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The cauliflower-like black crusts on sandstones: A natural passive sampler to evaluate the surrounding environmental pollution

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ABSTRACT

Black crust in buildings can be formed as a result of different kind of chemical and physical reactions between the stone surface and environmental factors (e.g. acid aerosols emitted to the atmosphere, airborne particulate matter, etc.). Moreover, biological colonizations can also be present on them. This kind of pathology is widely present in limestones, but fewer are the case study dealing with the characterization of black crusts on sandstones. In this work we present an innovative methodology based on the use of cauliflower-like black crusts formed on sandstone material as natural passive sampler to evaluate the environmental pollution related with the emission of natural (crustal particles and marine aerosol particles) and metallic elements in the airborne particulate matter from the surrounding atmosphere. To illustrate its usefulness, different cauliflower-like black crusts growing in areas protected from the rain growing in an historical construction, La Galea Fortress, made up of sandstone and placed in the Abra Bay (Getxo, Basque Country, Spain) were characterized. This area suffers the anthropogenic emissions coming from the surrounding industry, traffic, sea port, and the natural ones coming from the surrounding marine atmosphere. The applied analytical methodology began with a previous elemental in situ screening in order to evaluate and compare the presence of the metals trapped in black crusts from different orientations using a hand-held energy dispersive X-Ray Fluorescence spectrometer. After this preliminary study, samples of black crusts were taken in order to characterize them in the laboratory using molecular techniques (Raman spectroscopy and XRD) and elemental techniques (ICP-MS, SEM-EDS and micro energy dispersive X-Ray Fluorescence). With the last two elemental techniques, imaging analyses were performed at different lateral resolutions in order to observe the distribution of the metals and other kind of particles trapped in the black crust samples. Additionally, a biological colonization found beneath the black crusts was also characterized using Phase Contrast microscopy.

1. Introduction

On the surface of building materials included in constructions, different kind of crusts can be found. Among them, grayish or black crusts can be mentioned. Usually these kinds of crusts appear in the areas less exposed to the rainfalls. The chemical composition of them can vary greatly depending on the building material where they grow up (e.g. marble, limestone, sandstone, etc.), the geographical location of the building and the environment where the building is located. In this sense, the chemical composition of the black crusts on a building located in an urban (Matovic et al., 2012) or industrial environment (Graue et al., 2013), against those located in a coastal (Rivas et al., 2014), rural (Török et al., 2011) or volcanic one (Barca et al., 2011) can vary greatly. The anthropogenic emissions coming from maritime traffic (Rivas et al., 2014; Barca et al., 2011), industries (Ausset et al., 1998) or road traffic (Rodriguez-Navarro and Sebastian, 1996) can also have influence in the composition of black crust.

The matrix of black crusts is made up of gypsum ($CaSO_4 \cdot 2H_2O$). In the calcareous materials (e.g. limestone which main component is calcium carbonate), gypsum can be formed between the reaction of the calcium carbonate from the material itself and wet

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depositions of the SO_2 present in the atmosphere (Sarmiento et al., 2008). Considering that the concentration of this acid aerosol is higher in the urban-industrial environments, it is supposed that the black crust formations will be found principally in more polluted environments (Marszałek et al., 2014). The formation of gypsum crusts and by extension black crusts does not easily take place on sandstones. However, these kind of crust have been identified in limestones (Senesi et al., 2016), calcarenite sandstones (Barca et al., 2011) (calcium carbonate acting as cementing agent in the stone) or even in calcium-carbonate free sandstones (Marszałek et al., 2014). Apart from gypsum, different kind of airborne particulate matter can be trapped on its structure. Among these particles, natural particles emitted to the atmosphere and coming from the erosion of the surrounding siliceous and calcareous stones can be deposited on the gypsum crust. Apart from that, metallic particles emitted from anthropogenic sources on urban-industrial emissions (e.g. road traffic, industry, maritime traffic etc.) (Ozga et al., 2014; Barca et al., 2014; Belfiore et al., 2013) can also be trapped in its structure. Moreover, in the buildings placed in marine environments, salts transported by the marine aerosol can also be trapped in the gypsum matrix.

In the black crusts, the responsible of its grayish/black color are the carbon particles (shoot) trapped in the gypsum matrix (Bonazza et al., 2007). Additionally, organic carbon and organic pollutants such as polycyclic aromatic hydrocarbons, triterpenoid hydrocarbons, etc. can also be present in the black crusts (Prieto-Taboada et al., 2013; Saiz-Jimenez and Hermosin, 2004; Ghedini et al., 2006). Therefore, black crust located in urban-industrial environments can act as repositories of inorganic and organic pollutants acting as passive samplers useful to evaluate the pollution of the specific environment where they grow up.

