Characterization of Roman mortars from the historical town of Mertola

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ABSTRACT: Ancient mortars from two Mertola's important Roman monuments, the River Tower and the Cryptoportic, were characterized by optical microscopy, scanning electron microscopy, X-ray diffraction, thermogravimetric and chemical analyses. The results show that all mortars are calcitic aerial lime mortars and that the aggregates are composed of quartzitic river sand and crushed schist. Samples from the River Tower and particularly sample taken from the outer layer of the Cryptoportic show the presence of crushed ceramics and neoformation pozzolanic reaction compounds.

1 INTRODUCTION

Mertola is an historical town standing high on the rocky schist margins of Guadiana river (figure 1a), a natural frontier between the South of Portugal and Spain. The immense legacy from different periods including Roman, Islamic and Christian makes it unique among Portuguese cultural heritage and has been the subject of intense archaeological research.

In this communication, we report the study of ancient mortars from two important late roman monuments, the River Tower and the Cryptoportic.

The River Tower (figure 1b) are the remains of a fortified roman harbor dating presumably from V-VI AC. This enormous and solid structure had a total length of 45 m and was composed of six arches and six towers which were connected to the roman defense walls of the town. It was used during the roman period to protect the water supplies, to tax and control the merchant boats, to load and unload merchandises and to protect the town (Veiga,1880). The structure is composed of schist and clay masonry. Granite and marble blocks are also present. The very high quality, size and regularity of these blocks indicate that they belonged to a former building of very big proportions (from Imperial Period) whose location is uncertain but presumably from the Acropolis.

The Cryptoportic is a semi-underground gallery with very thick walls linked by a vault (figure 1c). This structure confined, at north, the roman forum and was an artificial platform which supported an important religious complex from the Bizantine period. The type of materials (schist and clay masonry with big granite and marble blocks) and the construction technology is similar to the ones used on the River Tower indicating that these structures were contemporary. Not long after its construction, the gallery of the Cryptoportic was sealed, the walls were covered with a waterproof mortar and it was converted to a cistern. This 32 m long and 2.7 m wide cistern had a water storage capacity of 138.000 liters.

The study and identification of the materials and the characterization and mapping of degradation forms are of utmost importance to guarantee the conservation of these monuments and can give valuable information about their history.

Figure 1. a) General view of Mertola; b) River Tower; c) Cryptoportic

2 SAMPLING METHODOLOGY

The sampling of the mortars was carried out with the aid of IPPAR technicians using a hammer and a small chisel. The size of each sample was the minimum that could guarantee the success of the analyses and the confirmation for future studies. To avoid contamination by capillary rise, two masonry mortars were taken from the upper joints of the inner walls of two pillars of the River Tower (MT1 and MT2 mortars). Two other mortars were taken from the Cryptoportic, one hydraulic mortar from the surface layer (MT3 mortar) and one mortar from the joint of the inner layer of the wall (MT4 mortar). All the samples showed high mechanical resistance and adhesion to the substrate.

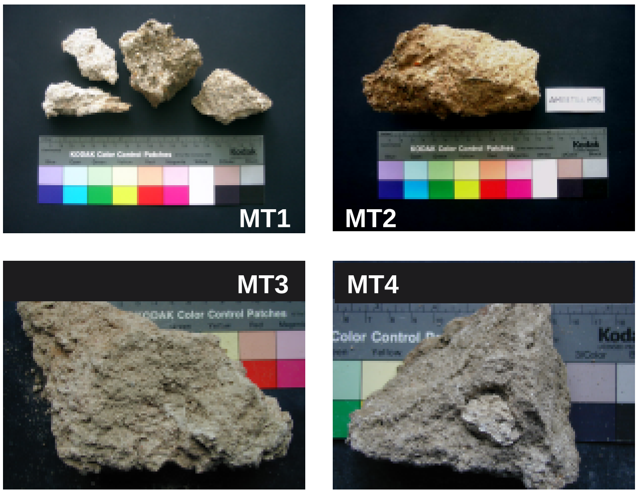

Figure 2. Detail of the mortar samples collected.

3 CHARACTERIZATION METHODOLOGY

The mortars were thoroughly observed in laboratory using an Olympus stereo-zoom microscope and disaggregated with care so as to avoid breaking the existing aggregates. During disaggregation, it was observed that all mortars exhibited high mechanical resistance.

Scanning electron microscopy observations were performed on a scanning electron microscope (SEM) JEOL JSM-6400 coupled with a OXFORD energy dispersive spectrometer (EDS) x-ray detector.

