

Raw Materials for Archaeological Pottery from the Campania Region of Italy: A Petrophysical Characterization

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We performed petrophysical analyses on 34 clayey samples of different geological origin within the Campania region of Italy in order to determine possible sources of raw materials used to produce ancient pottery. Possible raw material sources can be grouped into high-CaO clays (HCC) and low-CaO clays (LCC). HCC are mainly represented by more recent (Miocene-Pleistocene) basinal sediments whereas LCC tend to be associated with basinal, alluvial, and pyroclastic deposits. A chemical comparison between clayey raw materials, modern ceramic replicas, and Campanian archaeological ceramics of several typologies (common ware, cooking ware, fine tableware, amphorae, and bricks) from 8th century B.C. to the Middle Ages (a total of 350 ceramic samples) indicates that HCC were extensively used for common wares and that these were either mixed with temper or levigated. In contrast, most of the LCC were used for the production of cookware. We also analyzed the technological potential of the sampled raw materials, taking into consideration their actual and possible uses. We observed that most HCC deposits were well suited for tableware and amphorae, whereas LCC were better for cookware and some fine tableware. © 2013 Wiley Periodicals, Inc.

INTRODUCTION

The Campania region of southwestern Italy is renowned for its rich and extensive archaeological record. Inhabited by the Italic people (the Oscans and the Samnites), the Greeks, and the Romans, the area has long been praised for its fertile land and favorable position with several natural harbors and communication networks. The area also has a rich ceramic tradition. Up until the Late Roman period (3rd–6th century A.D.), and even later, the pottery produced in many Campanian workshops circulated in regional and extra-regional contexts (Grifa et al., 2013). This ceramic tradition continues today and in a few examples includes the exploitation of local clays. Surprisingly, despite many archaeological excavations and an increasing availability of archaeometric data, knowledge of ceramic raw materials (clay and temper) used in the past is far from understood.

The aim of this study is the search and petrophysical characterization of clayey raw materials used in the pro-

duction of ancient pottery in the Campania region. This information is relevant to archaeometric studies on Campanian ceramics where one of the most frequent questions asked by archaeologists is as follows: Where was this pottery produced? In some cases, the answer is obvious, especially where there are production indicators (kiln waste, spacers, etc.) or very distinctive temper grains easily recognizable in thin section. However, in cases where ceramic inclusions are not distinct or easily recognizable, as with finer fabrics, a comparison between the chemical composition of the ceramics with that of a local clayey raw material may be helpful. Complications in sourcing arise when the bulk composition of clayey materials have been modified by the removal of coarse grains. Since ancient times, potters have refined raw materials by sieving or, if necessary, by a more efficient levigation process in settling tanks (e.g., Cuomo di Caprio, 2007; Fowler, Fayek, & Middleton, 2011) where fine clays are locally absent. Clay levigation was frequently adopted in the production of fine wares, such as *Black-Glazed* ware and *terra*

sigillata. Thus, we also analyzed the chemical composition of the clay fraction (CF, $< 2 \mu\text{m}$) after the removal of coarser grains via sedimentation in order to investigate changes in chemical composition following the levigation process.

Another focal point of our work regards the technological potential of local clays. In the past, potters were able to choose the best clays for their wares simply based on experience. Today, the technological properties of ceramic end products can be predicted using mineralogical, chemical, and petrophysical analyses of clayey raw materials. Thus, a quantitative analytical approach is increasingly used to select raw materials, especially in modern industry where ceramics with very specific features and applications are produced (Dondi, 1997). To this purpose, we combined the geochemical data of different clayey sediments from the Campania region with their chemical composition and rheological properties.

OVERVIEW OF CAMPANIAN POTTERY

Many ancient production centers of pottery have been identified in Campania. A full review is beyond the scope of the current study, thus, we have focused our attention on well-documented production sites where archaeometric data sets are available. Other archaeological studies with important hypotheses related to local productions are also included to better understand the Campanian context of pottery manufacturing.

The Bay of Naples, defined here as the area extending from ancient *Cuma* to *Stabiae* (Figure 1), contains a rich archaeological record. Ceramic evidence dates as early as the 3rd millennium B.C. (e.g., pottery from the Gaudio Culture; Livadie, 1990), and the area later became a major cultural and economic center for the region. *Cuma*, the first Greek colony of the Italian peninsula (8th century B.C.) contains ceramics that evidence continuous occupation from the Archaic to the Middle Ages and highlight the city's fundamental role in trading and manufacturing technology (Morra et al., 2012). Recently, the ancient city has been part of a large archaeological research program (the *Kyme* projects) resulting in new archaeometric data for locally produced and imported pottery. Particular attention has been focused on cooking ware, taking into account that *Cuma* was the main center of a presumed manufacturing district referred to as the Campanian Cookware industry (Peña & McCallum, 2009a). Archaeometric analysis of ceramics, including *internal red-slip* cookware (*Rosso Pompeiano*), probably the *Cumanae Testae* of classical sources (Pucci, 1975), ranging in age from the 1st century B.C. to the 1st century A.D., sheds light on the peculiar technological aspects of this pottery and the

trading of (carbonate-free) clayey raw materials and volcanic temper from neighboring areas (e.g., De Bonis et al., 2009; Morra et al., 2012). High technological standards in pottery manufacturing and the careful selection of clays and temper is also evidenced in fine and common ware productions from *Cuma*, such as *Black-Glazed* ware (4th century B.C.; Munzi et al., 2012), Byzantine common ware (6th–8th century A.D.; Grifa et al., 2009a), and ceramic crucibles used for making Egyptian blue pigment (Grifa et al., 2012). For these productions, the most probable carbonate-bearing clay exploited from the Greek to Middle Ages (and possibly later) is on the island of Ischia (Figure 1; Grifa et al., 2009a; De Bonis, 2011; Morra et al., 2012). This recent research, combined with earlier archaeological data, has helped to redefine the role of the Bay of Naples as an important pottery production center (e.g., Monti, 1980, 1991; Olcese, 2010).

The Campi Flegrei area (Figure 1) north of Naples also contains important ancient ceramic production workshops. For example, *Puteoli* (modern Pozzuoli), produced *terra sigillata* from the latter years of the 1st century B.C. up until the middle of the 1st century A.D. (Soricelli, 2004; Porten Palange, 2009). *Misenum* (modern Miseno) hosted an ancient harbor of the Roman fleet, and produced High Medieval transport amphorae (Grifa et al., 2005a, 2005b). *Neapolis* (modern Napoli) was another pottery production center as demonstrated by the *Campana A* workshops from Corso Umberto and Vico S. Marcellino (Laforgia, 1988; Guerini & Mancini, 2007). Recent archaeometric investigations suggest the presence of locally produced *Thin-Walled* pottery (2nd century B.C.–3rd century A.D.) from *Neapolis* (Faga, 2010). Kiln waste remains of the so-called *Produzione A della baia di Napoli* (Soricelli, Schneider, & Hedinger, 1994; Soricelli, 2004; see also Kenrick, 1996, who defines it as *Campanian Orange Sigillata*) suggest that workshops were active in this town during the second half of the 1st century B.C. and the first half of the 1st century A.D. Thousands of common ware and amphorae fragments from the Carminiello ai Manesi excavation (Carsana, 1994) and cooking ware from Girolamini (Toniolo, 2012) suggest that ceramic production in *Neapolis* continued into the Late Roman period.

Pompeii (Figure 1) has also been the subject of multiple ceramic investigations where the study of pottery has helped archaeologists better understand the socioeconomic dynamics of the region. Almost one century of research on the large quantities and types of pottery found beneath the A.D. 79 pumice layer has revealed a well-organized distribution system of items within the city and proximal service area. However, where and how those workshops worked is still barely understood. The latest studies hypothesize the occurrence of fine ware

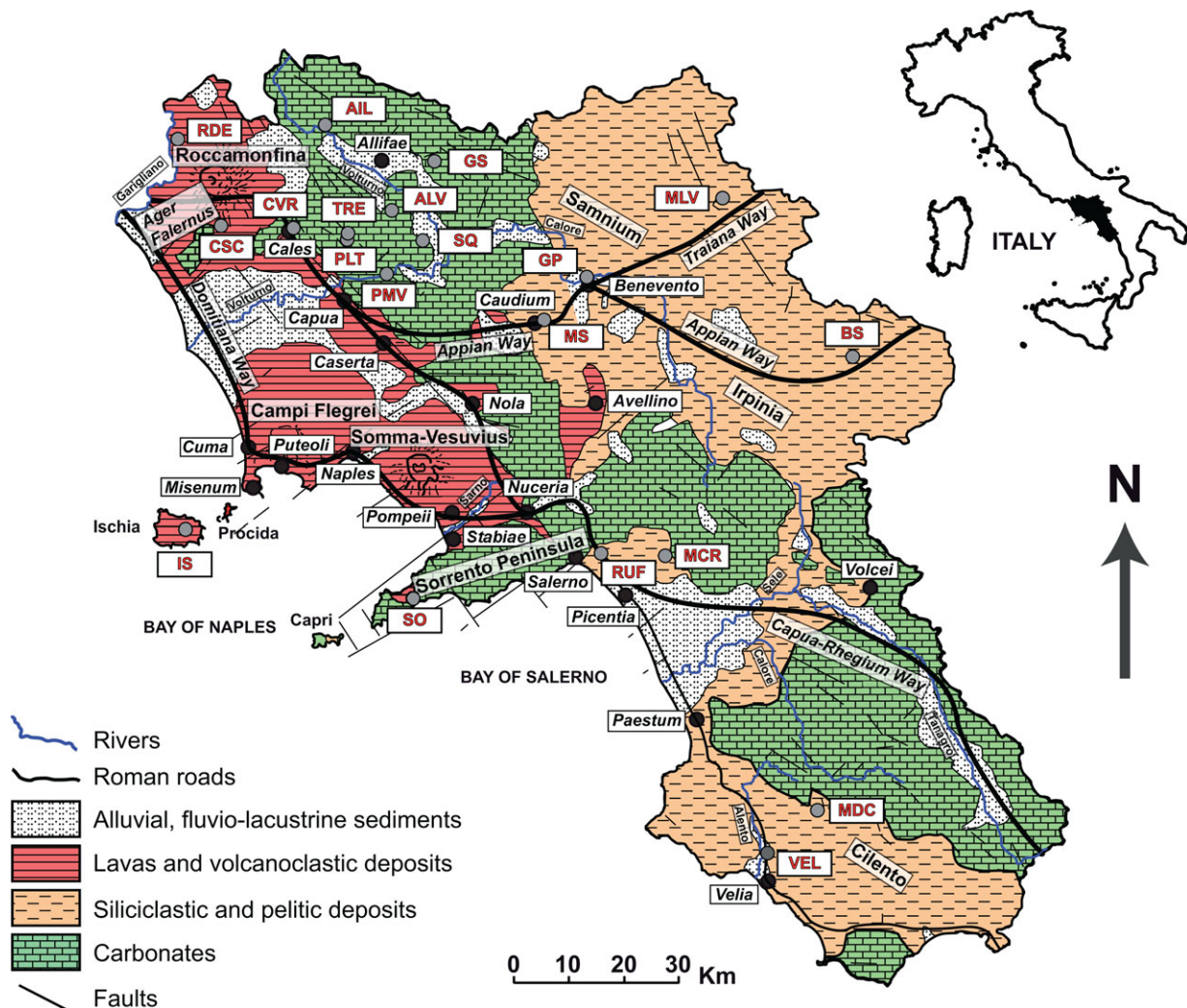


Figure 1 Simplified geological map of the Campania region (adapted from Grifa et al., 2013) showing the clayey deposits sampled in this study. ALL = Ailano; ALV = Alvignano; BS = Bisaccia; CVR = Calvi Risorta; CSC = Cascano; GP = Gran Potenza; GS = Gioia Sannitica; IS = Ischia; MCR = Montecorvino Rovella; MDC = Moio della Civitella; MLV = Malvizza; MS = Montesarchio; PLT = Pontelatone; PMV = Piana di Monte Verna; RDE = Rocca d'Evandro; RUF = Rufoli; SO = Sorrento; SQ = Squille; TRE = Treglia; VEL = Velina. The main ancient roads and archaeological sites are also reported (after Shepherd, 1911, modified).

workshops integrated within the urban network, intimately correlated with places of worship in the forum area (sanctuary/workshops model), at least up until a significant rebuilding activity occurred in the middle of the 2nd century B.C. (Cottica et al., 2010; Schneider, Daszkiewicz, & Cottica, 2010). Afterwards, ceramic production was probably organized in peripheral manufacturing districts that were well connected with the hinterland by a road network, as evidenced by a common ware kiln close to the *Porta di Stabia* (Cavassa, 2009; Grifa & Morra, 2009). The complete readaptation of the urban network and the consequent displacement of workshops to peripheral areas could be the reason for very limited

kiln structure finds at Pompeii. Despite recent archaeometric data on potsherds from Pompeii, the clayey raw materials exploited for ceramic production have yet to be accurately located. Peña and McCallum (2009a and 2009b) indicated the occurrence of a well-developed distribution network of pottery (either locally produced or imported) inside the city and hypothesized the exploitation of marine clays located in the Salerno province (the Ogliara and Montecorvino outcrops) and/or fluvial deposits from the Sarno flood plain, variably mixed with volcanic temper. Heavy weathered volcanic deposits may have been another source (e.g., Peña, 1992) for the production of cooking wares due to their good refractory

properties. Pottery production in the Vesuvius area continued after the A.D. 79 eruption and was part of a very active trading network between the coast and inland areas (Martucci et al., 2012; Grifa et al., 2013).

