

Surface Features of the Giovanni Rasori marble monument (1840, Milan): chemical characterization of degradation and past restoration interventions

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Abstract – The conservation of outdoor heritage in urban environments requires careful analysis of degradation processes induced by atmospheric pollutants. This study presents the results of a scientific investigation on the marble monument of Giovanni Rasori (1840), located in Milan, a city affected by heavy traffic and industrial emissions. Exposed for decades to an outdoor polluted environment, the monument exhibited visible signs of surface alteration. Analytical techniques, including SEM-EDX and ATR/FTIR, revealed that the primary degradation process was sulfation, confirmed by the presence of gypsum on the marble substrate. Moreover, the detection of Ti in localized areas of certain micro-fragments suggests the possible use of a whitening agent or pigment during past restoration works. Additionally, the co-presence of elements such as Si, Al, and Fe may be linked to atmospheric dust or to abrasive residues from earlier cleaning practices, such as micro-sandblasting, historically used in stone conservation. These findings contribute to a deeper understanding of marble surface transformations in polluted urban contexts.

I. INTRODUCTION

The conservation of monumental heritage in urban environments presents a complex challenge, particularly in highly industrialized areas. The city of Milan, located at the heart of the Po Valley, is subject to a combination of environmental and anthropogenic factors that make it one of the most polluted areas of the entire country. High urban

density, intense vehicular traffic, and significant industrial activity contribute to the accumulation and stagnation of atmospheric pollutants, which have well-documented effects not only on public health, but also on the preservation of historical materials exposed outdoors [1–3]. In the case of stone materials, prolonged exposure to such environmental conditions promotes multiple chemical and physical weathering processes, including the formation of black crusts [4–6], salts crystallization [6–8], atmospheric particulate matter deposition, and biological colonization. These phenomena can profoundly alter the original surfaces of stone artifacts, compromising both their aesthetic and structural integrity.

This study focuses on the Giovanni Rasori monument, a commemorative marble sculpture created in 1840 by Benedetto Cacciatori, a sculptor from Carrara, commissioned by the Ospedale Maggiore of Milan. Rich in symbolic iconography, the monument was originally located under the portico of the Ospedale Maggiore (now IRCCS Ca' Granda – Policlinico) and was later relocated in the courtyard of the Historical Archive during the 1960s, where it remained for decades, exposed to atmospheric agents and gradually undergoing visible deterioration (Fig. 1a). Following a conservation intervention carried out in 2024 by the Centro Studi e Conservazione del Piccolo Chiostrò, a scientific investigation was carried out aimed at characterizing the surface and the degradation patinas. The subject of this case study is the marble Monument to Giovanni Rasori, a renowned hospital physician who died in 1837 after a long and distinguished career. The decision

to commemorate him was made in 1838, followed by a public fundraising campaign in 1841. The monument construction was entrusted to the acclaimed sculptor Benedetto Cacciatori (1794–1871), a Neoclassical school artist from Carrara, who created the marble work with a rich symbolic iconography (Fig. 2).



Fig. 1. Location of the Giovanni Rasori monument before (a) and after (b) the 2024 restoration. a) outside the Historical Archive; b) inside the vestibule of the Archive, Milan.

The composition is dominated by a female figure, presumably Hygieia, the goddess of health and hygiene, embracing the sculpted bust of the physician. Above, the owl of Athena, resting on a book, symbolizes wisdom, while the Rod of Asclepius, entwined by a serpent, represents the medical profession. On the right, a stork symbolizes filial piety [9-10]. The monument is surmounted by a bas-relief depicting an owl resting on a bed of flowers. The marble monument measures 242 cm in height and 115 cm in width [9-10]. Originally located under the portico of the courtyard of the IRCCS (Scientific Institute for Research, Hospitalization and Healthcare) Ca' Granda Foundation, Ospedale Maggiore Policlinico, located in the centre of Milan, the monument underwent an initial restoration in 1918, limited to a surface cleaning. During the post-war reconstruction, likely in the 1960s, the monument was relocated (possibly also subjected to undocumented restoration) into the courtyard of the Historical Archive (Fig. 1a), where prolonged exposure to atmospheric agents and pollutants progressively led to various forms of deterioration, including corrosion, surface deposits, and biological growth. In 2024, the monument underwent a new conservation intervention, carried out by the Centro Studi e Conservazione Piccolo Chiostrò. The sculpture was dismantled and transferred to a controlled indoor environment for conservation operations and was later reassembled and relocated to its current position in the vestibule of the Archive (Fig. 1b).



