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Black crusts grown on varied stone substrata from historical buildings under different air quality scenarios (SE and NW Spain)

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***Abstract* – This work addresses the characterization of black crusts (BCs) collected from stones of different nature, i.e. granite and carbonate stones (limestone, marble and travertine) taken from diverse historical buildings located in NW (Vigo) and SE (Granada) Spain subjected to dissimilar environmental and air quality scenarios. Likewise, filters located adjacent to the sampling areas were analyzed to evaluate particle dry deposition components in order to assess the ambient air quality of the selected buildings and its impact on the growth of BCs (natural passive pollutants markers). To this end an array of complementary analytical techniques was used, i.e.: Stereomicroscopy (SM), Polarized Light Microscopy (PLM), High Resolution Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (HRSEM-EDX), X-ray Diffraction (XRD) and Fourier Transform-Infrared spectroscopy (FT-IR).**

I. INTRODUCTION

Deposition of carbonaceous particles and metals on surfaces of the urban edifications contributes to the formation of black crusts (BCs) which compromise their durability and aesthetic appearance [1, 2]. BCs are present on building materials typically found in industrial environments in areas protected from washout [3]. In addition to solid pollutants, mostly heavy metals, BCs are mainly composed of gypsum ($CaSO_4.2H_2O$) and/or other calcium sulfates [4]. BCs occurs principally in carbonate stones (marble, limestone, travertine, etc.) due to interaction of SO_2 gaseous pollutant with calcium from the calcite, which is the major forming mineral of these stones [2, 5, 6]. However, thick and compact BCs are also found in silicate stones, such as granite, despite the low calcium content of this stone [1]. These authors reported that the available calcium sources to form these BCs crusts are cement and mortar dissolution or old lime remains. Usually sulfur in the BCs comes from anthropogenic activities through the oxidation of sulfur from industry and traffic, but also from deposition of sea spray in cities with strong maritime influence [1].

Since BCs could be considered as a passive sampler of atmospheric pollution, compounds found in BCs can be used as an indicator of environment pollution [7]. Therefore, the correlation between air pollutants and the chemical composition of BCs seems plausible. In this work we discuss and correlate the analytical results of BCs from historical buildings made with either silicate- or carbonate-based stones located in contaminated and/or marine air masses in Spain (NE and SW), with atmospheric pollution components collected on filters placed nearby.

II. MATERIALS AND METHODS

A. Sampling locations: BCs and filters

The city of Granada (SE Spain) has a Mediterranean climate with continental influence and is located in a geological depression at the foot of the Sierra Nevada mountains that reach 3500m elevation. In spite of being a non-industrialized city, accumulation of fine natural and anthropogenic particulate matter (PM) is important due to heavy traffic, intensive construction works, its topography and low wind speeds [8, 9]. Likewise, as stated by the European Environment Agency, Granada is one of the cities with the highest SO_2 contamination in Western Europe, occasionally reaching 20μg/m^3 [10]. This pollution scenario is enhanced by the recurrent surface thermal inversions associated with stagnant wintertime weather conditions [11]. Carbonate stones (marble, limestone, travertine, etc.) are commonly found in the built Cultural Heritage.

The city of Vigo (NW Spain) which is one of the most important Atlantic port city in terms of industrial and shipbuilding activities, has a humid sub-tropical climate, with rainy winters (1200 mm rainfall) [12, 13] marked by low-pressure S-SW fronts from the Atlantic. Air quality data [14] indicate that Vigo has c.a. SO_2 average: 3μg/m^3.

PM is frequently lower than 20 μg/m^3. The ancient buildings in Vigo are constructed with granite.

BCs (Table 1) were collected in different buildings of the two cities.

Table 1: BCs sampled in Vigo and Granada cities. Samples were taken up to 2 m height. O: orientation. For Granada samples, after dash, C for calcarenite (type of limestone), T for travertine and MA for marble.