Other significant ceramic production sites have been identified in northern Campania. The ancient city of *Cales* (Figure 1) was an important center of ceramic production and a cultural and economic connection point between Rome and the southern provinces. *Calenan* workshops are generally identified for their shiny and finely decorated *Black-Glazed* ware and *terra sigillata* productions, widely diffused in the colonies of the Roman Empire (Pedroni & Soricelli, 1996; Langella & Morra, 2001; Guarino et al., 2011). Another important center of production, yet rarely considered until recent times, is the city of Alife (ancient *Allifae*), where recent studies have identified a large production of common and *Thin-Walled* wares, contemporarily active with *Cales* during Roman time (Soricelli, 2009). All the area commonly named *Ager Falernus* seems to have also been involved in intensive ceramic production, particularly devoted to local wineries, utilizing clayey deposits located between Falciano and Teano (Arthur, 1987). The way these presumed production centers interacted with the surrounding districts (e.g., *Cales*) is an important but yet to be determined aspect of pottery production dynamics in Campania.

Ancient pottery production centers have also been identified in ancient Roman settlements of northern Campania (e.g., Chiosi & Gasperetti, 1994; Chiosi et al., 1994a; 1994b; Livadie, 1994). Pottery productions from the Samnium and Irpinia regions (Figure 1), located along the Apennine chain, are widespread, due to the presence of large clay outcrops, together with the favorable location of many ancient settlements along two important Roman roads (the *Appian* and *Traiana* Ways), which crossed the Apennines reaching the eastern coasts of southern Italy. Almost all the settlements were located next to a clay source, as in the case of Caudium (De Bonis et al., 2010) and Benevento (Lupia, 1998; Grifa et al., 2006; Grifa, Morra, & Langella, 2007). In this region, ancient ceramic traditions are still practiced today in several centers, among which the most important are Cerreto Sannita (Di Cosmo, 2005) and Ariano Irpino (Giorgio & D'Antuono, 2010) where finely decorated majolica is produced.

The distribution of clay outcrops has also influenced pottery production in southern Campania. The Etruscan-Campanian site of Fratte, in the vicinity of Salerno (Greco & Pontrandolfo, 1990), is located along a natural road of communication connecting the plain of Pontecagnano (ancient *Picentia*) and Paestum with the *Agro Nocerino-Sarnese* and the Campanian Plain (Avallone, 2007). In this area are clay outcrops that were likely exploited at local

pottery production centers (e.g., Vietri sul Mare, Rufoli di Ogliara). Other production centers also occur along the Cilento coastline, such as the *Magna Graecia* colonies of Paestum and Velia (Figure 1; Gassner, Greco, & Sauer, 2003). Ceramic production has also been identified farther inland at ancient *Volcei* (modern Buccino), a Roman settlement (Rinaldi et al., 2007).

In sum, recent archaeological investigations have provided new archaeometric data regarding pottery production in Campania and surrounding regions.¹ Nevertheless, there is still a need to better determine the source of raw materials used in the production of Campanian pottery. Such information can provide greater insight into the production and exchange relationships of this important archaeological region.

GEOLOGICAL FRAMEWORK AND SAMPLING DESIGN

The geology of Campania is dominated by the Southern Apennine chain located between the Central Apennine chain to the north and the Calabria-Peloritani Terrane to the south (Bonardi et al., 2009). Clay deposits are exposed in several outcrops, and therefore we established the following criteria for choosing raw materials for this study: (1) proximity to ancient archaeological sites (most identified as production centers) and (2) the location of ancient roads by which materials could be easily transported (Figure 1 and Table I). Moreover, additional information was obtained from historical sources and from modern workers in the ceramic industry. In particular, as in other studies of this type (e.g., Fowler et al., 2011), information was obtained from potters who still employ traditional technology (e.g., the use of local clays and wood firing).

We collected raw materials from diverse geological contexts within Campania (Table I). Sampling was performed by removing the surface portion of the clayey deposit in order to minimize plant and faunal organic matter content. Geological information for the sample localities was obtained from maps provided by the Istituto Superiore per la Protezione e la Ricerca Ambientale at 1:100,000 and 1:50,000 scales² and, where possible, from

¹The *Immensa Aequora* project provides publications (Olcese 2010, 2012) and an on-line archaeometric database (<http://www.immensaaequora.org/>) on pottery (4th century B.C. to 1st century A.D.) from Campania and other regions of Italy. The on-line *Facem* resource organized by the Institute of Classical Archaeology of the University of Vienna (<http://www.facem.at/>) provides information on pottery (6th–2nd century B.C.) in the Southern Central Mediterranean area.

²1:100,000 scale maps available at http://193.206.192.231/carta_geologica_italia/default.htm; 1:50,000 scale maps available at <http://www.isprambiente.gov.it/Media/carg/index.html>.

Table 1 Sampling data.

Sample	Site (Province)	UTM (mE)	UTM (mN)	Geological Information	Description	Munsell Color
AIL1	Ailano (CE)	433,718	4,582,078	Caiazzo sandstone (lower Messinian)	Clayey sample with vegetable organic matter	2.5Y 5/3 (light olive brown)
ALV1	Alvignano (CE)	445,208	4,565,791	Pietraraja formation (middle-upper Tortonian)	Clayey sample from the external area of a recently disused quarry	2.5Y 5/3 (light olive brown)
ALV2	Alvignano (CE)	445,370	4,565,666	Pietraraja formation (middle-upper Tortonian)	Clayey sample from the quarry face	2.5Y 4/2 (dark grayish brown)
BS1	Bisaccia (AV)	530,875	4,540,919	Vallone del Toro Unit (Tortonian-Messinian)	Clayey sample coming from the badlands of the Ferrelli valley	GLE Y1 5/5G (greenish gray)
BS2	Bisaccia (AV)	530,875	4,540,919	Vallone del Toro Unit (Tortonian-Messinian)	Clayey sample coming from the badlands of the Ferrelli valley	10R 4/2 (weak red)
BS3	Bisaccia (AV)	530,901	4,540,919	Vallone del Toro Unit (Tortonian-Messinian)	Clayey sample coming from the riverbank in the Ferrelli valley	2.5Y 5/2 (grayish brown)
CSC1	Cascano di Sessa Aurunca (CE)	413,994	4,564,955	Weathered pyroclastics from the Roccamonfina Volcano	Clayey sample deriving from reworked piroclastic deposits, currently used for cookware production	7.5YR 5/3 (brown)
CVR1	Calvi Risorta (CE)	429,319	4,564,448	Pietraraja formation (middle-upper Tortonian)	Clay from road-work excavation	5Y 3/1 (very dark gray)
CVR2	Calvi Risorta (CE)	428,875	4,564,205	Pietraraja formation (Middle-Upper Tortonian)	Clayey deposit with arenaceous intercalations from the quarry face	2.5Y 5/1 (gray)
GP1	Gran Potenza (BN)	479,922	4,552,198	Ariano Unit (Andretta Synthème; lower Pliocene)	Clayey sample from the quarry face	2.5Y 6/1 (gray)
GP2	Gran Potenza (BN)	479,922	4,552,198	Ariano Unit (Andretta Synthème; lower Pliocene)	Clayey sample from the quarry face	2.5Y 6/1 (gray)
GS1	Gioia Sannitica (CE)	453,432	4,574,215	Argille Varicolori (Sicilide, Parasiclilide) olistostromes in thrust-top formation (Caiazzo sandstones, lower Messinian)	Reworked clayey deposit with sparse calcareous fragments	5YR 4/6 (yellowish red)
IS1	Ischia (NA)	408,334	4,509,367	Cava Lecce Unit (Sbrana et al., 2010)	Reworked clayey deposit	2.5Y 6/3 (light yellowish brown)
IS2	Ischia (NA)	408,275	4,509,357	Cava Lecce Unit (Sbrana et al., 2010)	Reworked clayey deposit with organic matter	2.5Y 5/3 (light olive brown)
IS3	Ischia (NA)	408,306	4,509,356	Cava Lecce Unit (Sbrana et al., 2010)	Clayey sample from a landslide deposit	2.5Y 7/3 (pale yellow)
IS4	Ischia (NA)	408,279	4,509,516	Cava Lecce Unit (Sbrana et al., 2010)	Clayey sample from a landslide deposit	2.5Y 7/2 (light gray)
IS5	Ischia (NA)	405,815	4,512,094	Likely Cava Lecce Unit (Sbrana et al., 2010)	Clay from an ancient kiln in the Santa Restituta excavations in Lacco Ameno	2.5Y 6/4 (light yellowish brown)
IS6	Ischia (NA)	408,283	4,509,355	Cava Lecce Unit (Sbrana et al., 2010)	Reworked clayey deposit with organic matter	2.5Y 6/3 (light yellowish brown)
MCR1	Montecorvino Rovella (SA)	497,019	4,502,773	Salerno-Montecorvino Basin Unit (Tortonian-lower Messinian; Pappone et al., 2010)	Clayey sample from the quarry face	2.5Y 5/1 (gray)
MDC1	Moio della Civitella (SA)	523,199	4,457,039	Gravity deposit (Upper Pleistocene-lower Holocene; Martelli & Nardi, 2005)	Reworked clayey deposit involving the substrate (presumably Liguride/Sicilide Unit)	5Y 6/1 (gray)
MDC2	Moio della Civitella (SA)	522,959	4,455,240	Gravity deposit (Upper Pleistocene-lower Holocene; Martelli & Nardi, 2005)	Reworked clayey deposit with sandstones fragments (presumably Pollica formation)	2.5Y 6/3 (light yellowish brown)

Table 1 Continued

Sample	Site (Province)	UTM (mE)	UTM (mN)	Geological Information	Description	Munsell Color
MLV1	Malvizza (AV)	505,818	4,566,605	Fortore Unit (Upper Cretaceous-Langhian)	Clayey sample from the mud volcano area <i>Bolle della Malvizza</i>	2.5Y 7/2 (light gray)
MS1	Montesarchio (BN)	472,032	4,545,528	Ariano Unit (Andretta Synthème; lower Pliocene)	Clayey sample from the quarry face	GLE Y1 6/10Y (greenish gray)
MS2	Montesarchio (BN)	472,048	4,545,557	Ariano Unit (Andretta Synthème; lower Pliocene)	Clayey sample from the quarry face	2.5Y 5/1 (gray)
PLT1	Pontelatone (CE)	437,226	4,560,674	Caiazzo sandstone (lower Messinian)	Clayey sample from the <i>Cretaccio</i> area	2.5Y 7/3 (pale yellow)
PMV1	Piana di Monte Verna (CE)	444,617	4,555,591	Alluvial sediments of the Volturno River	Clayey sample collected to a depth of about 1 m	10YR 6/3 (pale brown)
PMV2	Piana di Monte Verna (CE)	444,617	4,555,591	Alluvial sediments of the Volturno River	Clayey sample collected to a depth of about 2 m	10YR 4/3 (brown)
RDE1	Rocca d'Evandro (CE)	406,599	4,580,152	Pietraroja formation (middle-upper Tortonian)	Clay sample from the quarry face	5Y 6/1 (gray)
RUF1	Rufoli di Ogliara (SA)	484,288	4,505,216	Salerno-Montecorvino Basin Unit (Tortonian-lower Messinian; Pappone et al., 2010)	Sample collected at a depth of about 30 m during highway tunnel excavation	GLE Y1 5/10Y (greenish gray)
RUF2	Rufoli di Ogliara (SA)	484,379	4,504,975	Salerno-Montecorvino Basin Unit (Tortonian-lower Messinian; Pappone et al., 2010)	Clayey sample from the quarry face	2.5Y 6/1 (gray)
SO1	Sant'Agnello (NA)	449,430	4,497,255	Debris flow deposits of strong weathered pyroclastics of the Somma-Vesuvius activity (Sgrosso & Martelli, 2003)	Clayey sample deriving from a reworked pyroclastic deposits containing lithic fragments of calcareous/arenaceous bedrock. Currently used for wooden oven refractory brick production	10YR 4/2 (dark grayish brown)
SQ1	Squille (CE)	450,728	4,559,337	<i>Argille Varicolori</i> (Sicilide, Parasclilide) olistostromes in <i>thrust-top</i> formation (Caiazzo sandstones, lower Messinian)	Clayey soil with plant remains	7.5YR 3/2 (dark brown)
TRE1	Treglia (CE)	437,621	4,563,292	<i>Argille Varicolori</i> (Sicilide, Parasclilide) olistostromes in <i>thrust-top</i> formation (Caiazzo sandstones, lower Messinian)	Clayey soil with plant remains and sparse calcareous fragments	10YR 3/3 (dark brown)
VEL1	Velina di Castelnuovo Cilento (SA)	513,559	4,449,412	Alluvial sediments of the Alento River: <i>argille superiori</i> (Cinque et al., 1995)	Clayey material used for brick manufacturing	2.5Y 7/3 (pale yellow)

All the coordinates are given in the Universal Transverse Mercator (UTM) system in the 33 T grid zone. Unless otherwise specified, geological information is from Bonardi et al. (2009).

more detailed cartography or recent literary sources. Photographic documentation of the sample localities is available in De Bonis (2011).