Fig. 2. Design of the commemorative monument to Giovanni Rasori, 1840, pencil and ink on paper, Milan, Historical Archive of the Ospedale Maggiore.

The primary objectives of these study were to identify the nature of degradation patinas present on the marble surface and to assess the possible presence of gilding traces on decorative areas of the monument.

II. MATERIALS AND METHODS

Sampling was carried out by collecting powders and micro-fragments from various areas of the monument with a scalpel (Fig. 3). Areas 1 and 2, which were affected by the same degradation patina, were grouped and analyzed as Sample 1. Similarly, areas 3 and 4 were combined and designated as Sample 2. In contrast, Samples 3 and 4 were collected from distinct locations (area 5 and 6, respectively) and analyzed individually. Details of these samples are provided in Table 1.

Table 1. List of samples collected from the Giovanni Rasori marble monument.

Sample	Description	Area	Sampling site
1	Fragment/ Powder	Area 1-2	Left side of floral decoration under the left wing
2	Fragment/ Powder	Area 3-4	Owl's head/Floral decoration under the right wing
3	Powder	Area 5	Right side of the floral decoration
4	Powder	Area 6	Flat surface parts under the floral decoration

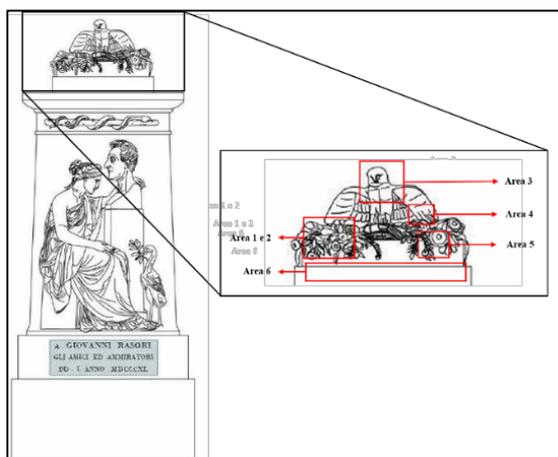


Fig. 3. Drawing of the Monument to Giovanni Rasori with the indication of the sampling areas. The image highlights the zones from which microsamples were collected for analytical investigation.

The morphology and chemical composition of the samples were investigated using SEM-EDX (Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy) to obtain qualitative and semi-quantitative elemental information. The instrument used was a Hitachi Tabletop Microscope - 4000Plus, equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED). Investigations were performed also with Fourier-Transformed Infrared Spectroscopy (FT-IR). Infrared spectra were collected with a JASCO FT/IR-4X spectrometer integrated with ATR PRO ONE 4X accessory equipped with a diamond crystal. The spectra were acquired in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1} .

III. RESULTS AND DISCUSSION

SEM was used to acquire representative images of the sample surfaces. As an example, an image of Sample 1 acquired in SE (Secondary Electrons) mode is presented in Figure 4 (left). Moreover, a false-colour elemental map was obtained using EDX (Fig. 4, right), illustrating the spatial distribution of the main chemical elements.

