Study of historical mortars from the Roman *Villa* of *Frielas* (*Loures*, Portugal)

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***Abstract* – The Roman *villa* of *Frielas* is an archaeological site from 3rd – 6th century AD located in *Loures*, Portugal. The *villa* is on excavation since 1997. A total of eighteen mortar samples were collected from the different structures of the *villa* with different functional uses (render, filler, and floor) and analyzed by a multi-analytical approach. The results revealed a similar composition of binder, while differences in aggregates allowed to establish several groups. The information was analyzed to understand if historic recipes from ancient Roman treatises as described by Vitruvius were followed in the manufacturing process, or if traditional formulae were adjusted and adapted to meet a specific demand or due to resource constraints.**

Key words: Mortars, Roman *villa*, materials, provenance, raw materials, archaeometry.

I. INTRODUCTION

The Roman *villa* of *Frielas* (*Villa Romana de Frielas*), is an archaeological site that is on excavation since 1997. Located on municipality of *Loures* under Lisbon District and on the right of the *Tagus* River across the *Trancão* River. It was part of the territory of *Olisipo* (present-day Lisbon) which included a vast area ranging from *Torres Vedras* to the north, to the vicinity of *Alenquer* in the east during the roman time [1]. The territory of *Loures* had a strong occupation in Roman times, namely in Imperial times, with little evidence from the 2nd century A.D during which there is an intense economic activity proven by the abundant import of *terra sigillata*. The *Frielas villa* fits into this chronological panorama, even revealing an extended occupation [2].

Analysis of amphorae material and *Terra sigillata* results in continuity in the consumption patterns of this *villa*, from the 1st century A.D. to the 5th century AD; following which there appears a set of indications that point to the gradual abandonment of the *villa* until the beginnings of the 7th century AD. Within the wide period of effective occupation of the *villa*, two construction phases initial 1st century AD- 3rd century AD and the 2nd phase 3rd century AD - 5th century AD had been distinguished [3].

A total number of eighteen mortar samples from the Roman *villa* of *Frielas* were collected. The samples were analyzed by employing a multi-analytical approach to determine and characterize the separate components, namely binder, aggregates, and additives. As the aim of the study, the samples were chosen from the different construction areas, functionality, and structures to be compared and find out the similarities and differences. To make a correlation with the chronological sequence of the site, the results were discussed as evidence of manufacturing techniques, production technologies, and possible raw materials provenance.

II. MATERIALS & METHODOLOGY

All the mortar samples were collected from the 2nd phase of the *villa*, as the other phases have no traces or availability of mortar according to the archaeological record. The samples were collected from the different structures (water channel, peristyle, staircase mosaic floor and mural painting wall) of the *villa* with different functional uses (render, filler, and floor). Before initiating any processual preparations, the samples were cleaned, dried and observed for macroscopic characteristics such as color, texture, identical stratigraphy, type of aggregates, and additives. Finally, all the samples were photographed and documented.

Two different types of powders were prepared by following different procedures. For the Thermo-Gravimetric Analysis (TGA), only global fraction (GF) and for X-ray diffraction analysis (XRD) both global and fine fraction (FF). Global fraction represents the bulk sample while the fine fraction, containing particles smaller than 0.063 mm has a higher probability of binder enrichment [4,5]. About 20g of a fragmented portion from each sample were used for acid attack and granulometric analysis. Polished sections (cross-section) for stereo-zoom microscopy and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectrometry (SEM-EDS), and thin sections for petrographic microscopy were prepared to identify the mineralogical composition of the mortar samples. XRD as a complementary to microscopical techniques was used [5,6].

