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

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**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 Na<sub>2</sub>O-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.).

La realizzazione di una banca-dati contenente analisi chimiche (XRF) ed analisi diffrattometriche (XRD) è risultata utile per interpretare i relativi processi produttivi nonché la natura dei materiali impiegati. I dati composizionali dei manufatti oggetto di studio, confrontati con i dati geochimico-mineralogici dei sedimenti affioranti nell'areale ferrarese, hanno confermato una provenienza locale delle materie prime, suggerendo un uso esclusivo di sedimenti argillosi legati ad eventi alluvionali del fiume Po (tipologia: High-Cr); fra questi si è riscontrato l'utilizzo preferenziale delle facies particolarmente ricche in CaO. L'uso di sedimenti ad affinità appenninica (tipologia: Low-Cr), benché affioranti nell'areale ferrarese, non è stata invece riscontrata in detti laterizi. Sistematiche differenze nelle concentrazioni di alcuni elementi maggiori (es.: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O, K<sub>2</sub>O) fra i laterizi investigati e le materie prime argillose, non imputabili a deidratazione/decarbonatazione durante la cottura, sono plausibilmente dovute a correzioni dell'originario impasto argilloso con sabbia quarzosa-feldspatica di provenienza locale, come indicato dai «trends» chimici e dai caratteri tessiturali-strutturali osservabili nell'analisi petrografica. In alcuni campioni è stato inoltre osservato un anomalo contenuto in sodio che non può essere spiegato con l'aggiunta di un degrassante di natura quarzosa-feldspatica, ma potrebbe essere imputabile all'uso di un fondente ricco in sodio. Campioni rappresentativi delle argille locali sono stati sottoposti a prove di cottura a temperature di 750, 800, 850, 900, 950, 1000 °C per verificare l'evoluzione della paragenesi mineralogica al variare delle condizioni termiche, e per interpretare poi le condizioni di cottura dei menzionati laterizi storici;

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sono state così 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-clastic 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 12<sup>th</sup>-16<sup>th</sup> centuries); the Church of Santa Maria in Vado (founded in the 10<sup>th</sup> century, extensively modified in the 15<sup>th</sup>-16<sup>th</sup> centuries); the Church of Santo Stefano (founded in the 10<sup>th</sup> century, re-built in the 15<sup>th</sup>-16<sup>th</sup> centuries); the Cathedral of Ferrara (apse, 15<sup>th</sup>-16<sup>th</sup> centuries); Schifanoia Palace («Hall of Stuccoes», 15<sup>th</sup>-16<sup>th</sup> 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 H<sub>2</sub>O/CO<sub>2</sub>-free basis), plotted on bivariate diagrams reporting SiO<sub>2</sub> 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 Al<sub>2</sub>O<sub>3</sub> content of the bricks is generally lower (and the SiO<sub>2</sub> 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 K<sub>2</sub>O vs. SiO<sub>2</sub> 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 Na<sub>2</sub>O 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 Na<sub>2</sub>O 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;  $\sigma$  = standard deviation. Analyses of local clays (samples 14 and 16) and sands (sample F8C4) also reported for comparison.

