

Petro-archaeometric characterization of historical mortars in the city of Ravenna (Italy)

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Abstract – During restoring operations of ancient buildings, datable between 1th and 16th century, in the city of Ravenna samples of mortars from different archaeological sites has been collected by the Superintendence for Archaeological Heritage of Emilia Romagna. Mineralogical and chemical analyses of these samples allowed to characterize mortars composition, comparing their features in order to highlight changes in construction technologies and chronological discrimination, by defining raw materials used and establishing their places of origin. In particular, mortars from: the Roman age San Zaccaria (Early Imperial period), the Cloisters of San Francesco (14th - 17th century and modern age) and Corte delle Antiche Carceri (dating back to Middle ages and modern age) were analyzed.

I. INTRODUCTION

According to recent studies concerning the origins of the city of Ravenna (North-East of Italy), the primitive human settlement in the area, where the urban center of Ravenna subsequently developed, dates back to the 4th-3th century BC [1]. A great economic and demographic increase in the city must be attributed to the first imperial period (1st century AD) when the Ravenna military and commercial port was developed by the will of the emperors. In this period the countryside around Ravenna, very productive, supplied the city and the harbor with food and timber, above all thanks to the production system of the villas.

Following alternation of periods of decline [2] and strong urban development [2], the city of Ravenna underwent significant changes over time. In the time of prosperity, some important buildings have been built, such as the Cathedral and the Episcopate dating back to the 4th and 5th centuries BC, that are still in use today [3], and then many churches, still visible, such as St. Apollinare Nuovo, St. Vitale and St. Apollinare in Classe dating to the 6th century BC [4].

In the Middle Ages, after the fall of the Exarchate, in

751, the history of Ravenna is not marked by particular events. Together with the 5th and 6th century buildings, which survived thanks to the acquisition by monastic and conventual orders and the transformation in monastic churches [5], some new buildings were constructed, often not surviving [6].

In 1441, after a period of crisis with the last members of the Da Polenta family, Ravenna came under the control of the Venetian Republic. In the following sixty years of Venetian domination, Ravenna was the subject of an important urban regeneration work [7]. Inside the ancient walls, the urban plan was raised and, in some parts, paved; many buildings were demolished, and the physiognomy of the road system built is still the one used today. The Venetians were also interested in the construction of some importance buildings for the city, such as the Rocca and the new Town Hall built after 1280 in the place of the medieval one, in the square which today takes the name of Piazza del Popolo.

After the Battle of Ravenna, fought near the city in 1512, Ravenna underwent a profound crisis, that only in the 18th was able to overcome.

In 1859 the city of Ravenna, which until then was under the protection of the Archiepiscopal Mensa [8], joined the Unification of Italy.

For some time, however, the protection of Ravenna's monumental buildings was considered an urgent problem, since the management of buildings rich in marble and ancient mosaics was very expensive. Restoration works were carried out only for the ancient buildings of worship that appeared decadent in the city of Ravenna. Until, in 1897, the problem of the protection of the monuments of Ravenna was taken on by the Superintendence of Monuments [9] that has the task of protecting monuments and which in Ravenna had the first example in the history of Italy. Thanks to this, the various restoration procedures were started in the buildings of the city which allowed the use of grouting the wall joints through the use of non-original but similar mortars. The use of this material

allowed to safeguard history, restore ancient constructions, and create continuity with the past.

Chemical and mineralogical characterization of mortars may be used to understand chronological aspects of the evolution of historical buildings [10]. Mineralogical and chemical data are useful tools for geoarchaeologists to relate the composition of historic artefacts to the provenance area, and a similar approach can be also used to study ancient mortars. Several studies comprising chemical and mineralogical composition of mortar components have been applied to answer questions related with formulation of repair strategies and replacement of mortars in built monuments, as well as in provenance and technological inferences [11,12,13,14,15]. This compositional approach has been widely used to characterize cultural heritage artifacts, and also mortars in restoration and treatment work and in studies of manufacturing technology and dating [16,17,18,19]. Furthermore, the types of raw materials can be identified and, hopefully, their provenance deduced. This allow to establish the differences between mortars through time and cultural context [20].