Campanian clayey deposits are mainly associated with siliciclastic and/or carbonate marine basinal sedimentary formations. The older sediments (e.g., Liguride, Sicilide, Parasicilide, Fortore, and Vallone del Toro units) are from the preorogenic/foredeep basinal domains of the Lower Cretaceous to the Upper Miocene (Bonardi et al., 2009; Vitale et al., 2011). Clay sediments associated with these successions generally outcrop as shales or overconsolidated clays (e.g., *ArgilleVaricolori*). However, it is also common to find them as plastic clayey masses in landslides (Di Pierro & Moresi, 1985). Clay deposits were sampled (1) close to the mud volcano known as *Bolle della Malvizza* in the Miscano River valley (MLV), (2) in the vicinity of the town of Bisaccia (BS) in the Irpinia area, (3) near the town of Gioia Sannitica (GS), and (4) close to the archaeological site of Moio della Civitella (MDC) in the Cilento area. Clayey deposits are also found in more recent (Miocene-Pliocene) successions deposited in synorogenic foredeep (e.g., Pietraraja formation) and postorogenic *wedge-top* basin domains (Bonardi et al., 2009; Vitale & Ciarcia, 2013). Most of the clays coming from these deposits have been used for different ceramic products. Sediments ascribed to the Pietraraja Formation were collected in the clay quarries of Alvignano (ancient *Compulteria*, ALV), Rocca d'Evandro (RDE), and Calvi Risorta (ancient *Cales*, CVR). Sediments from Ailano (AIL) were used in the Bourbon period for the manufacturing of tiles. Near the archaeological site of Treglia (ancient *Trebula*), in the Caserta province (Livadie, 1994), three different types of clayey intercalations in the Caiazzo Sandstone were sampled (TRE, PLT, and SQ). From the deposits of the *Gran Potenza* hill, near Benevento (GP) and Montesarchio (ancient *Caudium*, MS), blue-gray clays of the Ariano Unit have been exploited for brick manufacturing and ceramic art. In the Salerno province, clayey sediments ascribed to the Salerno-Montecorvino Basin Unit (Pappone et al., 2010) outcrop in Rufoli (RUF) near Ogliara, a small village of Salerno adjacent to the archaeological area of *Fratte*, where they have long been exploited for the traditional production of wood-fired floor tiles. Sediments of the same geological unit were sampled in a quarry near the town of Montecorvino Rovella (MCR). More recent marine clays (Upper Pleistocene) were sampled from the island of Ischia (IS, Cava Lecce Unit; Sbrana et al., 2010), which is considered one of the most important pottery production centers of the Bay of Naples.

Campanian clayey deposits can also be found in Quaternary alluvial/lacustrine sediments. Such deposits occur in the flood plains of major rivers (e.g., Volturno, Sarno, Sele, Alento), whereas minor deposits may be found in

the sediments of either small water bodies or active river valleys. These sediments reflect the composition of the lithologies eroded by rivers within their catchments. Two samples were collected in a clay quarry near the town of Piana di Monte Verna: the first sample (PMV1) was obtained 1 m below ground level, the second (PMV2) from 2 m below ground level where bricks from the Roman age were found. Sediments from the Alento River plain were sampled in a recently abandoned quarry, previously exploited for brick production (Cinque et al., 1995), near the site of Velia, the ancient Greek colony of *Elea* (VEL).

Clay deposits can also originate from intensive weathering of pyroclastic deposits associated with the volcanic centers of Campi Flegrei (including the islands of Ischia and Procida), Somma-Vesuvius, and Roccamonfina (see Conticelli et al., 2010 and Morra et al., 2010 for additional information). In the village of Cascano di Sessa Aurunca (Roccamonfina Volcano), these deposits (Cascano, CSC) are still used for handicraft cookware, following a semitraditional, wood-firing production. In the Sorrento Peninsula (SO), pyroclastic deposits deriving from the Somma-Vesuvius are exploited by a local workshop in Maiano, a small village of Sant'Agnello, to produce artisanal refractory bricks mainly used to build wood-burning pizza ovens. Unfortunately, we have no precise information on the exact location of the outcrops for the samples coming from these two places, because these materials were collected in the stores of the workshops. Due to the difficulty of finding suitable outcrops, the potters wait for occasional excavations (e.g., those associated with the construction of building foundations) to carefully select their clays.

ANALYTICAL METHODS

The chemical analyses for the major oxides (wt.% of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅) and the trace elements (ppm of Rb, Sr, Y, Zr, Nb, Ba, Cr, Ni, Sc) of the 34 bulk sediments were obtained by X-ray fluorescence (XRF) spectrometry on pressed powder pellets of the samples (PANalytical Axios instrument; PANalytical B.V., Almelo, The Netherlands). The chemical composition of the < 2 μm fraction was determined for 25 representative samples, selected on the basis of geological origin. Analytical precision is estimated to be within 1–2% for major elements and generally better than 5–10% for all trace elements in the observed compositional ranges. No analytical bias was observed between these and the XRF analyses reported in our earlier studies (Melluso et al., 2005, 2008).

CF analyses were also carried out in order to follow the chemical trend of the clayey materials after the removal of coarse fractions (very common during the preparation

of more refined pottery). Separation was performed via sedimentation in distilled water following the Stokes law for particle settling (Cavalcante & Belviso, 2005). Loss on ignition (LOI) was determined by heating 1 g of pre-dried (overnight at 110°C) sample powder at 1000°C.

Semiquantitative mineralogical analyses of bulk samples were performed by X-ray powder diffraction (XRPD). Samples were prepared with a McCrone Micronizing Mill (The McCrone Group, Westmont, IL, USA), which permitted obtaining an average particle size of about 10 μm (Bish & Reynolds, 1989). Data were acquired with a PANalytical X'Pert PRO 3040/60 PW (PANalytical B.V., Almelo, The Netherlands) diffractometer (CuK α radiation, 40 kV, 40 mA, scanning interval 4–50° 2 θ , step size 0.017° 2 θ , counting time 15.5 seconds/step). A careful identification of the clay phases on oriented aggregates (Cavalcante & Belviso, 2005) was conducted on 25 representative samples. Data were obtained with a Philips PW 1710 (PANalytical B.V., Almelo, The Netherlands) diffractometer (CuK α radiation, 30 kV, 40 mA, scanning interval 3–35° 2 θ , step size 0.020° 2 θ , counting time 2 seconds/step) on air-dried samples and after thermo-chemical treatments (ethylene glycol solvation, 550°C heating) in order to observe any structural change of the clay minerals (Moore & Reynolds, 1997).

Grain size analyses on nine selected samples were conducted by wet method using an Octagon 200 shaker (Endecotts, London, UK) and standard sieves (ASTM D2217–85; ASTM, 1985) for the determination of the > 74 μm fraction (No. 200 ASTM sieve). The passing fraction was complementarily analyzed by means of a sedimentation technique (ASTM D422–63; ASTM, 1972), allowing the evaluation of the CF passing 2 μm . In order to calculate the particle size via sedimentation, the specific gravity of the solid particles (G_s) was previously determined by the Gay Lussac pycnometer procedure (ASTM D854–10, ASTM, 1983). Soil samples were classified according to the USCS (Unified Soil Classification System) system (United States Corps of Engineers, 1960). The Atterberg limits were estimated to define the critical values of water content (w) controlling the different rheological stages of the fine-grained soils. More precisely, the liquid limit (w_L) was determined using the cone penetrometer (Wykeham Farrance Ltd, Slough, UK) method (BS 1377–2, 1990). The plastic limit (w_P) was estimated by measuring the water content when a hand-molded cylindrical stick of 3 mm in diameter begins to crumble (ASTM D4318–10, BS1377–2, ASTM, 1984). The shrinkage limit (w_S) was determined by the Monel shrinkage dishes (Matest S.p.A., Treviolo, Italy) method (ASTM D4943–08, ASTM, 1989), calculating the water content for which further loss of moisture will not cause a volume decrease of the clay sample. The plastic-

ity index ($PI = w_P - w_L$) and the activity ($A = PI/CF$; Skempton, 1953) were also estimated. Owing to the dependence of PI on both CF and clay minerals assemblage (Holtz & Kovacs, 1981), a correlation with soil mineralogy was also verified. Finally, the dry unit weight (γ_{dry}), the saturated unit weight (γ_{sat}), the submerged unit weight (γ'), and the specific surface (S) were also determined, the latter by the empirical correlation derived from the cone penetrometer test (Farrar & Coleman, 1967; Santamarina et al., 2002).

RESULTS

Chemical Analyses

Clay samples of the Campania region can be broadly clustered into two main groups considering their CaO content (Figure 2a; Table II). The high-CaO clays (hereafter HCC; CaO > 6 wt.% after Maniatis & Tite, 1981) are represented by 22 basinal clays (AIL1, ALV1, ALV2, BS3, CVR1, CVR2, GP1, GP2, IS1, IS2, IS3, IS4, IS5, IS6, MCR1, MDC1, MS1, MS2, PLT1, RDE1, RUF1, RUF2) and by one alluvial deposit (PMV1). The low-CaO clays (hereafter LCC; CaO < 6 wt.%) are represented by seven basinal (BS1, BS2, GS1, MDC2, MLV1, SQ1, TRE1), two alluvial (PMV2, VEL1), and two weathered pyroclastic (CSC1, SO1) deposits. The HCC samples show a wide range of CaO variation ($\sigma = 3.73$) in a relative narrow SiO₂ range ($\sigma = 2.74$), the two oxides being inversely related. The HCC samples can be further subdivided into three groups with CaO ranging from about 9 to 13 wt.%, from 13 to 18 wt.%, and > 18 wt.% (Figure 2a). It is worth noting that in the first group (9 to 13 wt.% CaO) all the Ischia samples and MDC1 are included, and that three northern Campania samples (PLT1, AIL1, and RDE1) are the richest in CaO (Table II).

The LCC samples show a wider and an almost continuous variation of SiO₂ and Al₂O₃ (from 15 wt.% up to 27 wt.%) contents. The lowest values of Fe₂O₃ for the LCC basinal clays were observed in the MDC2 (5.03 wt.%) and SQ1 (5.26 wt.%) samples, whereas the GS1 (10.1 wt.%) and BS2 (10.5 wt.%) samples account for the highest contents. In contrast, MgO, MnO, alkalis, and P₂O₅ show very small compositional variations ($\sigma < 1$), with the exception of sample MLV1, which is characterized by a significantly higher Na₂O (4.43 wt.%), most probably reflecting its peculiar outcrop conditions of a mud volcano environment, where gas emissions and highly saline (Na-Cl) thermal springs are present (Duchi et al., 1995). Similar behavior ($\sigma < 1$) can be observed for TiO₂, with the exception of three LCC samples (BS1, BS2, and GS1) showing higher concentrations. LOI values vary from 4.57 wt.% to 20.9 wt.%, generally showing a good positive relation with CaO contents.

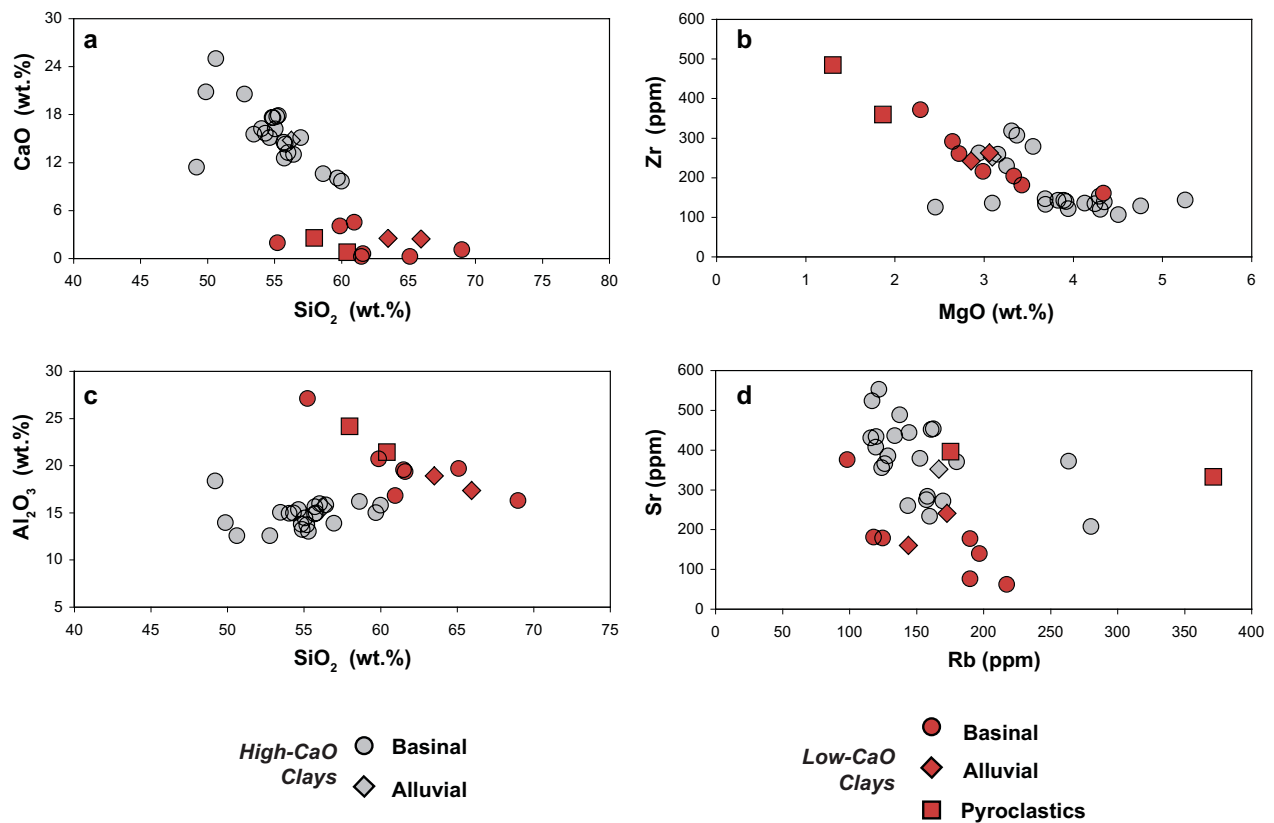


Figure 2 A selection of binary major oxides (wt.%) and trace elements (ppm) compositional plots of samples grouped according to their high-CaO (CaO > 6%) and low-CaO (CaO < 6%) chemical character and their geological origin (basinal, alluvial, and pyroclastic).

