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Communication

Chemical and mineralogical characterisation of historic mortars in Ferrara (northeast Italy)

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Abstract

Chemical and mineralogical analyses were carried out on historical mortars from Ferrara to characterise the nature of the related raw materials. Results indicate (a) the binder homogeneity ($CaCO_3$) confirming the widespread use of lime and (b) the remarkable heterogeneity of the silicoclastic skeleton, attesting heterogeneity of the fluvial sands available in the area. These data enable us to assign the distinct sand composition to the different rivers flowing in the Ferrara area. This investigation offers fresh insight into the historic building activity and related techniques and should provide knowledge useful for restoration and conservation processes.

Keywords: Mortar; Characterisation; Petrography

1. Introduction

Sedimentary geologists use mineralogical and chemical data to relate fluvial sand composition to the source mother rocks, thus establishing the related provenance. A similar approach can also be employed as an archaeometric tool in the investigation of ancient mortars. In this contribution, chemical and mineralogical data on mortars from Middle Age/Renaissance buildings of Ferrara (in the Po River plain, northeast Italy; Fig. 1) provide constraints on the raw materials employed.

Results are compared with the available information on the alluvial sediments of the area to constrain as far as possible the location of the quarry areas, to highlight the building techniques employed, and to provide guidelines for the utilization of new materials in the foreseen restoration processes.

In particular, the studied materials are interbrick mortars from the following buildings: 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 and extensively modified in the 15th–16th centuries), the Cathedral of Ferrara (apse, 15th–16th centuries), Palazzo Schifanoia ("Hall of Stuccoes," 15th–16th centuries), and Palazzo Canani (16th century), where bricks, tiles, and terracotta have already been investigated [1].

2. Chemical and mineralogical characterisation

Chemical composition (both major and trace elements) of mortars from the mentioned historic buildings of Ferrara was determined by X-ray fluorescence (XRF) using a Philips PW1400 spectrometer. Major element data (analyses recalculated to 100% on H_2O/CO_2-free basis) are plotted on variation diagrams reporting SiO_2 wt.% along the *x*-axis (Fig. 2) and show a wide compositional range with diverging chemical trends. This suggests the involvement of various amounts of distinct endmembers: the binder(s) and the different types of aggregates. Even within a single building, these chemical differences cannot be explained as the result of a different binder/inert ratio, thus implying a significant heterogeneity of the employed aggregates (i.e., sands). For example, in the samples from Sant'Antonio in Polesine, we recognised three groups of mortars: StA1, StA2, and StA3. StA1 and StA2 can be assumed to have been prepared with similar sands and merely reflect a different amount of cement. StA3 mortars, on the other hand, appear relatively depleted (for comparable SiO_2 and CaO contents) in Al_2O_3 and Fe_2O_3,

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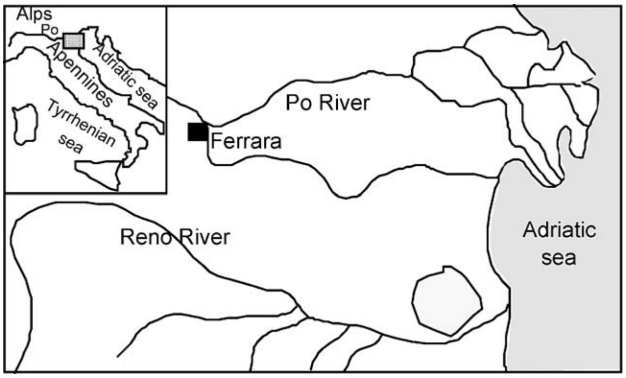

Fig. 1. The location of Ferrara.

