Double-pulse micro-laser-induced breakdown spectroscopy applied tothree dimensional mapping of stonemonumentsamples

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***Abstract* – In this study, double-pulse micro-laser-induced breakdown spectroscopy (DP-µLIBS) associated to optical microscopy was applied to obtain a microscale three dimensional compositional mapping of a limestone monument encrusted quoin before and after its laser cleaning treatment. Mapping was carried out microdestructively by scanning the laser beam across the stone sample rough surface without further preparation. The compositional maps of the elements were obtained from the intensity of their DP-µLIBS emission lines.DP-µLIBSmapping analysis of the limestonewas able to discriminate effectively between elements originating from alteration mineralogy and elements of the matrix.**

I. INTRODUCTION

Limestones are widely spread in the Apulian region (Southern Italy) and were used frequently to build relevant monuments in the region [1]. Limestones mainly undergo superficial degradation by dissolution of carbonatic components, sulphatation processes, and deposition of substances.This requires extensive, expensive and frequent cleaning works, of limestone monuments especially when located in urban areas [2].Two techniques are generally used to analyse geological samples and obtain X-ray compositional maps,i.e. electron-probe microanalysis (EPMA) and micro-x-ray fluorescence (µXRF). However, samples to be analyzed by EPMA must be flat, polished and require carbon coating, whereas the µXRFfeatures a low image and analytical spatial resolution. Thus, in general, mapping of stone samples involves a number of sample preparation and acquisition issues.

Laser-induced breakdown spectroscopy (LIBS) is a very promising analytical technique emerged inthe last decades in many application areas as a simple, fast and microdestructive technique that requires no sample preparation and can be performed in air[3]. This technique, combined with optical microscopy, allowed to obtainthree dimension compositional mapping and in-depth information of surfaces by improving the overall spatial resolution[4-5].

In this study, the use of double-pulse micro-laser-induced breakdown spectroscopy (DP-µLIBS) in conjunction with optical microscopywas usedto mapping and identifying the elemental composition of a limestone sample collected from a monument exposed for decades to urban environment. This approach combinesmicroscalethree dimensional (3D) compositional mapping with the compositional analysis of the sample.

II. MATERIALS AND METHODS

The sample used in this work is a limestone fragment collected from a quoin of the left jamb of the southern entrance gate to the courtyard of CastelloSvevo, Bari (Italy) (Fig. 1). This portion of the masonry blocks of the limestone castle appears particularly degraded showing a deposit of black crusts formed over the centuries.

The analysis of the limestone sample was performed usinga µ-Modì system produced by Marwan Technology (Pisa)which worked with a double-pulse Nd:YAG laser by Lotis that emitted two collinear pulses at 1064 nm (Fig. 2). The laser beams were directed through the Modì articulated arm to a Zeiss AxioPlan A1 optical microscope featuring a 10x magnification objective and then focused on the sample. The microscope plate was equipped with a two axis pc-controlled motors by ThorLabswhichensured the movement of the sample stage. A double spectrometer by Avantes, whichcoveredthe spectral range from 190 to 900 nm,was used. The LIBS signal was acquired by an optical fiber at 45° with respect to the laser direction using a ball lens positioned in the front of the fiber.A homemade software

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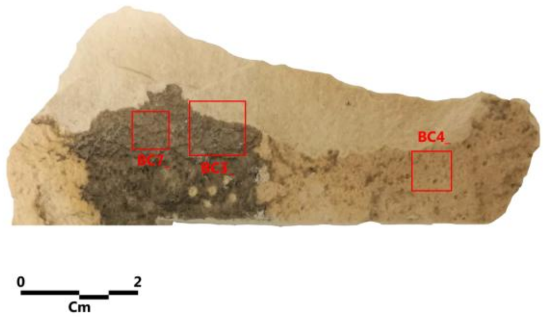

Fig. 1. The limestone fragment analysed using micro-LIBS 3D mapping. The sampled areas are highlighted in red squares.

Fig. 2. The μ-Modì- double-pulse instrument.

8.5) was used to synchronize the lasers, the spectrometer and the motors.

The elements were mapped in three different 5-mm^2 surface areas of the sample (BC 3, BC 4 and BC 7) (Fig. 1) (625 LIBS spectra) with a lateral resolution of 200 µm, and for 5 layers in depth. In particular, an area with an apparent superficial deterioration with presence of black crust (BC 7), an area covered by black crust and the unweathered rock (BC 3) and an area where the black crust was removed by the laser cleaning treatment (BC 4).The compositional mapping was performed microdestructively by scanning the laser beam across the stone sample rough surface without further preparation using a grid of analytical spots of about 20 μm diameter, spaced at 200 μm intervals.The in-depth (several microns) analysis was performed by impinging multiple laser pulses on the same sample point,which allowedto obtain the petrographical characterizationof the limestone sample. The 3D compositional map of each element was generated from the intensity of its DP-μLIBS emission line, with the dimensions x and y corresponding to the x and y steps of the raster (200 μm), and the z coordinate representing the depth of the laser crater. A spectrum was acquired for each analyzed point. As the dimension of the space was too large to be represented in a 2D or 3D space, an artifice was applied in order to reduce the dimensionality of the sample space.