In terms of trace elements, Sr strictly follows the CaO behavior, strongly concentrated in the HCC samples (up to 489 ppm), and depleted in the LCC group. Zirconium and niobium are strongly enriched in volcanic-derived samples (CSC1 and SO1, Table II), and in one LCC basinal sample (GS1). The Ischia samples are clearly recognizable among the HCC samples due to their high Zr enrichment (> 250 ppm), low Cr (< 100 ppm), and high Nb (> 25 ppm) contents. The SO1 sample is distinguished for its high Ba content (1010 ppm).

The results of the XRF analyses on the CF (< 2 μm) of 25 representative samples are presented in the diagrams of Figure 3 and in Table III. Separation of coarse fraction may cause strong compositional variations of clayey sediments such as for some HCC samples (IS1, IS2, IS4, IS6, MDC1) that merge into the LCC group. On the whole, all the samples show a CaO depletion (as also evidenced by Eramo et al., 2004), with the exception of BS1 and BS2. Moreover, strong depletion was noticed also for SiO₂, especially in the LCC samples (Figure 3a), whereas a general enrichment in Al₂O₃ was observed, along with a minor increase (except for MDC1) of Fe₂O₃. Potassium also shows a general increase, with the exception of samples

IS6, GS1, TRE1, PMV2, and the two weathered pyroclastic deposits (CSC1, SO1).

Trace elements show some variability with respect to the major oxides (Figure 3b). A quite regular trend was observed for Sr, which decreases in most samples (except for CVR2, GP2, BS1, BS2, MLV1, and VEL1). A strong Ba enrichment was noticed for MDC1 and MLV1. Weathered pyroclastics show a strong Zr enrichment, whereas only a slight Cr increase was recorded in sample CSC1. The concentrations of TiO₂, MnO, MgO, Na₂O, Y, Ni, and Sc remained substantially unchanged.

Mineralogical Analyses (XRPD)

All clayey samples are rich in quartz (Table IV), which is the most abundant phase. The only exception is represented by sample CSC1, in which feldspar prevails and quartz is scarce. The amount of feldspar generally varies from scarce to frequent, and it was detected (some as traces) in almost all the samples. Phyllosilicates of illite/muscovite type are ubiquitous. Carbonates are mainly constituted by calcite, which is abundant in many samples, whereas dolomite was detected, in very

Table II Major oxides (in wt.%, recalculated to 100% on a LOI-free basis), trace elements (in ppm), and LOI (in wt.%) for the analyzed clayey samples grouped according to their high-CaO (HCC, CaO > 6%) and low-CaO (LCC, CaO < 6%) chemical character and their geological origin (basinal, alluvial, pyroclastic). Average compositions and standard deviation (σ) for each group are also reported.

Origin	Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Rb	Sr	Y	Zr	Nb	Ba	Cr	Ni	Sc
HCC basinal	AIL1	49.86	0.71	13.97	6.61	0.11	4.76	20.87	0.45	2.53	0.13	20.10	137	489	29	129	12	307	138	78	40
HCC basinal	ALV1	55.17	0.70	13.75	6.32	0.12	3.09	17.80	0.44	2.48	0.13	17.43	124	356	27	136	12	285	131	41	37
HCC basinal	ALV2	55.04	0.74	14.48	6.48	0.09	3.83	16.22	0.42	2.57	0.13	16.95	126	366	29	143	14	267	133	44	34
HCC basinal	BS3	56.95	0.74	13.89	6.48	0.14	3.68	15.12	0.73	2.13	0.14	15.96	117	524	27	147	14	344	120	39	27
HCC basinal	CVR1	53.44	0.75	15.07	6.50	0.11	5.25	15.55	0.51	2.69	0.12	17.08	153	379	30	144	14	270	147	53	28
HCC basinal	CVR2	54.87	0.68	13.26	5.89	0.11	4.35	17.61	0.61	2.50	0.13	16.73	116	431	26	140	12	273	129	37	33
HCC basinal	GP1	55.79	0.78	14.99	6.09	0.07	4.29	14.33	0.79	2.73	0.15	14.15	163	453	26	153	14	261	144	44	35
HCC basinal	GP2	55.27	0.66	13.04	5.51	0.09	4.13	17.88	0.77	2.52	0.14	16.84	120	408	26	136	11	287	114	28	36
HCC basinal	IS1	56.40	0.79	15.86	6.65	0.14	3.55	13.02	0.64	2.80	0.15	15.34	180	371	39	279	31	374	88	53	28
HCC basinal	IS2	58.61	0.81	16.22	6.43	0.13	3.15	10.61	0.69	3.19	0.16	14.40	170	273	35	260	28	354	69	39	22
HCC basinal	IS3	56.00	0.82	15.97	6.93	0.12	3.25	13.25	0.52	2.98	0.15	16.13	157	275	33	231	25	270	91	44	24
HCC basinal	IS4	59.69	0.67	15.01	5.28	0.11	3.31	10.07	0.43	5.33	0.10	12.35	280	208	38	319	37	210	76	30	19
HCC basinal	IS5	55.71	0.82	15.64	6.90	0.14	3.36	12.56	1.58	3.12	0.16	19.70	263	372	33	308	31	319	82	40	23
HCC basinal	IS6	60.00	0.77	15.83	6.13	0.14	2.94	9.70	0.86	3.47	0.15	12.07	160	234	27	263	27	369	74	41	18
HCC basinal	MCR1	54.01	0.76	14.95	6.26	0.09	3.92	16.26	0.89	2.72	0.13	16.54	134	437	29	140	14	327	126	42	32
HCC basinal	MDC1	49.18	0.72	18.40	12.44	0.32	4.30	11.44	0.43	2.73	0.05	13.31	143	260	37	120	12	352	127	87	36
HCC basinal	MS1	54.80	0.71	13.81	5.75	0.07	3.69	17.66	0.86	2.50	0.15	18.52	120	434	27	133	13	246	122	29	32
HCC basinal	MS2	55.69	0.77	14.89	6.13	0.07	3.89	14.57	0.88	2.96	0.14	14.83	161	452	23	143	13	250	126	38	25
HCC basinal	PLT1	50.61	0.68	12.57	5.43	0.13	2.45	25.03	0.36	2.60	0.13	20.38	158	284	30	126	12	251	115	53	48
HCC basinal	RDE1	52.76	0.64	12.58	5.50	0.11	4.50	20.60	0.64	2.55	0.13	20.61	122	553	23	107	10	284	111	34	40
HCC basinal	RUF1	54.29	0.77	15.00	6.59	0.07	3.94	15.67	0.70	2.83	0.14	17.88	144	444	30	122	14	255	133	44	27
HCC basinal	RUF2	54.62	0.77	15.36	6.37	0.10	4.24	15.13	0.45	2.84	0.13	16.94	129	385	28	135	13	271	124	60	23
	Average	54.94	0.74	14.75	6.48	0.12	3.81	15.50	0.67	2.85	0.13	16.56	153	381	30	173	17	292	114	45	30
	σ	2.74	0.05	1.36	1.41	0.05	0.65	3.73	0.27	0.62	0.02	2.43	42.78	93.82	4.49	67.33	8.15	44.83	23.66	14.50	7.64
LCC basinal	BS1	61.59	1.13	19.37	8.76	0.07	4.34	0.63	1.03	2.83	0.25	7.62	125	179	33	161	21	167	183	56	19
LCC basinal	BS2	61.48	1.17	19.57	10.54	0.03	3.42	0.28	0.88	2.48	0.14	7.48	118	181	32	182	23	186	171	60	23
LCC basinal	GS1	55.21	1.05	27.12	10.14	0.13	2.28	2.00	0.16	1.85	0.06	18.74	190	77	61	372	52	469	120	68	23
LCC basinal	MDC2	65.10	0.65	19.72	5.03	0.02	3.33	0.26	0.86	5.01	0.02	4.57	217	63	28	205	17	343	79	22	13
LCC basinal	MLV1	60.95	0.90	16.85	6.96	0.12	2.99	4.57	4.43	2.04	0.19	11.63	98	376	30	217	21	386	113	45	17
LCC basinal	SO1	68.98	0.71	16.33	5.26	0.11	2.72	1.12	1.09	3.62	0.07	8.61	197	140	27	261	25	497	72	31	11
LCC basinal	TRE1	59.87	0.88	20.74	7.54	0.17	2.64	4.09	0.59	3.17	0.30	14.07	190	177	46	292	39	442	111	36	15
	Average	61.88	0.93	19.96	7.75	0.09	3.10	1.85	1.29	3.00	0.15	10.39	162	171	37	241	28	356	121	45	17
	σ	4.29	0.20	3.54	2.19	0.05	0.67	1.80	1.42	1.08	0.11	4.80	46.96	103.27	12.44	72.90	12.86	132.63	42.27	16.46	4.43
HCC alluvial	PMV1	56.30	0.76	15.54	6.14	0.18	3.10	14.73	0.70	2.41	0.15	15.47	167	351	39	251	24	518	101	40	30
LCC alluvial	PMV2	65.94	0.82	17.37	6.18	0.23	2.86	2.43	0.87	3.19	0.11	7.27	173	241	35	242	27	653	86	47	13
LCC alluvial	VEL1	63.50	0.91	18.90	6.47	0.16	3.06	2.50	0.90	3.48	0.13	8.49	144	159	35	262	24	531	80	38	13
	Average	64.72	0.87	18.13	6.33	0.20	2.96	2.47	0.89	3.33	0.12	7.88	158	200	35	252	26	592	83	43	13
	σ	1.72	0.06	1.08	0.20	0.05	0.14	0.05	0.02	0.21	0.01	0.86	20.36	57.77	0.00	13.86	2.62	86.76	3.61	6.01	0.21
LCC pyroclastic	CSC1	60.42	0.79	21.41	6.54	0.21	1.31	0.78	2.32	6.11	0.10	7.15	372	332	48	485	72	585	11	24	8
LCC pyroclastic	SO1	57.98	0.90	24.15	7.38	0.19	1.86	2.57	0.79	4.04	0.14	10.90	175	396	40	359	54	1010	34	26	10
	Average	59.20	0.85	22.78	6.96	0.20	1.59	1.68	1.56	5.08	0.12	9.03	273	364	44	422	63	798	22	25	9
	σ	1.73	0.08	1.94	0.59	0.02	0.40	1.27	1.09	1.46	0.03	2.65	138.66	45.11	5.94	88.81	12.23	300.24	15.91	1.63	0.99

low amounts, only in 11 samples. Scarce pyroxene and sporadic hematite and gypsum occurrences were also recorded. The pyroclastic origin of the CSC1 and SO1 samples is evidenced by the detection of pyroxene. The same phase was also observed in the Ischia samples, again consistent with the volcanic nature of the island. Both the pyroclastic and Ischia samples are also characterized by high feldspar contents. Other samples do not show a clear link with their specific sedimentary environment. The two reddish samples (BS2 and CSC1) are those in which hematite was identified, while the presence of gypsum in BS3 can be attributed to the evaporite-bearing pelitic succession of the Vallone del Toro Unit (Matano et al., 2005; Pescatore et al., 2008).