The objective of this study was to establish the chemical mineralogical constitution of historical mortars from different archaeological sites, to highlight eventual differences between them, and to correlate such differences with cultural changes at the archaeological site. The aim of this research was to contribute to the scientific knowledge of Ravenna archaeological mortars with a possible application to conservation or restoration work.

II. MATERIALS AND METHODS

Samples collected in three archaeological contexts, identified by the Superintendence for Archaeological Heritage of Emilia Romagna, were analyzed (Fig. 1).

- San Zaccaria (small town located about 20 km South-West of Ravenna): production plant of the Roman age (1th-2th century; samples VM2, VM9);

- Cloister of San Francesco (9th-10th century) [9]: the mortar samples collected have not undergone modern contamination (samples VM4, VM7, VM8, VM12 and VM13). In addition, other mortar samples were collected from modern construction walls not contaminated by restoration rework (VM3, VM5, VM10 and VM11).

- Corte delle Antiche Carceri: mortar samples form walls (Middle ages - sample VM6) located in the subsoil of the area occupied by the Palazzo Comunale complex and raised walls of recent production (modern age - sample VM1).

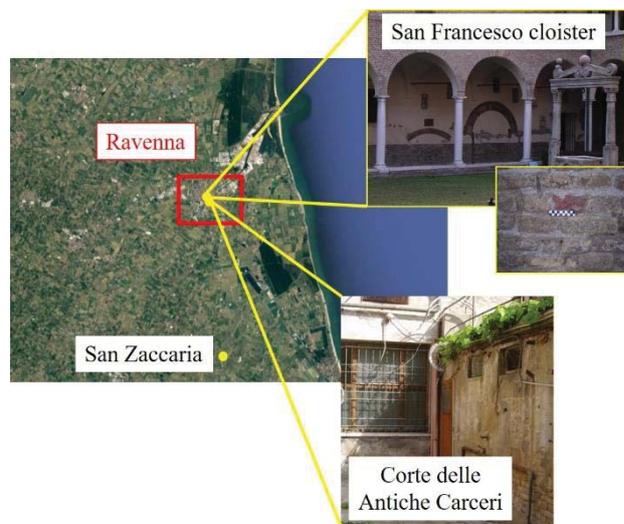


Fig. 1. Map of the sampling site. In red square the city of Ravenna in which San Francesco cloister and Corte delle Antiche Carceri are located. San Zaccaria is represented by the yellow circle at the bottom (20 km from Ravenna city center).

Samples were ground until a powder with a particle size less than 2 μm was obtained. The powders obtained were dried in an oven at 110° C and the L.O.I. (loss on ignition) of each sample were calculated. The powders were prepared by pressing the tablets on boric acid support for XRF analysis. The chemical characterization of the collected samples was determined by X-ray fluorescence (XRF) analysis, carried out at the Department of Physics and Earth Sciences, University of Ferrara with a wavelength dispersion spectrometer ARL Advant-XP (Thermo Fisher Scientific, Waltham, Massachusetts, USA) [21]. This technique allowed the determination of the major elements, expressed as a percentage by oxide weight (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5) and of the following trace elements reported in ppm (parts per million): Ba, Cr, Ni, Pb, Rb, Sr, V, Zn, Zr, Nd, S. The accuracy of the instrument, estimated on the basis of the results obtained on international standards of geological samples, and the precision, expressed as standard deviation of replicated analyses, were between 2% and 5% for the major elements and between 5% and 10% for trace elements. The detection limit (0.01% for major oxides) was estimated to be close to ppm for most trace elements, except for S for which 50 ppm was considered [22]. The processing of the acquired intensities and the correction of the matrix effect was performed according to the model proposed by Lachance and Trail [23]. The qualitative data obtained were ex-pressed as single element weight.