	StAPol		SMV		S.Stef		Schifa		Cathedral		Sediments from the Ferrara surroundings		
	n=10	$\sigma$	n=8	$\sigma$	n=7	$\sigma$	n=11	$\sigma$	n=21	$\sigma$	Clays		Sand
											14 Low-Cr	16 High-Cr	F8C4
SiO <sub>2</sub>	52.93	1.70	52.85	2.44	53.99	3.06	54.30	1.77	54.34	3.44	47.20	45.57	62.05
TiO <sub>2</sub>	0.69	0.04	0.68	0.04	0.68	0.04	0.73	0.04	0.65	0.04	0.68	0.67	0.41
Al <sub>2</sub> O <sub>3</sub>	14.67	0.65	15.19	1.32	14.63	0.79	15.02	0.48	13.66	0.85	15.90	14.94	9.96
Fe <sub>2</sub> O <sub>3</sub>	5.93	0.46	5.98	0.50	5.97	0.50	6.36	0.37	5.50	0.34	6.76	6.09	3.34
MnO	0.12	0.02	0.11	0.02	0.11	0.01	0.13	0.01	0.11	0.01	0.14	0.12	0.08
MgO	4.71	0.52	4.79	0.57	4.60	0.56	4.69	0.65	4.11	0.63	2.99	4.32	3.31
CaO	11.11	1.73	10.11	1.68	10.30	1.25	11.36	0.65	10.26	1.64	9.72	11.04	9.03
Na <sub>2</sub> O	1.64	0.36	0.95	0.13	0.83	0.21	1.35	0.20	1.39	0.25	0.48	0.53	1.79
K <sub>2</sub> O	2.39	0.34	2.41	0.30	2.28	0.17	2.36	0.14	2.35	0.22	2.58	2.22	1.91
P <sub>2</sub> O <sub>5</sub>	0.19	0.02	0.28	0.07	0.38	0.08	0.21	0.03	0.25	0.04	0.28	0.33	0.12
LOI	5.63	2.22	6.65	3.24	6.22	3.78	3.49	2.08	7.38	3.68	13.27	14.16	8.00
Pb*	28.5	13.8	30.8	4.68	43.7	10.4	65.8	39.4	42.0	27.5	19.4	19.6	16.4
Zn*	94.1	8.77	108	11.4	101	13.1	92.5	8.06	133	62.9	106	102	54.2
Ni	146	24.6	154	21.0	146	13.6	155	24.6	142	17.3	89	145	80.9
Co	19.7	2.02	21.0	2.96	19.9	1.77	21.2	2.08	17.4	4.02	18.4	20.7	10.5
Cr	206	41.3	228	30.6	254	31.4	224	38.7	201	25.3	122	210	124
V	109	13.9	114	15.2	101	11.3	109	8.36	102	10.9	144	124	55.1
Th	11.6	1.68	11.0	2.52	n.a.		9.93	2.83	9.87	2.48	17.8	15.4	7.83
Nb	14.4	1.31	14.8	3.55	n.a.		11.6	2.20	n.a.		14.8	15.4	n.a.
Zr	182	20.2	144	27.0	n.a.		122	27.6	184	20.0	126	131	109.3
Rb	121	11.0	127	15.9	n.a.		131	9.19	118	11.4	134	128	81.5
Sr	339	84.3	281	27.0	n.a.		293	39.3	318	45.9	272	301	233
Ba	411	34.3	437	48.6	n.a.		425	22.7	406	44.5	583	1017	293
Y	31.0	1.36	25.6	1.96	n.a.		26.7	3.43	28.9	3.09	20.3	22.3	16.4
La*	29.9	4.40	28.8	12.9	n.a.		28.9	2.92	29.5	12.2	n.a.	n.a.	19.7
Ce*	63.1	5.92	59.9	8.44	n.a.		65.8	14.0	52.9	14.6	n.a.	n.a.	40.1

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.