XRD data on the CF highlights that almost all samples are rich in chlorite, kaolinite, and illite-smectite mixed layers. Halloysite, a typical phase of weathered pyroclastic sediments (Adamo, Violante, & Wilson, 2001), was recorded in only two samples (CSC1 and SO1). As far as mixed layers are concerned, we estimated the relative amounts of illite and smectite and the statistical layer ordering variable (Reichweite; R), meaning that mixed-layer mineral may be randomly distributed ($R = 0$) or ordered ($R \geq 1$; Cuadros, Fiore, & Huertas, 2010). The adopted nomenclature (Cavalcante & Fiore, 2005) shows the component with the smallest d -value first (in our case illite) with its percentage, and then the layer ordering (R) of the sequence. Basinal sediments

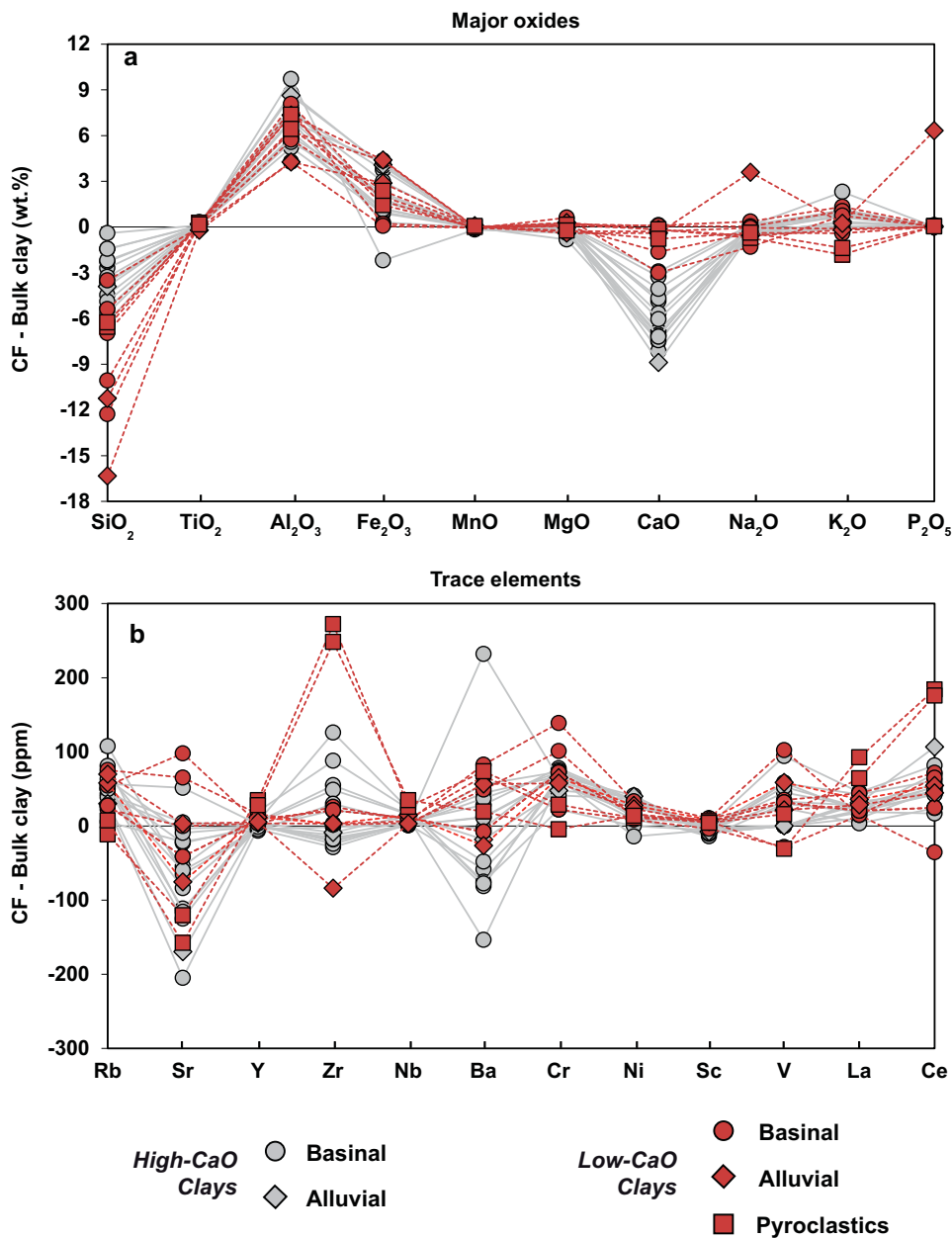


Figure 3 Spider diagrams showing compositional differences between the clay fraction (CF, < 2 μm) and the bulk clay for most representative samples: (a) major oxides; (b) trace elements.

are characterized by percentages of illite not exceeding 50% and *R* = 0 (Figure 4a). Five samples show both higher amounts of illite and *R* index: MDC1 (IS90R3), BS1 (Figure 4b), BS2, and GS1 (IS70R1), and MLV1 (IS60R1).

Grain Size and Physical Characterization

Laboratory tests for grain size (Table V) and physical and index properties (Table VI) characterization were per-

formed on nine representative samples of a basinal (BS1, CVR2, IS6, MDC1, MS1, RUF1), alluvial (PMV2), and pyroclastic (CSC1, SO1) origin. Basinal samples BS1, MS1, and RUF1 are characterized by the highest content of silt and CF (Table V), and their grain size curves show similar and quite regular patterns (Figure 5). Silt ranges from 51 to 54% and clay from 37 to 45%. Sand fraction is less than 4% in MS1 and RUF1, while it reaches ~11% in BS1. Gravel is always < 1%. The remaining basinal samples show a grain size mainly ranging from sand to clay.

Table III Major oxides (in wt.%, recalculated to 100% on a LOI-free basis), trace elements (in ppm), and LOI (in wt.%) for the clay fraction (CF, < 2 μm) of most representative samples grouped according to their geological origin (basinal, alluvial, pyroclastic).

Origin	Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Rb	Sr	Y	Zr	Nb	Ba	Cr	Ni	Sc
Basinal	AIL1	49.45	0.83	19.89	8.84	0.07	3.94	13.35	0.22	3.23	0.19	15.21	187	466	29	113	13	319	205	91	25
Basinal	ALV2	52.35	0.87	22.35	8.13	0.07	4.09	8.07	0.19	3.73	0.15	12.79	182	254	28	130	20	295	211	78	25
Basinal	BS1	51.51	1.38	27.03	8.97	0.03	4.41	0.74	1.39	4.16	0.37	7.45	200	244	49	163	25	216	284	68	29
Basinal	BS2	49.21	1.48	25.83	14.89	0.02	3.62	0.36	0.92	3.52	0.15	7.31	172	279	35	185	29	269	310	93	33
Basinal	BS3	55.50	0.82	19.11	7.37	0.10	3.89	10.26	0.62	2.20	0.13	13.58	122	503	23	119	16	285	161	76	24
Basinal	CVR2	50.41	0.84	20.30	7.69	0.09	4.44	11.94	0.51	3.62	0.16	14.52	173	482	28	119	15	318	196	78	24
Basinal	GP2	49.94	0.79	19.31	6.71	0.07	4.16	14.62	0.81	3.42	0.17	16.21	163	412	27	112	15	283	189	61	29
Basinal	GS1	51.70	1.02	31.39	10.21	0.07	2.00	1.70	0.10	1.73	0.07	13.33	212	77	65	398	61	536	142	76	19
Basinal	IS1	52.84	0.93	23.37	10.41	0.11	3.26	5.59	0.20	3.13	0.17	12.31	206	166	36	301	42	220	147	62	17
Basinal	IS2	52.95	0.98	24.99	10.42	0.13	3.14	3.80	0.21	3.20	0.19	12.92	221	148	40	315	45	273	136	68	19
Basinal	IS3	52.72	0.96	23.51	9.91	0.09	3.04	6.19	0.18	3.25	0.16	N/A	208	191	37	279	41	222	149	61	21
Basinal	IS4	57.41	0.78	20.58	7.37	0.07	3.39	4.02	0.13	6.16	0.09	8.89	361	92	44	445	60	135	98	30	13
Basinal	IS5	41.01	0.62	15.77	7.12	0.07	2.20	6.47	9.72	1.99	15.03	11.60	157	171	28	243	30	143	85	47	13
Basinal	IS6	53.76	0.98	22.76	10.34	0.15	3.13	5.03	0.27	3.39	0.19	12.47	230	179	46	351	50	292	135	67	19
Basinal	MDC1	46.98	0.74	28.10	10.24	0.15	3.91	4.26	0.52	5.04	0.06	12.40	251	195	31	150	16	584	191	73	30
Basinal	MLV1	53.98	1.08	24.91	8.67	0.05	3.60	1.57	3.13	2.79	0.22	9.53	159	451	33	175	26	584	205	71	21
Basinal	MS1	49.91	0.83	19.63	6.72	0.07	3.81	14.73	0.99	3.12	0.18	16.12	158	431	27	115	14	257	187	64	23
Basinal	RUF1	52.86	0.86	21.97	6.88	0.04	4.03	8.47	0.85	3.89	0.15	11.92	194	384	25	120	16	311	206	76	23
Basinal	RUF2	50.97	0.82	21.17	7.52	0.08	4.12	11.07	0.25	3.87	0.14	13.72	191	376	27	117	15	308	196	72	24
Basinal	TRE1	54.48	0.95	26.47	9.54	0.13	2.69	2.45	0.21	2.75	0.32	11.83	217	136	55	313	50	434	183	52	21
Alluvial	PMV1	52.39	0.96	24.17	10.21	0.18	3.06	5.84	0.23	2.77	0.19	11.00	197	181	43	242	38	500	149	80	22
Alluvial	PMV2	54.69	0.98	24.71	10.57	0.25	3.14	2.25	0.30	3.00	0.11	11.74	230	166	46	246	42	627	151	74	22
Alluvial	VEL1	47.16	0.69	23.16	9.35	0.24	2.65	2.10	4.49	3.72	6.44	9.21	214	162	40	178	27	587	138	61	19
Pyroclastic	CSC1	53.87	1.06	28.77	7.97	0.21	1.44	0.62	1.60	4.29	0.15	11.18	360	212	83	757	97	659	40	35	15
Pyroclastic	SO1	51.71	1.06	30.58	9.75	0.24	1.62	1.80	0.41	2.66	0.17	15.38	183	238	68	607	89	1030	29	40	14

Silt prevails in CVR2 and IS6 (around 45%), where sand is ~24%, clay ranges from 26 to 31%, and gravel does not exceed 4%. In the MDC1 sample, sand, silt, and clays are in comparable proportions (~30%), whereas gravel shows the highest percentage observed (~9%). The representative sample of alluvial clay is characterized by predominant silt (40%), followed by clay (32%) and sand (27%). Weathered pyroclastics (CSC1, SO1) are characterized by the lowest percentages of CF: 17% and 11%, respectively. Silt prevails in CSC1 (46%, against 35% of the sand fraction), whereas in the SO1 sample, silt is lower (33%) and sand is in the highest amount (53%) observed for all analyzed samples. The fraction passing the N. 200 ASTM sieve (74 μm) is > 50% for all samples except for SO1.

As for the physical characteristics (Figure 6a), most basinal samples revealed high liquid limit (w_L) values, basically ranging from 50.8% of MDC1 to 54.3% of BS1, with only the CVR2 sample showing a markedly lower value (36.9%). The shrinkage limit (w_S) shows a quite narrow range of variation, from 11.7 to 15.4%. Plastic limit (w_P) values of basinal clays vary between 23.4% of MS1 and 29.5% of IS6. The PI of most basinal clays ranges from 24.3% in MDC1 to 29.8% in MS1, with again sample CVR2 displaying a lower PI (13.5%). According to the

Casagrande plasticity chart (Figure 6b) and the USCS classification, basinal clays fall within the field of high plasticity inorganic clays (CH), with the exception of the CVR2 sample, which is classified as an inorganic clay of low to medium plasticity (CL). The activity of basinal clays straddles the boundary line separating normal (MDC1, IS6, BS1) from inactive (CVR2, RUF1, MS1) clays (Figure 6c). The representative sample of alluvial sediment shows w_P and w_S values falling in the field of basinal samples, with slightly lower w_L (48.5%) and PI (23.0%). It is classified as an inorganic clay of low to medium plasticity (CL, Figure 6b), lying just below the limit between normal and inactive clays (Figure 6c). The weathered pyroclastic sample CSC1 is characterized by the lowest w_L (36.5%) value, while w_S (19.7%) is higher than that of basinal clays. Sample SO1 shows the highest values of w_P (39.5%) and w_S (31.9%), whereas w_L falls into the basinal clays range. The two weathered pyroclastics samples are characterized by very low PI values (SO1 = 14.4%, CSC1 = 11.8%). The CSC1 lies on the boundary between inorganic clay of low plasticity (CL) and inorganic/organic silts and clayey silt from low to slight plasticity (ML-OL; Figure 6b). The fine fraction of SO1 (passing to 74 μm) falls into the field of organic clays and inorganic silts of medium to high plasticity (MH-OH) and therefore it can

Table IV Semiquantitative and qualitative mineralogical composition of the analyzed bulk samples and clay fraction (< 2 μm), respectively.

Origin	Sample	Quartz	Feldspar	Pyroxene	Illite/Muscovite	Hematite	Calcite	Dolomite	Gypsum	Illite-Smectite	Kaolinite	Chlorite	Halloysite
Basinal	AIL1	xxx	x	-	xx	-	xxx	-	-	IS30R0	o	o	-
Basinal	ALV1	xxxx	x	-	x	-	xxx	-	-	N/A	N/A	N/A	N/A
Basinal	ALV2	xxxx	Traces	-	x	-	xx	-	-	IS40R0	o	o	-
Basinal	BS1	xxxx	x	-	x	-	-	-	-	IS70R1	o	o	-
Basinal	BS2	xxxx	x	-	x	x	-	-	-	IS70R1	o	o	-
Basinal	BS3	xxxx	Traces	-	x	-	xxx	-	x	IS10R0	o	o	-
Basinal	CVR1	xxxx	x	-	xx	-	xx	x	-	N/A	N/A	N/A	N/A
Basinal	CVR2	xxxx	x	-	xx	-	xx	x	-	IS40R0	o	o	-
Basinal	GP1	xxxx	x	-	xx	-	xxx	-	-	IS30R0	o	o	-
Basinal	GP2	xxxx	x	-	xx	-	xxx	Traces	-	IS50R0	o	o	-
Basinal	GS1	xxx	-	-	xx	-	-	-	-	IS70R1	o	-	-
Basinal	IS1	xxxx	xx	x	xx	-	xxx	x	-	IS40R0	o	o	-
Basinal	IS2	xxxx	xx	x	xx	-	xxx	x	-	IS50R0	o	o	-
Basinal	IS3	xxxx	xx	x	xx	-	xxx	x	-	IS50R0	o	o	-
Basinal	IS4	xxxx	xx	x	xx	-	xxx	x	-	IS50R0	o	o	-
Basinal	IS5	xxxx	xx	Traces	xx	-	xxx	Traces	-	IS40R0	o	o	-
Basinal	IS6	xxxx	xx	x	xx	-	xxx	x	-	IS50R0	o	o	-
Basinal	MCR1	xxx	x	-	xx	-	xx	-	-	N/A	N/A	N/A	N/A
Basinal	MDC1	xxxx	-	-	x	-	xx	-	-	IS90R3	-	o	-
Basinal	MDC2	xxxx	x	-	x	-	-	-	-	N/A	N/A	N/A	N/A
Basinal	MLV1	xxxx	x	-	xx	-	x	-	-	IS60R1	o	o	-
Basinal	MS1	xxx	x	-	xx	-	xx	-	-	IS40R0	o	o	-
Basinal	PLT1	xxx	x	-	xx	-	xxx	-	-	N/A	N/A	N/A	N/A
Basinal	RDE1	xxx	Traces	-	xx	-	xxx	x	-	N/A	N/A	N/A	N/A
Basinal	RUF1	xxx	Traces	-	xx	-	xx	-	-	IS30R0	o	o	-
Basinal	RUF2	xxxx	x	-	xx	-	xx	-	-	IS20R0	o	o	-
Basinal	SQ1	xxxx	x	-	x	-	-	-	-	N/A	N/A	N/A	N/A
Basinal	TRE1	xxx	x	-	x	-	x	-	-	IS30R0	o	-	-
Alluvial	PMV1	xxxx	xx	-	x	-	xx	Traces	-	N/A	N/A	N/A	N/A
Alluvial	PMV2	xxxx	xx	-	x	-	Traces	-	-	IS60R1	o	-	-
Alluvial	VEL1	xxxx	Traces	-	x	-	-	-	-	-	o	-	-
Pyroclastic	CSC1	x	xxx	x	xx	Traces	-	-	-	-	-	-	o
Pyroclastic	SO1	xx	xxx	xx	xx	-	-	-	-	N/A	-	-	o

XXXX = very abundant; XXX = abundant; XX = frequent; X = scarce; o = present; - = not present; N/A = not available data.

be classified by the USCS as silty sand (SM). The CSC1 lies on the boundary between normal and inactive clays, whereas the SO1 lies between normal and active clays (Figure 6c).

