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Roman brick production technologies in Padua (Northern Italy) along the Late Antiquity and Medieval Times: Durable bricks on high humid environs

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ABSTRACT

Production technologies of Roman to Medieval times bricks on the city of Padua were addressed by means of a multi-analytical approach, consisting in Spectrophotometry, X-Ray Fluorescence (XRF), Powder X-Ray Diffraction (PXRD), Polarized Optical Microscopy (POM) and Scanning Electron Microscopy (SEM-EDS). The Early-Christian (5-6th centuries) and Romanesque (12-13th centuries) areas of the Basilica of Saint Justine of Padua (5/6-16th centuries), and the remains of the Roman necropolis (1-3/4th centuries) still preserved under the basilica, were selected to collect the bricks in order to define possible differences between the materials used for the various building phases. The walls are mainly shaped by yellow (with pale and dark hue) and beige colored bricks with an overall good conservation state. The ceramic bodies of this type of bricks showed the development of high-temperature phases but a low sintering degree was achieved. Moreover, secondary phases such as zeolites and calcite were formed, within almost the pale-yellow bodies and intensively precipitated through the groundmass of the beige bricks, respectively. Mg-rich calcareous clays and chloritic-illitic clays were used, firing temperatures of or over 900°C were reached and more porous ceramic bodies were produced when higher was the carbonate content on the raw clays. A lesser carbonate content of the base clays and/or the decrease in the firing temperatures were the main technological modifications progressively accomplished, leading to color changes on the ceramic bodies from yellow to beige hue. The Roman production technologies might be largely inherited by the brick makers during the Late Antiquity and Medieval times in the city and the reuse of more ancient bricks during the Medieval Times was confirmed. Such reuse operations have allowed to observe that under high humid conditions the yellow hue bricks have been rather good preserved, while when exposed to insolation and fluctuations of the environmental conditions a significant granular disaggregation -with the concomitance darkening of the color pastes- is developed. The color of bricks may entail an identifier of a specific construction period of the city and durable bricks from local clays, especially suitable for high humidity areas and that may preserve the aesthetical values of the city of Padua, may be currently produced.

1. Introduction

Interdisciplinary studies on ancient bricks provide a knowledge base loaded with a heritage and technological value that may entail a cultural heritage resource [1]. If the bricks are well preserved, could be transferred to current ceramic industry to produce durable bricks ensuring at the same time their aesthetical values [2]. Ceramic processing is largely influenced by the composition of the original clays and by the firing conditions [3,4]. Ceramic tech-

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nologies imply crystallization processes involving mineralogical and microstructural changes that are much more complex during the firing of calcareous-rich clays than of low -or free- carbonate clays [5–7]. Newly-formed phases such pyroxene-type or melilites represent the products of the solid-state reactions that take place at high firing temperatures between phyllosilicates and carbonates [5]. Besides the mineral phases preserved from the base clay and those formed during firing, ancient ceramics could contain secondary phases crystallised after firing [8–10]. Calcite and zeolites occur frequently as post-firing mineral phases on calcareous ceramic bodies [11,12] and may induce color, mineralogical and microstructural changes [13]. Moreover, environmental conditions may induce bricks decay, especially if they are exposed to high fluctuating environments [14].

1.1. About of Padua's environs, the fired brick in the city and the Basilica of Saint Justine

The city of Padua (Northern Italy) has a warm and tempered climate. There is significant rainfall throughout the year, with an average annual circa of 1000 mm. The average temperature is 15°C and the average annual relative humidity is 74% (Regional Agency for the Protection of the Environment, ARPAV). Due to its location in the eastern Po River plain, characterized by the abundance of clayey materials (mostly Quaternary alluvial deposits), and the lack of rock outcrops (except those of the nearby Euganean Hills), fired bricks have been extensively used as building material along the history of the city.

The Municipium of *Patavium* was a strategic trade area in Roman times, mainly due to its geographical centrality in the Veneto region and the fluvial system that run through the territory. The large demand of fired bricks from the middle of the 1st century BC determined the proliferation of numerous pottery workshops [15], as point out the stamps imprinted on clay elements found in the city and surroundings [16]. Once molded, the bricks were dried and the firing temperatures might reach the 900-1000°C in one week [17]. After the fall of the empire (end of the 5th century), the city was depopulated for long periods, chiefly due to invasions, abandonment as well as floods and earthquakes. To date, it is unknown the presence in the city of furnaces that produced bricks during the Late Antiquity, that would be built or reused from Roman times. Only after the 10th century, Padua began to be properly recovered and became an independent municipality.

During Medieval times, the so-called Communal Age (12-13th centuries) entailed a time of expansion of the city, being the reuse of building materials -both dimensioned stone and bricks- from ruined Roman constructions a very extensive practice [18–20]. Besides, specialized firms in the recovery of ancient materials from diverse places also procured reused bricks [21]. For a better manageability, in the Medieval Times the large and quadrangular Roman brick was changed to a smaller and rectangular module. However, the reduction of the size of the bricks may also suggest former reuse practices, since the Roman bricks were cut to be fitted within the new fabrics [22,23] and the builders were get used to work with smaller pieces [24].

