THE STATUES OF THE APOSTLES FROM THE MAIN DOORWAY OF THE CHURCH OF THE MONASTERY OF BATALHA (PORTUGAL): ANALYSIS OF DEGRADATION FORMS IN RELATION TO ANCIENT TREATMENTS

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ABSTRACT
The results of some investigations concerning the original statues of the apostles from the doorway of the church of the Monastery of Batalha are discussed.

The sculptures are generally in a bad condition, mainly noticeable through surface scaling, a great absence of cohesion of the underlying material and complete loss of certain parts.

Special attention has been turned to another phenomenon which may be related to decay: the intense brown-orange colour existing on most original surfaces or on those that have not suffered recent scaling. The different analyses carried out on surface samples excluded the presence of calcium oxalate, originally supposed. The orange colour is due to a surface layer where some elements like iron, silicium, magnesium, manganese and potassium were found; these elements may be related to pigments like brown earth and red ochre. Morphologically, this layer does not seem to have a true pictorial homogeneity, rather resembling a thin scialbatura coloured with brown pigments. The possibility of a natural element enrichment, caused by migration and deposition on the surface, cannot however be excluded, but the presence of traces of organic substances, like oils and waxes, established by FTIR analysis, would bear the hypothesis of surface treatment. Archive documents indicate that the Batalha monastery received various maintenance interventions in the last century, therefore it is possible to assume there is a direct relationship between old treatments and degradation forms.

1. INTRODUCTION

Batalha monastery, UNESCO word heritage, is a great monument of the late Portuguese Gothic art and one of the most beautiful European churches of the Middle Ages. The façade, erected between 1402 and 1438, is adorned with the manueline portal, by Mateo Fernandes. Twelve Apostles sculptures and about seventy statues of monarchs, biblical kings, prophets and angels stand out from pillars and archivolts (fig. 1).

At the beginnings of XX Century the apostle sculptures were dismounted and replaced with replicas. This operation is not documented but it is evident that at that time the statues must have been seriously damaged to justify their replacement.

The originals are today guarded in the adjacent monastery refectory, used as a museum. The statues are seriously damaged, with loss of elements and crumbling stone. The powdery material which collects at the base of the statues shows that damaging processes are still active.

2. MATERIALS AND METHODS

In order to limit the sampling, only two statues have been examined: respectively the second and sixth of the museum inventory.

In statue n.2 about 60% of the original surface (fig. 2) disappeared and arms are missing.
The head (fig. 3) presents some areas where the stone is crumbly and desegregated and some others where the original surface is preserved and sculpturing work traces are still evident. The original surface is orange to brown coloured and fairly strong. In some other parts we observe the detachment of a stack of flakes parallel to the stone surface that is replaced with some millimetres of decohesed stone material. The statue n.6 shows better preservation: most of the original surface is preserved; but in the case of the face and neck (fig. 4) evident stone alteration occurs. Also in this case the projecting parts, like arms, have been lost during time. The orange colour of surfaces not exposed to loss of material is less bright. The statues damage morphologies are summarise as:

- loss of parts in strong projection;
- loss of crust parallel to original surface;
- granular disintegration into sand;
- original surfaces are very compact and orange brown coloured.;
- alteration processes move in parallel direction to surfaces;
- frontal parts and those in the past more exposed to atmospheric agents, are particularly damaged.

The samples were analysed by the following analytical techniques:
- Optical Microscopy (OM);
- Scanning Electron Microscopy (SEM/ EDS);
- X-ray Diffractometry (XRF);
- Infrared Spectrometry (FTIR);
- Ion Chromatography (IC).

In addition to the samples of statues, we examined some fragments from the external wall of the cathedral, in order to compare the materials and verify if the surface orange colour of statues could be related with that of some areas of the external wall of the monastic complex. Addition analysis has been performed to characterise biological colonisation.

3. RESULTS OF ANALYSES

Statues are carved in white calcareous compact stone. The same material was employed for the construction of the facade. The lithotipe used is Bathonian oolite limestone that crops out in Batalha district. Considering the limestone breed of the region, Aires-Barros (Aires-Barros, 1991) recognises lithotipes as very similar to a mineralogical and petrographical point of view. Some physical variabilities, like open porosity and water permeability, permitted him to distinguish materials of different quarries.

Optical microscopy
Under optical microscope we observe the oolitic stone texture and structure. Oolite diameters are between 200 and 300 µm and present evident radial and concentric structures. They are stuck together by sparithmetic white calcite. Oolitic structures have partially gone lost on surface because of micrite processes. Cross sections (fig. 5) show an external coloured orange layer. The layer is rather homogeneous, generally adherent to the substrate and with a thickness between 50 and 150µm. Sub-parallel fissures and microcracks have been observed under the surfaces. They probably form the planes of discontinuity and weakness of scale which will detach (fig.6).

