Study and testing of the "Porta Férrea" stone materials University of Coimbra, Portugal

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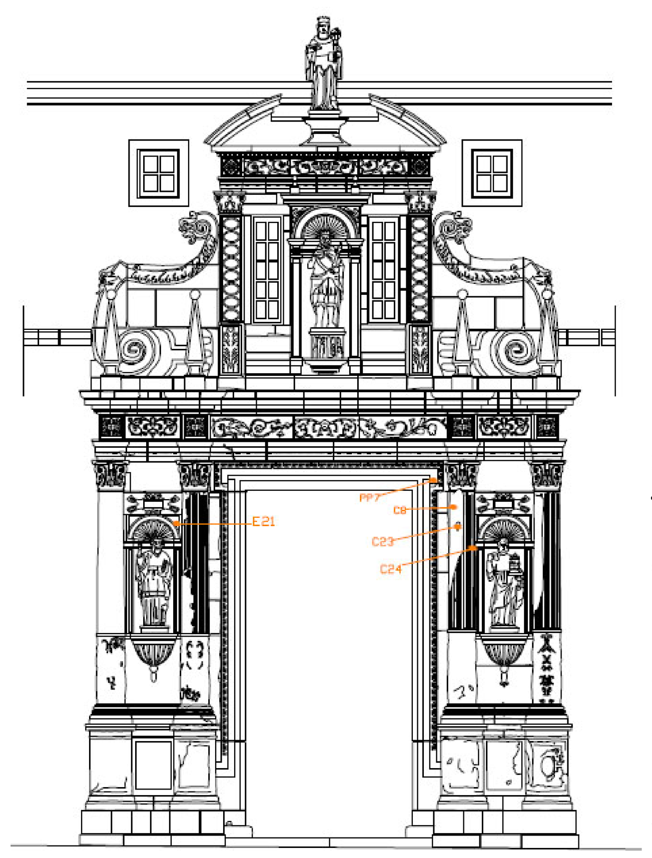


Figure 1 | Porta Férrea, West Portal.

Introduction

"Porta Férrea" (Iron Gate) was built from the initiative of the Rector of the University, Don Alvaro da Costa (1633-1637) in the beginning of his mandate. It corresponds to the access of the University in an edifice used before as the Royal Palace in Coimbra. In the present time "Porta Férrea" remains as one important symbol of the University (Universidade de Coimbra, 2014).
The architect António Tavares was the author of this double portal, connecting the two fronts through a vaulted inner gallery, with a rectangular vain. All sculptural groups are authored by Manuel de Sousa (Bonifácio *et al.*, 2006). The stone used to carve the sculptural groups and all the decorative elements was Ançã Stone, recognised by the simplicity of working, but with high porosity and water absorption.

