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Environmental impact on historical monuments: the black crusts of the Venice lagoon

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***Abstract* – Black crusts are typical decay forms on calcareous rocks in polluted urban environments. Their origin is due to "*sulphation*" reaction of calcium carbonate substrates ($CaCO_3$), as a consequence of pH value decrease caused by SO_2 in the polluted atmosphere. They can be therefore defined as a passive air pollution sampler. For the purpose of this work, samples from the historic center of Venice were analyzed. The city of Venice suffers in particular maritime and industrial pollution (Marghera industrial zone). By means of minero-petrographic and geochemical analyses, it was possible to obtain information on the mineralogy of the crust and its interaction with the underlying substrates, other than useful information on the chemical composition in terms of major and traces elements linked to the various sources of urban pollution.**

I. INTRODUCTION

Venice is an Italian municipality, whose territory includes both mainland and island territories. The two centers are Mestre (on the mainland) and the Venetian Lagoon. It is the 3rd Italian city with the highest annual tourist flow and the 42nd in the world.

In addition to being a famous tourist destination, the Venice area is also one of the most polluted areas in Italy. Over the years, an increase in air pollution has been observed. In 2017, for example, the city was ranked 8th with 94 total days of exceeding the limits set for atmospheric particulate matter (PM_{10}) and ozone (O_3) [1], while in 2018, it was ranked 4th with 139 days of exceeding limits [2].

The main sources of pollution in the area are attributable to:

• Industrial activity;
• Domestic wastes;
• Maritime traffic.

The main industrial area is *Porto Marghera* with its petrochemical center. In addition, domestic wastes/drains from lagoon inhabited centers without adequate purification systems are also present [3,4]. In terms of pollution, Venice is the 3rd in Europe and the 1st in Italy. On average, 68 large ships are stationed annually in the Venetian lagoon, with a resulting emission of sulfur oxides of about 27520 kg, 600337 kg of nitrogen oxides, 10961 kg of atmospheric particulate matter. To be noted that the sulfur oxide emission of 68 ships is about 5 times higher than that of 110000 cars [5,6].

In this paper, samples of black crusts [3,7-14] collected from several historical buildings in the city of Venice were characterized in order to improve the knowledge of their decay in the peculiar Venetian environment.

II. MATERIALS AND METHODS

The black crust samples examined in this paper come from various monuments of the historic center of Venice located in different areas of the Venetian lagoon (Fig. 1).

Fig. 1. Sampling points in the Venice area.

Table 1 reports a detailed list of analyzed samples with indication of sampling points (Fig. 2) and methodologies applied for their characterization.

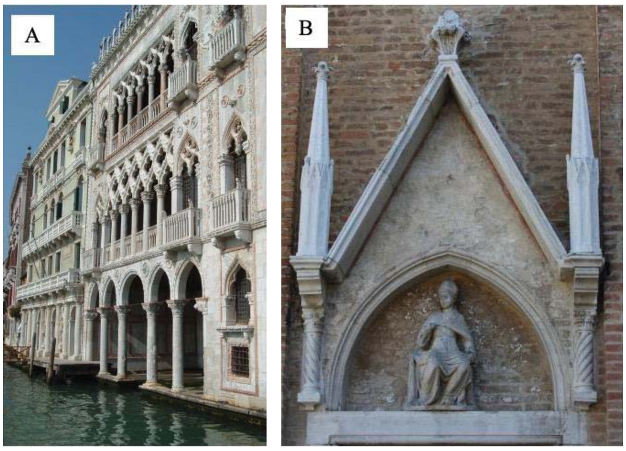

Fig. 2. Example of two sampling points: A) Ca' d'Oro Palace; B) Sant'Alvise Statue.

Table 1. List of analyzed samples.

Sample code	Year of sampling	Typology	Analytical Method	Monuments
SA1	1967	Substrate + black crust	OM	Sant'Alvise Statue
FSM1	1972	Substrate + black crust	OM	Basilica of St. Mark
FSM2	1972	Substrate + black crust	OM	Basilica of St. Mark
CD67 1	1967	Substrate + black crust	OM	*Ca' d'Oro* Palace
CD67 2	1967	Substrate + black crust	OM	*Ca' d'Oro* Palace
4MO	2018	Substrate + black crust	OM + FTIR	*Morosini del Pestrin* Palace
11MO	2018	Substrate + black crust	FTIR	*Morosini del Pestrin* Palace
PCAV2	2017	Substrate + black crust	FTIR	*Cavagnis* Palace
PCAV4	2017	Substrate + black crust	OM + FTIR	*Cavagnis* Palace
EP2101	1984	Substrate + black crust	OM + FTIR	Saint Mark Place

Optical microscopy (OM) was performed on thin sectioned lithotypes samples and stratigraphic sections by means of a Zeiss AxioLab microscope (Oberkochen, Germany) equipped with a digital camera.

Fourier-transform infrared spectroscopy (FT-IR) investigations were carried out to identify the mineralogical phases constituting the examined damage layers.