The Abbey of Saint Justine of Padua (5/6-16th centuries) nowadays includes a basilica and a Benedictine monastery and it stands next to the Prato della Valle square, where a Roman necropolis and theatre -named *lo Zairo*- were by the 1-3/4th centuries [25]. Around the 5-6th centuries, a small basilica where Saint Justine of Padua was buried and an attached chapel (*sacello*) were built. Of this Late Antiquity construction, the *sacello* and a mausoleum were the main remains preserved [26,27]. After major damages caused by the earthquake of 1117, the pristine basilica was rebuilt in the 12th century, with the extensive reuse of bricks and stones (mainly trachyte) [28]. During the 12-13th centuries, the Romanesque construction was focused on the presbytery, the bell tower and two chapels. During the 14-15th centuries, the choir, the sacristy and other chapel were built in Gothic style. The basilica rebuilt in the 12th century was demolished in 1502 and the current basilica was built during the 16th century, according to a Renaissance project. Currently, the entire complex is owned by the Italian state and is kept by the present Benedictine community (see Supplementary 1).

2. Research aims

With an interdisciplinary approach, the multi-analytical study of bricks from the Basilica of Saint Justine of Padua aims: i) to shed light about the manufacturing technologies used in the city during the Roman, Late Antiquity and Medieval times and ii) to state the main factors involved in the conservation and decay of the bricks. Considering previous multi-analytical studies performed on historic bricks used at the built heritage of Padua [29,30], the following research deepens on the production and conservation of fired bricks over a long period of time in the city.

3. Materials and methods

3.1. Bricks sampling

The remains of the Roman necropolis were mostly shaped by yellow bricks, the areas selected of the basilica dated to the Late Antiquity (Early-Christian basilica, 5-6th centuries) chiefly by pale-yellow bricks (some bricks with beige hue were also identified in these areas) and those from Medieval times (Romanesque walls, 12-13th centuries) were built overall with beige-colored bricks. The bricks fabrics were joined by lime mortars. Twenty bricks were sampled for analysis and the relative humidity and temperature of the areas were measured. The Roman remains, the Late Antiquity areas and the inner Medieval walls are exposed to high humidity. Furthermore, they are quite closed areas where the environmental conditions remain fairly constant throughout the day. The outer east Medieval wall is exposed both to a major fluctuation of the climatic values and to an important insolation degree during the summer. The bricks shown a good conservation state, except some used on such outer wall (see Supplementary 2).

3.2. Analytical techniques

The color was measured on fresh surfaces of bricks by spectrophotometry using a portable 3nh NS800 Spectrophotometer. The chromatic coordinates a* and b* (a*: +60 = red, -60 = green; b*: +60 = yellow, -60 = blue) were considered. Chemical analyses were performed by X-Ray Fluorescence (XRF) using a PANalytical Zetium compact spectrometer with a Rh anode and 4 kV X-ray generator. Major and minor oxides were determined. The mineralogical composition was determined by Powder X-Ray Diffraction (PXRD) using a PANalytical X'Pert PRO diffractometer in Bragg-Brentano geometry equipped with a cobalt X-ray tube and a X'Celerator detector. Mineral phases identification was performed using the X'Pert HighScore Plus software. The ceramic bodies were examined in thin sections by Polarized Optical Microscopy (POM), using a Nikon Eclipse E660 microscope equipped with a CANON 650 digital camera and the Camera EOS digital microphotography system. The microstructure and the chemical composition of the ceramic bodies were studied by High-Scanning Electron Microscopy coupled with a microanalysis of Energy Dispersive X-Ray

