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To cite this version:

Aurélie Verney-Carron, Mandana Saheb, Yassmine Ben Amor, Clarisse Bolou Bi Balland. Correlation between black crust formation on limestone monuments and air pollution. Goldschmidt 2019, Aug 2019, Barcelone, France. hal-02277446

HAL Id: hal-02277446

https://hal.science/hal-02277446

Submitted on 3 Sep 2019

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Correlation between black crust formation on limestone monuments and air pollution

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INTRODUCTION

Impacts of air pollution on health and environment are a major issue. The addition of pollutants in the atmosphere is responsible for 4.2 million deaths every year and threatens 91% of the world's population (according to the World Health Organization). It also causes the reduction of agricultural yields, damage to ecosystems and degradation of historical monuments.

On monuments out of calcareous stones, air pollution leads to the formation of black crusts in sheltered zones (Fig. 1). Black crusts result from a sulfation reaction (SO_2 reacts with calcite to form gypsum ($CaSO_4 \cdot 2H_2O$)) and the entrapment of particles (especially soot), causing its blackening [1-3].

In order to understand the first steps of this alteration and to investigate the influence of the environment, samples of limestone and marble were exposed in different sites for 1 year.

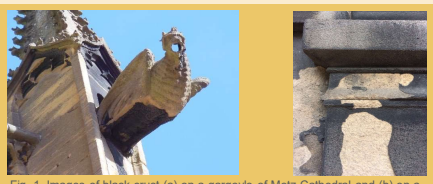

Fig. 1. Images of black crust (a) on a gargoyle of Metz Cathedral and (b) on a tomb of the Père-Lachaise Cemetery (France)

METHODOLOGY

EXPOSURE CAMPAIGN AND ENVIRONMENT

An exposure campaign was performed in the framework of the International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments (ICP-Materials, Chairs: J. Tidblad & P. Spezzano).

Samples of 'Saint Maximin roche fine' limestone and Carrara marble (6 x 6 x 1 cm) were exposed in sheltered conditions and in vertical position (Fig. 2) in 22 European sites and 1 site in USA (Fig. 3).

In parallel, environmental data were collected by each site: T° and RH for the climate and $[SO_2]$, $[NO_2]$, $[PM_{10}]$ using passive samplers (from IVL Swedish Environmental Research Institute) for pollution.

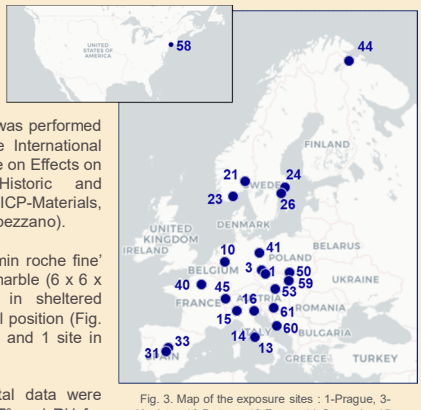

Fig. 3. Map of the exposure sites : 1-Prague, 3-Kopistry, 10-Bottrop, 13-Rome, 14-Casaccia, 15-Milan, 16-Venice, 21- Oslo, 23-Birkenes, 24-Stockholm, 26-Aspvreten, 31-Madrid, 33-Toledo, 40-Paris, 41-Berlin, 44-Svanvik, 45-Chaumont, 50-Katowice, 53-Vienna, 58-New Haven, 59-Zilina, 60-Zagreb, 61-Split

Fig. 2. Image of the limestone (at the top left), marble (at the bottom left) and glass (on the right) samples in the exposure box in Katowice (Poland)

GLOBAL MEASUREMENTS:

The samples were characterized by weighing (mass of deposit), optical microscopy coupled with image processing (percentage of covered surface) and spectrophotometry (percentage of reflectance change).

DEPOSIT CHARACTERIZATION:

The deposit was analyzed using SEM-EDS (Scanning Electron Microscopy – Energy Dispersive Spectrometer) and Raman spectroscopy. One piece of each sample (~ 10g) was cut and solubilized in an stirred vial of 20 mL of ultrapure water for 24h. Solutions were analyzed using ICP-AES (Indictively Coupled Plasma – Atomic Emission Spectrometry).

RESULTS AND DISCUSSION

MASS OF DEPOSIT

The mass of deposit was only measured for marble and glass (loss of material during handling and transport on the limestone samples). The available results are presented on Fig. 4a.

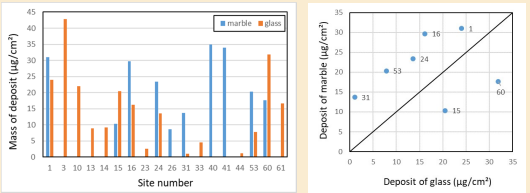

Fig. 4. (a) Mass of the deposit (in µg/cm²) on glass and marble for each site. (b) Correlation between the mass of deposit on glass and on marble.

⇒ **The deposit on marble is generally slightly higher than on glass (Fig. 4b), which indicates a higher reactivity (with gases) and/or a higher roughness (to fix particles).**

OPTICAL PROPERTIES AND COVERED SURFACE

The results of reflectance change are not relevant for the soiling measurement (Fig. 5) as the majority of the values indicates a gain of reflectance (due to a general lightning of the stone in contact with humidity), especially for limestone. However, particles are present on the surface (Fig. 6). The percentage of covered surface was calculated (Fig. 7).

