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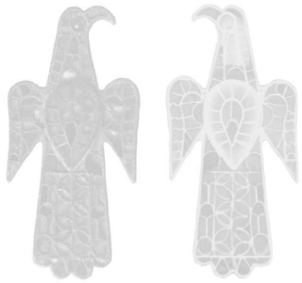

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NDT FOR THE DETECTION AND CHARACTERIZATION OF SUPERFICIAL TREATMENTS ON STONE MATERIAL FROM ARCHAEOLOGICAL SITES OF MERIDA (SPAIN)

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Abstract

Different treatments (consolidation and water-repellent) were applied on samples of marble and granite from the Front stage of the Roman Theatre of Merida (Spain). The main goal is to study the effects of these treatments on archaeological stone material, by analyzing the surface changes. X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy techniques, as well as Nuclear Magnetic Resonance have been used in order to study changes in the surface properties of the material, comparing treated and untreated specimens. The results confirm that silicon (Si) marker tracking allows the detection of applied treatments, increasing the peak signal in treated specimens. Furthermore, it is also possible to prove changes both within the pore system of the materialand in the distribution of surface water, resulting from the application of these products.

Introduction

The work described arises from the collaboration between different research groups, under the framework of the PICATA programme (CEI Moncloa):

- AIPA Research group (ETSAM, UPM),
- Petrology applied to Heritage Conservation, Instituto de Geociencias, IGEO (CSIC, UCM),
- Laboratorio di Fisica e Tecnologie Relative- UniNetLab (UNIPA).

The overall goal of the project is the study of the effects of conservation treatments applied on stone material from selected archaeological sites of Merida (Spain), in terms of superficial changes and effectiveness. In this sense, one of the first premises is characterizing the surface of the treated and untreated material in order to determine changes in physical and chemical properties.

Objectives

Selected archaeological sites of Merida, the Roman Theatre (Figure 1) and the House of Mitreo, have been subject of several restoration intervention, where different treatments were applied to natural stone material, including artificial stone materials - mortars, wall paintings and mosaics -. Some of these interventions have been accurately registered, some others not. In this sense one of the objectives of this work is to test the effectiveness of different analysis techniques to characterize the surfaces of new treated stone material. This will also allow us subsequently working on the detection of treatments applied on site, by using portable equipments.

Figure 1. Overview of the Roman Theater and Mitreo's House

Materials and methodology

Samples of white marble (Figure 2) and granite (Figure 3) which are present in the Front stage of the Roman Theatre (1), have been subject of different treatments documented in past interventions (2):

- Consolidative treatment with ethyl silicate TEOS (Estel 1000©)> S
- Siloxane water-repellent treatment (Tegosivin HL©)> H
- Consolidative + Water-repellent treatments (double application)> S+H
- Some other samples have been left as a reference with no treatment> N

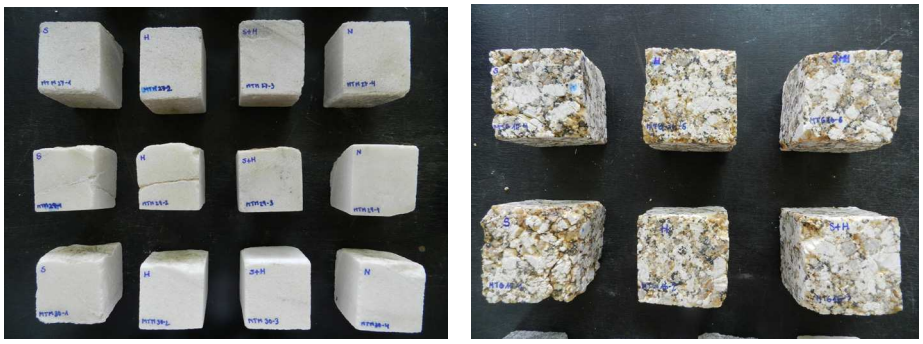

Figure 2 and 3. White marble specimens (4x4cm) mainly used in cornices and capitals. Granite specimens (5x5cm) are found in the basements of the Front stage.

