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## Study of the degradation of 18<sup>th</sup> century alabaster sculptures through accelerated aging on test samples

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# Study of the degradation of 18<sup>th</sup> century alabaster sculptures through accelerated aging on test samples

Marta Oliveira

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## Introduction

- 1 During the internship in the Sculpture Department of Conservation and Restoration of the Institute of Museums and Conservation (IMC) in Lisbon, Portugal, a set of two sculptures in gypsum alabaster was studied and restored (Fig. 1). The sculptures, dating from the eighteenth century and belonging to the collection of Grão Vasco Museum, in Viseu (inventory number 993/118 and 994/119, respectively) represent two mythological figures (Poseidon, the god of the sea, and Athena, the goddess of war). They are about 50 cm high and are carved on the front and on the sides with elegance and grace which points to influences from the Italian Baroque and Rococo.

Fig. 1 – The alabaster set: *Poseidon* and *Athena*



The set of gypsum alabaster, representing two mythological figures, *Poseidon* (left) and *Athena* (right).

Credits: Luis Piorro, Conservation and Restoration Department in the Direção-Geral do Património Cultural.

- 2 In general, the sculptures were in reasonable condition, presenting some fractures, adhesives from old collages and a few missing parts. However, during the preliminary observation, in the front areas, an unusual kind of degradation characterised by a roughening erosion (Fig. 2) has been detected which was thought might be related with the nature of the substrate – the alabaster.
- 3 This material consists mainly of gypsum, i.e., calcium sulphate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), a sedimentary rock of the group of evaporites, precipitated from ancient seas and lakes due to water evaporation in arid climates (Dimes 2001). Alabaster is a fine-grained and compact material, extremely soft (hardness 2 in the Mohs scale), and easily carved. As a rule, a pure alabaster is translucent, and has a whitish tone, although alabasters with beige or red tone or coloured veins, caused by traces of minerals such as iron oxides and other impurities, are also common. Another feature of alabaster, with great relevance for conservation, is its solubility in water which is why the works are usually found inside buildings (Cheetham 1984:11).
- 4 Based on the preliminary observation and taking into account the characteristics of a typical alabaster such as the solubility in water, it became clear that the roughening erosion should result from gypsum dissolution. However, for that dissolution at least two possible causes can be considered. The first is the dissolution caused by condensation of the atmospheric moisture, which, according to Larson, is one of the main causes of degradation of alabaster (Larson 2001). According to him, “the recurring movement of water droplets over a polished surface causes erosion similar to that of a river in a valley,

although a chemical reaction between water and stone is also involved” (Larson 2001). The second possibility is the direct exposure of the sculptures to weather conditions such as sun, wind, fog and especially rain, what could have happened if the sculptures had been placed in outdoor, for instance, in the cloisters of the Grão Vasco Museum or, before the works have entered that collection, in any open space.

- 5 To test these two hypotheses, accelerated aging tests were performed in samples of gypsum alabaster and the altered surfaces resulting from the exposure to condensation conditions and to tap water simulating the rain’s action were characterised with several analytical techniques and compared with the sculptures surface. This study, undertaken as part of the internship that took place at the Direcção-Geral do Património Cultural (Lisbon, Portugal) and was included in the Conservation and Restoration Master Course of the Polytechnic Institute of Tomar, Portugal, is described here.

## Experimental

### Alabaster samples

- 6 Alabaster samples for the aging tests were obtained from a block of a decorative column made of gypsum alabaster (identified by X-ray diffraction), cut in cube shapes approximately 4.0 cm high, 3.5 cm long and 4.0 cm wide. The upper side of the samples was polished in a polishing device (DP-U3, Struers). The polishing was finished with a 3 µm and 1 µm abrasive pads combining with paraffin wax. The mass of the samples was determined after dried at 70 °C during 24 h.

### Accelerating aging tests

- 7 Two series of tests have been carried out. The first, intended to test the condensation hypothesis, was done in a salt mist chamber (Ascott S120T model) that allows to control the fog and drying periods in addition to temperature and relative humidity. The samples were subject to six condensation cycles, each one composed by the following phases: 144 h of nebulisation at 35 °C and 24 h at 50 °C. Deionised water was used and the alabaster samples were labelled CT1 to CT4 (CT=condensation test). The second series was done to test the exposure to rainwater hypothesis. The alabaster samples were placed at the bottom of a washbasin and for the rain simulation a perforated bottle attached to the faucet with holes from which drops of water fell equally in all the surface of the samples has been used. In each cycle the samples were exposed to water with a slow flux during 8 h and after that were dried at 70° C for 24 h. The samples, labelled RS1 to RS6(RS=rain simulation), were exposed to three cycles.

