

The Provenance of Sand in Mortars from Roman Villas in NE Italy: a Chemical-Mineralogical Approach

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Abstract: The chemical- mineralogical composition of the sand fractions of mortars found in Roman villas dating from the 1st century A.C. located in Northern Italy has been investigated by optical microscopy, scanning electron microscopy plus energy dispersive spectroscopy microanalysis and x-ray diffractometry. The petrographic results on the mortar samples have been compared with mineralogical data available on recent fluvial sediments in rivers located near the archaeological sites investigated. The aim of this study was to assess the feasibility of this simple analytical approach as a useful tool in assisting in the determination of the provenance of the raw material used in Roman Age in the making of mortar for building construction purposes. Preliminary results indicate that a good correlation can be established between the mineralogical composition of the sand grains imbedded in the ancient mortars and the fluvial sand clasts present in rivers in areas nearby. This is particularly true when the river sands are characterized by distinct mineralogical markers.

Keywords: Roman villas, mortar, sand provenance, mineralogical analysis.

INTRODUCTION

Sediment provenance studies in sandstone rocks have been extensively used by earth scientists as a tool in tectonic and palaeogeographic reconstructions [1-5]. The petrography and mineralogy of the clastic fraction of sandstones of different ages and of modern beach sands have been studied in detail in order to determine the presence or absence of mineralogical markers that can be used to trace the primary sources of the original sediments and to define petrographical provinces: to that purpose, the sand mineralogical composition, the clay mineral assemblages and the heavy mineral suites together with their relative abundances have been shown to be extremely valuable tools [6-8]. In this preliminary study we have applied such petrographical analytical approach to the field of archaeometry in order to assess its value in tracing the geological sources of raw materials (in this case mortars) used in Roman Age in the construction of “domus” in the Xth regio (NE Italy). The results have been compared with detailed mineralogical data available on the petrography of fluvial sandy sedimentary deposits from rivers in the vicinity of the sites investigated [9-11], given the assumption that the mineralogical composition of the present river deposits are likely not to have changed in the geologically speaking very short period of time (approx. 2000 years) since Roman times. Moreover, it is well known that when the source rocks whose erosion provides the detritus for the fluvial drainage basins, are located in high-relief, temperate-

cold mountain settings where chemical weathering is negligible and sediment transport is rapid and short, (as it is the case in the Southern Alps setting), the river sand composition can be held as representative of the mineralogy of the parent rocks [11]. It should therefore be possible to establish also a “geological” correlation between the sand mineralogical composition in the mortar samples and the local geology of the area under study.

Chemical, isotopic and mineralogical analytical techniques have been often used to obtain compositional data on archaeological artefacts of different nature such as ceramics [12], stone [13], glass [14] and bronze [15]; chemical analyses of ancient mortars and plasters have also been performed in the past as part of the routine analysis of archaeological materials such as Roman and medieval wall paintings [16-22]: in some of these studies, mineralogical data on the inert sand-sized fraction of the mortars have been provided but very little research has been carried out to correlate the petrography of the sand-sized aggregates to that of the historical fluvial sources of the same clasts. A detailed chemical and mineralogical characterization of historic mortar components should prove extremely useful in the correct choice of materials for the restoration of Roman masonry and in assisting the archaeologists in the reconstruction of ancient building practices [17].

MATERIALS AND TECHNIQUES

Samples of mortars have been collected from painted wall paintings of Roman Age from villas in the following locations in NE Italy (Fig. 1): Verona (*via Rensi, via S.Cosimo*), Padova (*via S. Martino e Solferino*), Concordia