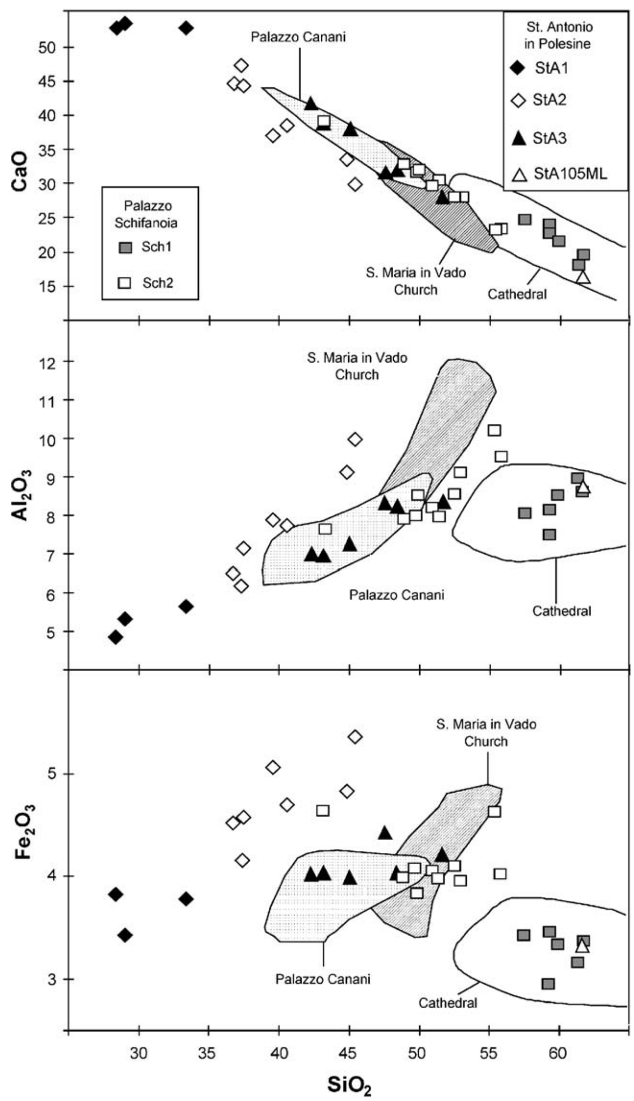

Fig. 2. Major element composition (wt.%) of mortars from historic buildings of Ferrara. Samples from the Monastery of Sant'Antonio in Polesine have been classified in three different groups (StA1, StA2, and StA3) plus the anomalous sample StA 105 ML. Samples from Palazzo Schifanoia have been divided in two groups (Sch1 and Sch2). Samples from Palazzo Canani, the Church of Santa Maria in Vado, and the Cathedral are reported as compositional fields.

suggesting a different mineralogical composition of the original sands. A further sample from Sant'Antonio in Polesine (StA 105 ML) is totally different, being extremely enriched in SiO_2 and depleted in both Al_2O_3 and Fe_2O_3, and represents a recent filling mortar.

Samples from Palazzo Schifanoia display two distinct populations: Sch1 and Sch2 were clearly prepared with two distinct batches of sand. Sch2 shows compositional analogies with the above-described StA3 samples, while Sch1 is prepared from SiO_2-rich (Al_2O_3-Fe_2O_3 poor) sands comparable with that employed in StA 105 ML.

Samples from Palazzo Canani and Santa Maria in Vado are roughly similar to the StA3 and Sch2 populations, whereas samples from the Cathedral are comparable with the SiO_2-rich (Al_2O_3-Fe_2O_3 poor) mortars Sch1 and StA 105 ML.

Optical observation of thin sections at the transmitted light microscope and available XRD results performed on tout-venant mortars (powdered without any preliminary preparation) confirm that samples StA 105 ML and Sch2 are enriched in quartz and depleted in femic minerals

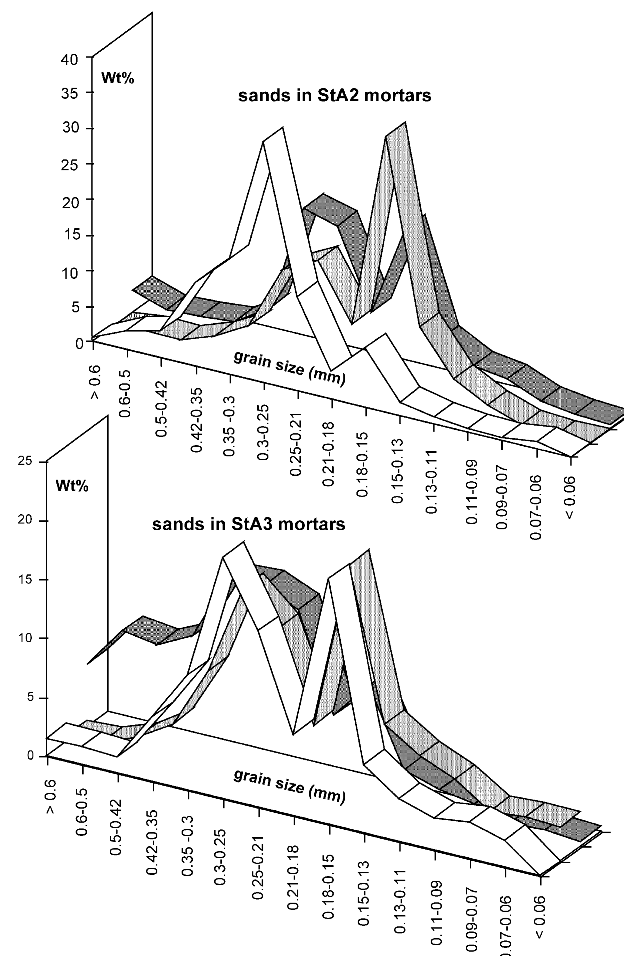

Fig. 3. Grain size distribution of sands employed in StA2 and StA3 mortars from Sant'Antonio in Polesine.

