity over time.

In-depth characterization with the routine analytical techniques used for archaeometric studies has provided the basis for implementing a new geochemical approach using TIMS and MC-ICP-MS, which includes for the first time three isotopic systematics: Sr, Nd and Pb. This method provided stronger feedback both in terms of provenance and clay-temper processing. This pioneering approach does not intend to replace the usual analytical routine that over the years has become a cornerstone for the ceramic characterization, but instead, aims to be a valid support to ceramic archaeometry.

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CHAPTER I

INTRODUCTION AND AIM

SUMMARY: 1.1. Introduction and historical background; 1.2. Archaeological context; 1.3. Aim

1.1. Introduction and historical background

The ancient city of Cales (modern Calvi Risorta) is located in the northern sector of the Campania region of Italy. The city was founded by the Ausoni, one of the oldest Italic people. Thanks to its geographical position Cales had an important strategic function for the Roman control of the *Ager Falernus*, the *Campus Stellatis* and the *Ager Campanus* (Fig. 1.1) (Pedroni, 1993; Ruffo, 2010), the so-called Capuan territory, also known as Campania Felix thanks to the fertile soil of the *Volturnum r*iver that runs through the plain.



Fig. 1.1 Sketch map of Campania Region with older rivers and Roman roads adapted from Grifa et al., 2013.

Cales became a Latin colony in 334 BCE. With the coming of the new colonist in 184 BCE, together with *Teanum Sidicinum*, Cales resumed its prosperity becoming one of the most important cities in the Inner Campania and finally after the Social War in 90 BCE it became a municipium (Ruffo, 2010). The territory of Cales, also known as Ager Calenus, is considered one of the most important production centers of fine-grained pottery, oriented towards the export of tableware. In particular, Cales was renowned for the production and distribution of black glazed ware a class of fine pottery first produced in Greece from the 5th century BCE and later in the western Mediterranean from the end of the 4th century to the middle of the 1st century BCE (Pedroni & Soricelli, 1996). In Cales the beginning of the production of black glazed pottery is probably connected, at least chronologically, with the arrival of the Latin colonists. The black glazed production was gradually replaced in specific areas of the Roman Empire by the so-called Terra sigillata, a class of fine red pottery with glossy slipped surfaces made (Soricelli, 2004).

Following the foundation of the Roman colony in the port of *Volturnum in* 194 BCE (Pedroni, 2001), it is presumed to be connected with the long-distance export of Calenian ceramics, directed mainly to North-Africa and the Iberian Peninsula, started already in the 3rd century BCE, while exchange with southern Gaul became more important in the 2nd and the 1st century BCE. The fine pottery from Cales was widely studied from an archaeological point of view (In particular Pedroni 1986; Pedroni 1990; Pedroni 2001) these studies highlighted the role of Cales in the production of fine-grained pottery and other types of pottery and ceramics in general.

In this regard, the town preserves conspicuous evidence of intense manufacturing activity covering a wide chronological span from the late 4th century BCE to the middle 1st century BCE, with a vast exportation throughout the Romanized world.

The city was also a benchmark for the manufacture of smooth black glazed pottery with several workshop structures identified both within the urban perimeter and in suburban areas.

For centuries the black glazed pottery has been considered the hallmark of Calenian production, in particular thanks to the availability of raw materials close to the city (De Bonis et al., 2013).

Numerous ateliers were active in the town and, among the most well-known, there are those of the Atilii, Gabiniie, and Paconii, which produced typical black glazed forms (Passaro, Carcaiso, 2006), such as umbilicate paterae, medallion cups, and characteristic gutti with pouring spouts.

The importance of the Calenian pottery production was further documented by the discovery, as a result of clandestine excavations in the 1980s, of a real craft district located outside the walls, a few hundred meters to the west, along the Via Latina.

In the same years J. P. Morel carried out a short excavation activity in this area that led to the identification of kilns active over a long period for the production of different ceramic classes exported on a large scale and competing with those of the nearby production centers of Teanum Sidicinum and Capua. Among these Calenian productions, tiles, oil lamps, and Dressel 2-4e amphorae are also attested and represent forms that do not seem to find evidence in other production centers (Morel 1989, Olcese 2015).

As a matter of fact, in such an important manufacturing center of ceramics, it is not surprising that the workshops also produced common ware, documented over a wide time span from the 3rd century BCE to the 2nd-3rd century CE. The collected data allow us to shed new light on the production activities of the Calenian workshops and document their remarkable continuity over time. The end of the production of black glazed pottery in the early imperial period does not determine the end of production activities, on the contrary there is an adjustment to new market demands with the manufacture of Sigillata pottery and a vast production of common ware. The continuity and liveliness of production testify to the role of an important craft center that Cales continued to play in the height of the imperial period, when the different senatorial families, linked to the imperial court, continued to boost the local economy, fitting into a market logic that managed to survive the strong economic changes that occurred during this period.

The production of most of these important ceramic classes, fine-grained pottery in particular, took advantage of the presence of large outcrops of clay next to the city of Cales (De Bonis et al., 2013), which represented important sources of raw materials. Thanks to Soprintendenza archeologica delle belle arti e paesaggio per le Province di Caserta e Benevento, the archaeological authority responsible for the site of Cales, it was possible to study ceramic finds from all relevant workshop areas and from recent excavations carried out on the so-called *arx* of Cales, excavated by the Soprintendenza in 2007.

1.2. The archaeological context

The investigated pottery samples come from two of the four sondages located on the NE slope of the tuffaceous plateau, where the ancient city was located (Fig. 1.2). The investigations have provided a complex and articulated stratigraphy that attests to an early phase of life in the Republican period, with the presence of imposing structures ascribed to public buildings, artisanal facilities, and remains of infrastructure, particularly in the sondage number three on the SE slope of the plateau.



Fig. 1.2. Satellite image with location of sondages 1-2-3 and 4.

The considerable presence of black glazed pottery, associated with kiln wastes, represented by deformed and misfired objects, cups and still stacked paterae,

along with the presence of tuff blocks and bricks with evident traces of a strong exposure to heat sources and several production wastes, indicate the occurrence of a production facility in the investigated area. The presence of a varied range of craft activities in the area is further attested by the discovery of a considerable amount of cattle bones, with well-sawn and polished ends.

Moreover, architectural elements, probably pertaining to a public building, along with evidence of craft activities with intense production rhythms, suggest the existence of a sacred building on the area with workshops annexed to it, according to a typology that would also seem to characterize the Calenian sanctuaries, in particular the Sanctuary of Ponte delle Monache.

A few archaeometric data are available so far and provided a preliminary overview on the compositional features of fine-grained pottery from Cales. L. Pedroni (2001) in his last volume on the Calenian black glazed pottery, gave a general description of the fabrics and glazed surfaces. He noted that the black glazed pottery from Cales is characterized by a high uniformity throughout the range of Calenian production from the beginning in the 3rd to the 1st century BCE and thus presumed a consistent "Calenian fabric". The homogeneity of these ceramic pastes was already suggested from the chemical and petrographic analyses carried out on few samples of production indicators by Langella and Morra (2001). A step ahead in the archaeometric knowledge about the Calenian fine-grained pottery was made by Guarino et al. (2011), who studied a selection of Terra sigillata. The study attested the circulation of Terra sigillata coming from productive areas in Central and Northern Italy along with locally produced samples, which showed affinity with local raw materials. This ceramic class is of great interest as it indicates important technological and cultural changes and the traceability of commercial paths in a crucial period just before the maximum expansion of Roman Empire. The production of Terra sigillata in the Campania region was influenced by new trends and technologies that spread out from the production centers in central Italy (e.g., Arezzo, Scoppieto) that probably converted their production from black glazed to Terra sigillata (Gómez-Herrero et al., 2008), also thanks to the use of the innovative wood-firing in muffle kilns

(Cuomo di Caprio, 2007). As a matter of fact, Cales was most probably the first regional centre that re-adapted the former facilities for the black glazed production to Terra sigillata and that took advantage from the availability of raw materials (Guarino et al., 2011), even before the production expanded to other centers, such as those in the Bay of Naples and Puteoli in particular (Soricelli, 2004; Grifa et al., 2019).

In addition to the considerable amount of fine-grained pottery produced at Cales, is also noteworthy the consistency of the Calenian production of common ware documented by the considerable amount of materials found in the area of sondage 3 (Fig. 1.2), located in a peripheral area on the northern slope of the ancient city, near the walls and a stream, thus in an area that was well suited to the presence of craft workshops. Evidence of the extensive ceramic production in the area is the presence at the proximity of the tuffaceous plateau, regularized in Roman period for defense reasons, falling within the current municipal territory of Pignatato Maggiore (CE), of a large ceramic dump, which record a high percentage of cookwares. It can be hypothesized that the intense production activity of the imperial period gave rise to the need to clear the plateau area, which was designated for craft activities, by dumping all the waste material resulting from processing in the area below.

The continuity that characterizes the intense production activity is also reflected in the use of raw materials and processing techniques.

1.3. Aim

The aim of the study is the definition of the local fine and coarse-grained pottery productions via in-depth minero-petrographic characterization of a large amount of samples from the 3rd century BCE to the 2nd century BCE, which include black glazed pottery, a minor selection of Terra sigillata and fine common ware, common cookware, internal red slip ware, thin walled pottery imitation and objects related to the production process. In fact, the focus of this work benefits from the finding and comparison with important production indicators represented by wastes of black glazed pottery and common cookware

along with spacers and supports used during the production process; these represent significant materials for defining with certainty the compositional features of local potteries.

This study also aims to increase the previous information concerning these important ceramic classes, also via the comparison with other fine ceramics found in the same context. Indeed, for the first time, three isotopic systematics were used to perform provenance studies, Sr-Nd and Pb respectively. This pioneering approach allowed us to understand the existing relationships between raw material and finished products. In the light of this, some Campanian clay raw materials Ca-rich and Ca-poor, well known in the literature, were selected and compared to the ceramics under study.

This approach highlights the importance of combining geochemical data to identify sources of raw materials and gave us back encouraging results that strengthening the previously experimental study, providing further confirmation of the validity of the method.

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CHAPTER II

GEOLOGICAL BACKGROUND

SUMMARY: 2.1. Geological and structural setting

2.1. Geological and structural setting

Campania is one of the most populated regions in Italy; it covers about 13.595 km² and according to ISTAT data (ISTAT, 2021) with almost 6 million inhabitants distributed in 5 provinces and 551 municipalities. The topography of the Campania landscape is very complex and depends on geological, morpho-structural and morphogenetic processes that have involved this region.

As mentioned above, the geological-structural setting of Campania region is very articulate due to the remarkable variety of geological processes that have affected the Apennine chain sector. The Apennine chain (Fig. 2.1) is a foreland fold-and-thrust belt which extends from the hinterland towards the Tyrrhenian coast and derive from the subduction of Neo-Tethys oceanic lithosphere under the Europa/AlKaPeCa plates (e.g. Carminati, Lustrino, & Doglioni, 2012; Cosentino, Cipollari, Marsili, & Scrocca, 2010; Vitale & Ciarcia, 2013 and references therein) with E ward migration of the thrust front as a consequence of downgoing slab-retreat (Malinverno & Ryan, 1986).

The Apennine chain is defined by the tectonic superposition of numerous thrust sheets constituted by Meso-Cenozoic deep basin to shallow-water successions, dissected by several Quaternary structural depressions located mainly in the Tyrrhenian direction (Vitale & Ciarcia 2018). It can be structurally divided into the northern and south-central segments. The latter is connected to the southern part of the Italian peninsula by the Calabrian orocline (Arco Calabro-Peloritano).



Fig. 2.1. Schematic geological map of the southern Apennines (Vitale et al., 2017).

Intense magmatic activity, both intrusive and effusive, widespread in the peri-Tyrrhenian zone from Tuscany to Campania, accompanied this new neotectonic regime. The distribution of magmatic provinces is illustrated in a structural model of the Apennines and back-arc regions as proposed by Peccerillo, 2020 (Fig. 2.2).



Fig. 2.2. Structural framework of the Italian peninsula and position of magmatic provinces (Peccerillo, 2020).

During the Quaternary post-orogenic extensional tectonic phases, the western side of the Apennines chain was faulted leading to the creation of semigraben structures and the beginning of a back-arc volcanic activity (Milia and Torrente, 2014; Milia et al., 2017). The volcanism started 700 k-year ago with the Roccamonfina volcano, in the northern part of the region, followed by the Ischia Island (150 k-year), the Phlegrean Fields (60 k-year) and the Somma-Vesuvius volcano (25 k-year). In the Quaternary, these structurally lowered zones, as well as other intermontane depressions, were filled by alluvial and volcanic deposits forming the Campanian, the Sele River and the Tanagro River alluvial plains. The tectonic pile is unconformably covered by Mio-Pliocene wedge top basin deposits and Quaternary post-orogenic sediments and volcanics (Ascione et al.,



2012; Vitale & Ciarcia, 2018). The geometrical relationships between the tectonic units present in the study region are schematized in fig. 2.3.

Fig. 2.3. Schematic representation of the geometric relationships between the tectonic units of the Southern Apennines in correspondence to Molise-Sannio and Cilento-Basilicata regions (Patacca & Scandone, 2007).

The lithologies mostly consist of sedimentary and volcanic rocks, spanning from the Triassic to recent times (Bonardi et al., 1998). The sedimentary rocks include: I) the stratigraphic Mesozoic Units, made up of limestones, dolostones, siliceous schists and terrigenous sediments (clays, siltstones, sandstones, conglomerates), which characterise mostly the external Apennine domains; II) the Neogene Units, mainly composed of siliciclastic, carbonate and evaporitic sediments along with Quaternary sediments represented by alluvial, lacustrine, coastal lake sediments and by pyroclastic fall and flow deposits (Buccianti et al., 2015).

The orogenic structure, consisting of allochthonous units can be grouped into three main tectonic complexes:

- I. Ligurian Accretionary Complex (LAC);
- II. Apennine Platform (AP) units;
- III. Lagonegro-Molise Basin (LMB) units.

The LAC occupies the tectonically higher positions by covering the AP units, which in turn overthrusting the LMB units. The foreland is represented by the Apulian Platform, but no outcrops are present in Campania (Fig. 2.4)



Fig. 2.4. Southern Apennine stratigraphy (Casero, 1988).

The volcanic rocks are characterized by potassic/ultrapotassic lavas and pyroclastics dated from about 600 ka to present, these rocks are produced by the four different volcanic centers (i.e., Roccamonfina, Mt. Somma–Vesuvius, Phlegrean Fields and Ischia Island) and by a fissure activity related to fractures activated in the Campanian plain from >315 to 18 ka that produced the Campanian ignimbrite (De Vivo et al., 2001; Rolandi et al., 2003). The latter covers the whole Campanian plain and also occurs on the Apennine Mountains (De Vivo et al., 2001).

The volcanic activity of the Campanian volcanoes shows variable volcanological features with predominantly explosive and less effusive activity as shown by the presence of lavas at Somma-Vesuvius (Santacroce, 1987). The erupted mafic products of the Somma-Vesuvius are mostly characterized by the presence of leucite, and the rock compositions are mafic ultrapotassic (basanites, tephrites, leucite-bearing shoshonites), intermediate (phonotephrites, latites) and evolved (trachytes and phonolites) (Melluso et al., 2022).

In this geological context, characterized by the presence of an important volcanic contribution rises the ancient city of Cales (currently Calvi Risorta).

The area is characterized by a carbonate platform succession that forms the Matese mountains and Monti Trebulani, also known as Matese-Mt. Maggiore-Mt. Camposauro unit (Bonardi et al., 2009). Extensive clay deposits crop out on the slope of the Trebulani muntains, just north of the town of Calvi Risorta (ancient Cales) (Fig. 2.5). These deposits belong to the foredeep succession of the Pietraroja Formation (Middle-Upper Tortonian) and were exploited up to modern times for brick production (Guarino et al., 2011). In more detail, Cales is located between two major volcanic districts, represented by the Phlegrean fields to the south and the Roccamonfina volcano to the north. The latter is a stratovolcano characterized by sector collapses and an apical central caldera (Cole et al., 1992; De Rita & Giordano, 1996; Giannetti, 2001; Rouchon et al., 2008) and is made up by lavas and pyroclastic rocks erupted in three main periods of activity (Ballini et al., 1989; De Rita and Giordano, 1996; Giannetti, 2001; Rouchon et al., 2008). In particular, the ultrapotassic leucite-bearing rocks are confined to the pre-caldera stage and show geochemical features similar to those of other volcanoes in the Roman Province (Peccerillo, 2017). After the major sector collapse of the volcano, occurred at ca. 400 ka, shoshonitic rocks erupted from cinder cones and domes both within the caldera and on the external flanks of the pre-caldera Roccamonfina volcano (Conticelli et al., 2009).

On the other hand, the volcanic history of Phlegrean fields has been characterized by several eruptions with the formation of mainly monogenic buildings, which erupted huge volumes of pyroclastic rocks and few lava flows. There were two high-magnitude eruptions, that of the Campanian Ignimbrite (39 ka; Fedele et al., 2008) and that of the Neapolitan Yellow Tuff (15.4 ka; Deino et al., 2004). Phlegraean products belong to the potassium series (KS) of shoshonitic affinity (Conticelli et al., 2004), among which trachytes are the most common lithotype. The archaeological area of Cales is located on pyroclastic flow deposits from Phlegraean Fields, represented by the Campanian Ignimbrite (39 ka, De Vivo et al., 2001; Fedele et al., 2008) and, subordinately, by the incoherent facies of the Neapolitan Yellow Tuff (15 ka, Deino et al., 2004).



Fig. 2.5. Geological sketch map of northern Campania sector modified after Vitale & Ciarcia 2018.

