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Metals distributions within black crusts sampled on the facade of an historical monument: the case study of the Cathedral of Monza (Milan, Italy)

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***Abstract* – This research deals with the characterization of black crusts collected from Dome of Monza. Black crusts (BC) can be formed as a result of different chemical and physical reactions between the stone surface and environmental factors (such as gaseous pollutants, aerosol particulate matter and its specific chemical constituents-the carbonaceous fraction and the metals); therefore, they are considered as a passive sampler of pollutants. The specific focus of the current work is the study of the metals and their distribution within the samples. To characterize BC, several techniques were used such as: HRSEM-EDX, IC and LA-ICP/MS. This integrated approach allowed us to gain information about the mineralogical phases and the elements within the crusts giving the possibility to identify the pollution sources causing the stone decay, as well as the variability in composition depending on the exposure of the analysed surfaces.**

I. INTRODUCTION

Air pollution is one of the most important causes of surface decay in urban environment. Deterioration is an irreversible and inevitable phenomenon and speed and modes where it occurs depends on the type of material, the surrounding environment and also from the chemical-physical processes involved. Water, soluble salts and atmospheric pollutants, such as carbonaceous particles and metals, are deposited on the surfaces by dry or wet processes and are the responsible for the degradation. The action of pollutants on the surface forms dark deposits called black crusts (BC) mainly present in areas protected from washout and exposed to polluting weathering agents. Among the degradation processes due to airborne pollutants, the formation of black crusts is one of the most dangerous one [1-8]. Currently, emissions from mobile combustion sources are the main agents responsible for pollution, although a significant decrease is expected in Europe in the next decade.

In this work the results obtained from the analysis of black crusts taken from the historical cathedral of Monza, placed in a polluted urban centre in the North of Italy, will be discussed. Although the black crusts of Monza cathedral have already been studied from the point of view of their morphology and the carbonaceous fraction [9], this paper will focus on the identification of the metals and main ions content.

The cathedral is located in the homonymous city placed ca. 20 km NE of Milan. Monza covers an area of 33.09 km^2 and has 123,776 inhabitants and it is the third largest city in the Lombardy region (N Italy). The city suffers from high pollution produced by the intense vehicular traffic, the high use of domestic heating, as well as the pollution produced by industrial and agricultural activities typical of the Po Valley. Several BC fragments have been sampled at different heights from the cathedral façade and then characterized.

II. MATERIALS AND METHODS

The façade of the Cathedral of Monza is a remarkable example of 15th century architecture, and divided into three parts, was designed and finished by Matteo da Campione between 1300-1350 AD; it is characterized by alternating dark and white-coloured rows of stone blocks. From the 18th to the 20th centuries several restoration works was carried out, involving only some areas [10]. The first restoration (1735) was carried out by Conca who replaced the dark and white-coloured degraded rows with new ones, and also integrated all the missing columns of white marble in the area above of the frieze; in particular, the 3 oculi and the 3 pinnacles were involved. Subsequently, the façade underwent an intense and very complicated restoration that could be distinguished in four phases. In the first phase (1892-1895) the works were directed by Beltrame who consolidated the façade and the rose window. Subsequently Landrini replaced Varenna marble on the facade and substituted the dark-coloured sandstone with serpentine stone from the Ojra quarries and some white marble slabs with Crevola marbles. Furthermore, some elements of the three-light windows and the quadrangular compartments on the black background of the rosettes in the central area were restored. In the second (1898) and in the third (1906) phase the restorations were directed by Mina who continued the work on the lower and upper cladding of the façade, in the central cusp and in the spire near the bell tower. In the fourth and final phase (1978-1983) a cleaning restoration was performed in the lower central and upper part of the façade. In 2017 the façade was restored once again.

