

# Air pollution impact on Mediterranean architectural heritage

## Molecular analysis of black crusts deposits

Saadia AIT LYAZIDI, Laboratoire de Spectrométrie des Matériaux et Archéomatériaux (LASMAR), Moulay Ismail University of Meknes, Faculty of Sciences, Morocco<sup>1</sup>

Mustapha HADDAD, Laboratoire de Spectrométrie des Matériaux et Archéomatériaux (LASMAR), Moulay Ismail University of Meknes, Faculty of Sciences, Morocco

Taibi LAMHASNI, Laboratoire de Spectrométrie des Matériaux et Archéomatériaux (LASMAR), Moulay Ismail University of Meknes, Faculty of Sciences, Morocco

Abdelouahed BEN-NCER, Institut National des Sciences de l'Archéologie et du Patrimoine (INSAP), Morocco

Alessandra BONAZZA, Institute of Atmospheric Sciences and Climate, ISAC-CNR, Italy

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## Introduction

The present investigation relates to air pollution impacts on architectural heritage; it is the continuation of the previous published works (*Lamhasni 2019 and Ozga 2013*). Black crusts deposits on four historical monuments at the Mediterranean region (Figure 1) were analysed by means of optical spectrometries. At the southern side, the investigation related to the “Burg Al-Klab” tower in the city of Salé and the Mosque Al-Qods of the Roches Noires neighborhood in Casablanca. These limestone buildings, dating back respectively to the late of the 12th and the beginning of 20th centuries, are highly exposed to road traffics and are suffering from air pollution. At the northern side, the monuments considered are: i) the cathedral of Milan, dating back to the XIV-XIXth centuries, which is one of the most attractive edifices of Milan and ii) the Santa Maria Del Fiore Cathedral of Florence, edified since the XIII<sup>th</sup> century, part of the most important monumental complexes in Italy. For the first time, the molecular/structural techniques of Synchronous fluorescence and ATR-FTIR spectroscopies were combined for the analysis of hazardous polycyclic aromatic hydrocarbons (PAHs) along with calcite degradation products in black crusts sampled on the exposed façades of the above Mediterranean monuments.

As in European areas, in the case of Morocco, the cities of Casablanca and Rabat–Salé are also subject to the problem of architectural heritage disfigurement; there are numerous buildings, dating back to different historical periods, suffering from air pollution. The expansion of industrial and urban areas is drastically increasing the atmospheric pollution and its harmful impacts on all environmental compartments.

Gaseous pollutants, suspended particulates matter (PM) and aerosols released from combustion processes are accelerating the deterioration of historical buildings in urban areas. Particulate matter (PM) and sulfur dioxide (SO<sub>2</sub>), in dry and wet depositions, are the most aggressive and dangerous agents for architectural heritage. In the case of limestone (the worldwide used ancient building material) as well as marbles, soiling, color changes and black crusts depositions followed by material loss are the most common observed alterations. Exposed to severe weather, limestone which is a naturally porous material behaves as a non-selective depository, passively entrapping airborne particulate matter, gaseous organics and carbonaceous particles. In particular, the entrapped carbonaceous particles act as catalysts in the calcite sulphation process and induce the blackening. They play thus the important role in the overall deterioration affecting the exposed façades of ancient buildings.

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<sup>1</sup> Author's address: Saadia Ait Lyazidi, Laboratoire de Spectrométrie des Matériaux et Archéomatériaux (LASMAR), Moulay Ismail University of Meknes, Faculty of Sciences, , Morocco; email: [aitlyazidisaadia@yahoo.fr](mailto:aitlyazidisaadia@yahoo.fr)