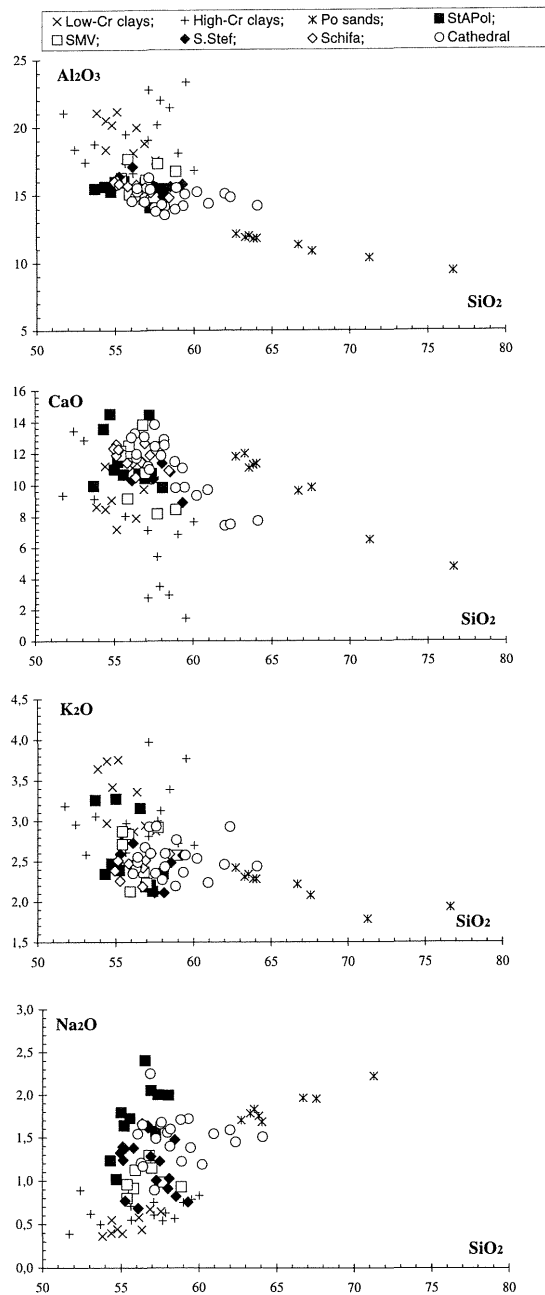


Fig. 1 – Binary diagrams of Al<sub>2</sub>O<sub>3</sub>, CaO, K<sub>2</sub>O, Na<sub>2</sub>O vs. SiO<sub>2</sub>.  
 Low-Cr clay = clays characterised by “Apennine” affinity; High-Cr clays = clays closely comparable to the present-day fine sediments of river Po; StAPol = bricks and terracotta elements 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 ( $\text{Cr} > 180$  ppm;  $\text{Ni} > 100$  ppm) and low ( $\text{Cr} < 180$  ppm;  $\text{Ni} < 100$  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 ( $\text{Sm} + \text{ML} / \text{Chl} > 1$ ); instead, High-Cr sediments are coarser and contain fewer clay minerals, with chlorite (Mg-rich chlorite in this group of samples) predominating over smectite + mixed layers ( $\text{Sm} + \text{ML} / \text{Chl} < 1$ ).

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<sup>th</sup>-16<sup>th</sup> centuries; Bondesan, 1990) in which some Apennine rivers (e.g., the Reno) were diverted into the southern branches of the Po river (flowing south of Ferrara at that time).

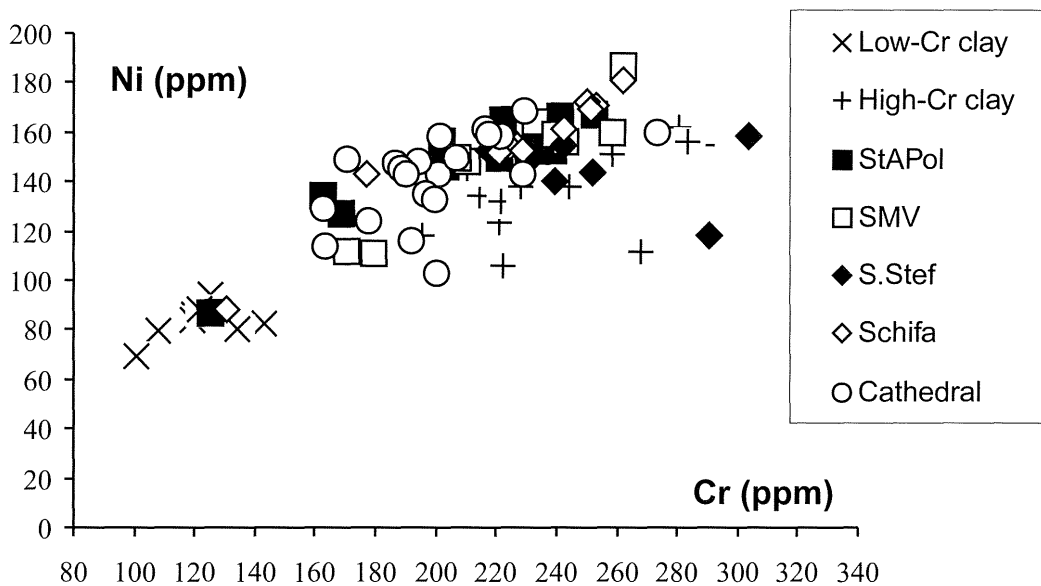


Fig. 2 – Binary diagram reporting Ni (ppm) vs. Cr. Symbols and labels as in Fig. 1.