### Analytical techniques

- 8 For the characterisation of the test samples, several analytical techniques were used. After each cycle, the test samples were weighed and the changes in the surfaces were observed by means of a binocular magnifier Leica IC 3DM2-16A.
- 9 At the end of each aging test, the colour surface was measured in the CIELAB system, that uses the coordinate  $L^*$  related to the lightness, the coordinate  $a^*$  to the red/green value and the coordinate  $b^*$  to the yellow/blue value. The samples were measured in three

areas with a 3 mm diameter with a spectrophotometer Datacolor Check II Plus®, with a D65 illuminant and a 10° observer. The average of the three measurements was recorded.

- 10 For each series, the samples were directly analysed, at the end of tests, by scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) (HITACHI S-3700 N microscope connected to a Bruker X Flash 5010 SDD, accelerating voltage of 20 kV, beam current of 0.1 mA, high vacuum). For each sample, the characterisation was done at three different areas.
- 11 For the identification of the minerals, X-ray diffraction analysis has been carried (Bruker, D8 Discover AXS, using a Cu K $\alpha$  radiation (40 kV, 40 mA and graphite monochromator), with a general area detector diffraction system (GADDS)). The diffractograms were obtained with a scanning angle of 8.0° to 70.0° (2 $\theta$  angle), a step size of 0.02° and a scan step time of 300 s.
- 12 The roughness increase due to alteration of the surface sample was measured in an area of approximately 6 mm<sup>2</sup> in a selected location of each sample. For that purpose a 3D optical profilometer, Talysurf CLI 1000, was used. The analysis has been performed with a laser of a diameter of 8 nm, 2 mm/s of measuring speed, 5 mm/s return speed and a 5  $\mu$ m spaced between lasers. Two roughness parameters were determined, *Sa* and *Sdr*. The *Sa*, expressed in  $\mu$ m, is the mean surface roughness and *Sdr*, expressed in percentage, is the increment of the interfacial surface area related to the area of the projected xy plane (for a completely flat surface *Sdr* = 0 % and for a non flat surface *Sdr* > 0 %) (Queiroz 2012).
- 13 In all cases, the results obtained on the test samples after aging were always compared with those obtained on the same samples before aging. Moreover, the degradation surface of the two sculptures was characterised with the binocular magnifier and with SEM-EDS and that degradation morphology were compared with the alterations of the test samples after aging.

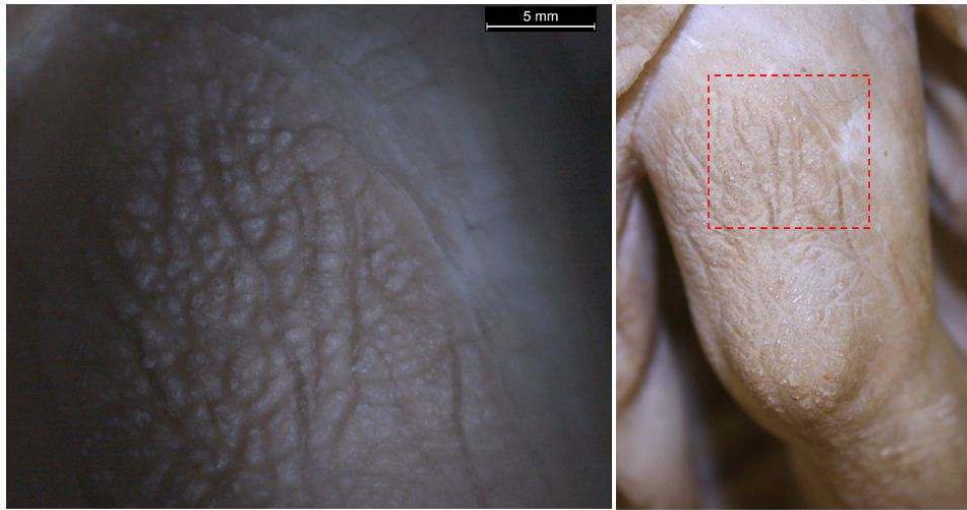
## Results

### Sculptures surface

- 14 The alteration only occurs in the front surface of the both sculptures, and more extensively on *Athena* sculpture. With the binocular magnifier, it was observed that the surface alteration occurs in a form of translucent tiny furrows randomly distributed, which gives a striated erosion surface, similar to that described by Larson (2001) (Fig. 2).



