

COMPOSITIONAL CHARACTERIZATION OF ETRUSCAN EARTHEN ARCHITECTURE AND CERAMIC PRODUCTION*

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This study presents the results of new research into Etruscan technology for earthen architecture as well as ceramic production in the upper Tiber Valley in central Italy, using as a case study the Etruscan settlement of Col di Marzo (Perugia). It determines the compositional differences of the raw material employed as building material and for ceramic production by X-ray powder diffraction (XRD), thermogravimetric analysis and differential thermal analysis (TG-DTG), Fourier-transform infrared analysis (FTIR) and geotechnical analyses. The research also advances the knowledge of ceramic manufacturing technology, with a focus on impasto production, at Col di Marzo between the fifth and mid-third centuries BCE and the surrounding territory on the left bank of the River Tiber. The compositional analysis of building material compared with the ceramics provides answers to questions related to their sourcing and deepens the understanding of the exploitation of natural resources.

KEYWORDS: EARTHEN ARCHITECTURE, COMPOSITIONAL CHARACTERIZATION, XRD, FTIR, TG, GEOTECHNICAL ANALYSIS, CERAMIC PRODUCTION, ETRUSCAN TECHNOLOGY, UMBRIA, ITALY

INTRODUCTION

The study of Etruscan domestic earthen architecture is traditionally limited to a few sites where the traces of such perishable material is preserved, especially after burning, although the use of raw earth for walling was a widespread technique in Italy from the Neolithic onward, as argued in many early studies (e.g., Ammerman *et al.* 1988: 125–128, Bietti Sestieri and de Santis 2001) and recently summarized by Amicone *et al.* (2020).

However, there are two main problems when discussing Etruscan earthen architecture (wattle and daub, pisé/rammed earth and mudbricks): first, the definition of the walling technology; and second, the structural components which in the literature are often misleading as, for instance, ‘wattle and daub’ is a term employed generally for all types of raw-earth walls and timber, as argued by Stoddart (2009) and Miller (2017). There are substantial compositional differences

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between the above techniques and the soils employed, as wattle and daub requires a more plastic clay than *pisé*, which uses silty sands with a small amount of clay, as will be discussed below.

Interdisciplinary analyses of raw-earth walling techniques are infrequent in the literature on Etruscan architecture in central Italy, with some exceptions on wattle-and-daub research conducted at the site of Forcello near Bagnolo di San Vito (Mantova) in the Po Valley (Croce *et al.* 2014; Amicone *et al.* 2020).

Therefore, this paper aims to broaden the discussion on Etruscan building materials through scientific analysis using as a case study the Etruscan settlement of Col di Marzo (fifth to third centuries BCE) overlooking the Tiber Valley in the territory of Perugia. Crucial to the discussion is the analysis of the processing of raw material in response to building construction requirements compared with the use in firing ceramics.

Although Etruscan ceramic technology has not received the same level of interest as Roman production, recently the research has applied a broader and more comprehensive approach to the analysis of production and firing technology of Etruscan ceramics. The pottery production from the main Etruscan cities was analysed by combining petrography, scanning electron microscopy (SEM), X-ray fluorescence (XRF) and X-ray powder diffraction (XRD) analysis, for example at Tarquinia (e.g., Cariati *et al.* 2001; Bruni *et al.* 2001; Bruni 2012) and Veii (Saviano *et al.* 2002; Ambrosini *et al.* 2009).

There are an extensive number of publications on the results of firing in oxidizing conditions, comprising non-calcareous ceramic and calcareous ceramic (Fabbri *et al.* 2014; Maggetti *et al.* 2011), as well as the effects on ceramic products in the presence of organic matter (Maritan *et al.* 2006). Also several studies have tested the firing temperature of ceramics to establish which kiln technology was used in antiquity by applying different approaches. Important examples of the study of phase transformations with temperature are El Ouahabi *et al.* (2015) and De Bonis *et al.* (2017). Conversely, firing in reducing conditions has received far less scholarly attention. Research has mostly focused on specific types of production, such as prehistoric artefacts near Naples (Di Maio *et al.* 2011), the sandwich-like structures of the Po Valley Etruscan pottery (Nodari *et al.* 2004) and Greek pottery (Rathossi and Pontikes 2010). The present paper provides an update on the debate on the production technology of Etruscan pottery, fired in both oxidizing and semi-reducing conditions, as well as introducing new data on the processing of raw material.

THE SITE

This study will focus on the upper Tiber Valley, and in particular on the territory of the Etruscan city of Perugia, which started to flourish from the fifth century BCE. The city achieved political importance from the fourth century BCE onwards, according to Livy who listed the city, together with Cortona and Arezzo, as representatives of the other Etruscan cities in Rome, after the Etruscan defeat in 310 BCE, when they requested a 30-year peace treaty (Livy 9.37.12). Archaeologically, the late fourth century BCE marks the monumentalizing period of the sacred area under the cathedral (Cenciaglioli 2014). In the same period, the first circuit of the city walls was built and the important families of Perugia achieved control of the territory of the right bank of the Tiber, as suggested by the location of some scattered tombs in the area of Ponte S. Giovanni (Ceccarelli and Stoddart in press).