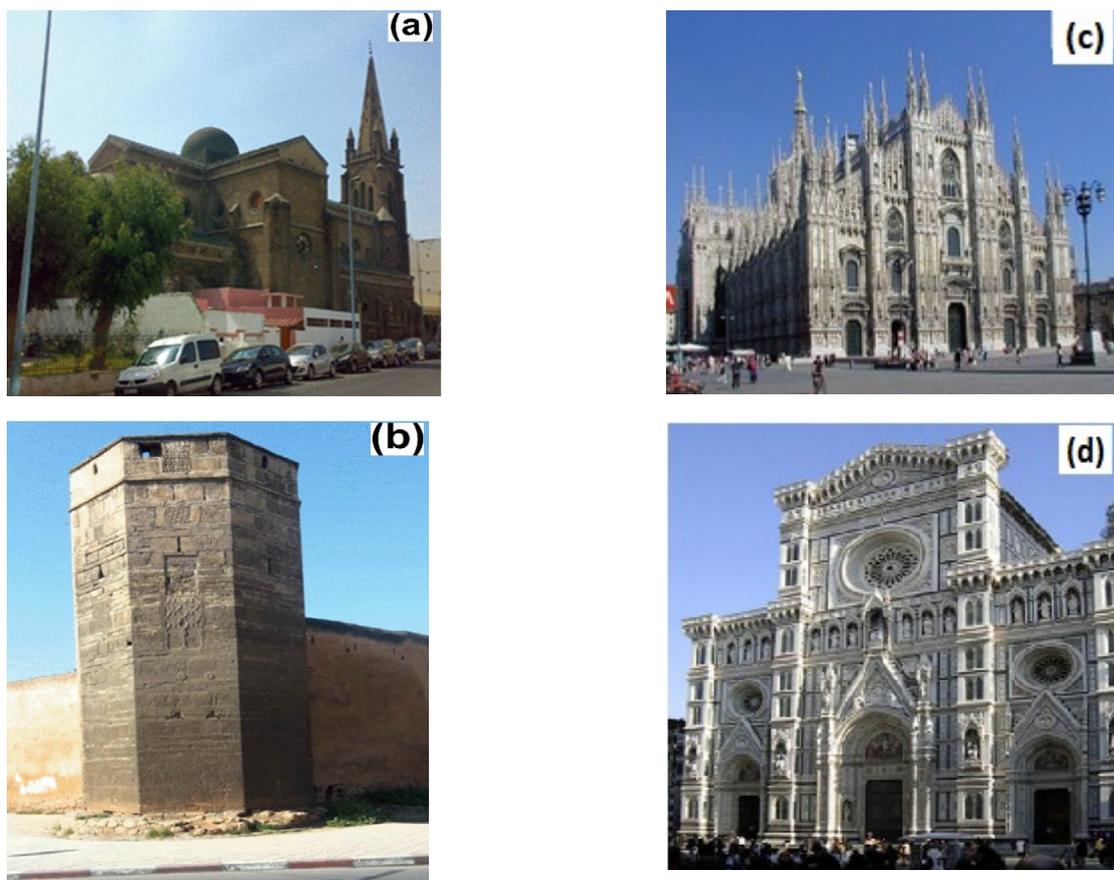


Fig.1. Mediterranean buildings: Moroccan buildings: a) Al-Qods Mosque and b) Burg Al-Klab tower. Italian buildings: c) Cathedral of Milan d) Cathedral of Florence

## Results and discussion

In the present case black crusts deposits collected on the monuments façades were studied by means of combining constant-wavelength synchronous optical fluorescence and ATR-FTIR spectroscopies. Figure 2 and figure 3 show respectively the synchronous fluorescence spectra (SFS) of black crusts dissolved in acetonitrile, and the ATR-FTIR spectra recorded directly on black crusts particles. All SFS were recorded at the same offset 10 nm value. In all cases, the comparison of the obtained synchronous fluorescence spectra (Fig. 2) with those formerly established for hazardous PAHs (*Lamhasni 2019*) permitted the identification of eight PAH groups: i) Fluorene ii) Acenaphthene, iii) Phenanthrene, iv) Chrysene and Pyrene, v) Anthracene, Naphthalene, Benzo (b) Fluoranthene, Dibenzo (a,h) Anthracene, Benzo (a) Anthracene, Benzo(k) Fluoranthene and Benzo (a) Pyrene, vi) Perylene, vii) Indeno (1, 2, 3, cd) Pyrene and viii) Fluoranthene. These PAHs groups are emitting respectively in the wavelength ranges 290-315 nm, 315-335 nm, 340-355 nm, 355-375 nm, 375-415 nm, 430-450 nm, 455-475 nm and 475-490 nm. The red sides, 500-600 nm, observed in all fluorescence spectra may be related to hydrocarbons with aromaticity degrees higher than those of the identified PAHs, crude oil from Iraq had been reported exhibiting fluorescence features in the same spectral range (*Naseer 2016*).