Fig. 2 - Striated erosion

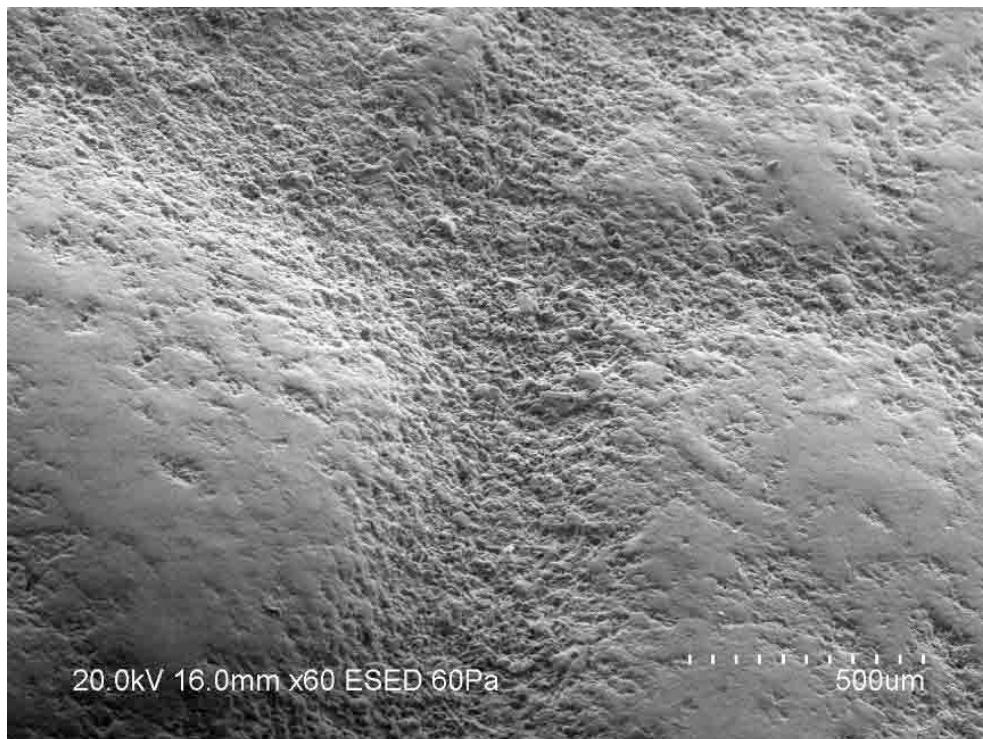


Degradation observed with binocular magnifier (left) and a photograph of the same place (right), located on the left leg of *Athena's* sculpture.

Credits: Inês Gomes and Marta Oliveira.

- 15 Due to its small size, the *Athena's* head, which was detached during the treatment, was placed in the SEM-EDS chamber and directly analysed on the right cheek. In the striated areas, the furrows show a loss of polishing and the surface is roughened (Fig. 3).

