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SCIENCE and ART: A Future for Stone

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Edited by
John Hughes & Torsten Howind

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Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

THE DIAGNOSTIC AND MONITORING APPROACH FOR THE PREVENTIVE CONSERVATION OF THE FAÇADE OF THE MILAN CATHEDRAL

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Abstract

The importance of preventive conservation strategies for the built heritage has been debated in the last years, but there still is a limited number of applied research involving complex architectural sites. The identification and monitoring of the decay processes after the restoration activities can provide valuable information on the degradation rate and extent, thus supporting the future planned conservation. In the present work the methodology and some selected results of the post-treatment diagnostic and monitoring of the façade of the Milan Cathedral are presented. The main conservation issues have been identified and studied. A non-invasive colorimetric monitoring of selected areas of the façade has been carried out during a two-year period in order to evaluate the soiling effect. Fragments of stone and samples of the particulate matter deposits have been collected and characterized in laboratory according to a multi-analytical approach. As the early stages of deposition and erosion at the end of the intervention are particularly relevant for the evaluation of the degradation rate, several set of stone specimens have been also exposed on the façade in different conditions. The results of the in situ monitoring, supported by the study of the specimens, confirmed that soiling is the main and most rapidly-evolving deterioration effect and it is therefore expected to have a significant impact in the next future. Moreover, beside the carbonaceous fraction responsible for the surface blackening, the deposits composition showed high content of potentially harmful soluble compounds which can react with the stone matrix and therefore needs to be monitored over time.

Keywords: monitoring, marble decay, deposition, surface erosion, stone blackening, preventive conservation

1. Introduction

The importance of preventive conservation strategies for the built heritage has been debated in the last years. Despite the theoretical studies available so far (Della Torre 2003), there is still a limited number of applied researches conducted in the field and involving complex

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architectural buildings and sites (Brimblecombe & Grossi 2005; Price 2007; Ghedini *et al.* 2011; Bortolotto *et al.* 2013). As far as the stone surfaces exposed outdoor are concerned, the identification and the monitoring of the decay processes after the restoration activities can provide valuable information on the degradation rate and extent. Indications for preventive conservation able to delay and possibly reduce the occurrence of the damage can be provided accordingly. In the present work, the diagnostic and monitoring strategy for the preventive conservation of the façade of the Milan Cathedral is presented. The Duomo is a major landmark of the city, a remarkable example of the late gothic architecture and a primary touristic resource. The continuous exposition to the highly polluted atmosphere of Milan city centre progressively damaged the Candoglia marble of the façade according to well-known deterioration mechanisms (Watt *et al.* 2009), so that extensive conservative interventions had to be performed during the last century in 1935-39 and 1972-74. More recently, due to the worrying state of conservation of the surfaces, particularly affected by soiling and black crust formation (Toniolo *et al.* 2009), a new and complex restoration project was carried out in 2003-2009. The post-intervention monitoring and diagnostic activity started two years later. The main conservation issues to be monitored have been identified and included: i) soiling and blackening effects due to the deposition of atmospheric pollutants and soil dust in sheltered areas; ii) surface erosion of the elements exposed to direct rain-wash. A non-invasive colorimetric monitoring of selected areas of the façade has been carried out during a 18-month period in order to evaluate the soiling and blackening effect. Fragments of stone and samples of the particulate matter deposits have been collected and characterized in laboratory according to a multi-analytical approach. As the early stages of deposition and erosion at the end of the intervention are particularly relevant for the evaluation of the degradation rate, several set of Candoglia marble reference specimens have been exposed on the façade in different conditions (height, orientation, superficial finishing, sheltered/non-sheltered condition) and monitored every 6 months.

2. Materials and methods

Colorimetric measurements have been performed by a Konica Minolta CM-600D instrument equipped with a D65 illuminant at 8° (400-700 nm range). Measurements were elaborated according to the CIE $L^*a^*b^*$ standard colour system; FTIR analyses were carried out with a Nicolet 6700 spectrophotometer with a DTGS (4000-400 cm^{-1} range) on powder samples in KBr pellets; XRD analyses were performed using a Philips PW1830 diffractometer with Bragg-Brentano geometry using a Cu anticathode and Kα radiation (λ = 1,54058 Å). ESEM-EDX analyses were performed using a Zeiss EVO 50 EP environmental scanning electron microscope, with an Oxford INCA 200-Pentafet LZ4 spectrometer. Anions analysis was carried out by means of a Ion Pac AS14A (Dionex) column and a detection conductivity system equipped with a ASRS-ULTRA suppression mode (Dionex). Cations determination was performed by means of a CS12A (Dionex) and a detection conductivity system equipped with a CSRS-ULTRA suppression mode (Dionex). Laser profilometry was performed by a UBM Microfocus instrument, with a 150 pts/mm density.