The ATR-FTIR spectra recorded on black particles did not show similar infrared spectra for all edifices (Fig. 3). While the spectra recorded on black crusts sampled on the Moroccan limestone buildings show bands characteristic of both of gypsum and oxalates degradation products, the spectra recorded on black crusts collected on the Italian marble buildings exhibit only bands characteristic of gypsum. The gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) signals are those located at 600, 672, 1109, 1684, 3397 and 3533  $\text{cm}^{-1}$ ; the oxalates (whewellite  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and weddellite  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) ones are observed at 1618 and 1321  $\text{cm}^{-1}$  along

with the large spectral block lying between 2900 and 3700  $\text{cm}^{-1}$ . Gypsum originates from calcite sulphation under wetness and  $\text{SO}_2$  rich oil fired soot, while oxalates are due to ancient biological weathering. The presence of oxalates in the case of the limestone buildings, against their absence in the case of the marble ones, indicates clearly that the porosity of the lime stone material may constitute a factor of its vulnerability compared to the marble one.

## Conclusion

Considering the remoteness of the four historical buildings, as well as the great difference between the northern and the southern Mediterranean climates, the similarity between the identified hazardous organic pollutants along with the degradation product gypsum, indicates that the weathering factors impacting negatively the building materials are of the same origin. These factors causing disfigurement of historical edifices are obviously carbonaceous particles originating from fossil fuel and oil combustion due to traffics expanding over decades.

Such results keeping track of air pollution, inducing degradation of architectural heritage, must alarm both cultural heritage and environmental decision makers.

## References

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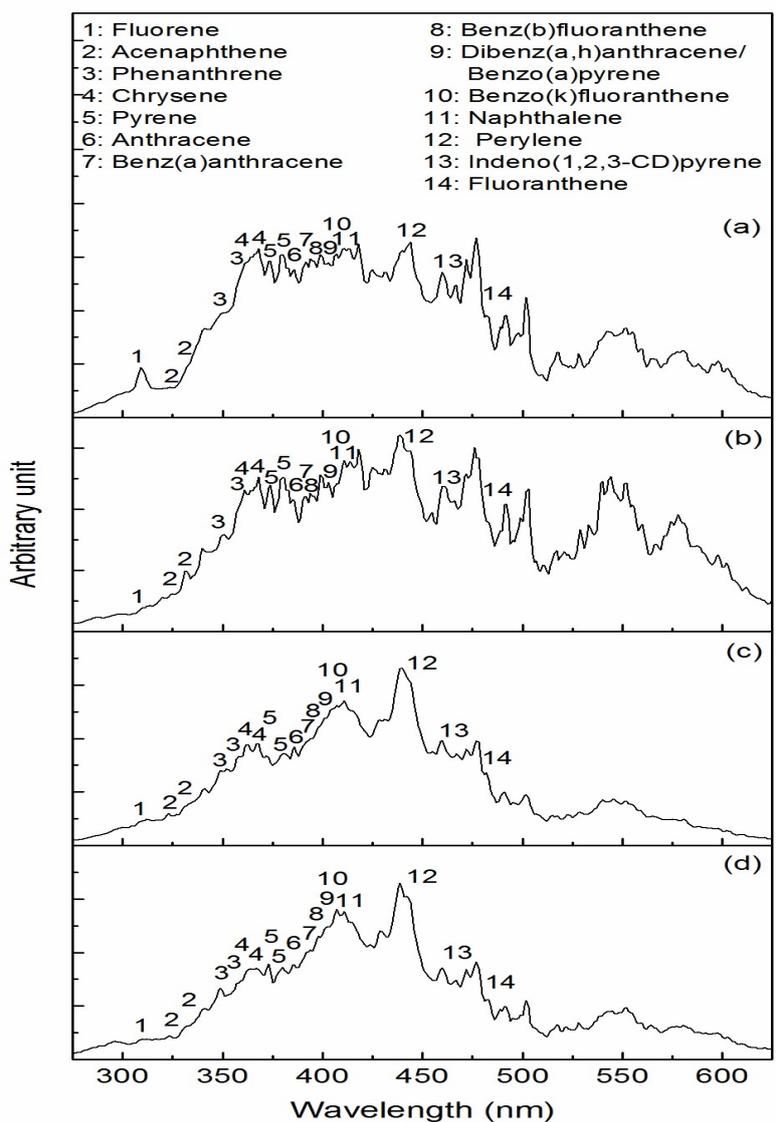


