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Mineralogical and chemical characterization of surface orange layers on the limestone of the Monastery of Batalha, Central Portugal

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***Abstract* – Samples of orange surface patinas found on the limestone balustrade and sculptures of the Batalha Monastery in Portugal, have been investigated by X-ray micro-diffractometry (µ-XRD) and Low-Vacuum Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry (LV-SEM + EDS). Aim of the study was to assess whether the orange layers have been intentionally applied or were resulting from stone weathering. Preliminary results suggest that the orange layer on the surface is mainly consisted of gypsum and hematite with halite and weddellite as minor components. This discovery implies the possibility that such orange patinas were applied intentionally instead of having been formed naturally by decay. A comparison was made between this patina and the "scialbatura", a protective coating often applied by conservators on limestones and marbles in monuments.**

I. INTRODUCTION

In the famous Batalha Monastery located in Central Portugal, an orange patina is commonly seen on the surface of sculptures, facades, column and walls (Figure 1). Few studies on this subject can be found in the literature. Rattazzi and coworkers examined two statues kept in the Monastery museum storage: the external orange layers were found to show a rather homogeneous texture with traces of gypsum and clay minerals; FTIR analysis showed bands of Al-silicates, and iron oxides, interpreted as Earth of Sienna natural and Red Ochre pigments [1]. Aires-Barros et al. investigated the original 15th century Saint Matthew statue and the external walls of the main façade. On the former, they revealed the presence of calcite, with nitrate, silicate and organic products like benzoic acid, while on the external walls the orange patina was found to be predominantly composed by calcium oxalates: whewellite ($CaC_20_4.H_20$) and some weddellite ($CaC_20_4.2H_20$), as well some hydroxyapatite ($Ca_5(P0_4)_3(OH)$), halloysite and nitrates [2].

With the term "Scialbatura" conservators refer to a superficial film covering the surface of Roman imperial marble monuments, its color is ranging between rose-brown and chamois. In late 1980's, researchers demonstrated that its principle components were Ca-oxalates, whewellite and weddellite, calcite from the underlying marble, quartz and feldspars as windborne soil dust, and gypsum related to the burning of oil and coal [3]. There was an intense debate of the origin of oxalates, with some authors regarding the oxalates as being due to the metabolic activity of living encrusting epilithic lichens producing oxalic acid, while others invoked non-bio-mediated chemical reactions between the calcareous stone substrate and a vast number of natural and manmade organic compounds found in the urban atmospheres [4]. It is also believed that "scialbatura" is a sacrificial shelter coat for the monuments which may lead to further deterioration [5]. In the following up studies, Fassina et al. revealed more varieties of such patina: lime is the main component of the traditional "scialbatura",

Fig. 1. Facade and sculptures with orange patina at the Imperfect Chapels, Batalha Monastery.

however in the yellow-pink layer titanium oxide was also detected. The yellow color is related to the presence of fluorite probably formed during the superficial consolidation using fluorosilicate treatments or alternatively to acid cleaning interventions [6].

Nearly one and half decades has passed since the last research carried out on this topic. In this research, two pieces from the Batalha Monastery – a sculpture and a balustrade section have been investigated. It is proposed to determine the composition of the orange layers on their surface, make a comparison between each other and with the previous discoveries.

II. METHODS AND MATERIALS

By special permission of the Direção-Geral do Patrimonio Cultural and the Mosteiro da Batalha authorities, 2 pieces were taken from the monastery to University of Evora to conduct the characterization - one is the sculpture “S-116” from 15th century which was once removed from the west portal of the monastery and stored indoor, the other is a section of fallen balustrade from the Royal Cloister west gallery, 3rd window outside. Complying the principle of non-destructive detection, the following methods were used.

A. X-ray micro-diffractometry (μ-XRD)

The identification of the mineralogical composition of the orange layer and substrate was assessed by μ-X-ray diffraction using a commercial Bruker AXS D8 Discovery diffractometer with Cu Ka radiation, Gadds detector, interval 3–708 2u, and step of 0.028/s [7]. The EVA code and Highscore Plus software were used for the identification of the peaks.