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-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Diffraction patterns were collected in the  $2\theta$  angular range  $5\text{-}50^\circ$ , with  $5 \text{ sec/step}$  ( $0.02^\circ 2\theta$ ). Two main mineral parageneses are envisaged:

a) carbonate-bearing mineral assemblages (calcite  $\pm$  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 ( $\text{SO}_2$ -rich); weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , probably due to metabolic activity of organisms on substances contained in the overlying paint layers); and

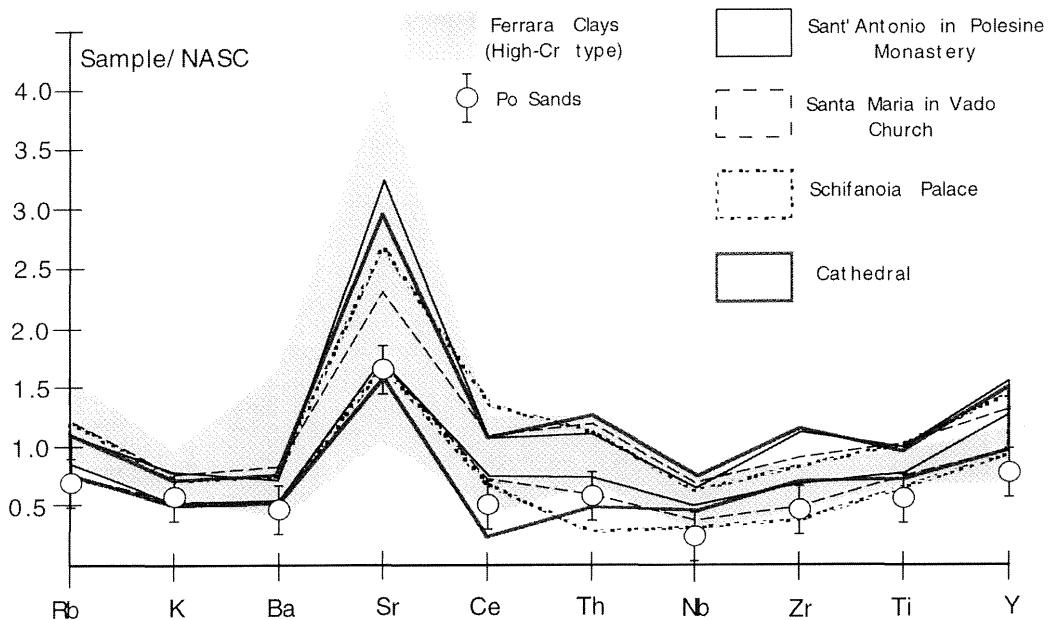


Fig. 3 – Trace element distribution in historical terracotta samples. Concentrations normalised to NASC coefficients (assumed as average composition for terrigenous sediments; Rollinson, 1993). Compositional field of High-Cr clays and averaged analysis of local sands also reported for comparison.

brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , 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 ( $65 < \text{liquid limit} < 79$ ;  $31 < \text{plastic limit} < 37$ ;  $16 < \text{shrinkage limit} < 21$ ;  $33 < \text{plasticity index} < 44$ ). 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 ( $2 \times 1 \times 0.5$  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 back ground intensity of the XRD diffraction patterns.

These results are summarised in Fig. 4, which highlights that the terracottas from Sant'Antonio in Polesine 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