Fig. 2. Synchronous fluorescence spectra of black crusts extracts in acetonitrile, recorded at the offset  $\Delta\lambda = 10$  nm. a) Mosque Al-Qos in Casablanca, b) Burg Al-Klab in Sale, c) Cathedral of Florence and d) Cathedral of Milan.

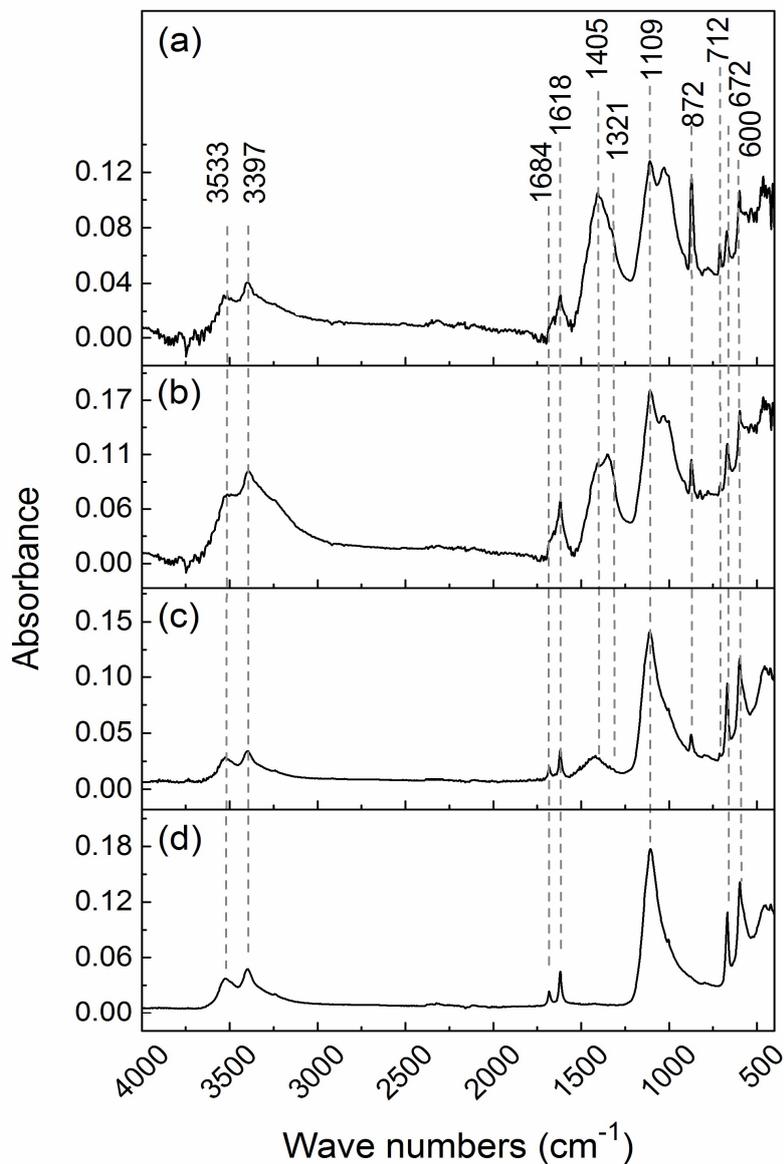


Fig. 3. ATR-FT infrared spectra of black crusts particles sampled on the facades of a) Mosque Al-Qos in Casablanca, b) Burg Al-Klab in Sale, c) Cathedral of Florence and d) Cathedral of Milan.