In all cases two lateral sides of specimens were free of treatment, intended to imitate the characteristics of the pieces preserved *in situ*, where only some faces are exposed.

Two techniques were used for the characterization and detection of superficial treatments: X-Ray Fluorescence (XRF instrument-Bruker AXS, mod. ARTAX 400). XRF measurements allow us to reveal the presence of treatment by monitoring the presence of silicon (Si) marker. The acquisition parameters used were voltage-40kV, X-ray tube current at 700 µA with an acquisition time of 200 seconds, under a flow of helium gas.

LIBS enables to analyse the stratigraphic sequence of different layers starting from the treated surface up to the bulk, thus, obtaining elemental information, not just the surface, but also in the inner layers (3, 4). The portable experimental apparatus for the LIBS measurements is the MObile Dual-pulse Instruments for LIBS material analysis (MODì) from Marwan Technolgy. It integrates a double Q-Switched Nd:YAG laser (Lotis, mod. LS-2131D) emitting, with pulsed emission, two collinear laser pulses at 1024 nm, whose energy can be set by varying the lamp flash voltage. The pulsed energy, focused on the sample surface by a 100 mm focal length Plano-convex lens, is within 50-120 mJ with a maximum repetition rate of 10 Hz and a reciprocal delay adjustable from 0 to 60 µs. The lateral spatial resolution of the LIBS measurements corresponds to the dimensions of the microcrater left by the laser on the sample surface. The microcrater diameter, whose dimensions are related to the laser energy, does not exceed 100 microns. Acquisition parameters selected for LIBS measurements were: GPD-2 µs, GPW-1 µs, and laser pulse energy-18J.

Besides, with Nuclear Magnetic Resonance the water content in the surface of the sample (depth of 2mm-5mm), and its distribution in the porous system have been measured. It allows the determination of the dimension of the pores in the surface material, and the interconnection between them (5). NMR measurements were performed by a single-side relaxometer mq-ProFiler (Bruker Biospin ®, Italy) operating at about 15 Mhz. Spin-spin relaxation time T2 of water protons were assessed by CPMG-8000 sequences with an echo time TE of 44 microsec. Each measurement is the average of 1024 accumulations acquired with a recycle delay of 2s. Specimens where vacuum-sealed and then saturared? with distilled water in order to fill the pores. All measurements were performed at room temperature and covering the sample by a film in order to avoid any leak of water. We have analysed for each sample the spin-spin relaxation trends of the NMR signal recorded and then calculated the distributions of the spin-spin relaxation time (T2) for the various samples studied.

All these equipments are part of the UniNetLab within Palermo University.

Measurements were performed in different points of three diverse faces of the samples (Figure 4), taking an average of three shots per point regarding XRF and LIBS (27 measurements per specimen), and two measures per face in NMR case.

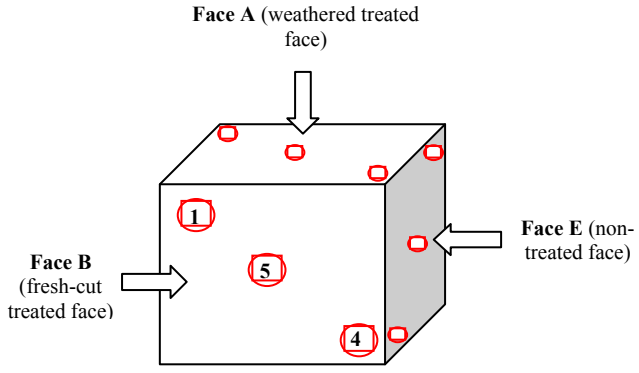

Figure 4. Schematic drawing in which the measured points in the marble and granite samples are indicated

Results

XRF

General results regarding marble samples confirm that the amount of Si varies increasingly when comparing treated and untreated samples, being purely clear only when confronted with S+H, and moderately distinguishable between untreated, and treated with S or H (Figure 5). If we analyze changes between the different faces of the specimen we can see that the Face A, being exposed to weathering, already has a natural silicon content, due to the rock impurities, which however increases in treated surfaces. Another observation is that the treatment has penetrated, or has been crept during application, in the free treatments sides (Face E), been very similar to treated Face B, and therefore can be considered that the entire specimen is treated.

