Environmental Earth Sciences (2018) 77:416
https://doi.org/10.1007/s12665-018-7587-z

THEMATIC ISSUE

Characterization and rehabilitation of the "Porta Férrea" stone materials, University of Coimbra, Portugal

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Received: 31 October 2017 / Accepted: 26 May 2018 / Published online: 5 June 2018

Abstract
The "Porta Férrea" (Iron Gate) is the main access to the "Paço das Escolas" (University Palace) at the University of Coimbra, Portugal. It has undergone several adaptations and reconstructions from an original castle gate until the present portal that was built in 1634. The inscription of "University of Coimbra, Alta and Sofia" in the UNESCO Word Heritage list increased the interest in developing conservation works and to do the characterization of the limestone materials of the "Porta Férrea" portal. To support the conservation works, a research project was developed. The intervention plan, the sampling and testing performed and the conservation developed are presented. The rock material in the portal is the Ançã limestone, showing very high porosity around 30%, creating quite important degradation and conservation problems. The deterioration pattern, analyses performed, and the conservative works are presented. In this study it can be confirmed that Ançã limestone of "Porta Férrea" do not decay according a theoretical predictable pattern in response to polluted environments, as the defined for Portland limestone, assuming erosion rates and forms controlled by a range of micro-environment conditions particularly related with architectural constraints.

Keywords University of Coimbra · Ançã limestone · Degradation process · Conservation studies

Introduction

University of Coimbra is recognized as the oldest university of Portugal and belong to the small group of the 15 universities dating back to the thirteenth century in Europe. As the oldest Portuguese university, Coimbra has become an important cultural pole with strong influence on its students and people from different geographical areas in country and overseas. The oldest nucleus of the actual university campus is located in the set of the "Paço das Escolas" (University Palace) and corresponds to the former Royal Palace of Coimbra (University of Coimbra 2016).

The inscription of the "University of Coimbra, Alta and Sofia" in the UNESCO Word Heritage list in 2013 (University of Coimbra 2016) requires a continuous effort to preserve and valuate the outstanding constructions and valuable architecture heritage, which illustrates significant periods of Portuguese history and of scientific progress. The "Porta Férrea" (Iron Gate) is the main access to the University Palace of Coimbra. It was built in 1634 to replace a castle gate and it has undergone several adaptations and reconstructions until the present portal.

In order to respond of the demands associated with the UNESCO classification, it was decided to realize some repairs in the "Porta Férrea". To support the intervention process of conservation (project and works), a characterization of the stone applied, properties and pathologies, was done. The similarity of the stone used in the sculptures of this construction, Ançã limestone, with the Portland limestone used as an ICP material in the International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments (Tidblad et al. 2012) allow us to

This article is part of a Topical Collection in Environmental Earth Sciences on "Stone in the Architectural Heritage: from quarry to monuments—environment, exploitation, properties and durability", guest edited by Siegfried Siegesmund, Luís Sousa, and Rubén Alfonso López-Doncel.

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compare both stones in terms of degradation process and verify if the degradation processes referred for this ICP material are related with this stone and its localization in the portal.

Constructive historical framework

The Mozarabic architecture in Coimbra (Portugal) was enhanced after Almansor have reconquered the city in 987 and marked decisively the monumentality of the Royal Palace, which would be the residence of successive Portuguese monarchs between the twelfth and the fifteenth centuries.

The transition from Royal Palace to University Palace was made through time. The main reforms started during the reign of King Manuel I (1495–1521) and lasted until the reign of King José I (1750–1777) by the administration of the Secretary of State of Internal Affairs, Marquis of Pombal. During this transitions the constructions were adapted, new areas created for the new university occupations and the buildings gained different functions.

The present monumental architectural composition of "Paços das Escolas" (Fig. 1) show a grandiosity, that goes from the finesse of the portals carved stones, to the elegance of Via Latina stairway and colonnade.

The white Ançã limestone and the yellow Coimbra dolomitic stone are characteristic of the historical buildings in the city, creating a quite rich heritage, from an architectonic and artistic point of view. The sculptors, stonemasons and carvers joined together to create an intersection of the nobility of the stone with the creativity and know-how.

The ancient fortification gate of the medieval fortress, the "Porta Férrea" portal, symbolize a very special way of accessing the courtyard of the oldest nucleus of the university campus, named "Pátio da Universidade" (Schools Courtyard). The actual portal was built by the initiative of the Rector Don Álvaro da Costa between 1633 and 1634. It is marked by Renaissance style with a mannerist influence and Flemish roots. The architect António Tavares was the author of this double portal, connecting the two fronts through a vaulted inner rectangular gallery (Fig. 1), flanked by Corinthian columns, with niches (in the East portal the statue of King João III and in the West portal the statue of King Dinis), both crowned by curved pediment with an image of Wisdom, the insignia of the University. In each portal symmetric niches

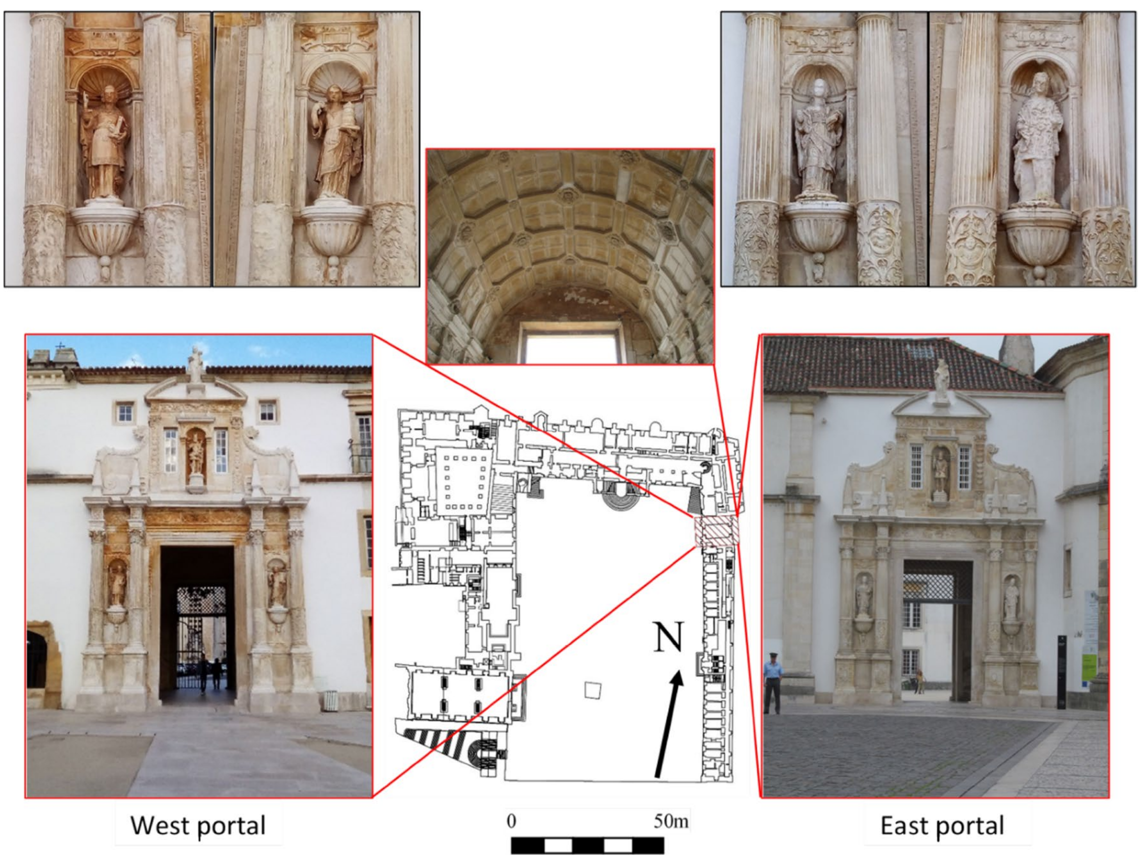


Fig. 1 General plan of "Paço das Escolas" with pictures of "Porta Férrea" (Iron Gate): East portal, vaulted inner gallery, West portal and detail of the four statues

present allegorical images with representations of the ancient colleges: Medicine and Laws on the East portal; Theology and Canons in the West portal. All sculptural groups are authored by Manuel de Sousa (Bonifácio et al. 2006). The Ançã limestone was used to carve the sculptural groups and all the decorative elements namely statues, columns, friezes and niches.