The chemical imaging technique used was able to analyse the surface composition and discriminate adjacent layers of the sample in relation to surface sensitivity and lateral and depth resolutions. These parameters are generally defined by sampling depth, area and shape of each individual analysis, and define the application niche of each surface analytical technique.

III. RESULTS AND DISCUSSION

A false color red, green, blue(RGB) map (Fig. 3)was then constructed to identify the elements chosen, i.e. Ca (red channel), Mg (green channel) and Si (blue channel). The yellow color was generated by the co-presence of Ca and Mg, magenta color by the co-presence of Ca and Si, and the cyan color by the simultaneous presence of Mg and Si. The yellow, cyan and magenta zones in the false color images corresponded to zones in which the relevant elements were present in higher concentrations, whereas the white spots corresponded to a high concentration of all the three elements considered. As the number of bands that can be visualized in a color image is limited to three, i.e. red, green and blue (RGB), these images could be easily represented.

The analysis of maps in Fig. 3 confirmed the presence of a number of layers of different elemental composition. The 5th, deepest layer of areas BC 3 and BC 7 featuring the presence of black crust was different from the 1st layer, i.e. the yellow zones would indicate an increase in red and green components (Ca and Mg, respectively).

The compositional maps discussed above showed clearly that the peak intensity of the emission lines detected, i.e. the concentration of each element, varied between the outer and inner part of the rock sample, and could be used to obtain a 3D reconstruction of the ablated volume. In particular,a stack was obtained from the whole maps element by element, and then the 3D volume of each element was calculated using some scripting language. The spacing between the layers was fixed as an arbitrary unit.However, bymeasuring the effective depth of each layer, it was possible to assign it to spacing. The cross sections obtained for the BC 3 area based on the reconstruction of the 3D volume (Fig. 4) showed interesting trends of the elements considered, which allowed to find the edge and variations between the black crust cover and the unweatheredunderlying limestone. In particular, the Fe line was present only in the black crust, and the corresponding line intensities decreased with increasing depth, disappearing almost completely in the unweathered limestone.

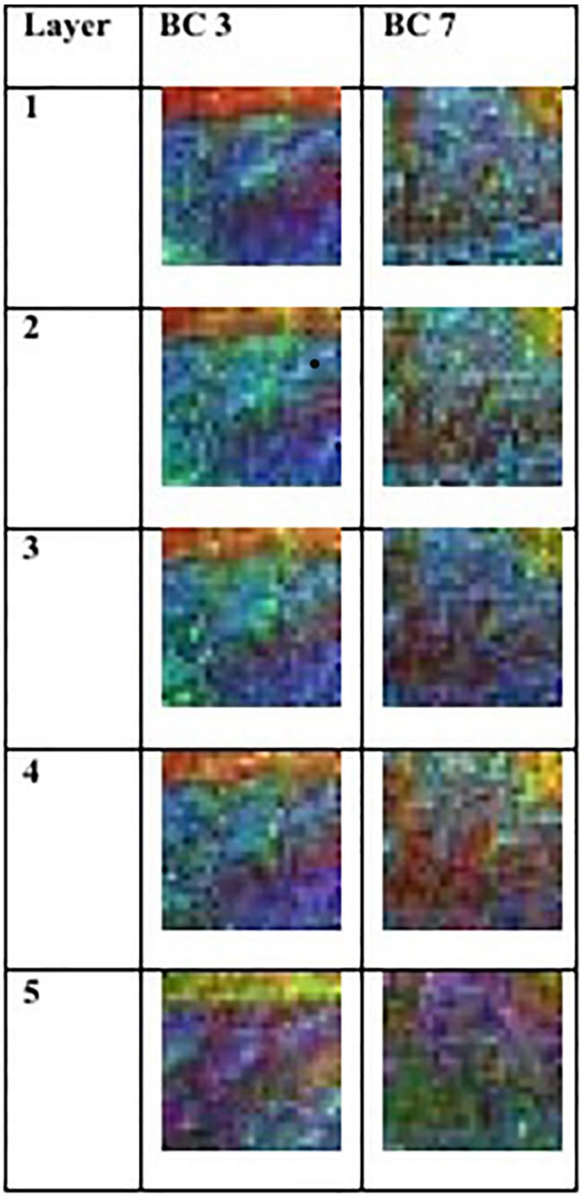

Fig. 3. False color RGB map of BC 7 and BC 3 from layer 1 to 5. Yellow areas indicate the simultaneous presence of Ca and Mg, magenta areas of Ca and Si, and cyano areas of Mg and Si.

