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A preliminary study on black crusts from the Monumental Cemetery of Milan

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Abstract **This study is aimed at the characterization of black crusts taken from funerary monuments placed in the galleries of the Monumental Cemetery of Milan. Black crusts are degradation patinas that formed on carbonate stone surfaces by sulphation reaction. Sulphates formed by this reaction produce incrustations which incorporate various polluting particles (such as carbonaceous particles and heavy metals) that are the catalysts of this reaction. For this reason, black crusts can be considered passive samplers of pollutants over time. To characterize black crusts, different techniques have been used such as SEM-EDS, FT-IR / ATR, IC and TGA. This methodological approach made it possible to obtain information on the chemical and mineralogical composition of the crusts, and also on the pollution sources that have induced the stone decay.**

I. INTRODUCTION

This research study is focused on the characterization of black crusts taken from different monuments located in the Monumental Cemetery of Milan with the aim to study the effects of atmospheric pollution on the stones surfaces.

The cultural interest in the Monumental Cemetery of Milan (built in 1864) has increased during recent years since the site is of great cultural interest and has become part of the tourist itineraries in Milan, as it has happened for other important cemeteries in other European capitals. Numerous architectural and sculpture works of art are present, some of which were created by important artists telling in this way the story (about 200 years) of the city and of the relevant historical figures who lived and worked in Milan.

Air pollution is the main responsible for the deterioration of the stone materials, and its impact on buildings and monuments has been extensively studied [1-12].

In fact, there is a growing awareness regarding the degradation produced on outdoor cultural heritage exposed to air pollution, especially in urban environments. Black crusts (BCs) are the result of the interaction between calcium carbonate, the main stone constituent, and SO_2 which reacting with humidity leads to the formation of gypsum [13-15]. In particular, this deterioration phenomenon is one of the most dangerous degradation processes due to airborne pollutants, both gases and particles, that can to interact with the stone surfaces. Indeed, particles of anthropogenic origin, such as carbonaceous particles (organic and elemental carbon, i.e. OC and EC) and metal oxides, are embedded into the degradation layer. Thanks to the crusts chemical characterization it is possible to get information on the contribution of the different pollution sources especially in urban areas [2-12].

In this preliminary study, five black crusts were collected from some monuments located in the galleries of the Monumental Cemetery of Milan. The samples present about 100 to 150 years of pollutants accumulation since they have all been picked up from dated monuments where the year of burial is reported. The characterization has been performed applying different analytical techniques such as Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS), Fourier Transform Infrared Spectroscopy/Attenuated Total Reflectance (FT-IR/ATR) and Ionic Chromatography (IC). Moreover, the crust's composition has been investigated focusing on the quantification of the carbonaceous fraction, i.e. OC and EC, using an approach based on thermogravimetric analysis (TGA).

This integrated approach has allowed identifying pollution sources responsible for the decay of the stone materials.

II. MATERIALS AND METHODS

Milan is the most industrialized and densely populated citiy of Northern Italy, and often aerosols concentration in this area exceed the legislative limits (Legislative Decree 155/2010) [16]. The city is located in the centre of the Po Valley which is characterized, due to its geological conformation, by the scarcity of rainy phenomena and weak or almost completely absent winds. The city of Milan, in particular, suffers from intense pollution due to vehicular traffic, domestic heating and industrial activities.

The Monumental Cemetery is placed in the city centre, surrounded by road arteries (Galileo Ferraries, Luigi Nono, Ceresio, Carlo Farini, Valtellina) and is near the Garibaldi train station. The cemetery was designed by the architect Carlo Maciachini and inaugurated at the end of 1866; it has been enriched over the decades with many works of funerary art of classical, contemporary and other original styles. The main entrance is through the large Famedio (fig.1a), a building in Neo-Medieval style made of marble and stone that contains the tombs of some of the city's and the country's most honoured citizens, including that of famous writer Alessandro Manzoni.