Specific gravity of solid particles (G_s) and unit weights (γ_{sat} and γ_{dry} , saturated and dry, respectively) of basinal clays range from the minimum values of IS6 (2.59 g/cm³) to the maximum of CVR2 (2.76 g/cm³). Other

Table V Grain size (%), AGI (Associazione Geotecnica Italiana; AGI, 1977), USDA (United States Department of Agriculture, 2007), and USCS (United States Corps of Engineers, 1960) classifications for a selection of nine representative clayey samples.

Origin	Sample	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	AGI classification	USDA classification	USCS classification
Basinal	BS1	0.61	11.39	51	37	Sandy silt with clays	Silty clay	CH
Basinal	CVR2	4.35	24.65	45	26	Sandy silt with clays	Loam	CL
Basinal	IS6	1.83	23.17	44	31	Sandy silt with clays	Clay loam	CH
Basinal	MDC1	9.54	31.46	29	30	Slightly gravelly sand with clay and silt	Clay loam	CH
Basinal	MS1	0.05	3.95	51	45	Silt with clay	Silty clay	CH
Basinal	RUF1	0.04	1.96	54	44	Silt with clay	Silty clay	CH
Alluvial	PMV2	0.60	27.40	40	32	Silt with clay and sand	Clay loam	CL
Pyroclastic	CSC1	1.94	35.06	46	17	Clayey silt with sand	Silt loam	CL/ML-OL
Pyroclastic	SO1	2.54	53.46	33	11	Clayey sand with silt	Sandy loam	SM

ML = inorganic silt; CL = inorganic clay; CH = inorganic clays of high plasticity; OL = organic silt, organic clay; SM = silty sand.

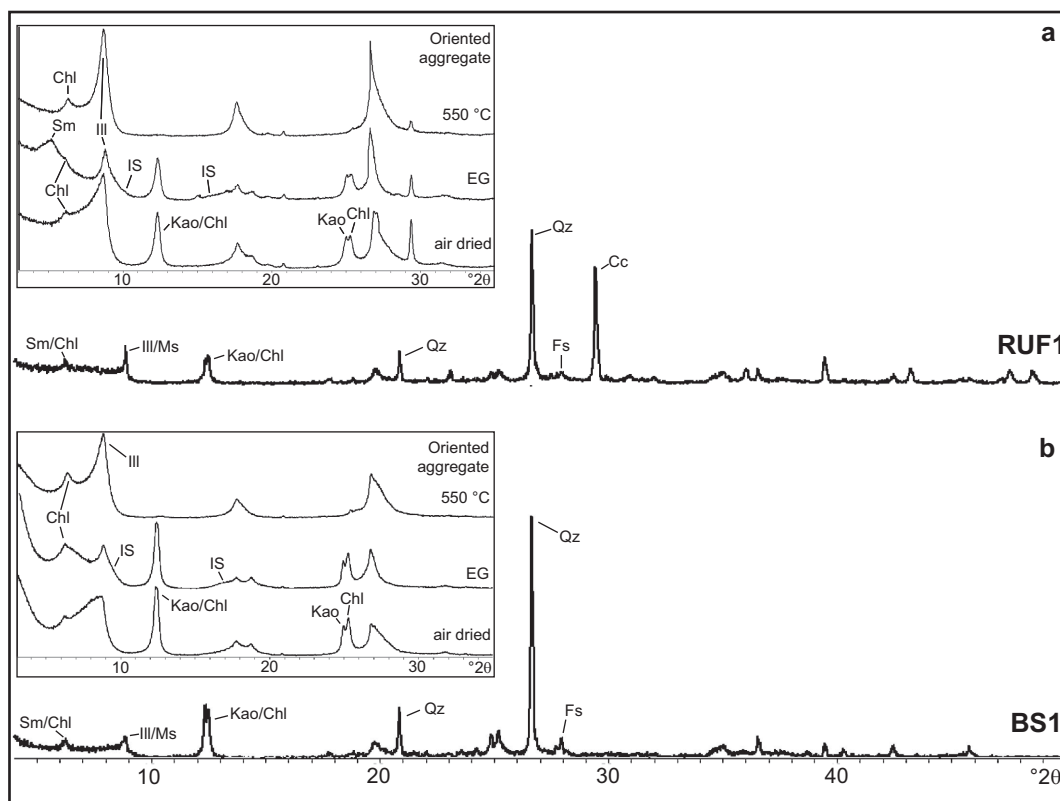


Figure 4 Representative XRPD patterns of bulk and oriented aggregates, air-dried, ethylene glycol solvated (EG), and heated to 550°C of clay fraction (inset at the top left corner) for the analyzed clayey samples. (a) RUF1, HCC basinal sample. (b) BS1, LCC basinal sample. Qz = quartz; Fs = feldspar; Cc = calcite; Ms = muscovite; Ill = illite; Sm = smectite; IS = illite-smectite; Chl = chlorite; Kao = Kaolinite.

physical parameters, as the void ratio (e) and porosity (n), show their minimum in CVR2 (0.65% and 39.36%, respectively) and their maximum in IS6 (1.01% and 50.20%, respectively), except for specific surface (S) that in BS1 reaches the highest value (68.38 m²/g) among all of the analyzed clays (Table VI). The physical parameters of the alluvial clay sample (PMV2) fall into the range of

the basinal clays. Specific gravity (G_s) and unit weights (γ_{sat} and γ_{dry}) of the weathered pyroclastics sample CSC1 (2.71 g/cm³, 1.98 g/cm³, and 1.55 g/cm³) are just below the highest values of the basinal clays (2.76 g/cm³, 2.07 g/cm³, and 1.67 g/cm³ for CVR2). In contrast, sample SO1 is characterized by the lowest observed values (2.49 g/cm³; 1.65 g/cm³; 1.08 g/cm³). The void ratio (e)

Table VI Physical and index properties for a selection of nine representative clayey samples.

Origin	Sample	w_L %	w_p %	w_s %	PI%	Activity	G_s (g/cm ³)	γ_{sat} (g/cm ³)	γ' (g/cm ³)	γ_{dry} (g/cm ³)	e	n (%)	S (m ² /g)
Basinal	BS1	54.29	24.62	13.69	29.67	0.80	2.66	1.91	0.91	1.45	0.84	45.53	68.38
Basinal	CVR2	36.87	23.39	11.67	13.48	0.52	2.76	2.07	1.07	1.67	0.65	39.36	46.51
Basinal	IS6	53.99	29.48	14.62	24.51	0.79	2.59	1.79	0.79	1.29	1.01	50.20	68.00
Basinal	MDC1	50.80	26.56	12.52	24.23	0.81	2.68	1.94	0.94	1.49	0.80	44.34	64.00
Basinal	MS1	54.13	24.31	13.30	29.82	0.66	2.68	1.94	0.94	1.49	0.80	44.37	68.17
Basinal	RUF1	54.01	28.72	15.36	25.29	0.57	2.64	1.86	0.86	1.39	0.90	47.43	68.02
Alluvial	PMV2	48.55	25.54	14.69	23.01	0.72	2.67	1.92	0.92	1.47	0.81	44.90	61.18
Pyroclastic	CSC1	36.47	24.58	19.68	11.89	0.70	2.71	1.98	0.98	1.55	0.74	42.65	46.02
Pyroclastic	SO1	53.97	39.53	31.94	14.44	1.31	2.49	1.65	0.65	1.08	1.32	56.82	67.97

w_L = Atterberg liquid limit; w_p = Atterberg plastic limit; w_s = Atterberg shrinkage limit; PI = plasticity index. G_s = specific gravity of solid particles; γ_{sat} = saturated unit weight; γ' = submerged unit weight; γ_{dry} = dry unit weight; e = void ratio; n = porosity; S = specific surface.

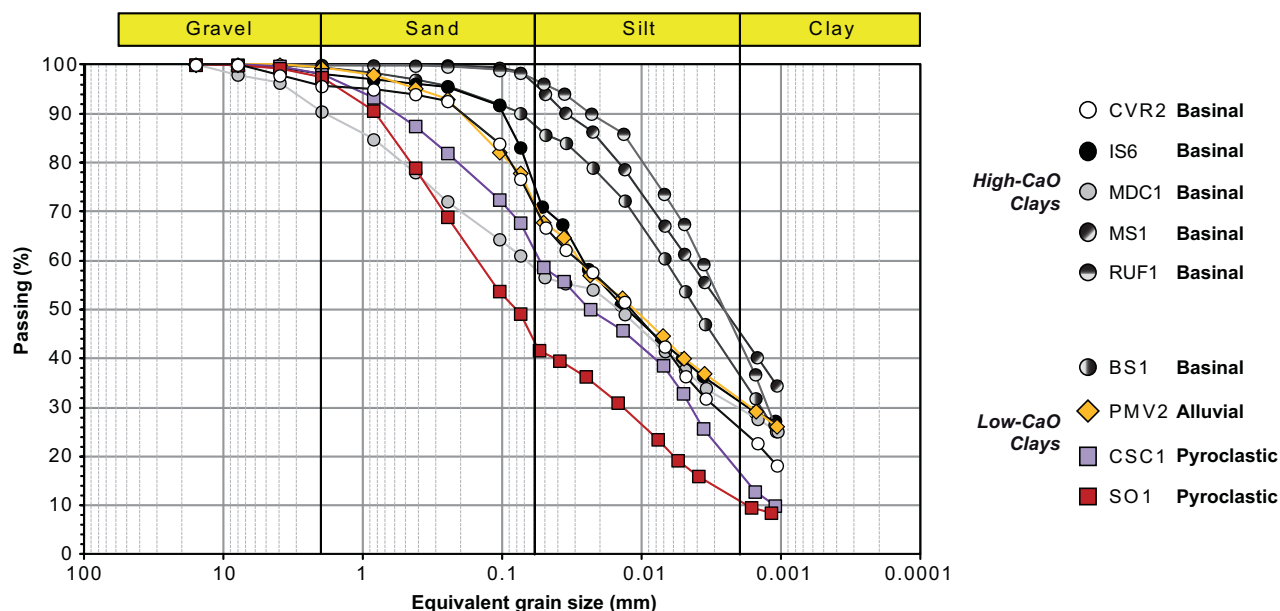


Figure 5 Grain size distribution of nine representative clayey samples according to their high-CaO ($\text{CaO} > 6\%$) and low-CaO ($\text{CaO} < 6\%$) chemical character and their geological origin (basinal, alluvial, and pyroclastic).

and porosity (n) of CSC1 (0.74% and 42.65%) are almost as high as the highest values of the basinal clays (CVR2), whereas sample SO1 is again characterized by the highest observed values (1.32% and 56.82%). Sample CSC1 shows the lowest specific surface (S) of all the analyzed clays (46.02 m^2/g), once more contrasting with the quite high value (67.97 m^2/g) obtained for SO1.

DISCUSSION AND CONCLUSIONS

Clayey Raw Materials

The clayey sediments of the Campania region are mainly located in the Apennine basinal successions and (to a lesser extent) in alluvial/lacustrine formations. Minor deposits also come from strongly weathered pyroclastic deposits. Such differences in origin and sedimentary environment are reflected in their geochemical, mineralogical, and physical properties. An important distinction, which can be made for all the basinal clayey sediments, is between the oldest (Lower Cretaceous–Upper Miocene) carbonate-free deposits, reflecting a low-CaO/high- SiO_2 composition, and the youngest (Miocene–Pleistocene) predominantly carbonate-bearing sediments, with a variable high-CaO content. Moreover, clay minerals of the oldest basinal deposits show a higher illite content ($> 50\%$ in the IS mixed layer) and R index values > 0 . All these differences are probably linked both to the depth of the deposition basins and to diagenetic processes.

