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A multi-analytical techinques for evaluation of black crusts formation on the façade of Al-Rifa'i Mosque, Egypt.

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Abstract

Al-Rifa'i Mosque is one of the most important mosques in Cairo. It suffers, like most of the historical buildings sited in urban areas, from many degradation phenomena related to the high level of pollution, especially soiling and the formation of the black crusts on the facades of buildings and monuments, which threaten their conservation.

An analytical study was conducted on the black crust samples collected from the external façade of the mosque in order to detect the morphological characteristics and the chemical and mineralogical compositions of these degradation products and to identify the pollutant sources and assess their impact on the stone material. For a complete characterization of the black crusts, several analytical techniques were carried out, including stereomicroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy.

The results showed that black crusts represent the most frequent and damaging surface degradation products affecting the walls of the mosque. Furthermore, the environmental pollution resulting from industrial activities and vehicle traffic has been identified as the main polluting source in Cairo city.

Keywords: black crusts; cultural heritage; limestone; Environmental pollution; carbonaceous particles.

1. Introduction

Cairo is one of the most important and largest heritage cities in the world and is characterized by a multiplicity of monuments and historical buildings reflecting Cairo's long history as a political, cultural, commercial, and religious capital, dominant and leading in the Middle East and the Mediterranean basin (El Rashidi; 2012). Cairo is, as they say, "the city of a thousand minarets and a world heritage city." It includes the greatest concentration of Islamic monuments in the world, and its mosques, mausoleums, religious schools, baths, and caravanserais, built by prominent patrons between the seventh and nineteenth centuries, are among the finest in existence. Actually, Cairo's Islamic monuments are part of an uninterrupted tradition that spans over a thousand years of building activity. No other Islamic city can equal Cairo's spectacular heritage. (Khallaf; 2011).

On the other hand, Greater Cairo is the largest city in Africa and the Middle East with a population of more than 15 million people, and it is one of the largest cities in the world (Robaa; 2003, Abbass et al; 2020). It was listed as one of the most polluted cities in the world (Gurjar et al; 2010). The sources of air pollution in the city vary and include the burning of rubbish, vehicle emissions (~4.5 million cars on the streets of Cairo) and industrial activities (Abbass et al; 2020). Air pollution is a powerful factor involved in the degradation of outdoor stone works, causing material transformation and the accumulation of surface deposits (Camuffo; 1998, Saiz-Jimenez; 2003, Doehne and Price; 2010). Several studies have

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stressed the importance of investigating first the building raw materials, mainly limestone. This stone type was widely used for the construction of historical monuments in the whole Mediterranean area due to its workability, durability, and aesthetic features (Fitzner et al; 2002, La Russa et al; 2013). Even so, it is frequently exposed to many decay processes such as black crust formation, salt crystallization, disintegration, pitting, cracks, and erosion (Davidson et al; 2000, Fitzner et al; 2002). In fact, buildings and monuments located in areas with high pollution rates are affected by the deposition of pollutants on the surface, especially carbon particles, and tend to darken over time. Soiling, color change, and black crust formation followed by material loss are considered the most common observed alterations in protected areas from rainfall (Saiz-Jimenez; 1993, Brimblecombe and Grossi; 2005, Fronteau et al; 2010).

The formation of black crusts is one of the most dangerous degradation forms produced by air pollution, which occurs mainly on carbonate substrates (marble, limestone, etc.). Their formation and development on the surface is closely related to levels of environmental pollution, specifically atmospheric pollution (Ausset et al; 1996, Grossi et al ;2003, Barca et al; 2010, 2014, Comite et al; 2012).