Thermogravimetric analysis (TGA) is a thermal method in which the mass of sample is monitored as a function of temperature, while the sample is subjected to a controlled temperature program. For mortar studies, the main weight loss is expected between 600°C and 900°C, confirming the decomposition of calcium carbonate ($CaCO_3$) into calcium oxide (CaO) and carbon dioxide (CO_2), which is indicative of a calcite composition of the lime-based binder [6]. Equation (1) is used to calculate the calcium carbonate content in terms of the percentage of calcite.

$$CaCO_3\% = [P\ (CO_2 \cdot M(CaCO_3)]/M\ (CO_2) \qquad (1)$$

P (CO_2) is the percentage of mass loss between 600° and 900°C, M($CaCO_3$) is the molar mass of calcium carbonate (100.082 $gmol^{-1}$), and M (CO_2) is the molar mass of carbon dioxide (44.02 $gmol^{-1}$).

SEM-EDS was used for elemental analysis, elemental mapping, and image acquisition of the mortar sample. SEM-EDS can show a higher magnification image up to x100,000 times with higher resolution and wider depth of focus, compared to optical microscopy [6].

The chemical process of attacking mortars with an aqueous solution of hydrochloric acid is used to obtain information about the ratio of the soluble fraction (carbonate binder, salts, and organic compounds) to insoluble residue (non-carbonated aggregates) present in the mortars [7]. According to the method developed by Hanna Jedrzejewska [8] the soluble fraction will be expressed as a percentage and calculated using the equation (2).

$$SF\ (\%) = 100 - \Sigma\,(IR\ (\%) + Carbonates\ (\%)) \qquad (2)$$

These parameters are the percentage of the "soluble" amount of sample in acid (without CO_2 generation), the amount of sand (the insoluble residue in acid), and the proportion of carbonates calculated by TGA [7,9].

III. RESULTS

According to the visual inspection, the samples were mainly divided based on their physical color. Group A, ceramic rich reddish mortar (*opus signinum*). Group B quartz (silicious aggregate) and brownish mortar (render) as group C that contains shell & black lithics. Upper layers of the stratified samples are in the group D. Some samples contain visible cracks, lime nodules and chromatic layers. The samples with ceramic fragments were the strongest in terms of physical strength, samples with siliceous aggregates were mostly with medium physical strength and the brownish samples were weak and fragile.

By means of the Optical Microscopy (OM), stereo zoom microscopy observation and insoluble residue from the acid attack analysis, the grain size and shape of the aggregates were observed mainly angular to sub-angular. The petrographic microscope and SEM-EDS shows the most abundant minerals in all samples were quartz and feldspars (K-feldspar and plagioclase). The presence of silicon and oxygen is corresponding to quartz while feldspar has been detected with the presence of aluminum and silicon, in association with either potassium that forms alkali feldspar, or sodium that forms plagioclase feldspar. X-ray diffraction (XRD) results confirms the mineralogical composition of K-feldspar (orthoclase and microcline) while microcline was more abundant compared to orthoclase (Fig.1).

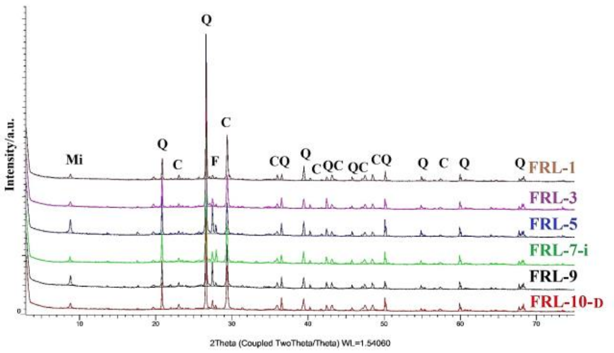

Fig. 1. XRD patterns (Global fraction) of ceramic rich samples (Group-A), (Q-quartz, C-calcite, F-feldspar, and Mi-mica).

Also, ceramic fragments were detected by their siliceous inclusions (e.g., quartz and feldspars) in an aluminum-potassium matrix according to clay mineral properties. In ceramic-rich samples, micas (muscovite and biotite) were also identified within the ceramic inclusions as well as in the binder matrix. Cracks developed alongside the ceramic fragments and sometimes within the binder matrix. Though, there is no significant zoning, boundary marks, or pozzolanic reaction observed in SEM-EDS images.

