Petro-archaeometric characterisation of “cotto ferrarese”: bricks and terracotta elements from historic buildings of Ferrara

GIANLUCA BIANCHINI*, ANNALISA MARTUCCI and CARMELA VACCARO

Dipartimento di Scienze della Terra - Università degli studi di Ferrara - Corso Ercole I D’Este 32, I-44100 Ferrara, Italy

ABSTRACT. — Petro-archaeometric characterisation of «cotto ferrarese», i.e., chemical-mineralogical investigation of bricks, tiles and decorative elements from historic buildings in Ferrara (NE Italy) enabled us to constrain the nature of the raw materials employed. These consist of clays closely resembling the present-day fine sediments of the river Po (High-Cr sediments); clays of plausible Apennine provenance (Low-Cr sediments), although outcropping in the area, were not used. Processing of chemical data reveals that, within the High-Cr clays, the most CaO-rich facies were preferred and mixed with minor amounts of the local sands; a Na₂O-rich flux component was then probably added.

After firing tests on these sediments, the related firing parageneses were compared to those recorded in the studied terracottas, indicating for the latter kiln temperatures between 850-1000°C, with significant variations among samples from different buildings.

RIASSUNTO. — In occasione di recenti interventi di restauro è stato possibile studiare dal punto di vista petro-archeometrico i laterizi di alcuni edifici storici del centro di Ferrara. In tale contesto, sono stati investigati mattoni ed elementi in cotto dei seguenti monumenti: Chiesa di Santa Maria in Vado (fondata nel X sec. e quasi totalmente riedificata nel XV-XVI sec.), Monastero Sant’Antonio in Polesine (XII-XVI sec.), Chiesa di Santo Stefano (fondata nel X sec. e riedificata nel XV-XVI sec.), Cattedrale di Ferrara (abside; XV-XVI sec.), Palazzo Schifanoia (Sala degli Stucchi; XV-XVI sec.).

* Corresponding author, E-mail: gbianch@liberto.it
sana state cost riscontrate temperature di cottura fra i 850-1000 °C, con significative differenze fra i laterizi appartenenti ai diversi edifici storici oggetto di studio.

**INTRODUCTION**

Geology (i.e., outcropping lithotypes) influences raw material availability, and thus building methods. In Ferrara (NE Italy), situated in the Po alluvial plain, the widespread presence of silico-elastic sediments (and the lack of any rock outcrops) led to the use of bricks («cotto ferrarese») and mortars as a dominant building technique.

As a proper evaluation of the state of conservation of historic buildings requires careful study of the building materials employed, we sampled terracottas (bricks, tiles, decorative elements) from the following monuments: the Monastery of Sant’Antonio in Polesine (built in several phases during the 12th–16th centuries); the Church of Santa Maria in Vado (founded in the 10th century, extensively modified in the 15th–16th centuries); the Church of Santo Stefano (founded in the 10th century, re-built in the 15th–16th centuries); the Cathedral of Ferrara (apse, 15th–16th centuries); Schifanoia Palace («Hall of Stuccoes», 15th–16th centuries).

Petro-archaeometric characterisation of these terracottas was carried out through petrographic observation of thin sections, XRF (X-ray fluorescence) chemical analysis, and XRD (X-ray diffraction) mineralogical investigation.

Results are discussed and compared with the chemical-mineralogical data available for the sediments of the area (Bianchini *et al.* 2000; 2002) in order to define the nature and provenance of the original raw materials.

Lastly, blunging and firing tests on local fine sediments were also carried out for a better understanding of the historic brick-making technology.

**CHEMICAL-MINERALOGICAL DATA SET**

Chemical compositions (major and trace elements) of terracottas sampled from the historic buildings of Ferrara were determined by X-ray fluorescence (XRF) using a Philips PW1400, according to the method of Franzini *et al.* (1975) and Leoni and Saitta (1975). Averaged analyses (plus the relative standard deviation) of terracotta samples from each studied building are listed in Table 1.

Major element data of the studied bricks and «cotto» decorative elements (analyses recalculated to 100% on a H₂O/CO₂-free basis), plotted on bivariate diagrams reporting SiO₂ wt% along the x-axis (Fig. 1), were compared with the composition of the local sediments. The relatively restricted CaO wt% typical of these terracottas (contrasting with the high CaO variability recorded in the local clays) suggests that the most carbonate-rich fine sediments were preferentially quarried as raw materials.