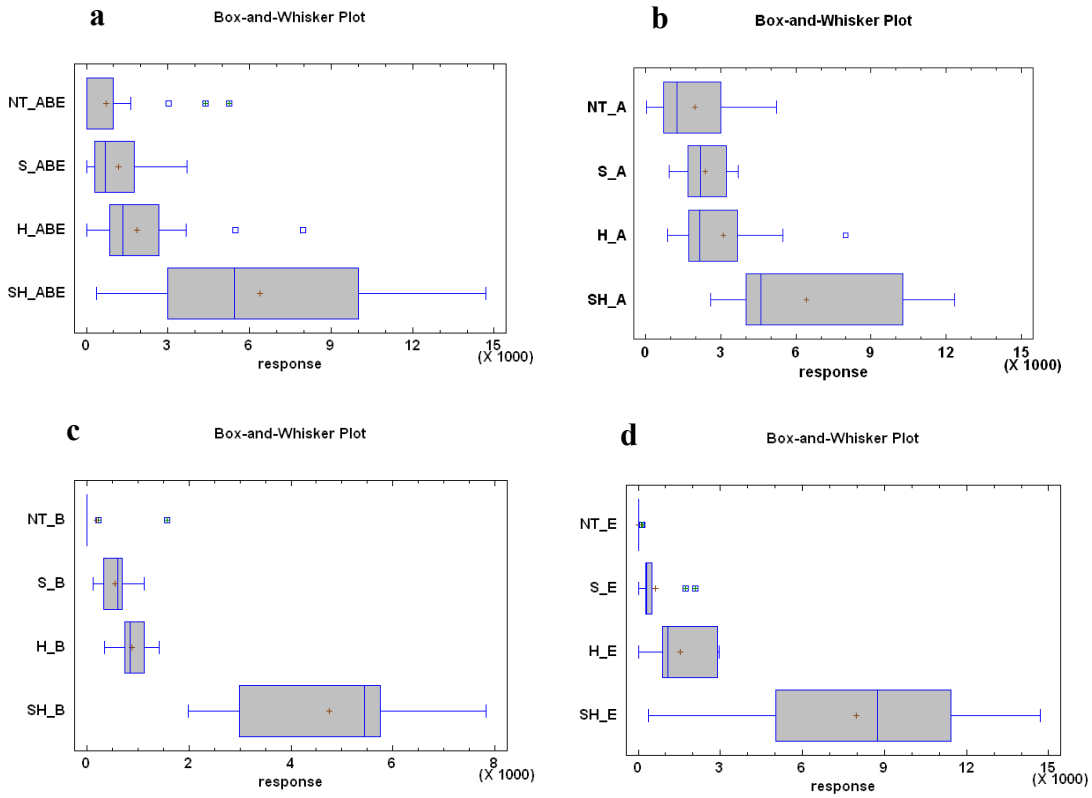

Figure 5. Box-and-Whisker graphs showing differential analysis of marble specimens (Si marker): (a) comparison of samples with data gathered from all faces; (b) weathered faces data, (c) freshly-cut inner faces data and (d) non-treated faces.

Regarding granites, the compositional heterogeneity of the grains is much higher than the difference between treated and untreated areas. Therefore the XRF analysis is unrepresentative in this sense, however it allows us to specify the majority of the element of grains (three grain types are distinguished) (Figure 6).