According to some scholars, the physical frontier between Perugia and the Umbrians was already defined by the river Tiber in the sixth century BCE (e.g., Sisani 2014, 100). However, passages of Strabo (5.2.1) and Pliny the Elder (*Hist. Nat.* 3.53) indicate that a portion of the territory on the left bank of the Tiber was under Etruscan control, as archaeologically documented by the

settlement of Arna, at least from the fourth century BCE (Donnini and Rosi Bonci 2008). A significant example of the frontier of Perugia, 10 km north from Arna, is offered by the settlement of Col di Marzo, located on a hilltop 645 masl overlooking the valley of Montelabate, which was excavated as part of the Montelabate Project (Stoddart *et al.* 2012; Stoddart and Redhouse 2014, 113–14; Malone *et al.* 2014; Ceccarelli and Stoddart in press) (Fig. 1).

The fortified hilltop site, whose foundation can be dated in the late fifth century BCE, flourished in the fourth century and was abandoned in the mid-third century BCE. Three successful excavation campaigns between 2011 and 2013, conducted by the University of Cambridge and the Queen's University Belfast, have revealed a series of substantial structures that extended over 1 ha forming part of a settlement on the top of a sandstone hilltop with several suggested activity zones, including weaving and cheese manufacture (Malone *et al.* 2014). The buildings are located at two different levels—Areas 2 and 3 at the upper level and Area 1 at lower level—separated by a retaining wall and arranged around two courtyards (Fig. 1, inset). The slope of the hill was exploited to collect rain water via two drainage systems, one running east–west and the other north–south, partially excavated but likely to converge in an underground cistern, although further excavation is necessary to confirm this idea. The buildings consisted of stone wall footings with floors and occupation deposits sealed by tile collapses, which also had evidence of burning.

The walls were constructed of wattle and daub, since during the excavation many fragments were recovered. These walls were built on a solid footing, probably pisé or mudbricks, to distribute the sideloads of the roof (for the latter on Etruscan monumental structures, see MacIntosh Turfa and Steinmayer 1996). Alternatively, as suggested for a house at Fidenae (Amoroso *et al.* 2009), the wattle and daub could have been built on a substantial wooden beam laid directly

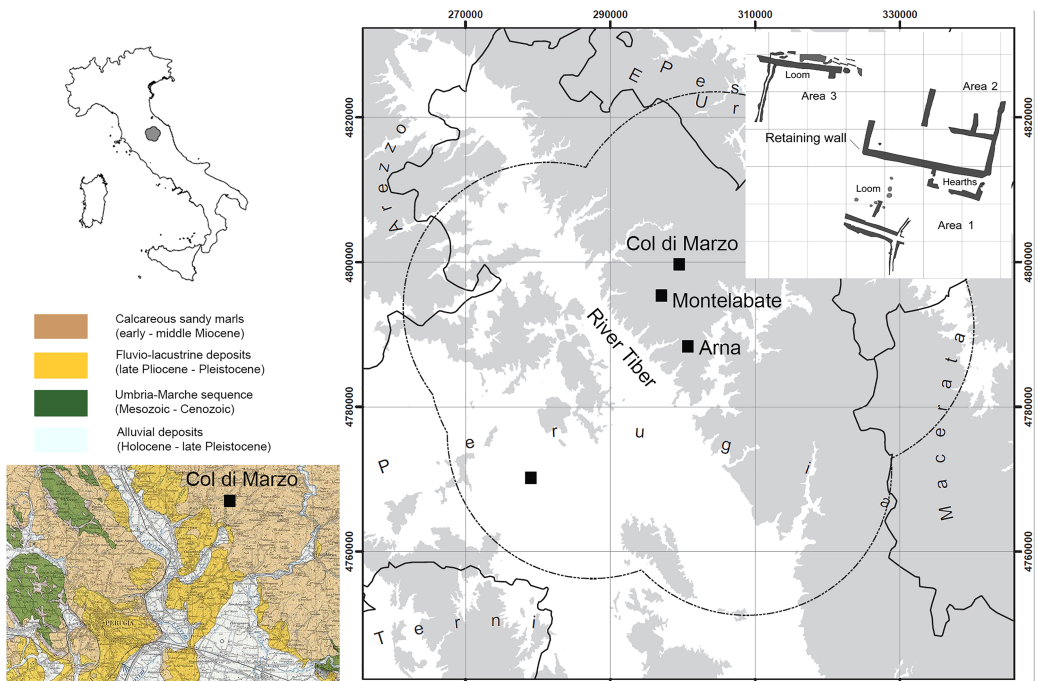


Figure 1 Geology and location of the site and other major sites mentioned in the text. Base map courtesy: David Redhouse. [Colour figure can be viewed at wileyonlinelibrary.com]

on top of drystone foundations, since no traces of postholes were discovered. Once the buildings at Col di Marzo were abandoned, the earthen architecture that held the weight of the tiled roofs might have collapsed after the decay of the walls, or could have been deliberately destroyed to recover iron nails. Currently, there is some evidence of pottery and tile waste, even if the presence of a kiln has not been confirmed. Therefore, a local production centre can be inferred from the availability of clay in the area and the similar characteristics of the products (tiles, impasto ceramics and grey impasto), as will be discussed below.