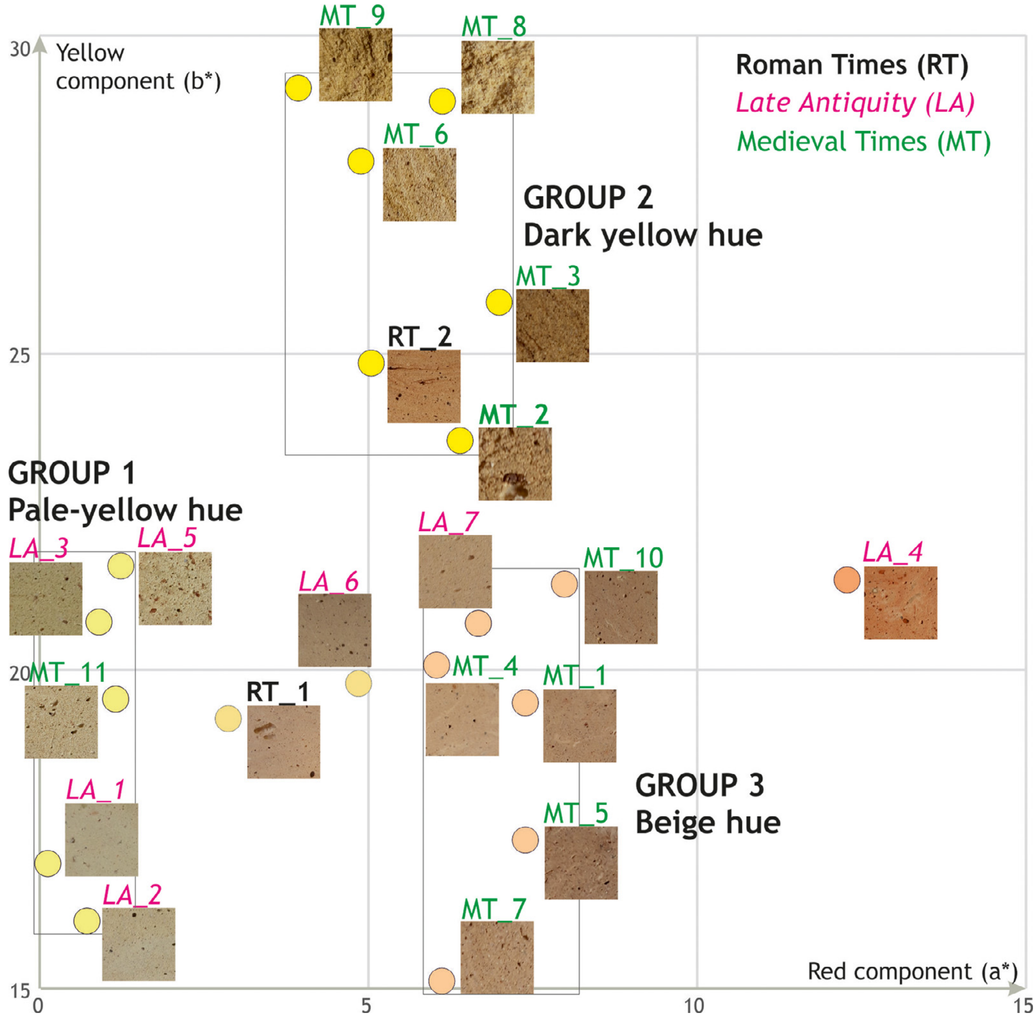


Fig. 1. The three main chromatic groups stated from the plotting of the a* and b* values measured on the fresh surfaces of the ceramic bodies. Many bricks from the Late Antiquity (LA) display a pale-yellow hue (group 1) and nearly all the bricks belonging to groups 2 and 3 were taken from the Medieval (MT) areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Spectroscopy (SEM-EDS), using a Camscan MX 2500 scanning electron microscope (see Supplementary 3).

4. Results and discussion

4.1. Brick production technologies based on the characterization of the ceramic bodies

4.1.1. Color measurement

Considering the values of the a* and b* coordinates, three main chromatic groups were clearly defined (Fig. 1): yellow-colored bricks, segregated in ceramic bodies with a pale-yellow (group 1) and a dark-yellow hue (group 2), and beige hue bricks (group 3). Bricks RT_1 and LA_6 remain between the pale-yellow and beige hue and brick LA_4 -with quite red hue- is out of these three groups. Bricks belonging to group 1 were mainly from the Late Antiquity areas and almost all the bricks with dark-yellow hue (group 2) and beige hue (group 3) have been sampled from the Medieval walls.

4.1.2. Chemical composition

From data show in Table 1, bricks are rather moderate rich in SiO_2 (36-48%) and in Al_2O_3 (11-15%). The restrained rich quantities of Fe_2O_3 (4-5%) chiefly correspond with iron oxides, present in the

Table 1
Chemical analysis of the major and minor oxides (expressed in wt.%) and zircon trace element (expressed in ppm) of the Roman bricks (RT) and of some bricks from the Late Antiquity (LA) and Medieval (MT) areas.

Brick	Color	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Zr	LOI*	TOTAL
RT_1	pale yellow	40.1	11.4	4.05	0.06	5.11	22.4	1.04	2.45	0.53	0.15	137.7	12.8	100.1
RT_2	dark yellow	47.3	14.0	5.21	0.09	7.54	16.9	1.91	1.46	0.71	0.17	174.7	4.43	99.7
LA_1	pale yellow	36.7	11.2	4.11	0.07	5.39	25.6	1.21	1.74	0.51	0.16	126.9	13.3	99.9
LA_4	red	46.7	15.1	5.44	0.09	4.63	15.4	1.24	3.02	0.63	0.18	159.5	6.95	99.3
LA_5	pale yellow	44.4	14.3	4.79	0.08	5.19	18.5	1.93	2.10	0.55	1.10	129.5	7.10	100.0
MT_4	beige	36.6	11.3	4.23	0.08	8.06	20.1	0.92	2.53	0.60	0.17	138.4	14.8	99.4
MT_8	dark yellow	45.8	12.9	4.66	0.08	8.57	18.3	1.78	1.41	0.69	0.33	160.9	5.31	99.9
MT_10	beige	46.3	14.4	5.00	0.08	5.06	13.7	1.32	3.55	0.52	0.13	153.3	5.92	95.9

*LOI = loss on ignition

base clays and/or developed during the firing [31]. The rather high alkaline-earth metals contents (MgO + CaO between 18-31%) may be related to Ca- and Mg-rich mineral phases formed during the firing and deriving from the carbonate rich clays used. The alkaline oxides (Na_2O and K_2O), occurring in quite moderate amounts (0.9-1.9% and 1.4-3.6% respectively), are probably related to the presence of Na-plagioclases, illite and/or K-feldspars naturally present in the base clays. The TiO_2 (< 0.8%) and Zr (125-175 ppm) contents are mostly related with the presence of Ti-bearing minerals and zircon. The chemical data point out that silica-rich clays with significant clay mineral and Ca-Mg-carbonate contents and diverse quantities of iron oxides were used.

Two main compositional types can be established: i) samples RT_1, LA_1 and MT_4, with lower quantities of silica (< 40.2%), alumina (< 11.5%) and iron oxide (< 4.3%), very high amounts of MgO + CaO (between 27-31%); and ii) samples RT_2, LA_4, LA_5, MT_8 and MT_10, with higher amounts of silica (> 44%), alumina (about > 13%) and iron oxide (> 4.5%), lesser contents of MgO + CaO (between 18-25%). Both compositional types were found in the Roman bricks and in those from the Late Antiquity and Medieval areas. No clear relation of such types with the grouping of bricks based on color measurements (Fig. 1) is observed, suggesting that the raw clays used were compositionally rather similar and that slight variations on the chemical composition were enough to yield a noticeable color change (see Supplementary 4).