X-ray diffraction (XRD) was carried out with a Phillips diffractometer with Co Kα radiation and a speed of 0.05 °/s, from 3 to 74, 2θ. Two types of fractions were analysed, the fraction corresponding to the mortar as collected, designated as *overall fraction* and obtained by grinding the disaggregated mortar to pass in a 106 µm sieve and the other fraction, designated as *fine fraction*, which has a higher binder concentration and was obtained from the fines of the disaggregated material passing a 106 µm sieve. The *overall fraction* of each sample was also used for thermal analysis (TGA-DTA) performed in a SETARAM TGA-DTA analyser, under argon atmosphere, with heating rate of 10°C/min, from room temperature to 1000°C.

Thin sections and polished surfaces of the mortars were prepared by vacuum impregnation with an epoxy resin. These were observed with a Nikon petrographic microscope in transmission, using crossed polarizers and images were recorded digitally.

For the chemical analysis, mortars were carefully disaggregated and all types of impurities and limestone grains were separated. Samples were afterwards attacked with warm diluted hydrochloric acid (1:3) to separate from the lime paste the fraction corresponding to siliceous aggregates.

All mortar samples, after being prepared, were dried at 40ºC for at least 12 hours, with exception of the samples for chemical analysis, which were dried at 105ºC.

4 RESULTS AND DISCUSSION

4.1 *Optical microscopy*

Preliminary observation of the samples and of polished surfaces under a stereomicroscope showed that all the mortars contain round nodules of lime which may indicate that the lime was slacked with a minimum amount of water to convert all CaO into $Ca(OH)_2$ (Schouenborg,1993 ; Elsen, 2004).

Samples MT1 and MT2 taken from the River Tower were quite similar. These mortars show a high degree of heterogeneity and the aggregates contrast in dimension and petrographic classification (mostly quartz and schist and smaller quantities of granitic lithoclasts and crushed ceramics). The roundness of the siliceous aggregates and the presence of schist are consistent with the use of river sediments combined with local crushed stones. The presence of crushed ceramics in these mortars was expected because its use was common in roman times particularly in a context of water-related constructions. These would enhance the hydraulicity of the mortars thus making them more watertight.

On the other hand, the mortars taken from the Cryptoportic (MT3 and MT4) were compact and homogeneous with aggregates of very small dimensions, mainly quartz, feldspars and mica. As in the other samples the roundness is consistent with river sand. The major difference between these mortars was that sample MT3 showed a higher amount of crushed and powder ceramics (*cocciopesto*), which rendered the mortar a reddish-pink color. This sample was taken from the outer layer of the inner wall of the Cryptoportic, which was used as a cistern, and must have hydraulic properties, while MT4 belonged to a load-bearing part of the construction which was not in contact with the water. This selective use of ceramics shows that by the fall of the Roman Era, the local populations still possessed a highly technical and semi-empirical knowledge that enabled them to formulate the mortars in accordance to their future use and functionality.

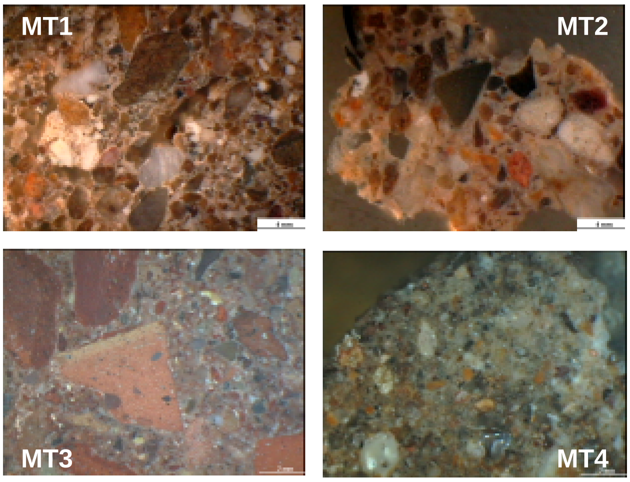

Figure 3. Detail of polished sections showing crushed ceramics (except for sample MT4), lime nodules and siliceous sand.

Observation of thin-sections under a petrographic microscope allowed a further insight on the mortars composition.

Samples MT1 and MT2 were very similar and presented a higher proportion of aggregates in respect to binder. The samples presented lime nodules and carbonate aggregates with irregular contours. The former indicate that the lime used was dry-slaked while the later indicate that the decarbonation of the calcareous rock during lime production was incomplete possibly due to low temperature or insufficient calcination time. The morphology of the aggregate grains varied from round to semi-angular and were dominated by quartz in its various forms (monomineral or quartzite rocks) along with feldspars and crushed ceramics and in smaller amounts schist, mica, chlorite, greywacke and amphiboles. It was possible to identify products of boundary reactions at the interface of both quartz and crushed ceramics.