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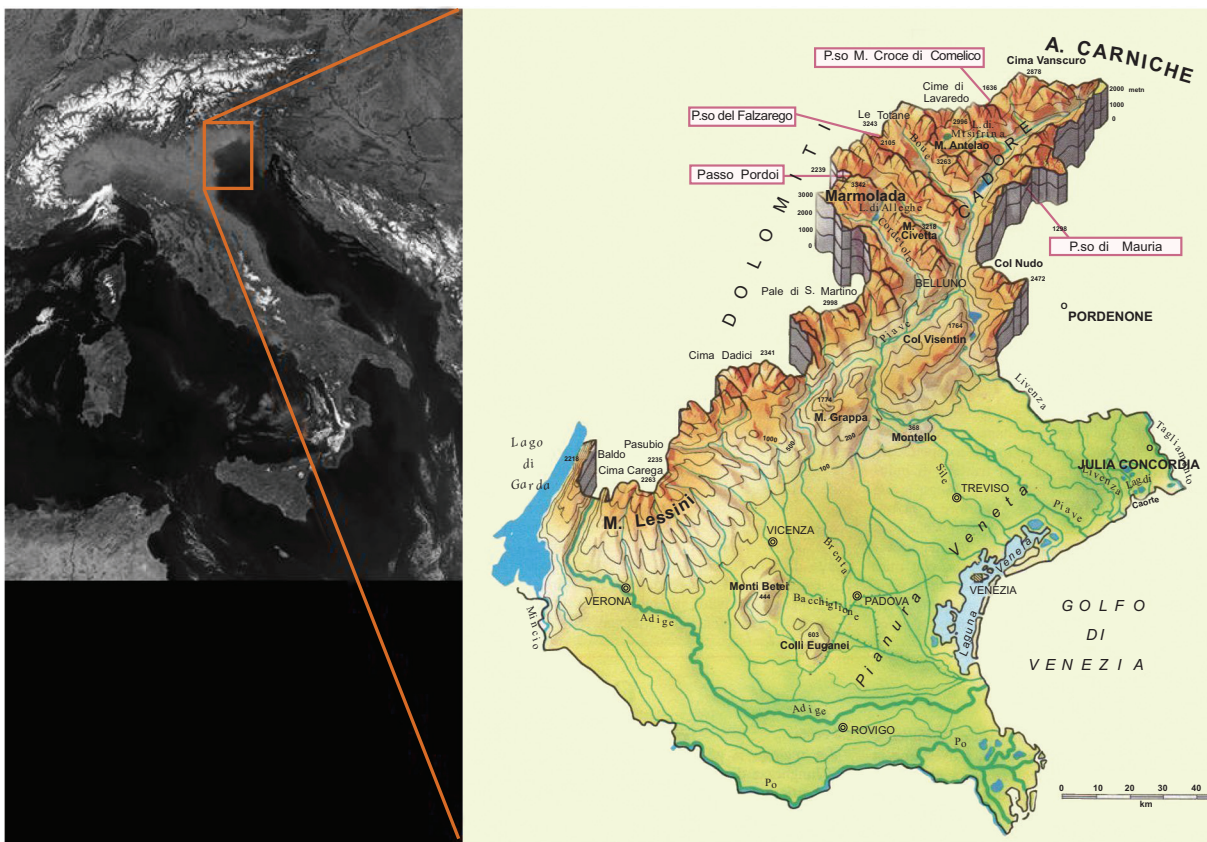


Fig. (1). Location map with sampling sites and possible sand supply rivers sources.

Sagittaria (the ancient *Thermae of Julia Concordia*) and Pordenone (Torre di Pordenone). The clastic sand fraction has been separated from the carbonate matrix by ultrasonic wet sieving. In order to concentrate the non carbonate fraction (which includes the heavy mineral content), selected samples of loose sand have been treated with cold 1M HCl solution to remove the carbonate matrix: this treatment removes also the carbonate (calcitic and dolomitic) clasts present as components of the sandy fraction and so these samples have not been considered in the calculation of mineralogical percentages. The mineralogy of sand-sized clasts has been investigated by Optical Microscopy (OM) using a Wild Leitz M8 Binocular Microscope (the samples were illuminated with a movable fibre glass system). Resin impregnated thin-sections of selected mortar samples were examined by Polarising OM using a Zeiss Microscope. Sand-sized clasts were also examined by Low-Vacuum Scanning Electron Microscopy (LVSEM) + Energy Dispersive Spectroscopy x-ray microanalysis (EDS) using a JEOL 5600 LVSEM interfaced with an Oxford Instruments 6587 x-ray detector. In low-vacuum SEM mode, samples do not display charging effects and therefore no Au or C pre-coating of samples was necessary. The presence of a C peak in some EDS analyses is due to residual mortar contamination. Mineralogical characterization of sand samples was performed on bulk as well as on 1M HCl-treated samples by x-ray Powder Diffractometry (XRD) using a Philips X'Pert vertical goniometer with Bragg Brentano geometry. XRD operating conditions: CuK α Ni-filtered radiation, graphite monochromator, 2 θ range (5-60 $^\circ$), step-scan mode (0.05 $^\circ$ step size) and 2 s by point.