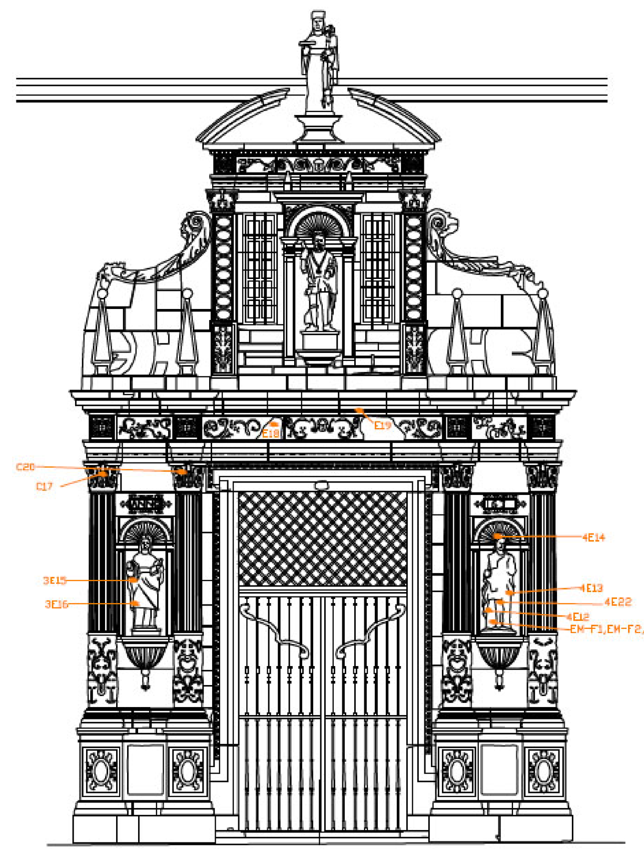
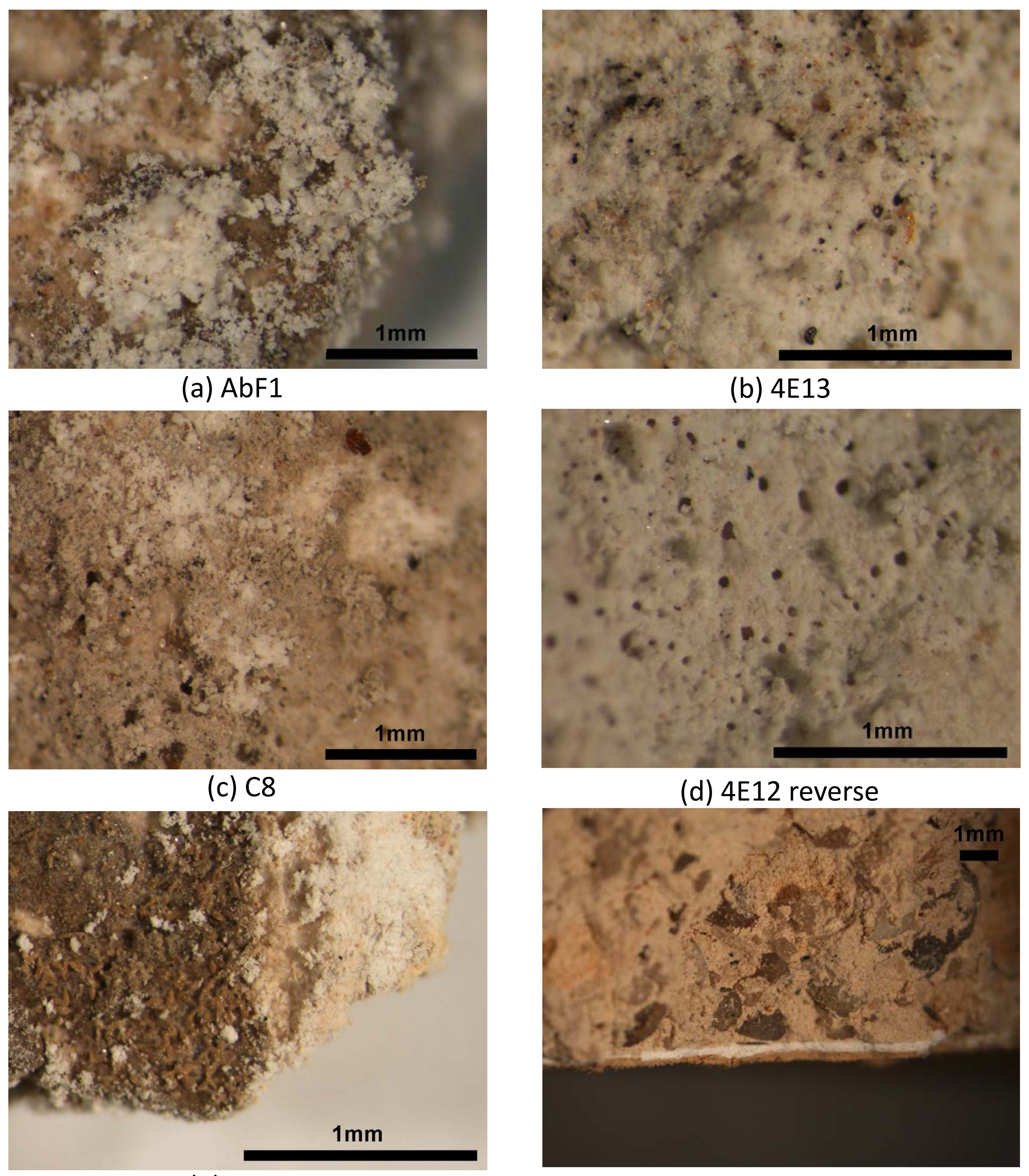


Figure 2 | Porta Férrea, East Portal.