BC samples	O	ID
Granada- Cathedral	NW	CAT-C
Granada- *Corral del Carbón*	E	CC-T
Granada- Monastery of *San Jerónimo*	S	SJ-C
Granada- Hospital of *San Juan de Dios*	S	SJD-MA
Granada- Church of *San Justo y Pastor*	NW	SJP-T
Vigo- old home for elderly *Ancianos Desamparados*	SE	AS
Vigo- building in a street close to the sea	N	A
Vigo- building in the heavily trafficked *Elduayen* street	NE	E
Vigo- building in the heavily trafficked *Tomás Alonso* street	NW	TA
Vigo- building in the heavily trafficked *Tomás Alonso* street	SW	TA2
Vigo- building in the heavily trafficked *Paseo de Alfonso* street	NW	PA

Moreover, quartz fiber filters were exposed vertically during 10 months in specific places at different height and orientations near the sampled buildings in order to collect aerosol particulate matter (PM) in a passive way to simulate what happens on the stone surfaces. Filters were kept inside an open box to protect them from direct rain impact; they were weighed before and after environmental exposure. Table 2 shows the filters placed in both cities.

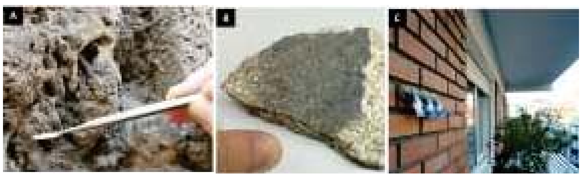

Fig. 1. A: BC from Granada (CAT-C sample). B: BC on granite collected in Vigo (As sample). C: Filters positioned in one balcony in Vigo.

A. Analytical techniques

The color and textural features of BCs were studied using a stereomicroscope (SM) model SMZ 1000 (Nikon, Japan) which incorporates a photomicrography system. A Polarized Light Microscope (PLM) in transmitted and reflected light (Carl Zeiss Jenapol U instrument, Germany) equipped with a digital camera (Nikon D-7000) was used to recognized the mineralogy, texture, structure and conservation state of the BCs. PLM was conducted on BCs bulk samples and cross sections prepared as polished thin sections.

Table 2: Filter placed in Vigo and Granada cities. O: orientation

Filters	Location	O
Granada- Filters 3 and 4	*Albaizín* quarter [15] set on a hill in front of the *Alhambra* monument in a first floor balcony facing a pedestrian street.	S
Granada- Filter 7	Second-floor balcony in the city center (Faculty of Science) facing a heavy traffic avenue and exposed to rain events.	E
Granada- Filter 8	First-floor balcony of a private house near the Monastery of San Jerónimo, in a pedestrian street. It was well protected from rain and direct impact of traffic pollution	NW
Granada- Filters 11 and 12	First-floor balcony of a private house located in the city center at the confluence of 4 heavy traffic streets. They were highly exposed to air pollution and rain impact	NE
Vigo- Filters 1, 2 and 3	Second-floor balcony of a private house located in the city center at the confluence of 2 heavy traffic streets. It was well protected from rain	SE
Vigo- Filters 4, 5 and 6	First-floor balcony of a private house facing a heavy traffic avenue. It was well protected from rain	NW
Vigo- Filters 7, 8 and 9	Fourth-floor balcony of a private house facing a heavy traffic avenue. It was well protected from rain	SE

The chemical composition and texture of the BCs were analyzed via a High Resolution Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (HRSEM-EDX) using a Supra 40Vp Carl Zeiss (Germany). The SEM was equipped with secondary electrons (SE) and backscattered electron detectors (BSE) that provide morphological and chemical images respectively, as well as a microanalysis system (Aztec 3) to deliver elemental information by EDX. BCs bulk samples and polished thin sections were carbon coated to be analyzed under high vacuum level. EDX single point analyses and X-ray maps were acquired from specific areas (thin sections) to better recognize the position, quantity and morphology of crystalline/amorphous phases present in the BCs.

X-Ray Diffraction (XRD) was applied to identify the mineralogy of the BCs using a Siemens D5000. To this end fine powdered BCs were analyzed and the semi-quantitative estimation of minerals present in the samples evaluated. Analytical set up conditions were: Cu-Kα radiation, Ni filter, 45 kV voltage and 40 mA intensity. Samples were explored in the range between 3° and 60° 2θ with 0.05° 2θ s^{-1} goniometer speed. The X'Pert HighScore software (Malvern Panalytical B.V., The Netherlands) was used to identify mineral phases.