Samples with shell fragments and calcitic bio-clasts (Ca rich) belongs to group C mortars. Samples containing basaltic rock fragments appear with minerals that might be associated with olivine and pyroxene which was further confirmed with the help of other techniques such as XRD and petrographic analysis. The presence of Mg and Fe with other elements associated with Si, Ca and Al, is indicative of mafic minerals and plagioclase, respectively. The rounded shape of this kind of aggregates is almost similar in the group C mortars. The morphological characteristics indicate their significant transportation from their source of origin.

The point and multipoint analysis revealed that the binder composition was similar to all samples which is mainly composed of Ca as an indicative of lime binder. A high amount of Ca in the binder composition with a very low percentage of Mg was noted. The presence of other elements such as K, Al, and Si, and Na may be influence from aggregates, or even it could be corresponding to a reduced detrital component of the calcined limestone. Multipoint and point analysis were performed to identify the lime lump composition of the samples; the result demonstrates that the lime lump is mainly composed of Ca, C and O (Fig.2).

(a)

(b)

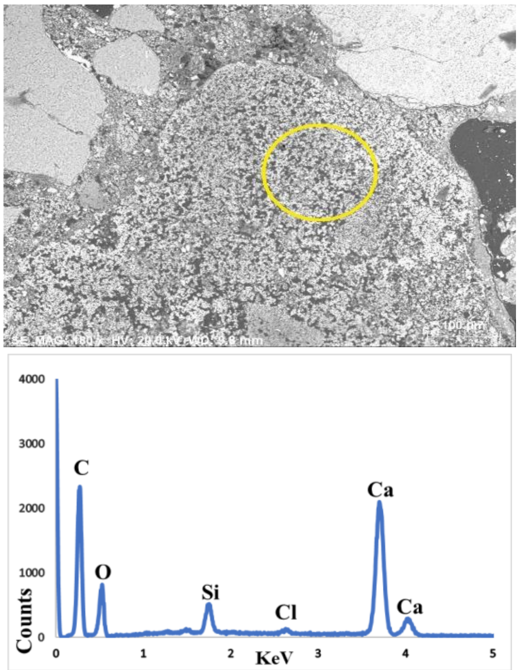

Fig. 2. Lime lump, FRL-17 (group-C) a) yellow line indicating lime lump, b) multi-point analysis spectrum of the spot marked in image 'a'.

In TGA the calculated percentage of calcium carbonate as a function of the mass losses in the temperature range between 600°-900°C, recorded from the thermogram showed that the $CaCO_3$ amount varies from 12.7% (FRL-5) to 64.6% (FRL-19-U) (Fig. 3) among the samples.

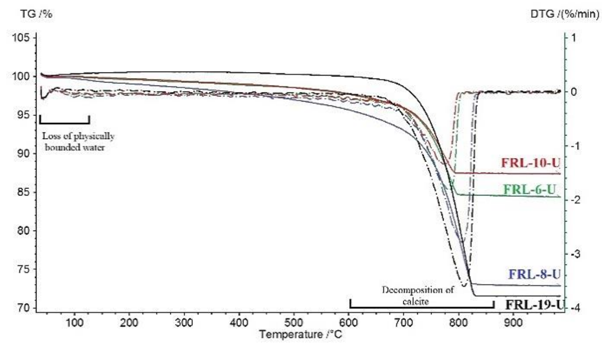

Fig. 3. TG/DTG curves of binder-rich upper layers (Group-D) samples FRL-6-U (green), FRL-8-U (blue), FRL-10-U (red), and FRL-19-U (black), continuous curves representing TG and dashed curve representing DTG data.