The presence of amphiboles was the most striking observation. According to the geological chart of Mertola and the geology of the South of Portugal it is unlikely that the original source of these aggregates came from the surroundings of Mertola. Considering that the most probable source is located 40km North of Mertola the most plausible explanation is the transport of this material by the nearby great water line, the Guadiana River.

For sample MT3 the aggregates were dominated by crushed ceramics and some quartz. The other aggregates were identical in composition and morphology to the ones observed in the previous samples, indicating a similar origin of the employed sands. What makes this sample unique is the extension and distribution of pozzolanic reaction products. Instead of being located at the lime-crushed ceramics boundary, they are spread all over the binder and in some cases there is a complete dissolution of the ceramics onto the lime, creating a binder composed of lime with high amounts of dissolved silicates and phyllosilicates.

Sample MT4 is different from the other samples because it does not have crushed ceramics and the aggregates are mainly quartz and schist. Traces of carbonates and amphiboles were also detected

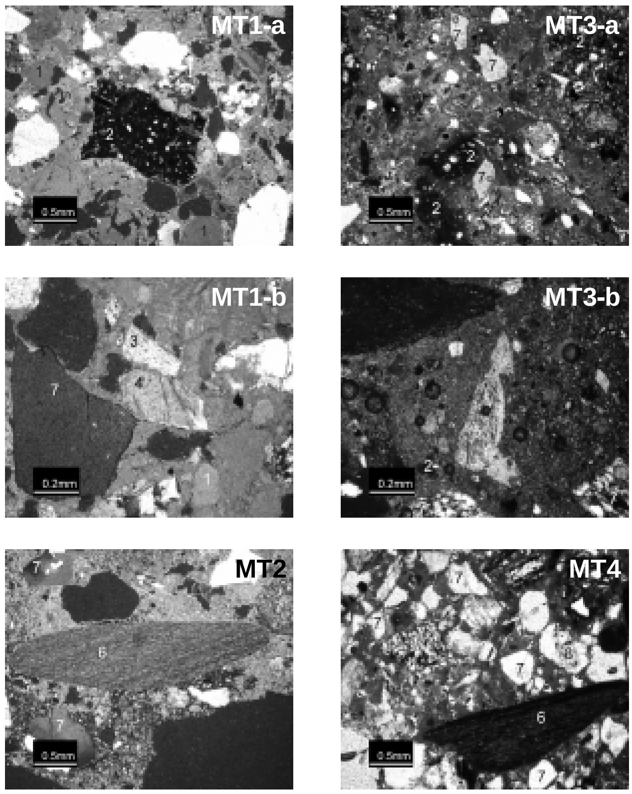

Figure 3. Thin-sections of the mortars. The MT1-a micro-photo shows a ceramic fragment, partially absorbed, between several quartz aggregates and two CaO nodules. These ceramic fragments are very abundant in MT3 (see MT3-a) frequently with an aureole around them. The presence of carbonate suggests an incomplete decarbonation (see MT3-b and text). The presence of schist (see MT2 and MT4 photos) are understandable if one considers the local geology but the widespread occurrence of amphibole is coherent with the use of sediments transported from geologically diverse areas.

1- CaO nodule; 2- Ceramic fragment, 3- Phyllosilicates, 4- Amphibole, 5- Carbonate, 6-Schist, 7 Quartz, 8-feldspar

4.2 *XRD analysis*

Table 1 presents the mineralogical composition of the overall fraction of the mortars determined by XRD analysis.

Table 1. Mineralogical composition of the mortars (wt%)

Crystalline phases	River Tower		Cryptoportic	
	MT1	MT2	MT3	MT4
Quartz	+++	+++	++/+++	+++
feldspars	+	+/++	+	++
Mica	+	+	vtg/+	+/++
Chlorite	vtg/+	vtg/+	vtg	vtg/+
kaolin	-	-	-	vtg
HCA *	vtg	vtg	vtg	-
Hematite	-	-	vtg	vtg
amphiboles	vtg	vtg	vtg	vtg
calcite	++/+++	++	++/+++	+/++

+++ abundant, ++ present, + small amount, vtg traces, - undetected

* HCA= Hydrated calcium carboaluminate

The results show that the binding material of the mortars is essentially calcite and that quartz is the main component of the aggregates. The presence of hydraulic compounds like hydrated calcium carboaluminates and chlorite confirm the thin-sections observations that showed the presence of chemical reactions at the ceramic-matrix interfaces (Moropolou, 1995). The results also confirm the presence of amphiboles which corroborates the thesis that the siliceous aggregates are river sediments.

