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The contribution of Archaeometric Analyses to the Multi-Disciplinary Research in Hierapolis of Phrygia, Turkey

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***Abstract* –In the frame of an integrated knowledge path applied to the archaeological site of Hierapolis in Phrygia (Turkey), several mortar samples were collected and analysed by means of a multi-analytical approach to study the production techniques and the conservation state, and to evaluate the possible dateability by means of the absolute radiocarbon dating method (^{14}C). This study was part of a collaboration research including structural engineering and geophysical investigations, aimed at evaluating the current conditions of the archaeological remains for the possible use of the whole site as an archaeo-seismic park.**

I. INTRODUCTION

In the context of the PRIN project 2015 "Archaeology of urban landscapes in Asia Minor between late Hellenism and Byzantine age. Multidisciplinary approaches to the study of Hierapolis in Phrygia", several research groups of the University of Padua joined their multidisciplinary expertise in materials science, structural engineering and geophysics, aimed at contributing to the interpretation of the archaeological data.

Advanced experimental analysis procedures and investigation techniques were used, which led to significant results on the characterization of mortars (composition and dating), soil (subsoil morphology in relation to possible fault activity) and structures (dynamic behaviour and seismic vulnerability).

This paper focuses on the results of a series of petrographic and microstructural analyses performed on the mortars sampled on two massive (large stone block) remains of the archaeological site, i.e., the Roman Baths, and the Temple of Apollo with its Nymphaeum (Fig.1). The possible absolute dating by means of the ^{14}C method was also attempted.

The archaeological site of Hierapolis is composed of the remains of the ancient Greco-Roman city (close to the modern Pamukkale, in Denizli region), located in Phrygia, the west-central region of classic Anatolia, Turkey. The site has been shaped by earthquakes occurred in the past centuries since its foundation (around the 3rd century BC), due to the presence of a system of faults, which are still active today [1]. After a severe earthquake occurred in the 7th century AD the city, which was at that time in the Byzantine age, lost its importance and up to the 14th century was gradually abandoned.

Since the late '50s the Italian Archaeological Mission in Hierapolis (MAIER) has played a fundamental role in bringing into light the ruins and in promoting restoration works for their valorisation and use [2].

The site extends over an area of about 75 hectares, including remains of several outstanding monuments, e.g., the theatre, the Martyrion of Saint Philip, the Ploutonion. Fig.1 shows the map of the archaeological area and the localization of the two case studies. Both monuments date back to the beginning of the 3rd century AD. The Roman Baths were built outside the north gate of the city. In the 4th century, a big earthquake damaged the buildings, and in the early Christian era the recovered ruins were transformed into a church [3]. Nowadays, two incomplete massive arcades (9 m in span) made of large travertine block stones (about 2.5 m in size) are still standing in the complex, together with other freestanding walls (about 7 m tall) and several collapsed elements (Fig.2.a).

The Nymphaeum is located at the lower terrace of the sacred area of the Temple of Apollo. It was a monumental fountain and it is made of multi-layer walls of travertine blocks and an inner core filled of a conglomerate of stone and mortar elements. The main body exceeds 30 m in length and 4 m in thickness, whereas the side wings are about 10 m long and 3 m thick [4] (Fig.2.b). The structure reaches currently about 12 m in height, including an upper layer that was probably rearranged in restoration works carried out after the 4th century AD earthquake.

Both monuments and their surrounding areas are currently closed to tourists, as the safety conditions of the structures are still under study. The analyses of mortars and of their constituents in those constructions, together with the other investigation techniques, could help in clarifying the building techniques and the possible use of recovering materials in the reconstruction phases.

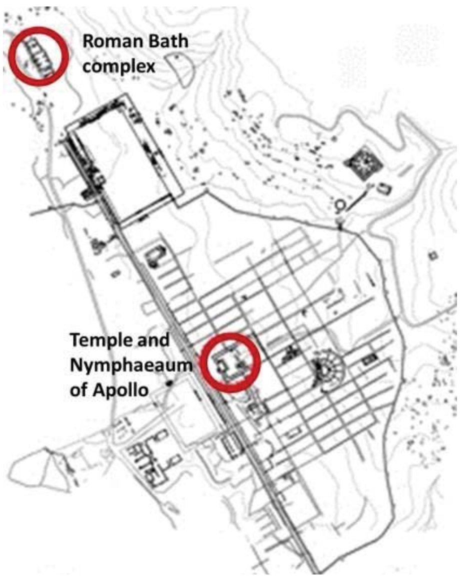

Fig. 1. Archaeological site of Hierapolis with identification of the case studies.