However, the Al₂O₃ content of the bricks is generally lower (and the SiO₂ content slightly higher) than that of the local clays, showing a trend towards the composition of the local sands. Coherent trends in other plots (see K₂O vs. SiO₂ diagram) suggested that these sands were used to temper the original clay body. This hypothesis was confirmed by thin section analysis, in which several samples were observed not to be homogeneous, being characterised by distinct textural domains (e.g., portions characterised by different grain-size; presence of detrital grains), thus revealing that the original raw materials were often mixed to yield a suitable composition.

The excess of Na₂O recorded in the studied materials (compared with the local clay composition) cannot be totally ascribed to the introduction of sand in the starting body clay, but may have been induced by introduction of soluble salts crystallised from Na-bearing aqueous solutions. However, the recurrent occurrence of this Na₂O excess appears to be unrelated to the spatial distribution of the bricks, some of which are located indoors and
TABLE 1

Major (wt%) and trace element (ppm) compositions (average analysis and standard deviation) of terracotta samples from historic buildings in Ferrara. * = semiquantitative analyses; n.a. = not analysed; n = number of available analyses; σ = standard deviation.

Analyses of local clays (samples 14 and 16) and sands (sample F8C4) also reported for comparison.

<table>
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<th></th>
<th>StAPol n=10 σ</th>
<th>SMV n=8 σ</th>
<th>S.Stef n=7 σ</th>
<th>Schifa n=11 σ</th>
<th>Cathedral n=21 σ</th>
<th>Sediments from the Ferrara surroundings</th>
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<td>Al₂O₃</td>
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<td>15.19 1.32</td>
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<td>5.97 0.50</td>
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<td>18.4 20.7</td>
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<td>n.a.</td>
<td>65.8 14.0</td>
<td>52.9 14.6</td>
<td>n.a. n.a.</td>
</tr>
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</table>

Labels: StAPol = bricks and terracotta elements from the Monastery of Sant’Antonio in Polesine; SMV = bricks and terracotta elements from the Church of Santa Maria in Vado; S.Stef = bricks and terracotta elements from the Church of Santo Stefano; Schifa = bricks and terracotta elements from Schifanoia Palace; Cathedral = bricks and terracotta elements from the Cathedral of Ferrara.
Fig. 1 – Binary diagrams of $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{K}_2\text{O}$, $\text{Na}_2\text{O}$ vs. $\text{SiO}_2$

Low-Cr clay = clays characterised by “Apennine” affinity; High-Cr clays = clays closely comparable to the present-day fine sediments of river Po; StAPol = bricks and terracotta elements from the Monastery of Sant’Antonio in Polesine; SMV= bricks and terracotta elements from the Church of Santa Maria in Vado; S.Stef = bricks and terracotta elements from the Church of Santo Stefano; Schifa = bricks and terracotta elements from Schifanoia Palace; Cathedral = bricks and terracotta elements from the Cathedral of Ferrara.
high above floor level (i.e., in positions not easily reachable by atmospheric and/or ground fluids). In this light, discarding any significant role played by the «secondary» introduction of soluble salts (not detected by XRD investigation), we suspect the addition of an «exotic» Na-rich component as a flux during the brick-making phase. For this purpose, excluding feldspar-rich lithologies (too rich in \( \text{Al}_2\text{O}_3 \)), and salts such as \( \text{Na}_2\text{CO}_3 \) (not available in the area, too expensive), it is speculated that vegetable ash rich in this element (probably obtained by burning seaweed; Chapman and Chapman, 1980; Stiaffini, 1999), or sea salt \( (\text{NaCl}) \) was employed.

To highlight in greater detail the nature of the fine sediments employed, the Ni vs. Cr diagram (Fig. 2) shows that the local clays may be grouped into two distinct populations, respectively characterised by high \( (\text{Cr}>180 \text{ ppm}; \text{Ni}>100 \text{ ppm}) \) and low \( (\text{Cr}<180 \text{ ppm}; \text{Ni}<100 \text{ ppm}) \) contents (hereafter, High-Cr and Low-Cr groups). Bianchini et al. (2000; 2002) report that Low-Cr sediments contain a higher proportion of clay minerals, in which smectite + mixed layers are more abundant than chlorite \( (\text{Sm+ML/Chl} > 1) \); instead, High-Cr sediments are coarser and contain fewer clay minerals, with chlorite \( (\text{Mg-rich chlorite in this group of samples}) \) predominating over smectite + mixed layers \( (\text{Sm+ML/Chl} < 1) \).