These damage layers are formed through the sulphation processes of stone surfaces as a result of the interaction between limestone and SO_2 airborne, which leads to the transformation of calcium carbonate $CaCO_3$, the main component of limestone, into gypsum $CaSO_4.2H_2O$ (Camuffo et al; 1983, Sabbioni; 2003, Doehne and Price; 2010, Belfiore et al; 2013, Barca et al; 2014, Comite et al; 2020a, 2020b). Gypsum formation is a quick process and can also be accelerated by the depositing of other atmospheric components, such as particles rich in minerals and metal oxides, which act as catalysts in the sulphating reaction (Ruffolo et al; 2015, La Russa et al; 2017, Fermo et al; 2020). In addition, during the crust formation, particulate matter, which contains amorphous carbon and several heavy metals, can be embedded into the gypsum, providing its characteristic black color (La Russa et al; 2018), which affects the artistic value and aesthetic appearance of the monuments. Regrettably, the fast increase in environmental pollution in the past century seriously threatens Cairo's archaeological surface in Al-Rifa'i Mosque. Built in the Mamluk style of the 19th and 20th centuries, it is located in buildings. Since the surfaces of buildings and monuments are the areas where air pollutants are deposited and interact with the stone, the chemical composition of black crusts reflects the change in pollution sources over time and could be used as an indicator for the environment, specifically near the monuments (La Russa et al; 2013, De Kock et al; 2017). Furthermore, several authors have stated that analysing trace elements in black crusts can aid in understanding the role of some pollutants in their formation (Barca et al., 2011, 2014, Comite et al., 2012, La Russa et al., 2013).For these reasons, it has become necessary to develop efficient strategies for the preservation and protection of built cultural heritage from the influence of air pollution.

The current study provides a detailed microscopic and chemical characterization of damaged limestone in order to emphasise the deterioration mechanisms that occur on archaeological buildings as a result of polluted environments.

Black crusts taken from Al-Rifa'i Mosque have been examined. This building is located in an urban setting characterized by high vehicular traffic. The crust samples were investigated using stereomicroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy.

This exhaustive analytical methodology made it possible to obtain the major features of the black crusts and stone substrate in terms of micromorphology, mineralogical composition, and major and trace elements. This inclusive characterization offered useful information on the formation processes of the black crusts as well as on the interaction between the stone and the environment around it, allowing us to evaluate the degradation degree influencing the stone substrate, which can contribute to the identification of the probable main pollutant sources in the study area that are responsible for the degradation of the surfaces over time.

2. Materials and Methods

2.1. Sampling

The study is based on the examination and analysis of samples of the black crusts formed on the limestone front of Sultan Hassan Mosque in the Citadel area of Ancient Egypt **(Fig. 1)**. It resembled buildings in

Europe at that time. The mosque was built from limestone, like most Islamic buildings in historic Cairo. The location of the mosque in Citadel Square affects the formation of soiling and black crusts on the surface due to the effect of air pollution with sulfur dioxide gas caused by traffic exhausts and the deposition of pollutants on the surface, which causes its blackening.

Samples involving black crust and the stone substrate were taken from some parts located on vertical surfaces of Al-Rifa'i Mosque, seriously influenced by degradation phenomena and exposed to high rates of environmental pollution. Therefore, all samples were taken from the mosque's exterior façade overlooking the Citadel Square. Sampling was carried out using stainless steel tools and surgical lancets.

A multi-analytical approach using different and complementary techniques was used to identify their morphologies and structures as well as their mineral and chemical compositions and interactions with the stone substrate.

2.2. Stereomicroscopy

Superficial samples and a polished cross section including both black crust and underlying limestone were observed using stereomicroscopy (Leica NZ6) to detect the degradation rate of superficial crusts by evaluating surface morphology, growth of black crusts, and the interaction between the substrate and the damage layer.

2.3. Scanning Electron Microscopy (SEM) coupled with energy dispersive X-ray spectrometry **(EDS)** analyses were performed on superficial samples and a polished cross section to obtain detailed information on the morphological features and the components of the examined black crusts (in terms of major elements) using a Quanta 250 FEG microscope. Furthermore, a mapping of specific microscopic areas in the sample is possible, allowing an evaluation of the distribution of elements over the sample.

2.4. X-Ray Diffraction

X-Ray Diffraction (XRD) analysis was carried out to identify the mineralogical phases constituting the black crust sample. Analysis was performed using an automated (Philips type: PW1840) diffractometer with a Cu Kα radiation source at a step size angle of 0.02°, a scan rate of 2° in 2 units, and a scan from 10° to 70°.