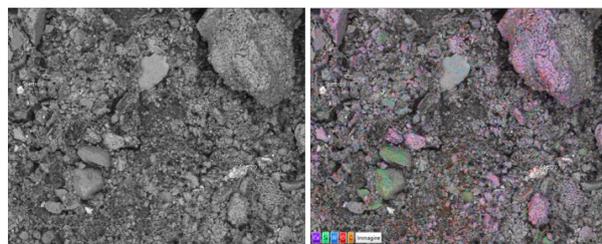


Fig. 4. SEM images of Sample 1. Left: micrograph in SE mode (Secondary Electrons). Right: false-color elemental map of the main chemical elements.

Overall, EDX analysis conducted on all samples revealed a chemical composition consistently dominated by C and Ca, consistent with a substrate primarily composed of calcium carbonate (Fig. 5).

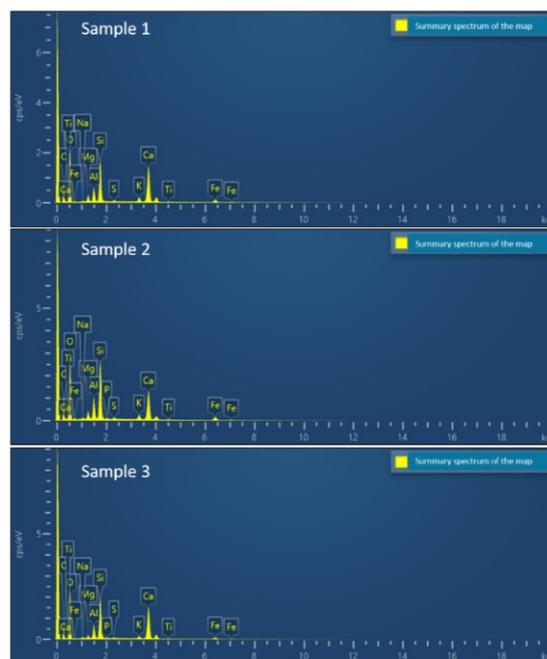


Fig. 5. EDX spectra of Samples 1, 2, and 3.

Of particular interest is the presence of titanium in all of the samples. The low intensity of the corresponding peak in the EDX spectra indicates a lower concentration compared to the other elements. However, additional analysis on micro-fragments (Fig.6) show a particular distribution indicating the intentional application of a titanium-based material, possibly used as a whitening agent or pigment during a past surface retouching or conservation treatment. Indeed, it is known that titanium dioxide (TiO_2) was widely employed in conservation and architectural coatings due to its excellent opacity and whiteness [11].

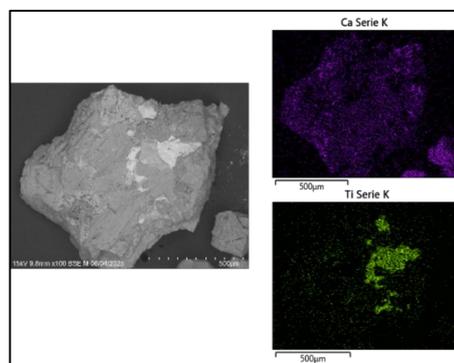


Fig. 6. SEM image and elemental maps showing the distribution of Ca and Ti of a micro-fragment.

Moving on, the simultaneous detection of aluminium, silicon, iron, potassium and magnesium, could be due to atmospheric particulate matter deposition (Fig. 7).

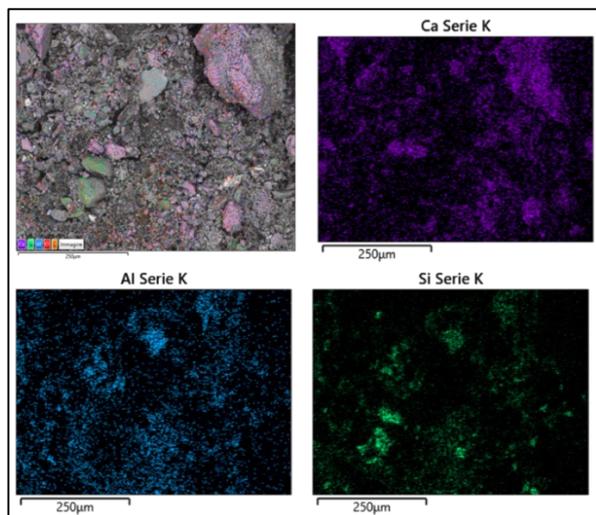


Fig. 7. SEM micrograph of a micro-fragment; false-colour elemental maps show the spatial distribution of calcium (Ca), aluminium (Al) and silicon (Si).