Most of the examined Middle-Age/Renaissance terracottas were prepared starting from High-Cr sediments with a chemical affinity with the present-day Po sediments, whereas Low-Cr compositions (recorded only in two terracottas) show analogies with the sediments of rivers flowing from the Bolognese Apennines. This fact probably means that Low-Cr clays were not available in the Ferrara surroundings at that time. Consequently, it is plausible to assume that Low-Cr clays were introduced into the area only after large-scale hydraulic works \( (14^{th}-16^{th} \text{ centuries}; \text{Bondesan, 1990}) \) in which some Apennine rivers \( (\text{e.g., the Reno}) \) were diverted into the southern branches of the Po river \( (\text{flowing south of Ferrara at that time}) \).

![Fig. 2 - Binary diagram reporting Ni (ppm) vs. Cr. Symbols and labels as in Fig. 1.](image-url)
Fig. 3 shows trace element analyses normalised to the NASC composition (reference composition for terrigenous sediments; Rollinson 1993), and reveals a good agreement between the trace element patterns of the terracotta samples and those of the High-Cr clays of local origin.

The mineralogical composition of the studied terracottas was investigated by powder diffractometric analysis (XRD) carried out on a Philips PW1860/00 diffractometer with graphite-filtered Cu-Kα radiation (λ =1.54 Å). Diffraction patterns were collected in the 2θ angular range 5-50°, with 5 sec/step (0.02° 2θ). Two main mineral parageneses are envisaged:

a) carbonate-bearing mineral assemblages (calcite ± dolomite), characterised by ubiquitous quartz, illite/muscovite, iron oxides, alkaline feldspar, plagioclase; amphibole, melilite and wollastonite may also be present (but are not ubiquitous); these mineral associations were identified in samples from the Monastery of Sant’Antonio in Polesine and the Church of Santa Maria in Vado;

b) diopside-bearing (carbonate-free) mineral assemblages, always characterised by quartz, alkaline feldspar, plagioclase, iron oxides, melilite and wollastonite; illite/muscovite is not ubiquitous and amphibole is rare; these mineral associations are typical in samples from the Church of Santo Stefano.

Both the above mineral parageneses occur in samples from the Cathedral of Ferrara; mineral analyses are not yet available for the samples from Schifanoia Palace.

Minerals of «secondary» genesis are: secondary calcite (filling pores and small fractures) due to the interaction with capillary water; gypsum probably induced by the aggressive urban atmosphere (SO₂-rich); weddellite (CaC₂O₄·2H₂O, probably due to metabolic activity of organisms on substances contained in the overlying paint layers); and...
brushite (CaHPO$_4$·2H$_2$O, perhaps resulting from bird excrement).

**Evaluation of Suitability for the Ceramic Manufacture: Shaping and Firing Tests**

Atterberg limits measured on the local clays indicate remarkable plasticity and low shrinkage (65<liquid limit<79; 31<plastic limit<37; 16<shrinkage limit<21; 33<plasticity index<44). Considering the high plasticity, these sediments do not appear suitable for manual moulding and shaping with traditional techniques (Marsigli and Dondi, 1997), confirming the need for temper correction (i.e., addition of small amount of local sands) to the starting body clay, as already hypothesised from the chemical data.

Clay samples 14 and 16 (see Table 1) were admixed with distilled water, worked until complete homogenisation, and used to shape small bricks (2 x 1 x 0.5 cm). Firing tests were carried out in an electric muffle furnace with an increasing thermal regime of 60 °C/hour, stabilising the temperature at 750, 800, 850, 900, 950, 1000 °C for 4 hours. After cooling to room temperature (in a dryer), different samples fired at the various temperatures were powdered and analysed by XRD, to evaluate the mineralogical evolution during the firing process.

