Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their composition

Mauro F. La Russa[a], Valeria Comite[b], Nevin Aly[c], Donatella Barca[a], Paola Fermo[b], Natalia Rovella[a], Fabrizio Antonelli[d], Elena Tesser[d], Silvestro A. Ruffolo[a*]

a Department of Biology, Ecology and Earth Science, Rende, Cosenza, Italy
b Department of Chemistry, Università degli Studi di Milano, Milano, Italy
c Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt
d Laboratorio di Analisi dei Materiali Antichi (LAMA), University Iuav di Venezia, Venice, Italy
e Department of Mulecular Science and Nanosystems, University Ca' Foscari, Venice, Italy

* Corresponding author: silvestro.ruffolo@unical.it

Abstract

This research deals with the characterization of black crusts collected from several historical buildings in the city of Venice. This city suffers from pollution from the industrial area of Marghera, as well as from the maritime traffic. Black crust can be considered as a passive sampler of pollutants, with particular reference to heavy metals. For this reason, in order to fully characterize those samples, several techniques were used, including scanning electron microscopy, thermogravimetric analysis, laser ablation inductively coupled plasma mass spectrometry, infrared spectroscopy and ion chromatography. 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 within the buildings, as well as the variability in composition depending on the exposure of the analyzed surfaces.

1. Introduction

Air pollution is one of the most important causes of stone decay in urban environment [1-7]. Among the degradation processes due to airborne pollutants, the formation of black crusts is one of the most dangerous one [1, 8-10]. They are formed thanks to a sulphating processes on the stone surface: calcium carbonate ($CaCO_3$), which is the main constituent of carbonate rocks, is transformed into gypsum $CaSO_4$ $2H_2O$. The other atmospheric components, such as metals and metal oxides, act as catalysts in the sulphating reaction. This process affects mainly stone materials having carbonate nature (for example limestone, marble, mortar). In addition, during the crust formation, particulate matter, which contains mainly amorphous carbon and several heavy metals, can be embedded into the gypsum, providing then, the characteristic black colour. Currently, emissions from mobile combustion sources (such as cars and boats) are the main agents responsible for pollution, although a significant decrease is expected in Europe within the next decade. Several authors [11-19] showed how the analysis of trace metals into black crust, as well as the characterization of the carbon, can provide insights on the influence of the pollution sources in the formation processes of this degradation product, moreover, they can act as passive samplers of air pollution. In this research, we characterized samples of black crusts collected from several historical buildings in the city of Venice. This city suffers pollution from the industrial area of Marghera, as well as from the maritime traffic. Samples were investigated by means of infrared spectroscopy to detect the main mineralogical phases; electron microscopy coupled with EDS to gain information about the micromorphology and the chemical composition in term of major elements; ion chromatography to investigate the soluble salts within the crusts; thermogravimetric analysis to obtain information on the carbon fraction; ion coupled plasma coupled with laser ablation to characterize the content of trace metals.

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2. Sampling

Eleven samples of black crusts were collected from the city of Venice, from different buildings located in different areas of the island (Fig. 1). For all samples, the stony substrate has been identified as Istria stone,

a limestones having low porosity, which is quarried in Istria peninsula. Before sampling on each monument, on-site surveys were carried out in order to identify the most representative points in order to assess pollution variations across the different areas of the island. Black crust micro-samples and stone substrate have been taken from several architectural elements (i.e. portals, frames and decorative elements) sheltered from meteoric water at a height of about 1.50 m, usually from vertical surfaces. There is not any reliable information about restorations performed in the past on sampled areas. Sampling is summarized in Table 1

Fig. 1. Map of Venice reporting the sampling points

Sample ID	Description of sampling point
V1	Private building located near Ruga Vecchia, window frame, vertical surface
V2	Next to Canal Grande, portal of a private building, vertical surface
V4	Private building located Rio Megio, portal
V5	Private building next to Rio Megio, decorative architectural element horizontal surface
V6	Via Corte Piossi, church of Santa Maria Mater Domini, lower part, vertical surface
V7	Piazza San Marco, vertical surface
V8	Piazza San Marco, inner part of the colonnade, vertical surface
V9	Campo San Maurizio, left side of private building next to Museo della Musica, vertical surface
V10	Next to Rio di San Pantalon left side of a portal belonging to a private building, vertical surface
V11	Next to Museo Guggenheim (Canal Grande), wall of private building, vertical surface
V12	Next to the curch of St. Moisè, inner part of a portal, private building, vertical surface