Although black crust is a well-known pathology in construction, in some cases, these kinds of crusts can act as protective layer of porous building materials or as barriers against the environmental stressors, which can react with the original material, promoting its degradation (Török, 2003). However, in some cases, these crusts can also have a destructive effect on the material, promoting for example exfoliations in the original stone (Zhang et al., 2013). Apart from possible physical damages on the material, black crusts usually give rise to aesthetical problems. During a restoration process of a specific building, construction, monument, etc. in where black crusts are present, it can be decided to remove these unsightly patinas. Two possible situations could happen if these crusts are removed from its support or stone matrix. On the one hand, a quick formation of a new gypsum crust on the stone could take place, slowing down its deterioration process (Smith et al., 2003). The formation of this new crust depends on numerous factors such as possible wetting-drying or freeze-thaw cycles that can undergo the stone (Smith et al., 2002) among others. On the other hand, the removal of the black crusts acting as a protective layer of the porous stone could make this material very unstable (Török, 2002) in a short period of time, promoting its quick deterioration (e.g. material loss).

According to literature, several works can be found dealing with the chemical variations of black crusts compositions through times, depending on the changes in the pollution levels (acid gases emission and particulate matter) of the atmosphere where the black crusts are present (Barca et al., 2014; La Russa et al., 2013). Moreover, there are some studies which determine if the gypsum present in the black crust comes from a natural origin or if it is formed due to the influence of wet SO_2 depositions from the atmosphere. In those works, sulfur and oxygen isotopes analyses were conducted (Rivas et al., 2014).

In general terms, there is a trend in the use of portable instrumentation for environmental studies (Galuszka et al., 2015) and also in the use of passive samplers for pollution studies (Mariusz et al., 2015a, 2015b, 2015c). Generally, the analytical methodologies applied up to now to characterize the composition of black crusts and the inorganic and organic pollutants accumulated on them compromise a combination of different elemental and molecular techniques. Several examples of multianalytical methodologies can be found in the literature. Among others, the combined use of SEM-EDS with FTIR on the characterization of black crusts on granites (Pozo-Antonio et al., 2015); ion chromatography applied together with SEM-EDS in the analysis of black crust formed on dolomitic rocks in a building of Milan (Fermo et al., 2015); FT-IR and SEM-EDS combined with LA-ICP-MS in black crusts formed on buildings from Milan and Florence and monument from Rome (Barca et al., 2014); XRD, SEM, TG/DTA together with ICP-OES, ICP-MS and INAA analyses on black crusts formed on sandstones from buildings in Kraków (Marszałek et al., 2014); FT-IR imaging combined with SEM-EDS and LA-ICP-MS analyses on black crusts formed on building from Seville (Ruffolo et al., 2015); optical microscopy, XRF, SEM, SEM-EDX, SEM-WDS, LA-ICP-MS, ion chromatography and GC–MS techniques applied to characterize the black crusts from the Cologne, Altenberg and Xanten cathedrals (Graue et al., 2013) etc., mutianalytical methodologies can be mentioned.

In this work we present an innovative methodology based on the use of cauliflower-like black crusts formed on sandstone material as natural passive sampler to evaluate the environmental pollution related with the emission of natural (crustal particles and marine aerosol particles) and metallic elements in the airborne particulate matter from the surrounding atmosphere. To illustrate its usefulness, different cauliflower-like black crusts growing in areas protected from the rain growing in an old building used to house the lighthouse keeper from La Galea Fortress, an historical construction made up of sandstone and placed in the Abra Bay (Getxo, Basque Country, Spain) were characterized. This area suffers the anthropogenic emissions coming from the surrounding industry, traffic, sea port and the natural ones coming from the surrounding marine atmosphere. This is the first time that a hand-held energy dispersive X-Ray Fluorescence spectrometer (HH-ED-XRF) has been applied in order to assess its usefulness in order to extract reliable conclusions about the presence/absence or higher/lower distribution of metals trapped on black crusts depending on the orientations were they are formed. After the in situ screening, samples of black crust were taken in order to characterize them in the laboratory using molecular techniques (Raman spectroscopy and XRD) and elemental techniques (ICP-MS, SEM-EDS and micro energy dispersive X-Ray Fluorescence (μ-ED-XRF)). With the last two elemental techniques, imaging analyses were performed at different lateral resolutions in order to observe the distribution of the metals and other kind of particles trapped in the black crust samples. Additionally, Phase Contrast microscopy was used to determine the nature of the main colonizer from the biological colonization found underneath the black crusts.

2. Materials and methods

2.1. La Galea site description and surrounded climatology

La Galea Fortress is located in the cliff overlooking the bay of Agra, in Getxo (Biscay, Basque Country, north of Spain) and about 50 m above the sea level (see Fig. S1 from the Supplementary material). In its origins (18th century), this construction acted as a fortress. This fortress undergoes two destructions and after that, in the year 1782, the fortress was reused as a lighthouse. The first lighthouse was substituted by a second one. In the year 1880, the lighthouse keeper house, where the black crust objects of research