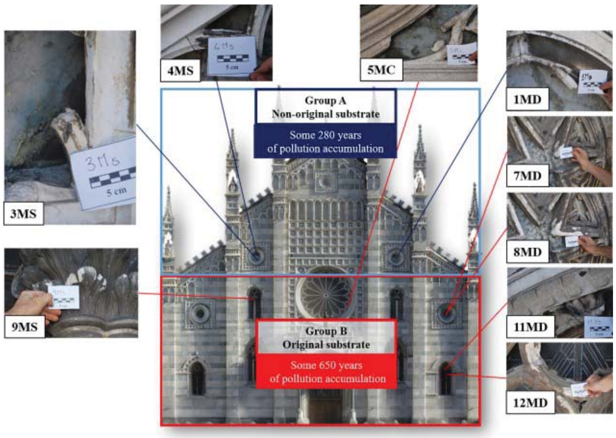

Figure 1. The locations of sampling points, and photographs of the black crusts collected from the façade of the Dome of Monza

During the last restoration carried out in 2017, 9 samples of black crusts developed on marble stones, were taken from the Dome façade at different heights (Fig. 1) Two groups of samples were identified:

-group A is formed by samples 1MD, 3MS and 4MS located at ca. 16m high (these crusts represent about 280 years of pollutants accumulation);

- group B is formed by samples taken from a height of ca. 12m, i.e. 5MC, 7MD, 8MD and 9MD, and samples 11MD and 12MD taken at ca. 5 m height (these crusts represent about 650 years of pollutants accumulation).

The micro-texture and chemical composition of the BCs and marbles substrates were analysed using a HRSEM-EDX. The instrument was a Supra 40Vp Carl Zeiss (Germany) furnished with BSE (backscattered electrons) and SE (secondary electrons) detectors (InLens) that deliver chemical and morphological images respectively, as well as a microanalysis system (Aztec 3) to provide elemental analyses by EDX (X-Max 50 mm detector). Ion Chromatography has been employed to quantify the main ions present in the BCs. Three milligrams of powder, withdrawn from the sample surface, were placed in a test tube and treated with 3mL of MilliQ water. 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_2^-, NO_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 [5,11]. BCs as well chemical analyses in terms of trace elements were performed by LA-ICP-MS. This method allows to investigate a great number of elements with spot resolutions of about 40–50 μm, also allowing the determination of micrometric compositional variations [12-13]. Analyses were carried out using an Elan DRCe instrument (Perkin Elmer/SCIEX) connected to a New Wave UP213 solid-state Nd-YAG laser probe (213nm). The analytical procedure to characterize the BCs is well- established in varied studies in the literature [14-15].

III. RESULTS AND DISCUSSION

The micro-morphological and chemical characterization through HRSEM-EDX was performed on representative samples of Group A and B. Information on the crusts morphology, as well as on the chemical composition in terms of major elements has been obtained. The images acquired show that in all samples the stone substrate is degraded, characterized by several fractures in which gypsum are evident in all samples. SEM micrographs of bulk 1MD and 4MS (belonging to group A) samples 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, attributed to gypsum (Fig. 2 a,b). X-ray maps acquired from 1MD thin section display the dissolution patterns of the calcite crystals nearby the marble surface and the crystallization of acicular gypsum crystals inside the calcite fissures (Fig. 2c,d). The gypsum crust embedded minute particles of variable composition such as silicates (Si/Al/Mg), Ba-sulfate, Ca-fosfate, Fe-rich particles, Pb-rich particles as well as particles containing Co and/or Zn and/or Cl (Fig. 2 e).

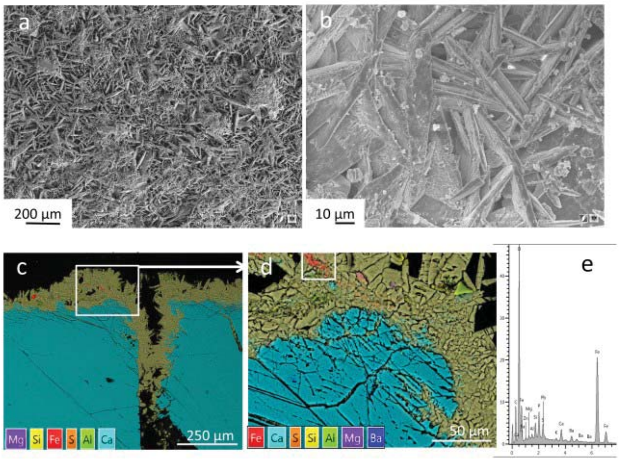

Figure 2. (a and b) SEM micrographs showing 1MD BC sample; note the crust made of rose-like clusters of gypsum crystals and the tiny particles placed in the BC. (c and d) SEM-EDX false-colour mineral map (thin section) of 1MD BC; note the dissolution patterns of the calcite crystals and the particles enclosed into the BC.(e)) average EDX spectrum of the box shown in 3d.