Table 1. Summary of collected samples

3. Analytical methods

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 Nicolet 380 (Thermo Electron Corporation) equipped with attenuated total reflection (ATR) accessory Smart Orbit and interfaced with a microscope FT-IR Nicolet Centaurus. The ATR accessory is equipped with a crystal diamond while on the microscope it is possible to mount an accessory with a silicon crystal (μATR), in the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. The technique was used to analyse small amounts of black crust drawn from samples surfaces using a scalpel.

In order to observe the micro-morphology, analyse the major elements and map the distribution of elements on a microscopic scale, an Electron Probe Micro Analyzer (EPMA) - JEOL- JXA 8230 – coupled with a spectrometer EDS – JEOL EX-94310FaL1Q - Silicon drift type - has been used. Elemental maps have been acquired with the following parameters: HV- 15 keV; Probe current - 10 nA; Working Distance - 11mm; Take off - 40°; Live Time - 50 sec.

Ion Chromatography (IC) has been employed for the quantification of the main ions. Three milligrams of powder, withdrawn from the sample surface, have been placed in a test tube and treated with 3 mL of MilliQ water. The test tubes have been 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. Anions analysis was carried out with an Ion Pac AS14A column using 8 mM Na_2CO_3/1 mM $NaHCO_3$, flow rate = 1 mL/min with for the detection a conductivity system detector working with an anion self-regenerating suppressor ULTRA (ASRS-ULTRA) suppression mode. Cations determination was performed using a CS12A (Dionex) column and 20 mM methane sulfonic acid (MSA) as eluent at a flow rate=1 mL/min and for the detection a conductivity system equipped with a cation self-regenerating suppressor-ULTRA (CSRS-ULTRA) suppression mode.

Thermogravimetric analyses (TG) were carried out on a selected group of samples by a Mettler Toledo TGA/DSC 3+ instrument, which allows simultaneous TG and DSC analyses. The analyses were conducted in the range 30°- 800° C, increasing the temperature with a rate of 20° C/minute, using about 0.2 mg of sample for each analysis. The samples were analyzed in the inert and oxidizing atmosphere, the latter made it possible to calculate the EC value.

Chemical analyses of the black crusts, as well as of the substrates, in terms of trace elements were performed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). This method can investigate a great number of elements with spot resolutions of approximately about 40–50 μm, which also allows the determination of micrometric compositional variations [20-22]. Analyses were carried out using an Elan DRCe instrument (Perkin Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 nm). Samples were ablated by a laser beam in a cell following the method tested by [23]. The ablation was performed with spots of 40–50 μm with a constant laser repetition rate of 10 Hz and fluence of ~20 J/cm^2. Calibration was performed using the NIST 612-50 ppm glass reference material as the external standard [24]. Internal standardization to correct instrumental instability and drift was achieved using CaO concentrations from SEM-EDS analyses [25]. The accuracy was evaluated on BCR 2G glass reference material and on an in-house pressed-powder cylinder of the standard Argillaceous Limestone SRM1d of NIST [13]. The resulting element concentrations were compared with reference values from the literature [26]. The accuracy, as the relative difference from reference values, was always better than 12 %, and most elements plotted in the range of ±8 %. Analyses were performed both on the black crust and on the unaltered substrate with the aim of better investigating the geochemical variability.