The Ançã limestone was exploited in a region close to Cantanhede in the surrounds of Coimbra, in Portugal, and corresponds to a carbonated formation of Bajocian–Bathonian (Middle Jurassic) (Trindade et al. 1998; Barbosa et al. 2008). It is almost composed by calcite, but the presence of silica in the form of quartz is also common (Ferreira Pinto and Delgado-Rodrigues 2008). It is a light-colored to yellow-white limestone, homogeneous fine-grained, bioclastic and calciclastic, showing oolitic tendency and containing very little spathized micritic cement (INETI 2017; Barbosa et al. 2008). In the portal, the stone presents a white color, sometimes with an ochre lime cover, that gives a yellow color tone to the facade.

The good workability of the Ançã limestone promoted its use in architecture and sculpture since ancient times, so it can be found in many monuments and important buildings all over Portugal. Due to its open porosity (20–27.2%), water absorption (10–14%), low mechanical strength and frost resistance (INETI 2017; Trindade et al. 1998; Ferreira Pinto and Delgado-Rodrigues 2008; Costa and Delgado-Rodrigues 2012; Delgado-Rodrigues and Ferreira Pinto 2015), it is very susceptible to deterioration by many degradation processes, including salt damage (Costa and Delgado-Rodrigues 2012).

For the structural elements of the "Porta Férrea", was applied a different stone from the same region named Outil limestone, due to its higher compression breaking load, lower porosity and water absorption (INETI 2017). The visibility of these stones is in small extension, because most of the portal is covered with decorative elements.

After its construction, many repairs have been done, with particular incidence in the decades of 30 and 40 of the last century, with replacement of four columns and three decorative slabs, in the East portal. This fact is documented, but can also be observed in situ, due to the much higher degradation of the original decorative elements when compared with the quite low degradation of the parts repaired in the same portal.

The World Heritage classification of the University of Coimbra—Alta and Sofia, includes important procedures to protect the built heritage. The conservation and restoration works of "Porta Férrea", one of the priority jobs in the proposed interventions in the candidature, took place between November 2014 and April 2015.

Intervention plan

As refereed before, the "Porta Férrea" is an iconic symbol of the University of Coimbra. As part of an enormous heritage edifice, its maintenance is an important work, always needed. Besides the importance of the portal for the people from academia, it is also an important touristic attraction, so the physical integrity and the aspect of the portal is of great relevance. The main aspects of the intervention plan, authored by F. Marques (2013), as part of the University team responsible for the conservative works of the campus buildings, included:

- Preliminary conservation status report, complemented with information in formats such as graphic/photographic/architectural;
- Architectural photogrammetric survey based on orthophotography and the cartography of pathologies;
- Historical/architectural research;
- Tests and investigations during the intervention work;
- Conservation and restoration project to implement;
- Intervention works;
- Maintenance plan;
- Final report.

The historical and architectural studies were provided by specialists related to the archeology of architecture both before and while the work was in progress. Following the authorization from the heritage authorities, a set of procedures was implemented, in order to minimize the impact and preserve the archeology in the site.

The planned intervention consisted of a soft cleaning (dry brush and aspiration; occasional soft brushing using deionized water), followed by the consolidation and protection of the materials. Previous conservative works done in University Palace, including the ones performed in the University Tower in 2010, allowed being aware of the needs for studies related with the degradation of rock materials, in order to understand the most suitable methodologies of intervention.

The research work here presented was started with the need to assist the rehabilitation work, particularly in the item "Tests and investigations during the intervention work".

Local atmospheric conditions

According the observed historical climatological values, in Coimbra from 1971 to 2000 (Table 1), the average temperature ranges from 9.5 °C in January to 20.8 °C in July.

Table 1 Normal climate of Coimbra from 1971 to 2000 (adapted from IGUC 2016)

Month	Average T (°C)	Average T max (°C)	Average t min (°C)	RH (%)	Rainfall (mm)	Wind
Jan	9.5	14.1	5.9	80	119.6	SE
Feb	10.7	15.7	7.0	78	114.2	SE
Mar	12.3	18.3	7.7	74	71.9	NW
Apr	13.4	19.2	8.9	75	88.6	NW
May	15.6	21.6	11.0	77	80.6	NW
Jun	18.8	25.5	13.8	75	42.6	NW
Jul	20.8	28.4	15.5	73	14.4	NW
Aug	20.7	28.7	15.4	73	16.5	NW
Sep	19.3	26.7	14.4	74	50.8	NW
Oct	16.2	22.0	12.0	78	104	NW/SE
Nov	12.7	17.4	9.0	80	113.3	S
Dec	10.7	14.7	7.4	81	139.8	SE
year	15.1	21.0	10.7	77	956.6	

The rain is present in 138 days with a total of precipitation of 957 mm, the air relative humidity (RH) ranges between 73 and 81% and the wind has preponderance from NW from March to October and S or SE in the four other months (IGUC 2016).

The conservation work was done in winter (November–April) and to control the atmospheric conditions, the air temperature and relative humidity in both portals were recorded (Fig. 2).

The temperature and relative humidity amplitudes in the West portal are higher than those observed in the East portal, promoting successive cycles of wetting–drying favored by sun exposure and incidence of NW winds. The West portal generally presents a temperature peak 10–18 °C higher than the East portal. When compared with the normal climate those values are also higher. Considering the relative humidity during the period of the conservative works, the East portal showed higher values, 30–40% above the values in the West portal were the amplitude is higher, but with values close to the normal climate.

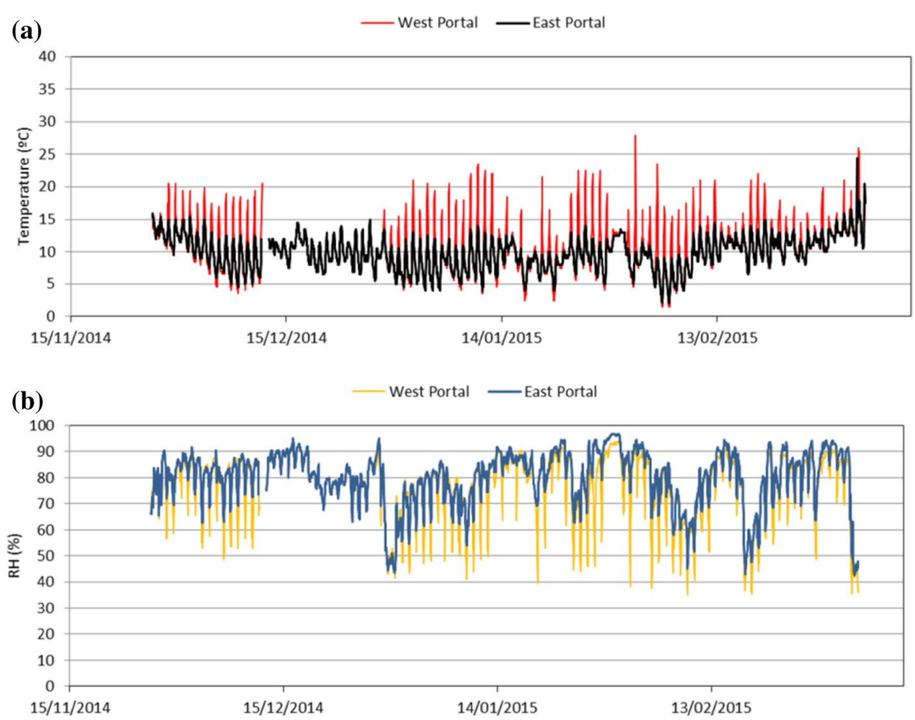


Fig. 2 Temperature (**a**) and relative humidity (**b**) values registered in East and West portals between November 2014 and March 2015

Deterioration patterns

According to the definitions of Illustrated Glossary on Stone Deterioration Patterns (ICOMOS-ISCS 2008), the deterioration patterns observed in the limestone of "Porta Férrea" are alveolization, scaling, exfoliation, fissures, powdering, and chipping (Fig. 3). Flacking, black crust and material loss are also present but not in range to be mapped at this scale. The biological colonization in the form of mosses, algae and plants is observed mainly in the cornices, lintels and pedestals, indicating problems of joint degradation but also problems to drain rainwater in the upper portals areas. The joints mortar was also degraded, but are not the main subject of this study.