4.1.3. Mineralogical composition

On the basis of the diffraction patterns (Fig. 2), it can state that quartz and K-feldspar are residual compounds of the raw clays; anorthite, a clinopyroxene (generic term), gehlenite (rather melilite), forsterite and hematite are the neo-formed phases; calcite, zeolites (mainly analcime) and aragonite are secondary phases. The pale and dark-yellow bricks display similar diffraction patterns, characterized by the significant presence of neo-formed phases, low contents of quartz and zeolite detection. The beige bodies shown a more heterogeneous mineralogical assemblage. Therefore, in the pale-yellow ceramic bodies (group 1) clinopyroxene, anorthite, calcite and analcime are predominant phases, gehlenite is well detected, forsterite is slightly present and quartz content is significantly low. In the dark-yellow bodies (group 2), the same mineral phases were detected but quartz concentrations are higher and an overall decrease of gehlenite and calcite is noted. In the beige bodies (group 3) the highest quartz concentrations and traces of K-feldspar are detected, anorthite and clinopyroxene are equally present but the definition of their main reflections is drastically reduced in some samples. Gehlenite and calcite presence is rather important, forsterite and aragonite are noted in some bricks.

The detection of anorthite, clinopyroxene and gehlenite point out that Mg-rich calcareous clays and chloritc-illitic clays were used and that firing temperatures between 900 and 950°C were reached. The illitic content in the raw clays should be low, so at 900°C no dehydroxylated illite phase remained and, besides, chlorite was completely disappeared. The high temperature mineral phases are more abundant in the yellow bodies -in concomitance with the lower presence of quartz- as well as the greater intensity of the anorthite and clinopyroxene main reflections with respect of gehlenite. This may indicate that they were produced using clays richer in carbonates and fired at higher temperatures -probably between 900-950°C- than the beige bodies -circa of 900°C- (see Supplementary 5). Besides the compositional differences on the base clays, the firing temperature was the main responsible of the color of the pastes. Hence, Fe^{3+} entrapment by the structure of calcium silicates inhibits hematite formation, so the color becomes lighter with increasing temperature [32–34].

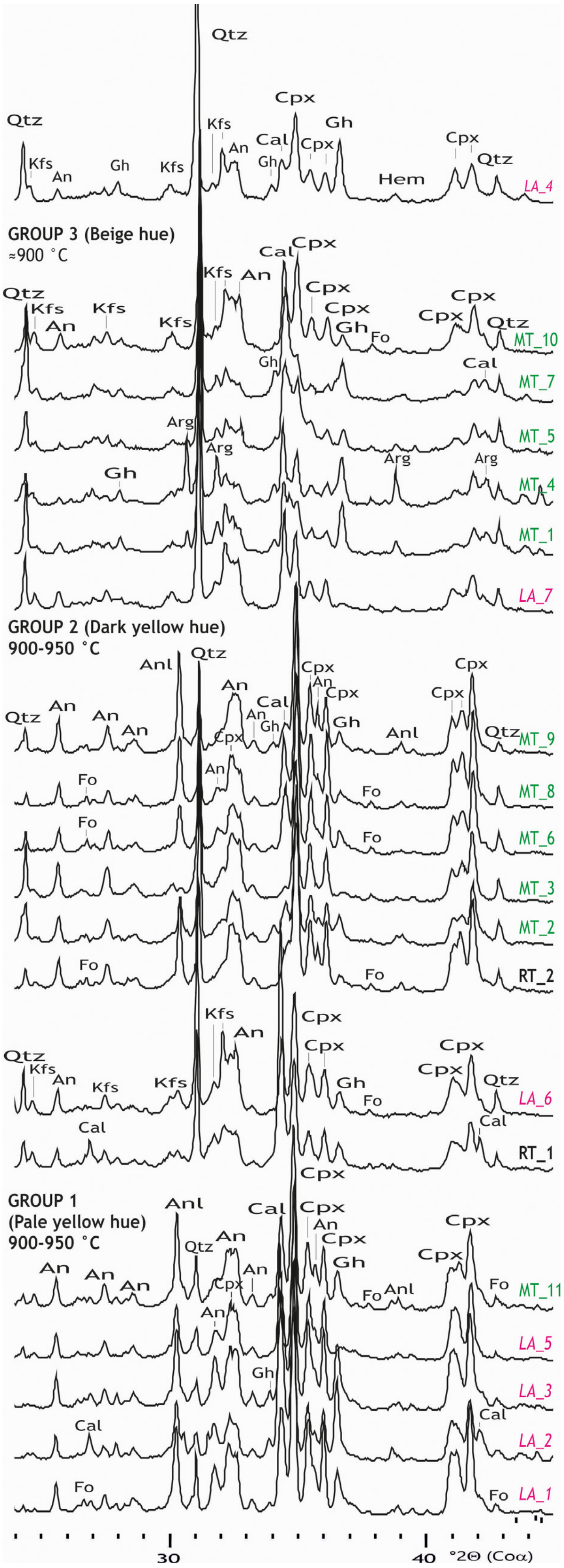


Fig. 2. Diffraction patterns and mineral assemblages detected by XRPD in the pale-yellow, dark yellow and beige hue ceramic bodies from Roman (RT), Late Antiquity (LA) and Medieval (MT) areas. Mineral abbreviations after [36]: quartz (Qz), K-feldspars (Kfs), anorthite (An), clinopyroxene (Cpx), gehlenite (Gh), forsterite (Fo), hematite (Hem), calcite (Cal), analcime (Anl) and aragonite (Arg). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