Fig. 3 – Furrow surface

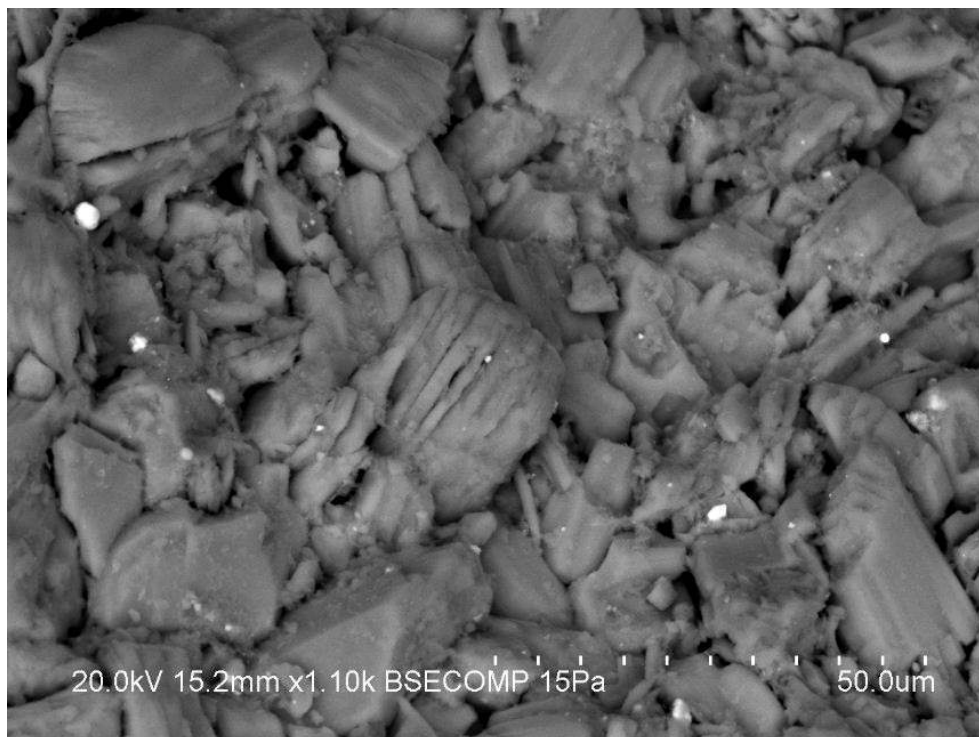


Electron secondary image (SEM-EDS) of the furrow surface, surrounded by polished areas, in the right cheek of *Athena's* sculpture.

Credits: António Candeias, Hercules Center.

- 16 The gypsum crystals shapes resemble fine slivers, due to their tabular cleavage (Fig. 4).

Fig. 4 – Gypsum grains

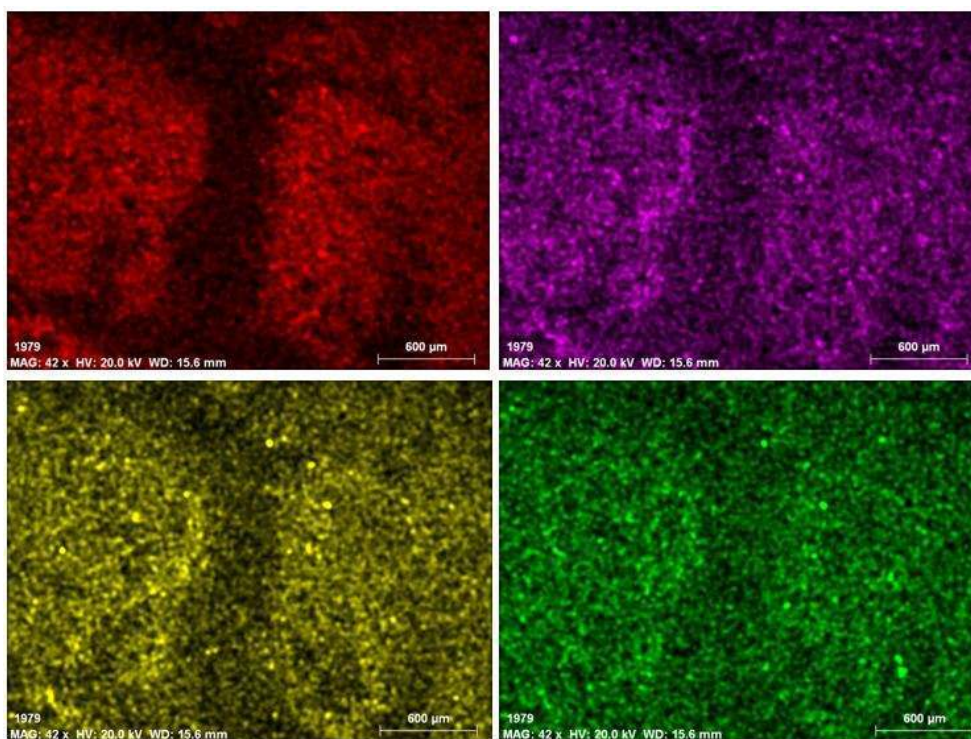


Backscattering electron image (SEM-EDS) of the gypsum grains of the furrow surface in the right cheek of *Athena's* sculpture.

Credits: António Candeias, Hercules Center.

- 17 The elemental data show differences in composition related to the alteration. In the non altered surface aluminium, carbon, sulphur, calcium, strontium and silicon were detected. The origin of the elements besides gypsum was inconclusive. Although it's possible that the elements can be derived from the abrasive pastes used during polishing by the sculptor or from the protective layer, which is a kind of wax. In the altered surface occurred a loss of carbon, aluminium, silicon and strontium, probably removed during the gypsum dissolution (Fig. 5).

Fig. 5 – Elemental analysis map



Elemental map obtained through SED-EDS for carbon, aluminium, silicon and strontium, respectively, on the same sample and area as Fig. 3.

Credit: António Candeias, Hercules Center.