Moreover, mineralogical determinations of some aggregates, previously grinded using water and then dried, were carried out through X-ray diffractometric powder analysis (XRPD) using a Philips PW1860/00

diffractometer, with a graphite filtered and a Cu K α radiation (1.54 Å) in a θ an-gular range 5-75°, with a 5 s/step (0.02° 2 θ) [21].

III. RESULTS

Table 1 shown the XRF data of major oxides expressed in weight oxide (%), instead of Table 2 shown the XRF data of trace elements expressed in ppm, obtained by all the analyzed samples of the three different sampling site.

Table 1. XRF data of major oxides expressed in weight oxide (%) in the analysed samples.

San Zaccaria			San Francesco cloister				
VM2	VM9		VM4	VM12	VM7	VM8	VM13
SiO ₂	39.16	33.57	38.88	41.02	49.61	51.07	33.29
TiO ₂	0.09	0.20	0.15	0.16	0.23	0.23	0.19
Al ₂ O ₃	3.16	6.74	4.25	4.70	5.64	5.77	4.49
Fe ₂ O ₃	1.13	1.51	1.67	1.77	1.95	1.83	2.27
MnO	0.07	0.07	0.09	0.10	0.06	0.06	0.10
MgO	1.10	1.12	1.55	1.65	2.06	2.16	1.76
CaO	31.39	29.07	29.23	27.60	21.84	20.24	34.17
Na ₂ O	0.41	0.37	0.61	0.66	0.97	1.01	0.51
K ₂ O	0.52	0.96	0.87	0.96	1.19	1.18	0.88
P ₂ O ₅	0.18	0.35	0.18	0.19	0.14	0.14	0.23
LOI	22.79	26.03	22.52	21.18	16.30	16.31	22.11
Tot.	100	100	100	100	100	100	100

San Francesco cloister				Corte delle Antiche Carceri		
VM3	VM5	VM10	VM11	VM1	VM6	
SiO ₂	50.53	54.07	51.84	41.87	43.02	26.43
TiO ₂	0.24	0.21	0.29	0.06	0.04	0.11
Al ₂ O ₃	6.55	6.31	7.14	2.63	1.40	2.84
Fe ₂ O ₃	2.17	1.81	2.31	0.81	0.62	1.27
MnO	0.09	0.08	0.09	0.07	0.03	0.06
MgO	2.39	2.18	2.61	1.05	0.81	1.39
CaO	19.01	17.73	17.33	29.09	35.53	40.12
Na ₂ O	0.90	1.09	0.98	0.49	0.18	0.39
K ₂ O	1.26	1.39	1.39	0.53	0.23	0.58
P ₂ O ₅	0.14	0.13	0.15	0.09	0.45	0.06
LOI	16.73	15.00	15.88	23.32	17.69	26.75
Tot.	100	100	100	100	100	100

Table 2. XRF data of trace elements expressed in ppm (n.d. = not detected) in the analysed samples.

	San Zaccaria		San Francesco cloister				
	VM2	VM9	VM4	VM12	VM7	VM8	VM13
Ba	85.5	201	139	154	151	151	145
Cr	5.70	1.71	14.4	16.0	26.9	25.2	22.1
Ni	4.30	0.38	12.4	13.9	21.6	22.0	14.9
Pb	14.6	40.1	29.6	27.5	19.4	25.6	26.0
Rb	15.2	42.6	24.7	27.6	33.3	32.0	29.7
Sr	436	474	395	417	292	277	458
V	10.5	22.7	18.2	22.4	27.6	30.4	27.9
Zn	9.30	35.4	21.0	20.7	20.6	21.9	26.0
Zr	59.4	234	108	104	131	116	114
Nd	56.9	26.9	55.8	57.6	81.3	77.1	59.5
S	n.d.	1154	n.d.	n.d.	n.d.	n.d.	621