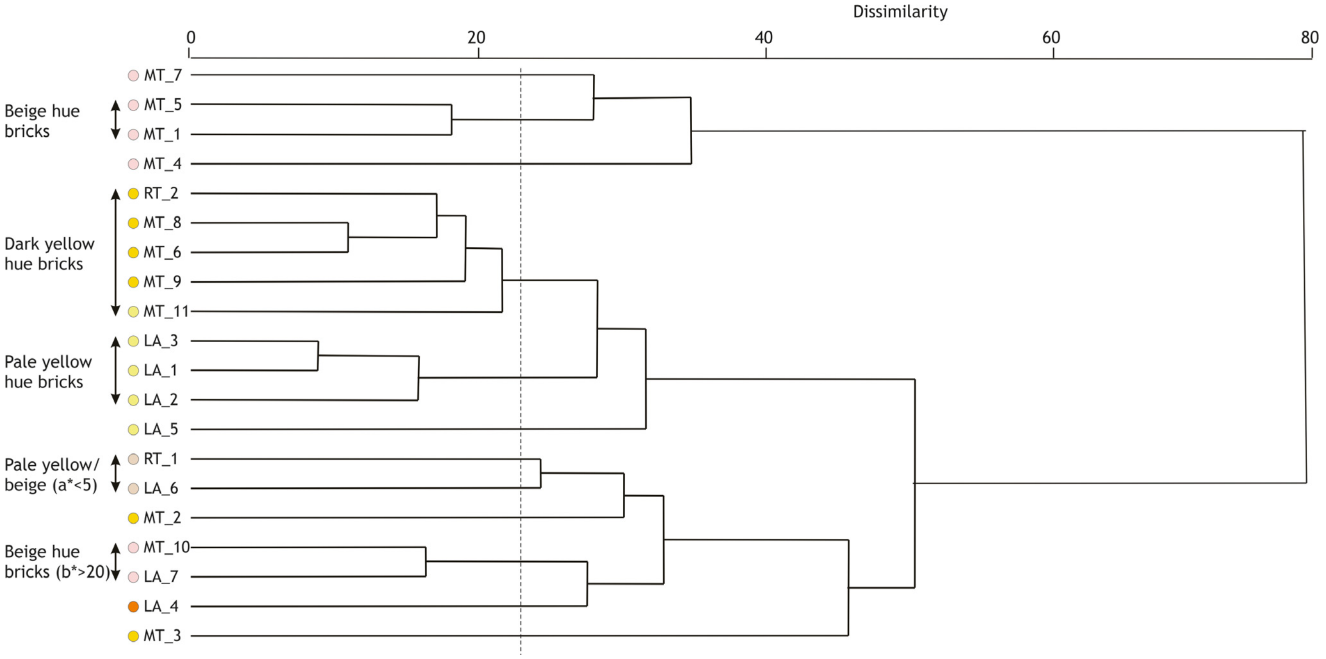


Fig. 3. Dendrogram obtained from the cluster analysis of the PXRD data according to Euclidean distance and average linkage method on position of peaks.

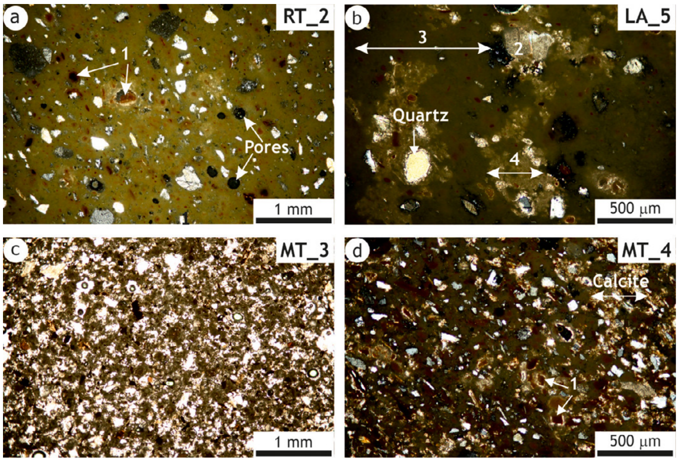


Fig. 4. Photomicrographs taken under the Polarized Optical Microscopy (POM) of the bricks. a: yellow bricks from the Roman necropolis (RT); b: pale-yellow from the Late Antiquity areas (LA); c: dark yellow and d: beige hue bodies, both from the Medieval walls (MT). Fe-rich clay pellets (1), decomposed carbonate grains (2), gelling portions (3) and high birefringent areas (4) of the matrix. Images taken in plain-polarized light (c) and crossed-polarized light (a, b and d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