II. CHARACTERIZATION AND RADIOCARBON DATING OF MORTARS

The multi-analytical study carried on archaeological mortars from Hierapolis consists of minero-petrographic, microchemical and microstructural characterizations aiming at studying the production techniques, conservation state and to evaluate the dateability of the mortars by the radiocarbon dating method (^{14}C), in order to contribute to the archaeological research [5], [6]. Radiocarbon dating on mortars exploits the C uptake during the carbonation process, where the atmospheric CO_2 signal is absorbed by reaction with lime putty, and then it is converted back into $CaCO_3$-binder containing the signature of the construction time [7]–[9]. The $CaCO_3$-binder must be isolated and our procedures in dating mortars includes, in brief: i) a multi-analytical characterization of the material in order to evaluate the materials' properties and the presence of potential dating contaminants; ii) a careful binder extraction by wet gravimetric sedimentation procedure to avoid aggregate contaminants; iii) characterization of the extracted binder fraction; iv) radiocarbon dating of the purified fraction.

The sampling of the binding materials (Table 1) was performed at the Roman Baths complex, Nymphaeum and Temple of Apollo, safeguarding the criteria of statistical representativeness of the materials used and minimal invasiveness (Fig.2.c, d, e).

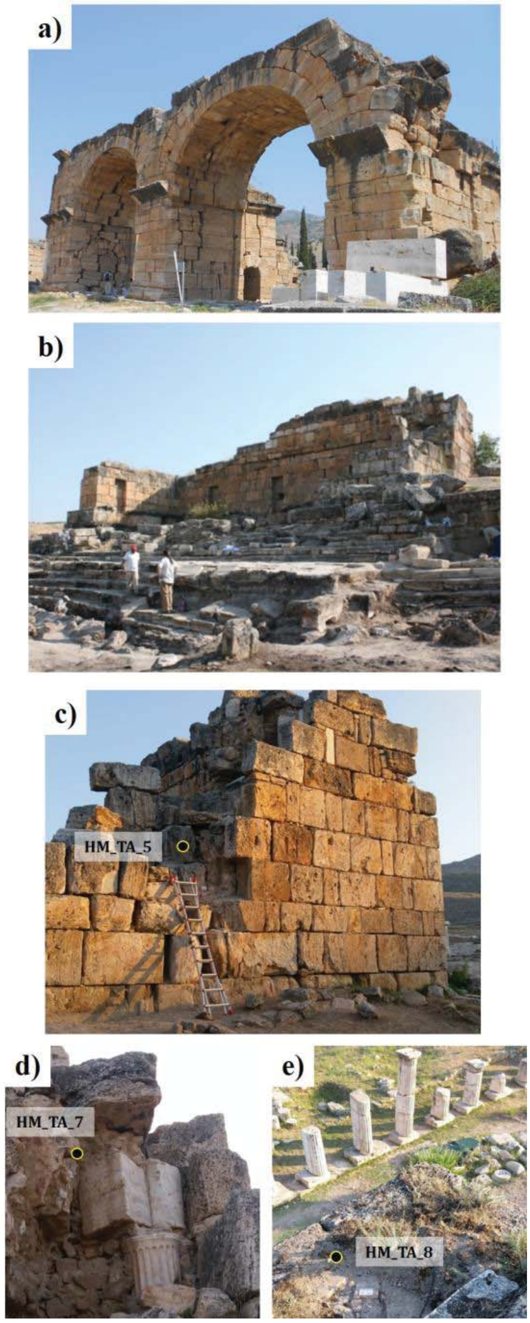

Fig. 2. View of main standing structures of Roman Bath (a), remains of Nymphaeum of Apollo (b) and some of the sampling points (c, d, e).

A. Characterization methods

Petrographic analyses were performed by optical microscopy (OM) on thin-sections under parallel and crossed polars using a Nikon Eclipse ME600 microscope equipped with a Canon EOS 600D Digital single-lens reflex camera. The thin sections, covered with an ultrathin coating of graphite, were microstructurally and microchemically characterized through a CamScan MX2500 SEM equipped with a LaB_6 electron source and an EDS probe used to collect elemental microanalyses through the SEMQuant Phizaf software, giving valuable information on the mineral phases and binder composition. Mineralogical quantitative phase analyses (QPAs) have been performed by X-ray powder diffraction (XRPD) on fine sample powders obtained by micronization. XRPD analyses were performed using a Malvern PANalytical X'Pert PRO diffractometer in Bragg-Brentano geometry, Co–Kα radiation, 40 kV and 40 mA, equipped with a real-time multiple strip (RTMS) detector (X'Celerator by Panalytical). Data acquisition was performed by operating a continuous scan in the range 3– 85° 2θ, with a virtual step scan of 0.02° 2θ. Diffraction patterns were interpreted with X'Pert HighScore Plus 3.0 software by Malvern PANalytical, reconstructing mineral profiles of the compounds by comparison with ICDD and ICSD diffraction databases. QPAs were performed using the Rietveld method [10] and refinements were accomplished using the TOPAS software (version 4.1) by Bruker AXS. The determination of both crystalline and amorphous content is calculated by means of the internal standard method with the addition of 20 wt% of zincite (ZnO) to the powders [11].