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CHAPTER III

MATERIALS AND ANALYTICAL METHODS

SUMMARY: 3.1. Materials- 3.2. Optical microscopy - 3.3. Modal analyses - 3.4. X-Ray Powder Diffraction (XRPD) – 3.5. Thermal analyses (TG-DSC)– 3.6. X-Ray Fluorescence (XRF)- 3.7. Field Emission Scanning Electron Microscopy (FESEM) and Microanalyses (EDS) - 3.8. Isotopic Analyses - 3.8.1. Sr and Nd isotopes (TIMS)- 3.8.2. Pb Isotopes (MC-ICP-

3.1. Materials

The study has focused on 125 samples of different ceramic classes (Table 3.1; Fig. 3.1 and 3.2) discovered during the excavations carried out at the so-called *Arx of Cales* by the *Soprintendenza* with the participation in 2007 of A. Tomeo who is currently the archaeologist in charge of the Ministry for the area of Cales and has provided his support and resources for this work.

The wide variety of selected material can be divided into two major groups based on inclusions grain size: fine and coarse-grained pottery. The designation of fine and coarse ware is generally used by archaeologist to mean certain ceramic assemblages on the basis of their macroscopic and textural features that are directly related to their intended use. At this purpose, fine ware refer to those materials for serving food and drink at table, as opposed for coarse wares to pots designed for cooking and food preparation, storage, transport and other common purposes. In this work this distinction is based on textural features (grain size), therefore the thin-walled pottery imitation that is a table ware, is included in the coarse-grained pottery.

	Class	Site	Chronology	n samples
	black glazed pottery	Cales	3rd-1st c. BCE	57
Fine-grained pottery	Terra sigillata	Cales	end 1st c. BCE/begin 1st CE	3
	fine common ware	Cales	undated	9
Fine-grained production indicator	Spacers	Cales	undated	8
	black glazed pottery - waste	Cales	undated	2
Coarse-grained pottery	common cookware	Cales	2nd c. BCE- 2nd c. CE	29
	internal red slip ware	Cales	2nd c. BCE- 1st c. CE	6
	thin-walled pottery imitation	Cales	from 2nd c. CE	3
	dolium	Cales	undated	1
Coarse-grained production indicator	Support	Cales	undated	4
	common cookware - waste	Cales	1st -2nd c. CE	3
	total			125

Table 3.1. Samples selected for the PhD project.

The materials selected for this PhD project are characterized by 79 samples of fine-grained pottery belonging to different ceramics classes (Table 3.1). The 57 samples are classified as black glazed pottery (Fig. 3.1a) that include paterae, pissidi, cups and bottle edge, characterized by a typical black surface coating. These samples are ascribed to a chronological span between the 2nd and 1st centuries BCE, just a few samples are characterized by forms attributable to the 3rd century BCE (35.46, 133.49, 35.56).

Interestingly, in the site of Cales the black glazed pottery in the late period (2nd and 1st centuries BCE) of production is characterized by the presence of several specimens that show a chromatic shading from black to red of the coating (Fig. 3.1a). These samples might be the results of a mistakes during the firing process and may allegedly represent the first attempts for the development of a technological innovation in terms of firing atmosphere, namely a shift from black glazed pottery (black coating) to Terra sigillata (red coating). The latter ceramic class was produced in several centers in the Roman Empire and is of great interest for archaeologists as it indicates important technological and cultural changes occurred in Roman ceramic technology (Grifa et al., 2019). This change was characterized by the implementation of the muffle-like furnaces where the flames and smoke are never in contact with the pottery, thus improving the technological production of the red coated wares (Picon, 1973; Cuomo di Caprio, 2007). Several samples that show this chromatic transition were selected for the analyses along with three specimens of Terra sigillata (Fig. 3.1b) that presented enough material for destructive analyses.

A selection of nine fine common wares (Fig. 3.1c) was also studied to provide a considerable contribution to define the local productions, along with 10 production indicators (Fig. 3.1d) represented by two kiln wastes and deformed pottery by the excessive firing and eight spacers that represent important materials to assess the compositional features of local potteries.



Fig. 3.1. Some representative ceramic samples of fine-grained pottery from the archaeological site of Cales. a) black glazed pottery; b) Terra sigillata; c) fine common cookware; d) production indicator.

In addition to the important production of fine pottery, samples of coarse pottery were also collected in the same archaeological context. The discovery provides a knowledge improvement about the history of this production center in northern Campania, which was not only focused only on fine wares, but also on coarse-grained pottery that have not been studied so far. The wide repertory of coarse-grained pottery from the context of the site "arx", included undecorated tableware and cooking wares that were selected for archaeometric analyses based on the amounts of materials found for each class. This work included the archaeometric investigation of 46 ceramic samples from the 2nd BCE to the 2nd century CE belonging to different ceramic classes as described below:

• 29 samples of common cookwares, represented by ollae, lids, pans and cups and consisting mainly of forms ascribable between the 2nd century BCE to the 2nd century CE, just few specimens show forms dated to the 4th-5th century CE (133.100 and 133.104, respectively) (Fig. 3.2a);

• 6 samples of internal red slip wares represented by pans with forms ascribable from the 2nd century BCE to the 1st century CE (Fig. 3.2b);

• 3 samples of thin-walled pottery imitation, which represents an extremely distinctive sample with forms dated from the 2nd century CE (Fig. 3.2c);

• 1 sample of wall of dolium with an undatable form (Fig. 3.2d);

• 7 production indicators represented by 3 samples of wasters of common cookware and 4 samples of supports, whose forms in many cases were not possible to date (Fig. 3.2e). These production indicators used during the production process represent significant materials to assess the compositional features of local potteries.



Fig. 3.2. Some representative ceramic samples of coarse ware from the archaeological site of Cales. a) common cookware; b) internal red slip ware; c) thin-walled pottery; d) dolium; e) production indicator.

Local clays and tempers have been collected and analyzed to find parallels with the end-products and localize the ancient sources of supply of raw materials. Raw materials of the area of Calvi Risorta were explored in the context of a study of clays from Campania by A. De Bonis (2011, 2013), which can be used as starting point and as a reference for the planned raw material studies of the region. The clays collected on that occasion will serve as important comparison for the local products of Cales and allow for better insights on the differences between the different productions in Campania region.

3.2. Optical microscopy (OM)

The 125 ceramic samples were selected for a minero-petrographic characterization. The color of ceramic body of the specimens was evaluated via a visual comparison with the Munsell Soil Colour Chart, 2000.

In order to shed light on the petrographic and textural features of the ceramic paste, the samples were investigated by means of polarized light microscopy (PLM) in thin section, very small slices of the material with thickness fixed at 0.03 mm (30 µm), using an OPTIKA V-600 POL microscope connected to ZEISS Axiocam 105 colour camera (ZEN 2.3 Lite software). The abundance, size range and roundness of the inclusions were estimated by reference to comparator charts (Terry & Chilingar, 1955; Quinn S.P., 2013). Sample preparation procedures was conducted at the Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR) of the University of Naples Federico II. The preparing processes starts with sample cutting (previously incorporated in epoxy resin if consisting of unconsolidated material) with a diamond-blade circular saw, to create a block of approximately 2x3 cm and with a thickness of about 0.5-1 cm. The block is sanded with carborundum abrasive discs to eliminate the irregularities caused by the cutting operations and to obtain a uniform and shiny surface. The surface of the block is then glued to a support glass slide using an epoxy resin as adhesive and then sanded again to remove excess resin and to reduce thickness up to 30 µm.

3.3. Modal analysis

In order to evaluate the percentage of inclusions, matrix and pores, a modal analysis was carried out on some representative samples of coarse-grained pottery selected on the basis of their minero-petrographic features, belonging to common cookware, internal red-slip ware, thin-walled pottery, dolium, and production indicators represented by support and wastes of common cookware. The analysis was carried out with the PC version 3.2.1 of the software "Leica Q Win", using a 15x15 mesh per field, for a total of about 1500 points per section and a magnification of 4.0X.

The choice to perform modal analysis on a few representative samples of coarse pottery was implemented in order to verify the correlation between the isotopic curve of binary mixing between raw material and temper as proposed in the experimental study on ceramic replicas by De Bonis et al. (2018).

3.4. X-Ray Powder Diffraction (XRPD)

X-ray Powder Diffraction (XRPD) was used to determine the bulk mineralogical composition using a Bruker D2 Phaser 2nd gen diffractometer (CuK α radiation, 30 kV, 10 mA, scanning interval 4-50°2 θ , equivalent step size 0.020°2 θ , equivalent counting time 66 s per step, Lynxeye 1D model detector), equipped with Diffract V6 5.0 data collector software (Bruker) for the first batch of 48 samples. The PANalytical X'Pert PRO 3040/60 PW diffractometer was used with analogous measurement conditions (CuK α radiation, operating at 40 kV, 40 mA, scanning interval 4-50°2 θ , using a step interval of 0.017°2 θ , with a step counting time of 66 seconds) for the second batch of 77 samples (Fig. 3.3). X-Ray Powder Diffraction (XRPD) is a technique primarily used for the qualitative and quantitative identification of the mineralogical phases and to



Fig. 3.3. The two instruments used for mineralogical analysis are shown in the figure. On the left is the Panalytical X'Pert PRO 3040/60 PW diffractometer and on the right is the Bruker D2 Phaser 2nd gen diffractometer.

provide information on unit cell dimension of crystals to investigate their structure and atomic spacing. In this work it has been particularly useful to investigate the fine-grained minerals that could not be recognized by optical microscopy, but also to obtain useful information about the production technology applied by the ancient craftsmen.

The X-Ray Diffraction is based on constructive interference of monochromatic X-Rays (emitted radiation) and a crystalline sample. Each electron of the atoms of a crystalline substance becomes a secondary source of X-rays with the same wavelength (λ) of the beam affecting the sample. This interference appears to be constructive only in those directions in which the waves diffused by all the atoms are "in phase". The rays that are thus created are the diffracted rays and the atoms define the diffraction lattice (three-dimensional, in the case of crystals). A crystal lattice has a large number of planes and the distance between these planes is called interplanar distance: it is unique for each mineral and can be determined by X-ray diffraction investigation, therefore the identification of this parameter allows for the recognition of the mineral species. The physical phenomenon of X-ray diffraction is described by Bragg's law:

$2d \sin\theta = n\lambda$

where d is the interplanar distance, θ is the incident X-ray angle and n is an integer number. According to this law, radiation is interpreted as a reflection from the atoms of a crystalline system and undergoes constructive interference. The samples preparation for XRPD analysis must allow the X-rays to intercept the lattice planes of the crystalline phases satisfying the Bragg's law. Approximately 0.5 g of sample, previously pulverized using an agate mortar was randomly placed in the center of the sample holder, in order to have a random distribution of lattice orientations (Cappelletti et al., 2019). The instrument used to perform measurements on powdered samples for the identification and quantitative study of crystalline substances is the diffractometer. It consists of: a source of X-rays (an X-ray tube), a sample holder, a detector and a "goniometer" (which provides precise mechanical motions of the tube, specimen, and detector). In addition, a "Soller" collimator eliminates all the X-rays diverging from the straight path, which is the most suitable for giving reflection under the conditions described by the Bragg's law. Therefore, the X-ray beam striking the sample could be considered as parallel.

The sample is placed at the center of the goniometer circle to facilitate the irradiation of a greater number of families of lattice planes. Simultaneously with the rotation of the sample, source and receiver can rotate on the unit circle with a double angular velocity, so any reflection produced at θ is recorded at 2 θ . This result in a pair of values angle - intensity of diffraction, called diffractogram.

3.5. Thermal analysis (TG-DSC)

The thermal behavior of ceramics and the loss on ignition (LOI) was performed on powdered bulk placed inside an alumina crucible by thermal analyses. The analyses were carried out by means of Netzsch STA 449 F3 Jupiter (Department of Science and Technology – University of Sannio; Fig. 3.4) thermal analyzer coupled with a FTIR BRUKER Tensor 27 for the Evolved Gas Analysis (EGA) by a transfer line heated at 200 °C.



Fig. 3.4 The Netzsch STA 449 F3 Jupiter instrument used for the thermal analysis.

The samples were heated from 40 to 1050 °C, with a heating rate of 10 °C/min in nitrogen atmosphere (flow rate 60mL/min). TG and DSC curves were acquired and processed with the NETZSCH Proteus 6.1 Software (Izzo et al., 2018; Germinario et al., 2019).

In order to evaluate the chemical and physical properties of the samples, Thermogravimetric Analysis (TGA) was performed. This measures the weight changes of a sample introduced into a specific atmosphere and subjected to temperature changes, generally progressive and linear increases as a function of time with its derivative declination (Derivative Thermogravimetry - DTG), which associates that particular reaction with a very precise temperature, and the analysis of gas species released (DSC) and Evolved Gas Analysis (EGA) during temperature changes. These instrumental methods represent, with probability, the oldest instrumental techniques for the analysis of minerals, in general, but in particular for those thermally reactive (for example: clay minerals as described by Bish & Duffy, 1990).

3.6. X-Ray Fluorescence (XRF)

Bulk chemical composition of the samples was performed via X-ray fluorescence spectrometry (XRF; AXIOS PANalytical Instrument) for measuring the concentration of 10 major oxides (wt% of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅) and 10 trace elements (Rb, Sr, Y, Zr, Nb, Ba, Cr, Ni, Sc, V, in parts per million [ppm]). Analytical uncertainties were in the order of 1-2% for the major elements and 5-10% for trace elements (Cucciniello et al., 2011). The method was applied on pressed pellets through the study of a fluorescent (or secondary) X-ray radiation. The standards employed are reported in Guarino et al., 2021.

The preparation of the pellets starts from a few grams of sample (usually 3-4 gr), previously powdered using a rotary mill equipped with agate spheres. Subsequently, the powders obtained are glued using MOWIOL polyvinyl alcohol prepared at DiSTAR's laboratories, which confers strength to the pellets, then the mixture is placed in an oven at a temperature of 90 °C to dryness for about 2 hours. The dry mixture is then poured into special aluminum containers of about 3 cm in diameter, above a layer of H_3BO_3 grains with a filler function (Fig. 3.5). Finally, a pressure of about 20 ton/cm² is applied for 20 seconds using a hydraulic press producing the pressed powder pellet for XRF analyses (Acquafredda & Laviano, 2019).



Fig. 3.5. AXIOS PANalytical Instrument and containers for powdered sample. From left to right: empty container; container with the layer of H₃BO₃; container with the powdered sample above the layer of H₃BO₃ (Acquafredda & Laviano, 2019).

When the sample is irradiated with high-energy X-rays, an atom in the sample is struck with an X-ray and an electron from one of the atom's inner orbital shells (K shell) is dislodged. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells (L or M shells). The electron drops to the lower energy state by releasing a fluorescent (or secondary) X-ray. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays, whose wavelength (λ) is unique, like a "fingerprint" for that specific element, according to the Moseley's law:

$$1/\lambda = k (Z-\sigma)^2$$

where Z is the atomic number and k and σ are constant characteristic of the specific spectral series. The instrument for XRF analysis is composed by: a generator; a tube emitting polychromatic, high-energy primary X-rays; a sample holder; one or more analyzer crystals of known d-spacing; detector transforming the X-rays reflected by the analyzer crystal into electrical impulses. Crystals of known d-spacings are used as analyzer crystals. Since the position of the sample

and the detector is fixed, the angular position of the reflecting crystal is changed in accordance with Bragg's Law so that a particular wavelength of interest can be directed to a detector for quantitative analysis. Every element has a discrete energy difference between orbital shells, such that every element will produce X-rays of a fixed wavelength. Therefore, by using analyzer crystals and positioning the crystals at a unique and fixed angle, it is possible to detect and quantify elements of interest based on the characteristic Xray wavelengths produced by each element. It is possible to determine the concentration of major elements and of some trace elements through this technique.

Multivariate statistical analyses were carried out using R (R Development core Team, 2014) software on chemical data standardized via log10 transformation. Hierarchical clustering analysis (HCA) was applied on the data set reduced by PCA (Principal Component Analysis) in order to cluster samples in a dendrogram using an agglomerative clustering algorithm (Euclidean distance and average linkage method).

3.7. Field Emission Scanning Electron Microscopy (FESEM) and Microanalysis (FESEM-EDS)

In order to define the degree of sintering and the microstructural features of the ceramic bodies according to different firing temperatures (Maniatis & Tite, 1981), observations of the fragments in fresh fracture via Field Emission Scanning Electron Microscope (FESEM; Zeiss Merlin VP Compact; Fig. 3.6) were performed. This analysis was carried out on 21 representative samples, chosen according to their mineralogical and petrographic features.

This technique is used for inspecting topographies, surface morphology of solid fragments through extremely detailed observations (high-resolved and high-zoomed, up to enlargements of $1-10 \ \mu m$).



Fig. 3.6 Field Emission Scanning Electorn Microscopy (FESEM) instrument in use at DiSTAR department.

The method is based on the interaction between an incident primary electron beam and the sample surface. The electron beam, produced by an electron gun, is accelerated and focused on the sample through magnetic lenses, and a system of coils allows the sample scanning. The interaction between the primary electron beam and sample surface generates several electromagnetic radiations, such as backscattered electrons, secondary electrons, Auger electrons, and characteristic X-ray. High-resolution imaging of surface morphology is generated by secondary electrons: since their energy is small, those generated at a deep region are quickly absorbed by the specimen, so secondary electrons are very sensitive to the surface and for this reason they are used to observe the topography. Backscattered electrons are those emitted when the incident electrons are scattered by the specimen. Since they have higher energy with respect to secondary electrons, they provide information about deeper regions. They are sensitive to the composition of the specimen and the efficiency of their production is strongly related to the atomic number: the higher the atomic number the brighter the material image. The samples investigated with the FESEM were covered with a conductive layer of gold, which facilitates the removal of electrical charges from the sample, avoiding their interference with the formation of the image.

Quantitative microanalyses of mineral grains and neoformed phases in the ceramic body were determined on polished thin sections by using the same instrument fitted with an energy dispersive X-ray spectrometer (EDS) and Oxford Instruments Microanalysis Unit (X Max 50 EDS detector operating at 15 kV primary beam voltage, 115–125 μ A filament current, and 60 μ m spot size, acquisition time 10s). The data was processed with an INCA Xstream pulse processor.