B. Low-vacuum scanning electron microscopy coupled with energy dispersive spectrometry (LV-SEM + EDS).

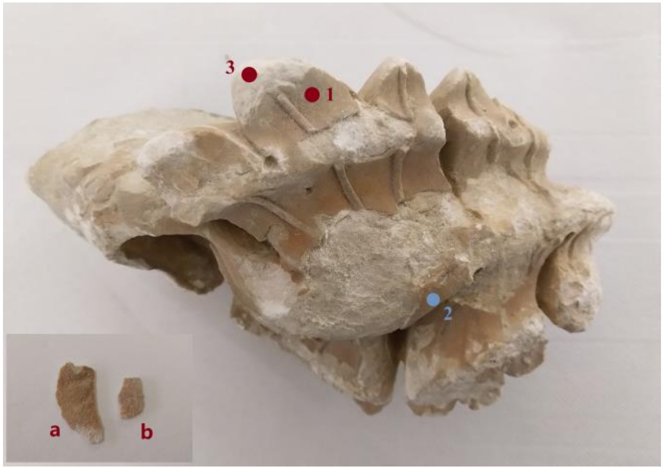

Fig. 2. Sculpture “S-116” covered with orange coating and the peeled off coating fragments.

Scanning electron microscopy coupled with energy dispersive X-ray spectrometry were carried out using a Hitachi S3700N (Tokyo, Japan) SEM coupled to a Bruker (Karlsruhe, Germany) XFlash 5010 SDD Detector system [8]. The fragment sample was characterized in situ, without any sampling or preparation, at a low vacuum of 40 Pa, an accelerating voltage of 20 kV.

III. RESULTS AND DISCUSSION

A. Sculpture “S-116” from Batalha Monastery

X-ray diffraction were conducted on three points of the sculpture “S-116” and peeled off coating fragment (a), as marked in Figure 2. The XRD pattern and peaks are shown in Figure 3., and a semi-quantitative evaluation is given in Table 1. A considerable amount of gypsum can be seen at point 1, point 2 and fragment a, where there is the orange coating. At point 3 where the coating is completely removed, gypsum cannot be found. Hematite

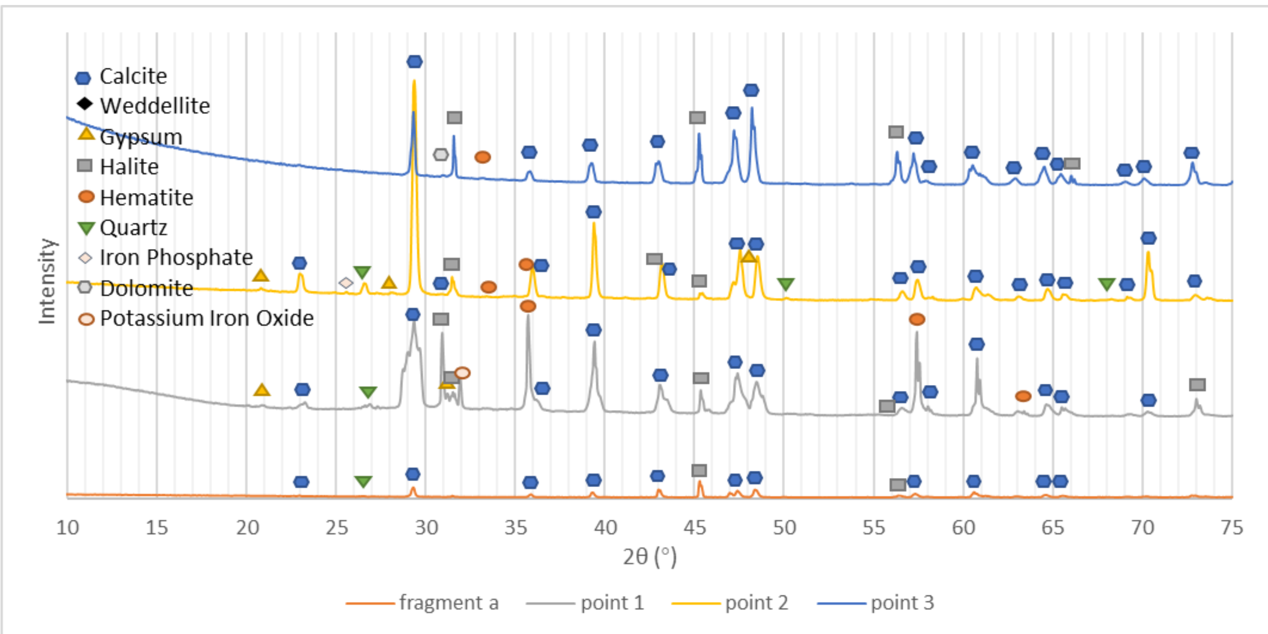

Fig. 3. XRD results on several points of sculpture “S-116” and fragment a.

