

Mineralogical Comparison Study of Old Mortars from Southern Portugal Cathedrals (Evora e Elvas)

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Abstract. The study of old mortars is a pluridisciplinary task which integrates the knowledge about the history of the monument with the detailed characterisation of the materials nature and properties. The production of mortars depended on the availability of raw materials and hence the mineralogical composition is especially relevant to establish direct correlation between provenance and use. This study on the two cathedrals (Elvas and Evora) underlined the importance of local resources as main source of aggregates. The raw materials for the production of lime seem to be related to trade routes rather than local provenance. The use of specific materials reflects the technological capabilities and developments of the society that built the Cathedrals.

Introduction

The study of cultural heritage materials is a pluridisciplinary task that requires the contributions of different branches of scientific knowledge. The value of Materials Science is underlined by the character of the objects, generally artefacts, pieces or buildings that can be seen as materials developed by the older societies using the technology at their disposal.

Historic mortars are composite materials made of combinations at different proportions of aggregates, binder and eventually some additives. Before the discovery of cement in the 19th century, aerial lime was the main binder. This material was produced by decarbonation of calcitic or dolomitic carbonate rocks followed by slacking with water. The aggregates are siliceous, carbonate sand, with various granulometric distributions, mainly from rivers or crushed rock. To increase the adhesion, mechanical response and durability some substances like brick powder and fragments, volcanic pyroclasts, among others were added. However, each component of the mortar has a geological origin and it is applied more or less processed.

The study of old mortars combines historical, conservation and materials science research which enables the identification of the materials and available technologies during the several construction stages, the diagnosis of the state of conservation and in some cases the knowledge of the commercial routes in the society that built the monument. Underlined to any conservation intervention is the fact that all materials used must be compatible to the original ones and reversible. The church of N^a Sr.^a of Assuncao or Elvas Cathedral is located in the historical centre of the town and is classified as national monument, since 1910. The construction was initiated in 1517 and even

though the building had some further modifications, the actual church still preserves the original structure. Particularly important were the interventions during the 17th and 18th centuries where numerous decorative works were done inside the church including mural paintings and glazed tile panels and marble and wooden baroque altars. The Bishopric of Elvas was extinct in 1881 and afterwards no major interventions were performed.

The church of Saint Maria de Evora or Cathedral of Evora is classified by UNESCO as World Heritage and is located in the historical town of Evora. The Cathedral has a Romanesque-Gothic or Gothic style with strong Cistercian and mendicant orders influence and its construction began in the 12th/13th century. The construction was inspired in Lisbon Cathedral's and in foreign Cathedrals, namely Spanish. The religious complex includes also a cloister. Like other buildings of this kind, after the construction period the Cathedral of Evora had restoration works and several increments that reflect the financial power of a particular period. The major intervention was produced in the 16th Century with the substitution of several renders and the construction of the high choir wooden chair structure.

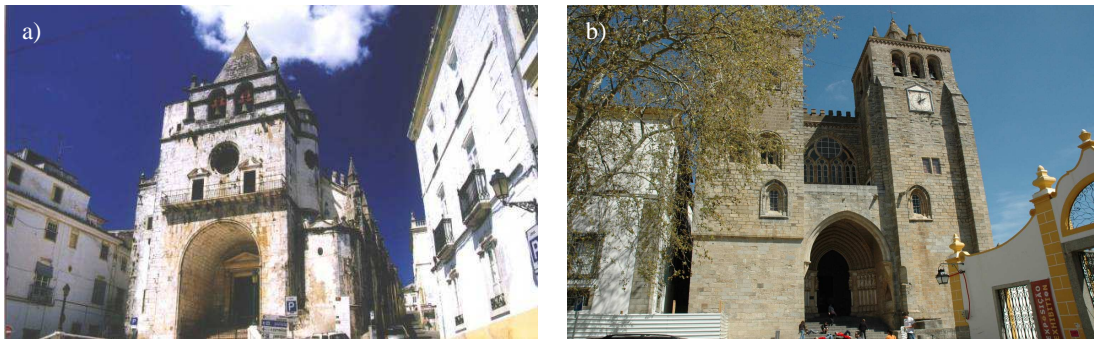


Fig 1. Churches studied in this work. a) Nª Sr.ª of Assuncao Church or Elvas Cathedral, b) Saint Maria de Évora or of Evora Cathedral

The two towns are located in the same region and distance each other only 100 km. However, Evora is located in the middle of a complex of granitoid rocks (gnaisses and granodiorites) with rare outcrops of more mafic rocks while Elvas is characterized by the abundance of high grade metamorphic rocks and alkaline igneous rocks. This work was developed to ascertain if the local geology and accessibility of raw materials was the major factor that influenced the type of materials used in the construction of these religious buildings.