4. Result and Discussion

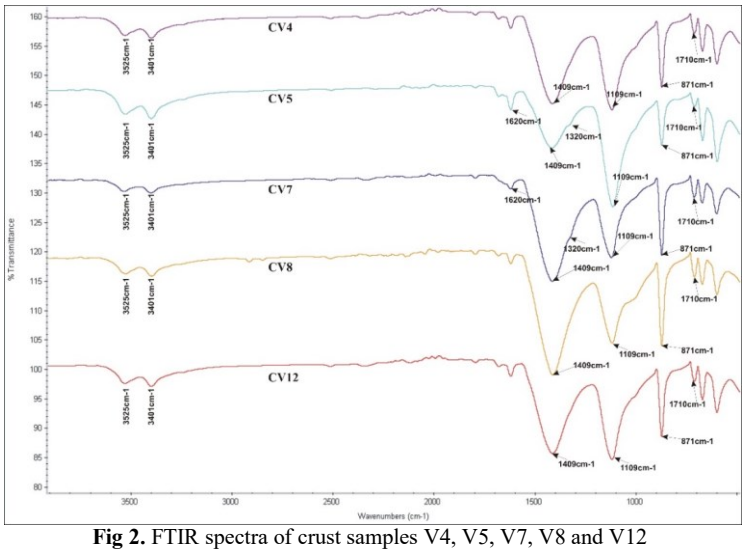


Fig 2. FTIR spectra of crust samples V4, V5, V7, V8 and V12

FTIR analysis showed the main inorganic components of the investigated samples. Spectra (Fig.2) shows the characteristic absorption peaks of gypsum, centered at 3525, 3401, 1682, 1627, 1109, 667 and 596 cm^{-1}, as well as the stretching and bending vibrations of the calcium carbonate, with peaks at 1409, 871 and 710 cm^{-1} can be certainly ascribable to the underlying substrate. The presence of oxalate (with peaks at 1630, 1320 and 780 cm^{-1}) in samples V5 and V7, according to the literature could be attributed due to restoration works carried out in the past or to the activity of microorganism colonies [26-33].

Electron microscopy coupled with EDS was performed in order to acquire information micromorphological (Fig. 3) and chemical (in terms of major elements) features of crusts. The microanalysis was carried out on spots of each sample.

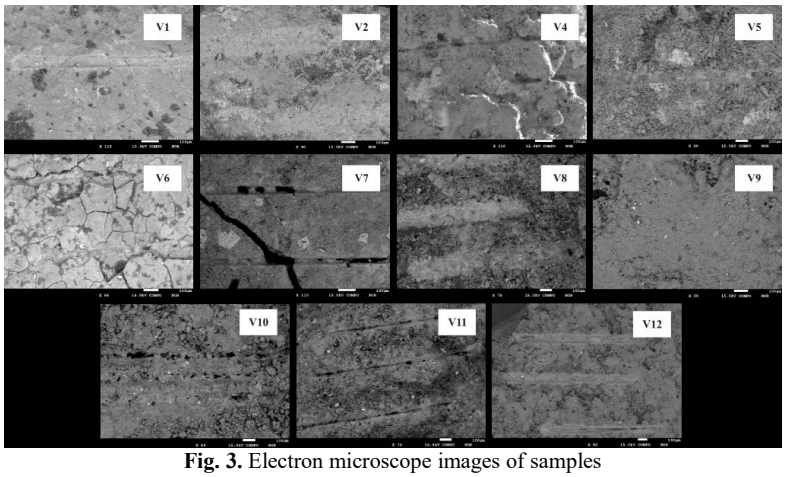


Fig. 3. Electron microscope images of samples

The analyzed crusts show in most cases, a heterogeneous, dendritic and irregular morphology (V2, V4, V5, V8, V9, V10, V11 and V12), while, few samples show a linear and compact morphology (V1, V6 and V7). The black crusts analyzed consist of gypsum crystals with acicular and lamellar habitus. Particles from combustion, having a spherical and sub-spherical shape with a smooth or porous surface were identified; they are heterogeneously distributed along the whole examined surface.
In general, the crusts examined show the same chemical composition with high levels of S and Ca, followed by Si, A1, Fe, Na, and smaller amounts of K, Mg and P (Table 2)

