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Surface and stratigraphic analysis of black crusts using Laser Induced Breakdown Spectroscopy

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***Abstract* – The interaction between atmospheric pollutants and architectural cultural heritage leads to several degradation processes, mainly the formation of black crusts. Numerous studies have highlighted that their elemental composition can be used to determine the main pollutant sources of the surrounding areas. Therefore, black crusts may represent actual "registries of pollution sources" and may help to understand the evolution of these sources and their impact throughout the years. In this study, Laser Induced Breakdown Spectroscopy was employed to study a series of black crusts from the Monumental Cemetery of Milan. Surface analysis was carried out in order to evaluate the feasibility of the technique, whereas stratigraphic analysis enabled to highlight the in-depth distribution of the detected elements. The elemental profile of the black crusts was used to identify the main pollution sources of the surrounding areas and the variation of their impact throughout the years.**

I. INTRODUCTION

Black crusts are amongst the most important degradation phenomena affecting stone materials. Several monuments, sculptures and other artworks of calcareous nature exposed to the outdoor environment and protected from washout, suffer from the formation of black crusts on the surface [1]. Over time, if left untreated, the deterioration can extend towards the bulk of the material, leading to irreversible aesthetic and structural damage. Indeed, different solar radiation absorption efficiency between the crust and the substrate, different linear expansion, and permeability reduction can cause several other secondary degradation processes, such as lamination of the surface and pulverization of the internal stone structure [2].

Black crusts are formed following the interaction between atmospheric pollutants and the calcareous substrate. Sulphur dioxide (SO_2) is emitted as a primary pollutant from a variety of sources, mainly combustion processes and other industrial emissions. This pollutant undergoes atmospheric oxidation to sulphuric acid (H_2SO_4), which reacts with the carbonate substrate ($CaCO_3$) in a process called sulphation. This reaction is catalysed by the metal-rich carbonaceous particles in the atmosphere (particulate matter (PM)), leading to the formation of gypsum ($CaSO_4 \cdot 2H_2O$) at the expense of the substrate. The characteristic black colour is due to elemental carbon (EC) present in particulate matter, which gets embedded in the structure [1].

Given that the composition of PM depends on the type of sources that generated the particles, black crusts can be used as tracers of the most impactful sources of the surrounding areas. Trace analysis of metals in black crusts has been used in several cases in the last years in order to determine the main pollutant sources and therefore enact targeted solutions for the protection of cultural heritage [3]. Amongst the numerous analytical techniques employed in the study of cultural heritage [4,5,6], one of the most widespread for this type of analysis is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), which has several benefits such as high resolution, low detection limits and a micro-destructive nature.

However, black crust samples need to be inevitably retrieved from the monument/sculpture/tombstone/etc. in order to carry out this type of analysis. Laser-Induced Breakdown Spectroscopy (LIBS) may represent a valid alternative, since it displays most of the technical advantages of LA-ICP-MS, with the additional possibility of carrying out analyses also *in-situ* and with the capability of semi-quantitative and stratigraphic characterization [7-9]. This would allow trace metal analysis of black crusts without the need to retrieve samples and therefore avoid removing pieces from the artwork. Indeed, these advantages have already been exploited in recent studies concerning the determination of the elemental profile of black crusts [10,11].

In the present study, black crust samples from the Monumental Cemetery of Milan (Italy) were collected and analysed using LIBS. The uniqueness of these samples lies in the fact that the timing of crustal accumulation is known, no restoration work has been done, and their position and that of their immediate surroundings have not changed. Therefore, one can potentially study the formation process in relation to the external environment. Initially, surface analysis was performed in order to evaluate the elemental composition of the black crust and determine the main pollutant sources of the area. Eventually, stratigraphic analysis was carried out to determine the in-depth distribution of the metals and therefore evaluate how the contribution of the pollutant sources changed throughout the years. The results highlighted the ability of the LIBS technique to identify the main pollutant sources of the area and their contribution to the formation of the black crust.

II. MATERIALS AND METHODS

A. Sampling site

The Monumental Cemetery of Milan is one of the symbols of the city, attracting large numbers of visitors from all around the world. This site was inaugurated in 1866 and since then it has been gradually enriched with different works of funerary art that have suffered various effects of degradation over the years, including the formation of black crusts. Indeed, the cemetery is directly exposed to different emission sources, such as those from the railway and several highly trafficked roads (Figure 1), in addition to being in one of the most polluted European cities.