Methods

A great number of physical and chemical techniques can be applied in the characterization of old mortars. The characterization methodology developed by the authors [1] comprises a wide range of techniques that complement each other. However, this work focus only on the mineralogical composition of these materials in what concerns to aggregates, binder and neoformation compounds and therefore the techniques presented are only X-ray diffraction (XRD), Thermogravimetric analysis with differential thermal analysis (TG-DTG) and optical microscopy.

The sampling was conducted under the control of IPPAR (Portuguese Institute of Architectural Heritage) technicians to assure the probable age of each sample.

After a drying period, each specimen was disaggregated and split into several fractions to be used by different techniques. The stereozoom and petrographic microscopes were used to identify the mineralogy and morphology of the aggregates and study the textural properties of each mortar. The X-ray diffraction was performed to allow a further insight on the mineralogy of the binder and aggregates. A Philips X'Pert diffractometer with Co K α radiation, step of 0.05 $^\circ$ /s, between 2 θ 3 $^\circ$ and 74 $^\circ$ was used. The thermo analytical techniques gave additional information on the composition of the binder. A Setaram TG200 equipment was operated under argon atmosphere and uniform heating rate of 10 $^\circ$ /min from room temperature to 1000 $^\circ$ C.

Results and discussion

Elvas Cathedral

Three samples were collected from Elvas Cathedral: SEL1- terrace pinnacle, SEL2- behind a glazed tile panel and SEL3- ceiling of the main church nave. Table 1 presents the mineralogical composition of the mortars determined by optical microscopy and XRD. By stereozoom microscope, it was possible to identify the most important aggregates like quartz, feldspars, micas and amphiboles. The presence of ceramics (fig. 2a) was also evident and has extreme importance since the addition of this material was a technological way of improving the mechanical quality of the material. The petrographic microscopy improved the capability to identify optically the aggregates and allowed the recognition of typical minerals from the geological igneous and metamorphic environment of Elvas, like amphiboles, pyroxenes (fig. 2b), sphene and staurolite. This technique enabled also evaluation of the spatial distribution of neoformation materials as result of pozzolanic reactions. It was clear that these new materials are preferentially positioned in the aggregate-binder interface. The capacities of optical techniques are unique and enabled the distinction between rocks like sienite, diorite and quartzite from the individual minerals (*i.e.* feldspars, quartz). Particularly important was the possibility to distinguish carbonatious aggregates (fig. 2c) from the binder (generally calcitic).

Table 1. Mineralogical composition of Elvas Cathedral mortars

	Microscopy identification*			Diffraction identification**		
	SEL1	SEL2	SEL3	SEL1	SEL2	SEL3
Quartz	xX	xX	xX	++	++	+
Potassium feldspars	xX	xX	xX	++	++	++
Plagioclases	X	X	X	++	+++	++
Micas	xX	xX	xX	+	+	+
Chlorite	X	X		Vtg.	Vtg.	Vtg.
Amphiboles	xX	xX			Vtg.	+
Pyroxenes	X	X				
Sphene	X	X				
Staurolite		X				
Hematite					Vtg.	Vtg.
Zeolite					+	Vtg.
Kaolinite				Vtg.	Vtg.	Vtg.
Calcite				+++	+++	+++
Dolomite					Vtg.(?)	
Aragonite					Vtg.	
Hydromagnesite					Vtg.	
Gypsum					Vtg.	+
Trona						Vtg.
Halite						Vtg.
Neoformation compounds	X	X				
Ceramic fragments	xX	xX	X			
Lime nodules	X	X	X			
Marble lithoclasts	X	X	X			
Sienite	X		X			
Diorite	X	X	X			
Quartzite		X	x			

* by stereozoom (x) and petrographic (X) microscopes

** +++ Very abundant; ++ Abundant; + Present; Vtg. Traces, ? Doubt

X-ray diffraction (XRD) can not differentiate a rock with quartz like quartzite from quartz grains but can recognise mineralogical phases finely distributed in the binder. Some of them as gypsum, trona, and halite are alteration mortar products and seem to be important in SEL3. Since the different carbonate minerals can not be identified by petrographic techniques, XRD was important

in the identification of the binder mineralogy. XRD showed that the mortars are mainly calcitic, with some contribution of aragonite and magnesium carbonates (dolomite and hydromagnesite) in the case of sample SEL2. These results were corroborated by TG-DTG which showed typical endothermic peaks characteristic of thermal decomposition of these carbonate specimens, particularly in SEL2.

