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Further Investigations on Limestone Artifact Surface Modifications by Laser-Induced Breakdown Spectroscopy Depth-Profiling

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***Abstract* – In the context of the preservation of cultural heritage, it is relevant to study the degradation mechanisms of materials of which historical constructions are made. Limestone was one of the most widely used materials in many monuments exposed to urban aggressive atmosphere that affected its durability. In this work, a limestone sample was collected from the masonry blocks of an ancient jamb of the historic entrance gate of Castello Svevo, Bari, Italy. The choice was based on its evident degradation, i.e. a deposit of black crusts. The laser cleaning process combined with laser-induced breakdown spectroscopy (LIBS) analysis was applied to remove and then characterize the altered limestone sample. The elemental composition of the ablated black crust and the underlying stone were determined by spectroscopic analysis of the plasma emitted using a double pulse (DP) LIBS configuration. The limestone sample was also subjected to a depth-profile analysis of the black crust area and the laser cleaned zones in order to identify and analyze the decrease or disappearance with depth of specific elemental components.**

I. INTRODUCTION

Limestones have generally homogeneous chemical characteristics and are dominated by $CaCO_3$ whereas physical characteristics such as hardness, fossil content and porosity may be highly variable [1]. In particular, physical characteristics, especially porosity [2], are the major responsible of the durability of limestones exposed to aggressive environmental conditions [3], whose decay occurs predominantly by gradual dissolution similar to the so-called karstic erosion of natural limestone outcrops [1].

Laser-induced breakdown spectroscopy (LIBS) has been recently used successfully [4-6] to perform chemical depth profiling to identify and analyze rock surface alteration features. Repeated laser pulses remove dust coatings and can provide accurate depth profiles through the weathering layers. This allows detailed investigation of rock varnish features as well as analysis of underlying pristine rock composition.

LIBS is faster and more accurate than other analytical techniques such as X-ray methods, which cannot be performed with control of depth penetration, and Scanning Electron Microscopy, Secondary Ion Mass Spectroscopy, X-ray Photoelectron Spectroscopy and nuclear particle irradiation, which can penetrate only a few micrometers below the surface.

The aim of this work was to explore the potential of ablative laser technology to obtain a depth profile of a limestone sample collected from a masonry block of the left jamb of the southern entrance gate to the courtyard of Castello Svevo, Bari, Italy. This, by impinging several laser pulses on the same spot to obtain the limestone chemical composition, and track rapidly elements such as Ca, Fe, Mg, Mn and Sr. In the first step, the laser cleaning technique allows to remove soiling and black crusts on the sample surface in a very selective way. In the second step, the depth profile study allows to evaluate the effect of different laser wavelengths on the limestone sample.

II. MATERIALS AND METHODS

The sample was collected from a selected block of the limestone masonry of Castello Svevo, Bari, Italy (Fig. 1), which is an historic multilayered monument built originally by Roger the Norman in 1131 on the remains of a Byzantine structure. The sample showed a surface degradation featured by a layer of black crust.

Laser cleaning was performed by a portable pulsed Nd:YAG Q-switched laser mod. Thunder Art of Quanta System equipped with a multi-articulated arm at a pulse width of 8 ns. Two different wavelengths, i.e., 1064 nm and 532 nm, were used at different pulse repetition frequencies (from 10 Hz to a maximum of 20 Hz), and varying the energy (maximum energy per pulse, 900 mJ at the wavelength 1064 nm and 400 mJ at 532 nm).

The LIBS system used consisted of two lasers

Fig. 1. The masonry limestone blocks of the jamb of the entrance gate of Castello Svevo (a) and area sampled (b). The red box inset shows the sample considered for the study.

operating at different wavelengths, i.e. 1064 nm (IR) and 532 nm (VIS). The IR pulse was generated by a Nd:YAG Q-switch Ultra (Quantel) at a maximum energy of 75 mJ and a width of 6 ns. The VIS pulse was generated by a Nd:YAG Q-switch Brillant (Quantel) coupled with a second harmonic generator module at a maximum energy of 180 mJ and a width of 4 ns. A 400-Butterfly Aryelle system was used to detect and select the wavelengths.