The more recent clay sediments were presumably deposited in a carbonate-rich basin (e.g., *wedgetop*) and have undergone a lower diagenetic process. Conversely, the lower CaO content of the oldest clays could be due to their deposition in deeper open basins, beneath or very close to the carbonate compensation depth, in agreement with the general interpretation of *Argille Varicolori* (Fiore et al., 2000). An alternative explanation could invoke the substantial absence of major calcite producers (foraminifera and calcareous nannoplankton) before the Cretaceous (Tateo, 1997). The higher illite content ($> 50\%$ in the IS mixed-layer) and the R index (> 0) systematically observed for the majority of the oldest sediments can lead us to infer a higher diagenetic grade, as suggested by some authors (Środoń, 2009). In particular, the involvement of old sediments (e.g., Liguride/Sicilide Unit) in the Quaternary gravity deposit of MDC1 could be evidenced by the occurrence of both high illite ($\sim 90\%$) and the R index (3) in the IS mixed-layer.

The samples from the island of Ischia represent a *unicum* for their chemical and mineralogical features. These deposits, outcropping on the northern flank of Mt. Epomeo, approximately 600 m above sea level, were deposited after the *Green Tuff* eruption (55 ka; Vezzoli, 1988; Barra et al., 1992) into a marine environment and then followed the Mt. Epomeo ascending resurgent block (Brown, Orsi, & de Vita, 2008). They represent a mixture of sediments from two different sources: a volcanic component, deriving from the very rapid erosion of the

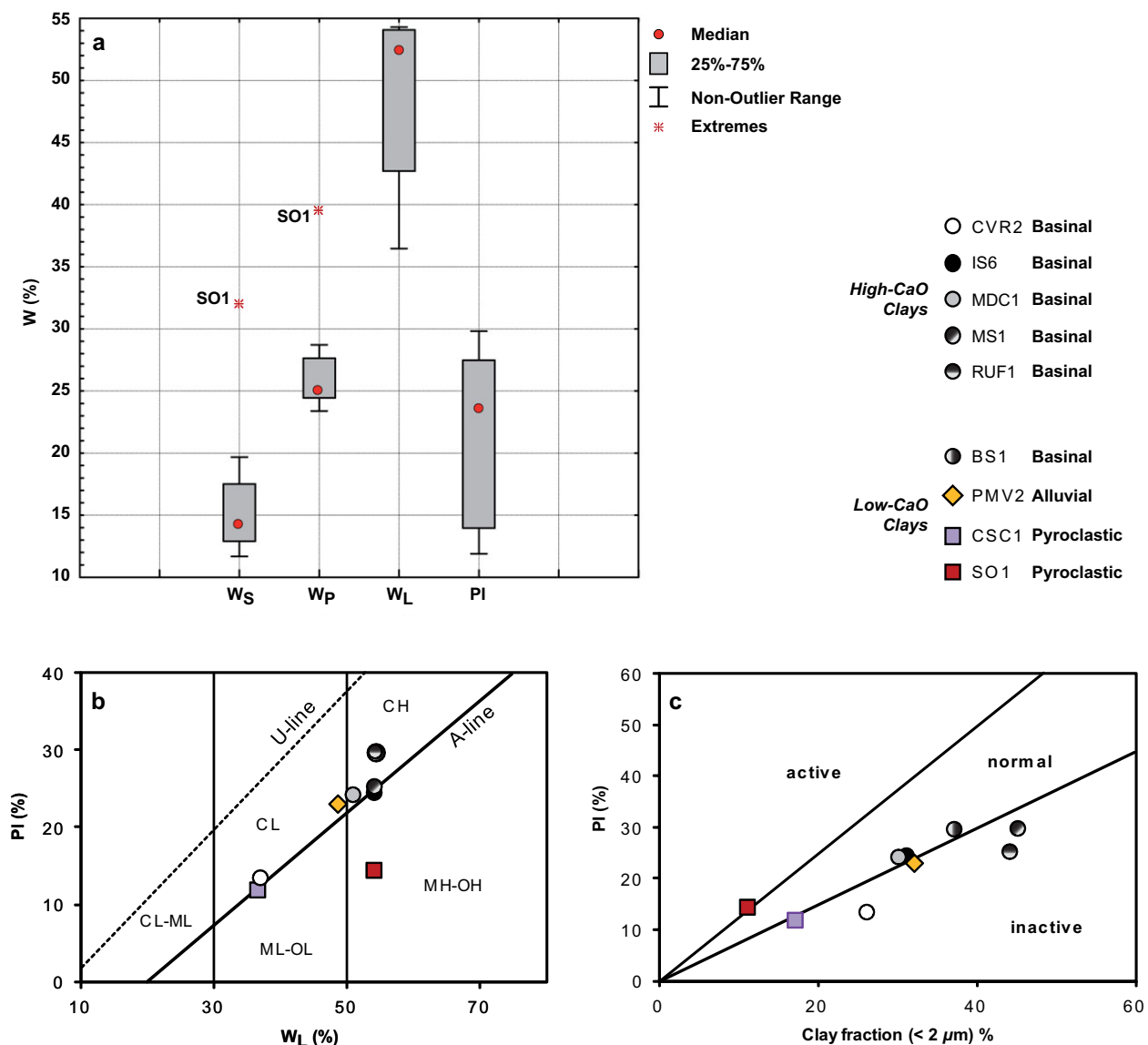


Figure 6 Physical characterization tests of nine representative clayey samples according to their high-CaO (CaO > 6%) and low-CaO (CaO < 6%) chemical character and their geological origin (basinal, alluvial, and pyroclastic). (a) Box plot of Atterberg limits (w_L = liquid limit; w_P = plastic limit; w_S = shrinkage limit) and PI (plasticity index). (b) Casagrande plasticity chart (PI vs. w_L). ML = inorganic silts from low to medium plasticity; MH = inorganic silts of high plasticity; CL = inorganic clays from low to medium plasticity; CH = inorganic clays of high plasticity; OH = organic clays from medium to high plasticity; OL = organic silts and clays of low plasticity. A-line separates clay-like materials from silty materials, and the organics from the inorganics; U-line indicates the upper limit for soils. (c) Activity chart (PI vs. clay fraction%) showing the fields for active, normal, and inactive clays.

Green Tuff deposits, and a siliciclastic component, probably originating from an inner Apennine area and deposited in the Phlegraean offshore by fluvial sedimentation. Abundant quartz, incompatible with the SiO₂-saturated to slightly undersaturated characteristics of Ischia's volcanics, along with clinopyroxene crystals, volcanic scoriae and lithics, and pumices (De Bonis, 2011; De Bonis et al., 2012), can confirm this hypothesis. The

chemical composition broadly falls between a basinal and a volcanic deposit, as evidenced by lower CaO and Sr contents and higher Rb, Zr, and Nb contents with respect to the other HCC basinal deposits (Figure 2).

The composition of alluvial sediments is more variable. The most significant example is given by PMV1 and PMV2 coming from the same site in Piana di Monte Verna, showing compositional change as a function of

stratigraphic height. More specifically, the CaO content of PMV1 is higher than that of PMV2, the latter coming from more than 2 m in depth. This difference is also reflected by the higher calcite content and by the presence of dolomite in PMV1. A change in the sedimentary supply can be thus inferred, also given the presence of a paleosol between the two sampling points, marking a sedimentation break and characterized by the presence of Roman brick fragments (Palmieri, 1998).

The volcanic-derived clays (SO1 and CSC1) inherited some important chemical features of the deposit from which they originated. They are characterized by high SiO₂, Al₂O₃, Ba, Nb, and Zr contents and by very low CaO. Depletion in MgO, Cr, Ni, and Sc reflects the evolved composition of the original pyroclastic products. These clayey materials also showed a peculiar mineralogical composition with high feldspar contents and the presence of pyroxene and halloysite. The presence of quartz in sample SO1 is likely due to the reworking of the arenaceous substrate of the hill above Sorrento (Sgrosso & Martelli, 2003), also evidenced by the occurrence of sandstone fragments (De Bonis, 2011; De Bonis et al., 2012).

Technological Features

Due to their different geological origin, all the clayey samples studied show different minero-petrographic compositions and physical features, which affect the workability of raw pastes and the technological characteristics of the end products. Ternary diagrams used in the modern Italian ceramic industry allow one to draw some interesting chemical considerations with respect to ceramic behavior and use. The first diagram (Vincenzini & Fiori, 1977; Figure 7a), which is currently obsolete due to the technological development of industrial plants, is nonetheless well suited to the purposes of this study, because it is focused on three types of ceramics (*majolica*, *cottoforte*, and red stoneware) generally prepared using only one type of clay and therefore similar to ancient and artisanal artifacts. The other diagram (Fabbri & Fiori, 1985 modified; Figure 7b) shows the chemical variation ranges of raw materials (illitic-chloritic clays) currently used in the ceramic industry and the compositional fields of clays for vitrified ceramic (red stoneware).

Taking into account these chemical diagrams (Vincenzini & Fiori, 1977; Fabbri & Fiori, 1985), most HCC deposits are suitable for the manufacturing of *majolica* (Figure 7a), whereas some LCC are best suited for red stoneware production (Figure 7b). In modern ceramics, only slight chemical variations of raw materials are allowed, but it is worth noting that most HCC are suitable for making products, such as *majolica*, which manifests technological characteristics very similar to those of

the majority of ancient common and fine wares (Grifa et al., 2006). Thus, the link between carbonate-free and carbonate-bearing clays for specific pottery productions is strictly connected to the different technological features of the end products. In particular, the HCC deposits were extensively employed due to their optimal molding and sintering attitudes (Šegvić et al., 2012).

In fact, as evidenced by several authors (Cultrone et al. 2001; Grifa et al., 2009b; Papachristodoulou et al., 2010), a high-CaO composition drives the reaction paths during the firing process, promoting early sintering and the formation of a stable ceramic microstructure over a wide firing temperature range. Thus, this provides optimal physical and mechanical properties for most common ware (e.g., liquid storage) or bricks (De Bonis, 2011; De Bonis et al., 2012). LCC deposits are, with some exceptions, suitable for cooking ware production due to their good thermal shock resistance, especially at low firing temperatures (< 850°C; Hein et al., 2008). Cooking ware was also produced by adding abundant temper to improve the toughness of the ceramic body (Tite, Kilikoglou, & Vekinis, 2001).

The grain size distribution of raw materials, along with the abundance and the type of clay minerals, strongly influences the plasticity properties and workability of clays, as well as the physical-mechanical properties of the end products. Considering the classification scheme proposed by Bender & Handle (1982), which suggests the particle size ranges for modern brick and tile productions, only three clayey samples (BS1, MS1, RUF1), among the nine studied, fall into the field of very clay-rich raw materials, slightly below the limit with roofing tiles. The grain size of these clays should be modified by adding coarser fractions in order to reduce the risk of shrinkage and to balance their very high plasticity (Figure 8). The correction of raw material grain sizes is currently performed on RUF1 clay for traditional floor tiles (*cotto*). Conversely, the MS1 sample is used for perforated bricks with no correction of the clay mixture, suggesting that these boundaries are purely theoretical and other parameters are to be considered (e.g., clay mineral composition, moisture content).

The remaining basinal clays samples (CVR2, IS6, MDC1) and the alluvial sediment (sample PMV2) are characterized by a higher sand fraction and can be employed to produce perforated bricks (Figure 8), as in the case of the CVR2 sample. All seven of these samples of clays could have been used in antiquity for most common ware (e.g., tableware) and amphorae productions, frequently mixed with temper in order to reach both the adequate plasticity for molding and physical-mechanical ceramic properties (Grifa et al., 2009b; De Bonis et al., 2010). Finer ceramics (e.g., *terra sigillata*, *Black-Glazed*