3. Results and discussion

3.1. Soiling and blackening effects

3.1.1. Deposits characterization

After few years from the last cleaning operations most of the marble surface of the bas-relief, of the sculptures and of all the areas sheltered from direct rainfall show slight to significant accumulation of deposit. Samples of the dark deposits have been collected from seven different locations which varied in height from the ground level to almost 20 meters. The XRD characterization of the deposit highlighted the presence of quartz, feldspar, gypsum and calcite as the main mineralogical phases, together with clay minerals in minor amount. Sodium chloride, as halite, has also been found in some of the samples collected from the lowest locations. The deposit has also been studied by SEM-EDX (Fig. 1). Metallic particles containing iron and titanium are the most diffused within the deposited material, with an average diameter which decreases with height: in the highest sampling site (almost 20 m), where the prevalent transport mechanism is the wind-driven deposition, the particles diameter ranges from 2 to 20 µm; in the lowest location (2 m), where anthropogenic and vehicular re-suspension of soil dust and particulate matter from the ground is also effective, their diameter rises to a range of 20 to 50 µm. Aluminosilicate particles have been traced as well, but their size distribution seems to be less effectively related to height. Only rare carbonaceous particles containing sulphur and vanadium have been found in the upper sampling sites.

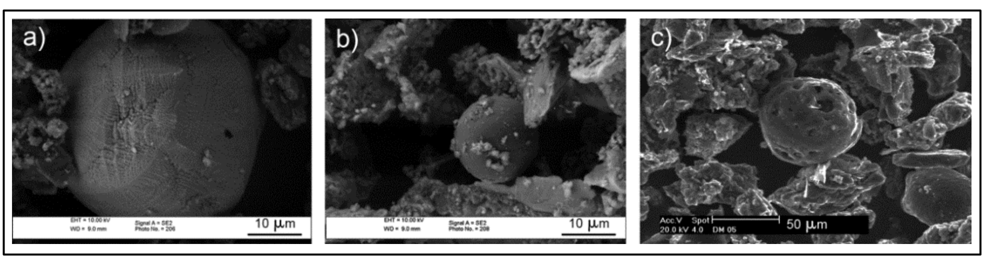

Fig. 1: ESEM micrographs of metallic (a), aluminosilicate (b) and carbonaceous (c) particles from the façade surface deposits.

The compositional characterization after FTIR analysis (Fig. 2) confirmed the prevailing presence of gypsum as the major component of the deposit (characteristic absorption doublets at 3532-3405, 1680-1622, 1140-1116 and 670-600 cm^{-1}). The sharp intense peak at 1385 cm^{-1} indicates the presence of high amount of nitrates and the smaller one located at 1323 cm^{-1} is related to the presence of calcium oxalate (most probably as weddellite). The calcite contribution is evidenced by the peaks around 1430, 875 and 715 cm^{-1}, present in minor amount together with silicates (Si-O characteristic peak around 1030 cm^{-1}) and quartz (779-799 cm^{-1}). The comparison between the deposits formed over the real sculpted surfaces (Fig. 2, grey line) as a result of the outdoor post-restoration exposition and the deposited material collected from the Candoglia marble specimens after six months of sheltered exposing condition on the façade (Fig. 2, black line) shows that no significant differences in the general composition are present.