The following standards, from Smithsonian Institute, were used for calibration: diopside (Ca K α), San Carlos olivine (Mg K α), anorthoclase (Al K α , Si K α), albite (Na K α), rutile (Ti K α), fayalite (Fe K α), Cr₂O₃ (Cr K α , chromite), rhodonite (Mn K α), orthoclase (K K α), apatite (P K α), celestine (Sr L α), barite (Ba L α), fluorite (F K α), sodium chloride (Cl K α), zircon (Zr L α , Hf L α), and pure vanadium (V L α). The utilized mineral standards are reported in Guarino et al. (2019) and Franciosi et al. (2019). Precision and accuracy of EDS analyses are reported in Rispoli et al. (2019).

The EDS instrument is used to analyze characteristic X-ray spectra by measuring the energy of the X-ray emitted from the sample via an energydispersive detector, a solid-state device that discriminates among X-rays energies, that is a Si (Li) crystal (Petrosino et al., 2019). This technique allows us to identify all the elements with atomic number between 4-Be and 92-U (Petrosino et al., 2019).

The energy released during the interaction between X-rays and detector depends on the number of shells the replacement electron has displaced from its original position, and to what shell the electron moves. This energy is emitted as X-rays and absorbed by the detector by ionization, yielding free electrons in the crystal that become conductive and produce an electrical charge bias. The energy of individual X-rays is converted into electrical voltage and the electrical pulses correspond to the characteristic X-rays of the element.

3.8. Isotopic Analyses

3.8.1. Sr and Nd isotopes (TIMS)

The Sr–Nd isotopic composition of representative ceramic and clay samples was determined via Thermal Ionization Mass Spectrometry (TIMS).

Isotopic analysis was performed on 40 representative samples divided according to the table 3.2. The choice of materials for this analysis was based on their petrographic characteristics, mineralogical assemblage, and chemical behavior. The raw materials were selected from the clay deposits investigated in De Bonis et al. (2013) from the most logistically advantageous deposits for large-scale production.

Sample ID	Class	Site	Chronology
133.3	black glazed pottery	Cales	undated
133.6	black glazed pottery	Cales	undated
133.14	black glazed pottery	Cales	undated
133.16	black glazed pottery	Cales	2nd-1st c. BCE
133.19	black glazed pottery	Cales	undated
133.27	black glazed pottery	Cales	second half 2nd- 1st c. BCE
133.37	black glazed pottery	Cales	end 2nd-begin 1st c. BCE
133.44	black glazed pottery	Cales	2nd-1st c. BCE
133.48	black glazed pottery	Cales	2nd c. BCE
133.57	black glazed pottery	Cales	2nd-1st c. BCE
35.75	Terra sigillata	Cales	end 1st c. BCE/begin 1st c. CE
35.76	Terra sigillata	Cales	end 1st c. BCE/begin 1st c. CE
133.114	fine common ware	Cales	undated
133.119	fine common ware	Cales	undated
16.36	black glazed pottery waste	Cales	undated
133.60	Spacers	Cales	undated
133.61	Spacers	Cales	undated
76.78	common cookware	Cales	2nd c. BCE- 2nd c. CE
76.79	common cookware	Cales	undatable
133.109	common cookware	Cales	2nd c. BCE- 2nd c. CE
133.112	common cookware	Cales	undatable
35.54	internal red slip ware	Cales	2nd c. BCE- 1st c. CE
145.59	internal red slip ware	Cales	2nd c. BCE- 1st c. CE
32.2801.72	internal red slip ware	Cales	2nd c. BCE- 1st c. CE
133.83	thin-walled pottery imitation	Cales	from 2nd c. CE
133.105	thin-walled pottery imitation	Cales	from 2nd c. CE

Table 3.2 Selected materials for isotopic analyses. Abbreviations: HC = high calcium oxide; LC = low calcium oxide. The table continues on the next page
Sample ID	Class	Site	Chronology
133.125	dolium	Cales	undatable
133106	common cookware waste	Cales	1st -2nd c. CE
133.70	Support	Cales	undatable
133.71	Support	Cales	undatable
CVR1	clay HC	Calvi Risorta (CE)	-
CVR2	clay HC	Calvi Risorta (CE)	-
PMV1	clay HC	Piana di Monte Verna (CE)	-
PMV2	clay HC	Piana di Monte Verna (CE)	-
ALV1	clay HC	Alvignano (CE)	-
ALV2	clay HC	Alvignano (CE)	-
CSC1	clay HC	Cascano (CE)	-
PLT2	clay HC	Pontelatone (CE)	-
AQM2	temper LC	Monte di Procida (NA)	-
DUG1	temper LC	Dugenta (BN)	-

Sample dissolution and Sr-Nd separation from the matrix, were carried out within a Plexiglas laminar flow hood equipped with two HEPA filters located in an ISO 6 class clean room at Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse (DiSTAR, Naples, Italy). Approximately 100 mg of powder was dissolved with Suprapur[®] grade HF-HNO₃-HCl acid mixtures (Fig. 3.7), the whole procedure lasting four days overall. Sr and Nd were the matrix through conventional separated from cation-exchange chromatographic techniques on quartz columns filled with either AG® 50W-X8 (for Sr and Rare Earth Elements) or Ln Spec[®] (for Nd) resins and using diluted Suprapur[®] grade HCl as eluant. Subsequently the obtained Sr and Nd fraction was loaded on a rhenium filament (single for Sr and double for Nd) and then inserted inside magazine equipped with 21 positions which is mounted inside the spectrometer.



Fig. 3.7 Suprapur acid used for the samples digestion, respectively HF, HNO₃, HCl.

⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd isotope ratios of CVR2, PMV2, CSC1 clays and AQM2 temper were determined at the Radiogenic Isotope Laboratory of the INGV–OV (Naples, Italy) with a ThermoFinnigan Triton TI multicollector mass spectrometer running in static mode to explore the potential that this method has for determining pottery provenance. The procedure involved the chemical dissolution of the samples, using suprapur grade HF-HNO₃-HCl mixtures described above, and Sr-Nd extraction by conventional ion-exchange chromatographic techniques. Average $2_{\sigma mean}$, i.e., the standard error with N = 180, was ± 0.000009 for Sr, and ± 0.000007 for the Nd measurements. The mean measured values of ⁸⁷Sr/⁸⁶Sr for the NIST SRM 987 standard and ¹⁴³Nd/¹⁴⁴Nd for the La Jolla standard were 0.710231 ± 0.000019 (2σ , N = 169) and 0.511845 ± 0.000010 (2σ , N = 55), respectively; external reproducibility (2σ) during the period of measurements was calculated according to Goldstein et al. (2003).

Measured ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios were normalized for within run isotopic fractionation to ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The final isotope ratio measured values were normalized to the recommended values of the NIST SRM 987 (⁸⁷Sr/⁸⁶Sr = 0.71025) and La Jolla (¹⁴³Nd/¹⁴⁴Nd = 0.51185) international standards, respectively De Bonis et al. (2018).

However, for the other 37 samples, the Sr–Nd isotopic composition of ceramics samples, clays and temper was determined at DiSTAR (Naples, Italy) through thermal ionization mass spectrometry (TIMS) techniques using a Thermo Scientific Triton Plus[®] mass spectrometer (Fig. 3.8).

The instrument is equipped with one fixed and eight adjustable Faraday cups for simultaneous acquisition of several ion beams in static mode. $2\sigma_{mean}$, i.e., the standard error with N = 150, was lower than ±0.000008 for Sr and ±0.000006 for Nd. In-run isotopic fractionation was corrected through normalization of measured ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios to ⁸⁸Sr/⁸⁶Sr = 8.37521 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219, respectively.



Fig. 3.8 Thermo Scientific Triton Plus[®] mass spectrometer used to define Sr and Nd isotope ratios of the samples.

During the period of analysis, replicate measurements of NIST–SRM 987 (SrCO₃) and JNdi–1 international reference standard were carried out to check for external reproducibility, 2σ (σ is the standard deviation of the standard results; Goldstein et al., 2003), obtaining the following mean values: 87 Sr/ 86 Sr = 0.710234± 0.00013 for NIST–SRM 987; 143 Nd/ 144 Nd = 0.512096± 0.000006 for JNdi–1. The measured Sr and Nd isotope ratios were normalized to the recommended values of NIST–SRM 987 (87 Sr/ 86 Sr = 0.710248 ± 0.000012 (σ); Zhang and Hu, 2020) and JNdi–1 (143 Nd/ 144 Nd = 0.512107 ± 0.000012 (σ); Zhang and Hu, 2020) standards, respectively.

In order to shed light on the isotopic features of raw materials (clays and temper) frequently mixed for ceramic productions the theory of binary mixing was adopted (De Bonis et al., 2018). The chemical and isotopic compositions of the resulting mixtures can be calculated by means of simple mixing models (Langmuir et al., 1978).

Considering a mixture of two components A and B having different concentration of the element X, and different isotopic composition Rx it is possible to construct the equation of an hyperbola:

$$R_{M}^{X} = \frac{R_{A}^{X} X_{A} f + R_{B}^{X} X_{B} (1-f)}{X_{A} f + X_{B} (1-f)}$$

Where Rx the isotope ratio of the element X in a mixture of components A and B and f is a mixing parameter.

3.8.2. Pb Isotopes (MC-ICP-MS)

Lead isotope analyses was applied on some representative ceramic samples and raw materials (both clays and temper from De Bonis et al., 2013). The analyses were conducted on a Nu Plasma II (Nu Instruments) Multi Collector - Inductively Coupled Plasma - Mass Spectrometer (MC-ICP-MS; Fig 3.9) in operation at the University of Missouri Research Reactor (MURR).



Fig. 3.9 Nu Plasma II (Nu Instruments) Multi Collector - Inductively Coupled Plasma - Mass Spectrometer (MC-ICP-MS) in use at the University of Missouri Research Reactor (MURR) to define Pb isotope ratios.

In order to make the samples viable for this analysis, ceramics and raw materials were powdered in an agate mortar and subsequently the clays were also calcinated at 550 °C for 4 hours. The surface of the ceramics was mechanically cleaned with a microdrill equipped with silicon carbide bits, rinsed with DI water and dried under heating lamps. Approximately 100 mg of powder were digested in closed Savillex[®] beakers (125 °C, 48 h) in 2.5 ml of 24 N Trace Metal Grade HF and 0.5 ml of Optima Grade 14 N HNO₃ and then evaporated at 90 °C overnight. The dry residues were digested in 1.5 ml of Optima Grade 14N HNO₃, vials were closed and heated at 125 °C for 48 h and then evaporated at 90 °C overnight. Lastly, the dry residues obtained were re-digested in 4 ml of 6N HCl at 125 °C for 48 h and subsequently evaporated at 90 °C overnight (Fig. 3.10).



Fig. 3.10 Digestion process of the samples before evaporation at 90 °C overnight.

The dry residues were finally dissolved in 2 ml 0.5M HBr (Renson et al., 2011). Lead extraction was realized via ion-exchange chromatography (IEC with Dowex AG1–X8 anion exchange resin) and was achieved by successive HBr and HCl additions following the protocol described in Weis et al. (2006). The eluted pure Pb solution was evaporated and stored. Prior to isotopic analysis, this purified Pb fraction was re-dissolved in 14N HNO₃ Optima, evaporated and finally dissolved in 0.05M HNO₃.

The instrument was optimized for ²⁰⁸Pb maximum intensity (minimum signal of 150 mV at mass 204). The samples and standard were spiked using a Tl solution to monitor and correct for mass fractionation. Sample solutions were prepared to measure Pb and Tl concentrations similar to those of the SRM 981 solution (approximately 200 ng g⁻¹ in Pb and 50 ng g⁻¹ in Tl). The SRM981 standard was measured several times at the beginning of each analytical session and after every two samples. Values were corrected for mass fractionation using the NIST value of 2.38714 for ²⁰⁵Tl/²⁰³Tl natural ratio.

A correction for mercury isobaric interference at mass 204 was also applied using a 0.229883 value for 204 Hg/ 202 Hg natural ratio. The mean values obtained for the SRM981 were 36.685 ± 0.012 (2SD), 15.488 ± 0.002 (2SD) and 16.936 ± 0.003 (2SD), for 208 Pb/ 204 Pb, 207 Pb/ 204 Pb and 206 Pb/ 204 Pb ratios, respectively.

The results were corrected by standard-bracketing (White et al., 2000; Weis et al., 2006) using recommended values from Galer & Abouchami (1998). Two duplicates (i.e. entire procedure applied twice to the same sample) and two replicates (second analysis of the same solution) were measured to evaluate the reproducibility of measurements.

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CHAPTER IV

RESULTS

SUMMARY: 4.1. Macroscopic and petrographic features - 4.1.1 Finegrained pottery- 4.1.2 Coarse-grained pottery- 4.2. Modal analyses - 4.3. X-Ray Powder Diffraction (XRPD)-4.3.1 Fine-grained pottery - 4.3.2 Coarsegrained pottery – 4.4 Thermal analyses (TG-DSC)– 4.4.1 Fine-grained pottery – 4.4.2 Coarse-grained pottery- 4.5. X-Ray Fluorescence (XRF)-4.5.1 Fine-grained pottery- 4.5.2. Coarse-grained pottery-4.6. Field Emission Scanning Electron Microscopy (FESEM)-4.6.1 Fine-grained pottery- 4.6.2. Coarse-grained pottery - 4.7. Microanalyses (FESEM-EDS)- 4.7.1 Finegrained pottery- 4.7.2. Coarse-grained pottery - 4.8. Sr and Nd isotopes-4.8.1 Fine-grained pottery- 4.8.2. Coarse-grained pottery - 4.8.3. Raw materials 4.9. Pb Isotopes-4.9.1 Fine-grained pottery - 4.9.2. Coarse-grained pottery – 4.9.3. Raw materials

The paragraphs **4.1.1**; **4.2**; **4.3.1**; **4.4.1**; **4.5.1**; **4.6.1**; **4.7.1**; **4.8**; **4.9** have been omitted from the text as they are in submission phase

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4.1. Macroscopic and petrographic features

To define the macroscopic and textural features (color, chromatic shades, hardness), the samples were subjected to a preliminary macroscopic examination via visual evaluation (Table 4.1 and Table 4.2) and then to optical microscope analysis in thin section with the purpose to define the petrographic characteristics (optical activity of the ceramic matrix, packing, grain size distribution, mineralogical assemblage, etc.).

From the last considerations, the 125 samples were divided into two main groups with similar features based on the size of inclusions, fine and coarse. In more detail, the first group is represented by 79 samples of fine-grained pottery (Table 4.1) made of fifty-seven samples of black glazed pottery; three samples of Terra sigillata; nine samples of fine common ware and ten sample of production indicators represented by eight samples of spacers and two welded plates of black glazed pottery.

Sample ID	Class	Chronology	Form	Wt. (g)	Inner Colour	Outer Colour	Hardness
133.1	BG	undated	patera	11.5	2.5YR 6/3	2.5YR 6/3	hard
133.2	BG	undated	patera	9.75	10YR 6/4	10YR 6/4	very hard
133.3	BG	undated	patera	12.2	7.5YR 6/4	7.5YR 6/4	very hard
133.4	BG	2nd c. BCE	pyxis base	10.6	7.5YR 6/4	7.5YR 6/4	very hard
133.5	BG	undated	patera	9.72	2.5Y 5/2	2.5Y 5/2	very hard
133.6	BG	undated	patera	9.75	10YR 6/4	10YR 6/4	very hard
133.7	BG	undated	patera	8.61	7.5YR 6/4	7.5YR 6/4	hard
133.8	BG	undated	patera	7.92	7.5YR 6/4	7.5YR 6/4	hard
133.9	BG	undated	patera	9.69	5YR 6/6	5YR 6/6	hard
133.10	BG	undated	cup	8.66	10YR 6/4	10YR 6/4	hard
133.11	BG	undated	patera	5.08	7.5YR 6/4	7.5YR 6/4	hard
133.12	BG	undated	patera	7.13	5YR 6/6	5YR 6/6	hard
133.13	BG	undated	patera	8.10	2.5YR 6/3	2.5YR 6/3	very hard
133.14	BG	undated	patera	7.84	5YR 6/6	5YR 6/6	very hard
133.15	BG	undated	patera	9.27	7.5YR 6/4	7.5YR 6/4	very hard
133.16	BG	2nd-1st c. BCE	cup base	9.26	7.5YR 6/4	7.5YR 6/4	very hard
133.17	BG	undated	patera	8.13	7.5YR 6/6	7.5YR 6/6	hard
133.18	BG	undated	patera	9.09	7.5YR 6/6	7.5YR 6/6	very hard

Table 4.1. Macroscopic features of 79 ceramic samples of fine-grained pottery object of the study. Abbreviations: BG = black glazed pottery; TS = Terra sigillata; FCW = fine common ware; BG-W = black glazed pottery-waste. The table continues on pages 42 and 43.