Fig. 1. Location of the Monumental Cemetery of Milan.

The Cemetery consists of a memorial chapel, located at the main entrance, and two side wings (west and east). In our case, sampling was performed in the Ponente wing, near bodies A, B, C, D, G, and in their respective galleries (Figure 2).

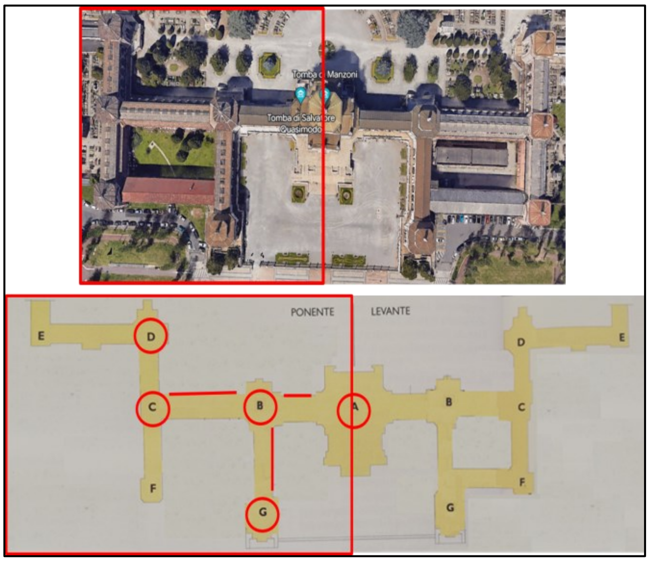

Fig. 2. Schematics of the Monumental Cemetery. The area highlighted in red indicates the sites in which sampling was carried out.

B. The samples

Five black crust samples were collected from five different funerary tombstones in the western wing of the cemetery (Figure 3, Table 1). The materials selected were natural stone (marble) on which the presence of black crusts or dust was observed. Only previously detached black crusts were selected in order to avoid compromising the aesthetics of the artwork. The samples all consisted of a layer of black crust and an underlying layer of substrate; easily distinguishable by the clear colour difference. The dimensions of the crusts were variable: around 10 mm in width and 3-5 mm in height.

Fig. 3. Bust on pillar funerary monument (sample GP) with the indication of the area (red circle) from which the collected black crusts were detached.

Table 1. Black crust sample details

Name	Years of pollutant accumulation
CM	150
LM	112
GC	114
FR	158
GP	130

Table 2. Elements detected in the black crusts using LIBS surface analysis

Sample	Elements in black crusts
CM	Fe, Mn, Ba, Ti, Cr
LM	Fe, Mn, Ba, Ti, Cr, Cu, Zn
GC	Fe, Mn, Ba, Ti, Cu, F
FR	Fe, Mn, Ba, Ti, Cr
GP	Fe, Mn, Ba, Ti, Cu, F

C. Laser-Induced Breakdown Spectroscopy

LIBS analysis was carried out on the surface and in-depth (stratigraphic study) of the considered samples using laser excitation at 266 nm (4th harmonic of a Q-switched Nd:YAG laser (Lotis TII, LS-2147), 15 ns pulses, 1 Hz repetition rate). LIBS spectra were recorded using a 0.2 m Czerny-Turner spectrograph (Andor, Shamrock Kymera-193i-A) equipped with a grating of 1800 grooves/mm (blazed at 265 nm) and coupled to a time-gated intensified charge-coupled device (ICCD) camera (Andor Technology, iStar CCD 334, 1024x1024 active pixels, 13 µm x 13 µm pixel). The laser beam was directed to the surface of the samples by the use of mirrors at an incidence angle of 45°. LIBS spectra were recorded in the 300-600 nm wavelength range using a step-and-glow mode at intervals of 30 nm.

In the surface analyses, each LIBS spectrum corresponds to the sum of 6 individual ones acquired in different areas of the sample covering a line of almost 1 cm. Instead, in the stratigraphic analysis (in-depth analysis), the LIBS spectra were recorded by applying several laser pulses in the same area of the samples at 30 nm wavelength intervals centered at 285, 325, 360, 400 and 500 nm. The spectra were recorded at a 0.17 nm resolution with a gate delay and width of 200 ns and 3 µs, respectively. A cut-off filter at 300 nm was placed in front of the entrance window of the spectrograph to reduce the scattered laser light and to avoid second-order diffractions.