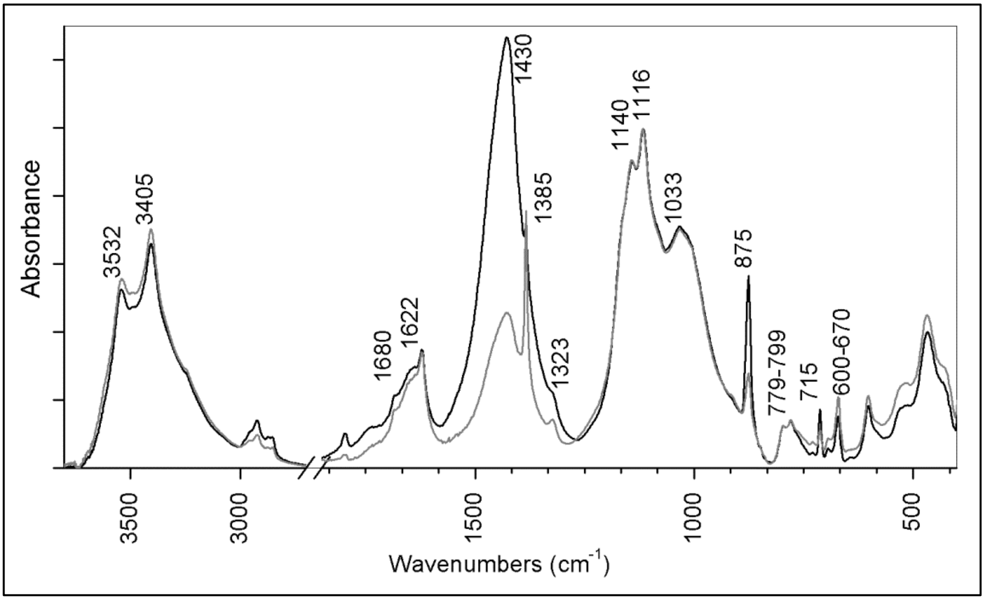

Fig. 2: FTIR spectra of samples of deposit from real façade surfaces (grey line) and collected from exposed Candoglia marble sample (black line).

The natural deposition over the sculpted surfaces is enriched in soluble compounds due to the longer exposition to the atmospheric pollutants and, as for gypsum, to the contribution provided by the partially sulfated substrate. It is worth noting that the overall composition of the latter deposits shows similar characteristics respect to the results of black layers and black crust characterization of samples of previous studies of the façade (Toniolo *et al.* 2009; Barca *et al.* 2014).

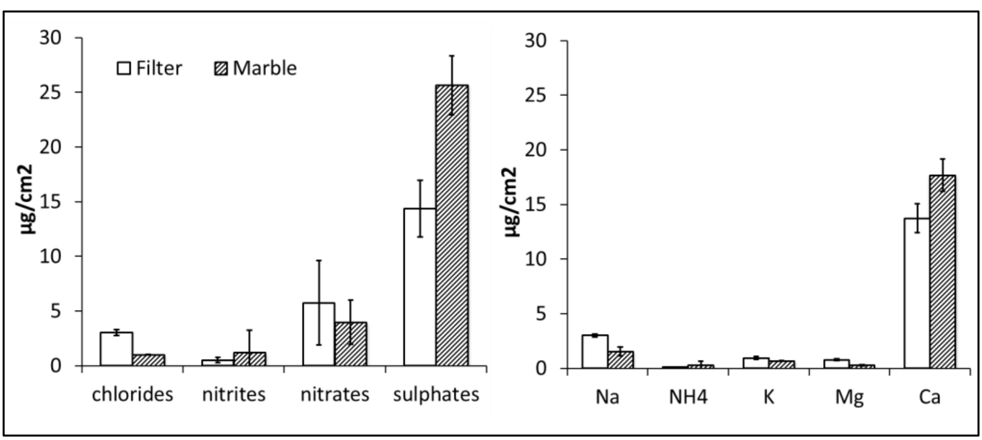

Fig. 3: Anions and cations content of deposit on quartz filter (white bars) and Candoglia marble specimens (grey bars) after six months of sheltered-condition exposition on the façade.

The evaluation of the soluble salts content of deposits collected on stone specimens and quartz filter after a six-month exposition period is reported in Fig. 3. The main ions concentrations determined in the two different cases are characterized by a comparable trend, thus confirming that the quartz filter represents a valid supporting material to collect the atmospheric particulate matter affecting the surfaces. Marble shows slightly higher concentrations of sulfate, nitrate and calcium. These differences could be partly due to early stage of sulfation process of the stone material.