Sample ID	Class	Chronology	Form	Wt. (g)	Inner Colour	Outer Colour	Hardness
133.19	BG	undated	patera	6.79	7.5YR 6/6	7.5YR 6/6	very hard
133.20	BG	2nd-1st c. BCE	patera	8.14	7.5YR 6/4	7.5YR 6/4	very hard
133.21	BG	half 1st c. BCE	patera	6.83	7.5YR 6/4	7.5YR 6/4	very hard
133.22	BG	2nd c. BCE	patera	6.46	5YR 6/6	5YR 6/6	hard
133.23	BG	half 1st c. BCE	patera	9.32	5YR 6/6	5YR 6/6	hard
133.24	BG	2nd c. BCE	patera	7.47	7.5YR 6/4	7.5YR 6/4	very hard
133.25	BG	2nd c. BCE	patera	8.84	7.5YR 6/6	7.5YR 6/6	hard
133.26	BG	2nd c. BCE	patera	5.52	7.5YR 6/4	7.5YR 6/4	hard
133.27	BG	second half 2nd-1st c. BCE	pyxis	4.18	7.5YR 7/4	7.5YR 7/4	hard
133.28	BG	second half 2nd-1st c. BCE	pyxis	5.65	7.5YR 7/4	7.5YR 7/4	hard
133.29	BG	second half 2nd-1st c. BCE	pyxis	5.79	7.5YR 7/4	7.5YR 7/4	hard
133.30	BG	second half 2nd-1st c. BCE	pyxis	3.33	7.5YR 7/4	7.5YR 7/4	very hard
133.31	BG	second half 2nd-1st c. BCE	pyxis	7.48	7.5YR 6/4	7.5YR 6/4	very hard
133.32	BG	second half 2nd c. BCE	pyxis	9.81	7.5YR 6/4	7.5YR 6/4	very hard
133.33	BG	2nd-1st c. BCE	pyxis	8.51	10YR 6/4	10YR 6/4	very hard
133.34	BG	2nd-1st c. BCE	pyxis	7.29	7.5YR 6/6	7.5YR 6/6	hard
133.35	BG	second half 2nd c. BCE	pyxis	5.50	7.5YR 7/4	7.5YR 7/4	very hard
35.37	BG	end 2nd cbegin 1st c. BCE	cup	7.87	7.5YR 6/4	7.5YR 6/4	hard
35.38	BG	end 2nd cbegin 1st c. BCE	cup	5.46	7.5YR 6/4	7.5YR 6/4	hard
35.39	BG	undated	cup	4.93	2.5Y 7/3	2.5Y 7/3	hard
35.40	BG	2nd c. BCE	patera	7.35	7.5YR 6/4	7.5YR 6/4	hard
35.41	BG	half 2nd c. BCE	patera	6.35	7.5YR 7/4	7.5YR 7/4	very hard
35.42	BG	2nd-1st c. BCE	patera	6.34	7.5YR 7/4	7.5YR 7/4	very hard
35.43	BG	2nd-1st c. BCE	patera	7.39	7.5YR 7/4	7.5YR 7/4	hard
35.44	BG	2nd-1st c. BCE	patera/ cup	5.31	7.5YR 7/4	7.5YR 7/4	hard
35.45	BG	2nd c. BCE	patera	6.66	7.5YR 6/4	7.5YR 6/4	very hard
35.46	BG	3rd-2nd c. BCE	cup	7.98	7.5YR 7/4	7.5YR 7/4	very hard
35.47	BG	1st c. BCE	patera	6.60	10YR 6/4	10YR 6/4	very hard
35.48	BG	2nd c. BCE	cup	4.74	10YR 7/4	10YR 7/4	hard
133.49	BG	3rd-2nd c. BCE?	cup	8.42	10YR 6/4	10 YR 6/4	very hard
35.50	BG	2nd-1st c. BCE	cup	10.5	7.5YR 6/4	7.5YR 6/4	hard
133.51	BG	undated	bottle edge	24.4	5YR 6/6	5YR 6/6	hard
133.52	BG	undated	parete	7.77	7.5YR 6/4	7.5YR 6/4	hard
133.53	BG	2nd-1st c. BCE	small patera	9.67	7.5YR 6/6	7.5YR 6/6	hard
35.56	BG	3rd-2nd c. BCE	cup	5.68	7.5YR 6/6	7.5YR 6/6	hard
35.57	BG	2nd-1st c. BCE	cup	17.8	7.5YR 7/6	7.5YR 7/6	hard
35.58	BG	2nd-1st c. BCE	cup	12.4	7.5YR 7/6	7.5YR 7/6	hard
76.74	BG	2nd-1st c. BCE	cup	7.78	10YR 6/4	10YR 6/4	very hard
133.87	BG	2nd-1st c. BCE	cup	9.38	7.5 YR 6/6	7.5YR 6/6	hard
35.75	TS	end 1st c. BCE/begin 1st c. CE	cup	5.6	7.5YR 6/6	7.5YR 6/6	hard
37.76	TS	end 1st c. BCE/begin 1st c. CE	cup	6.35	7.5YR 6/6	7.5YR 6/6	hard
27.77	TS	undated	base open form	5.79	5YR 6/6	5YR 6/6	hard
133.113	FCW	undated	ansa	6.88	5Y 5/1	5Y 6/4	very hard
133.114	FCW	undated	base closed form	8.85	7.5YR 6/6	7.5 YR 6/6	hard

Sample ID	Class	Chronology	Form	Wt. (g)	Inner Colour	Outer Colour	Hardness
133.115	FCW	undated	base closed form	6.75	7.5YR 6/6	7.5YR 6/6	hard
133.116	FCW	undated	base closed form	6.28	r	2.5YR 6/6	hard
133.117	FCW	undated	base closed form	7.79	5YR 5/8	5YR 5/8	hard
133.118	FCW	undated	base closed form	6.14	5Y 5/3	5Y 5/3	very hard
133.119	FCW	undated	base closed form	8.44	2.5Y 5/2	2.5Y 5/2	very hard
133.120	FCW	undated	base closed form	5.03	10YR 6/4	10YR 6/4	hard
133.121	FCW	undated	base closed form	6.91	10YR 6/4	10 YR 6/4	hard
16.36	BG-W	undated	cup basis	18.5	5Y 5/3	5Y 4/1	very hard
133.60	spacer	undated	ring spacer	9.40	10YR 6/3	10 YR 6/3	very hard
133.61	spacer	undated	ring spacer	8.22	10YR 6/3	10 YR 6/3	very hard
133.62	spacer	undated	ring spacer	8.75	2.5YR 6/3	2.5YR 6/3	very hard
133.63	spacer	undated	ring spacer	10.6	7.5YR 7/4	7.5YR 7/4	very hard
133.64	spacer	undated	cup spacer	8.68	7.5YR 7/4	7.5YR 7/4	hard
133.65	spacer	undated	cup spacer	7.12	2.5YR 6/4	2.5YR 6/4	very hard
133.66	spacer	undated	cup spacer	6.33	2.5YR 6/4	2.5YR 6/4	very hard
133.67	spacer	undated	cup spacer	8.35	5Y 6/3	5Y 6/3	very hard
76.73	BG-W	undated	cup basis	9.89	2.5Y 5/3	2.5Y 5/3	very hard

The second group is represented by 46 samples of coarse-grained pottery (Table 4.2) made of twenty-nine samples of common cookware; six samples of internal red slip ware; three samples of thin-walled pottery imitation; one sample of dolium and seven production indicators composed by four supports and three wastes of common cookware.

Table 4.2. Macroscopic features of 46 ceramic samples of fine-grained pottery object of the study. Abbreviations: CW = common cookware; PRW = internal red slip ware; TW = thin-walled pottery; CW-W = common cookware-waste; LC = dolium. The table continues on the next page.

Sample ID	Class	Chronology	Form	Wt. (g)	Inner Colour	Outer Colour	Hardness
76.78	CW	2nd c. BCE- 2nd c. CE	olla	9.19	5YR 5/6	7.5YR 4/1	hard
76.79	CW	undatable	olla base	10.6	7.5YR 4/1	5YR 5/6	hard
76.80	CW	2nd c. BCE-1st c. CE	olla	11.4	7.5YR 5/1	5YR 6/6	hard
133.84	CW	undatable	olla base	8.81	2.5YR 6/2	5YR 5/6	hard
133.85	CW	2nd c. BCE-1st c. CE	olla	olla 13.0 5		5YR 5/4	hard
133.86	CW	2nd c. BCE- 2nd c. CE	lid	7.67	7.5 YR 3/1	7.5 YR 6/6	hard
133.88	CW	from II cent. CE	small olla	10.2	5 YR 5/6	5YR 5/6	hard
133.89	CW	2nd c. BCE- 2nd c. CE	lid	9.43	2.5 YR 5/8	2.5 YR 5/8	hard
133.92	CW	2nd c. BCE- 2nd c. CE	lid	9.68	10YR 6/3	7.5YR 5/6	hard
133.93	CW	2nd c. BCE- 2nd c. CE	lid	10.9	2.5YR 5/6	7.5YR 6/6	hard
133.94	CW	2nd c. BCE- 2nd c. CE	lid	8.42	7.5YR 5/4	5YR 5/8	hard
133.95	CW	undatable	lid	8.71	10YR 6/3	5YR 5/6	hard
133.96	CW	undatable	lid	12.8	2.5Y 4/1	2.5Y 5/2	hard

Sample ID	Class	Chronology	Form	Wt. (g)	Inner Colour	Outer Colour	Hardness
133.97	CW	2nd c. BCE- 2nd c. CE	lid	9.98	5YR 5/6	5YR 5/6	hard
133.98	CW	2nd c. BCE- 2nd c. CE	lid	9.26	10YR 5/1	7.5YR 6/6	hard
133.99	CW	2nd c. BCE- 2nd c. CE	lid	9.80	10YR 6/6	7.5YR 6/6	hard
133.100	CW (coated)	4th -first half 5th c. CE	lath cup	9.62	10YR 5/1	7.5YR 6/6	hard
133.101	CW	undatable	base	9.22	5YR 5/8	5YR 5/8	hard
133.102	CW	1st -2nd c. CE	olla	6.87	5YR 5/6	5YR 5/6	hard
133.104	CW (African)	2nd-4th c. CE	pan	6.50	2.5YR 5/8	2.5YR 5/8	hard
133.107	CW	2nd c. BCE- 2nd c. CE	olla	9.62	2.5YR 5/8	2.5YR 5/8	hard
133.108	CW	2nd c. BCE-1st c. CE	olla	7.04	2.5YR 3/1	2.5YR 4/8	hard
133.109	CW	2nd c. BCE- 2nd c. CE	olla	10.8	2.5YR 5/1	2.5YR 5/8	hard
133.110	CW	2nd c. BCE- 2nd c. CE	olla	9.40	2.5YR 2.5/1	2.5 YR 5/3	hard
133.111	CW	2nd c. BCE- 2nd c. CE	lid	8.83	2.5YR 5/1	2.5YR 5/8	hard
133.112	CW	undatable	lid	11.8	7.5YR 4/3	7.5YR 2.5/1	hard
76.122	CW	1st -2nd c. CE	olla	8.37	5YR 5/1	5YR 5/6	hard
76.123	CW	2nd c. BCE-1st c. CE	olla	10.1	5YR 5/1	5YR 5/6	hard
76.124	CW	2nd c. BCE-1st c. CE	olla	9.06	5YR 5/4	5YR 5/1	hard
35.54	PRW	2nd c. BCE-1st c. CE	pan	11.1	5YR 5/6	5YR 5/6	hard
35.55	PRW	2nd c. BCE-1st c. CE	pan	15.7	5YR 5/6	10YR 4/1	hard
145.59	PRW	2nd c. BCE-1st c. CE	pan	8.60	5YR 5/6	5YR 5/6	hard
32.2801.72	PRW	2nd c. BCE-1st c. CE	pan	10.4	5YR 5/6	5YR 5/6	hard
133.90	PRW	2nd c. BCE-1st c. CE	pan	10.2	5YR 5/8	5YR 5/8	hard
133.91	PRW	2nd c. BCE-1st c. CE	pan	10.1	10YR 5/3	7.5YR 5/6	hard
133.82	TW imitation	from 2nd c. CE	small olla	6.25	2.5Y 5/2	7.5 YR 6/4	hard
133.83	TW imitation	from 2nd c. CE	small olla	6.26	5YR 6/8	5YR 6/8	hard
133.105	TW imitation	from 2nd c. CE	small olla	6.89	5YR 5/6	5YR 5/6	hard
133.125	LC	undatable	dolium wall	32.7	5YR 6/4	5YR 6/1	hard
133.68	support	undatable	spacer	15.0	10YR 6/3	10YR 6/3	hard
133.69	support	undatable	spacer	8.50	10YR 5/3	10YR 5/3	hard
133.70	support	undatable	spacer	9.25	2.5YR 6/2	2.5YR 6/2	hard
133.71	support	undatable	spacer	12.8	5YR 5/6	5YR 5/6	hard
133.81	CW-W	from 2nd c.	small olla	12.9	Gley 2 4/10B	Gley 2 4/10B	hard
133.103	CW-W	undatable	ansa	12.1	2.5YR 3/1	2.5YR 3/4	hard
133.106	CW-W	1st -2nd c. CE	olla	12.6	2.5YR 3/2	2.5YR 3/2	hard

4.1.2. Coarse-grained pottery

Common cookware

Twenty-nine samples of common cookwares (Table 4.2; Fig. 4.5a-i) are characterized by a very variable color of ceramic body, varying from reddish (5 YR 5/6, 5YR 5/4, 2.5YR 5/1, 5YR 5/4, 2.5YR 2.5/1, 2.5YR 5/8, 2.5YR 6/2; Table 4.2), brownish (10YR 6/3, 7.5YR 5/4, 7.5YR 4/3, 10YR 6/6; Table 4.2) to grayish (7.5YR 4/1, 2.5Y 4/1, 5YR 3/1, 7.5 YR 3/1; Table 4.2). Almost all the samples show a heterogeneous color of the clay paste with evident shades from the core toward the rim, except for the samples 133.85, 133.86, 133.88, 133.89, 133.97, 133.101, 133.102, 133.104, 133.107, 133.109, 133.110, 133.111, 76.124, that on the contrary show a homogeneous color of the clay paste. The optical activity of ceramic matrix is generally active, but with some exception recognized in the samples 133.85, 133.94, 133.100, 133.101, 133.109 and 76.123 which show an optically inactivity of ceramic matrix. The amount of inclusions ranges from 30 to 35 % with a bimodal distribution of grains. The inclusions are characterized by tiny quartz crystals, feldspar (Fig. 4.5a-i), clinopyroxene (Fig. 4.5b, c, e, f, g, h), evident lithics fragments of



trachyte (see Fig. 4.5a, h) and juvenile volcanic fragments represented by pumices and shards.

Fig. 4.5. Thin section images of common cookware samples. NX = crossed polars; NII = parallel polars.

Internal red-slip ware

Six samples of internal red slip ware (Table 4.2; Fig. 4.6a-f) are characterized by a yellowish red color (5YR 5/6; Table 4.2) of ceramic body, just one sample is characterized by a brownish color of ceramic body (133.91; 10YR 5/3; Table 4.2). Generally, the color is homogeneous, except for samples 35.55 and 133.91, which show a slight chromatic shading that varies from yellowish red (5YR 5/6; Table 4.2) to dark gray toward the rim (10YR 4/1; Table 4.2) in 35. 55 and from brown (10YR 5/3; Table 4.2) to strong brown (7.5YR 5/6; Table 4.2) in 133.91. The optical activity of the ceramic matrix is usually active, from weak to strong, with an amount of inclusions ranging from 30 to 35 % and a bimodal distribution on grains. The composition of the inclusions is consistent in all the samples analyzed, the presence of quartz, feldspar (Fig. 4.6c), clinopyroxene (Fig. 4.6d), juvenile fragments represented by evident pumices (occasionally > $400 \ \mu\text{m}$; Fig. 4.6a) and shards along with lithics fragments of volcanic origin consisting in trachyte fragments (Fig.4.6b, e). The samples are also characterized by the presence of a distinct red coating on the inner surface.



Fig. 4.6. Thin section images of internal red slip ware samples. NX = crossed polars; NII = parallel polars.

Thin-walled pottery imitation

Three samples of thin-walled pottery imitation (Table 4.2; Fig. 4.7a, b) are characterized by a reddish color (5YR 6/8, 5YR 5/6; Table 4.2) of the ceramic body for the 133.83, 133.105 samples and brownish for the 133.82 sample that also show an evident chromatic shade of the clay paste from the core (2.5Y 5/2; Table 4.2) toward the rim (7.5 YR 6/4; Table 4.2).

The optical activity of ceramic matrix varies from inactive as shown in the sample 133.82 to active in 133.105, with an amount of inclusions ranging from 20 to 25 % with a bimodal distribution of grains.

The grains are mostly characterized by tiny quartz crystals, plagioclase, alkali feldspar (Fig. 4.7a), clinopyroxene along with sporadic mica fragments (Fig. 4.7b).

Dolium

The only Dolium sample recognized in the archaeological site of Cales is characterized by a light reddish-brown color (5YR 6/4; Table 4.2) of ceramic body with an evident shade of ceramic paste from the core toward the rim, in which the color takes on a darker hue (5YR 6/1; Table 4.2). The optical activity of ceramic matrix is weakly active with an amount of the inclusions that varies from 30 to 35 % and a bimodal distribution of grains. The inclusions made of tiny quartz crystals, plagioclase, alkali feldspar, lithics fragments represented by evident trachytes and juvenile fragments represented by pumices (Fig. 4.7c), along with sporadic mica.



Fig. 4.7. Thin section images of thin-walled pottery (a, b) and Dolium (c). NX = crossed polars; NII = parallel polars.

Coarse-grained production indicators

Seven samples of coarse-grained production indicators are represented by four fragments of supports (Table 4.2; Fig. 4.8a, b, c) and three samples of wastes of common cookware (Table 4.2; Fig. 4.8d, e, f). They are characterized by a variable color of ceramic body that varies from reddish (5YR 5/6, 2.5YR 3/2), to brownish (10YR 5/3), to greyish (2.5YR 6/2, Gley 2 4/10B, 2.5YR 3/1). The optical activity of ceramic matrix referred to the supports is generally inactive (Fig. 4.8 a, b, c). The amount of inclusions are ~40 % with a bimodal distribution of grains. The coarse fraction (generally >200 μ m) is made of volcanic lithics and pumices, feldspar and clinopyroxene; on the other hand, the fine fraction (generally < 50 μ m) mainly consists by tiny quartz crystal and sporadic mica.



Fig. 4.8. Thin section images of production indicators represented by supports (a, b, c) and waste of common cookware (d, e, f). NX = crossed polars.