This approach, integrated with similar studies available in the recent literature (Capel et al., 1985; Brindley and Lemaitre 1987; Duminuco et al., 1996, 1998; Riccardi et al., 1999; Artioli et al., 2000; Cultrone et al. 2000) and compared with the mineralogical parageneses recorded in the studied terracottas, indicate that:

- illite is the only clay-mineral originally present within the fine-fraction of the local sediments (together with kaolinite, chlorite, smectite, mixed-layers) which persists at the investigated temperatures, being stable up to 950 °C;
- iron oxides appear to be newly formed minerals, stable throughout the tested thermal range;
- dissociation of calcite occurs around 800 °C; dolomite was never detected in our fired samples, probably because this phase dissociates at lower temperature (from 700 °C, according to Cultrone et al., 2000);
- crystallisation of melilite and wollastonite appears from 800 °C upwards, in agreement with the above-mentioned experimental studies; modal amounts of these minerals are significantly higher in sample 16 (with higher CaO content);
- amphibole (often observed in the local sediments) is recorded in some bricks of the studied monuments and in the firing tests of sample 16; its presence is generally antithetical with that of clinopyroxene, suggesting that its stability field is restricted towards higher temperatures;
- clinopyroxene (diopside) is recorded only in high-temperature samples (> 900-950 °C), probably due to progressive destabilisation of other CaO-bearing phases such as melilite and amphibole;
- plagioclase predominates over alkaline feldspar in the same thermal conditions of clinopyroxene formation (>950 °C), probably due to progressive destabilisation of both melilite and illite;
- loss of crystallinity at increasing firing temperature was evaluated from the steadily increasing background intensity of the XRD diffraction patterns.

These results are summarised in Fig. 4, which highlights that the terracottas from Sant’Antonio in Polessine and Santa Maria in Vado were fired at temperatures close to 850 °C, whereas those of Santo Stefano were fired at significantly higher temperatures (up to 1000 °C). Instead, samples from the Cathedral of Ferrara show a wide range of firing temperatures, probably indicating heterogeneous thermal conditions (different furnace kilns?) during their preparation.

For more reliable information, further starting compositions should be investigated in firing tests with monitored redox conditions. Moreover, considering the possible correction of the original clay bodies with sand (added to
Fig. 4 – Thermal constraints provided by firing tests (integrated with available literature data): stability fields of mineral phases recognised within the terracotta parageneses. Firing temperatures estimated in bricks of different historic buildings are reported, to identify the relative technological processes. See text for further details.
limit shrinkage) and/or with small amounts of a Na-rich flux (which may displace firing reactions towards lower temperatures), it would be interesting to simulate the effect of adding temper (and/or flux).

**CONCLUSION**

The presented data attest that the terracottas of the historic buildings of Ferrara were prepared with the CaO-richest clays occurring around Ferrara at that time (High-Cr clays). As shown in Fig. 5, these predominant materials were often corrected by adding local sands. Instead, the further addition of a Na-rich flux is suggested by the Na$_2$O excess (relative to the local sediment composition) of the studied materials.

Compositions are reported in the Fe$_2$O$_3$tot-(Na$_2$O+K$_2$O)-(CaO+MgO) ternary diagram (Fig. 6a), proposed by Fiori _et al._ (1989) to classify ceramic raw materials, and plot on the Cottoforte and Maiolica compositional fields. Further characterisation of these materials is provided by the (CaO+MgO)-Al$_2$O$_3$-SiO$_2$ diagram (Fig. 6b), which shows the composition of phases usually observed in bricks, as well as the tie-lines dividing the relative stability fields (Artioli _et al._, 2000); our samples and the local clay composition mainly plot in the subtriangle Si-Wo(Di)-An, indicating that quartz - wollastonite (diopside) - plagioclase is the predicted stable paragenesis for terracottas of similar bulk composition. In this light, the presence of carbonates and/or melilite (recorded in several Ferrara bricks and «cotto» elements) indicates that equilibrium...
Fig. 6 - a) Ferrara historical terracottas and local clay compositions plotted in $\text{Fe}_2\text{O}_3-(\text{Na}_2\text{O}+\text{K}_2\text{O})-(\text{CaO}+\text{MgO})$ diagram reporting geochemical characterisation for ceramic raw materials (Fiori *et al.*, 1989); b) Ferrara historical terracottas and local clay compositions plotted in $(\text{CaO}+\text{MgO})-\text{Al}_2\text{O}_3-\text{SiO}_2$ diagram reporting composition of phases usually observed in firing tests (with relative tie-lines; Artioli *et al.*, 2000).
conditions were not attained. This is ascribed to the lack of homogeneity of the original starting material, which consists of several micro-domains of different composition, and indicates limited mobility of the chemical species during firing (Duminuco et al., 1996, 1998; Riccardi et al., 1999).

For this reason, a detailed investigation of the reactions occurring during firing processes (and thus a better calibration of the estimated firing temperatures) would require integration of the reported «bulk» data with in-situ analyses.

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