The asymmetries of stone degradation can be related to the different exposures to the atmospheric conditions (sun, rain and wind). As an example, the sculpture of the north-east corner (4E—Medicine, East portal) present different pathologies when compared with the others located in the same portal (3E—Laws, East portal), but also with the ones located in the West portal (Fig. 1). The Medicine sculpture presents a homogeneous advanced degradation all over its surface, with powdering, alveolization and scaling (Fig. 4). In the remaining sculptures the degradation is in lower extension and intensity as can be observed in Fig. 3.

The differential degradation could be related with the particular atmospheric condition of the location of the statue. It is in a corner with poor ventilation and sun exposure that allow to maintain the moisture content due to rain and relative humidity in the stone. The intrinsic stone properties of the Medicine sculpture could also contribute to this difference, but it was not possible to confirm this assumption as no rock samples were possible to obtain from the sculptures.

The columns in the West portal show fissures, scaling and cavities, in a much more effective degradation when compared with the ones in the other portal, because they are original pieces, not replaced in earliest conservation works, as it happens in the East portal. However, if they were not substituted in the same occasion it can mean that, back then the degradation was not significant. In assumption, it can be said that the degradation process in both portals does not present the same rate.

Sampling methodology and tests

The selection of samples was based on two criteria: areas where the stone has not been replaced in previous restorations with obvious degradation and areas that presented different types of degradation. Thus, on the East portal, samples were removed from the two sculptures and areas with detachments and, on the West portal, samples were extracted from the columns with evident disintegration and alveolar cavities.

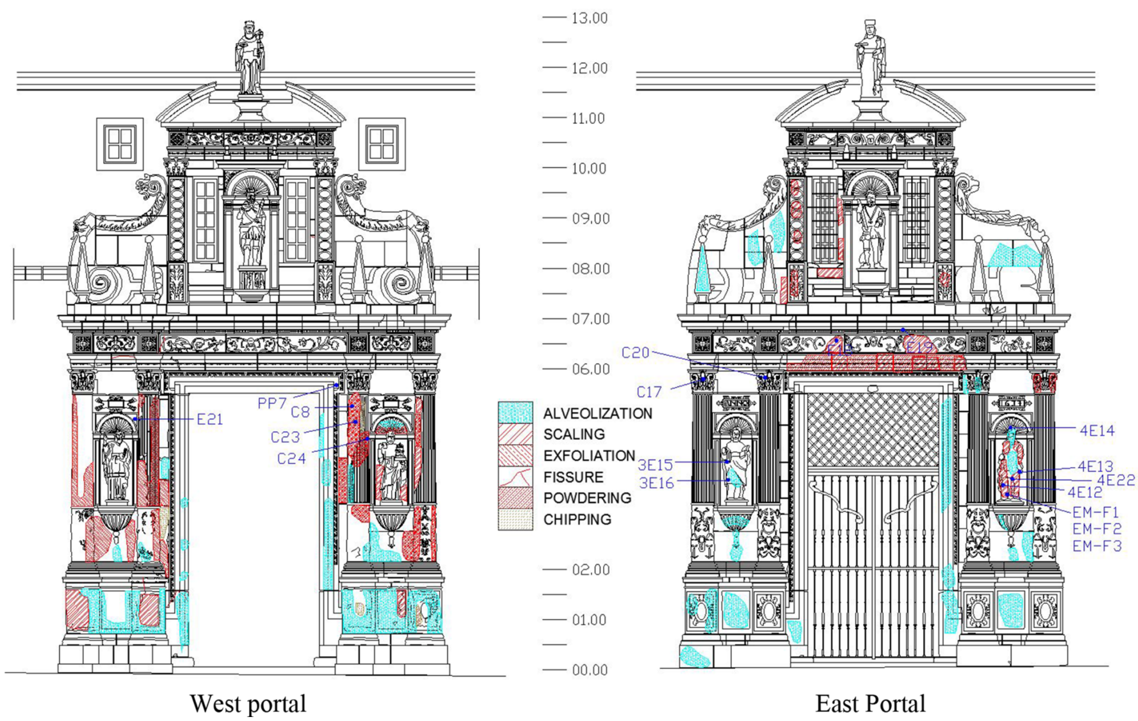


Fig. 3 More significant pathologies of the stone identified in "Porta Férrea" and sample location (adapted from Marques 2013)

Fig. 4 Details of pathologies of Medicine statue (4E) on the East portal showing powdering and scaling

Samples were collected by the conservation workers including: stone flakes, detaching parts from columns and dome; in surface weathering powder from sculpture 4E (Medicine, East portal) (Fig. 4) and yellow whitewash of sculpture 3E (Laws, East portal) summing 20 samples (Fig. 3). Additional 4 samples were collected to study the yellowish coloring in the East and West portals and to identify the pigments and binders. In order to evaluate the depth degradation of 4E sculpture, a small borehole with 3 cm depth in a non-visible location was also carried out, seeking to identify the presence of crystalline salts within the sculpture. For each centimeter of drilling a sample was collected (sample EM—F1, F2, F3).

For a first assessment of the presence of salts and sulfates in the stone, the samples were analyzed under a stereographic microscope. After, their composition was analyzed using the powder X-ray diffraction (p-XRD) technique, to identify the presence of crystalline compounds. In parallel, an elemental analysis was performed using the X-ray fluorescence (XRF) technique, in order to detect the presence of elements with atomic mass higher than sodium. This technique may indicate in some special cases, even non-crystalline substances. This is the case of heavy elements such as lead from atmospheric pollution. As a complement, some analyses were performed with micro-Raman spectroscopy, for the detection of compounds, in particular the pigments that give the color on the surface of some samples and binders.

Open porosity (EN-1936) and water absorption (EN-13755) were also determined in a few rock samples, as they are properties that can interfere with the application of consolidants, but can also give information about the stone characteristics.

In order to determine the better consolidant a few experiments of small broken cannelure of columns were also made with Lafarge© Hydrated Lime and Nanorestore© consolidants (rate 1:1 and 1:2 with isopropyl alcohol), by brushing and immersion. Both consolidants were selected taking into account the compatibility of its active components and the calcareous content of the stone (Oudbashi et al. 2008). Other consolidants have been tested and are referred in literature (Bracci et al. 2008; Pamplona et al. 2008; Costa and Delgado-Rodrigues 2012; Delgado-Rodrigues and Ferreira Pinto 2015), but the decision of technical staff was to use one with a chemical composition that does not introduce contaminant substances. The samples obtained were analyzed using the scanning electron microscopy (SEM) technique. The strength resistance was not determined due to the small size and irregular shape of the samples tested.

The conductivity of the immersion water with cannelure fragments from a column of West portal was tested, in order to evaluate the salinity present in the samples. The fragments were immersed in demineralized water (with conductivity of 3 μS/cm) and the variation of water conductivity with time was evaluated with a WTW Multi 340i equipment until stabilized. The water temperature varied between 15 and 18 °C.

The analysis plan, relevant to the work was defined as:

- Whitewash and burnish (on stone or on plaster): identification of pigments using X-ray diffraction (XRD) and/or X-ray fluorescence (XRF) and/or Raman spectroscopy;

determining the number and thickness of layers (under the stereographic microscope).

- Limestone weathering: identification of salts and oxides (XRD and/or XRF); measurement of porosity and water absorption.

The equipments used were XRD powder diffractometer Bruker D8 Advance in reflection mode with Bragg–Brentano geometry and Cu *k*-alpha radiation; fluorescence X-ray analyzer by high-sensitivity energy dispersive Hitachi SEA6000VX HSfinder with X-ray tube with *W* target and Si multi-cathode detector; micro-Raman spectroscopy, using a Jobin–Yvon T64000 equipment with focal length 0.64 m, diffraction gratings with 1800 g/mm CCD detector with 1024 × 256 pixels.