After its construction, many repairs have been done over time, with particular incidence in the decades of 30 and 40 of the last century. Since 2013 University of Coimbra — Alta and Sofia is classified with three criteria in the World Heritage list. Due to this classification many interventions were recognised as needed. In November 2014 started the work of conservation and restoration in "Porta Férrea", one of the priority jobs in the interventions defined. The research support was then requested to aid and assist the enterprise work.

Methodology

Samples were collected in: stone flakes and mortar detaching from columns and dome; surface weathering powder from sculptures and yellow whitewash in several places (figure 1, 2). Additional samples were collected to study the yellowish colouring to identify the pigments and binders. In order to evaluate the depth degradation of 4E sculpture was also carried out a small borehole with 3 cm deep in a non-visible site to identify the presence of crystalline salts.
The analysis considered relevant to the work were: determining the number and thickness of layers (under the stereographic microscope); identification of pigments /binders using X-ray diffraction (XRD) and/or X-ray fluorescence (XRF) and/or Raman spectroscopy; identification of salts and oxides (XRD and/or XRF); measurement of porosity and water absorption. Air temperature and relative humidity was also evaluated during the conservation work.
The equipment's used were: XRD powder diffractometer Bruker D8 Advance in reflection mode with Bragg-Brentano geometry and Cu k-alpha radiation; fluorescence X-ray analyser 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 1024x256 pixels.



(a) AbF1 (b) 4E13
(c) C8 (d) 4E12 reverse
(e) 3E16 (f) PW3

Figure 3 | Images of samples at stereographic microscope.

Acknowledgements

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Results

The observation on stereographic microscope reveals that several samples present powdery particles on surface (figure 3a, b, c). In the reverse of some stone samples that have been detached it is observed a recrystallization of calcite with holes (figure 3d). Small crystals with elongate form are also observed (figure 3e). XRD patterns allow to identify gypsum ($CaSO_4.2H_2O$), weddellite ($CaC_2O_4.2H_2O$) and halite (NaCl) (figure 4). The gypsum could be the result of a sulfation processes associated with cycles of wetting/drying. The weddellite is a calcium oxalate which can occur by reaction between the rock and lichens or other chemical reactions. Halite is also present in the mortar sample.
Yellow whitewash are present as a thin layer above a whitewash layer (figure 3f). In samples of the borehole in sculpture it was only detected calcite and quartz. If salts are present the quantity doesn't allow the detection by XRD. This may be due to the content of water, higher in deep than in surface.