The occupation of the territory did not cease with the abandonment of Col di Marzo. A detailed survey (Stoddart *et al.* 2012; Malone *et al.* 2014) has shown scattered rural farms towards the Tiber Valley that started in the third century BCE and continued into later periods. Excavation has also discovered some grey impasto fragments at the site of the nearby Roman kilns (for a description of the site, see Ceccarelli 2017). This pattern suggests an agricultural exploitation of the territory under the control of Perugia, the importance of which resonates with the passages of Livy (28.45) when in 205 BCE the city provided, together with Chiusi, wheat and wood to Rome, supporting Scipio's expedition in Africa.

The bedrock of the site of Col di Marzo consists of alternating layers of clay shales with calcareous sandy marls interbedded with Miocene sandstones (Regione Umbria 2013; Stoddart *et al.* 2012) (Fig. 1). The valley of Montelabate and Perugia are located on fluvio-lacustrine deposits, characterized by marine sediments with a high proportion of calcium carbonate of the Pleistocene to late Pleistocene (Fig. 1), as demonstrated also by detailed coring in the area conducted by S. Taylor (University of Cambridge personal comment). Clays constitute the base of the stratigraphic sequence and the CaCO₃ content is relatively high (marly clays), with a good percentage of micaceous silt. The area is part of Monti Vulsini Volcanic District, where rocks consist of pyroclastic products and minor lavas of potassic (trachybasalts and trachytes) to ultra-potassic (leucitites) rocks (Peccerillo 2017, 89).

The analysis of the hilltop settlement raw clayey material and the results of the compositional characterization of soils in the valley of Montelabate (Ceccarelli *et al.* 2018) allow the exploration of wider issues such as the technology of raw materials in building construction compared with their use for ceramic production, and the exploitation of resources in the Etruscan world, pivoting around the Upper Tiber Valley.

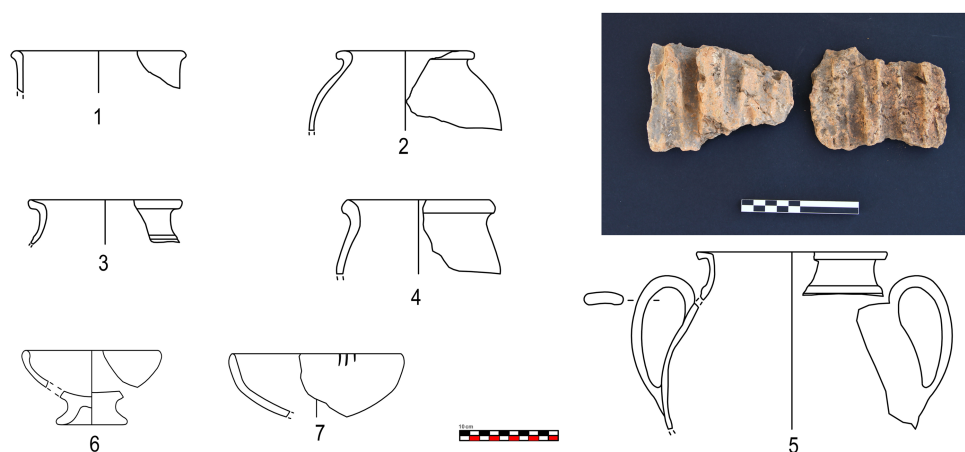


Figure 2 Col di Marzo: impasto pottery and (photograph) daub sample ER03. Pottery drawings courtesy: Marco Amadei. [Colour figure can be viewed at wileyonlinelibrary.com]

MATERIALS AND METHODS

Seven samples of daub and pisé employed in the construction of walls and a selection of the most representative raw earths from the area of the Roman kilns were analysed. Eleven fired samples covering the full diagnostic range of all the ceramics discovered at Col di Marzo were also selected. Daub, courseware impasto (Fig. 2: 1–5) and fineware ceramics (Fig. 2: 6 and 7, the so-called grey impasto which was fired with a similar technique as grey bucchero) fragments were chosen from different areas of the site (Fig. 1). In order to reconstruct the Etruscan building technology, specifically for the case study of Col di Marzo, the first step was to understand the procurement of the raw materials, which was likely based upon factors such as distance and accessibility. Therefore, three raw earths were selected for comparison with the samples collected at the site, while RR01 and RR02 came, respectively, from 3 and 4.5 km south-west of the settlement, near a Roman ceramic workshop (Ceccarelli 2017). Samples ER01 and ER02 are building materials, the latter possibly a pisé, from the same structure in Area 2. Daub ER03 originates from a deposit sealed by a substantial layer of tile collapse with evidence of destruction by fire in Area 1 (Figs 1 and 2: photograph). The larger fragments from this layer have a different thickness and are imprinted with the impression of small twigs with a 1.5–2.0 cm diameter, similar to those discovered at Chiusi, Petriolo (Gastaldi 2009, 33). The remaining samples ER04 and ER05 were discovered in the different areas of the rectangular structure in the eastern part of Area 1, belonging to the collapse of the walls (Fig. 1). Among the fired material samples, EF01 and EF02, a tile and a dolium were discovered in the same context as daub ER03, whilst the loom weight EF03 was collected from the topsoil. Several jars of cooking ware and tableware impasto fragments were sampled: the cooking ware EF04 and EF06 (Fig. 2: 1 and 2) came from Area 3 and the topsoil, respectively, whilst the tableware samples EF05 and EF07 (Fig. 2: 3 and 4) were discovered in Area 1. Finally, sample EF08 (Fig. 2: 5) came from the building above the retaining wall in Area 2. The grey fineware impasto bowls fragments, samples EF09–EF11 (Fig. 2: 6 and 7) from both Areas 1 and 2 are similar to the production from Todi which is dated from the fifth to the fourth centuries BCE by Tamburini (1985).