## Aging tests

### Microscopy

- 18 In the accelerating aging test in condensation conditions, all samples loss the polished surface and became roughened and less translucent after the first cycle. At the end of the second cycle the CT3 and CT4samples revealed a degradation similar to that found in the alabaster set with the same striated form (Fig. 6, Fig. 7), while this was not the case for the other samples of the CT-type.



Fig. 6 – Superficial degradation



Striated erosion, observed with the binocular magnifier, on *Athena*'s sculpture in abdomen area.

Credits: Inês Gomes and Marta Oliveira.

Fig. 7 – Alteration of CT4 sample

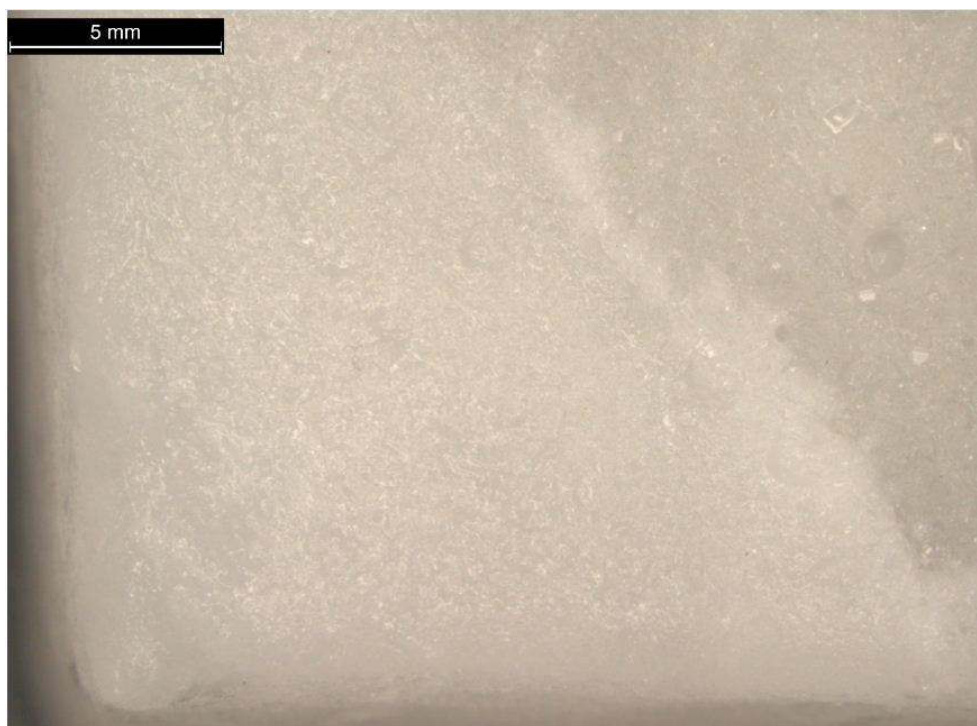


Alteration observed with the binocular magnifier of CT4 sample after the test.

Credits: Inês Gomes and Marta Oliveira.

- 19 After the following cycles there was an increasing development of the alteration in all samples, most pronounced in the CT2, CT3 and CT4 samples. The striated morphology first appeared at the edges of the upper side of the samples and at the end of the cycles it spreads to the centre. In the CT1 sample the surface alteration was much less obvious and restricted to the formation of a few tiny furrows. This difference might be explained by the heterogeneity of the block from which the samples were cut. The samples lost some weight at the end of the test, 3.84 % in average.
- 20 Different results were obtained on the test samples exposed to the action of rain water. At the end of the test, the surface of the samples became concave or tilted with a roughened texture (Fig. 8), and a significant loss of weight was observed (23.8 %, in average).

Fig. 8 – Alteration of RS3 sample



Alteration observed with the binocular magnifier of RS3 sample after the test.

Credits: Inês Gomes and Marta Oliveira.

### Colorimetry

- 21 According to the colorimetric measurements, the aging processes caused a significant increase in opacity (revealed by the increase in the lightness parameter,  $L^*$ ) and enhanced green and the blue tones (shown by the decrease in  $a^*$  and  $b^*$  parameters, respectively) (Tables 1-2). The changes were significantly more pronounced in the samples subject to the condensation conditions.