3.1.2. Blackening

Surface blackening has been evaluated by colorimetric monitoring of fifty selected areas of the façade. The main parameter related to the blackening effect is the variation of L^* which effectively describe the darkening of the surface as a result of the deposit accumulation. The real façade surfaces have shown a high dispersion of the initial values of this parameter due to the very different conditions of the substrate respect to: orientation, finishing, material heterogeneity and, most of all, presence of substituted elements as a result of the conservative interventions and of the regular maintenance activity of the building. The initial value of L^* of the "original" surfaces (those belonging to elements not recently substituted) ranges from 50 to 75 units, whereas the values of the substituted elements is always above 85. A general trend for such diverse situations therefore cannot be traced. In Fig. 4 is reported, as an example, the evaluation of two surfaces characterized by the same orientation, location and overall geometry but with significantly different exposition period. The "original" horizontal sheltered upper surface of the sculpted element shows an initial L^* value of 51, which decrease of about 5 units at the end of the first year of monitoring. The substituted element shows a similar trend but with a lower variation in the same period (3 units), which can be related to the different surface condition of the marble characterized by a less weathered surfaces (as confirmed by on-site qualitative microscopic observation). Such surface can be considered as less prone to deposit accumulation due to its lower surface roughness.

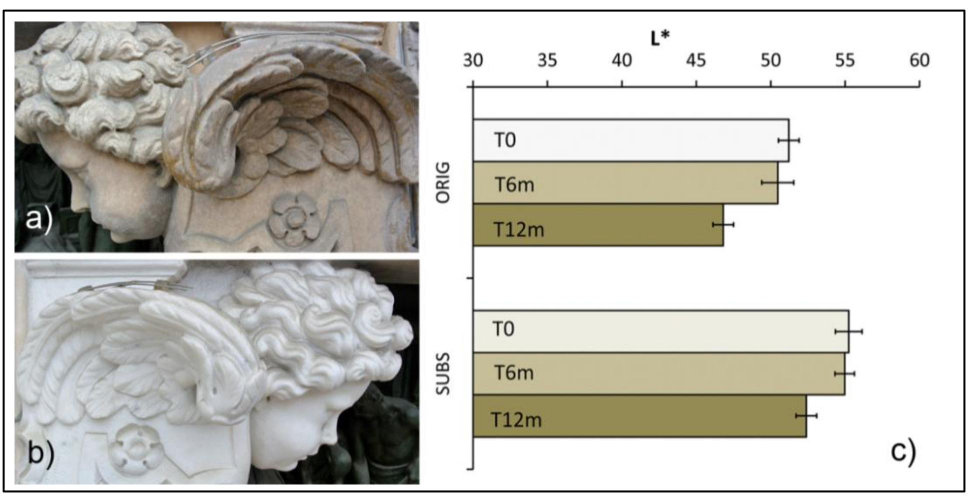

Fig. 4: Photographic documentation of two areas of the colorimetric monitoring characterized by the presence of "original" (a) and more recently substituted (b) marble elements; b) variation of the L parameter within the first year of monitoring.*

The generally limited *L** variations of the real areas have been compared to those of marble reference specimens, to properly take into account the non-linear trend of surface blackening (Brimblecombe & Grossi 2005). The results of the reference specimens exposed in the central area of the façade indicate a more significant and progressive reduction of the superficial lightness (Fig. 5, left). After the first exposition interval (6 months), the variation of *L** is around 4 units, thus being already barely detectable by the naked eye, and it reaches a final decrease of 14 units after 18 months. The *b** variations follow an opposite trend (Fig. 5, right) indicating that the deposit accumulation is characterized by a saturation of the yellow colorimetric coordinate, even though to a minor extent respect to the most relevant blackening effect. The final increase of the *b** value is limited to almost 4 units.

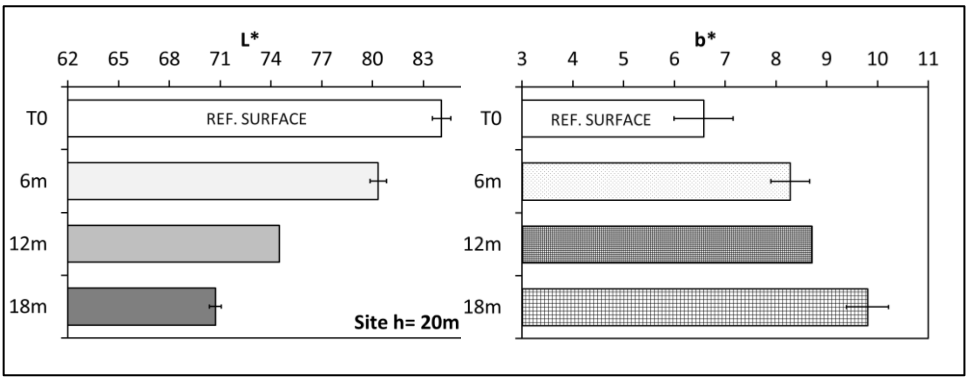

Fig. 5: variation of the L (left) and b* (right) parameters of Candoglia marble reference specimens within 18-month exposition in sheltered condition.*