San Francesco cloister				Corte delle Antiche Carceri		
VM3	VM5	VM10	VM11	VM1	VM6	
Ba	181	191	189	82.2	48.1	95.6
Cr	18.4	13.2	22.5	3.31	1.99	31.6
Ni	23.3	16.5	24.2	1.15	n.d.	4.73
Pb	23.7	21.7	31.8	19.0	13.6	24.8
Rb	37.9	40.0	43.6	13.0	6.14	16.5
Sr	371	359	350	456	181	363
V	34.0	24.5	38.7	7.77	0.23	21.5
Zn	35.0	26.1	37.1	5.79	12.0	21.6
Zr	97.0	105	125	48.5	17.7	112
Nd	62.8	72.2	67.0	56.5	94.2	55.8
S	n.d.	n.d.	n.d.	n.d.	n.d.	2507

XRF analyses showed a difference between the sands of the two mortars (VM2 and VM9) collected in the San Zaccaria sampling site. The two samples were characterized by Al content and less Fe (Table 1 and Fig. 2). One mortar is made with sand rich in quartz (VM2), while the other is made up of sand rich in phyllosilicates in which the average SiO₂: CaO ratio is 1.2.

The samples of the San Francisco cloisters, as can be seen from the binary diagrams in figure 2, were divided into three groups, two of which were essentially numerous while a single poor in silica (Table 1). The VM4 and VM12 samples have similar pattern. The sand is quartz-feldspathic in which the average SiO₂: CaO ratio is 1.4.

VM7 and VM8 samples were collected from two wall partitions to narrow a door (14th century). The chemical analysis shows equivalent data for the two samples, with an average SiO₂: CaO ratio of 2.4, confirming that the two

walls were built in the same period.

VM13 sample is different respect to the other samples, as it is poor in silica (Table 1). The SiO_2 : CaO ratio is 1.1.

The comparison between the samples VM3, VM5, VM10 and VM11 collected from masonry pertinent to the Franciscan cloisters currently in use (17th century) shows that they are characterized by similar chemical elements (only VM11 is poorer in silica – Table 1), with an average SiO_2 : CaO ratio of 2.6 that confirm that it is the same wall structure of the new cloisters.

The chemical results of the two samples (VM1 and VM6) collected in the Corti delle Antiche Carceri show that probably they come from different periods. VM1 sample, collected in modern masonry (Late Middle Ages) has an average SiO_2 : CaO ratio of 1.2 and rich in silica (Table 1). On the other hand, VM6 mortar is different and it dates from a more recent period (18th-19th century). It consists of sand rich in calcite (Table 1) in which the average SiO_2 : CaO ratio is 0.6.