The in-depth study of the crater profile was performed by using a double pulse (DP) LIBS by accumulating 110 shots on three different zones of the limestone sample, i.e. two laser cleaned surface from the black crust and black crust surface. The DP LIBS spectra were acquired by collinear geometry configuration using two laser beams, each with energy of 45 mJ, focused and aligned to hit the sample in the overlapping mode. The temporal parameters used in this experiment were optimized for the best LIBS signal, i.e. the delay time was 500 ns, the gate time 10 µs and the interpulse delay 500 ns.

In order to characterize the encrustation/limestone interface and the texture of the sample, a thin polished petrographic section of the sample was prepared and examined by a polarized optical microscope (OM) using a ZEISS Axioskop microscope equipped with a digital camera. Scanning Electron Microscope coupled with energy-dispersive X-ray spectrometry (SEM-EDS) analyses were performed using a JEOL (JSM-6510, Thermo Scientific) equipped with EDAX microanalysis working in energy-dispersive spectrometry and operating in the secondary electron mode at 15 kV accelerating voltage, 0.2 nA beam current, 100 s acquisition time and 30% dead time.

III. RESULTS AND DISCUSSION

A. Optical and scanning electron microscopy analysis

Preliminary petrographic, mineralogical and textural analyses were performed to recognize the petrographic nature, the type of degradation and the possible presence of "scialbaturas" of the sample before performing the cleaning process. The OM and SEM analyses provided information on the micromorphological characteristics of both the substrate and the black crusts and the interaction between stone and damage layer, while the use of SEM-EDS provided the chemical composition of crusts in terms of major elements.

The OM analysis indicated that the rock sample is a dedolomitizated limestone, i.e. the texture of the original rock was apparently canceled by a dedolomitization process (Fig. 2a). The typical lozenge form of dolomite crystals was replaced by recrystallization with pseudomorfa microcrystalline calcite. The black crust consisted mainly of cryptocrystalline gypsum mixed with calcite combined with quartz silt (Fig. 2b), together with deposits of soot and dust.

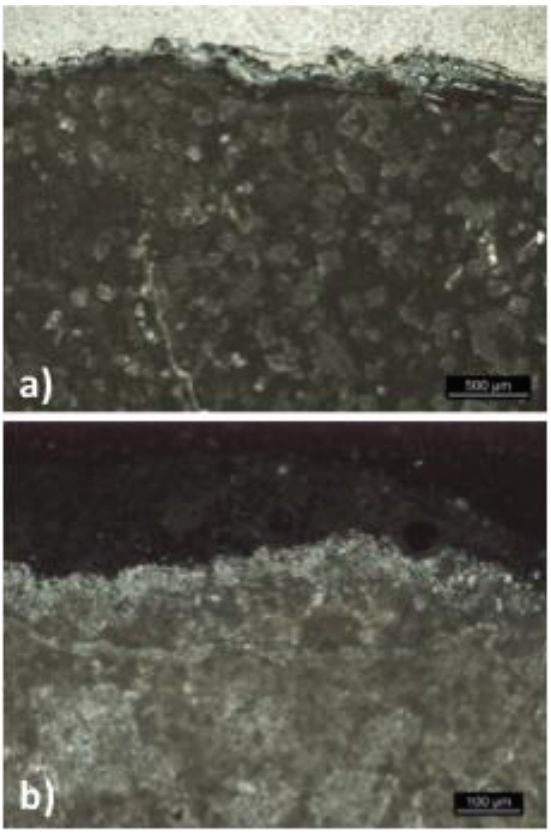

Fig. 2. Limestone sample analyzed by optical microscopy.

The gypsum crust formation and surface modification generally occur in the presence of particulate (dust) deposition, especially in areas sheltered from rain and rain-wash [7]. In particular, black crusts sampled from carbonate stone monuments subject to italian urban atmosphere contained an average of 76 % calcium sulfate dehydrated, 2 % carbon from carbonates, 2.5 % carbon other than carbonates (soot), and 19 % other components among which silica (mainly quartz) and aluminosilicates were very abundant [8].