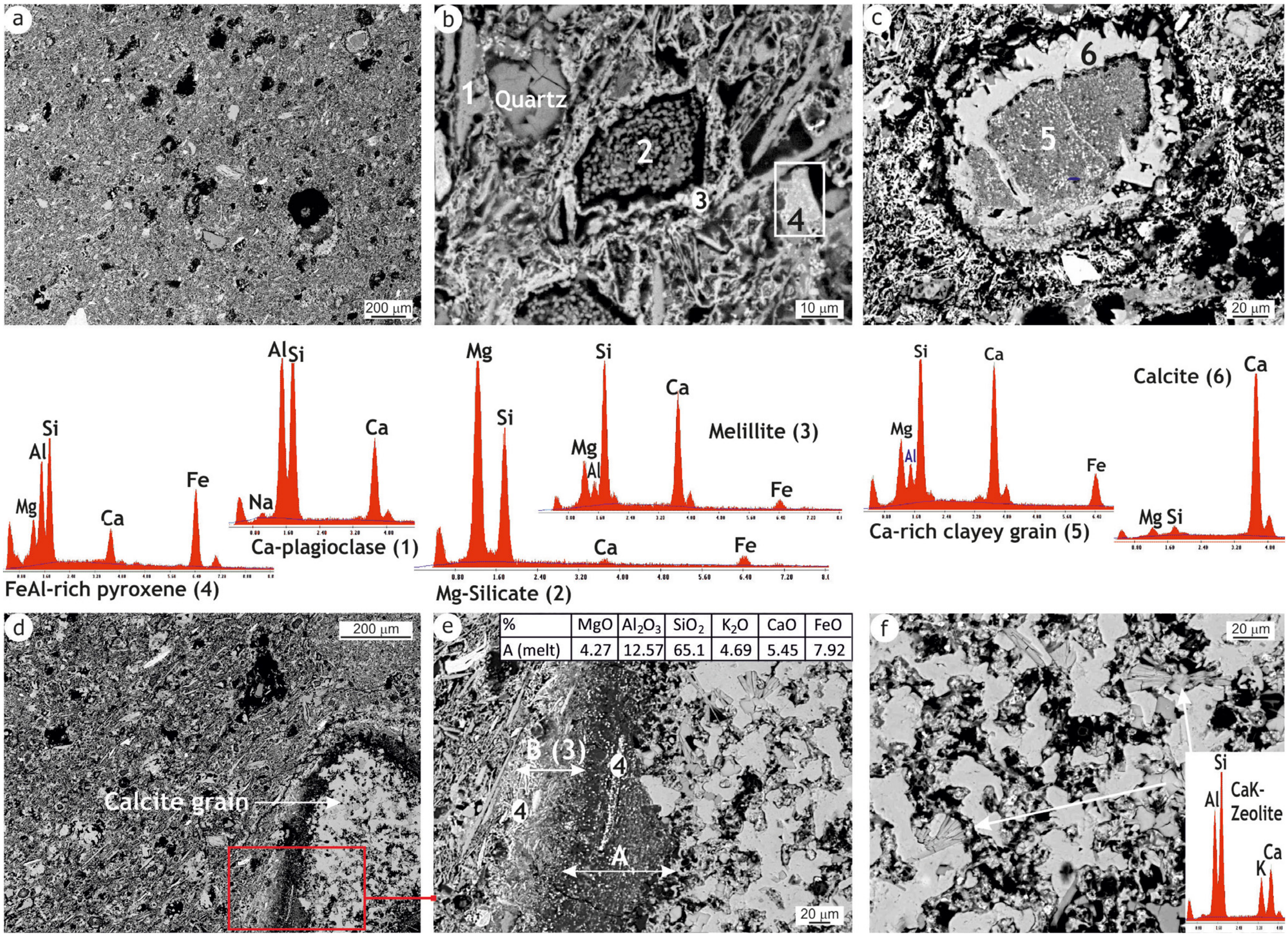
The calcite detected should mainly correspond to secondary calcite, in that new-formed phases and primary carbonates cannot be together [35]. Zeolite secondary hydration products have been detected by XRPD in other ancient bricks that shape the built heritage of the city of Padua [29,30]. The detection of such hydration secondary products only in the yellow bodies suggests that high calcium contents may foster their formation, so the nucleation of these type of zeolites also points out that calcite-rich clays were used.

When the PXRD data are statistically treatted by cluster analysis as proposed by [37], excellent grouping according to the firing temperature and/or composition of the raw materials could be provided [30]. Bricks tends to group according to their color, althought some of them tend to group separately or even being outliers (Fig. 3). The pale-yellow bricks cluster together, showing in one case a higher dissimilarity level (LA_5) with others or being more similar to the dark-yellow bricks (MT_11), which are also groupping in a unique cluster with the exception of samples MT_2 -with more analcime- and MT_3, where no zeolites were detected. The beige hue brick tend to group in two different regions of the cluster: samples MT_7, MT_5, MT_1 and MT_4, althought adjacent showed a high dissimilarity level, and MT_10 and LA_7, characterised by a higher clinopyroxene content, reflected by the higher yellow component ($b^* > 20$, Fig. 1). The post-depositional processes determined the crystallization of secondary phases, which affected their mineralogical composition and seems to have been less effective on the bricks color.

4.1.4. Petrological features

The Roman bricks (with yellow hue) and the pale-yellow bodies from the Late Antiquity areas display similar petrological features, showing a yellow-brown color and optically very low active groundmass (Figs. 4a and 4b). Highly dense gelling portions and high birefringent areas are segregated (3 and 4 in Fig. 4b). About 10-20% of inclusions is observed. The content of quartz and K-feldspar grains -both with occasional reaction rims- is low (5-10%), displaying sub-rounded and sub-angular morphologies and fine/medium sand-size. Clay pellets with porous rims are uniformly distributed (1 in Fig. 4a). Carbonate inclusions that have lost their birefringence (2 in Fig. 4b) and some coarse calcite grains with reaction rims are noted. The porosity (≈5%) corresponds to rounded and sub-rounded pores (Fig. 4a), mainly resulted from the decarbonization of the carbonate-rich clays during the firing [38], and to shrinkage rims formed due to the contraction of particles during the cooling (normally filled by secondary calcite). The groundmass of the dark-yellow bodies is highly porous (Fig. 4c), as the decay of these bricks has led the loss of almost both the gelling and the optically active portions of the matrix.

The beige bodies are characterised by a brown color and optically low active groundmass (Fig. 4d). Inclusions rather homogeneous in size are abundant (30-40%), mainly composed of clay pellets and carbonate grains associated with quartz and K-feldspar



%	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO
A (melt)	4.27	12.57	65.1	4.69	5.45	7.92

Fig. 5. SEM-BSE images combined with EDS spectra of the pale-yellow ceramic bodies (from the Late Antiquity areas). a: very fine-grained, dense and rather porous micromass with an early sintering degree; b: anorthite crystals (1), dark particles formed by Mg-silicate crystals (2) with melilitic reaction rims (3) and fassaite-type pyroxene crystals (4) within the melilitic composition matrix; c: Ca-rich clayey grain and shrinkage rim filled by secondary calcite; d: coarse calcite inclusion with corona-like microstructure; e: detail of the previous image, fassaite-type pyroxene crystals (4) nucleated in an aluminosilicate amorphous Fe-rich phase (A) and in a melilitic-like groundmass (B); f: CaK-zeolite formed within the coarse calcite grain. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that display a low alteration degree and almost no reaction rims. Scarce sub-rounded porous are observed and shrinkage rims were likewise formed, almost filled by secondary calcite, that is also significantly extended through the groundmass (Fig. 4d).