Table 1 – Results of the colorimetric analysis, before and after the accelerated aging test under condensation conditions

	$L^*$		$a^*$		$b^*$	
	Before test	After test	Before test	After test	Before test	After test
Mean	16.81	64.05	-0.13	-0.47	-0.47	-2.19
Standard deviation	4.19	4.31	0.11	0.08	0.32	0.57
Minimum	9.66	56.17	-0.29	-0.57	-0.95	-2.70
Maximum	23.48	69.50	0.04	-0.33	0.05	-1.11

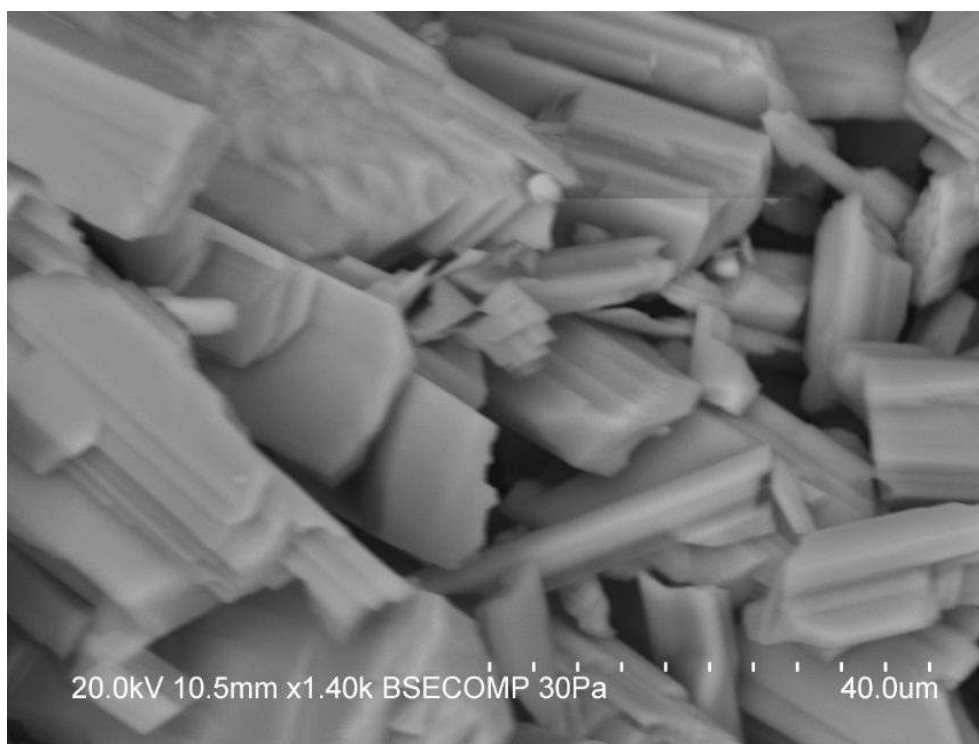
Table 2 - Results of the colorimetric analysis before and after the accelerating aging test with rain simulation

	$L^*$		$a^*$		$b^*$	
	Before test	After test	Before test	After test	Before test	After test
Mean	16.97	32.92	-0.05	-0.18	-0.65	-0.85
Standard deviation	4.19	5.37	0.16	0.13	0.22	0.57
Minimum	28.31	48.34	0.45	-0.03	-0.33	-0.04
Maximum	9.02	26.13	-0.21	-0.47	-1.27	-2.16

### SEM-EDS

- 22 The SEM-EDS images showed different changes in the two test series. In the samples aged by condensation a loss of polishing and the formation of gypsum crystals with flat and angular shapes were observed (Fig. 9) similar to those observed in *Athena's* sculpture (Fig. 4).