Sample	Na (% wt)	Mg (% wt)	Al (% wt)	Si (% wt)	P (% wt)	S (% wt)	Cl (% wt)	K (% wt)	Ca (% wt)	Fe (% wt)
V1	1.3	1.8	9.6	4.8	0.9	34.2	1.7	1.9	31.8	9.4
V2	1.3	0.8	2.7	11.8	0.6	42.1	1.3	0.9	33.2	5.0
V4	1.3	1.1	6.7	5.6	0.5	42.8	1.7	0.8	36.3	1.0
V5	1.1	1.3	2.8	9.8	0.0	40.4	1.6	1.0	40.1	1.6
V6	1.2	2.0	11.0	4.0	0.0	36.9	1.5	1.8	35.0	5.2
V7	1.1	1.1	2.4	4.7	1.7	40.5	5.8	1.3	41.1	0.0
V8	1.3	1.5	2.7	7.7	1.0	44.1	2.2	0.0	39.1	0.0
V9	1.3	1.0	3.3	8.5	0.5	45.7	1.0	1.8	34.0	2.5
V10	1.8	2.0	3.4	4.1	0.5	37.3	7.9	2.6	35.0	2.4
V11	1.4	2.1	6.3	7.0	1.0	37.2	3.2	2.8	33.4	4.7
V12	1.1	1.1	2.3	6.8	1.5	42.5	2.6	0.0	36.8	5.0

Table 2. Concentrations of major elements on black crust surfaces measured by EDS

In order to evaluate the distribution of the most abundant elements detected in the window analyzed (S and Ca), it has been performed false color maps of the two elements, as well as a combination of them (Fig 4).

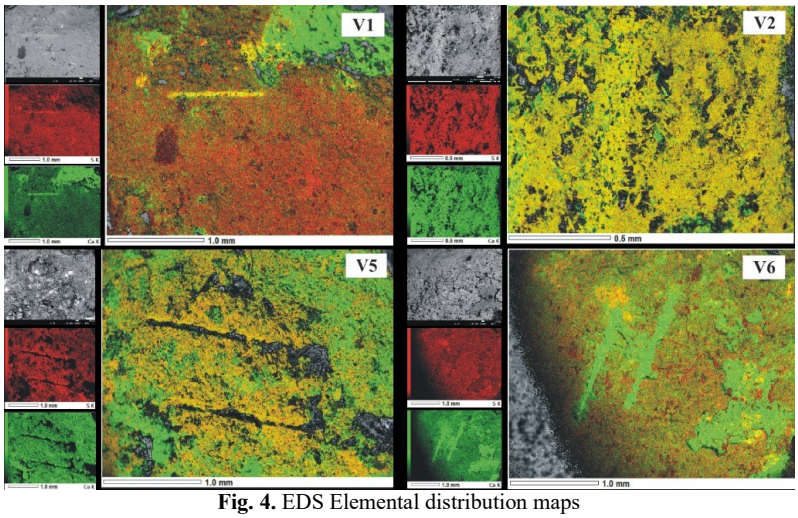


Fig. 4. EDS Elemental distribution maps

The analyses were performed on all samples, some of them are reported in Fig. 4 (V1, V2, V5 and V6). It is observed that the surface analyzed is mainly composed of gypsum, given by sulfur and calcium whose content varies from orange to yellow (overlapping of red colors indicating 100% of S and green indicating 100% of Ca) according to the greater or lesser quantity of them.
The samples showing a linear and compact surface (V1 and V6) have a higher sulfur content with a more homogeneous composition compared to those samples having dendritic irregular morphology (V2 and V5) which exhibits a heterogeneous gypsum distribution.
Results regarding the determination of ionic species measured by IC are reported in Fig. 5. As expected, the examined crusts contain large quantities of sulphate, coming from calcium sulphate [33-35]. It is worth noting that calcium and sulphate show exactly the same trend confirming the presence of gypsum. Among anions it is quite interesting the presence of high concentrations of nitrites (higher than nitrates for samples V7, V8 and V9). In the aerosol, particulate matter nitrites are not generally present in concentrations comparable to nitrates because of the oxidizing conditions so we can hypothesize that they form on the surface and perhaps can acts as oxidizing agents. Among cations the presence of ammonium is highlighted only in one case (sample V5), probably due to ammonium salts present in the aerosol PM reacted with the surfaces transforming into other species.