RESULTS

Verona

Mortar samples from Verona display an aggregate/ligand ratio = 2.8. The sand clasts from the Verona samples appear sub- to well-rounded and are well to very well sorted ($\sigma = 0.1-0.5$). They are coarse- to very coarse-grained with an average diameter of 1.5-2 mm, some of which occasionally may reach gravel dimensions up to 5 mm (Fig. 2). One sample (*via S. Cosimo*) display lower grain size values in the medium to coarse sand range (average diameter 0.5-1mm).

Mineralogically, the sand clasts can be grouped into three main classes in the following proportions:

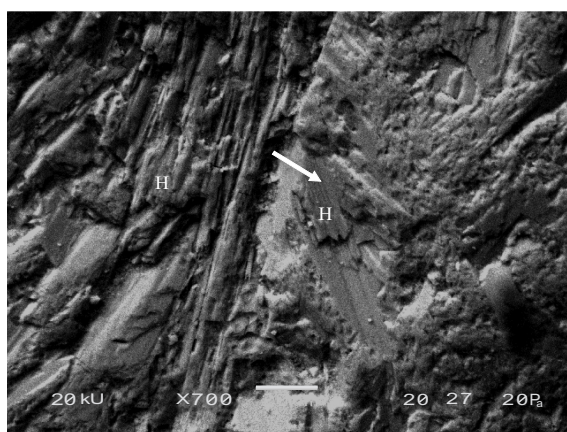
- 1) Carbonates (calcite + dolomite) 50-55%
- 2) Silicates (monocrystalline quartz + reddish-pink K-feldspar (Fig. 2), biotite, muscovite, clinopyroxene [augite] 20-25%.
- 3) Lithic fragments (LF). These include igneous LF both volcanic (porphyritic rhyolites, rhyodacites, andesites, basalts with degassing porosity) and plutonic (granites, tonalites), metamorphic LF (phyllites, micaschists, gneiss and green serpentinites) and sedimentary (micritic limestone, minor chert). 15-25%

In one sample (*via S. Cosimo*) quartz grains are more abundant and may reach 20% of the total clast population.

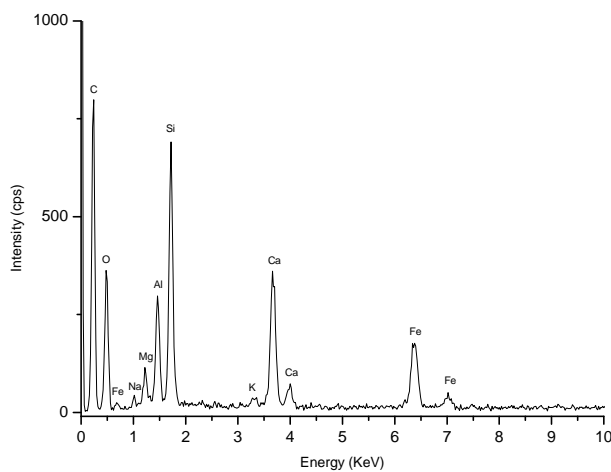
SEM + EDS analysis confirms the widespread presence of mineral grains of feldspars and other silicates such as



Fig. (2). Verona (Binocular OM image). Sand grains of reddish Feldspars (F), Quartz (Q), Calcite (C) and volcanic lithic fragments (LF).