These particles, deposited through atmospheric transport and precipitation, are commonly found on stone surfaces exposed to polluted urban environments and can lead to the accumulation of alteration layers. A second hypothesis considers the possible historical use of abrasive cleaning techniques, particularly micro-sandblasting with alumina (Al_2O_3). This method was widely employed between the 1940s and 1960s for the removal of encrustations and surface deposits from stone materials. The alumina-based abrasives used at that time were often not chemically pure, consisting of natural or synthetic corundum with significant impurities of silica (SiO_2) and iron oxides (Fe_2O_3). The presence of these elements in the analysed samples is consistent with residues potentially associated with such treatments. These abrasive materials are known to leave persistent micro-residues on treated surfaces and to alter the substrate's microstructure, increasing both porosity and susceptibility to further degradation [12-13]. It is plausible that this type of intervention occurred during the post-war relocation of the monument to the courtyard of the Historical Archive, likely in the 1960s. The presence in low concentration of K and Mg in all samples can also be attributed to biological activity, such as colonization by algae, lichens, or microbial communities. These organisms are frequently observed in outdoor stone monuments and are associated with biodeterioration phenomena, both through physical biofilm formation and chemical action via metabolic by-products [14].

Furthermore, the co-presence of calcium and sulphur in Sample 1 (Fig. 8) suggests the formation of gypsum

($CaSO_4 \cdot 2H_2O$), a common indicator of the sulfation processes typically observed on calcareous stone surfaces exposed to urban environments [15-16]. These processes generally result from the interaction of airborne sulfur oxides (e.g., SO_2) with calcium carbonate in the presence of moisture, leading to the formation of sulphate minerals, black crusts, and granular disintegration.

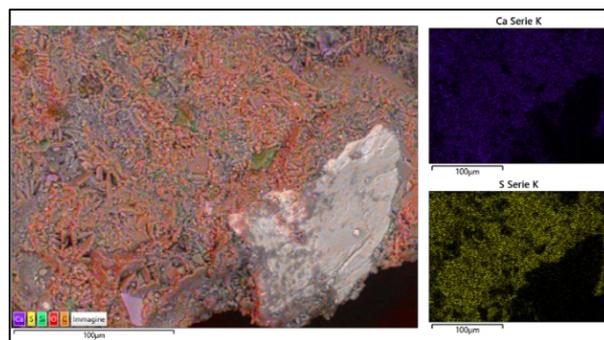


Fig. 8. SEM micrograph of sample 1; false-colour elemental maps show the spatial distribution of calcium and sulfur.

From the SEM images it was also possible to highlight the presence of several particles probably generated by combustion processes [15-16]. Most have a porous surface and a subspherical or irregular shape, around which newly formed gypsum crystals can be observed as in Fig. 9, while others are spherical with a smooth surface. SEM-EDX maps revealed that the porous particles were mainly composed of sulphur and carbon, with lower amounts of iron and, in some cases, also silicon and calcium. These were likely carbonaceous particles containing iron oxides, originating from the combustion of fuel oil used in domestic heating systems, as reported in the literature [15-16]. The smooth spherical particles, on the other hand, were mainly composed of iron and lower amounts of silicon and aluminium, with the typical composition of coal combustion particles (Fig. 7) [17].