The Ca line showed the highest intensity in the unweathered limestone (5th layer), which decreased at lower depth, while Mg showed an inverse trend, similar to Fe. The concentration of C initially decreasedand then increasedwith depth. The elements Fe and Si were used as markers to locate the black crust, showing that the crust was attenuated but not totally removed even after the fifth shot. The presence of these two elements in the black crust could be ascribed to atmospheric pollution and dust and particulate deposition,respectively.

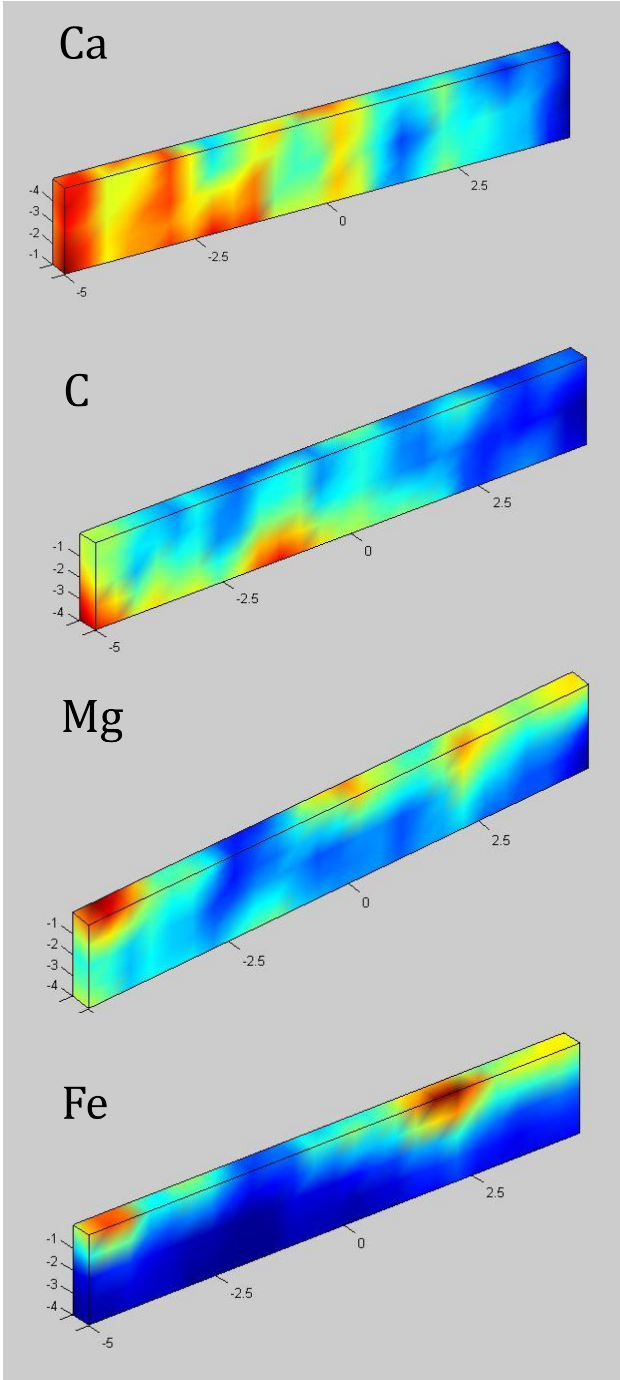

Fig. 4. 3D reconstruction of the ablated volume using the compositional maps of the BC 3 area for layers 1 to 5 for Ca, C, Mg and Fe.

IV. CONCLUSIONS

The results of this study confirm the effectiveness of DP-μLIBS as a mapping tool for chemical elements in monument stones, which can be used as a complement to other mapping techniques. Mapping of elements related to pollution effects of limestone minerals has important applications in the evaluation and remediation of weathered limestones.However, due to the inhomogeneity of the sample,the determination of the mineralogical nature of limestone layers is not an easy task.DP-μLIBS mapping analysis appears to be able to discriminate efficiently between elements originating from alteration mineralogy and elements of the matrix. In particular, the technique shows that Si and Fe are present only in the black crust originated from atmospheric dust and particulate deposition, whereas Ca, C and Mg signalintensitiesshow different trends in the black crust and in the limestone underneath.

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