2.5. FTIR analysis

FTIR analysis was performed to determine both inorganic and organic compounds present in the black crust. FTIR spectroscopy was performed using a 6100 Jasco (Japan) equipped with an attenuated total reflectance (ATR) accessory. ATR-FTIR spectrometer with a range from 400 to 4000 cm^{-1}, at a rate of 2 mm/s, with a resolution of 4 cm^{-1}. Each spectrum was obtained in the transmission mode with TGS detectors.

2.6. Raman spectroscopy

The phase composition of the deterioration products was determined using Raman spectroscopy. Raman spectroscopy was performed using a Bruker Senterra operating at 20 mW of power with an excitation wavelength of 532 nm.

Fig.1. (a, b) Al-Rifa'i Mosque, Egypt

3. Results and Discussion

3.1. stereomicroscopy

Microscopic observations proved helpful for understanding alteration mechanisms and evaluating the degree of damage. The observations of the cross section and superficial samples with stereomicroscopy allowed us to gain information regarding the adherence, thickness, and morphology of the damage layers. The cross section **(Fig.2a)** shows a continuous black crust with a dendritic and irregular morphology and a high thickness (up to 1.76 mm). The different superficial samples examined showed that the black crusts have good adherence to the stone substrate. The color varied from dark brown to black due to the deposition of atmospheric particles **(Fig. 2 b, c, and d)**. Stereomicroscopy observations also show that the substrate is classified as a biomicrite **(Fig. 2 e, f)** (Folk; 1959).

3.2. SEM-EDS analysis

The use of this methodology allowed us to obtain detailed information on the morphological features of the examined crusts and their interactions with the substrate, as well as information about the chemical composition of these damaged crusts. Regarding the morphology of the black crusts, SEM observations on the surfaces revealed that the crusts are mainly composed of gypsum, which appears in different morphological forms. Furthermore, rosette and acicular stable gypsum crystals were mostly found in black crusts.Aggregates of gypsum granules of different sizes related to early stages of gypsum formation were also detected, covering the surface of the stone completely and making the surface more porous. These crusts have good adherence to the stone substrate. SEM observations also revealed that the substrate is classified as a biomicrite (Folk ;1959) (**Fig. 3**). The EDS analysis carried out on the same sample showed that the examined damage crust is mainly composed of Ca, O, and S, followed by Al, Si, C, Fe, and smaller amounts of Na, Mg, Cl, and K. The results point to high concentrations of calcium and sulfur, which can be attributed to gypsum $CaSO_4.2H_2O$, the main component of the crust, with a lower content of calcite $CaCO_3$, coming from the substrate, while aluminum, silicon, magnesium, and potassium indicate the presence of quartz SiO_2 and clay minerals, sodium and chlorine due to the presence of halite NaCl, the most common salt in the subsurface water of Egypt, while iron can be attributed to iron oxides and clay minerals as shown in **Fig.4**. The EDS-Map was also used in order to evaluate the distribution of the most abundant elements detected in the black crust **(Fig. 5)**.