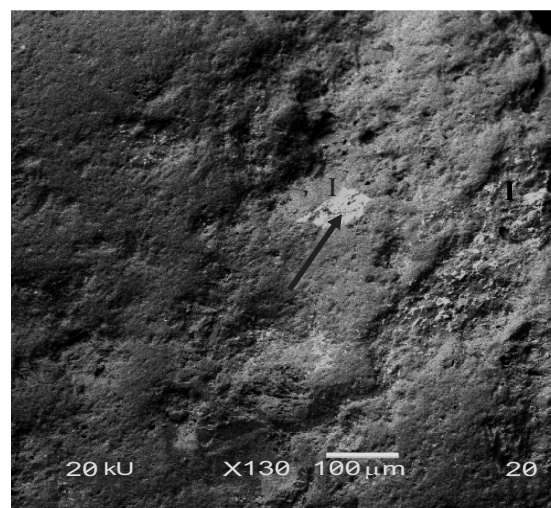
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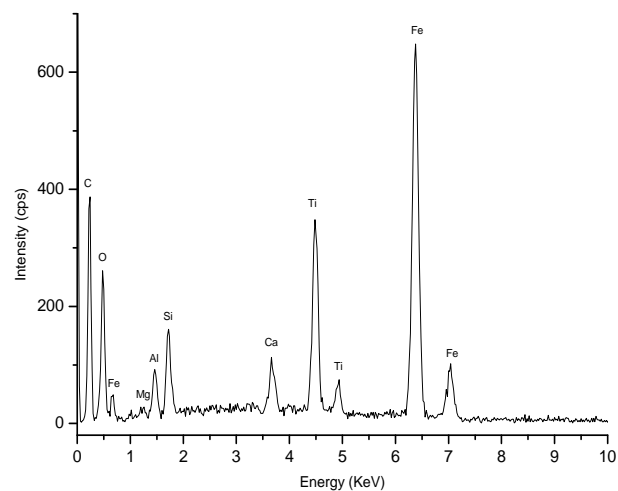
b

Fig. (3). **a**) Igneous LF sand grain with fibrous Hornblende (H). **b**) EDS spectrum (arrow in [a]).

platy biotite and fibrous hornblende (Fig. 3), besides grains of calcite and dolomite. Metamorphic LF often contains gar-



a



b

Fig. (4). Verona (BSEM image). **a**) Igneous LF sand grain with Ilmenite crystals (I) and **b**) EDS spectrum arrow in [a].

net (almandine) as an accessory mineral. Chert grains with typical conchoidal fracture can be found but are not common. A relevant feature (see discussion below) is the presence of igneous LF with Ti-rich crystalline oxides (ilmenite and rutile: (Fig. 4)).

XRD analysis shows peaks that can be ascribed to calcite, dolomite, albite, orthoclase and quartz. Qualitative estimates based on relative peak intensities confirm that dolomite is more abundant than calcite. The spectra of the HCl treated samples reveal the presence of chlorite and muscovite as minor components (Fig. 5).

Padova

Mortar samples from Padova display an aggregate/ligand ratio = 2.7. Sand clasts from Padova samples display average roundness values in the sub roundness class: the quartz fraction display lower roundness values (in the subangular to angular class). The sand appears very well sorted ($\sigma=0.35$). The grain size is in the coarse sand range with an average clast diameter of approximately 1 mm (Fig. 6).

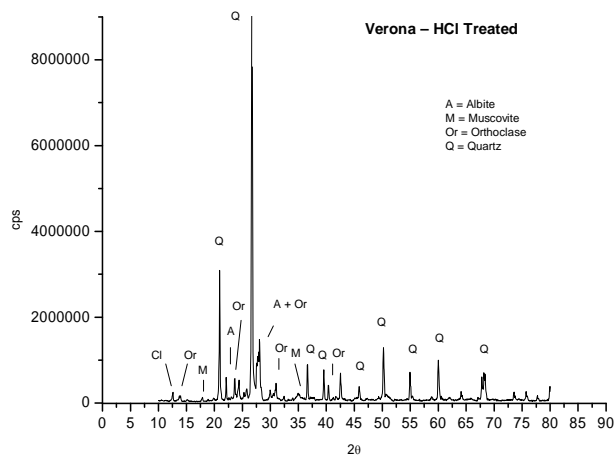


Fig. (5). XRD spectrum of HCl treated Verona sample. Beside peaks that can be ascribed to Albite, Orthoclase and Quartz, minor peaks of Chlorite (C) and Muscovite (M) can be detected: the latter ones were not visible in bulk samples analyses due to overlapping calcite and dolomite peaks.