Fourier Transform Infrared Spectroscopy (FT-IR) in Attenuated Total Reflectance (ATR) mode was used to ascertain the molecular composition of the BCs using a Thermo Nicolet 6700. The infrared spectra were recorded from 400 to 4000 cm^{-1} at 2 cm^{-1} resolution over 100 scans.

Quartz fiber filters and BCs samples were analyzed in order to assess their chemical composition as regards the main constituents, i.e. ions and carbonaceous fraction. Main ions analysis was performed by IC analysis using a ICS-1000 HPLC system equipped with a conductivity detector [2,16]. The determination of OC (organic carbon) and EC (elemental carbon) has been carried out on quartz fiber filters using a TOT (Thermal-Optical Transmittance) Sunset instrument following the methodology conventionally used for their determination in the aerosol particulate matter [16, 17]. The quantification of OC and EC in the BCs samples was performed in accordance with a procedure already set-up [2,18].

III. RESULTS AND DISCUSSION

Visual and PLM study of BCs from Granada reveal that they ranged in color from black to dark grey according to the pollution exposure position, and also in thickness, hardness and morphology features. The thicker and darker BCs grew on rough surfaces of travertine and calcarenite stones closely exposed to traffic, often showing cauliflower-like morphologies differently to the black laminated crust that developed on polished marble. As shown by PLM, BCs are primarily made by acicular gypsum crystals closely mixed typically with clay minerals and black soot particles (Fig. 2A). Also, all substrates display damage in different degrees (Fig. 2A).

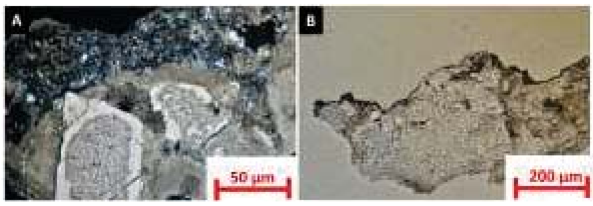

Fig 2. PLM photograph (parallel polars) of BCs (thin section) from A. Granada (CAT-C) showing the thick crust made of copious arrowhead-like gypsum crystals -embedding soot particles- growing on travertine. Note the calcite crystals surface (from the calcarenite) displaying dog´s tooth (secondary) calcite. B. Vigo (TA) where the thin and brownish BC is seen on top of the severely fractured granite.

HRSEM-EDX study reveals that, irrespective of the carbonate substrate, BCs from Granada consist of a dense structure of needle-like crystals made of Ca and S ascribed to gypsum, mixed with aluminosilicate minerals, dolomite and quartz (Fig. 3). This matrix embedded tiny particles of different chemical composition, most ubiquitously: NaCl and $NaNO_3$ salts, Pb-Cl and Ca-Cl-rich particles, Ca-phosphate particles, clusters of particles made either of Ba-sulfate with Co, Sr and P, or composed of K-sulfate and Fe, Cr, and Cl. Also C-rich, Si-rich, Fe-rich and Al-rich spherical particles are abundant, the latter two particularly in BCs taken from buildings very near to the impact of traffic (Fig. 3).

Visual and PLM examination of BCs from Vigo show that they varied in color from brownish to black and are thinner that those found in Granada (Fig. 2B). The As sample is an exception showing a well-developed BC made of acicular gypsum crystals trapping particles of different nature. All granite substrates are deeply deteriorated with gypsum precipitation driving feldspars delamination (Fig. 4A). HRSEM-EDX study discloses that the composition of the trapped particles is similar to those analyzed in Granada, though nitrate salts were not found and spherical particles are scarce. The following particles were identified: aggregates of Pb-Cl, Ca or K-phosphate particles, Ba-sulfate and NaCl (Fig. 4B-D). Other elements detected with EDX were Fe, Cu, Zn, Co, P and Ca which can proceed from the granite alteration.