The optical activity of ceramic body of the wastes of common cookware is generally inactive (Fig. 4.8d, e, f) with an amount of inclusions ~35 % characterized by a bimodal distribution of grains. The coarse fraction (>200 μ m) is made of volcanic lithics, pumices, feldspar and clinopyroxene; on the other hand, The fine fraction (< 50 μ m) mainly consists of tiny quartz crystal and sporadic mica.

4.3. X-Ray Powder Diffraction (XRPD)

4.3.2. Coarse-grained pottery

The mineralogical observation on twenty-nine samples of common cookware via X-Ray Powder Diffraction (XRPD) showed that quartz is the most abundant phase in all the samples analyzed, followed by feldspar, pyroxene from scares to abundant. Neoformed iron oxides are represented by Fe^{3+} oxide (hematite) was identified in a good percentage of the common cookware analyzed except for 76.78, 133.84, 133.88, 133.92, 133.93, 133.95, 133.96, 133.97, 133.98, 133.99, 133.100, 133.102, 133.108, 133.110, 133.112, 133.122, 76.124 (Table 4.5; Fig. 4.16). In addition, the presence of phyllosilicates represented by illite/mica, from sporadic to abundant, was identified in all samples analyzed except for 133.85 and 133.109.



Figure 4.16. XRPD representative spectra of common cookware samples. Abbreviations according to Whitney & Evans, 2010. Qz = quartz; Fsp = feldspar; Px = pyroxene; Cc = calcite; Hem = hematite; Mll = melilite; Mca = mica; Ilt = illite. Symbols as in Fig 4.9.

XRPD pattern of 6 samples of internal red slip ware indicate a very homogeneous mineralogy, in which the quartz is the most abundant phase recognized in all the samples analyzed, followed by feldspar, phyllosilicates represented by illite/mica, traces of pyroxene and iron oxides represented by Fe^{3+} oxide (hematite) in the samples 35.54, 35.55, 145.59, 32.2801.72, 133.90, 133.91 (Table 4.5; Fig. 4.17.).



Figure 4.17. XRPD spectra of internal red slip ware samples. Abbreviations according to Whitney & Evans, 2010. Qz = quartz; Fsp = feldspar; Px = pyroxene; Cc = calcite; Hem = hematite; Mll = melilite; Mca = mica; Ilt = illite. Symbols as in Fig 4.9.

The mineralogical observation made on three samples of thin-walled pottery confirmed the observations previously described in the optical microscopy section. Quartz appears to be the most abundant phase in all the samples, abundant feldspar, mica/illite, followed by pyroxene except in the 133.105 sample. Moreover, traces of hematite in the sample 133.83 were recognized Table 4.5; Fig. 4.18.).



Fig. 4.18. XRPD spectra of thin-walled pottery samples. Abbreviations according to Whitney & Evans, 2010. Qz = quartz; Fsp = feldspar; Px = pyroxene; Cc = calcite; Hem = hematite; Mll = melilite; Mca = mica; Ilt = illite; Chl = chlorite. Symbols as in Fig 4.9.

XRPD results obtained on the one dolium sample also showed in this case a mineralogy characterized by a predominant presence of quartz, feldspar, frequent pyroxene and calcite and mica. In addition, the presence of gehlenite was recognized along with hematite Table 4.5; Fig. 4.19.).



Fig. 4.19. XRPD spectra of Dolio sample. Abbreviations according to Whitney & Evans, 2010. Qz = quartz; Fsp = feldspar; Px = pyroxene; Cc = calcite; Hem = hematite; Mll = melilite; Mca = mica; Ilt = illite. Symbols as in Fig 4.9.

Lastly, the XRPD pattern of seven production indicators represented by four supports used inside the kiln and three samples of wasters of common cookware, once again, showed that quartz is the most abundant phase in all the samples analyzed, followed by feldspar, mica/illite in 133.69, 133.71 and 133.103 samples. The presence of bivalent iron oxide represented by hematite was identified in most of the samples analyzed except for 133.70 and 133.81. In addition, traces of gehlenite were recognized in 133.70 and 133.71 samples Table 4.5; Fig. 4.20.).



Fig. 4.20. XRPD spectra of production indicators represented by a) supports b) common cookware waste. Abbreviations according to Whitney & Evans, 2010. Qz = quartz; Fsp = feldspar; Px = pyroxene; Cc = calcite; Hem = hematite; Mll = melilite; Mca = mica; Ilt = illite. Symbols as in Fig 4.9.

Table 4.5. Semi-quantitative XRPD analysis on 46 sample of coarse-grained pottery represented by: CW = common cookware; PRW = internal red slip ware; TW = thin-walled pottery; CW-W = common cookware waste; LC = dolium. Abbreviations according to Whitney & Evans, 2010. Qz = quartz; Fsp = feldspar; Px = pyroxene; Ca = common cookware waste; Ca =

calcite; Hem = hematite; Mll = melilite; Mca = mica; Ilt = illite; Chl = chlorite. The table continues on the next page.

Sample	Class			Mir	neralo	ogical a	issem	blage	
Sample	Class	Qz	Fsp	Px	Cal	Hem	Mll	Mca/Ilt	Others
76.78	CW	xxxx	XX	tr.	-	-	-	xx	-
76.79	CW	xxxx	XX	tr.	-	х	-	х	-
76.80	CW	xxxx	xx	tr.	-	tr.	-	х	-
133.84	CW	xxxx	xx	tr.	-	-	-	xx	-
133.85	CW	xxxx	xxx	xx	-	XX	-	-	-
133.86	CW	xxxx	xx	tr.	-	tr.	-	Х	-
133.88	CW	xxxx	XX	tr.	-	-	-	XX	-
133.89	CW	xxxx	xx	х	-	Х	-	XX	-
133.92	CW	xxxx	xx	tr.	-	-	-	XX	-
133.93	CW	xxxx	xx	tr.	-	-	-	XX	-
133.94	CW	xxxx	xx	х	-	Х	-	х	-
133.95	CW	xxxx	xx	tr.	-	-	-	х	-
133.96	CW	xxxx	xxx	х	-	-	-	XX	-
133.97	CW	xxxx	xx	tr.	-	-	-	XX	-
133.98	CW	xxxx	х	tr.	-	-	-	х	-
133.99	CW	xxxx	х	tr.	х	-	-	XX	-
133.100	CW (coated)	xxxx	х	tr.	-	-	-	х	-
133.101	CW	xxxx	xx	tr.	-	Х	-	х	-
133.102	CW	xxxx	xx	tr.	-	-	-	XX	-
133.104	CW (African)	xxxx	XX	-	-	х	-	х	-
133.107	CW	xxxx	xxx	х	-	х	-	х	-
133.108	CW	xxxx	х	-	-	-	-	XX	-
133.109	CW	xxxx	х	-	-	х	-	-	-
133.110	CW	xxxx	XX	-	-	-	-	XX	-
133.111	CW	xxxx	xxx	-	-	tr.	-	х	-
133.112	CW	xxxx	XX	-	-	-	-	XX	-
133.122	CW	xxxx	XX		XX		Х	х	-
76.123	CW	xxxx	XX	XX	-	х	-	х	-
76.124	CW	xxxx	xx	tr.	-	-	-	Х	-
35.54	PRW	xxxx	XX	tr.	-	tr.	-	XX	-
35.55	PRW	xxxx	XX	tr.	-	-	-	XX	-
145.59	PRW	xxxx	xx	tr.	-	tr.	-	XX	-
32.2801.72	PRW	xxxx	xx	х	-	-	-	XX	-
133.90	PRW	xxxx	XX	х	-	tr.	-	XX	-
133.91	PRW	xxxx	xx	х	-	tr.	-	XX	-
133.82	TW imitation	xxxx	XX	х	-		-	-	-
133.83	TW imitation	xxxx	XX	x	-	х	-	Х	-
133.105	TW imitation	xxxx	Х	-	-	-	-	XX	Chl
133.125	LC	xxxx	XXX	xx	xx	х	Х	x	-
133.68	support	xxxx	XXX	XX	-	x	-	-	-

Sample ID	Class	Qz	Fsp	Px	Cal	Hem	Mll	Mca/Ilt	Others
133.69	support	XXXX	xx	XX	-	х	-	х	-
133.70	support	XXXX	xxx	xx	х	-	tr.	-	-
133.71	support	XXXX	xxx	х	х	х	х	х	-
133.81	CW-W	XXXX	xx	х	-	-	-	-	-
133.103	CW-W	XXXX	xx	XX	-	х	-	xx	-
133.106	CW-W	xxxx	xxx	х	-	х	-	х	-

4.4 Thermal analyses (TG-DSC)

4.4.2. Coarse-grained pottery

The simultaneous thermal analyses carried out on common cookware sample showed a weight loss due to an endothermic reaction between 40 and 300 °C (Table 4.7) thermal range, while between the 300 and 500 °C thermal range is evidenced by only a weight loss. Loss on ignition (LOI) was lower than approximately 3 wt.%.

The internal red slip ware shows a weight loss due to an endothermic reaction between 40 and 300 °C (Table 4.7) thermal range, while between the 300 and 500 °C only a weight loss was detected as already evidenced for common cookware described above. LOI was between 4 and 6 wt.%.

As far as the coarse-grained production indicators are concerned, the simultaneous thermal analyses detected, in all samples, a weight loss due to an endothermic reaction between 500 and 800 °C (Table 4.7), thermal range in which carbonates decompose. LOI was lower than approximately 3 wt. %.

Table 4.7 Results of simultaneous thermal analyses, showing weight-loss and enthalpy changes observed in the analyzed pottery. Legend: a - endothermic; b - exothermic; $\Delta w -$ mass loss; DSC: differential scanning calorimetry; DTG: derivative thermogravimetric curve; LOI: loss on ignition. Abbreviations: CW = common cookware; PRW = internal red slip ware.

		40)-300 °C		30	0-500 °C	2	50	0-800 °C	2	80	0-1050 °	°C	LOI
Sample	Class	Δw (%)	DTG	DSC ^a	Δw (%)	DTG	DSC ^a	Δw (%)	DTG	DSC ^a	Δw (%)	DTG	DSC ^{a,b}	Δw (%)
76.78	CW	1.78	109.5	99.5	0.95	433	-	0.38	-	-	0.11	-	-	3.22
76.79	CW	1.03	110.4	89.7	0.73	411.7	-	0.21	-	-	0.12	-	-	2.09
76.80	CW	0.47	242.7	80.4	0.35	-	-	0.00	-	-	0.04	-	-	0.86
35.54	PRW	3.41	102.2	101	1.07	421.5	-	0.3	-	-	0.03	-	-	4.81
35.55	PRW	2.65	112.9	94.4	1.06	432.2	-	0.48	-	-	0.08	-	-	4.27
145.59	PRW	2.69	112.3	97.4	0.96	414.1	-	0.32	-	-	0.11	-	1012 ^b	4.08
32.2802.72	PRW	4.01	113	112.1	1.2	410.9	-	0.43	-	-	0.13	-	-	5.77
133.68	support	0.38	116.2	86	0.24	-	-	0.94	694.3	698	0.01	-	-	1.57
133.69	support	0.38	119.7	76.2	0.18	-	-	0.19	627.9	-	0.01	-	-	0.76
133.70	support	0.56	114.5	86.5	0.35	-	-	0.81	679.1	685	0.00	-	-	1.72
133.71	support	0.75	116.6	91.6	0.39	-	-	2.13	702.6	706	0.1	-	-	3.37

4.5. X-Ray Fluorescence (XRF)

4.5.2. Coarse-grained pottery

Most of the samples belonging to the group of coarse-grained pottery show a low-CaO composition of the ceramic body as evidenced in the Fig. 4.22a (CaO 1.23-2.77wt. %; Table 4.9a) except the support samples, which, on the contrary show a high-CaO composition of the ceramic matrix along with the dolium sample (CaO 8.30-9.60; Fig. 4.22a, Table 4.9a).

The analysis of major oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅ in wt.%, Table 4.9a) and trace elements (Rb, Sr, Y, Zr, Nb, Ba, Cr, Ni, Sc, V in parts per million [ppm]; Table 4.9b) shows that the forty-one samples of common cookware, internal red slip ware, thin-walled pottery imitation and wastes of common cookware are characterized by a very homogeneous chemical composition (Fig. 4.22), with limited compositional variability in terms of both major oxides (SiO₂ 60.2-65.6 wt.%; TiO₂ 0.73-0.93 wt.%; Al₂O₃ 18.6-22.1 wt.%; Fe₂O₃ 6.06-7.44 wt.%; MnO 0.11-0.47 wt.%; MgO 1.53-2.08 wt. %; Na₂O 0.94-1.77 wt. %; K₂O 3.25-4.53 wt. %, P₂O₅ 0.07-1.42 wt. %) as shown in Fig. 4.22a, b, c and d (CaO vs. SiO₂; Al₂O₃ vs. Fe₂O₃; MgO vs. CaO; MgO vs. Zr, respectively) and trace elements (Rb 194-323 ppm, Sr 188-390 ppm, Y 27-46 ppm, Zr 252-417 ppm, Nb 25-51 ppm, Ba 603-1397 ppm, Cr 70-120 ppm, Ni 36-56 ppm, Sc 9-18, V 97-157 ppm) as shown in the chemical binary diagrams reported in Fig. 4.22d, e and f (MgO vs. Zr; Cr vs. Ni; Nb vs. Zr, respectively).

On the other hand, the production indicators represented by supports (133.68, 133.69, 133.70, 133.71) and the sample of dolium (133.125) shows different geochemical behavior than the previously described group, characterized by lower Al_2O_3 (15.2 to 17.4 wt.%) content and higher MgO (2.50 to 3.60 wt.%) values as shown in Fig. 4.22.



Fig. 4.22. X-Ray Fluorescence binary diagrams of coarse ware.

Table 4.9a. Major (wt. %) oxides for common cookware (CW), Internal red slip ware (PRW), thin-walled pottery (TW), dolium (LC); common cookware waste (CW-W). The major oxide analyses are recalculated to 100 wt.%. The Table continued.

Sample ID	Class	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P2O5	тот
76.78	CW	65.5	0.74	18.6	6.29	0.15	1.85	1.71	1.34	3.66	0.22	100
76.79	CW	62.5	0.77	20.5	6.54	0.15	1.91	1.79	1.42	4.25	0.21	100

Sample ID	Class	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P2O5	тот
76.80	CW	63.5	0.79	19.8	6.71	0.15	1.97	1.71	1.42	3.87	0.16	100
133.84	CW	63.6	0.82	20.2	6.65	0.15	1.65	1.91	0.96	3.64	0.34	100
133.85	CW	60.9	0.91	22.0	7.36	0.16	1.61	1.60	1.35	3.95	0.12	100
133.86	CW	64.5	0.82	19.8	6.60	0.16	1.77	1.32	1.25	3.56	0.13	100
133.88	CW	64.2	0.78	20.2	6.44	0.16	1.69	1.95	1.10	3.33	0.16	100
133.89	CW	61.1	0.82	21.9	7.11	0.17	1.62	2.04	1.09	3.86	0.23	100
133.92	CW	62.1	0.84	21.3	7.07	0.16	1.66	1.73	1.16	3.64	0.39	100
133.93	CW	64.0	0.78	19.5	6.16	0.22	1.73	1.93	1.38	4.03	0.18	100
133.94	CW	63.0	0.85	21.0	7.11	0.17	1.76	1.23	1.21	3.51	0.11	100
133.95	CW	64.2	0.78	20.2	6.44	0.17	1.59	1.89	1.04	3.47	0.25	100
133.96	CW	60.2	0.82	20.8	7.04	0.15	1.94	2.77	1.12	4.28	0.82	100
133.97	CW	61.7	0.82	21.4	7.00	0.15	1.61	2.16	1.08	3.89	0.18	100
133.98	CW	62.4	0.85	21.4	7.04	0.19	1.69	1.59	1.23	3.50	0.17	100
133.99	CW	63.9	0.79	19.7	6.25	0.19	1.74	1.82	1.27	3.99	0.36	100
133.100	CW (coated)	64.2	0.79	19.1	6.51	0.17	2.08	2.07	1.26	3.69	0.20	100
133.101	CW	63.6	0.82	20.0	6.87	0.19	1.85	1.90	1.32	3.27	0.12	100
133.102	CW	61.5	0.85	21.7	7.10	0.26	1.60	2.22	0.94	3.59	0.26	100
133.104	CW (African)	63.9	0.82	20.0	6.96	0.26	1.76	1.61	1.28	3.25	0.13	100
133.107	CW	62.6	0.81	21.6	6.68	0.11	1.53	1.52	1.23	3.85	0.10	100
133.108	CW	63.5	0.84	20.6	6.91	0.14	1.75	1.45	1.09	3.56	0.16	100
133.109	CW	64.4	0.81	19.7	6.67	0.19	1.75	1.42	1.25	3.65	0.12	100
133.110	CW	62.6	0.84	20.7	6.69	0.17	1.75	2.12	1.04	3.70	0.34	100
133.111	CW CW	64.0	0.76	19.1	6./9	0.19	1.80	1.00	1.57	3.8/	0.13	100
155.112	CW CW	03.0 64.0	0.74	18.0	0.27 6.20	0.13	1.89	1.90	1.32	5.41 2.71	0.18	100
76.122	CW CW	04.0 61.6	0.75	19.0 21.4	0.29	0.14	2.05	2.40	1.57	5./1 2.62	0.51	100
76.124	CW CW	65.0	0.80	10.0	6.45	0.10	1 70	1.04	1.27	3.62	0.17	100
/0.124 average	CW	63.2	0.74	20.3	6 73	0.15	1.79	1.00	1.41	3.00	0.17	100
std døv		1 38	0.01	1 01	0.33	0.03	0.14	0.33	0.15	0.26	0.25	0.00
35 54	PRW	63.6	0.04	19.9	6.36	0.05	1 72	2 19	1.16	3.91	0.15	100
35.55	PRW	62.3	0.70	20.7	6 75	0.15	1.72	2.19	1 11	4 01	0.20	100
145.59	PRW	62.8	0.79	20.9	6.71	0.18	1.60	1.82	1.17	3.74	0.31	100
32.2801.72	PRW	61.5	0.78	20.7	6.70	0.14	1.56	2.51	1.04	3.63	1.42	100
133.90	PRW	62.3	0.81	21.1	6.75	0.14	1.59	2.11	1.02	3.82	0.29	100
133.91	PRW	64.1	0.82	19.8	6.47	0.15	1.61	1.91	1.07	3.72	0.37	100
average		62.77	0.79	20.52	6.62	0.15	1.62	2.12	1.10	3.81	0.49	100
std.dev		0.94	0.02	0.56	0.16	0.02	0.06	0.25	0.06	0.14	0.45	0.00
133.82	Imitation TW	62.1	0.86	21.2	7.03	0.15	1.64	1.76	1.37	3.78	0.10	100
133.83	Imitation TW	64.6	0.81	19.5	6.52	0.20	1.69	1.52	1.38	3.65	0.14	100
133.105	Imitation TW	65.3	0.78	18.6	6.06	0.47	1.84	2.21	0.95	3.29	0.44	100
average		64.0	0.82	19.8	6.54	0.27	1.72	1.83	1.24	3.58	0.23	100
std.dev		1.71	0.04	1.34	0.49	0.17	0.11	0.35	0.25	0.25	0.19	0.00
133.125	LC	57.5	0.74	17.4	6.19	0.20	2.95	8.72	1.72	4.28	0.32	100
133.68	support	58.5	0.66	16.8	5.48	0.18	2.59	8.66	2.39	4.46	0.19	100
133.69	support	58.8	0.73	16.7	6.15	0.12	3.60	8.34	1.47	3.99	0.18	100
133.70	support	58.5	0.64	16.2	5.51	0.17	2.66	9.60	2.13	4.38	0.26	100
133.71	support	58.6	0.65	17.3	5.39	0.17	2.50	8.30	2.26	4.61	0.29	100
133.81	CW-W	61.3	0.93	21.7	7.44	0.19	1.53	1.47	1.44	3.90	0.07	100

Sample ID	Class	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P2O5	тот
133.103	CW-W	62.2	0.78	19.9	6.81	0.19	1.66	2.24	1.73	4.36	0.13	100
133.106	CW-W	61.8	0.82	19.8	7.04	0.18	1.61	2.30	1.77	4.53	0.14	100
average		59.9	0.75	18.3	6.26	0.17	2.31	5.84	1.88	4.32	0.18	100
std.dev		1.72	0.11	2.12	0.84	0.02	0.75	3.63	0.38	0.27	0.08	0.00

Table 4.9b. Traces (ppm) elements for common cookware (CW), Internal red slip ware (PRW), thin-walled
pottery (TW), dolium (LC); common cookware waste (CW-W). The table continued.