Analysis of bulk 7MD, 9MS and 12MD samples (group B) by SEM show that crusts have a powdered texture mostly made of granular and (hexagonal) plate-like gypsum crystals as well as tabular crystals in lesser amount (Fig. 3 a). Spheroidal spongy and/or smooth black carbonaceous particles (BCP) (Fig. 3 a, b) as well as metal particles are more abundant than in crusts from group A (1MD and 4MS). As revealed by EDX analyses, clusters of tiny metal particles (e.g. Cr and Fe) cover the smooth rounded BCPs (Fig. 3 b,c).

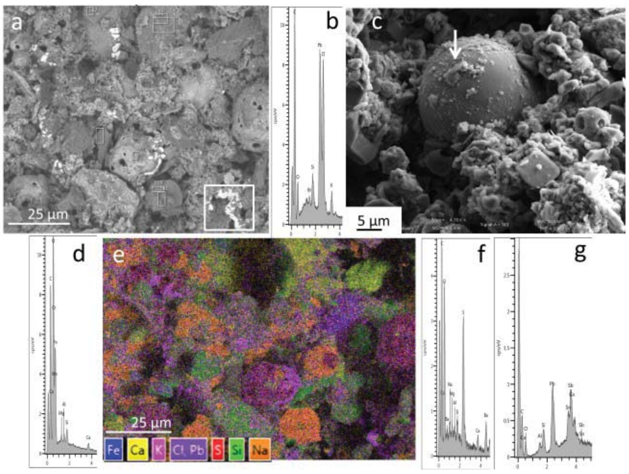

Figure 3 SEM micrographs of 7MD and 9MS BCs (bulk samples). (a) 7MD crust made of granular and tabular gypsum crystals enclosing copious rounded spongy-like BCPs and metal particles (white box) made mostly of Pb and Cl. (b) Smooth rounded BCP in 9MS crust. (c) EDX spectrum of metal particles (Fe, Cr) covering the CBP of image 4b (arrow). (d) average EDX spectrum of metal particles shown in the white box of image 4a; note the Pb-Cl rich composition. (e) SEM-EDX false-colour mineral map of image 4a. Note the enrichment on Pb-Cl, Fe, K and Na elements. f) and g) are average spectra of metal particles composition.

Other clusters of particles have variable composition such as: Pb-chloride always allied with K and occasionally with Br (Fig. 3 d, Fe-rich particles (Fig. 3 c,e) which in 12MD display framboid spherical morphology, Ba-sulfate (Fig. 3 f), glomerulus enriched by Sb, Sn, Pb and Al (Fig. 3 g), also K-sulfate, Ca-phosphate, Al, Zn, Ti, and V were detected in the particles embedded into the BCs.

All the analysed BCs samples showed low values of ions concentration can be attributed to the diminishing porosity inside the crusts.