The calculated average of the soluble fraction ranges from 18.35% (FRL-1) to 76.60% (FRL-19-U) whereas the insoluble residues vary between 23.30% (FRL-19-U) to 81.35% (FRL-1).

IV. DISCUSSION

Based on the results obtained from OM, XRD, TGA, and SEM-EDS, mortar samples from the Roman *villa* of *Frielas* presents in general a calcitic lime binder; the significant detection of calcite by XRD associated with the TGA thermogram, showing greater mass losses in the characteristic range between temperature 600°C - 900°C as well as the presence of Ca on elemental maps of EDS points to a binder with calcitic composition.

Moreover, the acid attack analysis allows the determination of the soluble fraction. Though, the partially dissolved carbonate aggregates (e.g., shell fragments) might overestimate the amount of calcium carbonate present in the samples. The amount of calcium carbonates from acid attack (soluble fraction), XRD, and TGA can be compared to see the differences (Fig. 4).

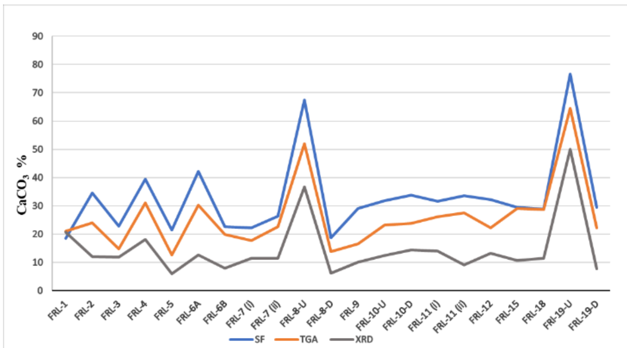

Fig. 4. Amount of $CaCO_3$ (weight %) of the studied samples. Comparison of TGA, acid attack (Soluble fraction), and XRD. XRD is giving semi-quantitative analysis from GF (Global fraction).

The samples containing crushed ceramic fragments correspond to the water channel structure as their functions are associated with a waterproofing mortar and *opus signinum* [10]. The inner faces of the water channel are coated with *opus signinum*, functioning as a waterproofing element (FRL-3 and FRL-5) that contains ceramic fragments (> 4mm). While a layer (FRL-2) shows different features which have a predominance of siliceous minerals aggregates, associated with very few and smaller random crushed ceramic fragments. That indicates a different preparation of mortars that can be a later renovation which is left unfinished.

According to several authors, the roman mosaic floor composition has several mortar layers (Fig. 5.a). The second layer as *'bedding'* is a thin layer which is rich in lime. Usually, in this layer the mosaic design is being marked and the tesserae design inserted before the mortar get hardened. The third layer *'Nucleus'* is an impermeable mortar layer of powdered pottery and lime, to protect the mosaic from the soil water (humidity) [11,12]. In that case, (FRL-8) shows differences, mainly in the layering and absences of ceramic in 'Nucleus' layer (Fig. 5 b and c).

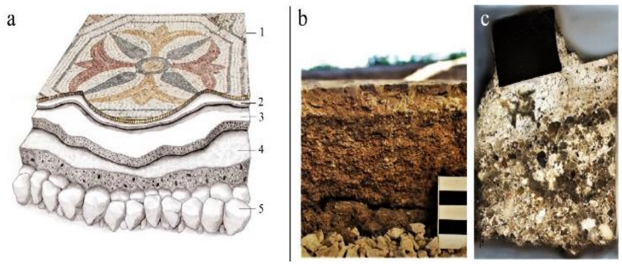

Fig. 5. a) Stratigraphy of a Roman mosaic floor according to Vitruvius's description. ('a' Adapted from Caldeira et. al., 2019). 1. Tessellatum, 2. Bedding, 3. Nucleus, 4. Rudus, 5. Statumen, b) section view of the sample FRL-8 (mosaic floor) in situ, from the site, c) prepared polished section of the sample FRL-8, containing stratigraphic layers of the floor.