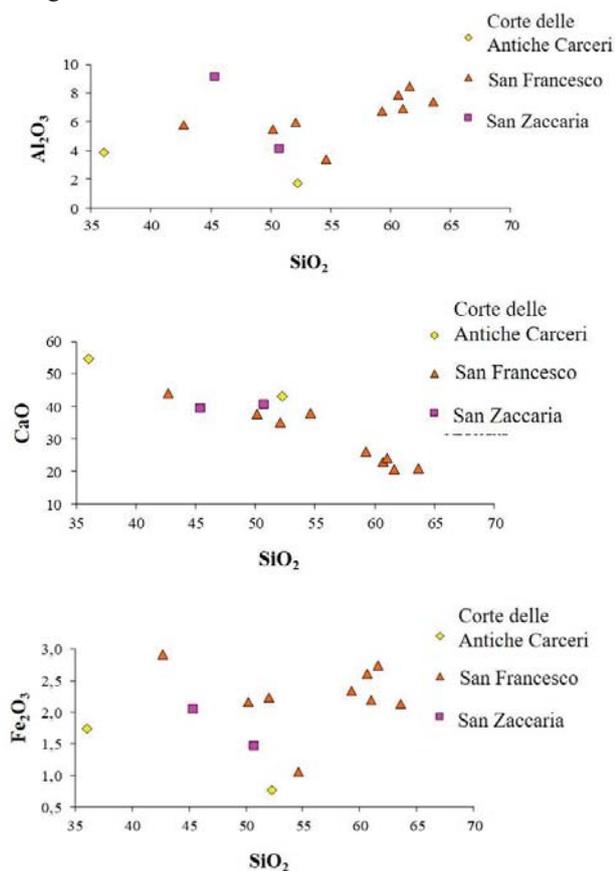


Fig. 2. Binary diagram obtained by XRF data of the samples collected in the three different sampling sites: a) SiO_2 (Wt%) – CaO(Wt%); b) SiO_2 (Wt%) – Al_2O_3 (Wt%); c) SiO_2 (Wt%) – Fe_2O_3 (Wt%).

The XRPD pattern of VM2 sample confirms that the sand has a quartz-feldspathic nature with quartz and

calcite, followed in less quantities by feldspars, zircons, epidotes and a low peak of phyllosilicates as main components (Fig. 3). With regard to this, the difference in the materials is probably due to different places of origin or to an addition of phyllosilicates in order to waterproof the decantation tank since, in the presence of water, the phyllosilicates sediment with a preferential orientation. The XRPD analysis of the VM9 sample is not present due to the lack of sampled material. The samples of the cloisters of San Francesco can be divided into three groups by chemical analogies.

VM4 and VM12 samples have similar characteristics, which confirms that the sections of the wall from which the samples were collected belong to a wall made in a single construction phase, probably belonging to the factories in the early Middle Ages (9th century). Proportionally the order of the mineral components is quartz, feldspar and calcite (Fig. 4a).

The diffractometric analysis of VM7 and VM8 samples revealed that in the VM7 (Fig. 4b) sample there is a presence of phyllosilicates, absent in the VM8 sample, and a difference in the proportions of the minerals which in the VM7 sample are quartz, feldspar, and calcite respectively, while in the VM8 they are quartz, calcite and feldspars (Fig.4c). The nature of the sand is quartz/feldspathic.

The VM13 sample was collected in the wall section built later (end of 14th century). VM13 sample is different respect to the other samples both in chemical and mineralogical composition, as it is poor in silica, which indicates a good quality mortar and which can hypothesize the presence of specialized workers in the Franciscan cloisters (Fig.4d).

The XRPD spectrum of Fig 4e shows the difference of the VM3 sample respect to the other (VM5, VM10 and VM11), characterized by quartz, feldspar and calcite while the remaining samples present quartz, calcite and feldspar. The nature of the sand is quartz/feldspathic.

The comparison between the samples collected in the Franciscan cloisters clarifies how, from the Middle Ages to the Modern era, there has been an impoverishment of materials due to a decrease in the use of calcite and in turn an increase in the use of sand.

The mineralogical differences between the two samples (VM1 and VM6) collected in the Corti delle Antiche Carceri confirmed that they come from different periods. The diffractogram of VM1 sample reveals that the main components are quartz, calcite, feldspar, epidote and a low peak of phyllosilicates (Fig. 5a). The nature of the aggregate is of the quartz/feldspathic type. On the other hand, VM6 (Fig. 5b) consists of sand rich in calcite. This data could confirm an excellent quality material due to evolutions in the technological knowledge supported by a possible economic growth of the city.