Results

The stereographic microscope observation reveals that several samples present powdery particles of salts on the surface (Fig. 5a–c). In the AbF1 sample, the crystals present higher size then the others, probably due to its location in the vaulted inner gallery, where the environment conditions are less exposed to the cycles of crystallization–dissolution. These bigger crystals can be correlated with the remains of trona ($Na_3(CO_3)(HCO_3)\bullet 2(H_2O)$) and gypsum ($CaSO_4\cdot 2H_2O$) detected by XRD (Fig. 6a).

Sample Am11 (Fig. 5b) shows a uniform distribution of white crystals when compared with sample C8. In the first case, the salt identified by XRD was halite (NaCl) and gypsum ($CaSO_4\cdot 2H_2O$) (Fig. 6b) and in the other one exists also a brown powdery crystals (Fig. 5c) corresponding to weddellite ($CaC_2O_4\cdot 2H_2O$) identified by XRD (Fig. 6c).

In the reverse of some stone samples that have been detached from the Medicine sculpture (sample 4E12 in Fig. 4), crust was observed due to the recrystallization of calcite and gypsum. Recrystallization was identified because of the presence of holes, due to the liberation of gases (CO_2 and H_2O) associated with the chemical reaction of transformation of calcium oxide in calcium carbonate and also with the process of sulfation of calcium carbonate to give rise to gypsum (Figs. 5d, 6d).

The XRD patterns of different sample powders allowed to identify several salts and sulfates: weddellite ($CaC_2O_4\cdot 2H_2O$), halite (NaCl) and gypsum ($CaSO_4\cdot 2H_2O$) (Fig. 6). The presence of trona is not very obvious (Fig. 6a), because it only matches two reflections in the diffractogram. The gypsum is the result of a sulfation processes associated with cycles of wetting/drying present in 8 of the 12 samples analyzed. Weddellite is a calcium oxalate which can occur by reaction between the rock and lichens (Wadsten and Moberg 1985; McAlister et al. 2000; Schiavon 2002; Giordani et al. 2003) or other chemical reactions (Cariati et al. 2000; Rusakov et al. 2017).

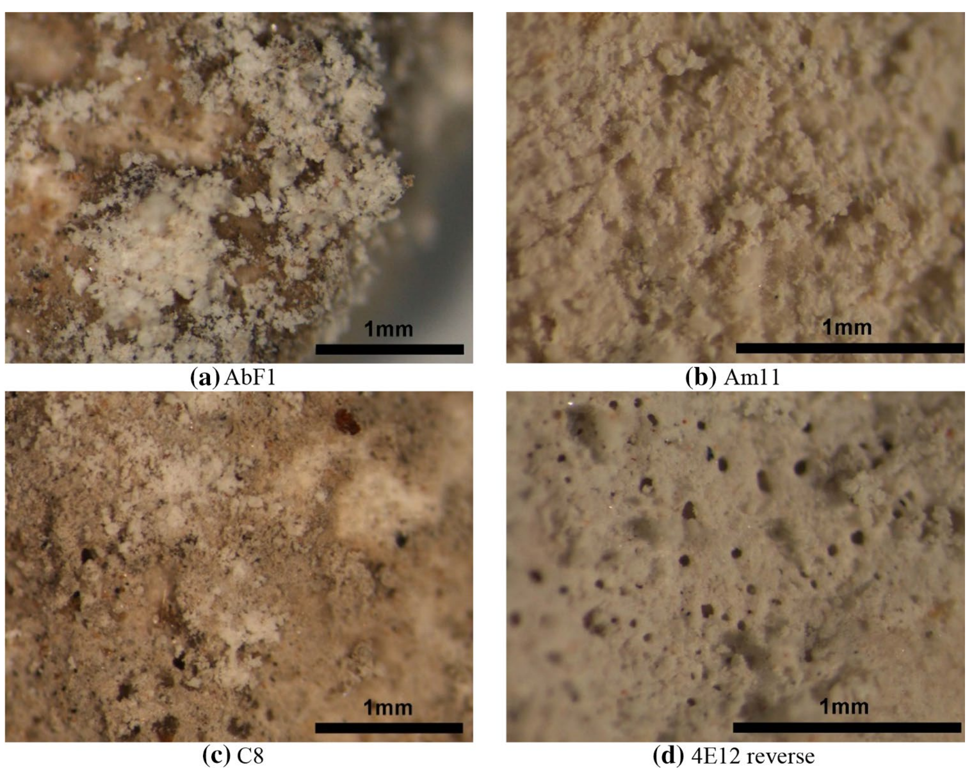


Fig. 5 Stereographic microscope observation of several samples: **a** crystals of trona and gypsum in sample AbF1; **b** uniform distribution of salts in sample Am11; **c** brown crystal of weddellite in sample C8; **d** reverse of stone sample 4E12 showing a crust with holes due to recrystallization

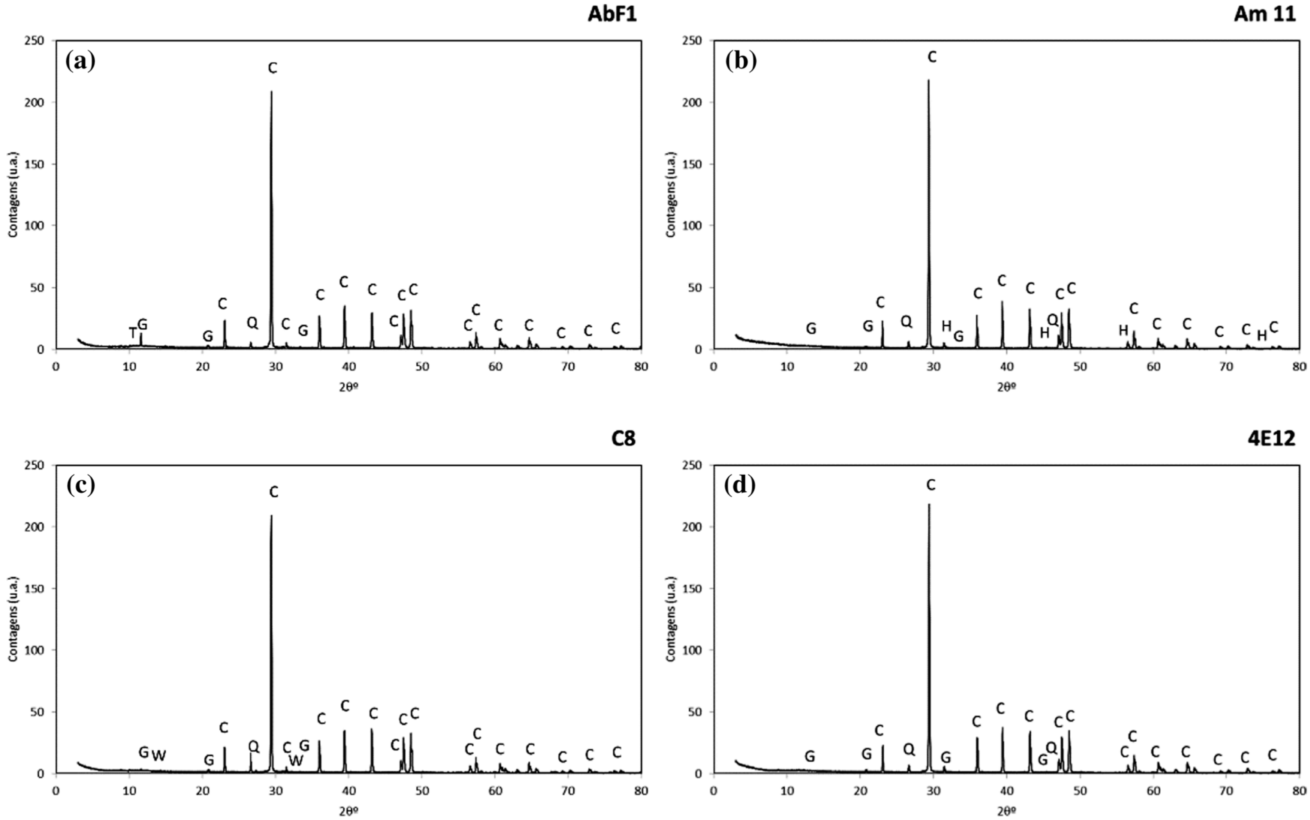


Fig. 6 XRD patterns of samples **a** AbF1, **b** Am11, **c** C8 and **d** 4E12 (*C* calcite, *Q* quartz, *G* gypsum, *H* halite, *W* weddellite, *T* trona)

The analysis obtained using the XRF equipment allows to identify other elements in small quantities. Some of these elements are lead (Pb), zinc (Zn), sulfur (S) and chlorine (Cl). The element lead is present in seven of the eight samples analyzed, with particular emphasis in the darker layers of the East portal sculptures (Fig. 7).