EXPERIMENTAL

Both unfired (daub) and fired samples were analysed using XRD, Portable X-Ray Fluorescence Spectroscopy (pXRF), thermogravimetric analysis and differential thermal analysis (TG-DTG), and Fourier-transform infrared analysis (FTIR). Moreover, geotechnical analysis was performed on selected unfired samples. X-ray powder diffraction patterns were recorded with a Bruker D8 Advance diffractometer using a graphite-monochromated Cu-K α radiation; the scan step was 0.02° 2 θ and the measurement time was 12 s per step. Diffractograms were analysed for qualitative phase composition with open-source software Profex (<https://profex.doebelin.org>; Döbelin and Kleeberg 2015), while quantification was performed through Rietveld refinement with the code GSAS (Larson and Dreele 2004). A 10 wt% of ZnO was added to all the analysed samples as an internal standard to quantify the crystalline and the amorphous fractions (Bish and Howard 1988). First, *in-situ* X-ray fluorescence spectra were collected using a portable Bruker Tracer III-SD instrument. All spectra were collected at 40 keV and 10.70 μ A with a collection time of 30 s following preliminary optimization. Quantitative data were obtained by means of a customized calibration (Ceccarelli *et al.* 2016). The sampling strategy for the majority of the samples comprised the analysis of sections which were prepared by making a fresh break to avoid any chemical contamination. The effective measured spot size was 8 mm in diameter and the analysis was

conducted with six readings on different spots to overcome the limits of the heterogeneity of the fabric, clay and temper. Compositional analysis was performed on the calibrated average net counts. Thermal analysis measurements (TG-DTG) were performed using a DTA-TG SEIKO 6300 thermal analyser. The experiments were conducted under flowing air in a temperature range of 25–1000°C; the heating rate was set at 10°C min⁻¹. The FTIR spectra were recorded with a Jasco model 615 spectrometer, using the KBr pressed-disk technique in the spectral range of 2000 to 400 cm⁻¹. The samples were ground with an Agatha mortar and a weighted amount of the resulting powder (200 mg) was mixed with KBr (Aldrich, spectroscopical grade) powder (700 mg). The mixture was pressed using a uniaxial press (10 tons) under vacuum for 5 min. The geotechnical analysis was conducted following the standard UNI CEN ISO/TS 17892-4: 2005, the Italian correspondent of European Standard CEN ISO/TS 17892-4. The analysis determines the grain size distribution curve of a soil and thus its granulometric fractions, that is, clay, silt, sand and gravel. The classification is based on particle size: clay is constituted by particles < 2 µm, silt includes grain sizes between 2 µm and 0.06 mm, sand comprises grains ≤ 2 mm, while dimensions between 2 and 4 mm are classified as gravel.

RESULTS AND DISCUSSION

Raw earths and earthen architecture building materials

Under the assumption that the characteristics of the soils employed in earthen architecture were related to the type of building construction with very limited processing, geotechnical analysis was performed. Samples ER04 and RR01 were selected because of the availability of material and to compare the differences. The resulting grain size distribution curves are plotted in Figure 3: it is possible to determine the granulometric fractions, that is, percentage of clay, silt and sand constituting the analysed soils. ER04 contains 12% of clay, 23% of silt and 65% of sand, while RR01

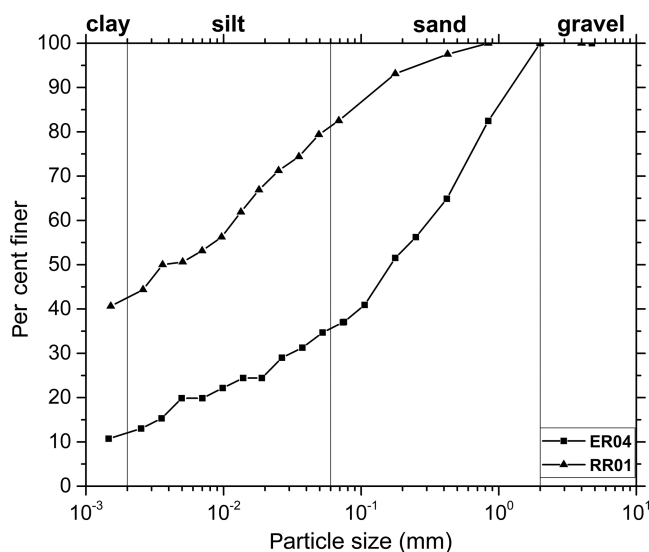


Figure 3 Grain size distribution of two raw earths (ER04–RR01).

contains nearly four times the amount of clay (42%), 39% of silt and the remaining 19% of sand. Hence, the analysis indicates that sample RR01 would be suitable for pottery-making because of its finer granulometry, whilst sample ER04 would be better as a building material. A lower degree of plasticity is required for raw earths employed as building material compared with those for pottery production. In addition, the soils most suitable for daub should contain a higher amount of sand, such as sample ER04, which has 65% of sand, with a small amount of clay, no more than 25%, on the basis that it would otherwise shrink too much during drying, even if the use of straw can somewhat counteract the shrinkage process (Russell and Fentress 2016). Moreover, an earth characterized by a smaller clay fraction can be suitable for this use because of its low liquid limit (Dumbleton and West 1966), a characteristic that implies limited shrinkage during drying.