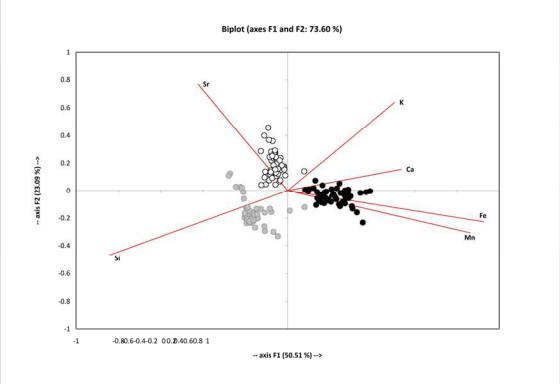

Figure 6. Principal Component Analysis (PCA) of XRF granite data from measurements of the principal macroscopic grains identified. Elements constituting grains can be associated to quartz, biotite and calcium

LIBS

LIBS measurements confirm what XRF showed, presenting higher presence of Si on treated surface. In addition, the Si content decreases as deepens the surface layer (sequence up to 15 shots) (Figures 7 and 8).

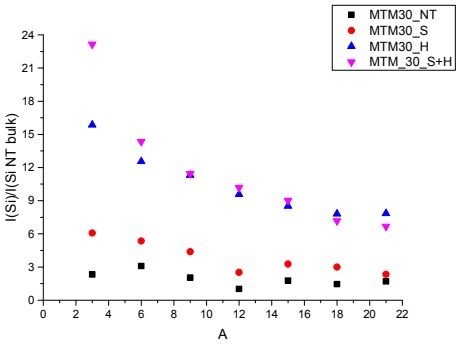

Figure 7. LIBS signal comparison among MTM30 samples undergone to different treatments. The I(Si)/I(Si NT bulk) ratio is reported for each specimen as function of laser shot number

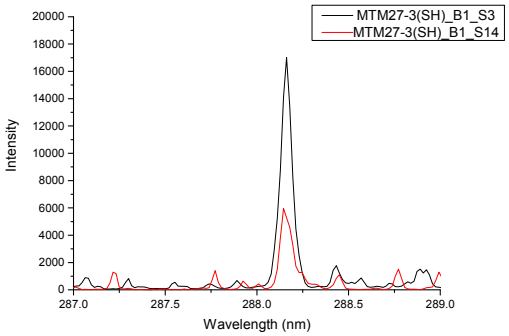

Figure 8. LIBS spectra shows the intensity of Si peak detected by LIBS at different points at the stratigraphic sequence: MTM27-3(SH) sequence 3 vs sequence 14.

NMR

Results of NMR measurements performed on granite sample are shown in figures 9, 10 and 11, where comparison of treated and untreated specimens have been carried out analyzing the distribution of the spin-spin relaxation time (T2).

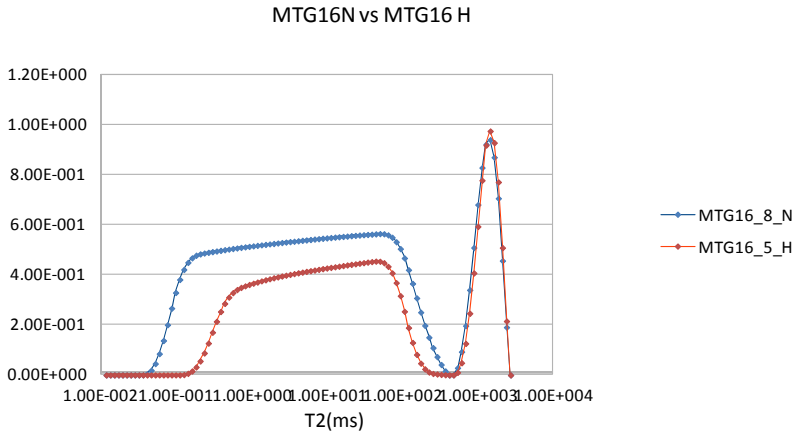

Figure 9. The treatment with a water-repellent product involves a reduction of the presence of water for T2 values smaller than 370 ms.