Fig. 9 – Gypsum grains of the CT3 sample

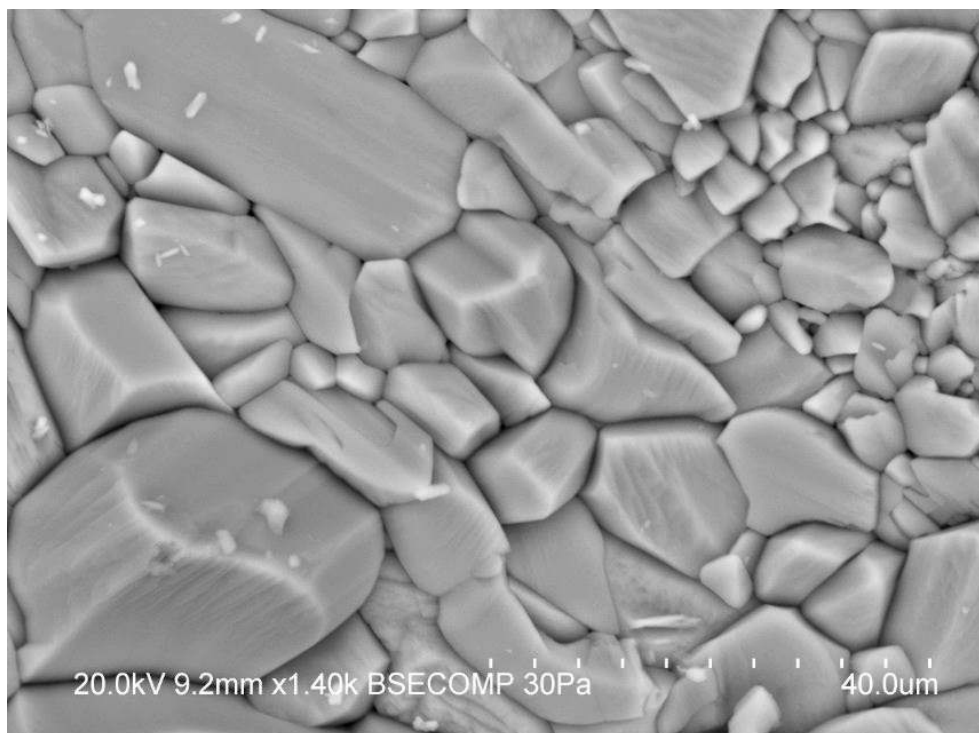


Backscattering electron image (SEM-EDS) of the gypsum grains of the CT3 sample after the test.

Credits: António Candeias, Hercules Center.

- 23 In the samples exposed to the rain simulation, the gypsum grains are round shaped due to the dissolution by the water flow (Fig. 10).

Fig. 10 – Gypsum grain of the RS2 sample



Backscattering electron image (SEM-EDS) of the gypsum grains of the RS2 sample after the test.

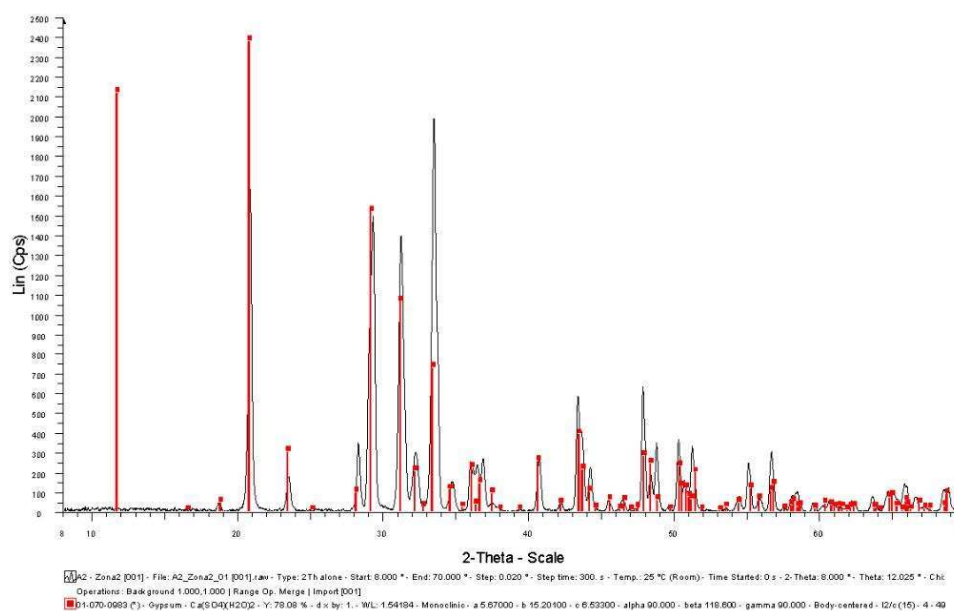
Credits: António Candeias, Hercules Center.

### X-Ray diffraction

- 24 With the aim of identifying the alteration products, X-ray diffractograms were obtained for the CT1, CT2, CT3, RS2 and RS6 samples. Each exposed surface were analysed in 5 or 6 locations, but all diffractograms showed only the presence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and no differences were observed in relation to the diffractograms of the gypsum before the tests (Fig. 11). Consequently, no alterations products were detected.