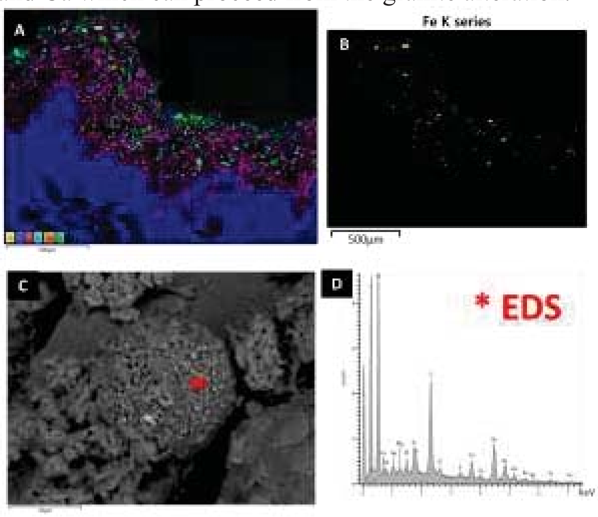

Fig 3. SJP-T black crust from Granada. A. SEM-EDX false color element map (X-ray map from thin section); note the copious gypsum crystals enclosing numerous Fe-rich particles (B), C. SEM micrograph and D. EDX spectrum of a rounded carbonaceous particle covered with tiny particles made of Ba-sulfate, K-sulfate, Sr, Al, Fe and Cl.

XRD and FTIR allowed the identification of gypsum in all the BCs regardless of the substrate (carbonate- and silicate-stones) with exception of the samples from Vigo, A and TA2 and from Granada, CC-T. Moreover, the amount of gypsum detected by XRD was notably higher in the BCs from Granada. In the BCs from Vigo, granite forming minerals were found (quartz, albite, microcline, and muscovite). Likewise, traces of calcite were identified in E crust, halite in A crust and hydroxide lead phosphate in TA2. The composition of BCs from Granada was much simpler: in addition to gypsum (SJD-MA), quartz was also detected in CAT-C and CC-T, as well as high amounts of calcite and some dolomite in the latter.

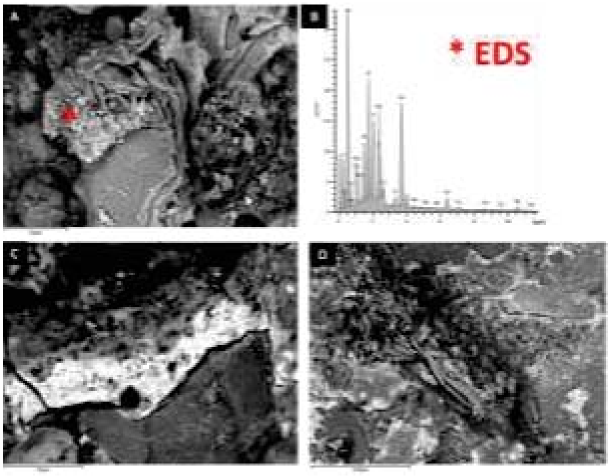

Fig 4. SEM micrographs of TA crust from Vigo (bulk sample). A. Detail of feldspars delamination due to growth of minute gypsum crystals. Note the copious metal (white) particles. B. EDX sprectrum of the above metal particles mostly made of Pb-Cl associated to Ca-phosphate and Ba-sulfate. C. Detail of a Pb-Cl/Ca-phosphate rich layer (white layer) covering the granite and D. the mentioned particles in relation to plate-like gypsum crystals.

As regards the carbonaceous components, i.e. organic carbon and elemental carbon, BCs from Granada turned out to be richer. In fact, OC represents 1.4wt% and 0.5wt% in Granada and Vigo sample respectively while EC represents in the two sites 1.12wt% and 0,18wt% (confirming what observed on Granada BCs, i.e. more abundant soot particles, i.e. elemental carbon).