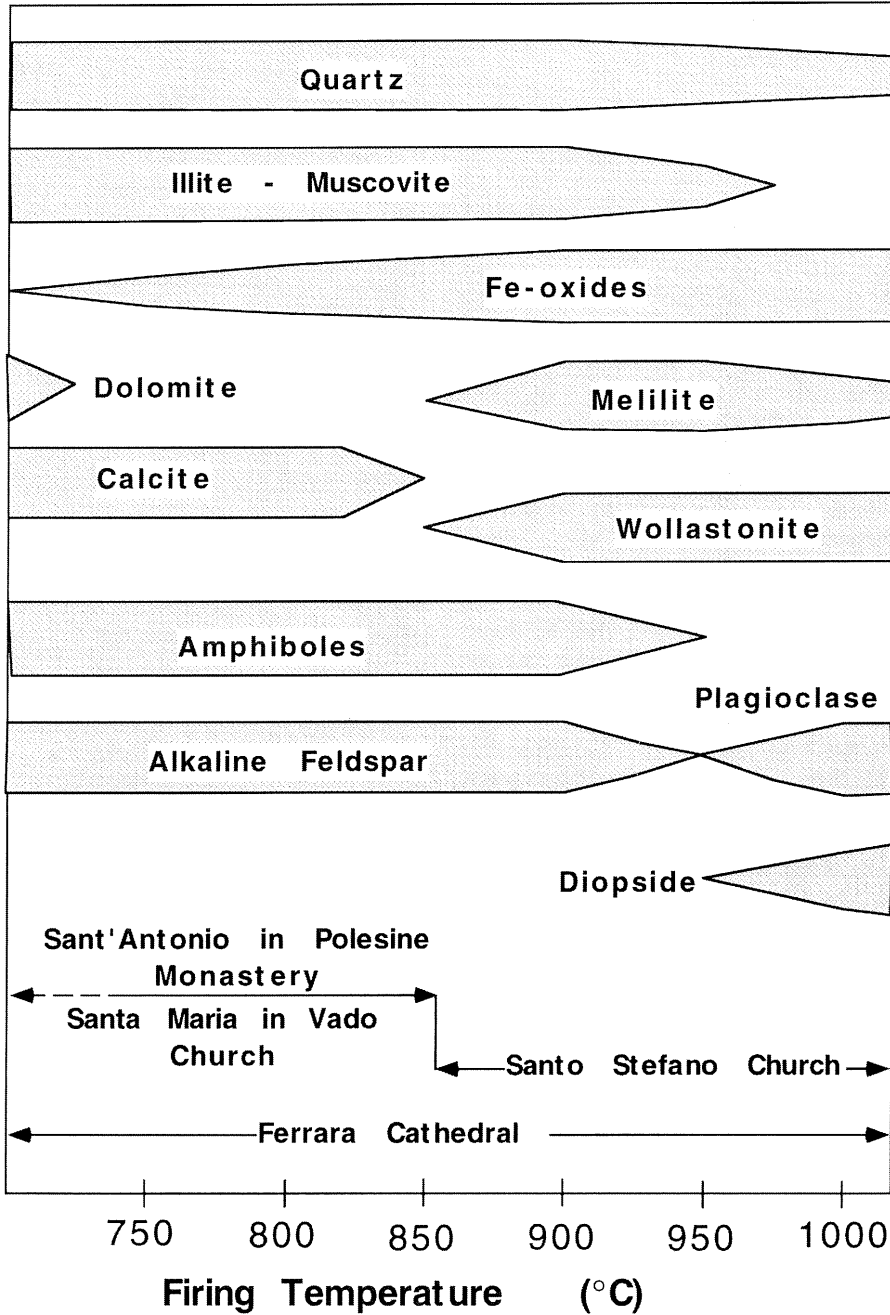


Fig. 4 – Thermal constraints provided by firing tests (integrated with available literature data): stability fields of mineral phases recognised within the terracotta parageneses. Firing temperatures estimated in bricks of different historic buildings are reported, to identify the relative technological 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  $\text{Na}_2\text{O}$  excess (relative to the local sediment composition) of the studied materials.

Compositions are reported in the  $\text{Fe}_2\text{O}_3$ -tot-( $\text{Na}_2\text{O}+\text{K}_2\text{O}$ )-(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)- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  diagram (Fig. 6b), which shows the composition of phases usually observed in bricks, as well as the tie-lines dividing the relative stability fields (Artoli *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