The presence of sulfur was also identified in many samples in dark areas, reaching high values. This element is directly related to the presence of gypsum (Graue et al. 2012), already identified by X-ray diffraction. The presence of chlorine (Cl) was also registered in a great number of samples in XRF determinations, related with the salt contents.

The presence of potassium (K) in the stone samples is not unusual, but the quantity is, in some cases, higher than expected. This could be attributed to repairs made in the beginning of twentieth century, because at that time one of the techniques used to promote the resistance and durability of limestone was the superficial application of potassium silicate with a paint-brush in concentrations allowing the natural penetration (Segurado 1932).

The architectural and sculptural surface layers present a pigmented lime in yellowish tones. It was detected by Raman spectroscopy calcite, ochre (iron oxide hydrate, α-FeO (OH)) and calcium oxalate monohydrate ($CaC_2O_4·H_2O$). The pigmented lime could have been applied soon after the portal was built (1634), with the following layers being due to maintenance interventions or, later, when the degradation of some surfaces of Ançã limestone took place. Although there was the expectation of finding organic binders with micro-Raman spectroscopy, it was not possible to confirm this fact.

Due to the huge powdering degradation observed at the surface of the statue Medicine (4E—East portal), we admit the hypothesis of the presence of salts, namely halite. However, the XRD analyses of samples EM-F1, F2, F3 only present calcite and quartz.

In spite of the absence of identified halite in the samples of the outer parts of the portals, the conductivity of cannelure fragments from detachments of a column of West portal was tested in order to evaluate the presence of salts. The concentration was obtained after the correction of the conductivity for the reference temperature of 25 °C (Hayashi 2004), and assuming the coefficient of 0.5 for the conversion of conductivity to concentration for sodium chloride (Foxboro 1999).

The cycle of immersion was also realized with a sample of a similar stone from the portal but not exposed to the exterior conditions, designated as reference limestone. In this experiment, the concentration obtained was 0.7% of salts.

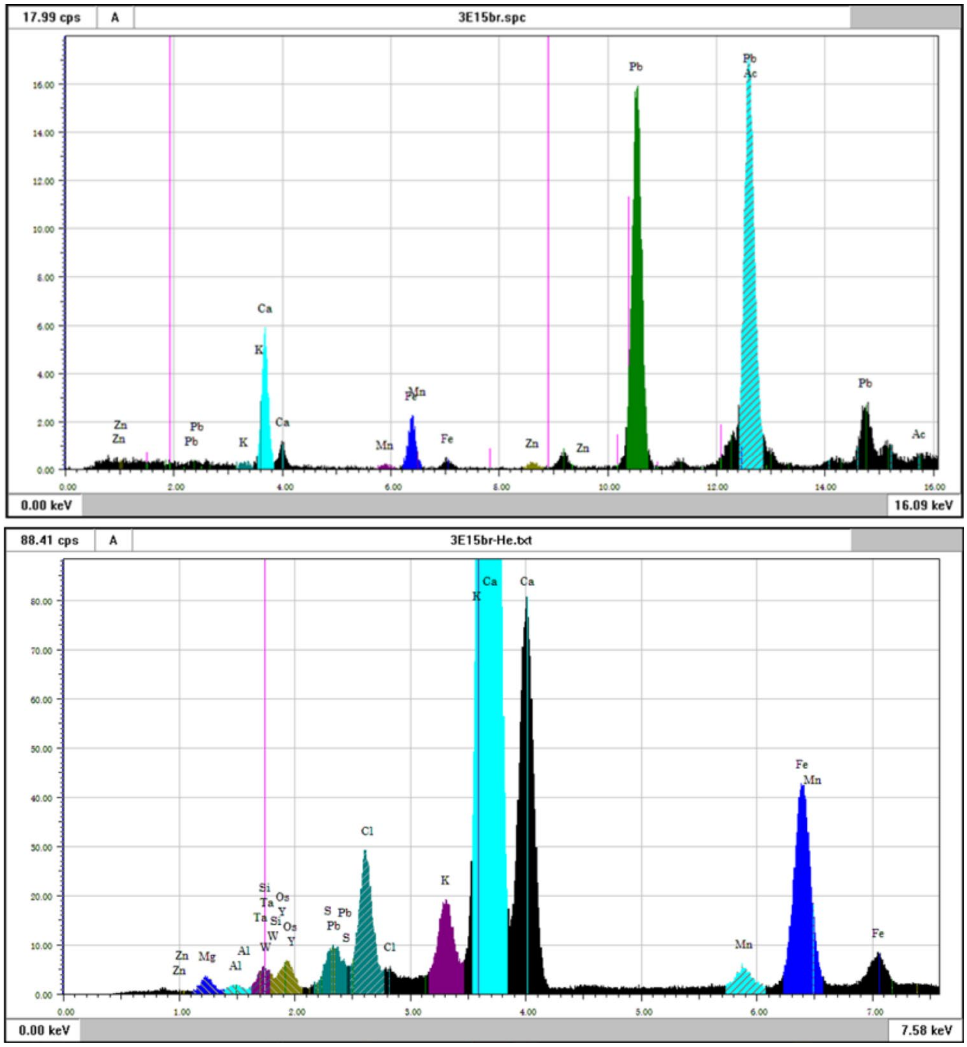


Fig. 7 XRF spectra of a sample from a sculpture 3E in East portal, at high (top) and low (bottom) X-ray energy

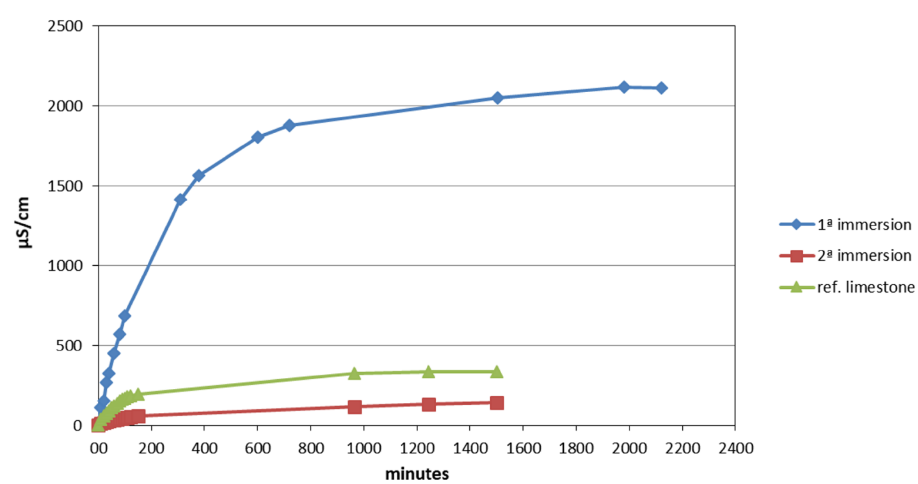


Fig. 8 Comparison between the water conductivity values in the 1st and 2nd immersion of a cannelure sample and with the reference limestone sample

The result obtained in the first cycle of the cannelure fragment (Fig. 8) reveals a content of salts in the sample, close to 5.2%. Assuming the value of 0.7% as the natural content of soluble salts in the reference stone, remaining 4.5% corresponds to the additional concentration of salts, due to environmental contamination.

To verify that removal of the salt content into the water had been effective, a second immersion of the sample was performed. According to the results, the conductivity of the water in the second immersion is much lower than the first immersion, lower than the result obtained in the reference limestone. With this experiment, the existence of salts in samples in lower content was evident and hence was not detected in XRD diffraction.