Sample ID	Class	Rb	Sr	Y	Zr	Nb	Ba	Cr	Ni	Sc	V
76.78	CW	208	271	34	267	28	697	107	50	17	123
76.79	CW	237	309	36	288	33	766	109	53	10	125
76.80	CW	213	267	36	281	30	707	97	49	17	134
133.84	CW	277	230	35	325	35	810	90	43	14	123
133.85	CW	295	279	46	408	49	826	79	38	13	145
133.86	CW	244	193	34	315	33	641	93	44	12	122
133.88	CW	278	223	34	321	33	758	87	44	15	109
133.89	CW	286	341	39	354	38	990	70	39	14	123
133.92	CW	265	236	42	360	39	804	89	42	14	132
133.93	CW	273	293	35	326	35	788	85	40	10	101
133.94	CW	264	228	39	345	37	718	92	47	11	129
133.95	CW	268	244	37	327	34	791	86	42	10	109
133.96	CW	308	337	35	306	35	1181	91	45	13	145
133.97	CW	297	303	33	342	38	802	87	43	12	113
133.98	CW	245	229	41	364	41	809	86	44	14	134
133.99	CW	256	216	37	314	34	698	95	46	10	119
133.100	CW (coated)	221	290	38	292	29	703	120	56	14	131
133.101	CW	231	214	39	330	35	659	102	50	11	132
133.102	CW	323	318	38	360	41	953	76	42	12	105
133.104	CW (African)	230	205	37	323	33	669	103	53	9	122
133.107	CW	252	390	39	339	32	820	74	36	14	125
133.108	CW	258	206	34	310	33	683	94	50	16	135
133.109	CW	232	261	40	323	35	760	96	48	12	130
133.110	CW	280	247	37	319	34	861	85	44	12	130
133.111	CW	208	259	33	273	28	665	119	56	16	139
133.112	CW	194	274	30	252	25	729	103	47	15	120
76.122	CW	209	390	31	256	28	738	83	40	13	117
76.123	CW	255	245	39	314	37	678	90	49	16	139
76.124	CW	212	218	27	269	28	603	99	48	16	117
average		252	266	36	317	34	769	93	46	13	125
std.dev		33.4	52.4	3.82	35.7	4.92	118	12.0	5.14	2.21	11.2
35.54	PRW	308	276	33	307	32	785	84	43	13	105
35.55	PRW	300	313	37	334	38	827	75	39	16	116
145.59	PRW	240	232	41	343	36	748	80	42	13	97
32.2801.72	PRW	281	344	40	335	37	1397	79	43	18	116
133.90	PRW	302	281	36	341	38	865	81	42	14	111
133.91	PRW	291	233	31	321	33	765	86	40	15	109

Sample ID	Class	Rb	Sr	Y	Zr	Nb	Ba	Cr	Ni	Sc	V
average		287	280	36	330	36	898	81	41	15	109
std.dev		25.0	44.3	3.67	13.5	2.37	248	4.02	1.65	1.81	7.13
133.82	Imitation TW	266	259	44	384	45	782	73	40	10	138
133.83	Imitation TW	242	277	39	338	35	789	84	46	12	127
133.105	Imitation TW	258	188	32	282	28	621	100	51	13	134
average		255	241	38	335	36	731	86	46	12	133
std.dev		12.5	47.3	6.09	50.9	8.58	94.7	13.3	5.52	1.45	5.69
133.125	LC	230	350	33	244	31	601	97	46	17	118
133.68	support	236	291	35	314	40	462	98	52	13	89
133.69	support	222	335	29	214	24	448	115	56	13	121
133.70	support	239	307	34	299	36	487	82	45	17	91
133.71	support	244	307	37	329	43	459	65	37	16	78
133.81	CW-W	296	274	45	417	51	823	73	37	14	156
133.103	CW-W	255	310	40	339	40	783	83	39	13	133
133.106	CW-W	261	318	43	352	40	780	82	40	12	136
average		250	306	38	323	39	606	86	44	14	115
std.dev		24.0	19.3	5.37	61.1	8.34	178.1	16.2	7.85	1.70	29.0

4.6. Field Emission Scanning Electron Microscopy (FESEM)

In order to define the degree of sintering, the microtextural features of the ceramic body and, subsequently, define the different EFTs (Equivalent Firing Temperatures) of the ceramic bodies, the microstructural observations of the fragments in fresh fracture were performed on 21 ceramics fragments, divided in: 12 fine-grained pottery and 9 coarse-grained pottery.

4.6.2. Coarse-grained pottery

The common cookwares show at the FESEM a microstructure represented by an extensive vitrification as in 76.79, 133.85, and 133.101 (Fig. 4.24a, b, c).

As far as the internal red slip ware is concerned, show a microporous structure characterized at the FESEM by initial vitrification (IV) as evidenced in 133.90 sample (Fig. 4.24d).

The thin-walled pottery shows a degree of sintering represented by a continuous vitrification with fine bloating pores (CV(FB)) in 133.82 (0.2-4 μ m; Fig. 4.14e). On the other hand, the sample of Dolium (133.125) shows a microstructure represented by an extensive vitrification (V) as reported in Fig. 4.24f.

The production indicators represented by the support show a microporous structure characterized at the FESEM by an extensive vitrification (V) in 133.68 and 133.69 (Fig. 4.24g). The waste of common cookware is characterized by a microporous structure at the FESEM by a continuous vitrification with fine bloating pores in 133.103 sample (0.2-4 μ m; Fig. 4.24h).



Fig. 4.24. FESEM images of freshly fractured samples: (a) 76.78. Extensive vitrification (V). (b) 133.85. Extensive vitrification (V). (c) 133.101. Extensive vitrification (V). (d) 133.90. Initial vitrification (IV). (e) 133.82. continuous vitrification with fine bloating pores (0.4-2 μ m; CV(FB)). (f) 133.125. Extensive vitrification (V). (g) 133.69. Extensive vitrification (V). (h) 133.103. Continuous vitrification with fine bloating pores (0.4-2 μ m; CV(FB)).

4.7. Microanalyses (FESEM-EDS)

Quantitative FESEM-EDS microanalyses were performed on 21 ceramic fragments divided in: 12 fine-grained pottery (133.3; 133.6; 133.8; 133.15; 133.16; 133.20; 35.75; 35.76; 27.77; 133.119; 16.36; 133.60) and 9 coarse-grained pottery (76.78; 79.79; 35.54; 32.2801.72; 133.105; 133.125; 133.70; 133.71; 133.106) in order to identify the chemical composition of mineral grains, the neoformed phases in the ceramic bodies and, in some cases, the chemical composition of the slips.

4.7.2. Coarse-grained pottery

The microanalyses performed on coarse-grained pottery samples showed that they are characterized by feldspars, clinopyroxenes, and juvenile volcanic fragments represented by pumices and glass shards. In more detail, the volcanic glass analyzed in the samples of common cookware (76.78 and 76.79) show a chemical behaviour that varies from trachy-andesitic to trachytic composition (Fig. 4.27a; Appendix C), the feldspars are represented by sanidine (Ab₁₃₋₃₁An₂₋ 9Or_{60-85;} Appendix D) and bytownite (Ab₁₃An₈₆Or_{1;} Appendix D), whereas the clinopyroxenes analyzed are classified as diopside (Wo₄₈₋₅₃En₂₃₋₄₃Fs_{8-25;} Fig. 4.27c; Appendix E).

As far as the Internal red slip ware is concerned (35.54 and 32.2801.72), the chemical composition of the mineral phases is represented by pumices characterized by a trachytic composition (Fig. 4.27a; Appendix C), feldspar represented by sanidine (Ab₁₋₄₄An₂₋₈Or₅₂₋₉₆; Fig. 4.27b; Appendix D) along with clinopyroxene classified as diopside (Wo₄₇₋₅₃En₂₅₋₄₃Fs₉₋₂₂; Fig. 4.27c; Appendix E). The thin-walled pottery imitation is characterized by feldspar classified as sanidine (Ab₈₋₅₂An₀₋₅Or₄₃₋₉₂; Fig. 4.27b; Appendix D), the clinopyroxene composition is represented by diopside (Wo₄₆₋₄₇En₃₆₋₄₉Fs₅₋₁₇; Fig. 4.27c; Appendix E). The Dolium shows a trachy-andesitic to trachytic composition (Fig. 4.27a; Appendix A) of the volcanic glass along with a clinopyroxene classified as diopside (Wo₄₈₋₅₁En₃₂₋₃₉Fs₁₃₋₁₇; Fig. 4.27c; Appendix E).

The coarse-grained production indicator represented by the waste of common cookware show a volcanic glass with a trachytic composition, the feldspar is represented by sanidine (Ab₃₁₋₄₂An₃Or₅₄₋₆₆; Fig. 4.27b; Appendix D), while the clinopyroxene is diopside (Wo₄₇₋₅₂En₃₀₋₄₂Fs₁₁₋₁₈; Fig. 4.27c; Appendix E). Lastly, the supports, show volcanic glass from trachy-andesitic to trachytic composition (Fig. 4.27a; Appendix C), the feldspars are represented by sanidine (Ab₃₃An₆Or₆₁; Fig. 4.27b; Appendix D) and bytownite (Ab₁₄An₈₄Or₁; Fig. 4.27b; Appendix D), while the clinopyroxenes are classified as diopside (Wo₄₁₋₄₆En₃₃₋₃₉Fs₁₄₋₁₉; Fig. 4.27c; Appendix E) and hedembergite (Wo₄₈₋₅₃En₁₆₋₂₂Fs₃₇₋₃₈; Fig. 4.27c; Appendix E).



Fig. 4.27. a) total alkali vs. silica; b) classified diagram of feldspar; c) classified diagram of clinopyroxene.

Noteworthy, FESEM-EDS analyses showed the presence of neoformed Casilicates represented by melilites (Fig. 4.28; Appendix F) observed in 133.125 (dolium) and 133.70 (support), that melilites have an intermediate composition between gehlenite and åkermanite (Gh. % 52.6-57.0, Na-mel. % 2.31-2.88, Ak. % 40.1-45.1) and are included in the compositional field of "ceramic" melilites as already evidenced for the melilites recognized in the fine-grained pottery.



Fig. 4.28. Composition of the neoformed phases analysed via FESEM-EDS. Ternary diagram of melilites.

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CHAPTER V

DISCUSSION

SUMMARY: 5.1. Provenance and procurement of raw materials- 5.1.1

Fine-grained pottery- 5.1.2 Coarse-grained pottery- 5.2. Pyrotechnology-

5.2.1 Fine-grained pottery- 5.2.2 Coarse-grained pottery

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CHAPTER VI

CONCLUSIONS

SUMMARY: 6.1. Fine-grained pottery - 6.2. Coarse-grained pottery

6.1. Fine-grained pottery

The proposed multi-analytical approach allowed us to confirm the local production of fine pottery at Cales and expand the previous knowledge about the black glazed pottery, a class of fine pottery widely distributed in central and western Mediterranean. In fact, for centuries the black glazed pottery has been considered the hallmark of Calenian production, in particular thanks to the availability of raw materials close to the city. Cales preserves conspicuous evidence of intense manufacturing activity covering a wide chronological span from the late 4th century BCE to the middle 1st century BCE, with a vast exportation throughout the Romanized world.

Despite several works were carried out on black glazed pottery, for the first time an accurate characterization of these artifacts was performed, including other fine-grained pottery and important production indicators from the same archaeological context with fine fabrics comparable to those of the investigated fine pottery.

- The set of techniques used for the archaeometric characterization showed the extreme homogeneity of these ceramic classes, including black glazed pottery, Terra sigillata, fine common wares and production indicators. The latter are represented by spacers and welded pieces of black glazed pottery, and, thanks to their historical importance linked to production, provided a great contribution in the definition of a local production of fine ceramics.
- The petrographic analysis showed an extreme compositional homogeneity of all the finds belonging to the different ceramic classes along with same mineralogical assemblage. The only difference was highlighted in the fine common ceramics and Terra sigillata samples, where the presence of trachyte was not recognized. The use of sporadic volcanic fragments in spacers and black glazed pottery may have been

used with the aim of imparting a technological correction (i.e., plasticity of the clay mixture) to the artifacts.

- The chemical analysis indicates that all samples are characterized by high concentrations of CaO which is compatible with the use of a local clay raw material from the Apennine chain sector. This is also confirmed by geochemical analysis thought the use of three different isotopic systematics, Sr, Nd and Pb isotopes, respectively.
- The application of Sr-Nd and Pb isotopic systematics to the fine-grained pottery from the archaeological site of Cales, for which a depth mineropetrographic characterization is available, suggests that the method enable discrimination between different ceramic productions and identify their respective sources of raw materials and it represents a valuable tool for investigating the provenance of ceramics. In detail, for fine-grained pottery, it was observed that their isotopic fingerprint is quite in line with the clay raw material used given the negligible manipulation of the starting clay.
- From a technological point of view, the samples of black glazed pottery exhibit an extreme variability of the EFTs. Three groups were identified based on their mineralogical assemblage, the qualitative abundances and degree of sintering. The two main groups (consisting of 21 and 32 samples, respectively) show an EFT from 850 to 1050 °C, just a few samples (133.22, 133.34, 35.44, 35.50) are characterized by an EFT lower than 850 °C. The three samples of Terra sigillata show an EFT from 750 to 900 °C along with a not well sintered slip, this contrasts with the technological features of Terra sigillata produced with the renowned Arretino modo that made use of muffle kilns (Cuomo di Caprio, 2007), for which the samples exhibit a well sintered slip and an EFTs above 900 °C (Mirti, Appolonia & Casoli, 1999). The fine common ware shows an EFT from 800 to 1000 °C except for the 133.119 samples where presence
of a continuous vitrification with fine bloating pores $(0.2-4 \mu m)$ suggests a slightly higher firing temperature. As far as the production indicators are concerned, the EFT ranges from 950 to 1050°C for spacers samples, whereas it turns out to be above 1050 °C for the waste of black glazed pottery, compatible with the fact that they are welded. For all the samples the presence of hematite suggests a prevailing oxidizing atmosphere. A short reducing phase may have been performed in the late stage of firing of black glazed pottery for blackening the coating. This important aspect will be further investigated in order to be able to discriminate the atmosphere condition inside the kiln and the Fe oxidation state through an accurate study of the coatings via specific state-of-the-art instrument, such as synchrotron beamlines as X-ray Absorption Near Edge Spectroscopy (XANES) that are successfully used in glazed and slip ceramic studies for tracing technological developments of specific workshops through the correlation of surface appearance and manufacture technology.

6.2. Coarse-grained pottery

The multi-analytical method used for the characterization of coarse-grained pottery from the archaeological site of Cales, allowed us to attest the local provenance of the coarse-grained pottery and assess the compositional features of the production, which can be now defined as a reference group (i.e., Maggetti, 2001) for this site. In addition to representing unpublished material from the archaeological site of Cales, this context allowed archaeologists to document the articulation of production over a wide time span. In this regard, the end of the black glazed pottery production did not determine the end of craft activities, which then oriented their manufacture to new market demands with Sigillata pottery and common ware. The production continued to highlight the role of Cales as an important craft center during the imperial period, when the most powerful families continued to enhance local economy, fitting into a market logic that managed to survive the strong economic changes that occurred during this period.