Fig. 11 – X-ray diffraction analysis



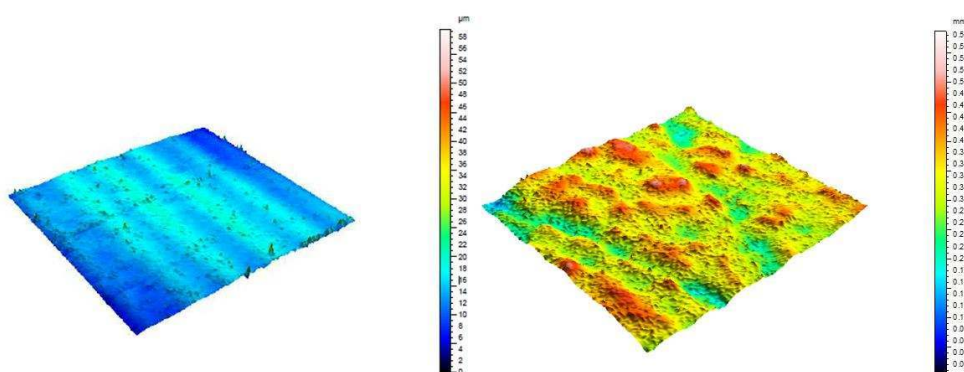
X-ray diffraction pattern of the CT2 sample after the test.

Credits: Maria José Oliveira, Conservation and Restoration Laboratory José de Figueiredo in the Direção-Geral do Património Cultural.

## Profilometry

- 25 As an example, Fig. 12 presents the 3D maps obtained for the sample CT3 before and after aging, which show a significant increase of the roughness and the development of a striated erosion morphology.

Fig. 12 - 3D maps



3D profile of the surface of the CT3 sample before (left) and after (right) the test.

Credits: Silvia Pereira and Luis Nunes of Stone & Ceramics Division from National Laboratory for Civil Engineering.

- 26 In general, the same was observed in the other test samples. The intensity of the alteration is also evident through the parameters reported in Table 3: both the roughness ( $S_a$ ) and the superficial area ( $S_{dr}$ ) parameters significantly increase during the aging tests for the samples of both series.

Table 3 -  $Sa$  and  $Sdr$  parameters of the samples analysed by 3D optical profilometry, before and after the aging tests

Samples	Before test		After test	
	$Sa$ ( $\mu\text{m}$ )	$Sdr$ (%)	$Sa$ ( $\mu\text{m}$ )	$Sdr$ (%)
CT1	2.441	4.128	11.27	62.84
CT2	3.906	2.680	27.66	110.7
CT3	2.232	0.9669	47.04	82.56
RS2	4.566	5.901	43.82	69.57
RS3	1.499	1.792	59.05	162.9

$Sa$ : mean surface roughness;  $Sdr$ : surface area ratio.

- 27 The mass loss of the samples made the earlier smooth and polished surface became quite rough, which is reflected in the results in these two parameters.

## Conclusion

- 28 The experiments were helpful to understand which conditions caused the striated erosion on the alabaster set, by the alterations on the surface samples after the tests. The results of the two series of aging tests were quite different and only the series that employed condensation conditions lead to an alteration pattern, characterised by a striated morphology, similar to that observed in the sculptures. This lead to the conclusion that the condensation exposure is the main cause of alteration. According to what Larson argues, this morphology results from the action of the water drops that condense on the polished surface through a chemical reaction of the gypsum that leads to its dissolution and to the formation of a net of tiny furrows (Larson 2001). Although the mechanism of this process remains to be determined, the present study documents a case that adds to the scant literature on the alteration of works in alabaster.

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## RÉSUMÉS

Deux sculptures en albâtre datant de la fin du 18<sup>ème</sup> siècle montrent une dégradation inconnue, caractérisée par une érosion striée de la surface, ce qui pourrait être dû à la condensation de l'eau ou bien à l'eau de pluie. Pour tester ces deux hypothèses, tests de vieillissement accéléré ont été effectuées sur des échantillons d'albâtre, et la morphologie de la couche de dégradation et sa composition ont été caractérisés. Les résultats suggèrent que les conditions de condensation ont été la cause principale de la dégradation.

Two alabaster sculptures dating from the late 18<sup>th</sup> century show an unknown superficial degradation characterised by striated erosion, whose cause seemed to be water condensation or, alternatively, rain water. To test these two hypotheses, accelerated aging tests were performed on alabaster samples, and the morphology of the degradation layer and its composition were characterised. The results suggest that the condensation conditions were the main cause of the alteration.

## INDEX

**Mots-clés :** albâtre, dégradation, érosion, rugosité, vieillissement accéléré, sculpture

**Keywords :** alabaster, degradation, roughening erosion, accelerated aging test, sculpture

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