This difference between the two cities could be due to both the chemical composition of the construction material, that in case of Granada are carbonatic stones, and the environmental conditions/atmospheric pollution (in Vigo for example SO_2 concentration is about an order of magnitude lower than in Granada). The confirmation that there is a significant contribution to BCs composition linked to the different environmental conditions in the two cities, is given by OC/EC ratio that is in the range 0.6-2 in Vigo while varies between 1.25 and 3.7 in Granada [19—21]

Furthermore, a certain variability is present within the same city among the BCs, mostly related to the particular exposure conditions of the monuments.

Comparing the chemical composition of the aerosol particulate matter collected on the filters with that one determined for BCs, has allowed to acquire information on PM sources. For example, as for the filters from Vigo, OC is much higher than EC with respect to what happens for the corresponding BCs samples, indicating how EC preferentially accumulates within the crusts.

Furthermore, in the PM samples collected in Vigo, chloride is the ion present in higher concentration (followed by sulphate and nitrate), even if remarkable differences among samples are evident. Vigo receives the direct influence of marine aerosol. Despite Granada is located ca. 50km from the coast, a marine influence has been proved in the city due to prevailing southwest winds; sulfate-rich PM are more abundant than chloride-rich PM [9].

On the contrary in BCs samples, sulphate is the main ion with notably lower concentrations of nitrate and chloride. In Granada, the high amounts of sulfate-rich PM is due to the fact that the city is characterized by high SO_2 levels. In Vigo, the industrial activity also produces SO_2 [1]. Consequently, as it is well-known, SO_2 can transform into sulfate in the atmosphere via the oxidation of SO_2 by the hydroxyl radical.

A deeper study of the results obtained, focusing the attention on the different monuments and the corresponding passive filters in the two investigated cities, will allow to better understand the relation existing between atmospheric pollution sources and black crusts formation process.

IV. CONCLUSIONS

Analytical results reveal that the composition and microstructure of BCs developed on substrates of different natures, i.e. granite, limestone, travertine and limestone, in NW and SE Spain, depend mainly on the accumulation time of pollutants on their surfaces and the air quality, rather than on substrate composition (carbonate or silicate composition). Thus, under the predominant dry environment of Granada, BCs on carbonate substrates have accumulated over greater time spans than in Vigo, were they are thinner because of frequent rain episodes. Consequently, BCs from Granada show more complex structure, particularly those sampled from substrates where vehicle pollution has been more intense. Moreover, though the city of Granada is ca. 50 km from the Mediterranean coast, sea-salt aerosols have been widely found embedded in the BCs, such as NaCl and secondary $NaNO_3$ salts (from NaCl-HNO_3 reactions), these last not found in BCs from Vigo. Additionally, though in all studied BCs from Vigo and Granada Pb-Cl and Ca-Cl-rich particles, Ca-phosphate particles, and clusters of particles made mostly of Ba-sulfate have been identified, metal-rich rounded particles are more abundant in Granada, including soot particles. This should be related to the pollution levels (mostly SO_2) of this non-industrialized city favored by its topography and semi-continental climate in contrast to the industrial but sea-exposed city of Vigo.

REFERENCES

[1] T. Rivas, S. Pozo, M. Paz, 2014. "Sulphur and oxygen isotope analysis to identify sources of sulphur in gypsum-rich black crusts developed on granites", Sci. Total Environ., vol. 482-483, pp. 137-147.

[2] V. Comite, J.S. Pozo-Antonio, C. Cardell, C. Randazzo,

M.F. La Russa, P. Fermo, “A multi-analytical approach for the characterization of black crusts on the facade of an historical cathedral”. Microchemical Journal vol. 158, nº105121, 2020.

[3] ICOMOS, Illustrated Glossary on Stone Deterioration Patterns, 2008, 78p.

[4] J.S. Pozo-Antonio, M.F.C. Pereira, C.S.A. Rocha. “Microscopic characterisation of black crusts on different substrates”, Science of the Total Environment vol. 584–585, 2017, pp. 291–306

[5] El-Gohary, M.A., “Investigations on limestone weathering of el-tuba minaret el mehalla, Egypt: a case study”, Mediterr. Archaeol. Archaeometry vol.10, 2010, pp. 61–79.