Two galleries start from the right and the left side of Famedio. Inside these galleries some funeral monuments of several illustrious Milanese families are placed. The five black crusts samples examined in the present work come from the left gallery protected from washout (fig. 1a) and, in particular, come from fragments fallen from some of the monuments (Fig. 1c). The sampled monuments have never undergone restoration and for this reason, the period of pollutants accumulation on the crusts is known with certainty and corresponds to the date of death of the illustrious person to whom the monument is dedicated. In particular, the examined crusts show pollutants accumulation that varies between 98 and 144 years.

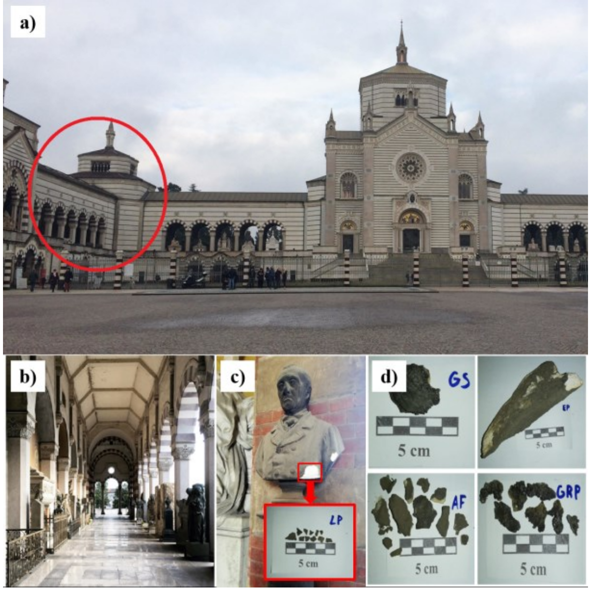

Fig. 1. Image of the Monumental Cemetery of Milan; a) image of the Famedio, the red circle indicates the left gallery; b) image of interior of the left gallery, c) image of a sampled statue and the LP crust sample; d) samples taken from monuments.

The samples (Fig. 1d) show variable color (from dark grey to black), morphology (linear compact and dendritic) and thickness, depending on the exposure position and on textural features of the underlying substrate.

A brief samples description accompanied by information regarding BCs sampling, year of exposure of the monument (indicated by the year of death) and period of accumulation of pollutants is summarized in Table 1.

Table 1. List of BC samples collected from Monumental Cemetery of Milan

Sample	Description	Year of exposure of the monument	Years of pollutants accumulation*
GS	Black crust on marble	1870	149
EP	Black crust on marble	1921	98
LP	Black crust on marble	1881	138
AF	Black crust on marble	1875	144
GRP	Black crust on marble	1900	119

*Difference between year of sample collection (2019) and year of exposure of the monument

The micro-texture and chemical composition of the BCs was analysed using SEM-EDS to obtain qualitative/semiquantitative information on the chemical composition. The instrument was a Hitachi TM1000 equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED). The spectra were directly acquired of the surface since no metal coating was required in this case to analyse non-conductive samples. Infrared spectra were collected with a spectrophotometer Nicolet 380 coupled with ATR accessory Smart Orbit equipped with a diamond crystal. The spectra have been acquired in the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

Chromatographic analysis has been carried out to quantify the main ions present in the black crusts. The test tubes were put in an ultrasonic bath for 1 h, then the solutions centrifuged and injected for IC analyses by means of an auto-sampler. Measurements of cationic (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anionic (NO_3^-, PO_4^{3-} SO_4^{2-}, Cl^-) species were carried out by using an ICS-1000 HPLC system equipped with a conductivity system detector. More details on the analytical procedure are reported elsewhere [8,17].

TGA was used to quantify the carbononaceous fraction. The analyses were carried out with a Mettler Toledo TGA/DSC 3 instrument that allows simultaneous TG and DSC analyses, in a range between 30–800°C, increasing the temperature with a speed of 20°C/minute in two different atmospheres, inert and oxidizing. Calculations were carried out for the determination of OC, EC and CC (carbonatic carbon) present in the crusts following the procedure described in [8].