4.3 *Chemical and grain size analysis*

Table 2 shows the chemical analysis of the soluble fraction which can give valuable information about the composition of the mortars and its environment.

Table 2 Chemical composition of the soluble fraction of the mortars (wt%)

Weight %	River Tower		Cryptoportic	
	MT1	MT2	MT3	MT4
CaO	19.28	11.25	21.75	18.05
Fe_2O_3	0.07	.13	0.46	0.20
MgO	0.36	0.58	0.62	0.59
K_2O	0.34	0.15	0.65	0.19
Na_2O	0.15	0.11	0.17	0.21
Cl^-	0.07	0.06	b.d*	0.13
SO_3	0.16	0.25	0.86	1.61

* b.d.=below detection limit

The high calcium contents contrast with the low magnesium contents showing that the ligand is essentially calcitic lime.

The overall low contents of chloride ion are similar to other studies (Alvarez, 2000, Bruno, 2004) and indicate low environmental salinity. The amount of soluble SO_3 is also low. Considering that SO_3 is an indicator of the presence of gypsum in the mortars (Maravelaki-Kalaitzaki, 2003), one can conclude that not only gypsum was not used during the formulation of the mortars but also that its formation by the reaction between the calcitic matrix and the atmospheric SO_2 is negligible, which is consistent with a non-polluted environment.

The grain size distributions of the insoluble residues are presented in figure 5. As was mentioned in other studies (Bakolas, 1998; Maravelaki-Kalaitzaki, 2003; Benedetti, 2004), it is an important analysis to obtain information on single components of mortars and their mixture ratio during mortar preparation. As can be seen, the majority of the aggregates of samples MT1, MT2 and MT4 have dimensions between 0.63 and 2.5 mm. Few fragments have diameters greater than 5 mm. The grain size distribution for sample MT3 reflects the fact that, unlike the other mortars, this mortar presented a large amount of ceramic fragments (cocciopesto) with dimensions between 2.5 and 5.0 mm.

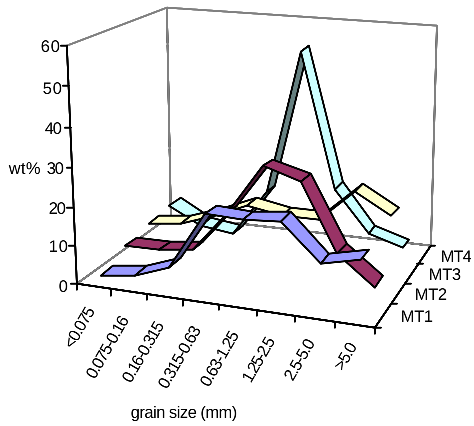

Figure 5. Grain-size distribution of the insoluble residues

4.4 *Scanning electron microscopy*

SEM analysis can give valuable information about the mortars materials namely binder, aggregates and reaction compounds and allows the observation of their forms, sizes, textures and distribution in the mortars.

Analysis of the mortars by SEM/EDS showed that all mortars have a compact microstructure with aggregates well embedded in the matrix. It was possible to identify aggregate fragments like quartz, mica and feldspars. Large areas of the surface and pores were filled with well defined calcite crystals formed possibly by a carbonate dissolution/recrystallization process of the binder. The river tower mortars (MT1 and MT2) presented biological microorganisms colonies and needle shaped calcium silicate crystals growing in small cavities formed by the pozzolanic reactions at the aggregate/binder interface. The aggregates of mortar MT3 were highly corroded and extensive areas of the binder presented a gel-like texture, typical of the formation of pozzolanic neoformation materials.