As a first step, XRF analysis demonstrated that two types of building raw material were employed at Col di Marzo: calcareous ($\text{CaO} = 11\text{--}31.5\%$) (see Table S1 in the additional supporting information) and non-calcareous ($\text{CaO} < 6\%$). Subsequently, all the raw earths were characterized using Powder X-ray diffraction (PXRD); the quantitative analysis results are listed in Table 1. Unfired materials contain a variable amount of quartz (12.7–39.0%), while the clay fraction is relatively low (13–27%) and both plagioclases and orthoclase are present. The amorphous fraction (20.0–37.6%) is a result of the presence of impure mineral phases determined by the low crystallinity of the materials, such as sand and silt. For instance, the results of geotechnical analysis prove that the soils contained considerable amounts of sand which is not entirely constituted by crystalline quartz. The clay fraction of all the samples is mainly constituted by illite, but small amounts of biotite, smectite, chlorite and kaolinite were also detected. The XRD clay fraction amount differs from geotechnical analyses that classify a soil only on the basis of granulometry, without considering the microstructure of the material or its chemical composition (Ceccarelli *et al.* 2018). For instance, different amounts of clay minerals in sample ER02 (15%) indicates that a lower degree of water content and plasticity was necessary for its use. Daub ER03 has an even lower amount of clay minerals (13%), which can be explained by its partial exposure to the fire that occurred in the building. The temperature was $< 550^\circ\text{C}$ because of the presence of chlorite, but temperatures in a fire can be uneven in relation to organic fuel, such as timber, or the amount of oxygen, as proved at the site of Forcello (Amicone *et al.* 2020).

In the assessment of different sourcing of material, the presence of carbonates and feldspars is crucial: samples ER01, ER03 and RR01 consist of non-calcareous materials, whilst samples ER02, ER04, ER05 and RR02 are calcareous soils (calcite content = 11.3–23.2%). The non-calcareous group from Col di Marzo (ER01–ER03) has homogeneous characteristics because of the presence of natural anorthite, whilst RR01 has a different source. In the calcareous group, the raw earths ER05 and RR02 are differentiated by their absence of natural anorthite. While the first sample also had double the amount of calcite, the latter had over double the amount of quartz (28.4%), suggesting different sources for both samples.

Col di Marzo raw earth samples were also analysed by FTIR and thermogravimetric analysis (TG), techniques discussed extensively in the literature (Vagenas 2003; Rodriguez-Blanco *et al.* 2011; Fabbri *et al.* 2014; Ihli *et al.* 2014, Li *et al.* 2017) for detection of calcite. The compounds identified in FTIR spectra are reported in Table S2 in the additional supporting information. In the spectra of samples ER02, ER04 and ER05, from the range of interest (2000 to 400 cm^{-1}) (see the examples in Fig. 4, a), the CaCO_3 main band of the natural calcite appears at 1428/1427 cm^{-1} together with those at 875 and 712 cm^{-1} , which are typical of primary calcite (see Table S2 in the additional supporting information). The analysis also confirms the presence of quartz and clay minerals, the latter's more intense absorption bands correspond to the stretching of the Si-O bond, its maximum recorded at 1031 cm^{-1} , and to the bending of the

Table 1 Phase compositions as determined by X-ray powder diffraction (XRD) Rietveld refinement of raw materials and fired ceramics (wt%)

ID	Quartz	Calcite	Albite	Orthoclase	Anorthite	Illite	Biotite	Smectite	Chlorite	Gehlenite	Hercynite	Amorphous
ER01	31.62	2.95	10.37	6.08	3.96	23.76	0.87	0.34				20.05
ER02	28.88	11.31	4.26	4.81	2.76	11.80	1.84		1.25			33.08
ER03	38.87	1.33	9.38	10.54	1.85	11.70			1.47			24.87
ER04	12.62	23.19	3.23	6.79	4.63	16.03	0.66					32.86
ER05	12.55	22.78	3.56	1.93		14.57	5.56	0.59	0.90			37.57
RR01	32.91	2.37	4.28	4.97		20.86	1.58	2.50	2.02			28.50
RR02	28.39	11.03	3.87	3.74		16.06	0.85		6.13			29.92
EF01	26.22	4.64	5.51	0.39		23.69	2.75	0.97	1.08			34.76
EF02	28.08	9.65	9.50	13.29	4.41	13.76				4.37		16.92
EF03	50.86	4.30	7.95	9.18	2.71	20.21						4.79
EF04	26.25	9.66	4.07	6.00	3.97	12.24	0.51			0.16		37.14
EF05	30.17		3.68	2.56		14.85	3.87		3.13			41.76
EF06	41.17	1.16	11.40	10.38	4.37	9.87				0.46		21.19
EF07	41.23	1.88	13.43	10.29		17.18	2.06					13.93
EF08	40.62		9.31	7.23		20.98	2.66	0.92				18.29
EF09	35.43		5.43	13.99	2.86	5.24					2.70	34.34
EF10	53.32		10.71	14.33							8.11	13.53
EF11	51.97		11.27	12.50							10.15	14.31