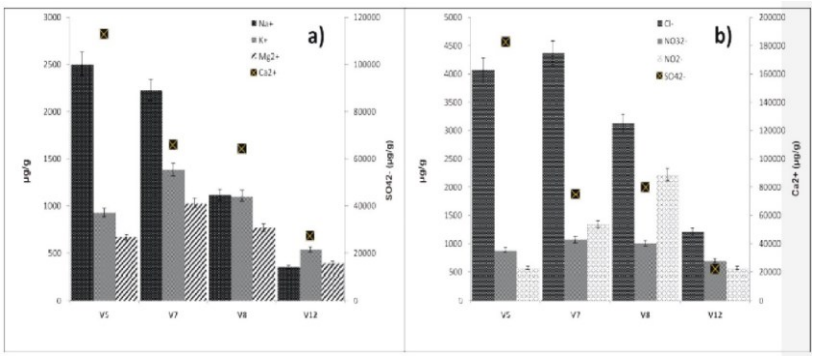
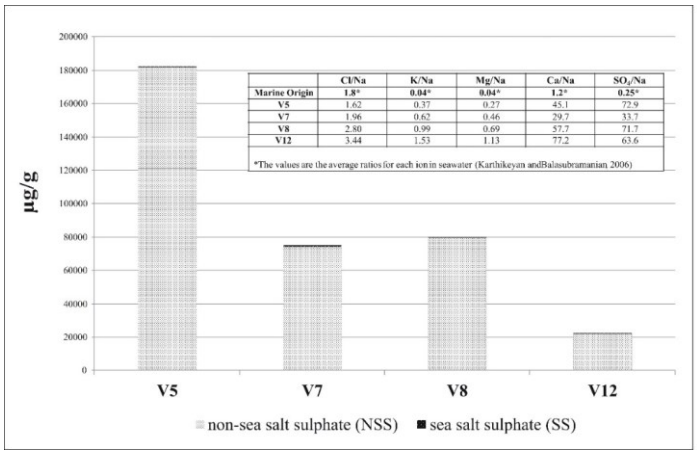


Fig. 5. Anions and Cations concentrations (µg/g) of the rapresentative black crusts samples V4, V5, V7, V8 and V12

In Fig. 6 it is shown the apportionment between sea salt sulphate (SS_SO4) and the non-sea salt sulphate (NSS_SO4) in accordance with what proposed by Keene et al. [36] and Hawley et al. [37], and based on the mass concentrations of the reference ionic species using the following algorithm: [NSS_SO4] = [SO4] - (0.25 * [Na]). As expected sulphate is mainly due to other sources different from see salt whose contribution is negligible. Nevertheless, it is worth noting that in a recent study carried out on particulate matter (PM10) sources due to ship contribution [38] approximately 60% of the total sulphate was attributed to secondary sources and around 20% was attributed to heavy oil combustion. As a consequence ships combustion emissions are an important sulphate source contributing to crusts formation.



Marine Origin	Cl/Na 1.8*	K/Na 0.04*	Mg/Na 0.04*	Ca/Na 1.2*	SO_4/Na 0.25*
V5	1.62	0.37	0.27	45.1	72.9
V7	1.96	0.62	0.46	29.7	33.7
V8	2.80	0.99	0.69	57.7	71.7
V12	3.44	1.53	1.13	77.2	63.6

Fig. 6. Histograms showing the sulfate concentrations subdivided in sea salt sulfate (SS_SO4) and the non-sea salt sulfate (NSS_SO4), the representative black crusts samples V5, V7, V8 and V12.

In order to determine the contribution of marine source to crusts composition, in accordance with what proposed by Karthikeyan and Balasubramanian [39], some ratios were calculated taking Na as reference element. In the inset of Fig. 6, the ratios (i.e. Cl/Na, K/Na, Mg/Na, Ca/Na and SO_4^{2-}/Na) typical for seawater are reported as a comparison together with the same ratios calculated for the four examined samples. Only Cl/Na ratios are in accordance with what observed in seawater confirming the presence of sodium chloride. Obviously, for Ca^{2+} and sulphate the ratios are significantly different, since Ca is among the main constituents of the crust and sulphate, as mentioned before, has secondary origin. In addition, potassium is linked to other sources such as biomass burning [40-42].

