

# Analysis of black crusts from the Church of Santa Maria delle Grazie al Naviglio Grande (Milan): A challenge to deepen the understanding of the relationship among microstructure, microchemical features and pollution sources

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Air pollution is one of the most important causes of surface decay in urban environment. Among the degradation processes due to airborne pollutants, the formation of black crusts is one of the most dangerous one. Currently, emissions from mobile combustion sources are the main agents responsible for pollution, although a significant decrease is expected in Europe within the next decade. During the crust formation, particulate matter, which contains mainly amorphous carbon and several heavy metals, can be embedded into the gypsum, providing then, the characteristic black colour. In particular, EC (elemental carbon) and OC (organic carbon), including hundreds of organic substances of different natures) are the two main constituents of particulate matter (PM) carbonaceous fraction. OC is emitted by combustion processes as a primary pollutant but it has also a secondary origin and can form starting from gaseous organic precursors (i.e. volatile organic compounds, VOC). Both OC and EC have been identified in the black crusts together with metal oxides that can catalyze the oxidation of SO<sub>2</sub>, promoting formation of the crust itself. Several authors showed how the analysis of trace metals into black crust, as well as the characterization of the carbon, can provide insights on the influence of the pollution sources in the formation processes of this degradation product, moreover, they can be act as passive samplers of air pollution (Barca et al., 2010, 2011, 2014; Belfiore et al., 2013; La Russa et al., 2013, 2017; Fermo et al., 2015; Ruffolo et al., 2015). This research deals with the characterization of black crusts collected from the Church of Santa Maria delle Grazie al Naviglio Grande of Milan, built in 1901 and located on the Naviglio Grande. This city suffers pollution from the industrial area, combustion processes (including biomass burning) as well as from the vehicular traffic. Black crusts can be considered as a passive sampler of pollutants. In particular, the monument was selected because it showed the formation of degradation surfaces on different substrates than the usual carbonate (marble, calcarenite). In fact, black crust samples were taken from surfaces such as mortars and bricks (Fig.1), materials commonly used for building churches. For this reason, in order to fully characterize those samples, several techniques were used, including scanning electron microscopy, thermogravimetric analysis, laser ablation with inductively coupled plasma mass spectrometry, infrared spectroscopy and ion chromatography. This integrated approach allowed us to gain information about the mineralogical phases and elements and species present within the crusts giving the possibility to identify the pollution sources causing the surface decay within the buildings, as well as the variability in composition depending on the exposure of the analysed surfaces.



Fig.1 Some representative pictures of the black crusts collected from the church of Santa Maria delle Grazie al Naviglio of Milan.

## References

- Belfiore, C.M., Barca, D., Bonazza, A., Comite, V., La Russa, M.F., Pezzino, A., Ruffolo, S.A., Sabbioni, C., Application of spectrometric analysis to the identification of pollution sources causing cultural heritage damage. *Environ. Sci. Pollut. Res.* (2013) 20, 8848–8859.
- Barca, D., Belfiore, C.M., Crisci, G.M., La Russa, M.F., Pezzino, A., Ruffolo, S.A., 2010. Application of laser ablation ICP-MS and traditional techniques to the study of black crusts on building stones: a new methodological approach. *Environ. Sci. Pollut. Res.* 17, 1433–1447.
- Barca, D., Belfiore, C.M., Crisci, G.M., La Russa, M.F., Pezzino, A., Ruffolo, S.A., 2011. A new methodological approach for the chemical characterization of black crusts on building stones: a case study from the Catania city centre (Sicily, Italy). *J. Anal. At. Spectrom.* 26, 1000–1011.
- Barca, D., Comite, V., Belfiore, C.M., Bonazza, A., La Russa, M.F., Ruffolo, S.A., Crisci, G.M., Pezzino, A., Sabbioni, C., 2014. Impact of air pollution in deterioration of carbonate building materials in Italian urban environments. *Appl. Geochem.* 48, 122–131.
- La Russa, M.F., Belfiore, C.M., Comite, V., Barca, D., Bonazza, A., Ruffolo, S.A., Crisci, G.M., Pezzino, A., 2013. Geochemical study of black crusts as a diagnostic tool in cultural heritage. *Appl. Phys. A Mater. Sci. Process.* 113, 1151–1162.
- Fermo, P., Turrion, R.G., Rosa, M., Omegna, A., 2015. A new approach to assess the chemical composition of powder deposits damaging the stone surfaces of historical monuments. *Environ. Sci. Pollut. Res.* 22, 6262–6270.
- Ruffolo, S.A., Comite, V., La Russa, M.F., Belfiore, C.M., Barca, D., Bonazza, A., Crisci, G.M., Pezzino, A., Sabbioni, C., 2015. Analysis of black crusts from the Seville Cathedral: a challenge to deepen understanding the relationship among microstructure, microchemical features and pollution sources. *Sci. Total. Environ.* 502, 157–166.
- La Russa M.F., Fermo P., Comite V., Belfiore C.M., Barca, D., Cerioni A., De Santis M., Barbagallo L.F., Ricca M., Ruffolo S.A., The Oceanus statue of the Fontana di Trevi (Rome): The analysis of black crust as a tool to investigate the urban air pollution and its impact on the stone degradation, *Sci. Total. Environ.* (2017) 593-594, p. 297-309.