The results of open porosity and water absorption of a cannelure sample and a reference limestone sample show mean values of 29.7% and 11.9%, respectively. The mean value for the bulk density was 1983 kg/m^3. These values are consistent with those of Ançã stone determined by other authors (Ferreira Pinto and Delgado-Rodrigues 2012; Delgado-Rodrigues and Ferreira Pinto 2015), but higher than other limestones including Portland limestone (Fitzner et al. 2002; Yates 2007; Hughes et al. 2013; Wilhelm 2016).

A sample of material that filled cavities in the columns of the West portal (sample C23 in Fig. 3) was also analyzed in order to recognize if that material was a result of the stone degradation. The diffraction pattern showed only the presence of quartz in abundant quantity and calcite. A more careful analysis of the sample has revealed quartz particles with size of very fine sand. It is possible that this material corresponds to an anthropogenic replacement, using fine white quartz sand associated with lime or stone dust, possibly to fill cavities on the rock block used to carve the column or due to later degradations. These replacements could also be related with repairs and conservation works made in the last century.

The experiments made with consolidants reveal that the Lafarge© Hydraulic Lime can penetrate easier in small holes (Fig. 9a), than Nanorestore© consolidant in a rate 1:1, but both can achieve a uniform aspect when are applied by brushing. However, the immersion in Nanorestore© consolidant presents a different kind of crystallization with the formation of elongated particles (2.2 × 0.35 µm) creating a coating surface (Fig. 9b).

Conservative intervention

The conservation and restoration work that was necessary to be done was adapted to the stage of degradation of each piece. In areas less degraded as the pavement in the inner gallery, pilasters, friezes and capitals in the interiors, the conservation works were less demanding. Some pieces originally in stones but already substituted by plaster, also present significant missing parts in friezes and capitals, were replaced when necessary.

The cleaning standardization was a quite important issue considering the portal yellowish details due to patina, as it was necessary to maintain the chromatic balance between cleaned and patina surfaces, in order to have a correct lecture of the portal. A final chromatic correction using lime water with ochre was applied in the areas affected by biological colonization, when the limestone presents white color. Along with the cleaning process, the closure of joints, cracks and fractures were common during all intervention. The disintegrated joint mortars were replaced and all the previous unwanted replacements in Portland cement were removed. The local corrections and reinforcements were made with fine sand plaster.

The biological colonization was not significant but plants, algae, mosses and lichens were removed using brushes or cutting tools. The decorative elements were in quite good conditions, except the one in the northeast side of East portal, Medicine. Cleaning and consolidation was the developed works in all the elements. Lafarge© Hydraulic Lime was applied in the restoration actions to fill gaps by paint brush and the Nanostore© consolidant, which was easier to injections, was used for detachment situations (Costa and Delgado-Rodrigues 2012; Allanbrook and Wilson 2012; Zornoza-Indart et al. 2012). The responsible team decided not proceeded with desalination, due to the low content and the difficulties of the operation.

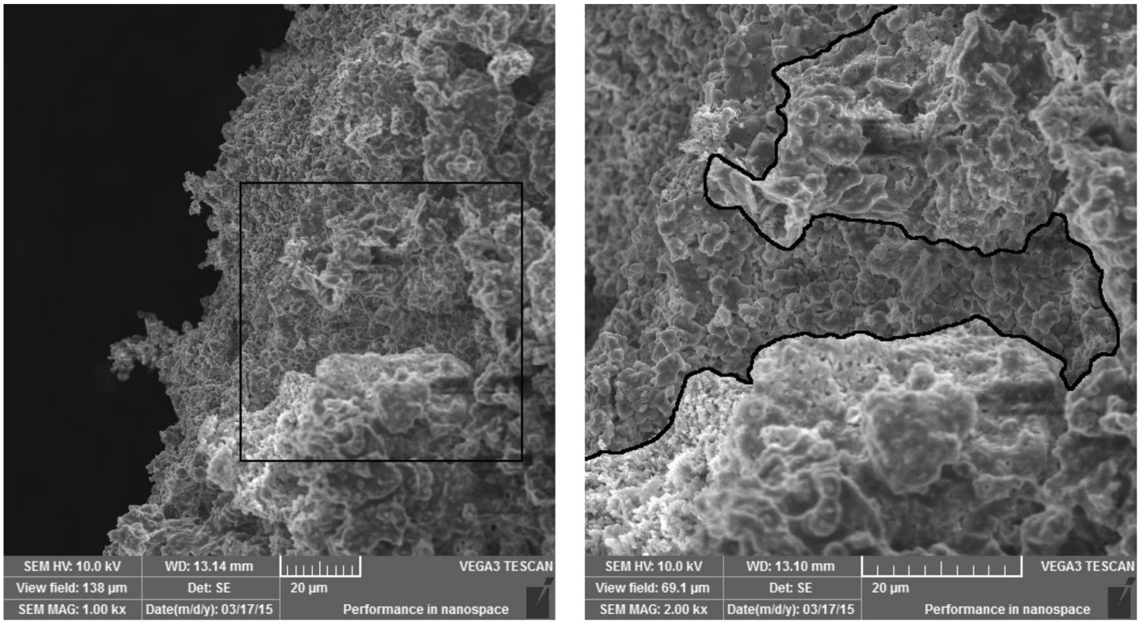
Discussion

The degradation of stone in urban areas is generally correlated to the air taking into account the dose–response functions (DRF). In the case of stones, DRF is only established for Portland limestone in a study realized all over the world from 1987 to 2009 (Tidblad et al. 2012). The DRF is defined as function of the concentration of sulfur dioxide, nitrogen oxide, hydrogen, ozone, PM10, rain, and relative humidity. As a remark, the authors observe that the last results compared to the first exposure, are obviously lower, but there is significant year-to-year variation and there is no obvious decrease since 1998.

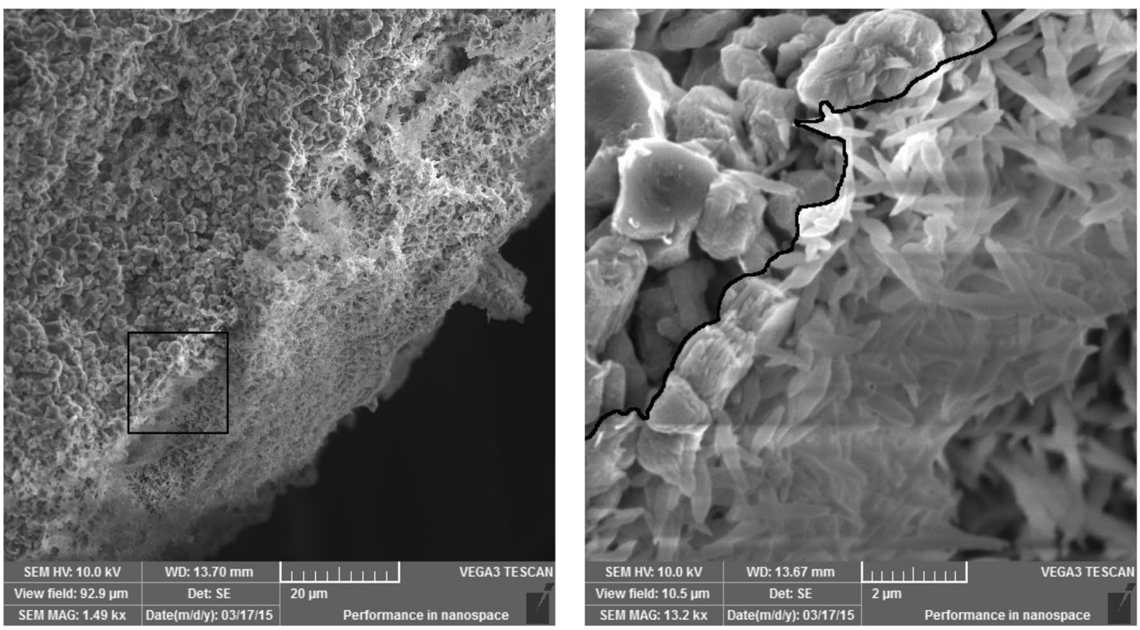
Pio et al. (1998) refer Coimbra as a region of low industrialization, where the sheltered specimens of Portland limestone used in tests increase in weight, while the unsheltered tablets lose weight, both in small amounts.