Table 1. Qualification and semi-quantification result of minerals and compounds on sculpture "S-116"

	Fragment a	Point 1	Point 2	Point 3
Calcite	37%	51%	85%	80%
Gypsum	43%	10%	10%	-
Weddellite	-	-	-	-
Quartz	1%	3%	2%	-
Hematite	3%	21%	1%	2%
Halite	15%	12%	1%	14%
Iron Phosphate*	-	-	1%	-
Dolomite*	-	-	-	4%
Potassium Iron Oxide*	-	4%	-	-

and halite are also seen at all analytical spots. The stone substrate is composed by calcite and quartz are the composition of the substrate, illustrated in previous study [9]. Small amount of iron phosphate, dolomite and potassium iron oxide were also found. Fragment b was observed under the low vacuum scanning electron microscope, with element mapping obtained by energy dispersive spectroscopy: results are shown in Figure 4. There is an absolute correlation between the distribution map of sodium and chloride, demonstrating the existence of halite (NaCl). Potassium (K), aluminum (Al) and silicon (Si) peaks imply the presence of quartz, feldspar and clays minerals as soil dust. The distribution of iron (Fe) is somehow uniform, and shows a correlation with sulfur (S), for instance, in the areas where there is a weaker signal of Fe, S is also hard to detect. The origin of sulfur is mainly due to the presence gypsum ($CaSO_4$), this indicates that Fe element is mixed and applied together with gypsum. Calcium (Ca) has a strong signal over the whole area, except where the NaCl and clay /feldspar / soil dust is located, which means halite and feldspar are on the surface of limestone or gypsum. This could also be seen from the SEM picture, the halite (up left) and feldspar (down central) show a well-formed crystalline habit with relatively large dimension grains (>50 μm), in contrast with the poorly crystallized gypsum grains . There are also two crystals close to the right edge of the map, where the Ca signal is stronger but Fe and S are less distributed, these should be other Ca-containing minerals such as calcite or oxalate instead of gypsum.

B. Balustrade from Batalha Monastery Royal Cloister

Figure 5. shows the balustrade piece, this sample has no fallen fragments, thus it was examined only by XRD as a bulk in order not to cause any damage. Figure 6. shows the XRD pattern. In Table 2 the main minerals are listed together with their semi-quantitative evaluation. It is illustrated that, at point 1, where an orange surface is still visible, there is a high content of gypsum and weddellite with minor amount of hematite. At point 2, where the orange surface is worn-out and the white substrate appears, the main composition is calcite, and the contents of gypsum and weddellite show a significant decrease, also hematite was not detected. At point 3, there is some dark orange powdered deposition, which has a different appearance than point 1, the result shows a majority of calcite (limestone), some weddellite and