Sample	OC_{TGA}%	CC_{TGA}%	EC_{TGA}%	OC/EC	EC/TC
V4	0.32	7.80	0.47	0.68	0.59
V5	0.41	5.11	0.32	1.28	0.44
V7	0.63	8.33	0.16	3.94	0.20
V8	0.99	7.60	0.82	1.21	0.45
V12	0.26	10.3	0.59	0.44	0.70

Table 3. TC (Total Carbon), OC (Organic Carbon), EC (Elemental Carbon) and CC (Carbonate Carbon) concentrations (wt%) determined for the five black crusts (V4, V5, V7, V8 AND V12) using the TGA methodology.

The quantification of TC (Total carbon), OC (Organic Carbon), EC (Elemental Carbon) and CC (Carbonatic Carbon) in the black crusts (Table 3) has been carried out using a new methodology based on TGA analysis and described in details in another paper in preparation. In particular, OC, EC and CC concentration have been determined taking into account the characteristic weight loss ranges typical of these species (range from 0.26 to 0.99 for OC; from 0.16 to 0.82 for EC and from 5.11 to 10.3 for CC). This methodology has been applied because it is not possible to quantify these species with this analytical method, Thermal Optical Transmittance normally used for this purpose [35]. Thermal Optical Transmittance cannot be applied to the analysis of powder samples since this method requires that the

powder is homogenously dispersed on a quartz fiber filter. In fact, this technique has been developed for the analysis of organic and elemental carbon in the aerosol particulate matter that is directly sampled on this kind of filters.

EC/TC ratios range from 0.2 to 0.70 and indicate an important contribution of fossil fuel combustion processes, likely due to primary emissions of the intense maritime traffic in the Venice lagoon [43].

Chemical characterization of samples in terms of trace elements was performed using LA-ICP-MS methodology. Three measurements were performed on the crust and on the substrate The average concentrations (in ppm) of the most representative chemical elements reported in Table 4.

Black Crust	Concentration (ppm)											
	As	Ba	Cd	Cr	Cu	Ni	Pb	Sb	Sn	Ti	V	Zn
V1	191.9	543.0	5.5	64.6	54.5	25.9	4105.6	15.4	71.0	1231.1	126.4	372.2
V2	93.1	1523.9	33.2	95.7	150.1	57.9	2468.6	28.6	30.2	2209.7	327.8	16996.8
V4	54.2	166.4	2.0	29.1	28.6	13.4	105.0	4.3	15.8	752.8	26.3	370.7
V5	56.2	568.7	3.3	59.5	62.7	22.9	658.5	7.5	29.6	730.0	64.0	626.1
V6	141.1	526.6	11.6	87.7	93.7	24.2	256.9	15.7	12.4	733.3	77.9	350.1
V7	431.9	564.7	5.0	66.9	145.1	355.4	18.3	64.5	943.9	4.5	137.7	169.2
V8	155.8	537.7	3.1	75.9	954.4	211.5	8.5	35.1	966.1	3.8	50.2	325.3
V9	286.5	1240.4	5.7	33.7	66.4	514.5	10.0	70.6	509.6	3.2	41.9	150.2
V10	75.1	2505.1	11.1	79.8	80.7	177.4	7.5	127.7	3082.6	3.0	58.7	716.2
V11	263.1	690.6	4.1	68.9	56.9	71.7	9.9	36.9	645.4	2.4	140.2	126.2
V12	123.3	331.2	4.0	55.4	76.2	504.6	12.6	41.4	336.9	11.4	33.1	126.9
Substrate	Concentration (ppm)											
	As	Ba	Cd	Cr	Cu	Ni	Pb	Sb	Sn	Ti	V	Zn
V1	215.4	75.0	46.9	41.0	344.3	83.2	11291.2	20.1	591.4	2778.7	70.1	2190.0
V2	10.4	105.9	25.1	13.4	65.8	12.1	76.8	6.0	4.7	1735.0	53.5	3546.3
V4	5.7	78.2	0.6	5.0	12.3	4.9	44.6	0.5	20.6	88.1	11.1	162.6
V5	38.5	50.7	0.6	13.8	11.5	4.5	40.6	0.4	11.9	149.9	7.1	99.0
V6	8.6	82.6	1.8	14.0	20.2	12.8	50.6	10.5	3.2	507.6	19.3	56.1
V7	53.7	159.8	1.3	13.7	38.8	45.0	1.0	7.4	127.9	1.2	14.0	43.8
V8	58.8	453.9	1.3	30.1	271.6	311.5	3.9	17.1	570.1	3.8	72.7	260.6
V9	35.7	177.7	0.7	10.0	83.2	66.8	1.7	6.1	815.5	3.4	19.0	104.5
V10	74.6	1471.2	6.2	111.0	279.0	935.2	9.6	31.9	1805.0	7.1	111.5	10915.7
V11	13.7	317.4	1.5	10.0	39.0	25.9	1.2	7.8	411.0	0.4	11.8	63.5
V12	31.8	69.6	2.6	37.6	92.4	493.2	2.8	13.4	364.4	6.4	44.6	475.0