III. RESULTS AND DISCUSSION

D. LIBS surface analysis

In order to select the characteristic elements of the black crust, a spectrum was recorded for both the black crust and the substrate parts of the sample. In almost all the samples, characteristic elements of the stone substrate such as Ca, Al, Mg, Na, O, Si and Sr were also found in the black crust, highlighting its embedment in the structure of the monument. Table 2 indicates those elements that were found exclusively in the black crusts, without considering the elements that were common to both the crust and the substrate. Instead, Figure 4 shows a comparison between the LIBS spectra of the substrate and of the black crust obtained for a representative sample.

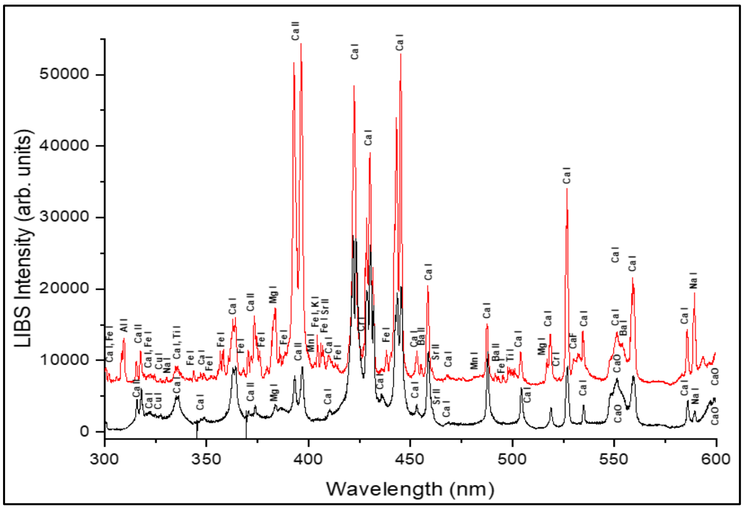

Fig. 4. LIBS spectra of the substrate (black) and of the black crust (red) for sample GP

Owing to the nature of the samples, calcium was by far the most abundant element in both the substrate and the black crust. However, the abundance of this element did not preclude the detection of several other ones in all the samples. As indicated in Table 2, Fe, Mn, Ba and Ti were common to all the samples, whereas Cr, Cu, Zn and F (detected as CaF) were found only in some of the crusts. With regard to elemental composition, no significant relationships could be observed in terms of years of accumulation. This is probably due to the limited penetration depth of surface LIBS analysis, which enabled the elemental characterization of the more recent parts of the crust, which share common characteristics between the samples.

However, all the elements detected using LIBS in the various samples are specific tracers of pollution sources surrounding the Monumental Cemetery. With regard to Fe and Mn, when found together, these two elements are specific markers of particulate matter deriving from railroad traffic [12]. This finding can be directly linked to the presence of one of the main railway stations (Garibaldi) of the city less than 1 km away. Moreover, some of the main markers of vehicular traffic were also found in the black crusts surface, such as Zn, Cu, Cr and Ba [3,12].

These elements derive from brake wear, tire wear, and tailpipe emissions. Specifically, Ba is one of the key markers of new generation diesel cars.

In support of this finding, all samples were also characterized by the presence of Ti. Indeed, titanium can be linked to roadside dust and resuspended soil, which derives mainly from vehicular movement [12]. Once again, these results agree with the location of the cemetery, which is close to some of the main traffic arteries of the city. Finally, fluorine was also detected as the molecular species CaF in some of the samples. To the knowledge of the authors, this is the first study in which this element was found in black crusts above the limits of detection. Based on the nature of the sampling site and on the other results, the authors hypothesize a common source with Fe and Mn. This is because fluorine is used as a flux in the manufacture of steel [13], which is the material with which train wheels and rails are made. It is possible that the proximity of the cemetery to the intensely trafficked railway station could be the source of fluorine found in the black crusts.

These results highlight the ability of the LIBS techniques to detect all the main markers of vehicular and railway traffic, which are the main sources of pollution in the surrounding area. This is particularly true for fluorine, which is usually not an easy element to detect, especially at the low concentrations in which it is present in black crusts. However, the calcium-rich nature of the black crusts makes this task easier, as fluorine is detected using the CaF molecular emission, which is a valid alternative when the concentrations are in the low ppm range [14].