The infrared spectra were collected with a spectrophotometer Perkin Elmer Spectrum 100 (Waltham, MA, USA), equipped with an attenuated total reflectance (ATR).

The ATR accessory is equipped with a diamond crystal, in the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

The technique was used to analyze small amounts of black crust drawn from samples surfaces using a scalpel.

III. RESULTS AND DISCUSSION

Polarizing optical observations allow to obtain information on textural and mineralogical features of analyzed samples together with details about their state of conservation.

Firstly, it was possible to recognize the type of substrate interested by black crusts deterioration.

In particular, these are marbles for samples SA1, FSM1, FSM2, CD67-1, CD67-2, EP2101 while the substrate of sample 4MO is a mortar and that of sample PCAV4 is a brick.

Table 2 summarizes the main petrographic characteristics of the substrates.

Table 2. Summary of some mineralogical and textural characteristics of the studied substrates.

Sample code	Typology	MGS (mm)	Texture	GBS
SA1	White Marbles	0.6	He, I	Cr, L
FSM1		0.4	Ho, I	Cr
FSM2		0.4	Ho, I	Cr
CD67-1		0.6	He, I	St
CD67-2		0.7	He, I	St
EP2101		1.5	He, I	St
Sample code	Typology	Aggregate	Binder/groundmass	Notes
4MO	Mortar	Qtz, Ms, Limestone fragments	Lime binder with sporadic lumps	Primary and secondary porosity
PCAV4	Brick	Qtz	Inactive	Voids/cracks
MGS = maximum grain size; Texture: He, heteroblastic; Ho, homeoblastic; I, isotropic. GBS (grain boundary shape): St, straight; Cr, curved; L, lobate; Qtz=quartz; Ms=muscovite.				

By means of petrographic analysis it was also possible to define the different state of conservation of the samples.

In particular, the best-preserved samples are those from the statue of *Sant'Alvise* (SA1), *Morosini Palace* (4MO) and *Cavagnis* Palace (PCAV4).

Black crusts grown on the surfaces of these samples have limited thickness and less interaction with the underlying substrate (Fig. 3).

The most degraded ones are those coming from *Ca' d'Oro* (CD67 1-2), from Saint Mark Place (EP2101) and the Basilica of San Mark (FSM1 and FSM2).

Black crusts that develop on these samples show good adhesion to the substrate, with penetration phenomena within the substrate itself causing discontinuities and fractures (Fig. 4).

The greater or lesser degradation may be due to various reasons, one of which is the severe exposure to pollutants.

In fact, observing the location of the monuments from which the samples were taken (Fig. 1), it can be seen that the most degraded samples are those most in close contact with the *Canal Grande*, which is the main canal of Venice, with traffic related to small boats for public and private service but also to large cruise ships.

Another feasible reason could be related to the period of accumulation of the crust.

For example, FSM1 and FSM2 samples, which are among the most degraded, have a long period of accumulation of the crust with about 552 years of exposure to pollutants. *Cavagnis* Palace instead is a building dating back to 1600, the sampling was carried out in 2017 following several restorations works so it has better conservative characteristics.

Finally, one of the reasons could be the presence of wrong consolidating interventions prior to the time of sampling.

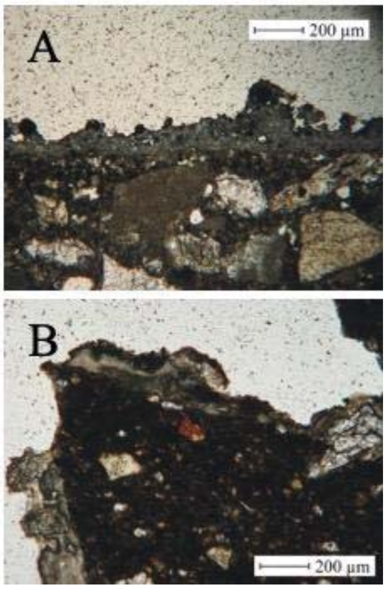

Fig. 3. Thin section microphotographs: A = sample 4MO, B = sample PCAV4.

FT-IR analysis was used to define the different mineralogical phases present in black crusts samples. The latter method provided important information: 4 samples out of 5 showed similar spectra.

In particular, the mineralogical phases identified are gypsum ($CaSO_4$*$2H_2O$) with the typical vibrational bands at 3401.9 cm^{-1}, 1621.5 cm^{-1}, 1116.4 cm^{-1} and 671.5 cm^{-1}, calcite ($CaCO_3$, 1434.5 cm^{-1} and 875.4 cm^{-1}) and calcium oxalate (CaC_2O_4, 1323.9 cm^{-1}).