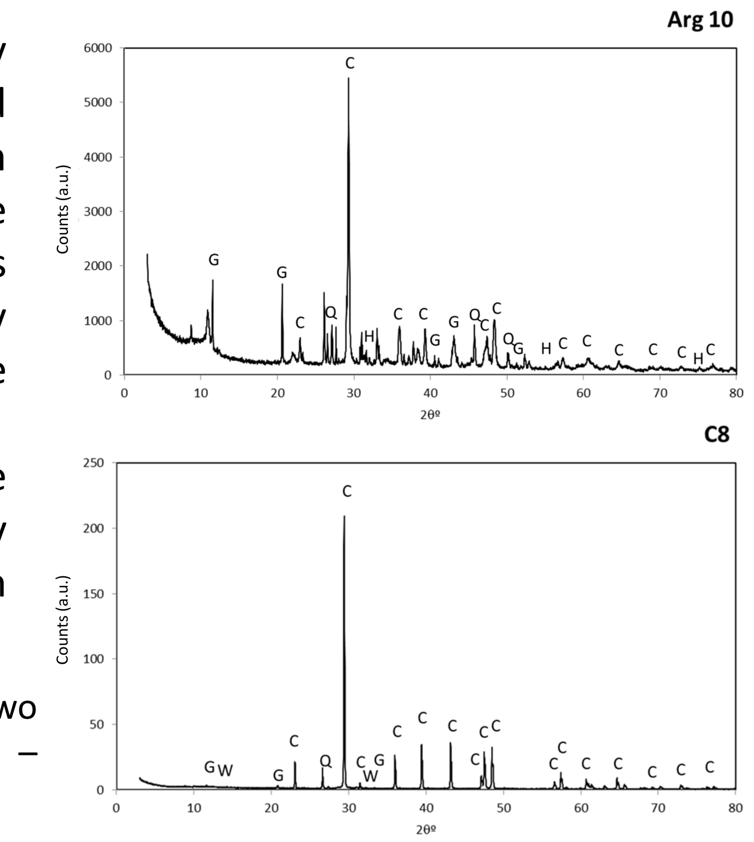

Figure 4 | XRD patterns of two samples (C – calcite, Q – quartz, G – gypsum, H – halite, W – weddellite).

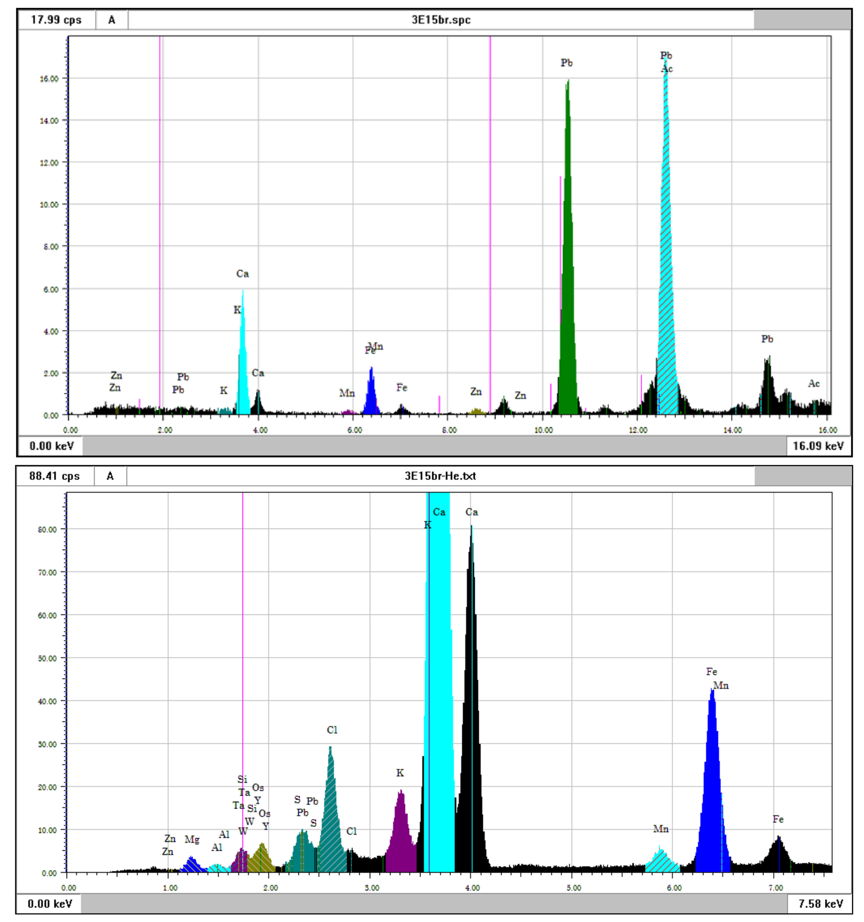

Figure 5 | XRF spectrums of a sample from a sculpture in East Portal, at high and low X-ray energy, respectively.

The element lead (Pb) is present in many samples, with particular emphasis on the darker layers of sculptures in East Portal (figure 5). This element is present in the air as a contamination of the gases released by the combustion of fuels. Currently fuels contain less or no lead, but until the 90s of last century it was an important additive. The zinc element (Zn) seems to be associated with the presence of lead, which is also understood to be present in the chemical composition of lubricating oil of hydraulic motors and systems.
In the areas of yellowish tone of whitewash, the presence of iron indicates that the mineral pigment is ochre, identified by XRD and micro-Raman spectroscopy. Although there was the expectation of finding organic binders with micro-Raman spectroscopy, it was not possible to confirm this fact. It was detected only calcite, ochre (iron oxide hydrate, α-FeO (OH)) and calcium oxalate monohydrate ($CaC_2O_4.H_2O$).
The results of open porosity and water absorption show mean values of 29.7% to 11.9% respectively. These values are consistent with those of Ançã Stone.