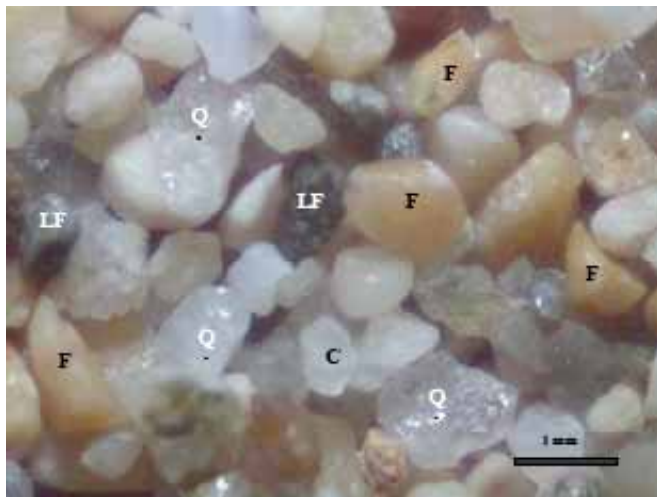


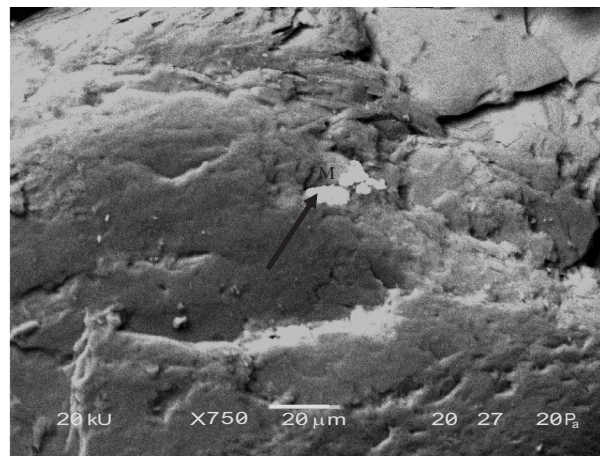
Fig. (6). Padova (Binocular OM image). Sand grains of reddish Feldspars (F), Quartz (Q), Calcite (C) and volcanic lithic fragments (LF).

Mineralogically, sand clasts can be grouped into the same main classes as in the Verona samples with the following relative percentages :

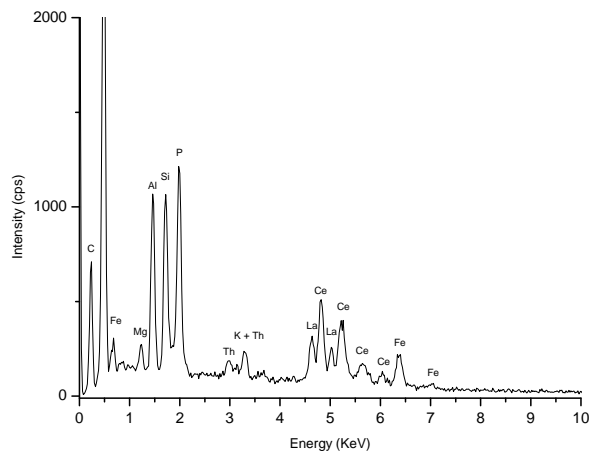
- 1) Carbonates (calcite, both in flat rhombohedra or in red microcrystalline masses + pink coloured dolomite) 50-55%.
- 2) Silicates (quartz, vitreous, translucent, colourless with conchoidal fracture + pink-reddish K-feldspar + plagioclase + clinopyroxene [augite] + platy brownish biotite, silver-grey muscovite and green chlorite 15-20%.
- 3) Lithic fragments (LF). These include igneous LF from volcanic (rhyolite-trachyte-andesite-basalt) and plutonic rocks (pink granite), metamorphic LF (micaschist, greenschist and serpentinites) and sedimentary LF (micritic limestone, minor chert).

Metamorphics LF are less abundant compared to Verona samples. 20-25%

Besides calcite and dolomite clasts, SEM + EDS analysis confirms the widespread presence of mineral grains of quartz and feldspars. To note the common presence of volcanic igneous RF with Ti-rich accessory minerals (rutile, and its polymorphs anatase and brookite, and ilmenite) associated with epidote. In granitic LF, massive monazite has been found as an accessory mineral (Fig. 7).



a



b

Fig. (7). Padova (BSEM Image). **a**) Igneous LF sand grain with Monazite crystals (M) and **b**) EDS (arrow).