Moreover, the presence of Ba in all the samples suggests that the pollution sources detected from the surface analysis are only the most recent ones. This hypothesis is further supported by the absence of Pb, which was used as an additive in leaded gasoline until around thirty years ago. Indeed, other studies found the presence of Pb in black crusts [3], however, the analysis was not restricted to the surface of the sample. Also, the fact that no difference was observed in terms of elemental composition despite the different ages of the crust is a further indication that the pollutants observed derive from modern sources common to all the samples.

E. LIBS stratigraphic analysis

In order to evaluate the in-depth distribution of the metals within the black crust, stratigraphic analysis was performed on all samples. The elements chosen were the ones that were common to all the samples: Fe, Ti, Mn, and Ba. This was done in order to be able to carry out significant comparisons between the different black crusts. The main results were a common trend in all the samples: that is, a decrease in the emission intensity with increasing laser pulse number (Figure 5).

As can be seen in Figure 5, the intensity of the selected emission lines for Fe and Mn displays an exponential decrease with increasing laser pulse number. Ti and Ba also showed similar trends to the one shown in Figure 5 for Fe and Mn. This result highlights a decrease in concentration of the species from the surface to the bulk of the black crust, underlining surface accumulation in the "younger" regions of the crust. This result could be due to several factors. Considering also the outcome of the surface analysis, it is possible that higher concentrations of the species close to the surface, therefore in the "youngest" parts of the black crust, could be due to the increase in pollutant activities in the last decades. Moreover, as mentioned in the previous section, most of the elements observed are tracers of relatively recent pollutant sources whose impact was inevitably less or even null in the "older" parts of the crust. Finally, also in the stratigraphic analysis, no differences were observed in terms of years of accumulation of the black crusts.

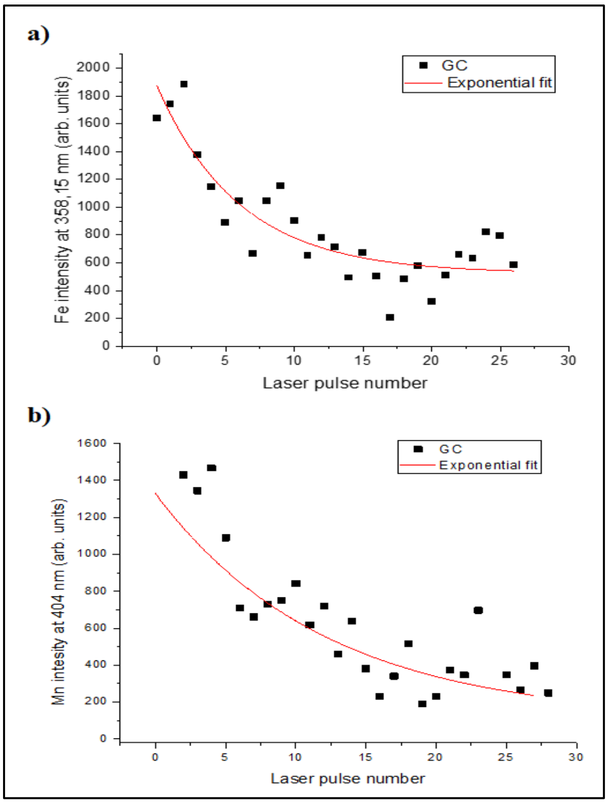

Fig. 5. Stratigraphic LIBS analysis of iron (a) and manganese (b) for sample GC.

IV. CONCLUSIONS

The results obtained in this study highlight the ability of the LIBS technique in the detection of the main elements in black crusts, since all the species found could be traced to a specific source of the surrounding area. Moreover, the in-depth distribution of the metals determined with stratigraphic analysis gave interesting insights on the variation of the impact of these sources throughout the years.

Further developments will include the study of a broader range of elements with the stratigraphic analysis. Indeed, based on the results of previous studies, it is likely that black crusts, like the ones in question, contain other elements such as Pb and As, typical tracers of “older” pollutant sources. This could also help to shed light on another unresolved issue in this field, which is the determination of the mechanism of the sulphation process; in particular, which elements specifically are responsible for the catalytic action that leads to the formation of the black crusts.

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