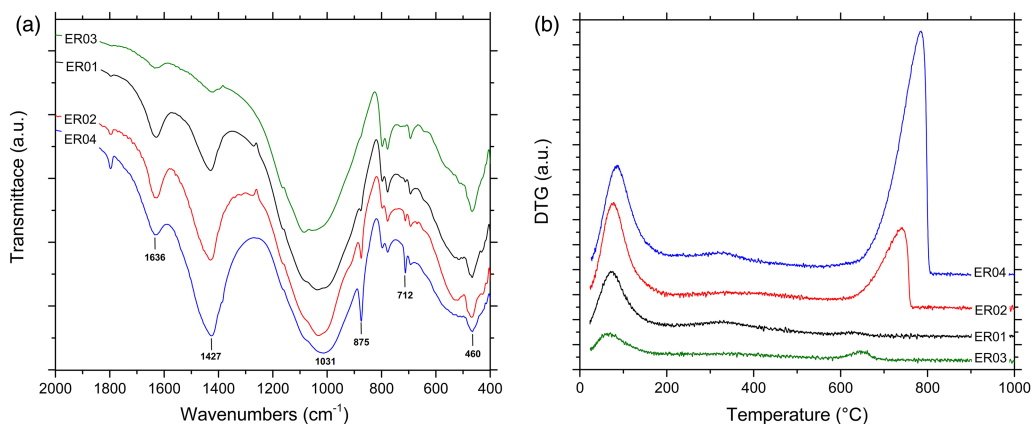


Figure 4 Analysis of the raw earths from Col di Marzo: (a) Fourier-transform infrared (FTIR) spectra; and (b) differential thermal analysis (DTG). [Colour figure can be viewed at wileyonlinelibrary.com]

O-Si-O bond, recorded at 460 cm^{-1} . These large bands are characterized by the presence of many shoulders because of the overlapping of the vibrational modes of compounds with similar structures and chemical composition. The same observation can be extended to the feldspars because of their similar compositions (Wilson 1987; De Benedetto *et al.* 2002; Shoal and Paz 2013; Bayazit *et al.* 2014).

In the thermogravimetric analyses, three different temperature ranges were considered: 25–250, 250–450 and 600–850°C, to determine the thermal decomposition of the samples (Fig. 4, b, and see Table S3 in the additional supporting information). In the first temperature range, all the samples behave very similarly, and the decomposition can be attributed to physi-sorbed water evolution. The second range is typical of chemi-sorbed water evolution and the decomposition of organic matter which determines weight losses. In particular, samples ER01, ER02 and ER04 show a loss between 2.04% and 2.70%, whilst the other samples have a range of 1.10–1.38%, which suggests that such raw earths have a higher organic component than other daubs. In the third temperature range, the strong decomposition phenomenon near 800°C, detected in samples ER04 and ER05, is related to primary calcite decomposition to give CaO (Fabbri *et al.* 2014). In this interval, the weight loss, ranging between 0.30% and 16.64% of the initial weight, is directly related to the amount of carbonates drawn from XRD analysis. The shift of decomposition temperature from samples ER04 (783°C) and ER02 (744°C) in Fig. 4 (b) can account for both the spread of the crystal size dimensions or the low purity of the calcite.

Fired samples

The main characteristics of the ceramics discovered at Col di Marzo and in its environs are (1) the use of different sources of raw material, both calcareous (CaO = 6–12%) and non-calcareous clays; and (2) the oxidizing or semi-reducing atmospheres used to produce objects. The quantitative XRD analysis of the fired samples in Table 1 shows that they are generally constituted by quartz (26–53%), plagioclases and orthoclase with an amorphous phase ranging from 4.8% to 41.0%. The latter is related to two factors: the variability of the clay composition (non-uniform grain-size distributions) and the mineralogical processes during thermal transformation which are affected by time and temperature, resulting sometimes in an incomplete mineralogical reaction

with low crystallinity at lower temperatures or in glassy material at high temperatures, both generating a high amorphous phase. This is because of uneven temperatures, non-homogeneous heat variations in the kiln and firing time. Therefore, it is crucial to focus on the firing process as the ceramics show incomplete or complete phase transitions providing important information on the methods and the technology of their production (Heimann and Maggetti 2019).