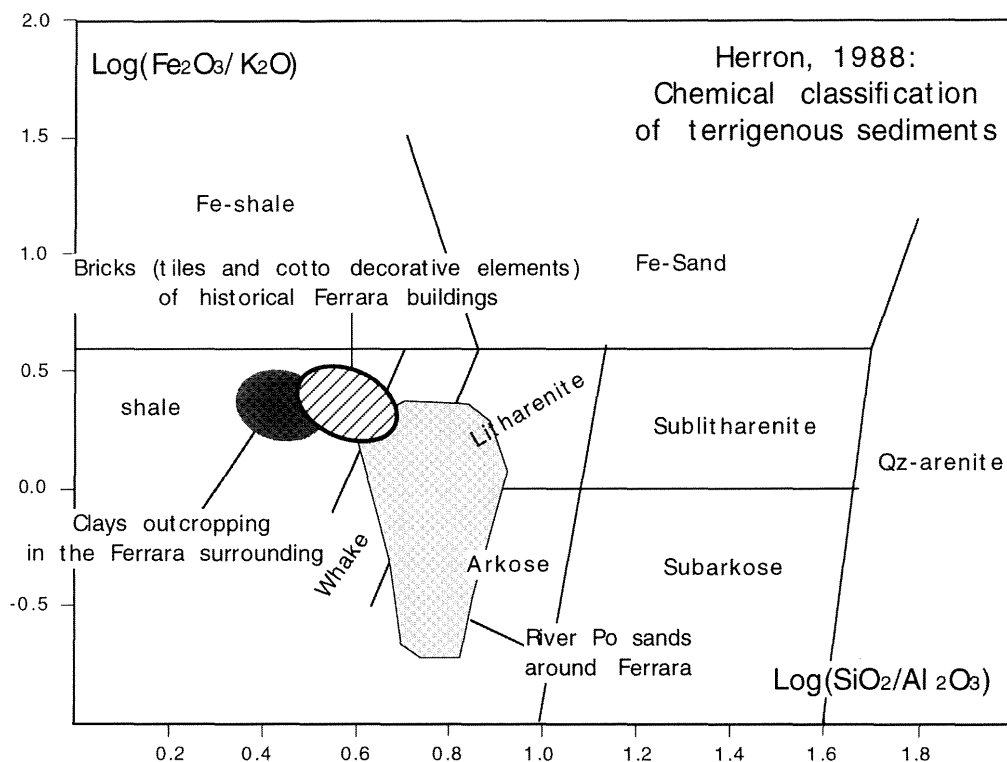


Fig. 5 – Bricks and local clay composition plotted in  $\text{Log}(\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$  vs.  $\text{Log}(\text{SiO}_2/\text{Al}_2\text{O}_3)$  diagram reporting compositional fields for various terrigenous sediments (Herron, 1988).

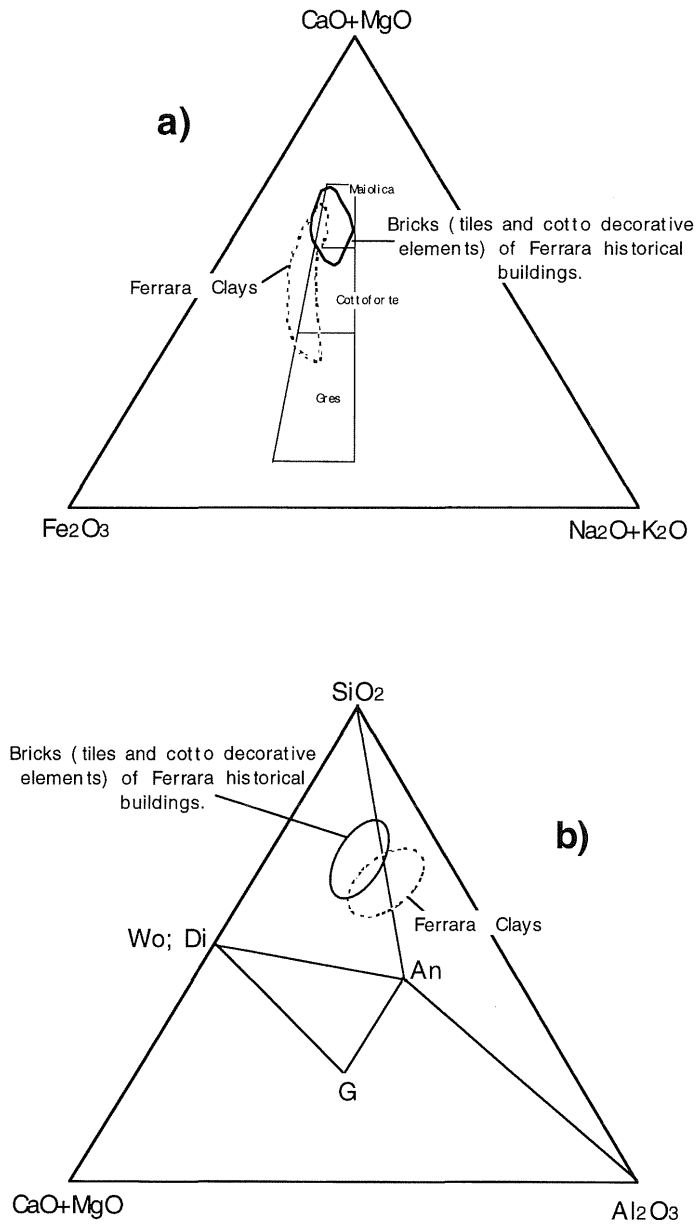


Fig. 6 – a) Ferrara historical terracottas and local clay compositions plotted in  $\text{Fe}_2\text{O}_3$ - $(\text{Na}_2\text{O}+\text{K}_2\text{O})$ - $(\text{CaO}+\text{MgO})$  diagram reporting geochemical characterisation for ceramic raw materials (Fiori *et al.*, 1989); b) Ferrara historical terracottas 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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#### REFERENCES