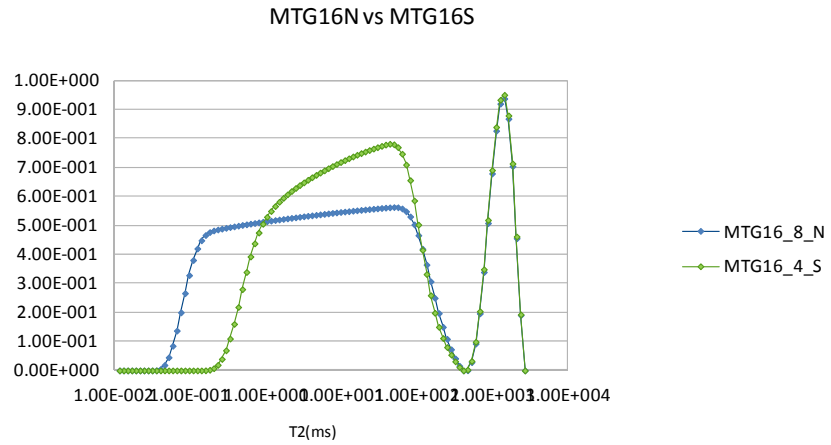

Figure 10. The effect of the silicate-based treatment consists in a reduction of the microporosity in favour of mesoporosity. The presence of TEOS reduces the accessibility of water to micropores in granite specimens.

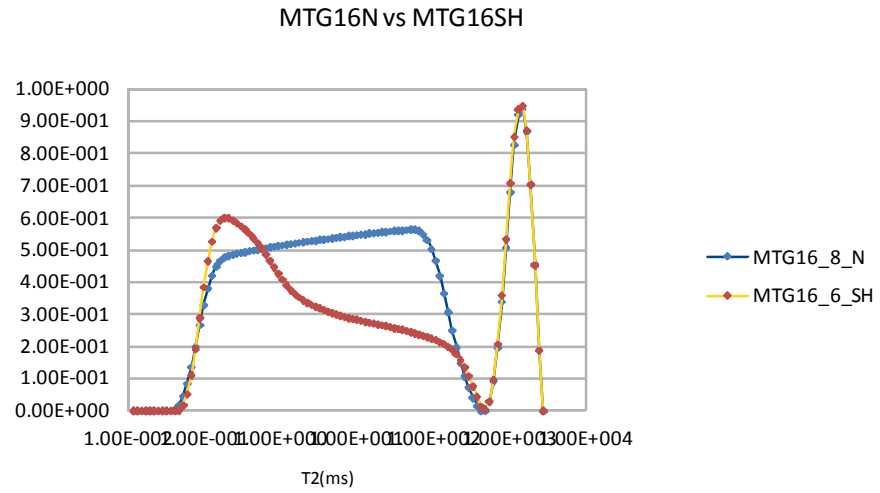

Figure 11. The combined effect of TEOS and water-repellent treatments involves a reduction of the average pore size because both obstruct the mesopores and the percentage of smaller pores increases respecting the untreated specimens.

Conclusions

Regarding the identification of treated surfaces, we have found that only the mineralogical homogeneity of marble allows differentiation between the treated and untreated specimens. It is due to, not only this homogeneity, but to its high granular compaction, which provoked the treatment to remain in surface, while in the case of granite intergranular spaces are considerable, allowing greater penetration of the treatment and, therefore, the lower superficial retention (this is confirmed by NMR tests). Taking into account that Si is the marker for the detection of treatments; another limitation is the presence of Si on the exposed surface of the stone material (Face A on marble samples). It can be concluded that, despite these considerations, increasing of Si is distinguishable between treated and untreated samples, though being only unmistakable when comparing N and S+H specimens. However, when this comparison is made over recently cut faces the differences in Si content become much clearer, enabling to distinguish between the three different treatments and the untreated specimens, both in the case of XRF as in LIBS analysis.

Comparing the hydric behaviour of treated and untreated material, some general conclusions are:

- Water-repellent treatments, in most cases, tend to homogenize the presence of water in the pores of varying size and reduce the overall presence of water.

- Silicate based treatments involves a variation in the distribution of water between pores of varying size but does not significantly change the presence of water .

- The heterogeneity of each sample (and therefore its water absorption capacity) must be considered, varying when considering one face or another of each specimen.

- In all cases, the water permeability of the treated samples markedly reduces.

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