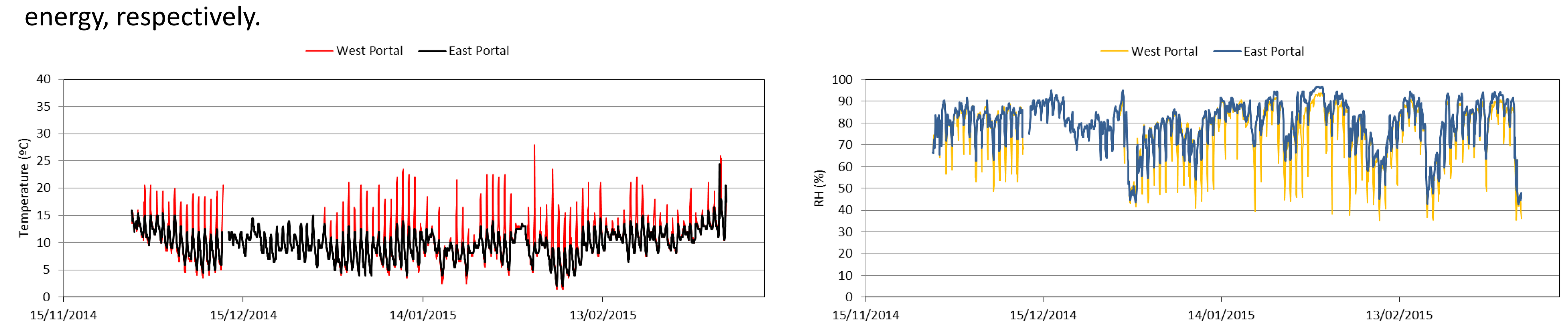

Figure 6| Air temperature and RH records obtained during the conservation works in East and West Portal.

Figure 7| Porta Férrea, East Portal, before intervention (Ribeiro, 2009)

The temperature and relative humidity amplitudes in the West Portal are higher (figure 6), promoting successive cycles of wetting-drying favoured by sun exposure and incidence of NW winds.

Conclusion

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, high water absorption and atmospheric contamination induce degradation by dissolution;
- 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 sulphur and zinc, due to atmospheric contamination.

The results allowed a more comprehensive and wised intervention in order to preserve a monument (figure 7, 8) that is part of the UNESCO Word Heritage.

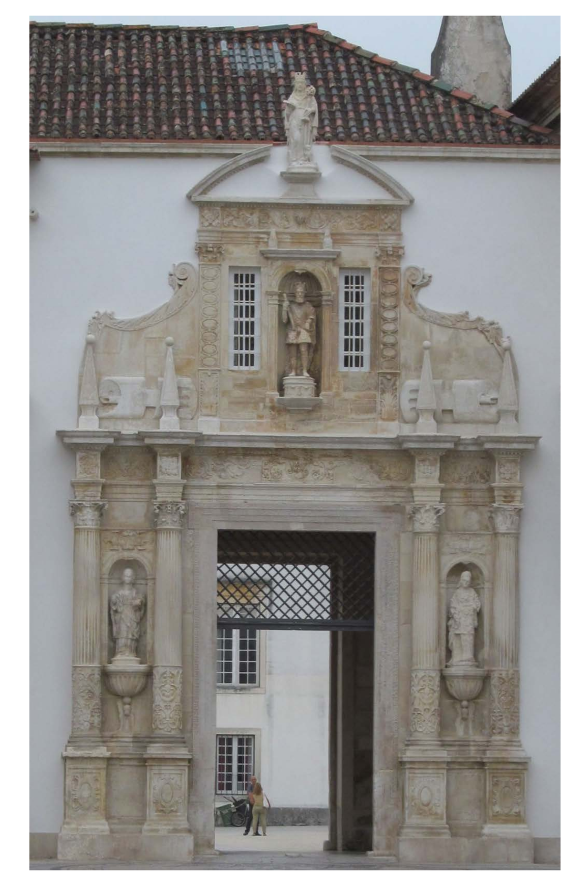

Figure 8| Porta Férrea, East Portal, after intervention.

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