3.2. Surface erosion

The surface erosion of marble due to the effect of direct rain wash and of run-off water flowing over the flat cladding slabs represents a major conservation issue that all the previous interventions had to deal with. Such mechanism is particularly efficient on the elements located on the top of the façade, such as the spires, and on the prominent sculpted figures of the lower register. The progressive erosive effects on the Candoglia microstructure are visible in Fig. 6, where the reference non-exposed material (Fig. 6a) is compared to fragments coming from a recently substituted element (Fig. 6b) and an "original" one (Fig. 6c). The grain morphology of the freshly sculpted marble is characterized by a very compact appearance, where the single grains show well defined regular borders and no discontinuities are present.

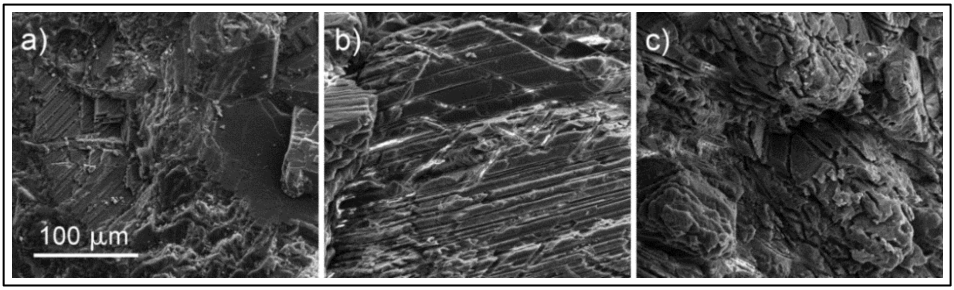

Fig. 6: ESEM documentation of the marble microstructure of a reference non-exposed material (a), compared to fragments from a recently substituted element (b) and from an "original" one (c).

As a result of the outdoor exposition, the erosive effect can be identified in the rounding of the grain edges and in the typical accentuated cleavage planes (Weber *et al.* 2007), which can be observed as parallel fissures. The prolonged exposition further enhances this deterioration pattern, leading to dramatic rounding of the grain and loss of material even on a macroscopic scale. The erosion extent has been monitored by laser profilometry on polished marble reference specimen exposed to the most severe non-sheltered façade condition.

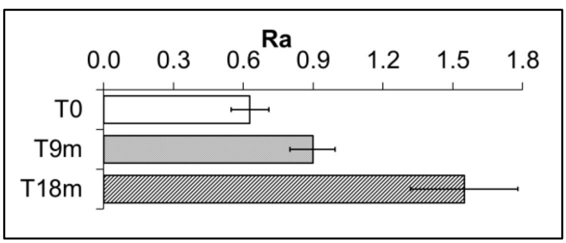

Fig. 7: Average surface roughness (Ra) of marble reference specimens evaluated after laser profilometry.

The decay effect has been evaluated respect to the variation of the surface roughness, as an indicator of the state of conservation of the superficial microstructure. The results show an increment of the average roughness as a result of the exposition, which is more than twice the initial one after 18 months of exposition (Fig. 7). Moreover, the higher standard deviation calculated for the final measurements is related to the increased surface irregularity (loss of material, formation of fissures, rounding effects) which is confirmed by the ESEM observations.

4. Conclusions

The diagnostic and monitoring approach for the real surfaces, supported by the study of the marble reference specimens, indicates that soiling is the main and most rapidly-evolving deterioration effect and is therefore expected to have a significant impact in the next future. Beside the carbonaceous fraction responsible for the surface soiling and blackening, the deposits composition showed high content of potentially harmful soluble compounds, which can react with the stone matrix leading to crystallization damages and crust formation. It therefore needs to be monitored over time. The deposition rate is confirmed to be particularly effective during the first stage of the exposition of the cleaned surfaces and tend to slow down over time. This suggests the importance of a proper planning of the monitoring activity, which should start at the very beginning of the post-restoration period. The enhancement of the surface roughness potentially leading to loss of material at a macroscopic scale is the main effect of the erosion mechanism in the non-sheltered areas. With respect to preventive conservation indications, the results point the attention to the need for further research to set-up sustainable methodologies for the periodic removal of the deposits and for surface protection to mitigate the marble corrosion effects.

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