III. RESULTS AND DISCUSSION

By SEM-EDS the micro-morphological and chemical characterization (in terms of major elements) was performed on the surface of the black crust samples. The images acquired (Fig. 2) show that almost all the samples (except for sample LP) show that crusts are made of an interlocked structure of lenticular and/or hexagonal plate-like crystals arranged as rose-like clusters composed of Ca and S (Fig. 2), attributed to gypsum. Gypsum crust embeds minute particles of variable composition containing Si, Al, Mg and Fe.

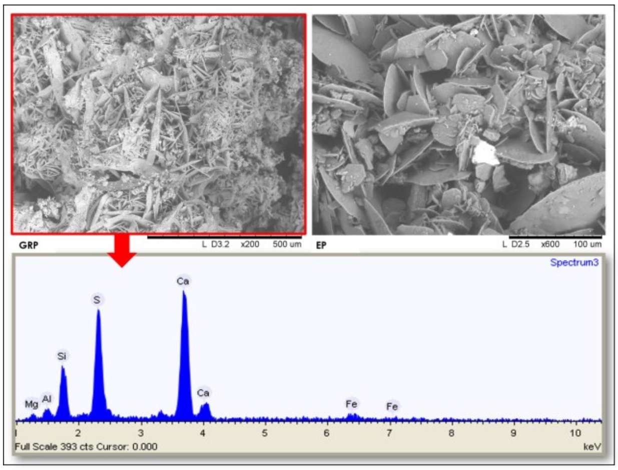

Fig. 2 SEM micrographs showing GPR and EF samples; note the crust made of rose-like clusters of gypsum crystals and the tiny particles embedded. The EDS spectrum shows the chemical composition of the surface

Figure 3 shows the results obtained from FT-IR/ATR analysis. It is possible to observe that all the samples exhibited the characteristic absorption peaks of gypsum, calcite and oxalate, which are typical of black crusts. In particular, the peaks due to the presence of gypsum are at around 3525, 3400,1627, 1109, 667 and 590 cm^{-1} and they have been observed for all the samples. Moreover, the most intense bands have been observed for samples GS and GPR (Fig. 3), confirming EDS analysis. Furthermore, the stretching and bending vibrations of calcium carbonate at 1409, 871 and 710 cm^{-1} were observed (except for the GRP sample); the presence of these peaks is to be attributed to the underlying carbonate substrate. Oxalate was recognized due to the typical absorption peaks at 1630, and 1321 cm^{-1} which, according to the literature, can be attributed to previous restoration interventions, or to a biological degradation (metabolism of microorganisms) [18-21]. In this case, the first hypothesis is to be excluded since restoration works have never been carried out on these monuments.

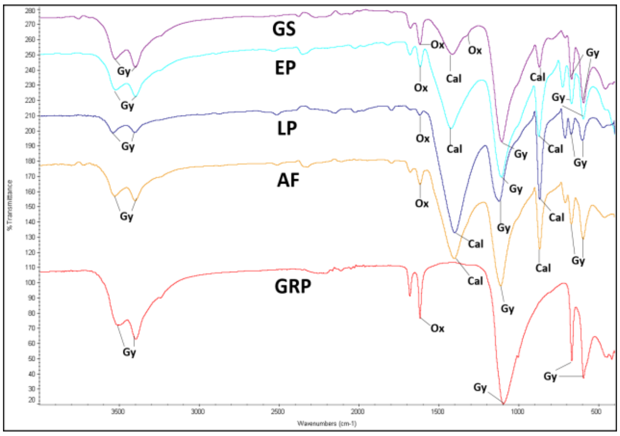

Fig. 3 FTIR spectra of black crust samples.

In table 2 results regarding the determination of ionic species determined by IC, have been reported. As expected, the examined samples contain large quantities of sulphate, coming from the conversion of calcium carbonate, the main constituent of the stone [21].

Table 2. Concentration of ions (ppm) in the examined black crusts.