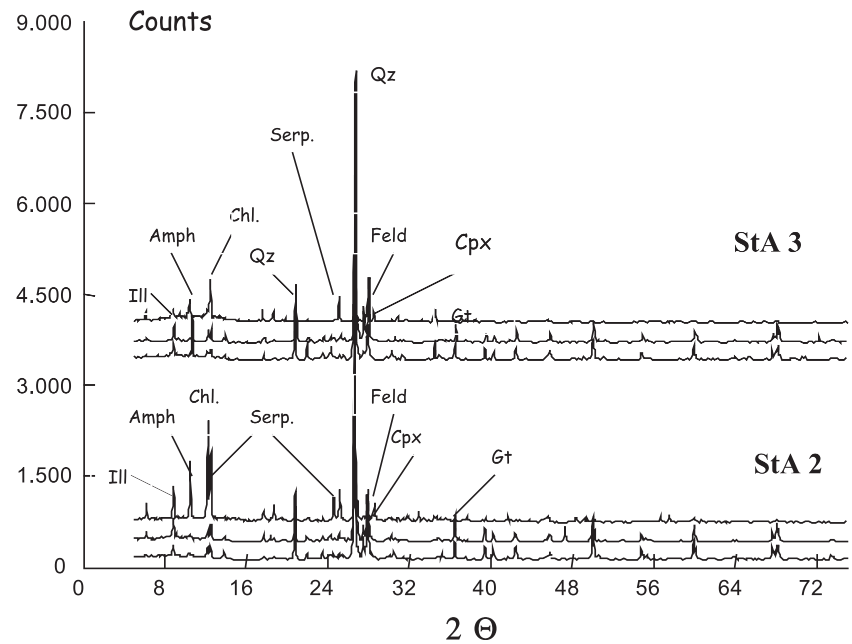

Fig. 4. XRD diffractometric analyses for the silicate-skeleton (obtained by HCl leaching) of StA2 and StA3 mortars from Sant'Antonio in Polesine. Analyses have been carried out by a Philips PW1860/00 diffractometer with graphite-filtered CuK_α radiation ($\lambda = 1.54$ Å). The diffraction patterns were collected in the 2θ angular range 5–50° with 5 s/step (0.02° 2θ). Mineral abbreviations: Qz, quartz; Cpx, clinopyroxene; Amph, maphibole (tremolite); Ill, illite/muscovite; Chl., chlorite; Serp., serpentine; Feld, feldspar; Gt, garnet.

compared with sample groups StA2, StA3, and Sch2. As concerns the binding component, XRD indicates that carbonate is ubiquitous and preponderant, indicating the typical employment of lime. Traces of gypsum, found only in few samples, could derive from the plasters originally covering the considered wall portions or else could represent secondary mineralisation induced by the current SO_2-rich (polluted) atmosphere. Diffractometric discrimination of accessory heavy minerals (key indicators of sand provenance) is hampered by the dilution effect of the main components (typically quartz and calcite). For this reason, to appreciate the difference between populations StA2 and StA3, mortars were leached with HCl to disgregate the samples, thus eliminating the binding effect of the carbonate. This treatment "concentrates" the silicoclastic skeleton, preserving grain size of the original sand, relative percentage of mafic and sialic minerals, quartz/feldspar ratio, and nature of the occurring femic minerals. Subsequent grain sieving indi-