For the determination of the provenance study of the samples, the lime used in the mortars of the Roman *villa* of *Frielas* is calcitic in nature, thus corresponding to an aerial lime. The degree of purity of the lime, without a significant siliceous (detrital) contribution, suggests limestones as the raw material been used. This lithology according to available cartography is abundant in the surrounding geological context. Namely represented by limestones of formations from *'Calcário de Alfornelos'* and *'Formação de Bica calcário'* [13,14].

The morphology of the aggregates of the samples are mainly angular to sub-angular or even poorly rounded that might indicate a short distances transportation from the source of origin but in the geological context and surroundings of the *villa*. On the right bank of the Tagus River, sand is available in the lower Miocene units between *Lumiar*, *Ameixoeira*, *Aeroporto*, *Charneca*, and *Camarate*. Therefore, it can be assumed that the possible sources of sand (quartz and feldspar) are from the right bank of the Tagus River.

The basaltic rock fragments are observed almost in rounded shape confirming by SEM-EDS, petrographic and visual observation. These rounded basaltic rock fragments indicate significant transportation from their source of origin. In geological context, the *'Formação de Benfica'* is based on volcanic discontinuity over the *'Complexo Vulcânico de Lisboa'* (CVL). Since it is in the vicinity of the studied site that conforms the possible geological sources of these basaltic rock fragments can be from CVL.

Samples with shell and basalts were previously described as group C contain carbonated organic materials e.g., shell fragments. Their sources can be assumed from a similar deposit with higher influence of CVL and presence of shells. The sample with crushed ceramics corresponding to the hydraulic structure and *Opus signinum*. Their size and shape differ from the functionality of the mortar. These ceramic fragments are assumed as brick and tiles fragments.

To reveal the production technology of mortar, technique of Jedrzejewska [8] was used to determine the binder to aggregate ratios. The ratios obtained from the results show two different patterns, 1st pattern of samples ratio is 1:3, and 2nd pattern of samples ratio is 1:1 to 1:7. According to Vitruvius's description, 1:3 can be an ‘ideal proportion’ in the case of pit sand. While the studied samples are resulting in the analysis that can comply with the river sand. The binder to aggregate ratio 1:3 can be considered as a pattern of contemporary structural mortar which might be prepared following roman recipe, while the rest of the samples, with other proportions, can be an indication of repair, rebuild (extension), or renovation of the structures.

The inaccuracy of the proportions of aggregates added to the mixture can also be due to the inaccessibility to traditional recipes and a construction based on empiric and intuitive knowledge and a “trial and error” practice or the result of an inexperienced laborer. The remoteness of this rural environment might have influenced the lack of qualified masons, who were most likely to live in the bigger cities [9].

Samples were also studied in terms of their level of hydraulicity. The hydraulicity of the mortars was calculated based on the results obtained by TGA analysis. It was determined that the “inverse trend of hydraulicity of mortars is being augmented exponentially with CO_2”, in which the lower the ratio is, the higher the hydraulicity. If the ratio of CO_2/H_2O is between 1 and 10, mortars can be accepted as hydraulic [15,16]. The calculation of CO_2/H_2O in relation to CO_2 most of the studied samples including ceramic-rich samples have hydraulic characteristics.

V. CONCLUSION

The study focused on analyzing the mortars from the Roman *villa* of *Frielas* to gain insights into their composition, origin, chronology, and production techniques. The research aimed to characterize the materials used, compare them to ancient recipes provided by Vitruvius, and assess their suitability for future consolidation and repair. The findings revealed that the mortars exhibited uniformity in their chemical, mineralogical, and microstructural composition across different structures, suggesting contemporaneity. However, it was evident that the masons did not strictly adhere to Vitruvius' guidelines for production, relying instead on their intuition and available resources.

VI. ACKNOWLEDGEMENTS

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