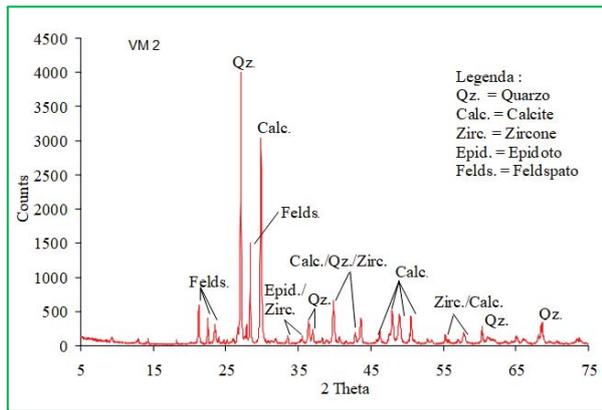
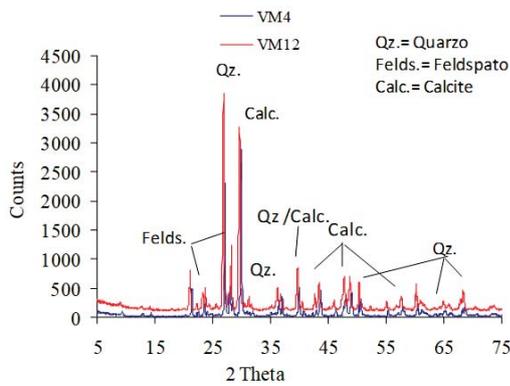
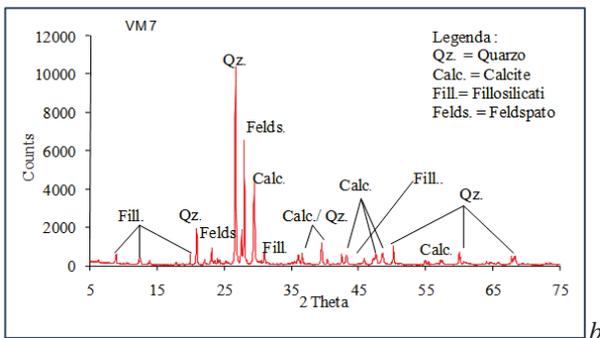


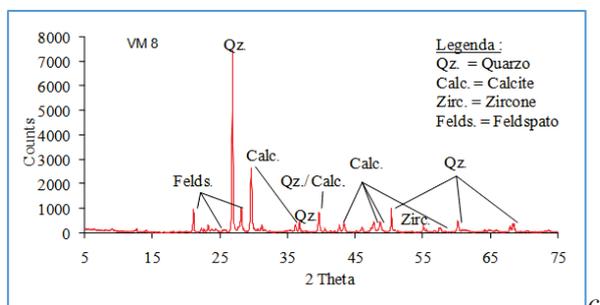
Fig. 3. XRPD spectrum of the sample VM2 collected in San Zaccaria area.