Table 4. Average concentration (ppm) of metals in black crusts and unaltered substrates of samples measured by LA-ICP/MS.

In general, the crusts show higher concentrations of trace metals in comparison with unaltered substrate for almost all metals, such as As, Ba, Cd, Cu, Ni, Pb, Sb, Sn, V and Zn. Some relevant ranges of concentrations are: As (max: 263 in V11 and min: 41.1 in V6), Ba (max: 1523 in V2 min: 116 in V4), Cd (max: 11.6 in V6 and min: 1.97 in V4), Cr (max: 95.7 in V2 and min: 29.1 in V4), Cu (max: 150 in V2 and min: 28.6 in V4), Ni (max: 355 in V7 and min: 13.4 in V4), Pb (max: 2469 in V2 and min: 7.50 in V10), Sb (max: 128 in V10 and min: 4.30 in V4), V (max: 328 in V2 and min: 26.3 in V4) Zn (max: 16997 in V2 and min: 126 in V11). In substrates: As (max: 215 in V1 and min: 5.17 in V4), Ba (max: 1471 in V10 min: 50.7 in V5),

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Cd (max: 46.9 in V1 and min: 0.55 in V5), Cr (max: 41.0 in V1 and min: 5.04 in V4), Cu (max: 344 in V1 and min: 12.3 in V4), Ni (max: 935 in (Max: 31.9 in V11 and min: 0.54 in V4), V (max: 70.1 in V1 and min: 11.1 and min: 5.54 in V5), Pb (max: 11291in V1 and min: 1.16 in V11), Sb in V4), Zn (max: 10916 in V10 and min: 43.8 in V7). In order to better understanding the enrichments of the analyzed metals in black crust compared with the stony substrate, it has been calculated the enrichment factors as the ratios of crust/substrate metals' concentration. Results are reported in Table 6.

	Enrichment factor EF											
Element	**As**	**Ba**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Sb**	**Sn**	**Ti**	**V**	**Zn**
V1	0.9	7.2	0.1	1.6	0.2	0.3	0.4	0.8	0.1	0.4	1.8	0.2
V2	9.0	14.4	1.3	7.1	2.3	4.8	32.2	4.7	6.4	1.3	6.1	4.8
V4	9.5	2.1	3.1	5.8	2.3	2.7	2.4	8.4	0.8	8.5	2.4	2.3
V5	1.5	11.2	5.9	4.3	5.5	5.0	16.2	21.1	2.5	4.9	9.0	6.3
V6	16.3	6.4	6.5	6.3	4.6	1.9	5.1	1.5	3.9	1.4	4.0	6.2
V7	8.0	3.5	3.8	4.9	3.7	7.9	19.2	8.8	7.4	3.7	9.8	3.9
V8	2.6	1.2	2.3	2.5	3.5	0.7	2.2	2.0	1.7	1.0	0.7	1.2
V9	8.0	7.0	8.3	3.4	0.8	7.7	5.8	11.7	0.6	1.0	2.2	1.4
V10	1.0	1.7	1.8	0.7	0.3	0.2	0.8	4.0	1.7	0.4	0.5	0.1
V11	19.2	2.2	2.7	6.9	1.5	2.8	8.5	4.7	1.6	6.4	11.9	2.0
V12	3.9	4.8	1.6	1.5	0.8	1.0	4.4	3.1	0.9	1.8	0.7	0.3

Table 6. Enrichment factors (EF) of trace metals in black crusts with respect to the substrates

Samples show an enrichment ranging from moderate (EF from 3 to 8 in most samples) to high (EF up to 32 for Pb and 14 for Ba in sample V2).