The higher firing temperatures for the yellow bricks is confirmed, represented by: i) loss of optical activity of the groundmass, ii) a low content of silicate inclusions, in turn with more rounded shapes and smaller in size, as they were progressively consumed to form the high-temperature phases, and iii) inclusions more altered and a higher development of reaction rims.

4.1.5. Microstructural and micro-chemical analysis

The pale-yellow bodies show a very fine grain and uniform microstructure where inclusions are dispersed in a dense micromass (Fig. 5a). Despite the high temperatures reached (between 900-950°C), an early sintering stage was achieved since the melting process was inhibited by carbonates that reacted at high temperature [39,40], yielding rather porous bodies.

The dense micromass is mainly constituted by elongated crystals -chiefly pristine plagioclase that achieved an anorthitic composition (1 in Fig. 5b) during firing [41]- embedded by a matrix with a melilitic composition, largely corresponding to a Ca-aluminosilicate vitreous phase. Quartz and K-feldspar residual inclusions show dissolution and phase transformations at grain boundaries (Fig. 5b) and shrinkage rims filled by secondary calcite. Dark aggregates composed by Mg-silicate crystals and with melilitic reaction rims (2 and 3, respectively in Fig. 5b) are noted. Within the melilitic micromass, the nucleation of bright Fe-rich crystals that may correspond to a fassaite-type pyroxene is observed (4 in boxed area in Fig. 5b). Ca-rich silicate grains with calcite rims (5 and 6 in Fig. 5c) are observed.

Coarse calcite inclusions (circa 1 mm of size) with corona-like microstructures, developed during firing, were also observed (Fig. 5d). Due to their coarse size, they may correspond to primary calcite that were partially preserved during the firing process. Compositionally “stratified” newly formed mineral phase can here be noted, with abundant fassaite-type pyroxenes crystalized from an aluminosilicate amorphous Fe-rich phase (major point analysis of Fig. 5e) in the contact with the inclusion (inner rim, A), and grown within a melilitic groundmass in the outer portion (outer rim, B, Fig. 5e). Inside these calcite inclusions, acicular and fan-shaped crystals corresponding to CaK-zeolite were identified (Fig. 5f).

The microstructure of the beige bricks showed a coarse texture with abundant inclusions -many with calcite rims- and an early sintering degree was likewise attained (Fig. 6a). Ca-plagioclase are noted in a lesser extent while Fe-rich phyllosilicate pseudomorphs are observed. Quartz and K-feldspars residual grains are rather

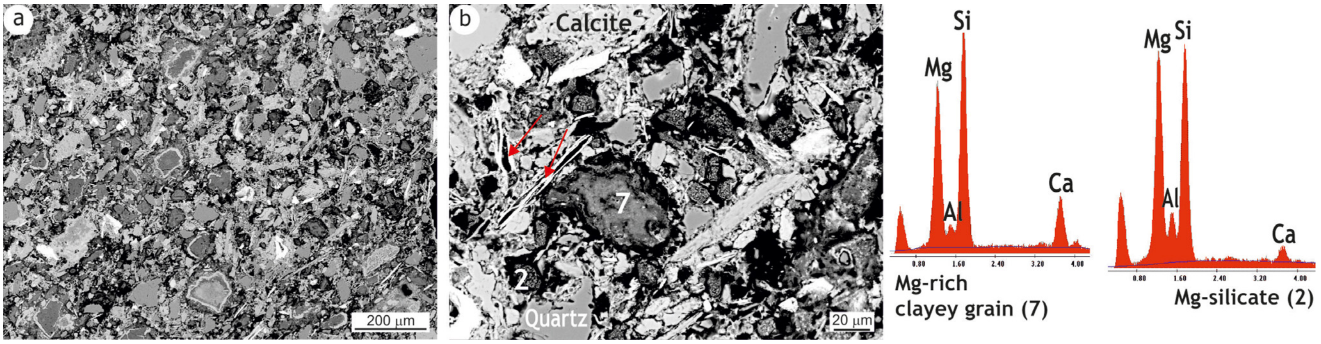


Fig. 6. Representative SEM-BSE images combined with EDS spectra of the beige bricks from the Medieval walls. a: general view of the low sintered groundmass with abundant coarse grains and scarce porosity, mainly because secondary calcite fills the shrinkage rims and extends through the micromass; b: Mg-rich clayey grains (7), smaller grains composed by Mg-silicates crystals (2) and Fe-rich phyllosilicate pseudomorphs (marked with arrows).

abundant, displaying sub-angular morphologies and scarce reaction with the evolving phases. Abundant Mg-bearing clayey grains with variable calcium content are noted and Mg-silicates crystals were only detected within the very small grains (Fig. 6b). A low porous texture is observed, partly due of the lesser carbonate content on the used base clays, but mainly because of the abundant secondary calcite that was also precipitated through the micromass (Fig. 6a), which determined the partial sealing of the porous system.