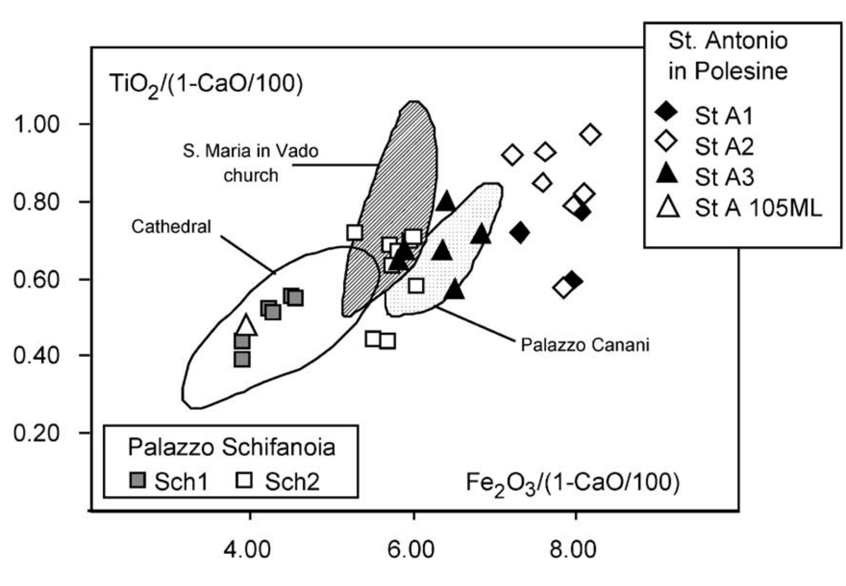

Fig. 5. TiO_2 vs. Fe_2O_3 diagram in which mortar compositions (expressed as wt.%) have been normalised to the parameter 1 − CaO/100. This allows a better comparison of the silicoclastic portion of the employed sands.

cates that the recorded difference cannot be ascribed to significant variation in the grain size, as both StA2 and StA3 sands show similar bimodal distribution in the 0.595–0.06 mm dimensional range (Fig. 3). Weight analyses of magnetically separated fractions indicate that the amount of femic minerals is 14–19% and 18–24% in sands StA3 and StA2, respectively. XRD results on the separated mineral fractions (Fig. 4) indicate that amphibole (mainly tremolite), chlorite (mainly chlinoclore), and traces of serpentine, clinopyroxene, and garnet are ubiquitous in both groups, while muscovite is typically recorded only in StA2 samples. Traces of orthopyroxene and olivine have also been sporadically detected in some StA2 samples.

Traces of melilite and wollastonite, usually present in terracotta mineral assemblages [1,2], have also been recorded in a few samples, indicating that crushed bricks (locally named "cocciopesto") were sporadically used as a further skeleton component during mortar preparation.

3. Origin of the employed sands

A direct comparison of chemical analyses (as reported in Fig. 2) could be misleading, considering that each mortar was prepared mixing different proportions of slaked lime and inert. To overcome this problem when investigating the nature of the sands employed, analyses were normalised to the parameter 1 – CaO/100. Accordingly, recalculated analyses plotted in the TiO_2 vs. Fe_2O_3 diagram of Fig. 5 confirm that the sands from mortars StA1 and StA2 in Sant'Antonio in Polesine were particularly rich in femic components (and thus in femic minerals). Mortars classified as StA3 (Sant'Antonio in Polesine) and Sch2 (Palazzo Schifanoia) as well as those from Santa Maria in Vado and Palazzo Canani were prepared with a relatively homogeneous type of sand, slightly less femic than the previous one. On the other hand, Schifanoia mortars classified as Sch1, those from the Cathedral, and sample StA 105 ML from Sant'Antonio in Polesine are significantly depleted in femic components.

These differences can be related to the two distinct sources of sediments available in the surroundings of Ferrara, represented by the alluvial sediments of the Po River and those of the Reno River that flows down from the Bolognese Apennine [2,3]. It has been envisaged that Po sediments are typically enriched in femic components compared with the Reno sediments. This is understandable considering that mafic and ultramafic rocks are widespread within the Po drainage basin, whereas they do not outcrop within the hydrogeological basin of the Reno River (characterised by silicoclastic terrigenous formation).

Sands employed in StA1 and StA2 mortars are clearly related to the Po River. Despite the lower content in femic minerals and the paucity of mica in mortars StA3 and Sch2 besides those from Palazzo Canani and Santa Maria in Vado, the typical heavy mineral assemblage (including