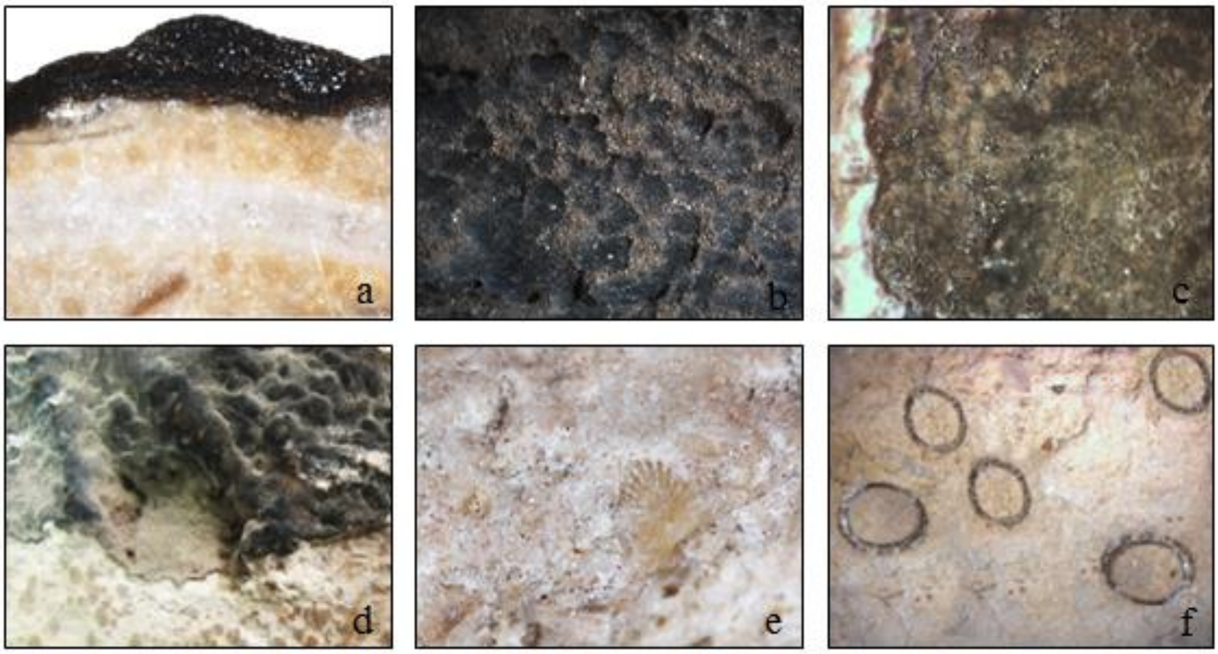


Fig. 2. The samples under stereomicroscopy, **(a)** cross section, **(b, c, d)** superficial samples of the black crusts, **(e, f)** limestone consisting of bioclasts set in a micrite matrix.

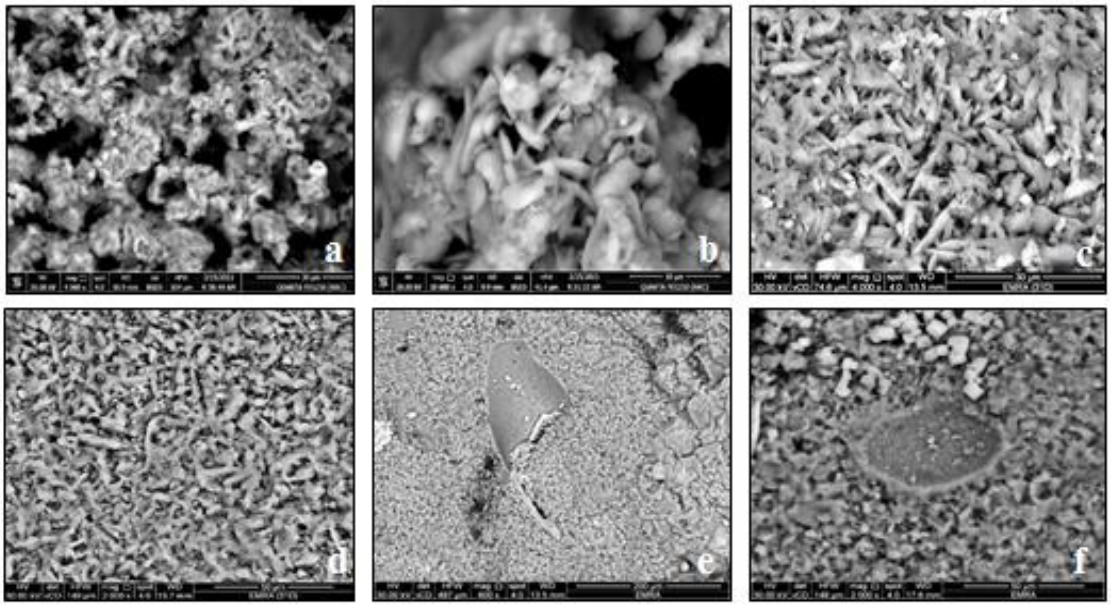
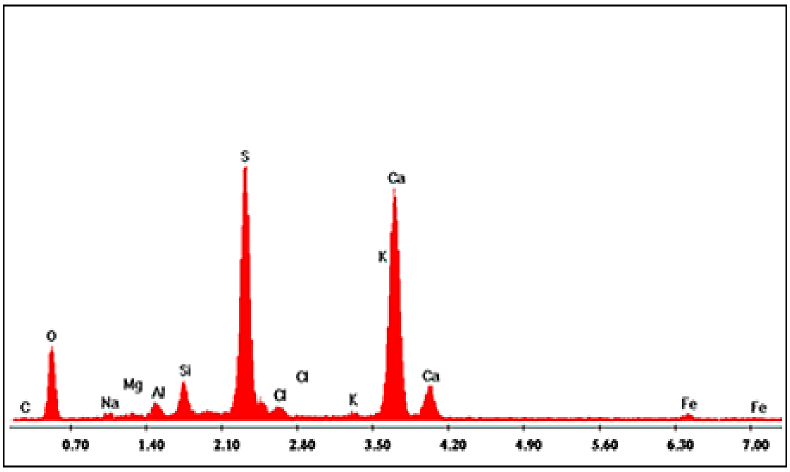