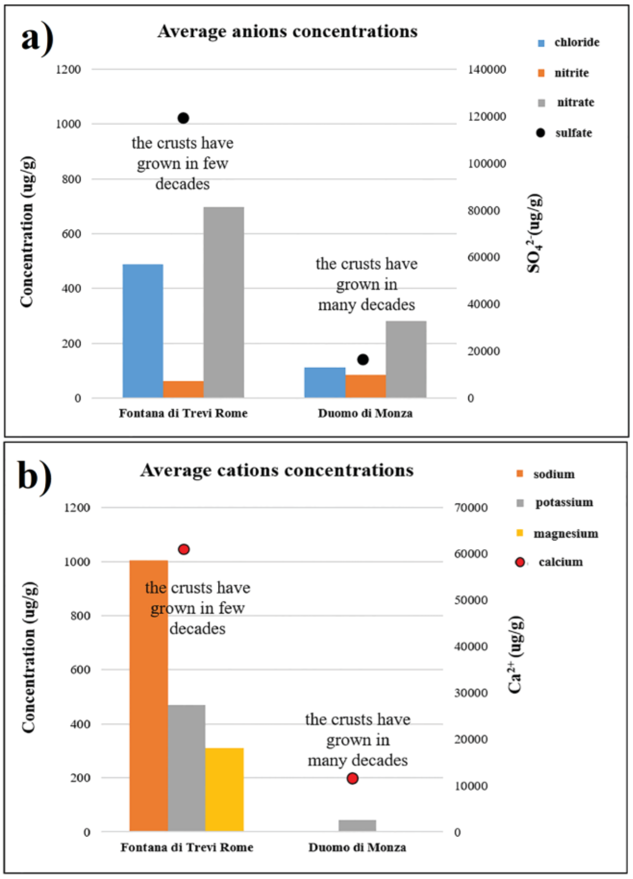

Figure 4 Comparison of the (a) anions and (b) cations average concentrations (μg/g) obtained from the Dome of Monza and Fontana di Trevi in Rome (Italy).

The average concentrations have been compared with what obtained in a recent study carried out on another monument having a similar substrate, i.e. Fontana di Trevi [5], even if the period of crusts growth is different. The differences observed in figure between the two monuments can be attributed to the diminishing porosity inside the crusts from Dome of Monza. In fact, many authors [16-18] suggest that when BCs tend to thicken over time, their porosity decreases. This would lead to a minor interaction with the gases environmental, also accentuating the diversity of mechanical and thermal behaviour with the underlying stone. This hypothesis is validated at least in part, since when collecting samples, the underlying substrate was so decayed, that the calcite crystals of the crystalline matrix were completely incohesive.

A deeper investigation of the geochemical features was obtained by measuring the average concentrations of trace elements by LA-ICP/MS. Fig. 5 shows the concentrations of the main elements on some selected samples.

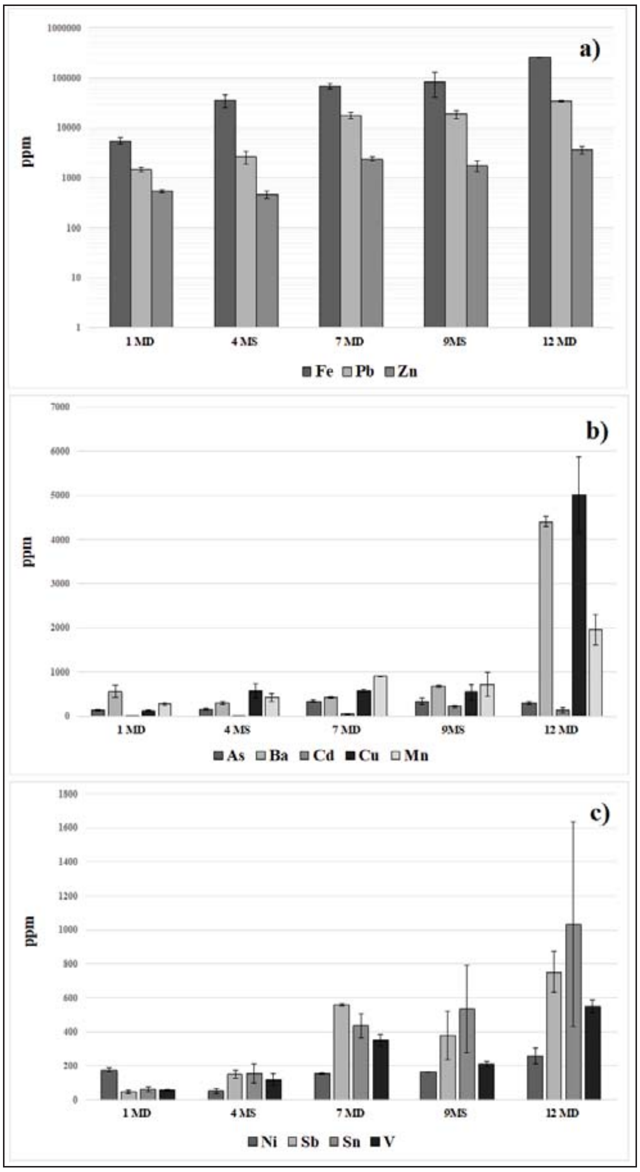

Figure 5 Histograms showing the average concentrations (ppm) of heavy metals in representative BCs. (a) Behavior of Fe, Pb and Zn. (b) Behavior of As, Ba, Cd, Cu and Mn. (c) Behavior of Ni, Sb, Sn and V.