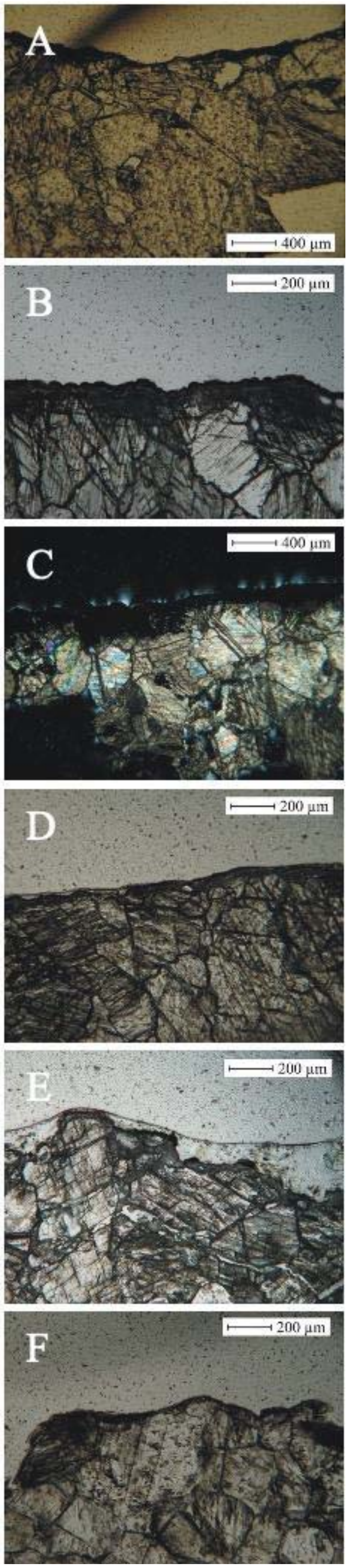

Fig. 4 Thin section microphotographs: A = sample SA1, B = sample FSM1, C = sample FSM2, D =sample CD67-1, E = sample CD67-2, F = sample EP2101.

Figure 5 shows the IR spectra of all analyzed samples.

The only exception is represented by the sample EP2101 (Fig. 6) which shows only the absorption bands of calcite (1408.0 cm^{-1} and 873.2 cm^{-1}) and quartz (1037 cm^{-1}).

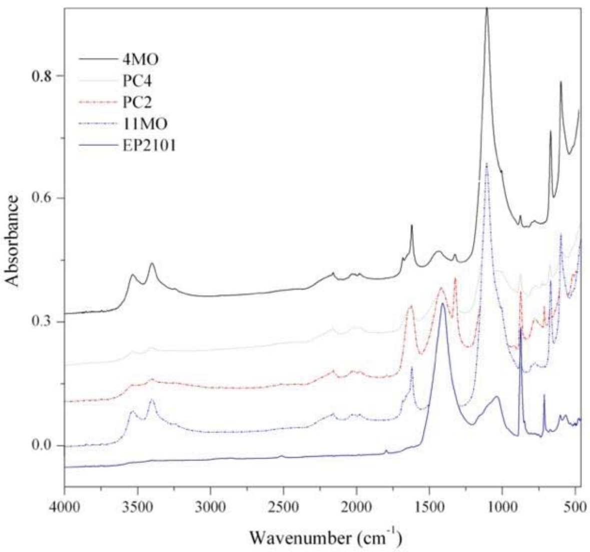

Fig. 5. IR spectra of analyzed black crusts.

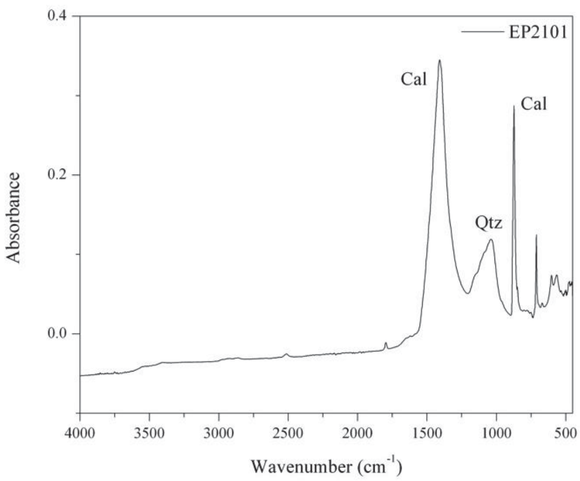

Fig. 6. IR spectrum of EP2101 sample.

IV. CONCLUSIONS

Minero-petrographic investigations carried out on black crusts from the historical center of Venice confirmed that they mainly consist of gypsum, calcium oxalates and calcite.

The origin of calcite can be attributed to the carbonate substrate. The presence of gypsum is due to the exposure of the building materials to pollutants that have determined sulfation reactions.

The presence of calcium oxalate can be considered a consequence of the oxidation of natural organic material applied as protective [15].

It has also been observed that the most degraded samples are those in closest contact with places where the concentration of pollutants is greater.

In particular, the historic center of Venice suffers industrial and maritime pollution, i.e. both fixed and mobile pollution.

In order to identify the sources of pollution in this particular environment, in a future work chemical analyzes of the trace elements will be carried out using LA-ICP-MS.

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