B. Extraction of the binder fraction

The purification treatment consists of a wet gravimetric sedimentation in a 500 ml cylinder in order to obtain a Stokes' Law-based dimensional separation of the particles, as reported by the authors [12]–[14]. The result is a solid separate of fine-grained particles (SG) corresponding to the "pure" binder fraction separated from the aggregates and contaminants present in the mortar mix.

C. Radiocarbon dating of mortars

The pure carbonate binder was digested under vacuum by orthophosphoric acid attack and converted into CO_2 [15]. The extracted CO_2 was reduced to graphite according to the CIRCE sealed tube reaction protocol [16] and the ^{14}C isotopic ratios was measured [17]. The obtained data were corrected for fractionation and blank according to their graphitised mass, normalised and R.C. ages were estimated and calibrated to absolute ages by means of OxCal 4.2 and INTCAL 13 calibration curve [18], [19].

Table 1. Mortars collected from Hierapolis site.

	Sample code	Notes
Nymphaeum and Temple of Apollo	**HM_3**	Tank bottom, under pre-Byzantine bricks
	HM_4	
	HM_9	internal tank, base cast of the tank bottom
	HM_10	internal tank, earthenware mortar under the bricks of the floor of the tank
	HM_12	internal tank, tank wall - mortar between the blocks with river sand
	HM_13	internal basin, wall of the basin - coating in *cocciopesto*
	HM_14	external tank, base layer under the travertine blocks
	HM_15	external tank. mortar between blocks of travertine US5020 and the first floor of the tank US 5017
	HM_16	external tank, mortar between the first floor of the tank US 5017 and the second floor US 5014
	HM_17	external tank, under the recycled column that is part of the wall
Roman Baths complex	**HM_TA_1**	Floor plan, US 4021, Augustan age
	HM_SO_1	Roman phase, possible ancient restoration from the Byzantine era
	HM_SO_2	I Byzantine phase
	HM_SO_3	
	HM_SO_4	
	HM_SS_5	Roman phase, possible ancient restoration from the Byzantine era
	HM_CE_6	I Byzantine phase
	HM_NS_7	
	HM_SE_8	
	HM_SE_10	II Byzantine phase, vertical joint
	HM_SE_11	II Byzantine phase
	HM_N_9	Roman phase, possible ancient restoration from the Byzantine era
	HM_SN_12	
	HM_SE_13	
Nymphaeum	**HM_TA_2**	Above the supporting arch, west side, Severian age
	HM_TA_3	North side foundation, Augustan age
	HM_TA_4	North side foundation, Severian age
	HM_TA_5	South side wall, Severian age
	HM_TA_6	
	HM_TA_7	South side wall, Proto-Byzantine period
	HM_TA_8	Top of the north-east corner wall, Severian age
	HM_TA_9	Top of the east corner wall, Proto-Byzantine period

D. Results and discussion

The analysed mortars under OM are characterized by a binding matrix with microcrystalline texture, homogeneous structure and interference colours typical of carbonate minerals, indicating the use of air lime as a binding material. The presence of lime lumps is observed (1 to 7 mm); the inert fraction appears not well selected with a bimodal distribution, mainly consisting of quartzites and large *cocciopesto* fragments (as in the case of the HM_10 sample). The mineralogical profile obtained by XRPD analyses, shows the calcite as the predominant mineralogical phase (up to 70 wt%) ascribable mainly to the binding fraction. Dolomite, quartz, feldspars, micas and amphiboles can be associated with the aggregate fraction. The small quantities of phyllosilicates and oxides detected can be associated with accidental additions to the mix together with the aggregate. The presence of diopside in the HM_10 sample confirms the presence of *cocciopesto* in the mortar, as already highlighted by the petrographic analyses. The calcium sulphates (gypsum and bassanite) detected in some samples could indicate the presence of alteration forms probably related to the thermal waters adjacent to the archaeological site.

The SEM-EDS observations of the selected samples highlighted the nature of the binder used (see Fig.3): most of the samples present a compositionally homogeneous binder matrix consisting mainly of calcium. However, in some samples, the calcic binder is associated with clayey phases in which the microanalysis detects the presence of calcium, silicon, aluminium, and iron. The micro-analyses carried out on the analysed lumps detected the presence of calcium, suggesting the use of aerial lime, and of silicon, probably migrated within the porosity of the same lump. In the HM_10 sample, in which fragments of *cocciopesto* have been detected, the matrix is not homogeneous and it consists of calcium in localized points, and aliquots of silicon, aluminium, magnesium and iron attributable to the reaction occurred with the clay phases present in the mixture. In the samples in which the presence of dolomite was detected by XRPD, a probable dedolomitization process occurred: the dolomite aggregates present reacted edges and the magnesium is detected mostly inside the crystal.