The different EF values in the 11 samples can be due to several factors, such as: sampling height, different morphology of sampled surfaces (vertical or horizontal), different exposure to agents pollutants, atmospheres, wash out and marine aerosols.

In general, the enrichment observed is mainly due to mobile emission sources, since the samples have been collected at a height of about 1.50 m. The stone substrate at this height is significantly influenced by the exhaust emitted by the maritime transport vessels (motorboats and boats) that cross the Grand Canal and the roads, which by spraying and deposition of marine aerosols. In fact, the marine water in Venice is enriched in metals, mainly Zn, Pb and Cu.

Specifically, the highest values were achieved for the V2 sample taken on the Grand Canal in a heavy traffic area. V5 sample shows high enrichment both for its position near to the Grand Canal, and because it was sampled from a horizontal decorative surface, where the deposition of the pollutants is higher. V1 and V10 samples show the lowest concentrations (with EF values even below 1), because they come faraway from direct emission sources.

Specifically, the high concentrations of Pb, and Zn, observed, are in agreement with the use of leaded gas [44], used up to a few decades ago. In addition, heavy metals such as Ba, Cu, Ni, Cr and V can be attributed to the use of other fuels such as fuel oil, diesel and gasoline [44-46], widespread after the abolition of leaded gasoline.

Moreover, it has to be taken into account the contribution of the various industries (such as glassworks, oil refineries and metallurgy production) located between Porto Marghera and Mestre [47-49], which emit large amounts quantities of: As, Cd, Sb, Pb, Zn, Cu, Sn, Ni, Cr and V [50-52].

In Fig. 7, it has been shown the good correlation between enrichment factors for V and Ni respectively. These two elements are the typical markers for fossil fuel combustion [38, 43]. In particular, V and Ni can

be used as valid tracers of shipping emissions confirming again the role of maritime traffic in the lagoon in the black crusts formation.

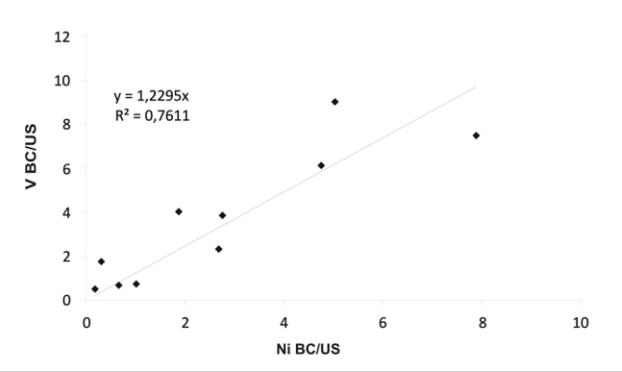

Fig 7. Correlation between the enrichment factors for V and Ni in the examined samples.

Conclusions

Black crusts, which are formed on stone materials, have been collected from several historical buildings in the city of Venice and analysed by several analytical techniques. This city suffers pollution from the industrial area of Marghera, as well as from the maritime traffic. Results indicated that the crusts are mainly composed by gypsum with lower content of calcite and oxalates. In terms of major elements, beside calcium and sulphur, Si, Al, Fe, Na, and smaller amounts of K and Mg were identified. Sulphates are mostly ascribable to fuel and biomass combustion, rather than to sea spray, while carbon into the crusts coming from fossil fuel combustion. Regarding trace metals in all samples, As, Ba, Pb and Zn are the most abundant, moreover, the correlation between Ni and V content measured in black crusts, suggests that heavy oil combustion from ship traffic, represent a significant pollution source. It has been observed different pattern of metal concentrations within the crusts in function of the exposure of the sampled surfaces. In particular, those surfaces next to the canals are more enriched in heavy metals, especially Pb, As and Sb, this suggest that also the sea spray can play also a significant role in the deposition of such metals on the stone surface.

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