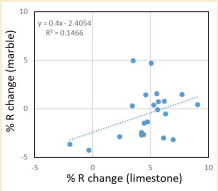

Fig. 5. Correlation between the percentage of reflectance change for limestone and for marble.

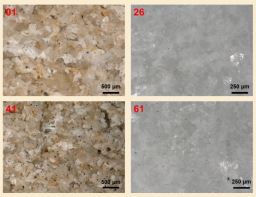

Fig. 6. Optical microscopy images of the surface of 2 limestone samples (Prague 01 and Berlin 41) and 2 marble samples (Stockholm 26 and Zagreb 61).

The % of covered surface is higher for limestone than for marble as some dark zones initially present in the limestone were counted as particles. The values are low on glass due to its very low roughness.

⇒ **The % of covered surface allows quantifying the soiling of stones.**

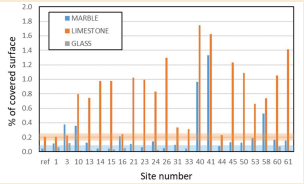

Fig. 7. % of covered surface for each site and for non exposed references (bands).

CHARACTERIZATION OF DEPOSIT

Raman spectroscopy and SEM-EDS

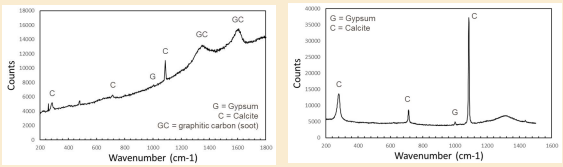

Fig. 8. Raman spectra of the marble from Split (Croatia)

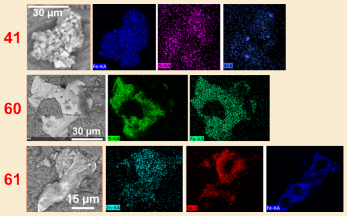

Fig. 9. SEM-EDS mappings of 3 particles found on the marble samples from Berlin 41, Split 60, Zagreb 61.

⇒ **The majority of the particles analyzed using Raman is composed of graphitic carbon typical of soot particles (Fig. 8). Gypsum is detectable on some samples. Metallic and mineral particles can also be observed using SEM-EDS (Fig. 9).**

Solution analyses using ICP-AES

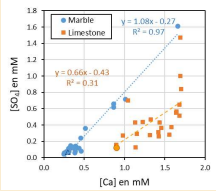

Fig. 10. Correlation between Ca and SO_4 concentration in solution after the solubilization protocol.

⇒ **The very good correlation between [Ca] and $[SO_4]$ for marble highlights that the extraction dissolves mainly gypsum (Ca and S release) and only a few calcite ([Ca] = 0.25 mM) (Fig. 10). For limestone, both minerals are dissolved.**

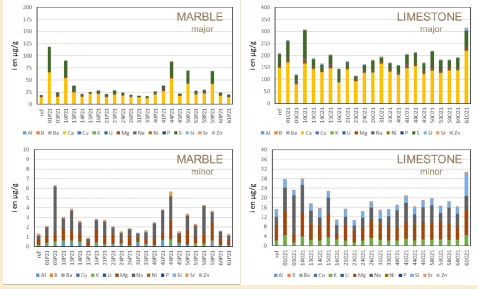

Fig. 11. Major and minor elements (in g/g of rock) on marble and limestone.

⇒ **Elements can be released by the dissolution of minerals (correlation between Ca, Mg, K for marble / Ca, B, Sr, Ba, K, Li, Mg, Na, P, Sr for limestone) or by air pollution (Cu, Ni, Zn) (Fig. 11).**

CORRELATION WITH AIR POLLUTION

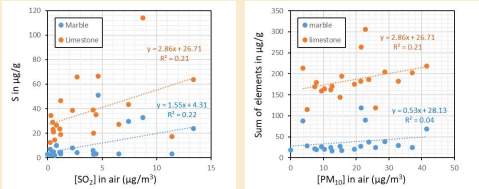

Fig. 12. Correlation between: (a) $[SO_2]$ in air and S in the deposit, (b) $[PM_{10}]$ in air and the sum of all elements analyzed using ICP-AES.

The quantity of S on the stones (coming from gypsum) is slightly correlated to SO_2 concentration in air (annual average), which highlights that black crust are formed in polluted zones (Fig. 12.a). On the same way, the sum of all elements detected in ICP-AES is slightly correlated to PM_{10} concentration for limestone, but not for marble (Fig. 2.b).

⇒ **The characterization of the deposit has to be pursued to improve the correlation of results with environmental data (not all available at this stage).**

CONCLUSION

- ✓ The percentage of the covered surface is the best parameter to assess the general soiling of stone materials.
- ✓ The deposit is mainly composed of soot, metallic and terrigenous particles. After 1 year, gypsum is already formed on the samples (Raman, ICP-AES).
- ✓ The study is in progress to complete the characterization of the deposit (Ion chromatography, C speciation) and to improve the link to air pollution.

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Acknowledgements – The authors would like to thank all the partners involved in the ICP-Materials program and the Ile de France Region (DIM MAP) for its financial support.