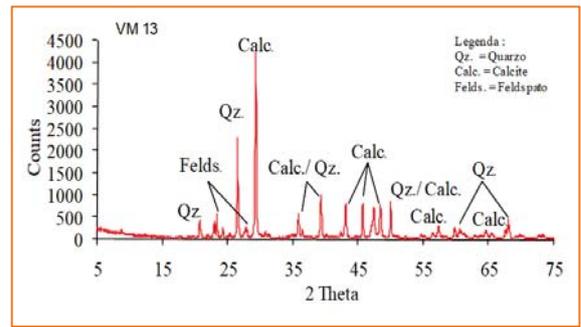
a



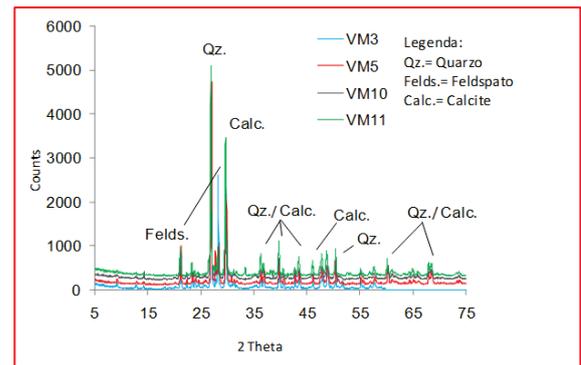
b



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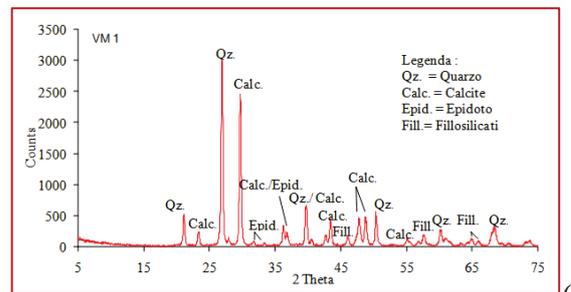


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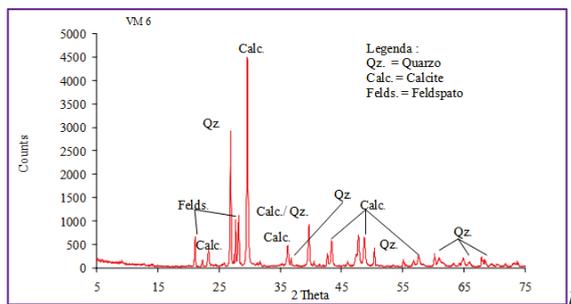


e

Fig. 4 a, b, c, d, e. XRPD spectrum of the samples collected in the cloister of San Francesco.



a



b

Fig. 5 a, b. XRPD spectrum of the samples collected in Corte delle Antiche Carceri

IV. CONCLUSION

Mineralogical and geochemical characterization of mortars from three different sites of the Ravenna area allowed to acquire data on the samples from chemical-mineralogical characterization.

All the hypotheses put forward by archaeologists have

been confirmed here. From a chronological point of view, it is essential to underline how from the I-II century up to the Modern age, changes in mortars are found, with a progressive impoverishment of the material due to the decrease in the use of lime and increase in the use of sand. Data shows that VM6 sample is different to the other samples because it is richer in calcite, suggesting that it is a good quality material and chronologically more recent (18th - 19th century). The remaining samples present mortars with quartz/feldspathic sands. Similar compositional characteristics in the mortars analyzed lead us to speculate that the raw materials were found in local quarries.