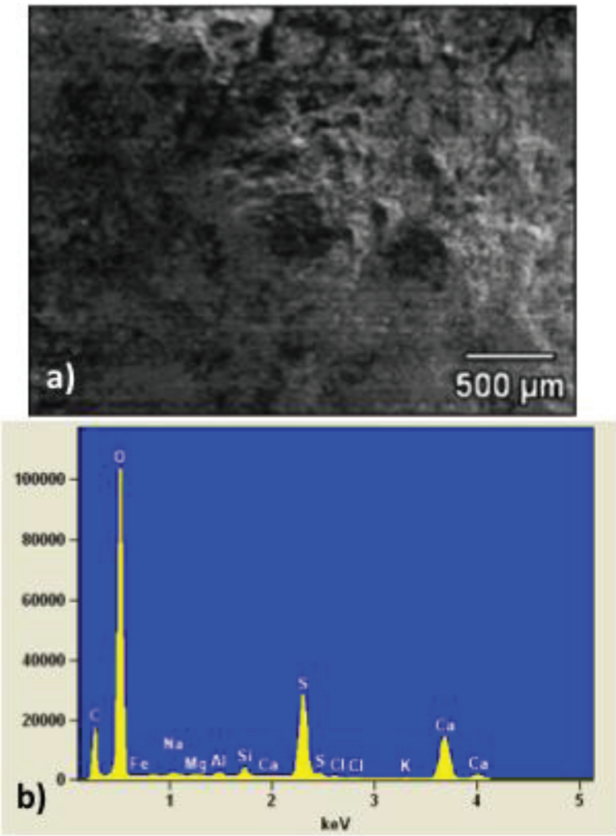

Fig. 3. SEM image (a) and EDS spectrum (b) of the examined black crusts present on the limestone sample.

The SEM image of the limestone sample examined shows the collapse of its internal structure and salt crystallization between grains (Fig. 3a). The SEM-EDS analysis of the black crust confirms the presence of sulfur corresponding to gypsum, $CaSO_4\ 2H_2O$ (Fig. 3b).

B. Laser cleaning

Two different procedures were applied to remove the black encrustations from the limestone [9]. The sample surface was divided into three areas that were subjected to different laser treatments. The first test was performed at the wavelength of 1064 nm (Fig. 4, left zone), and a second one by applying two consecutive wavelengths, the first at 1064 nm and the second at 532 nm (Fig. 4, right zone). The two tests showed a different level of cleaning with a better whitening effect when two consecutive laser wavelengths were used. The Nd:YAG laser provides pulses of typically few ns at the 1064 nm wavelength, which are preferentially absorbed by the stone soiled layers, thus producing a rapid increase of surface temperature and vaporization of the black crust. A further irradiation with the second laser harmonic (532 nm) of the areas previously cleaned with the fundamental wavelength resulted in a more complete removal of dust particles.

Fig. 4. The sample after laser cleaning using different wavelengths: 1064 nm (left zone) and first 1064 nm and then 532 nm (right zone). The centered zone is covered by the original black crust.

C. Depth profile analysis

The limestone sample was then subjected to depth profile analysis of each cleaned zone and the black crust area using the DP configuration in collinear LIBS mode, which allowed to evaluate the decrease or disappearance with depth of specific elemental components. The estimated crater depth after 110 shots was ~ 1 mm, i.e. 11 µm per shot.

In particular, the Mn peak at 259,82 nm and the Fe peak at 273,95 nm in the three zones generally show a systematic decrease of intensity with depth with increasing the shot number. Obviously, Mn and Fe peaks show a higher intensity in the black crust zone, whereas in the two other zones are greatly attenuated by previous laser cleaning. The decrease of Mn and Fe peak intensities with increasing the number of shots is especially evident in the black crust zone (Fig. 5). However, a signal attenuation is expected with depth where the plasma can be confined in the crater.