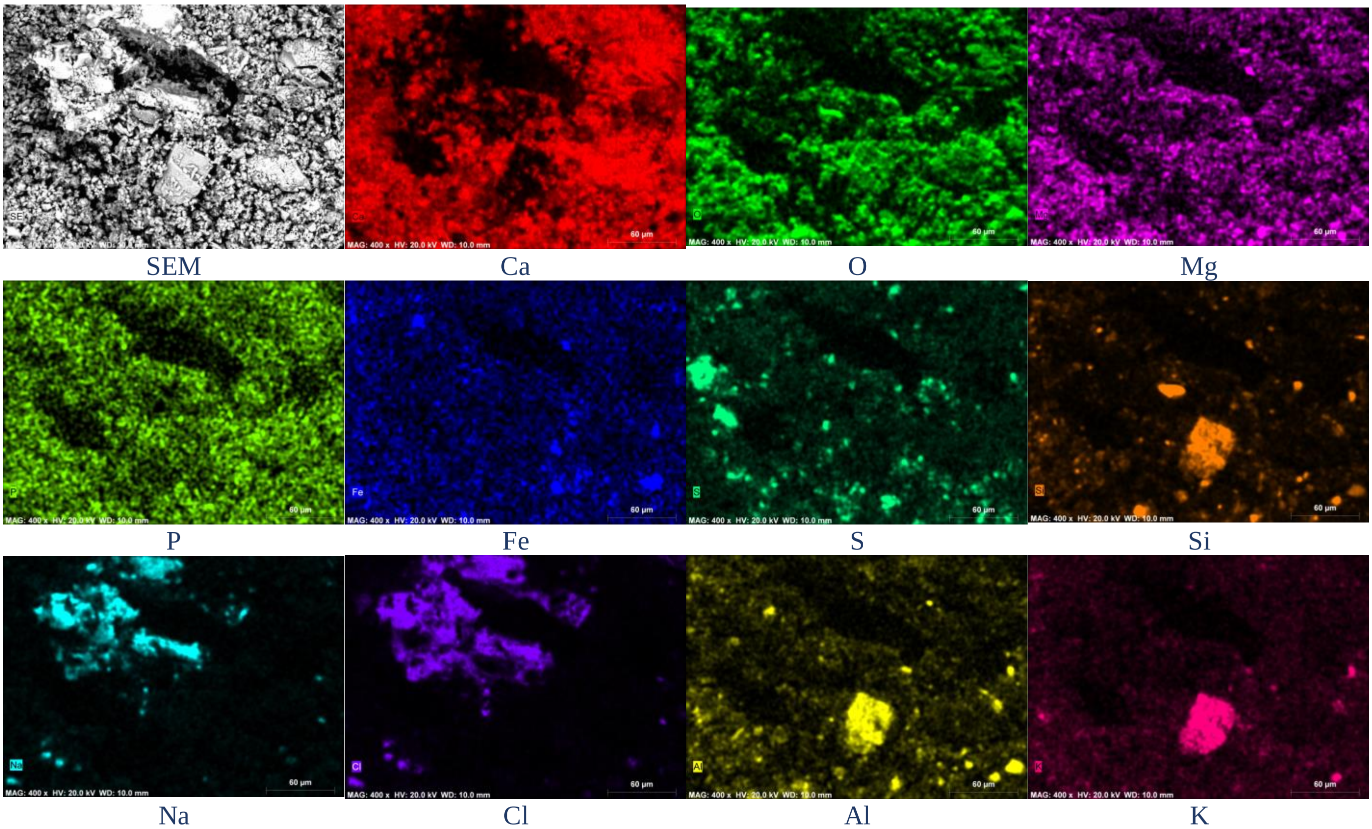

Fig. 4. Element mapping of sculpture "S-116" fragment b.

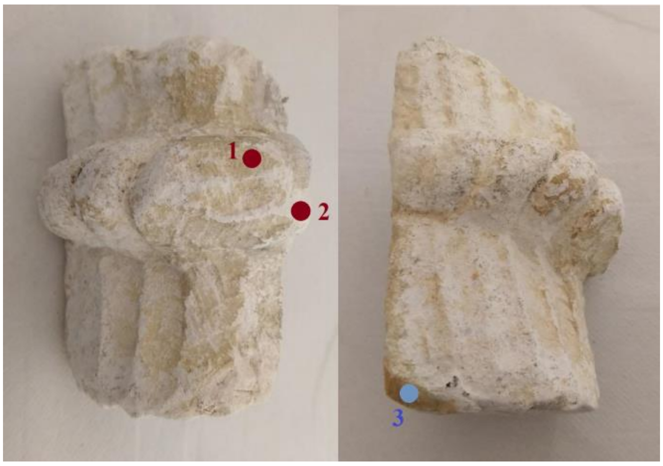

Fig. 5. Balustrade piece from Royal Cloister, Batalha Monastery.

hematite, the presence of halite at point 3 is distinct from point 1 and point 2.

C. Comparison between the two samples

Though both were named "orange patina", there is significant difference between the two samples investigated. For the sculpture "S-116", the orange layer has an imprint of shaping, for example, the ridging stripes spreading out from the center, which does not exist on the substrate. There are traces of K-aluminosilicates, which, if excluding feldspar or soil dust, is highly possible to be clay. For the Royal Cloister balustrade, the orange patina is closely adherent to the limestone substrate, instead of a separate lamination visible on "S-116". And there is an abundant weddellite on the balustrade surface, which was not found on "S-116".

The decay pattern of this orange layer on the two samples is also different. On sculpture "S-116" sample, the surface layer is flaking, from the white substrate

Table 2. Qualification and semi-quantification result of minerals and compounds on sculpture "S-116"

	Point 1	Point 2	Point 3
Calcite	21%	78%	86%
Gypsum	50%	13%	-
Weddellite	23%	8%	10%
Quartz	3%	1%	1%
Hematite	3%	-	1%
Halite	-	-	2%

under the peeled off lamination, a higher content of halite is detected. This indicates a typical salt decay process, that the salt solution evaporated and crystallized at the interface between the coating and the substrate, leading to detachment eventually [10]. In this case, the salt that is related to this process is mainly halite (NaCl), the contribution of nitrates and phosphates may also be presented.

Considering the Royal Cloister balustrade, the patina is lost preferentially at the ridges and bulges but is more preserved in flat areas, marks of scratches can also be seen. Two possible explanations can be inferred: a) the evaporation rate of salt solutions is higher at the geometrically protruded parts due to a larger specific surface area, resulting in higher crystallization pressure inside the stone pores and more severe decay [11]; b) the protrusion endures more mechanical abrasion from rain, wind, sands, and human activities, thus accelerating the decay processes.