Roof tiles are characterized by a clay containing carbonates (CaO 6% in Table S1 in the additional supporting information) fired at a very low temperature (sample EF01), as shown by the presence of chlorite indicating a firing temperature at approximately 550°C, corresponding to the chlorite breakdown temperature, as experimentally demonstrated in pit-firing conditions (Maritan *et al.* 2006, 6–7). Impasto pottery is produced either with calcareous clay or with non-calcareous raw material, fired at higher temperatures. For instance, calcareous samples EF02, EF04 and EF06 show the presence of calcite (1.2–9.6%), an amount of illite (9.9–13.8%) and gehlenite (0.2–4.3%), which begins to form at 850°C (Fabbri *et al.* 2014; Rathossi and Pontikes 2010). At such temperatures, calcite should have decomposed completely, but, as suggested by Fabbri *et al.* (2014), calcite could reform in ceramics after firing, so the nature of calcite can be determined by thermogravimetric analysis (Fig. 5, a, and see Table S3 in the additional supporting information) where the carbonates decomposition peaks range between 670 and 728°C, indicating re-formed calcite. The original carbonate content, subject to a proper calcination process, was totally decomposed to CaO (free-lime) and in turn reacted with atmospheric moisture that was rehydrated to form calcium hydroxide (Ca(OH)₂). Subsequently, Ca(OH)₂ can react with atmospheric CO₂ and the re-formed calcite crystallized. The presence of gehlenite, which is a Ca-containing high-temperature phase, implies not only its formation during the firing but also that it was decomposed because the ceramics were buried in humid conditions. This has been demonstrated in experimental tests which show that in very humid acidic soils the decomposition of gehlenite may lead to the formation of secondary calcite (Heimann and Maggetti 1981). Interestingly, in all the above samples, a *dolium* and two cookware impasto fragments, fired at similar temperature contain similar amounts of anorthite (3.9–4.4%), which can be assumed as naturally present, as in the raw earths, with a minimal increase because of the firing temperature. Newly formed Ca-silicate mineral phases such as gehlenite and anorthite can occur in a ceramic body obtained from a calcareous clay, The formation of the latter together with diopside, however, requires temperatures > 900°C. Therefore, calcareous ceramics that do not

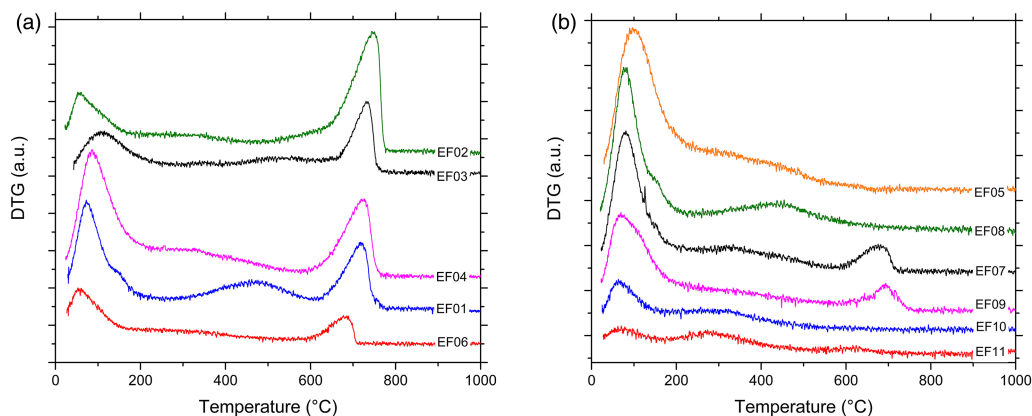


Figure 5 (a) Differential thermal analysis (DTG) of the calcareous impasto pottery; and (b) DTG of the non-calcareous impasto samples. [Colour figure can be viewed at wileyonlinelibrary.com]

contain diopside are supposed to be fired below such temperatures, assuming a lower heating rate and short reaction time preventing the expected reactions (Heimann and Maggetti 2019). Moreover, the formation of these phases by a reaction of a substantial dehydroxylation of phyllosilicates in calcareous clays reduces the amount of the free-lime in the ceramic body and consequently the possibility of the formation of secondary calcite (Fabbri *et al.* 2014), both of which are still present in samples EF02, EF04 and EF06.

The calcareous sample EF03 (a loom-weight) presents a significant quantity of illite, indicating a firing temperature $< 850^{\circ}\text{C}$. Therefore, the presence of calcite can be assumed as newly formed. This is confirmed by the differential thermal analysis (DTG) analysis (Fig. 5, a), where the carbonate decomposition is observed at around 720°C since the decarbonation of the reformed calcite appears at lower temperature than primary calcite.

The other samples, tableware and fineware fragments (EF05 and EF07–EF11) were produced with non-calcareous clays, and they can be divided into two groups on the basis of the estimated firing temperatures. Samples EF05 and EF08 were fired at lower temperature, as proved by the low amount of orthoclase and high amount of clay minerals, which are similar to the composition of the raw material. Therefore, a firing temperature $< 750^{\circ}\text{C}$ should be assumed for these samples and also $< 700^{\circ}\text{C}$ for sample EF05, which still contains 3.13% of chlorite (dehydroxylation around 650°C). Sample EF07 may have been fired at a higher temperature compared with the previous samples.