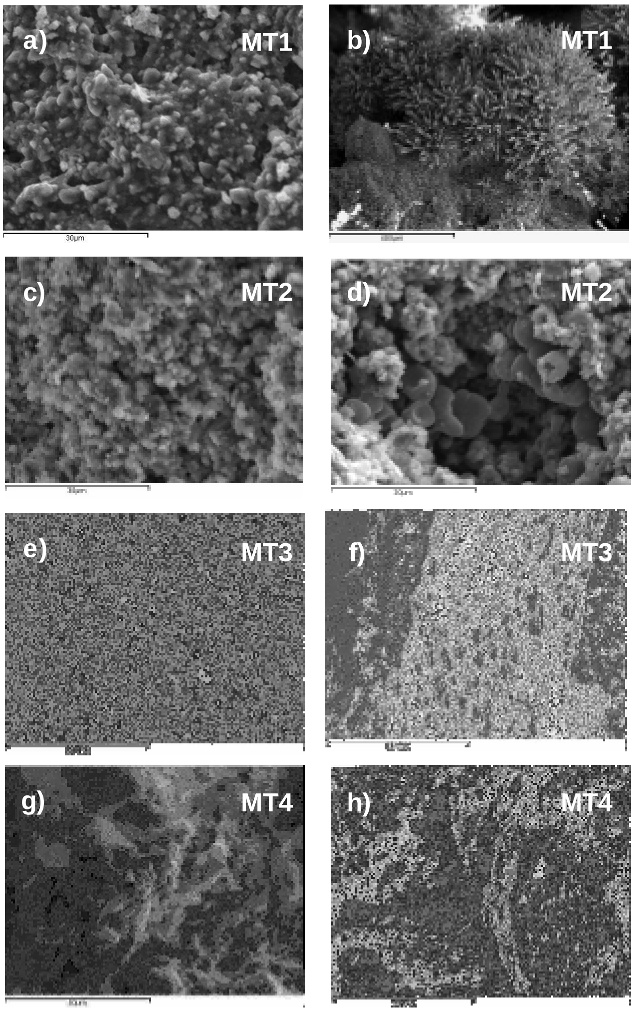

Figure 6. SEM micrographs of the mortars; a), c), e) and g) microstructure of the lime matrices showing the presence of well defined calcite crystals; b) hydrated calcium silicate crystals growing at the surface of an aggregate; d) biological colonization; f) surface of an altered plagioclase from a ceramic fragment h) quartz crystal embedded in the binder.

4.5 *Thermal analysis and mortar composition*

Table 3 presents the weight loss estimated from the TGA curves within the selected temperature ranges and the calcium carbonate content calculated in the temperature range 500 to 900ºC.

Table 3. Weight losses (in %) obtained by TG/DTG and estimated % of $CaCO_3$.

Temperature range (ºC)	River Tower		Cryptoportic	
	MT1	MT2	MT3	MT4
20-220	1.66	1.38	2.02	1.29
220-500	1.06	1.15	1.90	1.32
500-900	14.46	8.99	16.25	10.11
900-1000	0.05	0.05	0.06	0.12
% $CaCO_3$	35	20	37	23

The thermograms are typical of ancient lime mortars with the general absence of important weight loss before the calcite decarbonation at 650-820ºC. Sample MT3 shows higher weight losses for temperatures ranging between 200 and 500ºC which can be attributed to water chemically bound to hydrated aluminum silicates originated from pozzolanic reactions (Moropolou, 1995, Silva, 2005)

The simplified compositions of the mortars (see table 4) were calculated on the basis of the method designated as "Jedrzejewska" (Jedrzejewska,1960) referring to old lime mortars combining the calcium carbonate % estimated by TG/DTA with the residue analysis. This method considers three type of components: "carbonates", acid "soluble fraction" (compounds soluble in acid without formation of carbon dioxide) and "aggregates" (corresponding to insoluble residue of the acid attack).

Table 4. Simplified composition of the mortars (wt%)

Sample	Aggregates (sand + brick)	Carbonates	Soluble fraction
MT1	61	35	4
MT2	75	20	5
MT3	53	37	10
MT4	64	23	13

5 CONCLUSIONS

This study provided interesting information and allowed a further insight on the mortars materials and preparation techniques. In all cases, the binder used was calcitic lime. The presence of round lime lumps indicates that the lime was dry-slaked. Partially dissolved calcium carbonate aggregates were found and are indicative of an incomplete decarbonation during the lime production.

Thin section and polished surface microscopy observations along with XRD analysis showed that two types of natural aggregate sources were used: river sand mainly composed of quartz with smaller amounts of mica, feldspars and amphiboles and crushed schist from the surroundings of the town. It was also possible to observe the addition of ceramic fragments (cocciopesto) and the presence of pozzolanic reaction hydraulic compounds on samples MT1, MT2 and MT3.

Sample MT3 showed an unusual amount of ceramic fragments and fine particles partially dissolved in the binder while sample MT4 had no ceramic fragments. This difference in the formulation of the mortars has certainly to do with the fact that the former was conceived as a watertight superficial layer, possibly when the Cryptoportic was converted to a cistern, and needed to have hydraulic properties while the later was used as a filling mortar.

The use of the same type of aggregates and binder in the formulation of all the mortars is consistent with the archaeological evidence that these monuments were built in the same period.

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