D. Comparison with the previous research

Through the above-mentioned results and analysis, the orange layer on the Royal Cloister balustrade is similar to the "scialbatura" for the composition, texture and color, except that the presence of titanium oxide and fluorite is

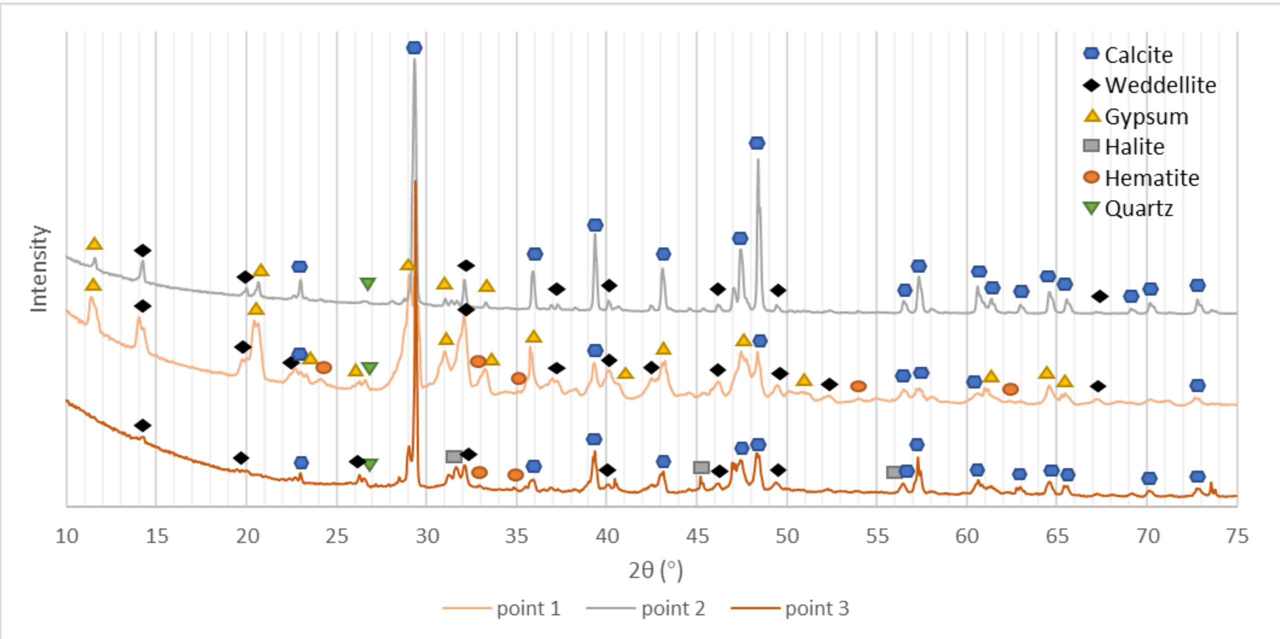

Fig. 6. XRD results on Royal Cloister balustrade.

not yet confirmed in this study. The coating on the sculpture "S-116" matches the description of that on the original apostle statues from the church doorway [1]. Considering they were both crafted in the 15th century, it is feasible that the same coating procedure was used, despite they were located differently in the Batalha Monastery. Although it is commonly believed that in this type of surface layers, the gypsum occurring on calcareous stones is either the result of lime-plaster applications or the reaction product of calcareous or silicate stones in a SO_2 polluted urban atmosphere [12], the possibility of artificial gypsum coating cannot be completely excluded [13]. In fact, the homogeneity of the layers supports the conclusion of them being artificial.

IV. CONCLUSION

In this research, characterization of the mineralogical and chemical composition was carried out on the orange layers in two limestone samples from the Batalha Monastery in Portugal. The homogenous and decorative layer on sculpture "S-116" is mainly composed of calcite, gypsum and hematite with traces of Al-K-Si silicates which comes from clay or windborne soil dust. It is highly likely to be applied intentionally, and its delamination with the substrate is a typical phenomenon of salt decay. The layer on the Royal Cloister balustrade is similar to the "scialbatura", which contains gypsum, calcite and abundant weddellite. More evidence is needed to confirm whether this colored layer was man-made or generated by the biochemical reactions with the environment.

Restricted by the prohibition of destructive test, some methods can hardly be applied and thus slow down the pace of seeking answers. In the future study, more attention could be put on the experiment design, to derive the answer via cohering information obtained.

V. ACKNOWLEDGEMENT

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