Anions concentration				
Sample	**Cl^-**	**NO_3^-**	**PO_4^{3-}**	**SO_4^{2-}**
GS	662	743	49	433860
EP	729	780	23	92370
LP	671	1024	3	82370
AF	717	1168	2	179545
GRP	899	877	47	674305
Cations concentration				
Sample	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**
GS	16509	7469	271	160532
EP	592	686	5877	40743
LP	6363	3237	523	95516
AF	4481	2195	444	123451
GRP	897	1012	0,00	212020

In fact, sulphate is the main component of the crusts (as also evidenced by FT-IR analyses previously) and in the five samples it shows the same trend of calcium (Fig. 4), in accordance with FTIR. All the samples reach quite high nitrate and chloride concentration.

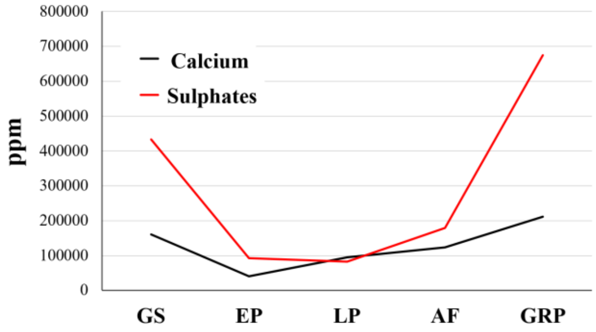

Fig. 4. Concentration trends of Ca^{2+}/SO_4^{2-} in the examined black crusts.

All the samples show quite high nitrate and chloride concentration. Among cations Mg^{2+} and K^+ probably come from dust resuspension.
The identification and quantification of the carbonaceous species are reporter in table 3.

Table 3. OC (Organic Carbon) EC (Elemental Carbon), CC (Carbonate Carbon), and TC (Total Carbon=OC+EC+CC) concentrations (wt%) of the examined black crusts.

Sample	Years*	OC	EC	CC	TC	EC/TC	OC/EC
GS	149	0.63	1.36	2.43	1.99	0.68	0.46
EP	98	1.38	0.44	4.10	1.82	0.24	3.16
LP	138	0.30	0.54	3.72	0.85	0.64	0.56
AF	144	0.30	0.54	3.97	0.84	0.64	0.56
GRP	119	0.38	0.35	0.14	0.73	0.48	1.08

***Years of pollutants accumulation**

Almost all samples show high concentrations of EC compared to OC, except for EP sample. The higher EC values indicate that primary emissions are probably the main sources of carbonaceous species. In fact, Milan is characterized by a high traffic responsible for the high values of these pollutants. Various studies [22-24] have indicated that sources identification is possible on the base of OC/EC ratio. Relatively low values, less than or equal to 1, are due to primary emissions from combustion of fossil fuels [25] while ratios greater than 1 are instead attributed to secondary emissions. The ratios reported in Table 3 are lower than 1 for all the samples except for EP which is also the sample with the lower period of pollutants accumulation indicating probably as a change in the contribution of the different sources has occurred. Obviously to confirm this hypothesis the analysis of a higher number of samples would be necessary. Comparing EC/TC values with what observed in other cases for black crusts samples collected in the city of Milan [9,25] and showing a ratio that varies from 0.5 to 0.7, it can be observed that they are in agreement indicating an important contribution due to vehicular traffic emissions. Finally, from Table 3 we note how the ratio EC/TC increases with the years of exposure (GS and AF samples that have longer exposure periods show the highest EC/CT).

IV. CONCLUSIONS

In this preliminary work black crusts collected from five monuments located in the Monumental Cemetery of Milan have been analysed. To our knowledge it is the first time that such a study has been carried out on this important Milanese monument. The analytical methodologies applied have provided information on their composition. The formation of these degradation layers is essentially due to the pollution coming from vehicular traffic. The black crusts are mainly composed of gypsum, with some traces of oxalate and calcite, the latter coming from the substrate. The presence of heavy metals mainly due to anthropogenic emissions, has also been disclosed.

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