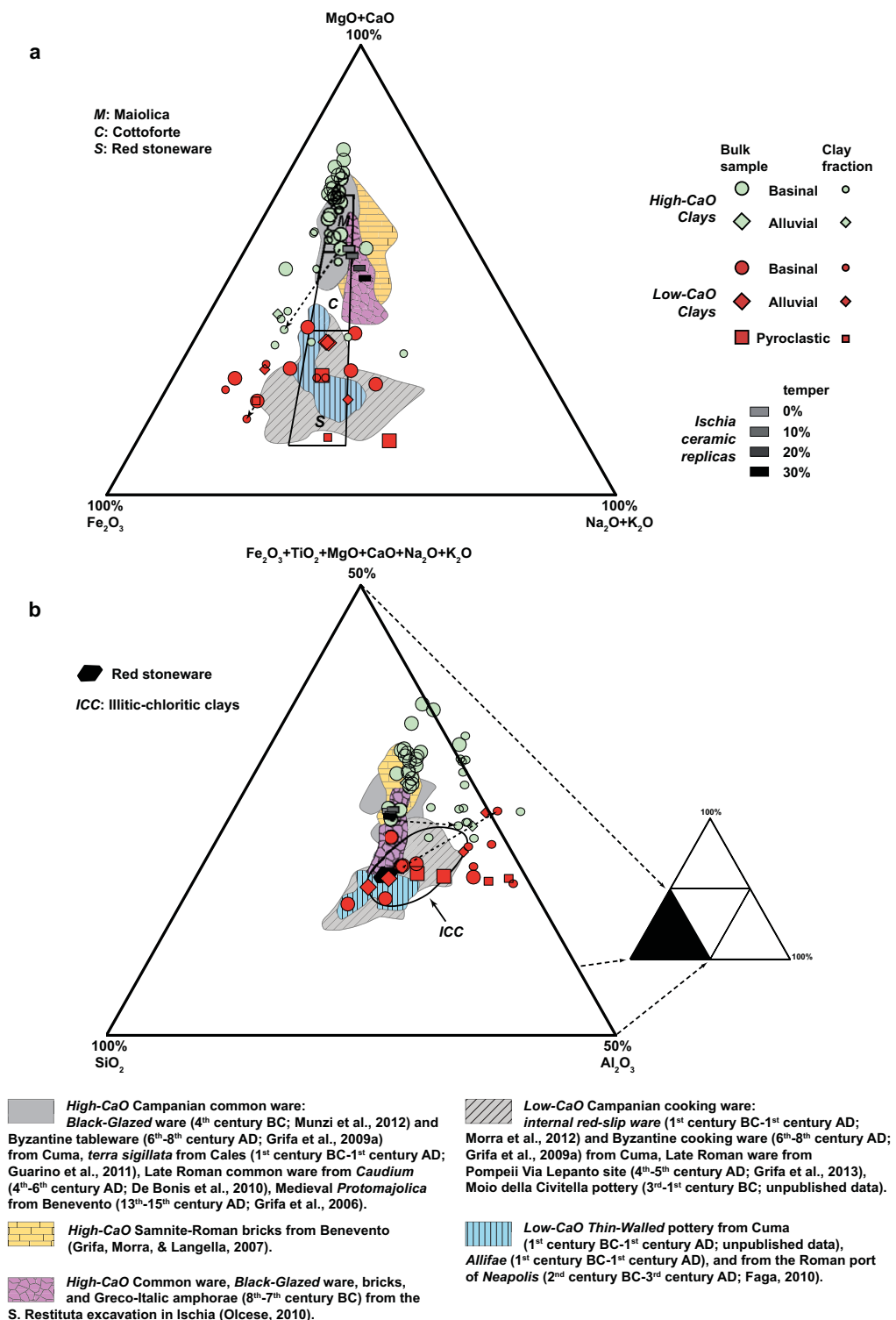


Figure 7 (a) Ternary diagram (Vincenzini & Fiori, 1977) showing the chemical composition fields of modern ceramics (*M* = majolica, *C* = cottoforte, *S* = red stoneware). (b) Ternary diagram (modified from Fabbri & Fiori, 1985) with the chemical composition field of illitic-chloritic (ICC) clays used for modern red stoneware production (black symbol). Both diagrams report the chemical composition of bulk clayey raw materials (bigger symbols) and their respective clay fraction (smaller symbols) obtained via levigation. Compositional changes related to the levigation of high-CaO (IS6) and low-CaO (BS2) representative clays are indicated by dashed arrows. Compositions of the four ceramic replicas, mixed with increasing proportions (0, 10, 20, 30%) of volcanic sand as temper, are represented by rectangles in grayscale. Compositional fields of archaeological ceramics are also reported for comparison.

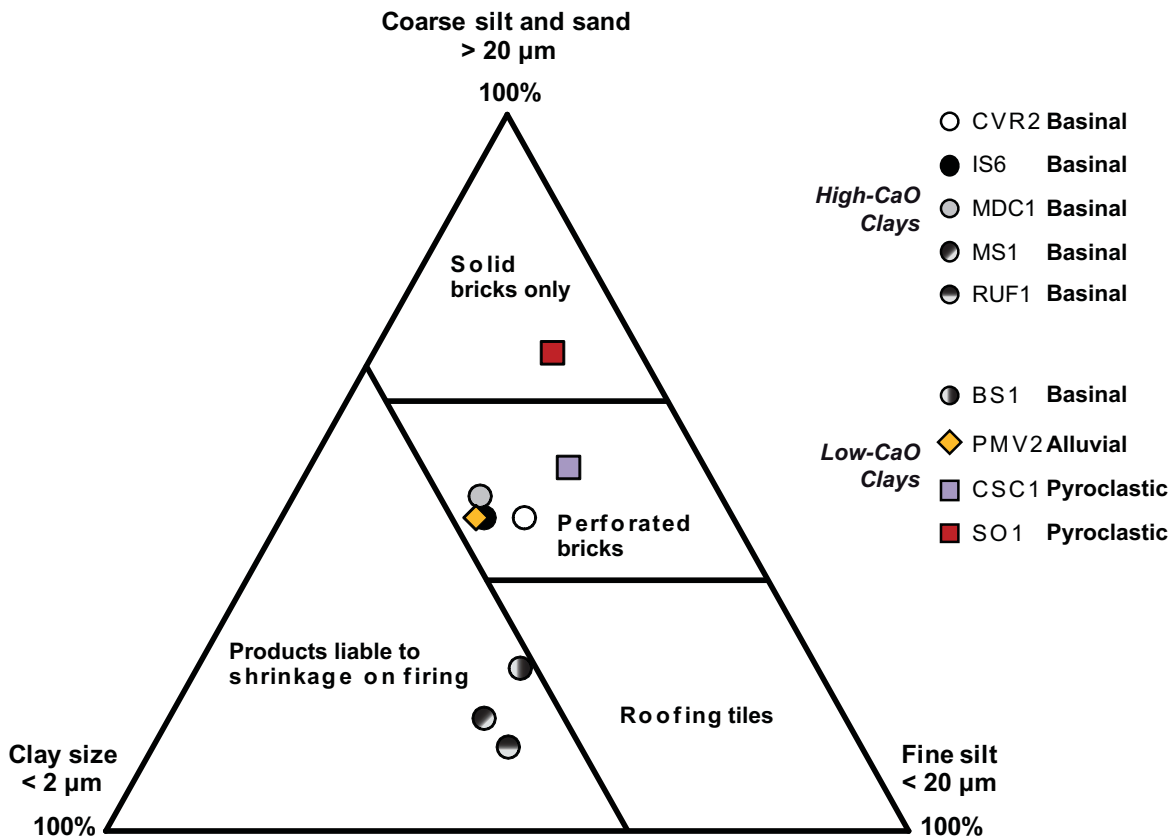


Figure 8 Recommended raw materials grain sizes for the production of bricks and tiles (Bender & Handle, 1982). Samples are illustrated according to their high-CaO (CaO > 6%) and low-CaO (CaO < 6%) chemical character and their geological origin (basinal, alluvial, and weathered pyroclastics).

ware) could have also been produced with raw materials refined via levigation.

As far as the alluvial clays are concerned, these sediments are now extensively used for the production of bricks, especially for their easy extraction and low lithification (Tateo, 1997), as in the case of the Alento flood plain deposit (sample VEL1). Furthermore, alluvial and lacustrine/marsh sediments as well, due to their widespread distribution, could have also represented an important raw material for ancient ceramic production. As highlighted for samples PMV1 and PMV2, a change in the sedimentary supply, often due to paleoenvironmental changes (e.g., rapid geomorphological evolution in volcanic areas), makes these materials suitable for different ceramic typologies. Hence, alluvial deposits should be carefully investigated, also by means of core drilling sampling to reach clayey sediments in (pre)historical levels.

Weathered pyroclastics from Cascano (sample CSC1) show technical characteristics suitable for perforated bricks, while the higher sand content of pyroclastic deposits from the Sorrento Peninsula (SO1) makes them appropriate only for solid bricks. Nevertheless, these sam-

ples are characterized by very low plasticity indices pointing to a narrow range of optimum workability, and they are mainly used for their good refractory properties. In fact, in Cascano (sample CSC1), these kinds of raw materials are today used for handicraft cookware (pots, saucepans), mainly made by using a press molding technique. In contrast, in the Sorrento Peninsula (sample SO1), they are only used for simple-shaped bricks for wooden ovens and not for construction purposes. This demonstrates that other parameters involved in the sintering process are to be considered in addition to the grain size (e.g., type and abundance of clay minerals, CaO content).

Such a broad minero-chemical spectrum of raw materials (clays and temper) available in the Campania region enabled the potters to produce ceramics for different end-uses. This has led to a flourishing manufacturing activity in Campania and to a high degree of specialization of potters. The use of volcanic temper found in the majority of the ceramics of the Bay of Naples area, where pyroclastic deposits are widespread, is typical of these productions. Particularly, in the Bay of Naples, potters

paid special attention in selecting well-sorted volcanic temper (Grifa et al., 2013). They preferred Vesuvian temper, which would have even been traded with *Cuma* for renowned cookware productions (Morra et al., 2012).

In conclusion, the data collected in this study highlights the technological potential of Campanian clayey raw materials most probably used in ceramic manufactures from prehistoric times to the present day. Future petrophysical investigations on firing ceramics with different types of Campanian clayey raw materials should be conducted to test the observations presented in this study.

Provenance of Some Relevant Campanian Archaeological Ceramics

One of the most challenging issues in the study of Campanian pottery is the precise identification of clayey raw materials exploited by ancient potters. The present set of geochemical data for Campanian clayey raw materials may represent a useful tool for such provenance studies. A comparison of the chemical composition of clayey raw materials (bulk and CF) and that of several regional ceramic and pottery productions (Figure 7) was made as a preliminary attempt to find a link between them.

The ceramics considered in this comparison are those for which an archaeometric data set is available and a local production is confirmed (*reference groups*) or is strongly supposed. We represented graphically the compositional fields of carefully selected chemical data, which are homogeneous and analytically consistent. It should be noted that other analytical chemical data exist (e.g., Rinaldi et al., 2007; Peña & McCallum, 2009a), but were produced with different analytical procedures making it difficult to compare with our data set.

We selected several ceramic productions among those mentioned in the introduction, which cover a wide range of typologies and span a large production period (from the 8th century B.C. to the Middle Ages). We again employed the ternary diagrams (Vincenzini & Fiori, 1977 and Fabbri & Fiori, 1985) commonly used to compare the chemical composition of raw materials with that of modern ceramic materials, such as majolica, cottoforte, and stoneware. The HCC and LCC group of samples can be well distinguished in the two diagrams of Figure 7. HCC show a remarkable similarity with the compositional fields of tableware productions and bricks. On the contrary, most of the LCC samples fall into the fields of cooking ware, and several in that of *Thin-Walled* productions from Campania.

These ceramics show different fabrics in thin section, most of them characterized by a variable amount of inclusions, most likely deliberately added to ceramic pastes by ancient potters as temper, predominantly represented by

volcanic grains in pottery from the Bay of Naples (*Cuma*, Ischia, Pompeii) and from the Samnium area (Caudium, Benevento). Modal analyses on thin sections show an abundance of inclusions in the order of 10–20% in tableware and 20–30% (sometimes slightly higher) in cooking ware (De Bonis et al., 2010; Morra et al., 2012).

Grifa et al. (2009b) and De Bonis (2011) evidenced via ceramic replica experiments that the presence of local volcanic inclusions does not significantly affect the bulk composition of the products up to values of ~30 wt.%. In this case, the chemical comparison between raw clays and tempered handiworks is suitable as a provenance test. Figure 7 shows the compositions of the four replicas made with the IS6 clay from the island of Ischia, also mixed with increasing proportions (0, 10, 20, 30 wt.%) of a volcanic sand from the Campi Flegrei volcanic area as temper. As the amount of inclusions increases in replicas, only a low CaO + MgO depletion and an alkali enrichment, due to the trachytic composition of the volcanic sand, is recorded (Figure 7a). In Figure 7b, the compositional change is barely noticeable due to the similar contents of Al₂O₃ and SiO₂ between the IS6 clay and the trachytic volcanic sand, whereas the variation of the other oxides (Fe₂O₃, TiO₂, MgO, CaO, Na₂O, K₂O) does not significantly affect the plot position.

The chemical analyses of the < 2 μm fraction of clayey samples highlight that the removal of the majority of coarse fraction can strongly affect the composition of the original clayey raw materials (Figure 7). The levigation process promotes the separation of some detrital minerals (e.g., quartz, calcite) causing a SiO₂ and CaO decrease, and an indirect enrichment in Al₂O₃ (clay minerals) and Fe₂O₃ in almost all the samples. CaO depletion can be quite strong for the HCC samples, which in some cases (e.g., the Ischia clays) switch to a low calcium composition (Table III). The LCC samples generally show a stronger SiO₂ depletion and a minor decrease of CaO due to the lower original content of quartz and calcite (Figure 7).

The refining of raw materials performed in this study was carried out by retaining, via sedimentation, the very fine fraction (< 2 μm). This is probably an excessive process if compared with a common levigation process for pottery manufacturing, and would be more similar to that carried out for the preparation of slips and enamels. It should be noted, however, that in ancient workshops, levigation was often performed to obtain a particularly fine clay for delicate or high-quality pottery (e.g., *Black-Glazed ware* or *terra sigillata*). Therefore, raw chemical data useful for determining the provenance of archaeological fine artifacts should be carefully weighed for the possible large discrepancy of chemical patterns between raw clays and potsherds. Chemical comparisons should

always be supported by archaeological (kiln waste, furnace structures), geological, and minero-petrographic evidence (e.g., thin section inspection, XRPD, scanning electron microscopy).

This study is a first attempt to compare the archaeological pottery of the Campania region with their possible clayey raw material sources. Data presented here might be considered in the future to better understand the technological properties of Campanian raw materials and to more confidently confirm the local provenance of ceramic production for which a complete and comparable archaeometric data set is available. It is evident that precise attribution regarding provenance cannot disregard the historical and archaeological contexts of the ceramics. Despite the growing interest of archaeologists in the archaeometric approach for pottery investigation, the available data are still limited and often difficult to compare due to the absence of an investigation protocol and evaluation standards (Frahm, 2012). Following the model of other Mediterranean archaeological projects (e.g., *Immensa Aequora* and *Facem*), it would be useful to gather all the archaeometric data so far available from the studies on Campanian pottery and raw materials for better accessibility and sharing of archaeometric data.

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