REFERENCES

- [1] P. Novara, A. Luparini. *Storia di Ravenna. Dalla preistoria all'anno Duemila*, Cesena 2016, pp. 9-32.
- [2] P. Novara, A. Luparini. *Storia di Ravenna. Dalla preistoria all'anno Duemila*, Cesena 2016, pp. 32-56.
- [3] P. Novara. *Palatium domini archiepiscopi. Appunti archeologici sull'area circostante la cattedrale di Ravenna attraverso alcuni fondi speciali*. In Benericetti R. 2005. *Colligite fragmenta*, 2005, pp.131-183.
- [4] P. Novara. *L'edilizia di culto ravennate dei secoli V-XI*. *Fonti e ricerche*, Ravenna 2008, pp. 5-19.
- [5] P. Novara. *Ad religionis claustrum construendum. Monasteri nel medioevo ravennate*. *Storia e archeologia*, Ravenna 2003.
- [6] P. Novara. *Luoghi di culto, vita comune consacrata e di assistenza nella Ravenna dei secoli XII-XIV*. Note si storia e archeologia. In R. Benericetti. *Storia e tradizione. Ricerche sulla Romagna medievale*, Faenza 2008, pp. 47-97.
- [7] V. Fontana. *De instauratione Urbis Ravennae. Architettura e urbanistica durante la dominazione veneziana*. In Bolognesi D. *Ravenna in età veneziana*, 1986, pp. 294-304.
- [8] P. Novara. *Appunti di cantiere. L'interesse archeologico nei riguardi delle antichità ravennate nel XIX secolo*. *Notizie, personaggi e immagini*, 2002.
- [9] A. Ranaldi, P. Novara. *Restauri dei monumenti paleocristiani e bizantini di Ravenna patrimonio dell'Umanità*, Ravenna 2013.
- [10] M. Vendrell-Saz, S. Alarcon, J. Molera, M. Garcia-Valles. *Dating ancient lime mortars by geochemical and mineralogical analysis*. *Archaeometry*, 1996, 38, 1, pp. 143-149.
- [11] J.I. Alvarez, I. Navarro, A. Martín, P.J. García Casado. *A study of the ancient mortars in the north tower of Pamplona's San Cernin church*. *Cement and Concrete Research*, 2000, 30, pp. 1413-1419.
- [12] J.J. Hughes, S.J. Cuthbert. *The petrography and microstructure of medieval lime mortars from the west of Scotland: implications for the formulation of repair and replacement mortars*. *Materials and Structures*, 2000, 33, pp. 594-600.
- [13] A. Moropoulou, A. Bakolas, K. Bisbikou. *Investigation of the technology of historic mortars*. *Journal of Cultural Heritage*, 2000, 1, pp. 45-58.
- [14] L. A. Ortega, M. C. Zuluaga, A. Alonso - Olazabal, M. Insausti, A. Ibáñez. *Geochemical characterization of archaeological lime mortars: provenance inputs*. *Archaeometry*. 2008, 50, 3, pp.387-408.
- [15] L. Barba, J. Blancas, R. Manzanilla, A. Ortiz, D. Barca, G.M. Crisci, D. Mirello, A. Pecci. *Provenance of the limestone used in Teotihuacan (Mexico): a methodological approach*. *Archaeometry*, 2009, 51, pp. 525-545.
- [16] P. Maravelaki-Kalaitzaki, A. Bakolas, A. Moropoulou. *Physico-chemical study of Cretan ancient mortars*. *Cement and Concrete Research*, 2003, 33, pp. 651-666.
- [17] F. Casadio, G. Chiari, and S. Simon. *Evaluation of binder/aggregate ratios in archaeological lime mortars with carbonate aggregate: a comparative assessment of chemical, mechanical and microscopic approaches*. *Archaeometry*, 2005, 47, 671– 89.
- [18] I. A. Meir, C. Freidin and I. Gilead. *Analysis of Byzantine mortars from the Negev Desert, Israel, and subsequent environmental and economic implications*. *J. Archaeol. Sci*, 2005, 32, 767– 73.
- [19] D. Nawrocka, J. Michniewicz, J. Pawlyta, and A. Pazdur. *Application of radiocarbon method for dating of lime mortars*. *Geochronometria*, 2005, 24, 109– 15.
- [20] D. Miriello, D. Barca, A. Bloise, A. Ciarallo, G.M. Crisci, T. De Rose, C. Gattuso, F. Gazineo, M.F. La Russa. *Characterisation of archaeological mortars from Pompeii (Campania, Italy) and identification of construction phases by compositional data analysis*. *J. Archaeol. Sci.*, 2010, 37, 9, pp. 2207-2223
- [21] E. Marrocchino, D. Rapti-Caputo, C. Vaccaro. *Chemical–mineralogical characterisation as useful tool in the assessment of the decay of the Mesola Castle (Ferrara, Italy)*. *Construction and Building Materials*, vol.24, 2010, pp.2672-2683.
- [22] E. Marrocchino, C. Telloli S. Caraccio, C. Guarnieri, C. Vaccaro. *Medieval Glassworks in the City of Ferrara (North Eastern Italy): The Case Study of Piazza Municipale*. *Heritage, special issue Geosciences for Cultural Heritage and Archaeology*, vol.3, 2020, pp.819-837.
- [23] G.R. Lachanche; R.J. Traill. *Practical solution to the matrix problem in X-ray analysis*. *Canadian Spectroscopy* vol.11, 1996, pp.43-48.