- The set of techniques used for the archaeometric characterization showed the compositional homogeneity between the common cookware, internal red slip ware, thin-walled pottery imitation, including the production indicators. The latter are represented by wastes of common cookware that provided a great contribution to the definition of a local production of coarse pottery.
- The chemical analysis highlights that common cookwares, internal red slip ware, thin-walled pottery imitation and wastes of common cookware are characterized by Ca-poor character, compatible with the use of an Alluvial clay raw material from the Volturnum river plain with similar features with the alluvial clay of Piana di Monte Verna (PMV2). On the other hand, the supports and the dolium are characterized by Ca-rich character, compatible with the use of an Alluvial clay raw material from the Volturnum river plain the use of an Alluvial clay raw material from the dolium are characterized by Ca-rich character, compatible with the use of an Alluvial clay raw material from the Volturnum river plain with similar features with the alluvial clay of

Piana di Monte Verna but collected in a level with higher CaO values (PMV1) and Pontelatone (PLT2). These affinities were closely confirmed by isotopic analysis of Sr, Nd and Pb isotopes.

- As observed for fine-grained pottery, the use of three different isotope systems is a valuable tool for investigating the provenance of ceramics, even when considering and expecting the addition of temper to reduce plasticity, in particular for the coarse-grained pottery production. In this regard, the method allowed us not only to discriminate the origin of the raw material, but also to be able to define its mix design (temper-clay ratio).
- This pioneering approach is not proposed to replace traditional methods for characterizing archaeological ceramics, but rather to provide more support to the normal analytical routine used for provenance studies.
- From a technological point of view, the samples of common cookware were fired at temperatures varying from 750 to 900 °C in a prevailing oxidizing atmosphere. Only three specimens were fired at slightly higher temperatures (850-950 °C). As far as the internal red slip wares are concerned, they are characterized by a narrow variability of firing temperatures (750-850 °C) and oxidizing atmosphere. These features highlight a great attention paid by potters during the production process, just as was the case of the internal red slip ware manufactured in Cuma (Morra et al., 2013; Izzo et al., 2021; Verde et al., 2022). On the contrary, samples of thin-walled pottery imitation exhibit a greater variability in terms of firing temperatures (from <750 °C to 950 °C). Production indicators clearly show higher temperatures than those of other investigated ceramic classes, occasionally exceeding 1000 °C.</p>

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APPENDIX

The chapter have been omitted from the text as they are in submission phase

References

Ascione, A., Ciarcia, S., Di Donato, V., Mazzoli, S., & Vitale, S. (2012). The Pliocene–Quaternary wedge-top basins of southern Italy: An expression of propagating lateral slab tear beneath the Apennines. Basin Research, 24, 456–474.

Ballini, A., Barberi, F., Laurenzi, M.A., Mezzetti, F., & Villa, I.M., (1989). Nuovi dati sulla stratigrafia del vulcano di roccamonfina. Boll. Gruppo Naz, Vulcanol. 5, 533-555.

Bish, D. L., & Duffy, C. J. (1990). Thermogravimetric analysis of minerals.

Bonardi, G., Ciarcia, S., Di Nocera, S., Matano, F., Sgrosso, I., & Torre, M. (2009). Carta delle principali Unità Cinematiche dell'Appennino meridionale. Nota illustrativa. Italian Journal of Geosciences, 128, 47–60, scale 1:250,000, 1 sheet.

Brown, R. J., Civetta, L., Arienzo, I., D'Antonio, M., Moretti, R., Orsi, G., Tomlinson, E. L., Albert, P. G., & Menzies, M. A. (2014). Geochemical and isotopic insights into the assembly, evolution and disruption of a magmatic plumbing system before and after a cataclysmic caldera- collapse eruption at Ischia volcano (Italy). Contributions to Mineralogy and Petrology, 168, 1–23. https://doi.org/10.1007/s00410-014-1035-1.

Buccianti, A., Lima, A., Albanese, S., Cannatelli, C., Esposito, R., & De Vivo, B. (2015). Exploring topsoil geochemistry from the CoDA (Compositional Data Analysis) perspective: The multi-element data archive of the Campania Region (Southern Italy). Journal of Geochemical Exploration, 159, 302-316. Carminati, E., Lustrino, M., & Doglioni, C. (2012). Geodynamic evolution of the central and western Mediterranean: Tectonics vs. Igneous petrology constraints. Tectonophysics, 579, 173–19.

Carter, S.W., Wiegand, B., Mahood, G.A., Dudas, F.O., Wooden, J.L., Sullivan, A.P., & Bowring, S.A., (2011). Strontium isotopic evidence for prehistoric transport of grayware ceramic materials in the eastern Grand Canyon region, USA. Geoarchaeology 26, 189–218. <u>https://doi.org/10.1002/gea.20348</u>.

Cascella, S. (2018). Nota sulla produzione della terra sigillata calena alla luce di alcuni frammenti inediti. Archeologia Classica, 69, 719-732.

Casero, P., Roure, F., Endignoux, L., Moretti, I., Muller, C., Sage, L., & Vially, R. (1988) Neogene geodynamic evolution of the Southern Apennines. Mem Soc Geol Ital 41:109–120

Cole, P.D., Guest, J.E., Duncan, A.M., Chester, D.K., & Bianchi,R., (1992). Post-collapse volcanic history of calderas on a composite volcano: an example from Roccamonfina, Southern Italy. Bull. Volcanol. 54, 504-520.

Conticelli, S., Marchionni, S., Rosa, D., Giordano, G., Boari, E., & Avanzinelli, R. (2009). Shoshonite and sub-alkaline magmas from an ultrapotassic volcano: Sr–Nd–Pb isotope data on the roccamonfina volcanic rocks, Roman Magmatic Province, southern Italy. Contributions to Mineralogy and Petrology, 157, 41– 63. https://doi.org/10.1007/s00410-008-0319-8. Conticelli, S., Melluso, L., Perini, G., Avanzinelli, R., & Boari, E., (2004). Petrologic, geochemical and isotopic characteristics of shoshonitic to potassic and ultrapotassic alkalic magmatism in central-southern Italy: inferences on its genesis and on the nature of its mantle source. Period. Mineral. 73, 135–164.

Cosca, M.A., & Peacor, D.R. (1987). Chemistry and structure of esseneite (CaFe3+AlSiO6), a new pyroxene produced by pyrometamorphism. American Mineralogist, 72, 148–156.

Cosentino, D., Cipollari, P., Marsili, P., & Scrocca, D. (2010). Geology of the central Apennines: A regional review. The geology of Italy: Tectonics and life along plate margins. In M. Beltrando, A. Peccerillo, M. Mattei, S. Conticelli, & C. Doglioni (Eds.),

Cucciniello, C., Melluso, L., le Roex, A.P., Jourdan, F., Morra, V., de Gennaro, R., & Grifa, C. (2017). From nephelinite, basanite and basalt to peralkaline trachyphonolite and comendite in the Ankaratra volcanic complex, Madagascar: 40Ar/39Ar ages, phase compositions and bulk-rock geochemical and isotopic evolution. Lithos. 274-275, 363–382. https://doi.org/10.1016/j.lithos.2016.12.026.

Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., & De La Torre, M. J. (2001). Carbonate and silicate phase reactions during ceramic firing. European Journal of Mineralogy, 13, 621–634. <u>https://doi.org/10.1127/0935-1221/2001/0013-0621</u>.

Cuomo di Caprio, N. (2007). Ceramica in Archeologia 2: Antiche tecniche di lavorazione e moderni metodi di indagine. Roma, IT: L'Erma di Bretschneider.

D'Antonio, M., Mariconte, R., Arienzo, I., Mazzeo, F. C., Carandente, A., Perugini, D., Petrelli, M., Corselli, C., Orsi, G., Principato, M. S., & Civetta, L. (2016). Combined Sr-Nd isotopic and geochemical fingerprinting as a tool for identifying tephra layers: Application to deep-sea cores from Eastern Mediterranean Sea. Chemical Geology, 443, 121–136. https://doi.org/10.1016/j.chemgeo.2016.09.022.

D'Antonio, M., Tonarini, S., Arienzo, I., Civetta, L., Dallai, L., Moretti, R., Orsi, G., Andria, M., & Trecalli, A. (2013). Mantle and crustal processes in the magmatism of the Campania region: Inferences from mineralogy, geochemistry, and Sr-Nd-O isotopes of young hybrid volcanics of the Ischia island (South Italy). Contributions to Mineralogy and Petrology, 165, 1173–1194. <u>https://doi.org/10.1007/s00410-013-0853-x</u>.

D'Antonio, M., Tonarini, S., Arienzo, I., Civetta, L., & Di Renzo, V. (2007). Components and processes in the magma genesis of the Phlegrean Volcanic District, southern Italy. In L. Beccaluva, G. Bianchini, & M. Wilson (Eds.), Cenozoic volcanism in the Mediterranean area. Geological Society of America Special Papers (Vol. 418, pp. 203–220). https://doi.org/10.1130/2007.2418(10).

De Bonis, A., Arienzo, I., D'Antonio, M., Franciosi, L., Germinario, C., Grifa, C., Guarino, V., Langella, A., & Morra, V. (2018). Sr-Nd isotopic fingerprinting as a tool for ceramic provenance: its application on raw materials, ceramic replicas and ancient pottery. Journal of Archaeological Science. 94, 51–59. https://doi.org/10.1016/j.jas.2018.04.002.

De Bonis, A., D'Angelo, M., Guarino, V., Massa, S., Anaraki, F. S., Genito, B., & Morra, V. (2017a). Unglazed pottery from the masjed-i jom'e of Isfahan

(Iran): Technology and provenance. Archaeological and Anthropological Sciences, 9, 617–635. <u>https://doi.org/10.1007/s12520-016-0407-z</u>.

De Bonis, A., Cultrone, G., Grifa, C., Langella, A., Leone, A.P., Mercurio, M., & Morra, V. (2017b). Different shades of red: The complexity of mineralogical and physicochemical factors influencing the colour of ceramics. Ceramics International, 43, 8065–8074. <u>https://doi.org/10.1016/j.ceramint.2017.03.127</u>.

De Bonis, A., Febbraro, S., Germinario, C., Giampaola, D., Grifa, C., Guarino, V., Langella, A., & Morra, V. (2016). Distinctive volcanic material for the production of Campana A ware: the workshop area of Neapolis at the Duomo Metro Station in Naples, Italy. Geoarchaeology 31, 437–466. https://doi.org/10.1002/gea.21571.

De Bonis, A., Cultrone, G., Grifa C., Langella, A., & Morra, V. (2014). Clays from the Bay of Naples (Italy): New insight on ancient and traditional ceramics. Journal of The European Ceramic Society. 34, 3229–3244. <u>https://doi.org/10.1016/j.jeurceramsoc.2014.04.014</u>.

De Bonis, A., Grifa, C., Cultrone, G., De Vita, P., Langella, A., & Morra, V. (2013). Raw Materials for Archaeological Pottery from the Campania Region of Italy: A Petrophysical Characterization. Geoarchaeology. 28, 478–503. https://doi.org/10.1002/gea.21450.

De Rita, D., & Giordano, G. (1996). Volcanological and structural evolution of roccamonfina volcano (southern Italy). In W. J. Mc Guire, A. P. Jones, & J. Neuberg (Eds.), Volcano instability on the earth and other planets. Geological

Society, London, Special Publications, 110, 209-224. https://doi.org/10.1144/GSL.SP.1996.110.01.16.

De Vivo, B., Rolandi, G., Gans, P.B., Calvert, A., Bohrson, W.A., Spera, F.J., & Belkin, H.E. (2001). New constraints on the pyroclastic eruptive historyof the Campanian Volcanic Plain (Italy). Mineralogy and Petrology, 73, 47-65. https://doi.org/10.1007/s007100170010.

Deino, A.L., Orsi, G., de Vita, S., & Piochi, M. (2004). The age of the Neapolitan Yellow Tuff caldera forming eruption (Campi Flegrei caldera - Italy) assessed by 40Ar/39Ar dating method. Journal of Volcanology and Geothermal Research, 133, 157-170. <u>https://doi.org/10.1016/S0377-0273(03)00396-2</u>.

Di Renzo, V., Arienzo, I., Civetta, L., D'Antonio, M., Tonarini, S., Di Vito, M. A., & Orsi, G. (2011). The magmatic feeding system of the Campi Flegrei caldera: Architecture and temporal evolution. Chemical Geology, 281, 227–241.

Di Renzo, V., Di Vito, M. A., Arienzo, I., Civetta, L., D'Antonio, M., Giordano, F., Orsi, G., & Tonarini, S. (2007). Magmatic history of Somma-Vesuvius on the basis of new geochemical and isotopic data from a deep borehole (Camaldoli della Torre). Journal of Petrology, 48, 753–784.

Dondi, M., Ercolani, G., Fabbri, B., & Marsigli, M. (1998). An approach to the chemistry of pyroxenes formed during the firing of Ca-rich silicate ceramics. Clay Minerals, 33, 443-452. <u>https://doi.org/10.1180/000985598545741</u>.

Fabbri, B., Gualtieri, S., & Shoval, S. (2014). The presence of calcite in archeological ceramics. Journal of the European Ceramic Society, 34, 7. https://doi.org/10.1016/j.jeurceramsoc.2014.01.007.

Fedele, L., Scarpati, C., Lanphere, M., Melluso, L., Morra, V., Perrotta, A., & Ricci, G. (2008). The Breccia Museo formation, Campi Flegrei, southern Italy: geochronology, chemostratigraphy and relationship with the Campanian Ignimbrite eruption. Bulletin of Volcanology, 70, 1189-1219. https://doi.org/10.1007/s00445-008-0197-y.

Franciosi, L., D'Antonio, M., Fedele, L., Guarino, V., Tassinari, C.C.G., de Gennaro, R., & Cucciniello, C. (2019). Petrogenesis of the Solanas gabbrogranodiorite intrusion, Sàrrabus (southeastern Sardinia, Italy): Implications for Late. International Journal of Earth Sciences volume, 108, 989–1012. https://doi.org/10.1007/s00531-019-01689-8.

Galer, S. J. G., & Abouchami, W., (1998), Practical applications of lead triple spiking correction of instrumental mass discrimination, Mineralogical Magazine, 62A, 491–2.

Germinario, C., Cultrone, G., Cavassa, L., De Bonis, A., Izzo, F., Langella, A., Mercurio, M., Morra, V., Munzi, P., & Grifa, C. (2019). Local production and imitations of Late Roman pottery from a well in the Roman necropolis of Cuma in Naples, Italy. Geoarchaeology, 34.

Germinario, C., Cultrone, G., De Bonis, A., De Simone, G. F., Gorrasi, M., Izzo, F., Langella, A., Martucci, C. S., Mercurio, M., Morra, V., Vyhnal, C. R., & Grifa, C. (2021). Production technology of late Roman decorated tableware

from the Vesuvius environs: Evidence from Pollena Trocchia (Campania region, Italy). Geoarchaeology, 36, 34–53.

Germinario, C., De Bonis, A., Barattolo, F., Cicala, L., Franciosi, L., Izzo, F., Langella, A., Mercurio, M., Morra, V., Russo, B., Cicchiello, I., & Grifa, C. (2022). Ceramic building materials from the ancient Témesa (Calabria region, Italy): Raw materials procurement, mix-design and firing processes from the Hellenistic to Roman period. Journal of Archaeological Science: Reports, 41, 103253.

Giannetti, B., (2001). Origin of the calderas and evolution of Roccamonfina volcano (Roman Region, Italy). J. Volcanol. Geoth. Res. 106, 301-319. https://doi.org/10.1016/S0377-0273(00)00259-6.

Goldstein, S.L., Deines, P., Oelkers, E.H., Rudnick, R.L., & Walter, L.M.,(2003). Standards for publication of isotope ratio and chemical data in ChemicalGeology.Chem.Geol.202,1-4.https://doi.org/10.1016/j.chemgeo.2003.08.003.

Gómez-Herrero, A., Urones-Garrote, E., López, A. J., & Otero-Diaz, L. C. (2008). Electron microscopy study of Hispanic Terra Sigillata. Applied Physics A, 92(1), 97-102.

Greco, G., Tomeo, A., Ferrara, B., Guarino, V., De Bonis, A., & Morra V. (2014). Cumae, the forum: Typological and archaeometric analysis of some pottery classes from sondages inside the Temple with Portico. In G. Greco & L. Cicala (Eds.), Archeometry. Comparing experiences (pp.37–68). Quaderni del

Centro Studi Magna Grecia 19, Università degli Studi di Napoli Federico II. Pozzuoli (NA), IT: Naus Editoria.

Grifa, C., Germinario, C., De Bonis, A., Langella, A., Mercurio, M., Izzo, F., Smiljanic, D., Guarino, V., Di Mauro, S., & Soricelli, G. (2019). Comparing ceramic technologies: The production of Terra Sigillata in Puteoli and in the Bay of Naples, Journal of Archaeological Science: Reports, 23, 291–303. https://doi.org/10.1016/j.jasrep.2018.10.014.

Grifa, C., Cultrone, G., Langella, A., Mercurio, M., De Bonis, A., Sebastián, E., & Morra, V. (2009). Ceramic replicas of archaeological artefacts in Benevento area (Italy): Petrophysical changes induced by different proportions of clays and temper. Applied Clay Science, 46, 231–240. https://doi.org/10.1016/j.clay.2009.08.007.

Guarino, V., de' Gennaro, R., Melluso, L., Ruberti, E., & Azzone, R.G. (2019). The transition from miaskitic to agpaitic rocks as marked by the accessory mineral assemblages, in the Passa Quatro alkaline complex (southeastern Brazil). The Canadian Mineralogist. 57, 339–361. https://doi.org/10.3749/canmin.1800073.

Guarino, V., De Bonis, A., Grifa, C., Langella, A., Morra, V., & Pedroni, L. (2011). Archaeometric study on terra sigillata from Cales (Italy). Periodico di Mineralogia, 80, 455–470. <u>http://dx.doi.org/10.2451/2011PM0030</u>.