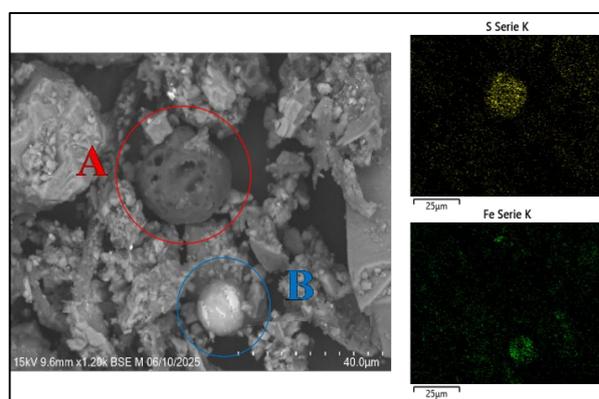


Fig. 9. SEM micrograph in BSE (Back-Scattered Electrons): (A) sub-spherical particle with a porous

surface; (B) spherical particle with smooth surface;
sulphur and iron chemical distribution map of the same
area.

ATR-FTIR spectroscopy performed on the powdered samples enabled the identification of the main mineralogical components as well as some organic functional groups (Fig. 10). All samples exhibited intense signals attributable to calcite, with characteristic peaks located at approximately at 1796, 1397–1403, 871, and 713 cm^{-1} , confirming the predominance of calcium carbonate (CaCO_3) as the primary lithic substrate. In Sample 1, the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was clearly identified based on its diagnostic OH and sulfate bands at 3525, 3395, 1682, 1618, 1106, 1001, 669, and 599 cm^{-1} . This finding supports the hypothesis of sulfation-related alteration, as previously suggested by the results of SEM-EDX analysis.

Moreover, quartz was detected in both Sample 1 and Sample 3, as indicated by the bands at 798 and 779 cm^{-1} , and in Sample 3 additionally at 1083 and 513 cm^{-1} . Moreover, Sample 3 exhibited a band at 1030 cm^{-1} , consistent with the presence of silicates. These mineral species may derive from terrigenous dust deposited on the surface or be attributed to residues from previous restoration treatments, such as abrasive materials.

Finally, all samples showed a weak but distinct carbonyl ($\text{C}=\text{O}$) band in the range of 1745–1750 cm^{-1} that could be due to the presence of organic residues, such as degraded binders or conservation products. Nevertheless, the absence of characteristic aliphatic $\text{C}-\text{H}$ stretching bands around 2900–2800 cm^{-1} makes the presence of a well-preserved organic component unlikely.

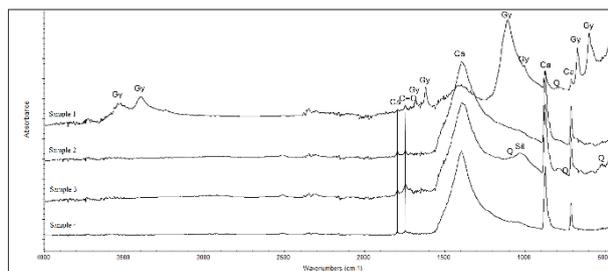


Fig. 10. ATR-FTIR spectra of the analysed samples. Gy = Gypsum; Ca = Calcite; Q = Quartz; Sil = Silicates; Q = Quartz.

IV. CONCLUSIONS

The diagnostic investigations conducted on the marble monument to Giovanni Rasori allowed the identification of the main degradation processes affecting the marble surface. SEM-EDX and ATR-FTIR analyses revealed that sulfation, with the formation of gypsum is the predominant phenomenon, associated with the interaction between the polluted urban environment and the carbonate-based

substrate of the artwork. The localized detection of titanium suggests the possible application of titanium dioxide-based products. Similarly, the co-presence of silicon, aluminium, iron, magnesium and potassium may be attributed to atmospheric terrigenous or anthropogenic dust, as well as to residues of siliceous abrasives, potentially associated with undocumented micro-sandblasting practices, which were commonly used in the past for cleaning stone surfaces.

These findings highlight the complexity of the observed alteration phenomena and the influence of previous undocumented treatments on the conservation history of the monument.

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