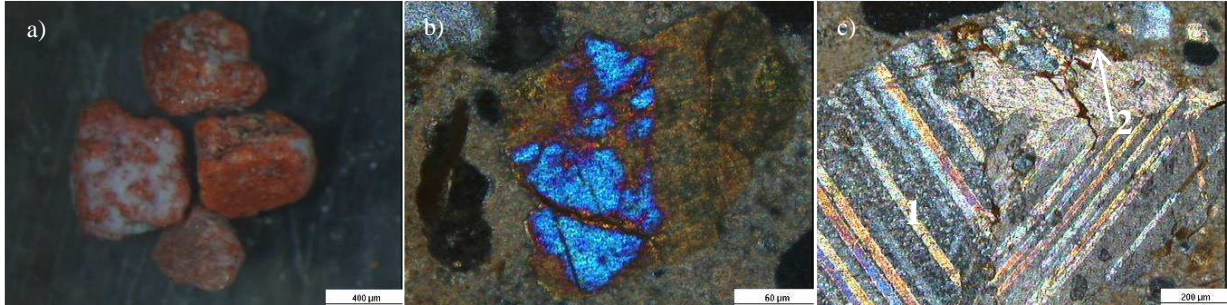


Fig 2. Micrographs of mortars aggregates from Elvas Cathedral a) ceramic fragments (SEL1), b) weathered pyroxene (SEL1) –thin section, and c) marble clast (1) with neoformation compounds (2) between aggregate and binder (SEL1) - thin-section.

Evora Cathedral

Five samples from Evora Cathedral were selected for this work: SEV1: terrace (exterior), SEV2: north side nave, SEV3: south side nave, SEV6: inner wall of the Zimborium tower and SEV8: High Choir (behind wooden chair structure). XRD data (Tab. 2) underlines the regional granitoid character of the aggregates with major minerals like quartz, feldspars and micas. The presence of minerals like chlorite or zeolites can be interpreted as result of rock alteration before their application. Gypsum is possibly the result of *in-situ* sulphate reactions from gaseous SO₂, while halite, due to its high content, is more probably to be an intentional addition to accelerate lime hardening during the mortars production.

The binder of SEL6, the 14th century mortar, is clearly calcitic while the more recent mortars (from 16th century) have a component of magnesium carbonates (magnesite and dolomite) which render them higher mechanical properties.

Table 2 Mineralogical composition of Evora Cathedral mortars by XRD.

	16 th century				14 th century
	SEV1	SEV2	SEV3	SEV8	SEV6
Quartzo	+++	+++	+++	+++	+++
Feldspatos	+ / ++	++	++	++	++
Mica (moscovite)	+	+	+ / ++	+	+ / ++
Clorite	-	-	+	-	vtg
Anfíbolos	vtg / +	vtg	vtg / +	vtg / +	-
Mineral zeolítico	vtg	vtg	vtg	-	-
Halite	-	vtg	?	vtg	-
Calcite	++	+ / ++	++	+ / ++	++
Magnesite	vtg	vtg	+	vtg	-
Dolomite	? / vtg	vtg	vtg	vtg	-
Hidromagnesite	+	vtg	-	vtg	-
Aragonite	-	vtg / +	-	-	-
Gesso	-	-	-	vtg	-

The presence of granitoid rocks is underlined by its direct observation on stereozoom microscope (Fig. 3a). In some cases it was also possible to find ceramic fragments (Fig. 3b). Under petrographic microscope, some minerals that were not detected by XRD, were identified, such as olivine (Fig. 3c). The presence of this mineral is particularly important, since it allowed the establishment of the probable source of the aggregates, the S.Bento quarries in the vicinity of Evora Town, which held some olivinic gabros outcrops.



Fig 3. Micrographs of mortars aggregates from Evora's Cathedral a) granitic rock fragments (SEV6), b) ceramic fragments (SEV8) and c) olivine crystal (SEV1) - thin-section (30x).

The contrast in the binder mineralogical composition between 16th and 14th century mortars from Evora Cathedral is underlined by the thermo analytical data (Tab. 3). The strong weight loss between 550 and 900°C of both mortars is due to the decomposition of the binder calcitic (CaCO_3) component [2]. But the 16th century have another strong weight loss between 340-550°C interpreted as decomposition of magnesium carbonates.

Table 3 Weight losses by temperature range in the samples SEV6 and SEV3.

	Temperature (°C)						
	20→240	240→340	240→500	340→550	550→900	900→1000	20→1000
SEV6 (14 th century)	0,60		1,04		8,54	0,05	10,22
SEV3(16 th century)	1,55	0,67		7,50	7,79	0,17	17,68

Final remarks

This work shows that in the two studied Cathedral, the aggregates are sand from the region and reveal the local geology. The relative abundance of each mineral component of the aggregates reflects its natural regional abundance and the resistance to weathering processes. The lime manufacture shows a greater selectivity of raw materials and the use of magnesium carbonates on the later mortar can be interpreted as a technological advance from medieval times [3]. Other technological advances comparatively to earlier medieval mortars can be alleged like the use of crushed or powder ceramics in lime mortars that was recognized in renaissance as a useful roman technique [4] or halite as a natural lime hardener.

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