Regarding fineware grey impasto samples EF09–EF11, their semi-reducing conditions during the firing process at high temperatures led to the formation of hercynite (an iron spinel, $\text{Fe}^{2+}\text{Al}_2\text{O}_4$), which is a phase forming at temperatures $> 900^{\circ}\text{C}$ (Heimann and Maggetti 2019). The occurrence of these reactions does not exclude the possibility of temperature variations inside a kiln, and newly formed phases may occur at lower temperatures when firing in a reducing or partially reducing atmosphere. However, samples EF10 and EF11 were probably fired at temperatures $> 950^{\circ}\text{C}$ because clay minerals are totally dehydroxylated. The lower amount of the amorphous phase (13–14%) in the above samples with respect to EF09 (34%) is not because of the firing temperature, but rather due to the larger amount of crystalline phases contained in these materials, as, for example, feldspars, hercynite and especially the larger amount of quartz.

Beyond temperature, another key factor to determine the surface colour, when considering the type of reactions taking place in firing ceramics, is the supply of air and the amount of O which influences the transformations of the Fe oxides into hercynite. Moreover, carbonaceous organic matter in oxidizing conditions begins to carbonize at 300°C and combined with O forms CO_2 , which is removed from the ceramic body (Quinn 2013, 198). In reducing or partially reducing conditions, the carbonized organic matter remains in the clay and contributes, as well as hercynite, to the grey colour of ceramics. In the analysed samples, the residual presence of organic matter is recorded through TG analysis: samples EF09–EF11 show a mass-loss (1.02–1.23%) in the interval $240\text{--}450^{\circ}\text{C}$ (see Table S3 in the additional supporting information). To support these observations, examples of DTG curves are plotted in Fig. 5 (b). The grey colour results under partially reducing firing conditions in an atmosphere rich in CO_2 , preventing the complete combustion of C in the ceramic fabrics, as well as the presence of the spinel phase hercynite (Heimann and Maggetti 2019).

CONCLUSIONS

The study examined nine raw materials, six of which were fragments of earthen architecture and three a selection of samples representing the main diagnostic group of pottery produced at Col di

Marzo near Perugia, Italy. They were analysed using multiple techniques, which have provided new insights into raw-earth building techniques and ceramic production technologies. This integrated methodology produced the following results:

- At least two different sources of raw material, both calcareous ($\text{CaO} = 9\text{--}31.5\%$) and non-calcareous ($\text{CaO} < 6\%$), were collected for building material at Col di Marzo, without preliminary refining of the soils. A low degree of plasticity is an essential characteristic for raw earths employed as building material. From a geotechnical viewpoint, the soils most suitable for daub should contain a higher amount of sand (65% in sample ER04) with a smaller clay fraction, no more than 25%, because of its low liquid limit, a characteristic that implies limited shrinkage during drying. As illustrated by the XRD analysis, sample ER05 (which came from the same building and context as the previous one) has similar characteristics with a ratio between quartz and calcite of nearly 1:2 (12.5–23.0%). Inversely, sample ER02 displayed compositional and texture differences compared with the other daub fragments, so could potentially be interpreted as a fragment of pisé. The non-calcareous daub samples (ER01–ER03) originated from the same source, but with a high amount of quartz (31.7–38.9%), suggesting that such a characteristic made it suitable as building material and therefore employed in several buildings, in both Areas 1 and 2 of the site (Fig. 1).
- The impasto at Col di Marzo was produced with both calcareous and non-calcareous raw clayey material, the latter of which was mainly chosen for tableware impasto. The firing technology suggests the use of a different type of kiln: the lower temperature of tiles is compatible with a bonfire kiln, whilst the rest of the samples were fired in a vertical kiln. The calcareous raw material was employed for large storage containers and for cooking ware, as calcite acts as flux reducing the firing temperature and provides mechanical strength to the ceramics to sustain the thermal shock when used for cooking. Samples EF02, EF04 and EF06 showed the presence of calcite and gehlenite, newly formed Ca-silicate mineral phases which begins to form at 850°C. At such a temperature, calcite should have totally decomposed, but this is also related to its granulometry. Furthermore, in the case of ceramics buried in very humid acidic soils, the decomposition of gehlenite may lead to the formation of secondary calcite. The nature of the calcite was determined by the thermogravimetric analysis as the carbonates decomposition peaks at $< 750^\circ\text{C}$ indicate re-formed calcite in all the samples. Non-calcareous tableware seems to have been fired at relatively lower temperatures $< 800\text{--}850^\circ\text{C}$.
- Fineware grey impasto at Col di Marzo was manufactured with non-calcareous raw clayey material at a high temperature. The occurrence of the Fe-spinel hercynite, a high-temperature phase, implies a firing temperature $> 900\text{--}950^\circ\text{C}$, as in samples EF10 and EF11 the clay minerals were totally dehydroxylated. However, this does not exclude the possibility of temperature variations inside a kiln, and newly formed phases may have occurred at lower temperatures when firing in a partially reducing atmosphere. The grey colour, as well as being because of residual organic carbon in the ceramic fabrics (indicated in the thermogravimetric analysis), is because of the partial reduction of firing conditions that influence the transformations of the Fe oxides into hercynite.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Table S1. Chemical composition as determined by X-ray fluorescence (XRF) analysis. All data are expressed as per cent.

Table S2. Assignment of the main absorption bands of Fourier-transform infrared analysis (FTIR) spectra.

Table S3. Weight losses measured through thermogravimetric analysis (TG) analysis.