XRD analysis shows peaks that can be ascribed to calcite, dolomite, albite, orthoclase and quartz. Again, qualitative estimates based on relative peak intensities suggest that dolomite is more abundant than calcite. In the spectra of the HCl treated samples, peaks ascribed to chlorite and muscovite and epidote have been identified (Fig. 8). Although the evidence is not conclusive due to peak overlaps, three minor peaks at 25.2°, 25.6° and 30.66° 2θ that can be tentatively attributed to the mineral brookite have also been identified.

Concordia Sagittaria (Julia Concordia)

Mortar samples from the Thermae of Julia Concordia display an aggregate/ligand ratio = 2.48. Sand clasts are very

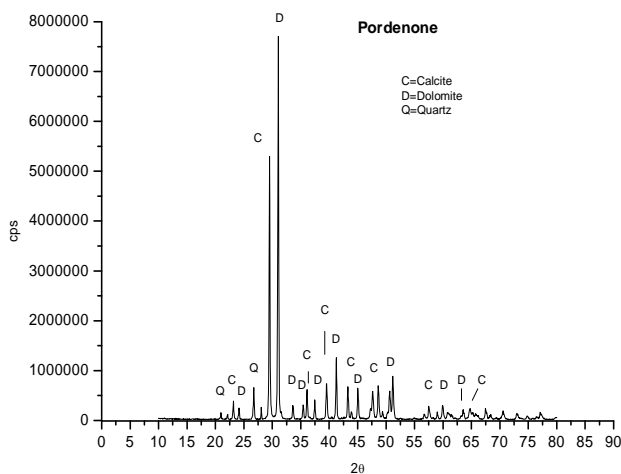


Fig. (11). XRD of Pordenone bulk sample.

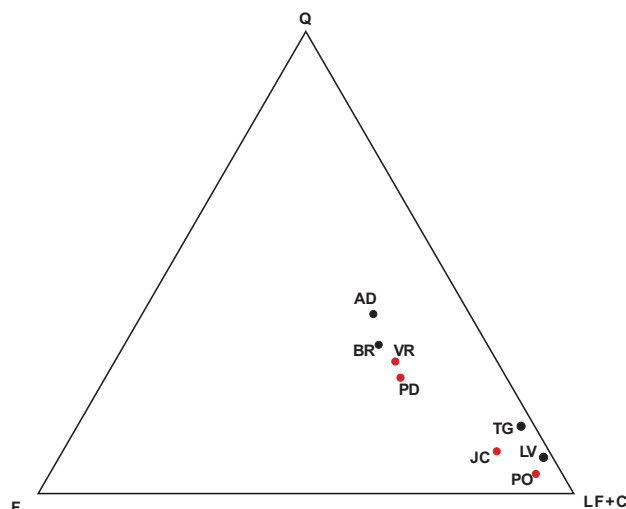


Fig. (12). QFL diagram comparing sand fraction composition in the mortar samples investigated (red circles) and in the river sources investigated (black circles). AD=Adige river; BR= Brenta river; LV=Livenza river; TV=Tagliamento river; VR=Verona; PD=Padova; JC=Julia Concordia; PO= Pordenone. Note that the LF apex includes also terrigenous carbonate rock fragments (C).

dolomite) grains observed here are too coarse for marble dust which for plaster use were very fine grained (i.e. < 1 mm in diameter). The well to very well rounded nature of the sand grains examined in this study indicates a river sand origin as the most likely. The aggregate/ligand ratios range from 2 to 2.8 and are consistent with those typical of Roman mortars of Augustean age [23].

The rivers that are the most likely sources of the sandy materials used in the mortar samples investigated are respectively (going in an eastward direction; (Fig. 1)): Adige (Verona), Brenta and Bacchiglione (Padova), Livenza (Concordia Sagittaria) and Tagliamento (Pordenone). The mineralogy/petrography of the fluvial deposits from these rivers has been examined in detail by Gazzi and coworkers [10], Jobstraibizer and Malesani [9] and by Garzanti and co-workers [11]. These authors indicate that, while the river deposits under investigation are similar in terms of clay mineral content, their sand fraction presents noticeable mineralogical

markers/features that can be useful in distinguishing between the different fluvial sands. When comparing the results of the current study with the data from the papers quoted above, the following considerations can be made (see also Fig. (12)):

In terms of mineralogical composition, the mortar samples from Verona and Padova can be clearly distinguished from the Julia Concordia and Pordenone ones. Higher content of carbonate grains (dolomite and calcite) and of chert lithic fragments in the Pordenone mortars as compared with the Verona and Padova samples, together with the lower content of feldspar and quartz grains, is consistent with known changes in the mineralogy of river sands in an eastward direction from Veneto region to the Friuli Venezia Giulia one [9,10].

