

# Surface Degradation of Indoor Stonework in an Ancient Roman Church: XPS and SEM/EDS Investigation

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### Abstract

The action of this work carried within the Italian Cultural Heritage framework was aimed at defining the main diagnostic aspects functional to the restoration of the interior of an ancient roman church - located near the centre of Rome along the river 'Tevere'.

The recourse to combined surface and sub-surface techniques, like XPS (X-ray Photoelectron Spectroscopy) and SEM (Scanning Electron Microscopy) equipped with EDS (Energy Dispersive Spectroscopy) for the X-ray microanalyses, has allowed to associate the surface chemical speciation (XPS) and elemental analysis (EDS) with the morphology and structure as revealed by SEM images, for each analysed sample. In the final step, the whole results were discussed and, having achieved a quite consistent interpretation of the experimental data, hypotheses could be formulated on the causes of degradation and properly considered for implementing rules in the subsequent restoration phases.

### Introduction

Detailed investigations on degradation phenomena represent the basic start for projects devoted to the protection and conservation of the cultural and artistic world heritage. The new technologies [1] that provide information down to the nanometres scale nowadays assume a key role in complementing the use of traditional disciplines for the subsequent restoration action to be taken accurately.

At the beginning of this diagnostic project, historical and artistic information of the church were merged with accurate 'in loco' examinations. Appropriate sampling modalities -in line with the international recommendations in the field- were then used for enabling 'ex-situ' analyses of the surface and sub-surface degradation products formed over the centuries onto structural and decorative materials inside the church - see figure 1.

The combine of sophisticated spectroscopic and microscopic techniques has provided results on degraded materials from either physical and chemical point of view. Moreover, chemical speciation and semi-quantitative analysis of XPS data were performed using a well tested curve-fitting procedure [2] that accounts for both intrinsic and extrinsic photoemission-related processes.

## Materials & Methods

The powdered samples for surface analyses were properly classified on the basis of the number of sampling and of the composition (marble or plaster marbles) and function (structural or decorative) of the architectural component and artistic stonework from which they were taken.

The XPS spectra were acquired with a Leybold spectrometer (LH X1) using the achromatic AlK $\alpha$  (1486.6 eV) and MgK $\alpha$  (1253.6 eV) double source at a constant power of 260 W. Wide and detailed spectra were collected using the FAT (fixed analyzer transmission) mode of operation with a Pass Energy of 50 eV and a channel width of 1.0 and 0.1 eV, respectively. The peak assignments (uncertainty on BEs of +/- 0.2 eV) refer to literature data and to the NIST standard reference database available on line (http://srdata.nist.gov/xps/).

SEM images and microanalyses were either carried in Rome (Università La Sapienza) and in Potenza (Università della Basilicata) using LEO1450VP and ESEM XL30 PHILIPS LaB6 microscopes, respectively, both implemented with EDS/ EDAX probes.

An accurate data elaboration was finally required to fully characterize the studied materials by properly taking into account the specific lateral and in-depth resolution of each technique.

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### Results

The experimental results were elaborated and rationalized in relation to internal microclimates and locations as well as samples and techniques characteristics: see an example of combined analyses in figure 1. Based on these correlations and by also considering that carbonaceous components were steadily distributed on surfaces, the 'degraded compounds' could be grouped into three main classes.

1-reprecipitated CaCO<sub>3</sub>

The surface products formed on 'isolated' marbles artefacts located near the entrance (right aisle, bottom) are the results of hydration and carbonation (dissolution and re-precipitation of calcium carbonate due to the combined action of water vapours and carbon dioxide)

 $2-CaSO_4$ 

The surface products formed on marble slabs adjacent to plaster columns or walls are prevalently composed of calcium sulphate (chapels, second right aisle and upper left aisle) mixed with sulphites and carbonates and are likely the results of slow processes induced by sulphur-containing components probably favoured by the internal activity of the church (i.e. lighting of the candlestick) and the local microclimate of the chapels.

3- Mixed efflorescent salts.

The surface products on artificial marbles (plaster slabs, upper right aisle and upper left aisle) are made of sodium nitrate and oxalate prevailing on others variable ionic compounds depending on the given location. In such cases, is sought that capillary forces induce migration of water and soluble salts from the ground and in wall efflorescence at different heights from the floor with the crystallization phenomena visible at the marble/plaster interfaces and on plaster surfaces because of their interior pronounced porosity.



Figure 1; centre: one sampling zone and elemental analysis of the degraded surface product (*EDS*), right: S2p curve-fitted region (*XPS*), left: secondary electrons micrograph (*SEM*)

### Conclusions

We have shown interesting and consistent relationships between degrading processes occurring at the surface of the analysed materials and their chemical-physical characteristics and environment.

The use of surface and sub-surface techniques in the field of cultural heritage allows to collect morphologic and chemical information useful- when united to others from the more traditional means of investigation- for achieving the completeness of diagnostic projects[3].

Work is in progress to extend the sampling to other indoor locations of the church and to complete the data elaboration with the help of PCA (Principal Component Analysis) statistics.

### References

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