- ARTIOLI G., BAGNASCO GIANNI G., BRUNI S., CARIATI F., FERMO P., MORIN S. and RUSSO U. (2000) — *Studio spettroscopico della tecnologia di cottura di ceramiche etrusche dagli scavi di Tarquinia*. In Atti del I Congresso di Archeometria (Patron Editore- Bologna), 335-349.
- BIANCHINI G., LAVIANO R., LOVO S. and VACCARO C. (2000) — *Clay sediments in the area surrounding Ferrara (Italy): a contribution for the environmental monitoring*. Plinius (Italian supplement of the Eur. J. Mineral.), 24, 38-39.
- BIANCHINI G., LAVIANO R., LOVO S. and VACCARO C. (2002) — *Chemical-Mineralogical characterisation of clay sediments around Ferrara (Italy) a tool for an environmental analysis*. Forthcoming publication.
- BONDESAN M. (1990) — *Evoluzione geomorfologica ed idrografica della pianura ferrarese*. In G. Corbo Ed., «Terre ed acqua-Le bonifiche ferraresi nel delta del Po», 13-20.
- BRINDLEY G. and LEMAITRE J. (1987) — *Thermal, oxidation and reduction reactions of clay minerals*. Mineral. Soc. Monograph. 6, A.C.D., Newman ed.
- CAPEL J., HUERTAS F. and LINARES J., (1985) — *High temperatures reactions and use of Bronze Age pottery from La Mancha, Central Spain*. Miner. Petr. Acta, 29-A, 563-575.
- CHAPMAN V.J. and CHAPMAN D.S. (1980) — *Seaweeds and their uses*. Chapman and Hall.
- CULTRONE G., SEBASTIAN-PARDO E., CAZALLA O., RODRIGUEZ-NAVARRO C. and DE LA TORRE M.J. 2000 — *Mineralogical changes during brick production in laboratory experiments*. In Quarry-Laboratory-Monument International congress, Pavia 2000 (proceeding volume n.1), 253-258.
- DUMINUCO P., RICCARDI M.P., MESSIGA B. and SETTI M. (1996) — *Modificazioni tessiturali e mineralogiche come indicatori della dinamica del processo di cottura dei manufatti ceramici*. Ceramurgia, XXXVI, 281-288.
- DUMINUCO P., MESSIGA B. and RICCARDI M.P. (1998) — *Firing processes of natural clays. Some microtextures and related phase compositions*. Thermochemica acta, 321, 185-190.
- FIORI C., FABBRI B. and RAVAGLIOLI A. (1989) — *Materie prime ceramiche vol. I*. Biblioteca Tecnica Ceramica, Faenza ed.
- FRANZINI M., LEONI L. and SAITTA M. (1975) — *Revisione di una metodologia analitica per fluorescenza-X basata sulla correzione completa degli effetti di matrice*. Rend Soc. It. Min. Petrol., 31, 365-378.
- HERRON M.M. (1988) — *Geochemical classification of terrigenous sands and shales from core or log data*. J. Sed. Petrol., 58, 820-829.
- LEONI L. and SAITTA M. (1975) — *X-ray fluorescence analysis of 29 trace elements in rocks and mineral standards*. Rend Soc. It. Min. Petrol., 32, 497-510.
- MARSIGLI M. and DONDI M. (1997) — *Plasticità delle argille italiane per laterizi e previsione del loro comportamento in forgatura*. L'industria dei laterizi, 46, 214-222.
- RICCARDI M.P., MESSIGA B. and DUMINUCO P. (1999) — *An approach to the dynamics of clay firing*. Applied Clay Science, 15, 393-409.
- ROLLINSON H. (1993) — *Using geochemical data: evaluation, presentation, interpretation*. Longman Publishers Ltd.
- STIAFFINI D. (1999) — *Il vetro nel Medioevo*. Fratelli Palombi Eds.