In general, the results are characterized by a certain variability on each BC sample. Fe, Pb and Zn are the most abundant elements (Fig. 5a), while As, Ba, Cd, Cu, Mn, Ni, Sb, Sn and V were always present at a lower amount (in terms of average concentrations) (Fig. 5 b and c). This difference among the analysed samples can be due to several factors such as: various accumulation time of pollutants, diverse height of sampling, different exposure to different sources of pollution and to wash out. The enrichment observed in group B (7MD, 9MS and 12MD) is mainly due to the high vehicular traffic that characterizes the city of Monza and the metropolitan area of Milan, although the cathedral has been located in a pedestrian zone in the last decades. On the contrary, group A (1MD and 4MS) samples collected from 16m from the ground, often display lower concentrations of the same heavy metals. The correlation between different metal contents can provide additional information on pollutant sources. Correlation values, calculated for the main metals within the two groups of BCs are shown in Fig 6.

a)

Group A	As	Ba	Cd	Cu	Fe	Mn	Ni	Pb	Sb	Sn	Sr	V	Zn
As	1,00												
Ba	-0,03	1,00											
Cd	0,79	-0,29	1,00										
Cu	0,15	-0,35	-0,17	1,00									
Fe	-0,08	-0,44	0,01	0,62	1,00								
Mn	0,12	-0,19	0,16	0,41	0,84	1,00							
Ni	-0,15	0,42	0,01	-0,79	-0,73	-0,38	1,00						
Pb	-0,40	-0,27	-0,23	0,36	0,63	0,76	-0,51	1,00					
Sb	-0,07	-0,55	0,17	0,34	0,42	0,63	-0,69	0,85	1,00				
Sn	0,62	-0,40	0,69	0,23	0,42	0,28	-0,65	0,17	0,61	1,00			
Sr	-0,35	-0,04	-0,67	0,65	0,37	-0,01	-0,68	0,38	0,29	-0,03	1,00		
V	-0,20	-0,29	-0,02	0,46	0,94	0,87	-0,48	0,25	0,78	0,22	0,20	1,00	
Zn	-0,68	0,01	-0,48	-0,25	-0,04	-0,04	0,49	0,25	-0,06	-0,75	0,04	0,15	1,00

b)

Group B	As	Ba	Cd	Cu	Fe	Mn	Ni	Pb	Sb	Sn	Sr	V	Zn
As	1,00												
Ba	-0,34	1,00											
Cd	0,38	0,06	1,00										
Cu	-0,09	0,81	0,38	1,00									
Fe	-0,53	0,82	0,16	0,84	1,00								
Mn	-0,13	0,77	0,20	0,91	0,84	1,00							
Ni	-0,03	0,64	0,36	0,94	0,76	0,89	1,00						
Pb	0,02	0,67	0,36	0,82	0,91	0,58	0,70	1,00					
Sb	-0,19	0,36	0,62	0,94	0,72	0,70	0,73	0,52	1,00				
Sn	-0,01	0,47	0,41	0,81	0,73	0,70	0,82	0,64	0,82	1,00			
Sr	0,50	-0,15	0,66	-0,04	-0,22	0,02	-0,09	-0,13	0,03	-0,44	1,00		
V	-0,26	0,78	-0,19	0,79	0,78	0,89	0,77	0,93	-0,56	-0,12	-0,31	1,00	
Zn	-0,27	0,90	0,14	0,94	0,86	0,91	0,89	0,91	-0,56	-0,51	0,49	0,89	1,00

Figure 6 Correlation values among the element concentrations detected in the representative BCs; a) Group A and b) Group B.

Fe shows a good correlation with almost all heavy metals in both groups A and B and all these are connected to the combustion of heavy fuels [19-20] used mostly in industries and for domestic heating. A high correlation between Pb and Fe (0.91), Pb and Zn (0.91), Fe and Zn (0.86), Cu and Sb (0.94) and Zn and Ni (0.89) in group B confirms that these elements are probably emitted by a similar pollution source such as vehicular traffic, as stated above. Cu and Sb could come from brake pad emissions and other parts of friction and machine wear [21-23] while Zn and Ni come from worn tires [19-20].

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