It is known that the concentration of pollutants in the city of Coimbra have decreased during the last decade and this can be seen in the pH of rain water: through 1978–1980 the value turns around 5.3–5.8 (Branco and Formosinho 1983) but from 2011 to 2014 the average value fits 6.85–6.86 (Silveira et al. 2016). Data of governmental institute available on-line (http://qualar.apambiente.pt/) with measures of the principal contaminants of air also can demonstrate that, with no exceedances after 2011, following the global decrease of contaminants since the last decade of the twentieth century (Doehne and Price 2010; Urosevic et al. 2012).

In the XRF results obtained with the samples analyzed (Fig. 7), it was observed elements such as lead, zinc, and



(a)



(b)

Fig. 9 SEM images of experiments made with consolidants **a** Lafarge© Hydraulic Lime applied by brushing, **b** Nanorestore© consolidant applied by immersion

sulfur, elements that are not present in fresh stone. Those elements are present in the air as a contamination from combustion of fuels (Graue et al. 2013). At present fuels do not contain lead, but until the 90 years of last century it was an important additive in gasoline. It is also important to mention that until 2001 cars were allowed to enter in University Courtyard through the "Porta Férrea", and intense traffic was present around. The zinc seems to be associated with the presence of lead, and can also be present in the chemical composition of lubricating oil of hydraulic motors and systems. It is expectable that future conservative works prove the absence of this kind of contaminants in the stone.

The characteristics of the Ançã limestone and the Portland limestone are similar in terms of water absorption, porosity, mineralogical and chemical composition, despite the different location and age. Portland limestone is an oolitic limestone with a fine-grained texture and an intergranular porosity of about 22–23% and is quarried on the isle of Portland in Dorset, England (Yates 2007; Hughes et al. 2013; Wilhelm et al. 2016). Under that point of view the correlation between them is possible. The response of Portland limestone to the detrimental effect of air pollution and meteorological factors is expressed by the DRF as surface recession. No DRF could be derived for the soiling of Portland limestone because the data revealed too much scatter (Watt et al. 2008). The average of surface recession observed in the last campaigns varies between 6 and 11 µm per year (Tidblad et al. 2012).

However, regarding the degradation pattern of the decorative elements in "Porta Férrea" (Fig. 3) it can be observed that recession surface and soiling are not important deteriorations. On this topic and focus in the four statues, they also present different behaviors. Particularly, the Medicine and Laws in the East portal, present a very different degree of deterioration, despite they are in a similar architectonical condition and at a distance of 5.5 m. Medicine statue showed a high level of surface disintegration, mainly powdering, scaling and alveolization. Intrinsic (stone-related properties) and extrinsic (environmental related variables such as exposure and micro-climatic conditions, pollution, etc.) factors can contribute to this difference (Pio et al. 1998) but assuming that the raw material was quarried in the same exploitation, at the same time, and the atmospheric condition are also identical, it is difficult to understand these process unless it is related with extrinsic factors.

Taking into account the NE location of the statue in the East portal (Fig. 1) and the predominant direction of the wind from NW (Table 1), it can be confirmed that the place corresponds to a corner where the wind have small importance in the drying effect of moisture content. Furthermore, when the small borehole was done in this statue for remove samples to identify salts, it was noticed that surface was dry despite the winter time, but at a 3 cm deep the stone was pasty with a great quantity of water. The problem was defined in a different condition as time of "wetness" (Smith et al. 2011) in response to the wet/drying cycles and related with the biological colonization. In our case, the biological colonization is not present but the presence of water in deep with a long residence time allow to a powdering disintegration favored by high porosity (29%) and water absorption (12%) of the Ançã limestone. The freeze–thaw cycles do not represent a problem in this case (De Kock et al. 2012) since the average temperatures in the city do not often reach negative values (Table 1). Due to the absence of wind this powder remains on the surface.

In this study, it can be confirmed that limestone of "Porta Férrea" do not decay according a theoretical predictable pattern in response to polluted environments, as the defined for Portland limestone, assuming erosion rates and forms controlled by a range of micro-environment conditions (Smith et al. 2010) particularly related with architectural constraints.

Conclusions

Based on the research performed and on the works accomplished, a few main considerations can be pointed out:

- The East portal is less exposed to temperature variations, promoting the retention of both rainwater and air moisture, that combined with the high porosity and high water absorption of the Ançã limestone inducing mainly degradation by dissolution incremented by environmental contamination;
- The yellow pigments match with ochre (α-FeO (OH)), which is consistent with the results obtained by XRD, XRF and micro-Raman spectroscopy;
- No organic substances could be identified by the Raman spectroscopy;
- Lead was identified particularly in the East portal, associated with sulfur and zinc, due to atmospheric contamination;
- The presence of crystalline salts particularly halite is related with the atmospheric conditions because in reserved environment it is present but when exposed to higher moisture content it is present in a soluble form, detected only by the conductivity of the water and the presence of the chlorine element. If this work was developed in the summer, probably the results could be different;
- Erosion rates and deterioration patterns are controlled by a range of micro-environments conditions particularly related with architectural constraints.

The results allowed a more comprehensive and wise intervention, seeking to preserve a monument that is part of the UNESCO Word Heritage and a quite strong icon of the University of Coimbra.

Acknowledgements We thank AOF Lda company (Dr. Telma Teixeira and David Llanos) for the information provided. Access to TAIL-UC facility, funded under QREN-Mais Centro project ICT_2009_02_012_1890 is gratefully acknowledged. This work was supported by FCT—Fundação para a Ciência e a Tecnologia, I.P., through Portuguese funds, in the research project UID/Multi/00073/2013 of the Geosciences Center of the University of Coimbra.

References

Allanbrook T, Wilson A (2012) Conservation of architectural marble at the New York Public Library. In: 12th International congress on the deterioration and conservation of stone Columbia University, New York. http://iscs.icomos.org/pdf-files/NewYorkConf/allawill.pdf. Accessed 11 Feb 2018

Barbosa B, Soares A, Rocha R, Manuppella G, Henriques MH (2008) Carta Geológica de Portugal na escala de 1:50,000. Notícia explicativa da folha 19A—Cantanhede. INETI, Lisboa

Bonifácio H, Gordalina R, Oliveira L, Pessoa L (2006) Paço da Universidade de Coimbra. http://www.monumentos.pt/. Accessed 12 Mar 2016

Bracci S, Sacchi B, Pinto APF, Delgado-Rodrigues J (2008) Inorganic consolidants on stone artefacts: optimisation of application procedures for marble and limestones. In: Delgado Rodrigues J, Mimoso JM (eds) Proceedings of the international symposium "Stone Consolidation in Cultural Heritage. Research and Practice", Lisbon, LNEC, pp 81–90

Branco JB, Formosinho SJ (1983) pH of rain water in Coimbra, Portugal: the seasonal variation. Tellus 35(B):237–239

Cariati F, Rampazzi L, Toniolo L, Pozzi A (2000) Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation. J Stud Conserv 45(3):180–188. https://doi.org/10.1179/sic.2000.45.3.180

Costa D, Delgado-Rodrigues J (2012) Consolidation of a porous limestone with nanolime. In: 12th International congress on deterioration and conservation of stone, at New York (USA), November 2012. https://www.researchgate.net/publication/257919278. Accessed 6 Mar 2014

De Kock T et al (2012) Monitoring frost susceptibility of limestone facies. In: 12th International congress on the deterioration and conservation of stone Columbia University, New York. http://iscs.icomos.org/pdf-files/NewYorkConf/dekoetal1.pdf. Accessed 11 Feb 2018

Delgado-Rodrigues J, Ferreira Pinto AP (2015) Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones. J Cult Heritage 19:467–476. https://doi.org/10.1016/j.culher.2015.10.002

Doehne E, Price C (2010) Stone conservation: an overview of current research, 2nd edn. Getty Conservation Institute, Los Angeles. https://doi.org/10.1007/s12665-016-5661-y

EN 13755 (2006) Natural stone test methods—determination of real density and apparent density, and of total and open porosity. European standard

EN 1936 (2008) Natural stone test methods—determination of water absorption at atmospheric pressure. European Standard