Fig. 3. (a, b, c, d) the morphology of the studied black crusts, **(a, b)** rosette-like gypsum crystals on limestone, **(c) a** dense network of acicular gypsum crystals, **(d)** aggregates of gypsum granules, **(e, f)** limestone consisting of bioclasts set in a micrite matrix.



Element	Weight %
C K	2.35
O K	42.27
NaK	1.02
MgK	0.55
Al K	1.47
Si K	2.83
S K	20.62
Cl K	0.94
K K	0.41
Ca K	26.29
Fe K	1.24

Fig. 4. EDS spectrum showing the presence of elements Ca ,S, O, Al, Si ,C, Fe , Na,Cl ,Mg and K.

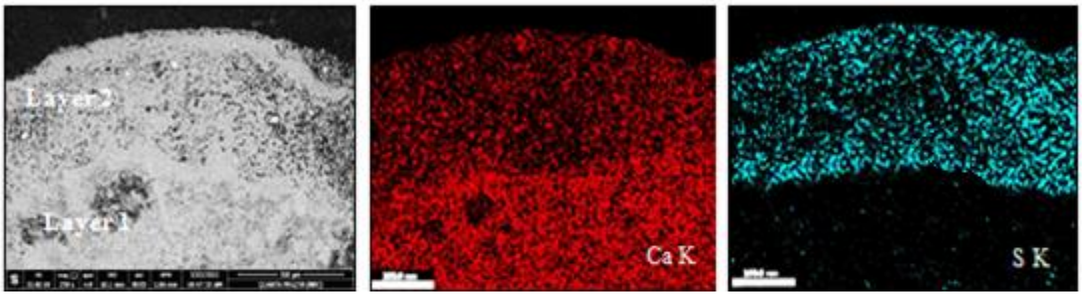


Fig. 5. EDS elemental distribution maps for the cross section.

3.3.X-ray diffraction

The results of EDX analyses were also confirmed by XRD, showing that the analyzed sample consists mainly of calcite ($CaCO_3$) 65%, gypsum ($CaSO_4.2H_2O$) 22%, and halite salt (NaCl) 13%. Gypsum originates due to the interaction of sulfur oxides with calcium carbonate in the substrate, calcite attributable to the substrate, and the presence of halite salts due to the effect of groundwater as shown in **Fig. 6**

3.4. Fourier Transform Infra Red.

Regarding the mineralogical composition of the analyzed damage crust, the infrared spectra of the crust sample showed that gypsum is the main mineral phase in the black crust. The presence of this mineral is confirmed through the bands assigned to the OH functional group related to the hydration state of the mineral and the S–O vibrations. Regarding S–O vibration, the sharp band centred at 1132 cm^{-1} is assigned to S–O stretching and the lower intense bands at 671 and 600 cm^{-1} correspond to S–O bending vibration, as well as the stretching and deformation vibrations of the O–H bond of water at 3538, 3405, 3246 cm^{-1} and at 1681 and 1627 cm^{-1}, respectively (La Russa et al; 2009, Pozo-Antonio et al; 2021). Gypsum originates from the transformation of calcite in the presence of Sulfur oxides. The characteristic bands of calcite are also present, the sharp one at 875 cm^{-1} is due to its asymmetric bending. Calcite FTIR spectrum shows peaks at 1425, 1392, and 875 cm^{-1} due to carbonate C–O stretching, indicating the substrate (Kiros et al; 2013). The Si–O symmetrical stretching vibrations observed at the doublet 797/779 cm^{-1}, the Si–O symmetrical bending vibration at 695 cm^{-1} and the asymmetrical bending vibration observed at 455 cm^{-1} indicate the presence of quartz (Anbalagan et al; 2010), attributable to the substrate and to the deposited particulate have also been identified. Furthermore, weak absorption bands at 2929 and 2865 cm^{-1} attributed to the stretching of CH_3 and CH_2 groups were detected, which confirms the presence of organic contaminants coming from the atmospheric deposition as shown in **Fig. 7**