The wet binder extraction procedure was carried on selected and significant mortar samples and the characterization of the fine binder fractions (SGs) was performed by XRPD. The presence of calcite, amorphous phases (very abundant in the sample HM_10_SG), clayey phases and phases related to the presence of LDH (layered double hydroxides, hydrated neoformation phases) have been detected. LDHs can be formed by pozzolanic reaction between lime and reactive clay minerals which, associated with the presence of relevant fractions of the amorphous phase (73%), allow the identification of pozzolanic reaction processes.

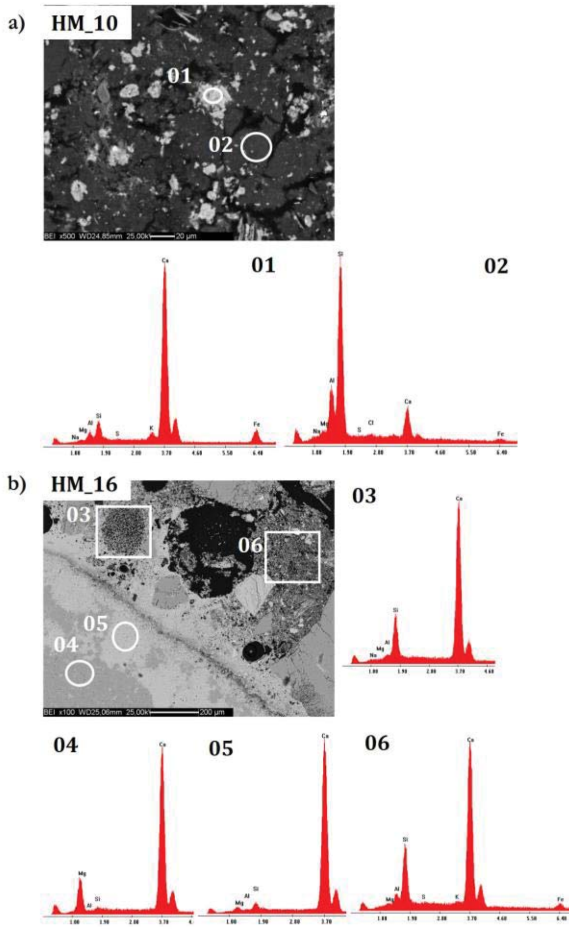

Fig.3. Backscattered electron micro-images of the binding matrix and EDS microanalysis of the highlighted portions: a) mortar sample HM_10 with microanalysis of the binding matrix 01 and 02; b) sample of mortar HM_16 with microanalysis of lump (03), dolomite crystal (04 and 05) and of the binding matrix (06).

The LDH phases represent a problem in radiocarbon dating mortars as they can capture CO_2 over time by introducing a younger carbon into the system and therefore post-dating the analyses compromising the final result [13], [20], [21]. For these reasons, a further purification process by heat treatment (at 550°C) for the elimination of the LDH phases was performed [13]. The binding fractions obtained with the appropriate purification procedures are apparently free of pollutants that could post- or back-date the radiocarbon age.

The radiocarbon dating results, where the radiocarbon age was calibrated and is expressed in BC, are unreliable, dating the mortars more than 10000 years ago (i.e. BC 8543 – 8266 with 2σ range). The problem was identified in the presence of the thermal baths nearby the archaeological site, from which the water could have been taken during the preparation of the building mixes, polluted itself by the presence of geogenic carbonate of about ten thousand years ago.

III. CONCLUSIONS

The archaeometric study presented and discussed regarding the analysed mortars at the archaeological site of Hierapolis of Phrygia in Turkey was complex from a scientific and methodological point of view. Nevertheless, it was possible to obtain significant data in terms of characterization of the binding material and absolute dating, able to contribute to the interpretation of the architectural structures. On the light of the analyses carried out, the binding mortars of the structures are in the most cases of an aerial type, with a very similar composition, suggesting the selection of nearby local raw materials and the use of coherent production techniques. The ^{14}C results of the selected mortars show unreliable dates due to the probable use of the thermal waters polluted by the old geological signal.

The research will progress with the analyses on the travertine elements of the remains, to complete the characterization of the masonry. Then, results on constitutive materials (mortar and stone) will also contribute at setting parameters needed for the implementation of analytical and numerical models able to assess and/or simulate the mechanical behaviour of the still standing structures of the archaeological site, to promote possible interventions able to recover the safety conditions needed for their use.

IV. ACKNOWLEDGMENT

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