Izzo, F., Grifa, C., Germinario, C., Mercurio, M., De Bonis, A., Tomay, L., & Langella, A. (2018). Production technology of mortar-based building materials from the Arch of Trajan and the Roman Theatre in Benevento, Italy. The

European Physical Journal Plus, 133, 363. <u>https://doi.org/10.1140/epjp/i2018-12229-1</u>.

Kemp, R.A. (1985). Soil micromorphology and the quaternary. Quaternary Research Associationtechnical guide no. 2. London, UK: Birkbeck College, 80 pp.

Kibaroğlu, M., Kozal, E., Klügel, A., Hartmann, G., & Monien, P. (2019). New evidence on the provenance of Red Lustrous Wheel-made Ware (RLW): Petrographic, elemental and Sr-Nd isotope analysis. Journal of Archaeological Science: Reports, 24, 412–433. <u>https://doi.org/10.1016/j.jasrep.2019.02.004</u>.

Langella, A., & Morra, V. (2001). Cenni sulla morfologia del territorio e sulla composizione della ceramica. In: L. Pedroni (Ed), Ceramica calena a vernice nera. Produzione e diffusione. Napoli, IT: Petruzzi Editore, 487 pp.

Langmuir, C.H., Vocke Jr., R.D., & Hanson, G.H., (1978). A general mixing equation with applications to Icelandic basalts. Earth Planet Sci. Lett. 37 (1), 380–392. <u>https://doi.org/10.1016/0012-821X(78)90053-5</u>.

Maggetti, M., (2001). Chemical Analyses of Ancient Ceramics: What for? CHIMIA Int. J. Chem. 55, 923–930.

Maggetti, M., Neururer, C., & Ramseyer, D. (2011). Temperature evolution inside a pot during experimental surface (bonfire) firing. Applied Clay Science. 53, 500–508. <u>https://doi.org/10.1016/j.clay.2010.09.013</u>.

Makarona, C., Nys, K., & Claeys, P., (2014). Sr isotope analysis for the provenance study of ancient ceramics: an integrated approach. In: Scott, R.B., Braekmans, D., Carremans, M., Degryse, P. (Eds.), Proceedings of the 39th International Symposium for Archaeometry, ISA 2012, Leuven (Belgium), pp. 149–156.

Malinverno, A., & Ryan, W. B. F. (1986). Extension in the tyrrhenian Sea and shortening in the Apennines as result of arc migration driven by sinking of the lithosphere. Tectonics, 5, 227–245.

Maniatis, Y., & Tite, M.S. (1981). Technological examination of Neolithic-Bronze Age pottery from central and southeast Europe and from the Near East. Journal of Archaeological Science, 8, 59–76. <u>https://doi.org/10.1016/0305-</u> <u>4403(81)90012-1</u>.

Maritan, L. (2020). Ceramic abandonment. How to recognise post-depositional transformations. Archaeological and Anthropological Sciences, 12, 199. <u>https://doi.org/10.1007/s12520-020-01141-y</u>.

Melluso, L., Scarpati, C., Zanetti, A., Sparice, D., & de'Gennaro, R. (2022). The petrogenesis of chemically zoned, phonolitic, Plinian and sub-Plinian eruptions of Somma-Vesuvius, Italy: Role of accessory phase removal, independently filled magma reservoirs with time, and transition from slightly to highly silica undersaturated magmatic series in an ultrapotassic stratovolcano. Lithos, 430, 106854.

Melluso, L., de' Gennaro, R., Fedele, L., Franciosi, L., & Morra, V. (2012). Evidence of crystallization in residual, Cl-F-rich, agpaitic, trachyphonolitic magmas and primitive Mg-rich basalt-trachyphonolite interaction in the lava domes of the Phlegrean Fields (Italy). Geological Magazine, 149, 532–550. https://doi.org/10.1017/S0016756811000902.

Milia, A., & Torrente, M. M. (2014). Early-stage rifting of the southern Tyrrhenian region: The Calabria–Sardinia breakup. Journal of Geodynamics, 81, 17–29. <u>https://doi.org/10.1016/j.jog.2014.06.001</u>.

Milia, A., Torrente, M. M., & Iannace, P. (2017). PlioceneQuaternary orogenic systems in central Mediterranean: The Apulia–Southern Apennines–Tyrrhenian Sea example. Tectonics. <u>https://doi.org/10.1002/2017TC004571</u>.

Mirti, P., Appolonia, L. & Casoli, A. (1999). Technological Features of Roman Terra Sigillata from Gallic and Italian Centres of Production. Journal of Archaeological Science, 26, 1427-1435.

Molera, J., Pradell, T., & Vendrell-Saz, M. (1998). The colours of Ca-rich ceramic pastes: origin and characterization, Applied Clay Science, 13, 187–202. https://doi.org/10.1016/S0169-1317(98)00024-6.

Morel, J. P. (1989). Un atelier d'amphores Dressel 2-4 à Cales. In F. Zevi (Ed.), Amphores romaines et Histoire èconomique: dix ans de recherches (pp. 558-559). Rome (RM). Italy: École française de Rome.

Morimoto, N. (1988). Nomenclatura dei pirosseni. Mineralogia e petrologia 39, 55-76. <u>https://doi.org/10.1007/BF01226262</u>.

Munzi, P., Guarino, V., De Bonis, A., Morra, V., Grifa, C., & Langella, A. (2014). The fourth century black-glaze ware from the northern periurban sanctuary of Cumae. In G. Greco & L. Cicala (Eds.), Archeometry. Comparing experiences (pp. 69–87). Quaderni del Centro Studi Magna Grecia 19, Università degli Studi di Napoli Federico II. Pozzuoli (NA). Italy: Naus Editoria.

Olcese, G. (2015). Produzione e circolazione mediterranea delle ceramiche della Campania nel III secolo a.C. Alcuni dati della ricerca archeologica e archeometrica. In A. Siciliano & C. Mannino (Eds.), La Magna Grecia da Pirro ad Annibale. Atti del Convegno di Studio sulla Magna Grecia (pp.159-210). Taranto. Italy: ISAMG - Istituto per la Storia e l'Archeologia della Magna Grecia (Taranto).

Pappone, G., Casciello, E., Cesarano, M., D'Argenio, B., & Conforti, A. (2010). Note Illustrative della Carta Geologica d'Italia alla scala 1:50000. Foglio 467 Salerno. ISPRA, Servizio Geologico d'Italia.

Passaro, C., & Carcaiso, A. (2006). Una patera a medaglione di K. Atilius e tre firme vascolari di TI.L. Albanius dall'area dell'ex Pozzi di Sparanise. Notizia preliminare. In D. Caiazza (Ed), Samnitice loqui. Studi in onore di Aldo Prosdocimi per il premio I Sanniti (pp. 287-293). Piedimonte Matese (CA). Italy: Libri campano-sannitici.

Patacca, E., & Scandone, P. (2007). Geology of the southern Apennines. Bollettino della Società Geologica Italiana, 7, 75-119. Peccerillo, A. (2020). Campania volcanoes: petrology, geochemistry, and geodynamic significance. In Vesuvius, Campi Flegrei, and Campanian Volcanism (pp. 79-120). Elsevier.

Peccerillo, A., (2017). The Roman Province, in: Peccerillo, A. (Ed.), Cenozoic Volcanism in the Tyrrhenian Sea Region. Advances in Volcanology. Second ed. Springer, Cham. <u>https://doi.org/10.1007/978-3-319-42491-0_4</u>.

Pedroni, L. (2001). Ceramica calena a vernice nera. Produzione e diffusione. Napoli, IT: Petruzzi Editore

Pedroni, L., & Soricelli, G. (1996). Terra Sigillata da Cales. Archeologia Classica, 48, 180–188.

Pedroni, L. (1993). Problemi di topografia e urbanistica calena. Samnium, 66, 208-230.

Pedroni, L. (1990). Due bolli in 'planta pedis' da Cales e la ceramica a vernice nera terminale. Samnium, 63, 169-181.

Pedroni, L. (1986). Ceramica a vernice nera da Cales. 2.[Tavole]. Liguori Ed..

Picon, M. (1973). Introduction à l'étude technique des céramiques sigillées de Lezoux, Centre de Recherches sur les techniques Gréco-romaines, 2.Archeologia Classica, 27, 153-160. Quinn, S.P. (2013). Ceramic petrography: the interpretation of archaeological pottery & related artefacts in thin section. Oxford, UK: Archaeopress. https://doi.org/10.2307/j.ctv1jk0jf4.

R Development Core Team (2012). R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing. Vienna, Austria. <u>https://www.r-project.org</u>.

Rathossi, C., & Pontikes, Y. (2010a). Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments. Part I: reaction paths, crystalline phases, microstructure and colour. Journal of the European Ceramic Society, 30,1841–51. https://doi.org/10.1016/j.jeurceramsoc.2010.02.002.

Rathossi, C., & Pontikes, Y. (2010b). Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments: part II. Chemistry of pyrometamorphic minerals and comparison with ancient ceramics. Journal of the European Ceramic Society, 30, 1853–66. https://doi.org/10.1016/j.jeurceramsoc.2010.02.003.

Renson, V., Jacobs, A., Coenaerts, J., Mattielli, N., Nys, K., & Claeys, Ph. (2013). Using lead isotopes to determine pottery provenance in Cyprus: Clay source Signatures and comparison with Late Bronze Age Cypriote pottery. Geoarchaeology, 28 (6), 517-530. <u>https://doi.org/10.1002/gea.21454</u>.

Rispoli, C., De Bonis, A., Guarino, V., Graziano, S.F., Di Benedetto, C., Esposito, R., Morra, V., & Cappelletti, P. (2019). The ancient pozzolanic

mortars of the Thermal complex of Baia (Campi Flegrei, Italy). Journal of Cultural Heritage. 40, 143–154. <u>https://doi.org/10.1016/j.culher.2019.05.010</u>.

Rolandi, G., Bellucci, F., Heizler, M. T., Belkin, H. E., & De Vivo, B. (2003). Tectonic controls on the genesis of ignimbrites from the Campanian Volcanic Zone, southern Italy. Mineralogy and Petrology, 79(1), 3-31.

Rouchon, V., Gillot, P.Y., Quidelleur, X., Chiesa, S., & Floris, B., (2008). Temporal evolution of the Roccamonfina volcanic complex (Pleistocene), Central Italy. J. Volcanol. Geotherm. Res. 177, 500-514. <u>https://doi.org/10.1016/j.jvolgeores.2008.07.016</u>.

Ruffo, F. (2010). La Campania antica. Appunti di storia e di topografia. Parte I dal Massico-Roccamonfina al Somma-Vesuvio. Napoli, IT: DLibri.

Santacroce, R. (1987) Somma-Vesuvius. Quad Ric Sci CNR, Rome, 114, 8, pp 249.

Sbrana, A., Toccaceli, R.M., Faccenna, C., Fulignati, P., Giudetti, G., Marianelli, P., Deino, A., Bravi, S., & Monti, L. (2010). Carta Geologica d'Italia alla scala 1:50000. Foglio 464 Isola d'Ischia. ISPRA, Servizio Geologico d'Italia.

Schneider, G., & Zabehlicky-Scheffenegger, S. (2016). Sigillata from the Insula II and a private house in the Eastern quarter of Velia – chemical analysis and archaeological discussion. <u>http://www.facem.at</u>.

Shoval, S., & Paz, Y. (2013). A study of the mass-gain of ancient pottery in relation to archeological ages using thermal analysis. Applied Clay Science, 82, 113–120.

Soricelli, G. (2004). La produzione di terra sigillata in Campania. In J. Poblome, P. Talloen, R. Brulet, & M.Waelkens (Eds.), Early Italian Sigillata, Proceedings of the First International ROCT-Congress (Leuven, May 7–8, 1999) (pp. 299– 307). Leuven and Paris and Dudley, MA: Peeters

Soricelli, G., Schneider, G., & Hedinger, B. (1994). L'origine della "Tripolitanian Sigillata/ Produzione A" della Baia di Napoli. In: Olcese, G. (Ed.), Ceramica romana e archeometria: lo stato degli studi. Atti delle giornate di studio (Castello di Montefugoni, Firenze). Quaderni del Dipartimento di Archeologia e Storia delle Arti, Sezione archeologica (pp. 67–88). Firenze, IT: All'insegna del Giglio.

Terry, R.D., & Chilingar, G.V. (1955). Summary of 'concerning some additional aids in studying sedimentary formations by M.S. Shvetsov. Journal of Sedimentary Research, 25, 229-234. <u>http://doi.org/10.1306/74D70466-2B21-11D7-8648000102C1865D</u>.

Verde, M., De Bonis, A., D'Uva, F., Guarino, V., Izzo, F., Rispoli, C., Borriello, G., Giglio, M., Iavarone, S., & Morra, V. (2022). Minero-petrographic investigation on Roman pottery found in a dump in the workshop area of Cumae (southern Italy). Journal of Archaeological Science: Reports, 42, 103-376. https://doi.org/10.1016/j.jasrep.2022.103376. Vitale, S., & Ciarcia, S. (2018). Tectono-stratigraphic setting of the Campania region (southern Italy). Journal of Maps, 14, 9–21. https://doi.org/10.1080/17445647.2018.1424655.

Vitale, S., Tramparulo, F. D. A., Ciarcia, S., Amore, F. O., Prinzi, E. P., & Laiena, F. (2017). The northward tectonictransport in the southern Apennines: Examples from theCapri Island and western Sorrento Peninsula (Italy).International Journal of Earth Sciences, 106, 97–113.

Vitale, S., & Ciarcia, S., (2013) Tectono-stratigraphic and kinematic evolution of the southern Apennines/Calabria-Peloritani Terrane system (Italy). Tectonophysics 583:164–182

Weis, D., Kieffer, B., Maerschalk, C., Barling, J., de Jong, J., Williams, G. A., Hanano, D., Pretorius, W., Mattielli, N., Scoates, J. S., Goolaerts, G., Friedman, R. M., & Mahoney, J. B., (2006), High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP–MS, Geochemistry, Geophysics, Geosystems, 7, Q08006. <u>https://doi.org/10.1029/2006GC001283</u>.

White, W. M., Albarède, F., & Télouk, P., (2000), High-precision analysis of Pb isotope ratios by multi-collector ICP–MS, Chemical Geology, 167, 257–70

Whitney, D.L., & Evans, B.W. (2010). Abbreviations for names of rockforming minerals. American Mineralogist. 95, 185–187. https://doi.org/10.2138/am.2010.3371. Williams, D.F. (1990). The study of ancient ceramics: the contribution of the petrographic method. In: T. Mannoni, & A. Molinari (Eds.), Scienze in archeologia. Quaderni del Dipartimento di Archeologia e Storia delle Arti, Università di Siena (pp. 43–64). Firenze, IT: All'insegna del Giglio

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to everyone who has contributed to the successful completion of my doctoral dissertation.

First and foremost, I would like to thank my supervisors **Prof. Alberto De Bonis** and **Prof. Vincenzo Morra** for their invaluable guidance from my bachelor's degree, support, and encouragement throughout my PhD studies. Their expertise and insight have been instrumental in shaping my research, and I am deeply grateful for their mentorship.

Thank you, **Alberto**, for your constant availability and support throughout the development of my thesis, even when you had a busy schedule. Your patience and willingness to listen to my concerns and questions have been invaluable, and I have learned so much from our discussions. Most of all, I appreciate your honest and constructive feedback. You have always challenged me to think critically and to strive for excellence, and your insights have helped me to become a better student and a better person. Thank you also for putting up with my endless questions and occasional meltdowns.

Thank you, **Prof.** Vincenzo Morra, for your patience and understanding during challenging times, as well as for your unwavering belief in my potential. Your expertise and knowledge have been invaluable to me, and I am constantly impressed by your dedication to your work and your willingness to go above and beyond to help your team succeed. All of this has been a source of great inspiration for me. I also want to express my gratitude for the support and encouragement you have provided me, whether it be through constructive feedback, opportunities for growth, or simply a kind word when I needed it most.

Thank you both for your extraordinary contributions to my academic and personal development. I will always cherish the knowledge, skills, and values I have acquired under your supervision. No thanks will be enough to express my gratitude.

I would like to express my gratitude **Dr. Antonella Tomeo** for providing me with the materials for this study, for her availability, and for being fundamental to the completion of my research work.

I am grateful to my colleagues and all the staff at DiSTAR for their stimulating discussions, insights, and friendship. In particular, for their helpful advice and support.

I would like to acknowledge the **reviewers of my PhD thesis**, **Prof. Celestino Grifa** and **Prof. Gianluca Soricelli,** for having approved and enjoyed my work; I thank them for their advice, which have surely contributed to the improvement of the thesis. I would like to thank **Dr. Virginie Renson**, who has welcomed me at MU-Research Reactor and supervised my abroad research activities in Columbia, Missouri (USA). I am grateful for the opportunity to work under her supervision, and I will always cherish the knowledge and skills I have acquired. Thank you for all the wonderful times we've had together, especially the delicious meals you've shared with me. Your hospitality and warmth have made me feel so welcome in a new and unfamiliar place, and I truly appreciate all the effort you've put into making my stay comfortable and enjoyable.

I would like to express my deepest appreciation to the entire **staff of MU-Research Reactor**. Their collaboration, companionship, and hard work have made this journey more meaningful and enjoyable. Their friendship and support have made a significant impact on my life. I will always cherish the memories we have created together, thank you all for being a part of my journey.

I would like to thank my dear friend **Gayla M. Neumeyer**, for the unforgettable experience of living together during my period abroad. Her friendship, kindness, and support have been instrumental in making this adventure a truly memorable one. I will always cherish the moments we shared, from exploring new places to trying new foods, from laughing until our stomachs hurt to comforting each other during tough times. I am so grateful for having had the chance to live with you. Thank you for everything, my dear friend. I will always treasure our time together.

THANK YOU ALL FOR YOUR INVALUABLE CONTRIBUTIONS TO MY DOCTORAL RESEARCH.