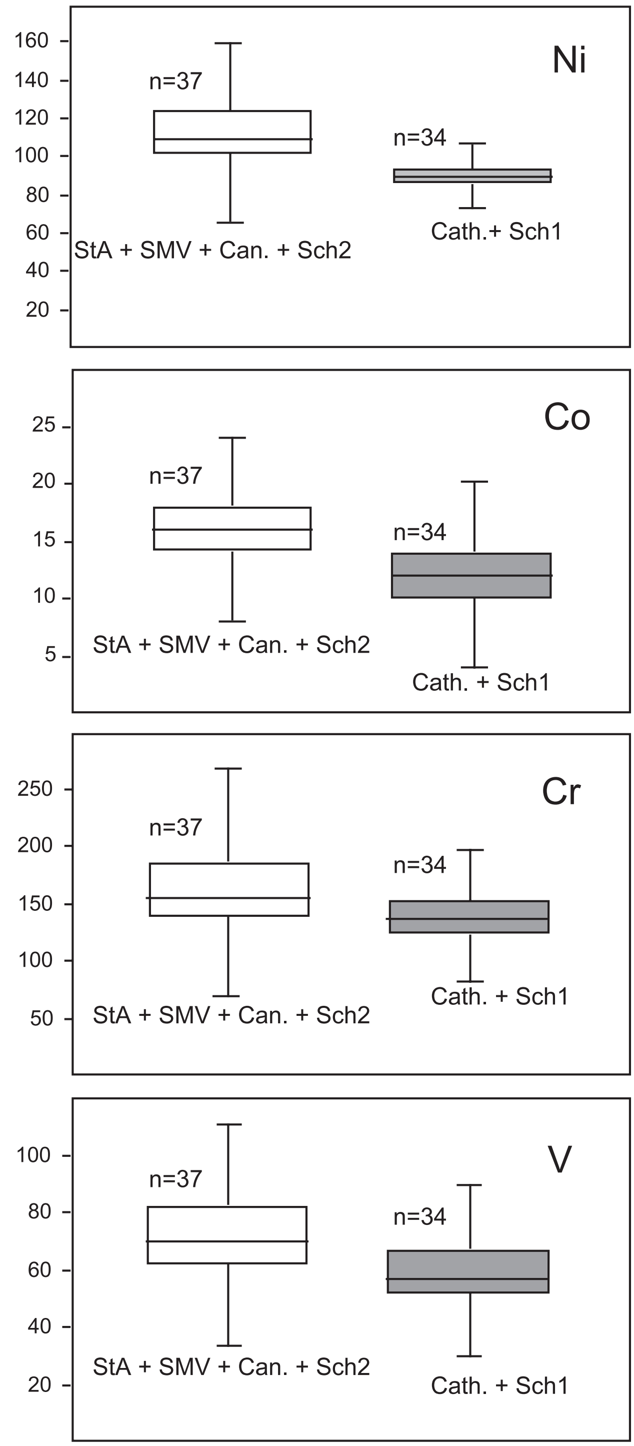

Fig. 6. Ni, Co, Cr, and V concentrations (expressed as ppm) of the studied mortars, normalised to the parameter 1 – CaO/100, are plotted as box plots. Two different populations of sands characterised by relatively high and low content of transition element can be envisaged. High Ni-Co-Cr-V sands are assumed to be Po River sediments, while low Ni-Co-Cr-V sands represent the sedimentary input of the Reno River. StA, Sant'Antonio in Polesine; Cath., Cathedral; SMV, Santa Maria in Vado; Can., Palazzo Canani; Sch1 and Sch2, Palazzo Schifanoia.

abundant amphibole; see Ref. [4]) also attests a connection with the Po sediments. In this case, significant chemical differences of Po sediments suggest that fluvial-dynamic processes [5] had a role in differentiating the sand mineralogical composition in adjacent sectors of the same riverbed. As concerns the working techniques, manual refinement of the sands by sieving is ruled out by the observed grain size curves, while sand pretreatment by flotation processes cannot be excluded (and could explain some of the observed mineralogical differences).

On the other hand, a completely different chemical and mineralogical fingerprint (Apenninic affinity) characterises sands employed in Sch1 and those from the Cathedral (as well as sample StA 105 ML from Sant'Antonio in Polesine). This interpretation is supported by the transition element distribution reported in Fig. 6, where two distinct populations can be clearly envisaged.

4. Conclusion

Different sands were used as aggregates in the mortars from several historic buildings of Ferrara. Some of them are clearly related to the Po alluvial sediments, while others display an Apennine affinity and should be linked to the Reno River. This indicates the historic availability of raw materials in different epochs. For Sant'Antonio in Polesine (the oldest building), we envisage only geomaterials from the Po River. Reno-type sediments are recorded only in younger masonry. This is coherent with the morphological evolution of the area: two different branches of the Po River surrounded Ferrara in the Middle Ages; Reno-type sediments were available only after the important hydraulic modification (15th–16th centuries) that diverted the Reno waters into the vanishing southern branch of the Po River [6].

As concerns the binder, XRD results confirm the sole presence of $CaCO_3$. Coherently, historic chronicles indicate that limestone was mainly quarried within the Berici hills (around 100 km northward), burnt and prepared as quicklime, and then transformed into slaked lime.

We emphasise that, as also highlighted by other authors [7,8], similar contributions should be taken into account during restoration activities to select the most appropriate materials. Moreover, we stress that similar chemical and mineralogical investigations could also be applied to present-day building materials to relate technical characteristics to compositional features.

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