[6] S.A. Ruffolo, V. Comite, M.F. La Russa, C.M. Belfiore, D. Barca, A. Bonazza, G.M. Crisci, A. Pezzino, C. Sabbioni, “An analysis of the black crusts from the Seville cathedral: a challenge to deepen the understanding of the relationships among microstructure, microchemical features and pollution sources”, Sci. Total Environ. vol 502, 2015, pp.157–166.

[7] T. De Kock, J. Van Stappen, G. Fronteau, M. Boone, W. De Boever, F. Dagrain, G. Silversmit, L. Vincze, V. Cnudde, “Laminar gypsum crust on lede stone: microspatial characterization and laboratory acid weathering”, Talanta vol. 162, 2017, pp. 193–202,

[8] C. Horemans, C. Cardell, L. Bencs, V. Kontozova-Deutsch, K. De Wael, R. Van Grieken, “Evaluation of airborne particles at the Alhambra monument in Granada, Spain”, Microchem. J. vol. 99, 2011, pp. 429–438.

[9] M. Urosevic, A. Yebra-Rodríguez, E. Sebastián-Pardo, C. Cardell, “Black soiling of an architectural limestone during two-year term exposure to urban air in the city of Granada (S Spain)”, Sci. Total Environ. vol. 414, 2012, pp. 564–575.

[10] EEA. European Environment Agency, accessed 5 July 2020, http://www.eea.europa.eu/themes/air/interactive/so2

[11] D. Patrón, H. Lyamani, G. Titos, J.A. Casquero-Vera, C. Cardell, G. Močnik, L. Alados-Arboledas, F.J. Olmo, “Monumental heritage exposure to urban black carbon Pollution”, Atmos. Environ. vol. 170, 2017, pp. 22–32.

[12] A. Martínez-Cortizas, “Zonas agroecológicas de Galicia; zona climática FAO”, An Edafol Agrobiol vol. 46, 1987, pp. 521–38.

[13] A. Martínez-Cortizas A, Pérez (editors), “Atlas climático de Galicia”, Consellería de Medioambiente, Xunta de Galicia, 1999. p. 210.

[14] Xunta de Galicia, Accesed in August 2020. Conselleria de Medioambiente e Ordenación do Territorio. Website: <http://www.meteogalicia.gal>.

[15] UNESCO World Heritage site, 1984

[16] Piazzalunga, A.; Bernardoni, V.; Fermo, P.; Vecchi, R. “Optimisation of analytical procedures for the quantification of ionic and carbonaceous fractions in the atmospheric aerosol and applications to ambient samples”. Anal. Bioanal. Chem., vol. 405, 2013. 1123–1132. DOI: 10.1007/s00216-012-6433-5.

[17] Fermo, P., Piazzalunga, A., Vecchi, R., Valli, G., Ceriani, M. “A TGA/FT-IR study for measuring OC and EC in aerosol samples”. Atmos. Chem. Phys. vol. 6, 2008, pp 255–266.

[18] Fermo, P., Turrion, R.G., Rosa, M., Omegna, A. “A new approach to assess the chemical composition of powder deposits damaging the stone surfaces of historical monuments”. Environ. Sci. Pollut. Res. vol 22, num. 8, 2015. pp 6262-6270.

[19] Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Jarvi, L., Keronen, P., Kerminen, V.M., Hillamo, R., “Sources of organic carbon in fine particulate matter in northern European urban air”, Atmos. Chem. Phys. vol 8, 2008, pp 6281–6295.

[20] Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermitzaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A.F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C., Burrows, J.P., Ladstaetter-Weissenmayer, A., Moubasher. H., “Review Megacities as hot spots of air pollution in the East Mediterranean”. Atmos. Environ. vol. 45, num. 6, 2010, pp.1223-1235.

[21] Cheng, Z., Luo, L., Wang, S., Wang, Y., Sharma, S., Shimadera, H., Wang, X., Bressi, M., De Miranda, R.M., Jiang, J., Zhou, W., Fajardo, O., Yan, N., Hao, J. “Status and characteristics of ambient PM2.5 pollution in global megacities”. Environ. Int. vol. 89–90, 2016, pp. 212–221.