3.5. Raman spectroscopy

Raman results confirmed and completed previous analyses. Raman spectroscopy allowed us to identify gypsum ($CaSO_4{\cdot}2H_2O$) as a common mineral in the black crust on the limestone surface. The presence of this salt has been inferred from its main band at 1007 cm^{-1} (ν_1 symmetric stretching), also minor bands at 416 cm^{-1} and 621 cm^{-1} (ν_2 symmetric and ν_4 antisymmetric bending of SO_4^{2-}, respectively) and 1167 cm^{-1} (ν3 antisymmetric stretching). The carbonaceous matter is also a significant component of the black crust, identified in analyses by the broad Raman bands at ~1600 and ~1300 cm^{-1} as shown in **Fig. 8**. The organic substance is probably soot, an airborne pollutant. Its presence results in further damage (Marszałek; 2016, Morillas et al; 2016).

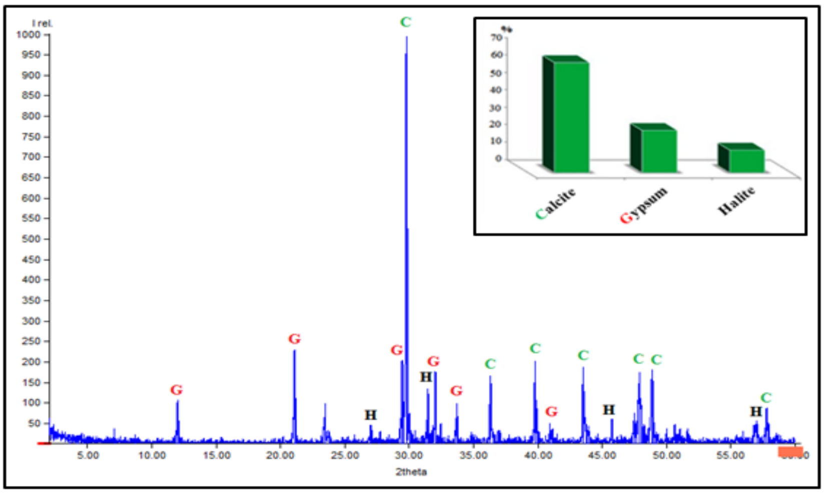


Fig. 6. XRD patterns of black crust sample showing the presence of (**calcite**, card number :05-0586, **gypsum**, card number: 33-0311, and **halite**, card number: 05-0628).