Ferreira Pinto AP, Delgado-Rodrigues J (2008) Stone consolidation: the role of treatment procedures. J Cult Heritage 9:38–53. https://doi.org/10.1016/j.culher.2007.06.004

Ferreira Pinto AP, Delgado-Rodrigues J (2012) Consolidation of carbonate stones: influence of treatment procedures on the strengthening action of consolidants. J Cult Heritage 13:154–166. https://doi.org/10.1016/j.culher.2011.07.003

Fitzner B, Heinrichs K, La Bouchardiere D (2002) Limestone weathering of historical monuments in Cairo Egypt. In: Siegesmund S, Weiss T, Vollbrecht A (eds) Natural stone, weathering phenomena, conservation strategies and case studies, vol 205. Geological Society, London, pp 217–239 **(Special Publications)**

Foxboro (1999) Conductivity ordering guide. EXW Foxboro, Massachusetts. http://myweb.wit.edu/sandinic/Research/conductivity%20v%20concentration.pdf. Accessed 15 Feb 2018

Giordani P, Modenesi P, Tretiach M (2003) Determinant factors for the formation of the calcium oxalate minerals, weddellite and whewellite, on the surface of foliose lichens. Lichenologist 35(3):255–270. https://doi.org/10.1016/S0024-2829(03)00028-8

Graue B, Siegesmund S, Simon K, Licha T, Oyhantcabal P, Middendorf B (2012) Environmental impact on stone decay: crust formation at the Cologne cathedral. In: 12th International congress on the deterioration and conservation of stone Columbia University, New York. http://iscs.icomos.org/pdf-files/NewYorkConf/grauetal1.pdf. Accessed 11 Feb 2018

Graue B, Siegesmund S, Oyhantcabal P, Naumann R, Licha T, Simon K (2013) The effect of air pollution on stone decay: the decay of the Drachenfels trachyte in industrial, urban, and rural environments—a case study of the Cologne, Altenberg and Xanten cathedrals. Environ Earth Sci 69:1095–1124. https://doi.org/10.1007/s12665-012-2161-6

Hayashi M (2004) Temperature–electrical conductivity relation of water for environmental monitoring and geophysical data inversion. Environ Monit Assess 96(1–3):119–128

Hughes T, Lott GK, Poultney MJ, Cooper B (2013) Portland Stone: a nomination for "Global Heritage Stone Resource" from the United Kingdom. Episodes 36(3):221–226

ICOMOS-ISCS (2008) Illustrated Glossary on Stone Deterioration Patterns. In: International council on monuments and sites/international scientific committee for stone. Edition V. Vergès-Belmin. Monuments and Sites XV, English-French edition

IGUC (2016) Normal climatological and actinometric values 1971–2000. Instituto Geofísico da Universidade de Coimbra. http://www1.ci.uc.pt/iguc/dados_cllima/norm7100.htm. Accessed 29 Oct 2016

INETI (2017) Catalogue of Portuguese Ornamental Stones, RS-CA 601 Ançã = Pedra de Ançã; RS-CA 601b Pedra de Outil. http://rop.lneg.pt/rop/index_en.php. Accessed 6 May 2017

Marques F (2013) Conservação e Restauro da Porta Férrea, Paço das Escolas. Internal document GNI/GCU, Universidade de Coimbra

McAlister JJ, Smith BJ, Neto JAB (2000) The Presence of Calcium Oxalate Dihydrate (Weddellite) in street sediments from Niterói, Brazil and its Health Implications. Environ Geochem Health 22:195. https://doi.org/10.1023/A:1026593729453

Oudbashi O, Siapoosh B, Siapoosh M, Shekofte A (2008) Consolidation of Limestone by Lime Method in Sangneveshteh Historic Monument, Khoramabad, West of Iran—a Practical Case. In: Delgado Rodrigues J, Mimoso JM (eds) Proceedings international symposium "Stone Consolidation in Cultural Heritage. Research and Practice", Lisbon, LNEC, pp 289–297

Pamplona M, Kocher M, Snethlage R, Wendler E (2008) Consolidation effectiveness of TEOS on Ançã limestone from Portugal—a laboratory study. In: Delgado Rodrigues J, Mimoso JM (eds) Proceedings international symposium "Stone Consolidation in Cultural Heritage. Research and Practice", Lisbon, LNEC, pp 183–192

Pio CA, Ramos MM, Duarte AC (1998) Atmospheric aerosol and soiling of external surfaces in an Urban Environment. Atmos Environ 32(11):1979–1989

Rusakov AV, Kuzmina M, Frank-Kamenetskaya O, Vlasov D (2017) Crystallization medium variations as a factor of oxalate patina formation. IUCr 2017 E-Abstracts. http://eabstracts.iucr2017.org/. Accessed 15 Feb 2018

Schiavon N, (2002) Biodeterioration of calcareous and granitic building stones in urban environments, vol 205. Geological Society, London, pp 195–205. https://doi.org/10.1144/GSL.SP.2002.205.01.15 **(Special Publications)**

Segurado JES (1932) Materiais de Construção. Biblioteca de Instrução Profissional. Livrarias Aillaud e Bertrand, 2ª edn

Silveira A, Lima JLMP, Lima MIP, Silva GCO, Naspolini BF (2016) Análise comparativa da qualidade da água da chuva precipitada e coletada em coberturas em dois locais no Brasil e em Portugal. Engenharia Civil UM 52:23–32

Smith BJ, Gomez-Heras M, Viles HA (2010) Underlying issues on the selection, use and conservation of building limestone. In: Smith BJ, Gomez-Heras M, Viles HA, Cassar J (eds) Limestone in the built environment: present-day challenges for the preservation of the past, vol 331. Geological Society, London, pp 1–11. https://doi.org/10.1144/SP331.1 **(Special Publications)**

Smith BJ, McCabe S, McAllister D, Adamson C, Viles HA, Curran JM (2011) A commentary on climate change, stone decay dynamics and the 'greening' of natural stone buildings: new perspectives on 'deep wetting'. Environ Earth Sci 63:1691–1700. https://doi.org/10.1007/s12665-010-0766-1

Tidblad J et al (2012) Effects of air pollution on materials and cultural heritage: ICP materials celebrates 25 years of research. Int J Corros. https://doi.org/10.1155/2012/496321

Trindade MF, Ferreira MOQ, Oliveira R (1998) Contribution to the study of Ancã limestone. In: Moore D, Hungr O (eds) Eighth international congress international association for engineering, geology and the environment, proceedings, vol 1–5, pp 2945–2952

University of Coimbra (2016) University of Coimbra Alta and Sofia—world heritage list. http://worldheritage.uc.pt/. Accessed 20 Oct 2016

Urosevic M, Yebra-Rodríguez A, Sebastián-Pardo E, Cardell C (2012) Black soiling of an architectural limestone during two-year term exposure to urban air in the city of Granada (S Spain). Sci Total Environ 414:564–575

Wadsten T, Moberg R (1985) Calcium oxalate hydrates on the surface of lichens. Lichenologist 17(3):239–245 https://doi.org/10.1017/S0024282985000305 **(Published online: 28 March 2007)**

Watt J, Jarrett D, Hamilton R (2008) Dose–response functions for the soiling of heritage materials due to air pollution exposure. Sci Total Environ 400(1–3):415–424

Wilhelm K, Viles H, Burke O, Mayaud J (2016) Surface hardness as a proxy for weathering behaviour of limestone heritage: a case study on dated headstones on the Isle of Portland, UK. Environ Earth Sci 75:931

Yates T (2007) Results from the 2005–2006 trend exposure program. Corrosion attack of limestone after 1 year exposure, vol 8. Building research Establishment Ltd., Garston. http://www.corr-institute.se/ICP-Materials. Accessed 19 Feb 2018

Zornoza-Indart A, López-Arce P, Gómez-Villalba LS, Varas-Muriel MJ, Fort R (2012) Consolidation of deteriorated carbonate stones with $Ca(OH)_2$ nanoparticles. In: 12th International congress on the deterioration and conservation of stone Columbia University, New York. http://iscs.icomos.org/pdf-files/NewYorkConf/zornoza.pdf. Accessed 11 Feb 2018