Scanning electron microscopy
The previous cross-sections were analysed by SEM interfaced with microprobe analysis. In backscattering mode the external layer is discernible from the substrate for the clear colour due to the presence of higher number atomic elements (fig.7). On the surface an higher concentration of sodium, magnesium, aluminium, silicon, sulphur, potassium, chlorine and iron, were found.
X-ray maps and profiles-line of sulphur show that it is located on the surface and in the spaces between fissures (fig.8).

Small cubic crystals of Halite are observed on the surfaces.

**X-ray diffractometry**

The stone is made from calcite; X-ray diffraction patterns of surface samples show gypsum and clays mineral traces.

This technique was unable to determine new-formation phases different from the gypsum ones.

**Infrared spectrophotometry**

The brown external layer has been analysed by infrared Spectrophotometry (FTIR). The analysis was carried out at first on powered samples and then on NaCl attack residue. The first spectra indicates the predominant presence of calcite, with absorption bands in correspondence with 1425-1428; 875; 713 cm\(^{-1}\). After CaCO\(_3\) removal the spectra shows characteristic bands of silicates, silicoalluminates, iron oxides, which compared with know pigment spectra are similar to Earth of Sienna natural and Red Ochre (fig.9).

This technique determines the presence of organic substances such as oils and waxes (fig.10). Some bands of absorption have been finally ascribed to potassium nitrate.

**Ion chromatography**

The samples were analysed by Ion chromatography, for a quantitative determination of water-soluble salts.

Chlorides, nitrates, sulphates are found in average percentage of 1\% (in weight). Traces of fluorides have been found (Arnold 1984).

Finally some analyses were carried out on the fragments taken from the external wall of the cathedral: surfaces have an orange colour similar to the one of the apostles statues.

Surfaces are affected from biological colonisation. Lichen was identified as *Rinodina Gennari* and *Caloplaca sp.* (fig.11). Cross sections where the lichens grows show a penetration of the fungal hyphae into the limestone substrate. Hypae penetrate very deeply into the substrate (5mm). Ooites and calcite cement are indiscriminately crossed and contoured by hyphae (fig. 12).

Compact deposit, orange brown coloured tracing the morphology of the stone surface were found.

XRD FTIR analyses show presence of calcium oxalates in monohydrate bi-hydrate form, Whewellite and Weddellite, alluminosilicates and iron oxides traces.

### 4. DISCUSSION OF RESULTS AND CONCLUSIONS

In our opinion weathering forms and original surfaces' colouring of apostles statues are closely related. The granular disintegration into sand and powder is due to the loss of calcite which provides the binder action. This weathering form is the consequence of the sulphation processes and of water-soluble salts action.

Batalha monastery was subject to several restorations in the past: those of the nineteenth century are in detail described by Albuquerque (Albuquerque, 1881). In that occasion acid substances were employed to clean the surfaces, particularly to remove the biological colonisation. Albuquerque reports also data concerning the wish to maintain the "aged" appearance of the surfaces. For this reason it was probably required to treat the surfaces in order to make uniform tonalities of stone cleaned or not.

This hypothesis is confirmed by the brown orange layers present on original surfaces which can be ascribed to an ancient scialbatura brown earth's and red ochre's-based. Organic substances like oils and waxes were also applied probably with consolidant and protective function.

The surface colour of the cathedral walls is due to the lichens colonisation and to ion migration of iron oxides from limestone. Morphology and the composition of surface colouring of the walls have different origins in respect to those then compared on the statues.
In conclusion: after a drastic cleaning of the statues, a scialbatura has been applied in order to conform the shade of the surface and provide protection. However weathering processes were accelerated by old maintenance work. The stone structure was deeply damaged by unfit use of acid employed to clean the surface. Consolidant action of scialbatura was not able to contrast the resultant decay, on the contrary it involved the loss of surface crusts.

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REFERENCES
Fig. 1 Overall view of portal apostles (replicas)

Fig. 2 Original apostle statue n. 2
Fig. 5 Cross section showing calcitic substrate (A) and external orange layer (B).

Fig. 6 Cross section showing surface sub-parallel fissures and micro-cracks.

Fig. 7 Cross section SEM BSE image and EDS analysed zone.

Fig. 8 SEM/EDS Sulphur line profile.
Fig. 9 Comparison among surface sample 1, brown earth and red ochre FTIR spectra

Fig. 10 Comparison among sample 1, linseed oil and beeswax FTIR spectra

Fig. 11 Cathedral wall surfaces colonised by lichen

Fig. 12 Penetration of hifhae into the substrate