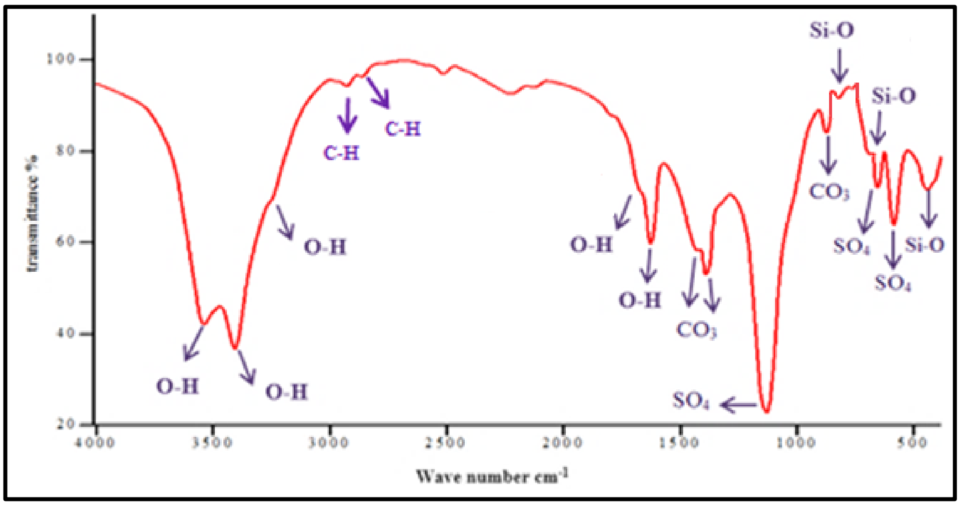


Fig. 7.FT.IR spectra of a black crust sample showing the presence of calcite, gypsum, quartz, and organic matter.

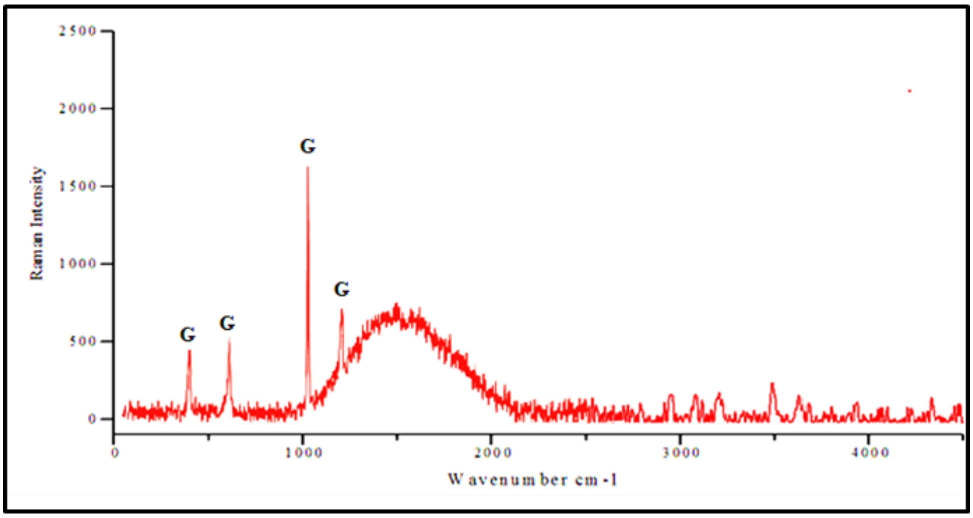


Fig.8. Raman spectra of a black crust sample shows organic matter, probably soot (broad band ~1300 to ~1600 cm^{-1}) and gypsum, the essential mineral in the black crust

4. Conclusions

In this work, black crusts taken from Al-Rifa'i Mosque have been analyzed. The characterization of these degradation products, carried out by means of multi-analytical techniques, provided information on their structures and morphologies as well as their chemical and mineral compositions. Detailed information is also given about the mechanisms of their formation and their interactions with the substrate, which allows the determination of the degradation state of the substrate due to the formation of soiling and black crusts. The black crust formation on the façade of Al-Rifa'i Mosque is essentially due to the pollution coming from industrial activities and vehicular traffic since the mosque is located in Citadel Square. Results indicated that the crusts are mainly composed of gypsum with a lower content of calcite coming from the substrate. In terms of major elements, besides calcium and Sulfur, Si, Al, Fe, Na, Cl, Mg, and K were identified as coming both from the substrate and external sources. Carbonaceous matter is also a significant component of the black crust, identified in Raman analysis, which comes from fossil fuel combustion. This study underlines how the built cultural heritage in Historic Cairo is influenced by various harmful degradation phenomena closely associated with environmental pollution. The results confirm the deep connection between the atmospheric composition and the degradation processes influencing the stone materials used. This work highlighted the importance of chemical characterization of black crusts formed by atmospheric pollutants in order to evaluate the risk of degradation of archaeological buildings in urban areas when exposed to environmental pollution. In this regard, the study stresses the significance of the reduction of SO_2 gas emissions in the atmosphere as a primary step for an effective conservation strategy of the built cultural heritage as well as to protect the environment and human health at the same time. This is followed by appropriate restoration interventions that are based on suitable cleaning procedures, consolidating and protective materials.

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