It is suggested that the high dense domains -largely with a melilitic composition- might act as a binder agent and have provided some cohesion to the constituents of the ceramic bodies. The major secondary calcite formation observed on the beige bricks might enhance the cementation of the bodies. The lime required for its formation could come from the lime binders of the brick fabrics and/or the aqueous solutions circulating in such a system. Moreover, the own production technologies might enhance the precipitation of secondary calcite, as such calcite could be formed from the carbonation of the lime produced during the firing of the calcareous clays and/or of the portlandite (derived from the large carbonate inclusion decomposition) that could be formed if the bricks were soaked in water. Due to the significant calcite rims observed, this practice -used in order to avoid lime blowing [42]- might have been applied.

4.2. Bricks manufacturing changes and reuse, preservation and decay of the bricks

For many centuries, specific areas within the alluvial deposits might have supplied the clayey materials, Mg-rich calcareous chloritic-illitic clays, to manufacture the bricks used in the city of Padova. The Roman manufacturing technologies that produced yellow bricks were probably inherited during the Late Antiquity, especially for the use of raw clays with high Ca-Mg-carbonates and the firing at temperature exceeding 900°C, yielding likewise yellow hue bricks. However, lighter and much more homogeneous textured bodies were achieved, mainly by the predominant use of carbonate-rich raw clays and higher firing temperatures. Both changes may point out a different production process, although the reuse of Roman bricks during the Late Antiquity cannot be discarded. At the Medieval Times, a lesser carbonate content on the starting raw clays and/or the decrease of the firing temperatures were progressively accomplished, yielding to beige hue bodies.

The similar mineralogical composition and petrological features of the pale and dark-yellow bricks point out that they were produced according to analogous technologies. These dark-yellow bricks seem to correspond with former bricks -Roman or produced during the Late Antiquity- that were reused on the Medieval walls, being probably lighter when they were replaced. Both may correspond to the same type of brick, being the pale-yellow bricks rather well-preserved and the dark ones very decayed.

The manufacturing technologies and the secondary phases -overall calcite, as has increased the cementation of the bodies- have been involved both in the conservation and decay of the yellow and beige bricks, playing the surrounding environment in turn an important role. In the yellow bricks, the high carbonate content of the raw clays might act as porosity enhancer during the firing process. Moreover, despite the abundance of high-temperature phases detected and the high densification of the groundmass, the early sintering and rather porous texture of these bodies have yielded bricks highly susceptible to the environmental conditions. On one hand, such porosity might foster bricks conservation in fairly constant humid environs, as facilities the entrance of humidity inside the bricks where remains uniformly distributed because of the high and uniform humid conditions of the environs. Hence, it is suggested that the retaining of humidity within the pale-yellow ceramic bodies, in a pretty equilibrium with the surrounding humid environs, has preserved the bricks. Besides, this porous texture has also enhanced the formation of zeolite hydration products within the bodies when exposed to humid conditions, as more humidity was retained within.

On the other hand, the same porous texture has enlarged the susceptibility of bricks to the granular disruption process, increasing in turn the overall porosity of the bodies and, subsequently, the darkening of the surfaces. Even though the original location of these dark-yellow and decayed bricks is unknown, neither the environmental conditions that they were originally exposed to, they were rather susceptible to the fluctuating environmental conditions existing in the outer East Medieval wall, where they were moved. This decay form has also induced the loss of the melilitic micromass formed during the firing and, conversely, its binder action. The beige bricks placed at this wall shown a good conservation state when exposed to the same environmental conditions, mainly because of the lower porosity formed during the firing and the abundant secondary calcite precipitation that has acted as a cementing agent. As zeolites were remained within the pale-yellow bricks exposed to the changing conditions of the outer East Medieval wall, their detection points out that these bricks should be previously exposed to high humid environs, so their movement (re-use) could be also confirmed.

5. Conclusions

The Roman production technologies might be largely inherited by the brick makers during the Late Antiquity and Medieval times and for many centuries rather similar clayey materials were used to produce the bricks used on the construction of the basilica. As the Late Antiquity areas are mainly shaped by pale-yellow color bricks and the Medieval walls by beige ones, the color may entail an identifier of specific construction period. In this regard, the use of beige bricks in the mausoleum -traditionally assigned as belonging to the Early-Christian basilica (5-6th centuries)-, could suggest that this construction was built later.

The lower carbonate content of the base clays and the reduction of the firing temperatures were the main technological modifications progressively accomplished. The reuse of ancient yellow bricks -from Roman times or produced during the Late Antiquity- in the Medieval walls of the basilica have been confirmed. From such reuse operations, the implication of the manufacturing process on the conservation and decay of these yellow bricks has been stated.

The high dense ceramic bodies, chiefly achieved by the formation of a melilitic composition micromass during the firing (Ca-aluminosilicate vitreous phase), and the rather porous texture of the pale-yellow bricks, largely due to the early sintering and the high carbonate content on the raw clays, have led to bricks highly susceptible to environmental conditions. Therefore, they have been rather well preserved when exposed to fairly constant humid conditions but they suffered a significant decay under insolation and changing conditions. Such porous texture has prompted the granular disaggregation of the bodies, triggered in turn due to the loss of the cohesion action provided by the melilitic groundmass.

As the use of calcite-rich clays and high humid conditions foster the formation of zeolite, its presence represents a marker of raw clays composition and environmental conditions. In the study addressed the reuse of yellow bricks has been also confirmed by the identification of such secondary hydration product.

The results achieved may be transfer to current ceramic industry to produce durable bricks especially suitable for humid environments, both for restoration and new constructions purposes. These new bricks may entail an identity mark of Padua, as they would preserved the aesthetical values of the city and would be produced from local raw clays and following the ancient techniques.

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Supplementary materials

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