Tracking plasma stability with depth is important to ensure that changes in LIBS signal with depth are due to change in elemental concentrations relevant to diagenesis and not to changes in ablation. Although the relationship between peak size and element abundance may result not linear due to chemical and/or physical matrix effects [10], large differences in peak sizes would be related to a true difference in abundance of the element in question. However, LIBS analyses based on multiple shots per location, may result in an overall attenuation of signal as the laser impinges deeper into the target. This effect is due to plasma becoming confined within the ablation crater, thus less photons are returned to the spectrometer. As a result, decreasing trend shown by many peaks with depth can be not only ascribed to a change of composition, but rather to an overall lowering of the returned signal [5].

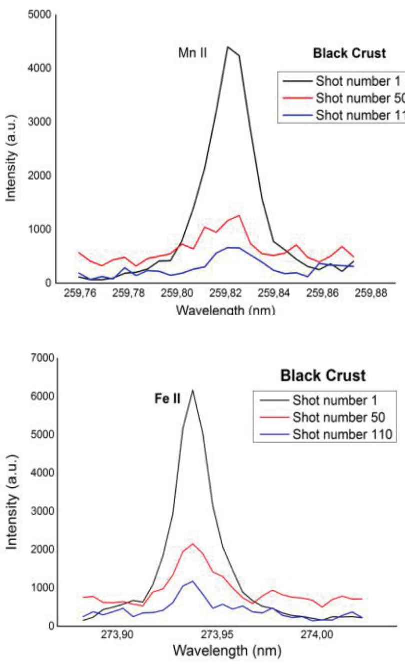

Fig. 5. Mn II and Fe II peak intensity changes in the black crust zone as a function of shot numbers/depth.

In order to determine whether trends observed for Mn and Fe peaks are actually significant, they were compared with the total emission spectra, i.e. the sum of all counts from the spectrometer at every wavelength prior to normalization, for the sampling location (Fig. 6).

Further, a decreasing concentration of Sr with depth was measured in the external layers up to 20 laser shots. Finally, the variation of the Sr/Ca ratio vs. Mn concentration suggested that the diagenetic alteration occurred in an open geochemical system.

IV. CONCLUSIONS

The laser cleaning process was confirmed to be appropriate and efficient for achieving the removal of unwanted layers from the surface of limestone with minimal damaging effects. The use of hundreds of shots on a single location, allows to penetrate thin rock coatings and tunneling into any weathered layer present beneath.

LIBS was also confirmed to be a powerful diagnostic technique able to monitor and control the laser cleaning process of limestone, which allows to replace traditional invasive laboratory analyses and provide a prompt compositional response in situ. A systematic decrease of Fe and Mn peak heights was measured downward the limestone profile, which indicates the higher content of these elements in the coating than in the rock.

The DP LIBS configuration stratigraphy was also used successfully to assess the decrease or disappearance with depth of specific elemental components that indicate the presence or absence of any protective layers (“scialbature”) on the quoin of the masonry.

As a whole, the results of this study confirmed that LIBS is a promising technique for studying rock alteration processes due to environmental factors.

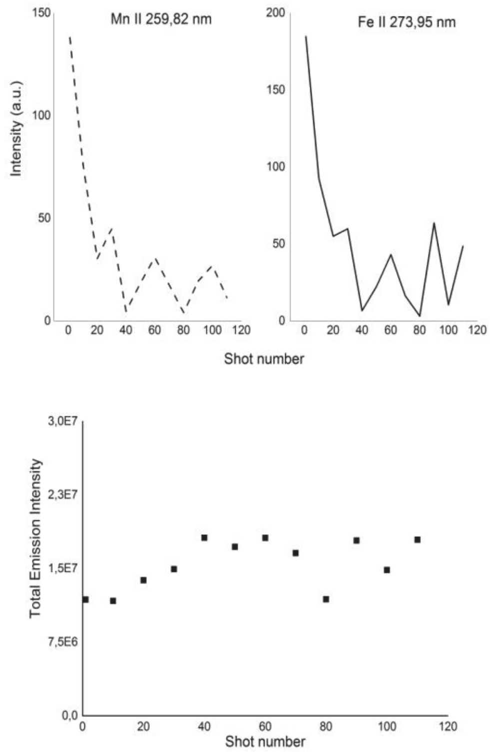

Fig. 6. Comparison of Mn II and Fe II peak intensities for the black crust zone with total emission intensity.

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