The widespread presence of reddish feldspars grains in the samples from Verona and Padova (Fig. 2) is consistent with these mineral grains being typical components of fluvial deposits of the Adige and Brenta rivers. Permian volcanics (Foiana-Luco lavas for example) containing dark red K-feldspar minerals as phenocrysts are typically outcropping along the drainage basins of these two rivers flowing southwards from Trentino-Alto Adige region to the Veneto region. These grains are absent in the Pordenone and Julia Concordia mortars.

The abundance in samples from Verona and Padova of igneous lithic fragments of acid volcanic (porphyritic rhyolites, rhyodacites, trachytes) and plutonic (granites, tonalites) rocks correlates well with the widespread presence of lithic fragments of this type in river deposits from the river Adige. The magmatic source rocks for these grains are a common geological feature of the Trentino-Alto Adige Region and belong to the well-known late Hercynian Atesina- Cima d’Asta volcano-plutonic complex of Permian age. The mono-crystalline nature of quartz grains in the Verona samples further suggests a volcanic origin for the same clasts which is consistent with a derivation from same igneous parent rocks outcropping in the Trentino region. Volcanic rock fragments (trachytes) have been reported as common aggregate components also in Roman mortars of Neronian age from the town of Montegrotto near Padova [21].

The widespread presence of Ti-rich inclusions (rutile and ilmenite) in the sand clasts from Verona and Padova samples (Fig. 4) and of garnets of the almandine species in Verona sands is consistent with above mentioned published data on the mineralogy of river deposits from the Adige and Brenta rivers.

The exclusive presence of brookite, monazite and of epidote mineral species in samples from Padova (Fig. 7) is consistent with published data on the mineralogy of modern sand deposits from the river Brenta: brookite and monazite have indeed been indicated as mineralogical markers for this river [9] and the widespread presence of monazite-bearing rocks in the Cima d’Asta plutonic complex (granodiorites) and in the Atesina volcanic complex (ryolites) from the Trentino region within the Brenta

drainage basin is well documented [24]. It is relevant to note that the Cima d'Asta plutonic rocks have also been indicated as the source of sand for the historic mortars used by the medieval painter Giotto in the making of frescoes of the Cappella degli Scrovegni, a world famous monument situated in Padova town center [19].

Despite a certain homogeneity in sand mineralogical composition between Verona and Padova mortar samples which in turn reflects similarities in their respective river sources (Adige vs Brenta), a discriminating parameter between these two locations can be found in the higher content in Padova samples of mineral grains of phyllosilicates (muscovite + biotite + chlorite: see XRD spectrum in Fig. (8)).

The calcitic versus dolomitic nature of the carbonate clasts present in the sand fractions does not represent a viable parameter that can be used to differentiate between the possible river sources inasmuch as dolomite content exceeds that of calcite in all the samples examined (both mortar and/or river-derived) where calcite/dolomite ratios estimated from XRD relative peak intensities range from 0.64 (Verona) to 0.43 (Padova), 0.36 (Julia Concordia) and 0.66 (Pordenone).

CONCLUSIONS

The medium to coarse grain size sands display high roundness values and moderate to very well sorting, suggesting a fluvial origin from rivers nearby the sites investigated such as the rivers Adige (Verona), Brenta (Padova), Livenza (Concordia Sagittaria), and Tagliamento (Pordenone).

The overall mineralogical composition of all sand fractions is fairly uniform and include calcite, dolomite, quartz, feldspars (albite and orthoclase), chert and igneous and metamorphic lithic fragments.

Despite the apparent mineralogical uniformity, compositional trends can be recognized that enable to distinguish between the different fluvial sources of the sand materials.

Preliminary results indicate the simple, and rapid, mineralogical-analytical approach adopted in this study as a potentially useful tool which may complement additional evidence gathered from archaeological and archaeometric research and assist in the assessment of the provenance of building materials used in the making of historic mortars.

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