



Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en



Modern and contemporary art

The deterioration of Apuan white marble in contemporary architectural context

Francesca Gherardi^{a,*}, Chrysi Kapridaki^b, Marco Roveri^a, Davide Gulotta^a,
 Pagona Noni Maravelaki^b, Lucia Toniolo^a

^a Politecnico di Milano, Department of chemistry, materials and chemical engineering “Giulio Natta”, Piazza Leonardo da Vinci 32, 20133 Milan, Italy

^b Technical University of Crete, School of architecture, Polytechniopolis, Akrotiri, 73100 Chania, Crete, Greece

ARTICLE INFO

Article history:

Received 31 January 2018

Accepted 29 June 2018

Available online 19 July 2018

Keywords:

Marble

Discoloration

Contemporary architecture

Cladding

Granular decohesion

ABSTRACT

The conservation of contemporary buildings is particularly challenging as only few information about their degradation and guidelines for their maintenance are available and at the same time, despite their architectural importance, the attention and caring procedures are not adequate to safeguard standards. The Oslo Opera House is a high-standing contemporary architecture (opening 2008) characterized by a large ornamental pavement mainly made of Apuan marble slabs. After a few years, large parts of the marble surface suffered from a marked yellow discoloration and dirt accumulation. In this context, the current research was carried out aiming at assessing the state of conservation of the marble slabs and investigating the causes of their discoloration, to suggest possible remediation and adequate maintenance procedures. Due to the extreme microclimatic conditions, a severe inter- and intra-granular decohesion of the calcite grains can be observed by microscopic analyses, while a surface corrosion phenomenon of the crystals is in progress. The chemical analyses of surface stone material from the slabs allow the detection of deteriorated organic by-products, as a result of the degradation of previous protective treatments, excluding the correlation of iron ions concentration with the discoloration. The state of conservation gathered so far was the starting point for the development of a tailor-made cleaning methodology of the marble cladding and a complete revision of the protective treatments and ordinary maintenance protocol.

© 2018 Elsevier Masson SAS. All rights reserved.

1. Research aim

This paper reports the results obtained from the analyses carried out on marble slabs used as floor, cladding and sloping roof of the Oslo Opera House in order to understand the causes of the intense yellow discoloration and to investigate their state of conservation, aiming to define new guidelines for the maintenance of the building.

2. Introduction

In modern and contemporary architecture, natural stone cladding has become the standard technology to protect and decorate concrete structures [1]. For high standard buildings, natural stones and particularly marbles with specific features, have been used by the architects in order to achieve desired external

aesthetical effects. Nevertheless, despite their coating function, it is well known that cladding materials generally exhibit a shorter service life than the building structure [2]. Several different deterioration patterns can occur depending on the atmospheric conditions to which they are exposed and on the nature and mineralogical characteristics of the material; the cladding technology and the used bedding and sealing materials should be also taken into consideration [3].

Metamorphic stones, and particularly white Carrara marble, a granoblastic crystalline calcitic material, is subjected to environmental deterioration because of the exposure in outdoor conditions to thermal excursions, solar irradiation, atmospheric pollution, rain washing and salt crystallization [4–6].

The deterioration of the Carrara marble façade of Alvar Aalto's Finland Hall in Helsinki, has been a very important case study and was deeply investigated [7]: in that case the most important decay phenomenon of the cladding slabs (30 mm thick) was an early pronounced bowing; the inter-granular decohesion of the marble (mainly on the convex surface), due to large thermal excursions in the northern climatic conditions, was assessed as the main cause

* Corresponding author.

E-mail address: francesca.gherardi@polimi.it (F. Gherardi).

of the deterioration of that specific marble quality; also a strong surface inter- and intra-granular decohesion was pointed out, due to chemical corrosion by acid rain washing [7] which concurred to increase the mechanical damage.

The Norwegian National Opera and Ballet was designed by Snøhetta Architects and built in Oslo in the period 2000–2008. The building represents a connection of the city with the fjord landscape: “Its low-slung form became a link within the city rather than a divisive sculptural expression. Its accessible roof and broad, open public lobbies make the building a social monument rather than a sculptural one” [8]. The construction of the Opera House is the largest single culture-political initiative in contemporary Norway, and is therefore of outstanding importance for the country and its population.

The building walkways and roof are paved by white Italian marble slabs (about 20,000 m² of horizontal slabs, 100 mm thick: roofs, floors and edges), while vertical surface cladding have been realized both with the same white marble (about 2000 m² of vertical slabs, 50 mm thick) and aluminum sheets (Fig. 1a–c) [9]. The selection of the stone material (among four different lithotypes) was carefully carried out after several aesthetic and durability tests and the white marble (commercial name: “Bianco Carrara La Facciata”) was supplied by Campolonghi Italia Spa (Carrara, Italy) [10]. The Architects at Snøhetta worked closely with different artists for the shape and size of the slabs and the surface finishing of marble [8]: actually, the slabs are forming a complex pattern of different surface textures (smooth, cuts, sharp edges, bush hammered) which give rise to a different light reflection and valorise the natural diversity of the metamorphic stone. In this respect, the coating slabs of the Oslo Opera House have an important artisanal value and their maintenance assumes a particular significance.

The problem of maintenance and cleaning of such a huge, highly frequented surface, has been pointed out since the very beginning of the construction. Actually, as reported in the official documentation, the marble slabs have been mounted with suitable technology

(different for horizontal and vertical surfaces) and once placed on-site (2008) all the surfaces were impregnated with Faceal Oleo HD (PSS Interservice AG, Switzerland), a fluoro acryl copolymer in an aqueous phase, to protect the crystalline structure, to prevent the accumulation of solid particulate and facilitate the cleaning operations. On the vertical surfaces, this treatment was followed by the application of PSS20 Clear (or Industry) (PSS Interservice AG, Switzerland), which is based on aqueous dispersion of vegetable polysaccharides for anti-graffiti purposes [9]. In addition, a siloxane-based product was also applied on the marble slabs in 2012.

Washing with high pressure (up to 150 bar) and hot water (60–70 °C) by manual and mechanical devices was carried out for the current maintenance in the period spring-fall on the sloping roof and roof areas, whereas a more frequent cleaning (three times per week) was followed in the square outside the entrance of the theatre. In the winter period, the horizontal surfaces are generally covered with snow.

The maintenance of marble surfaces in historical architecture (mostly vertical surfaces) and the specific requirements for cleaning procedures are well established [11], the main concept being the total respect of the original surface, especially of decorated and sculptured ones, and the set-up of a safe methodology in the specific context [12]. In the present case study, the great challenge is to protect and maintain a marble surface subjected not only to the atmospheric stresses connected to the severe climatic conditions but also to the mechanical damage (wear stress) caused by walking. The specific appearance, geometry and surface finishing of the large amount of slabs of this big, high value contemporary architecture, deserve particular attention for their conservation.

Soon after the opening in 2008, a light yellowing of some marble slabs in different areas on the roof (especially on the floor slabs of the sloping roof and of the roof) was evidenced by the curators. In the following couple of years, the color alteration increased in intensity and diffusion, and the phenomenon became more and

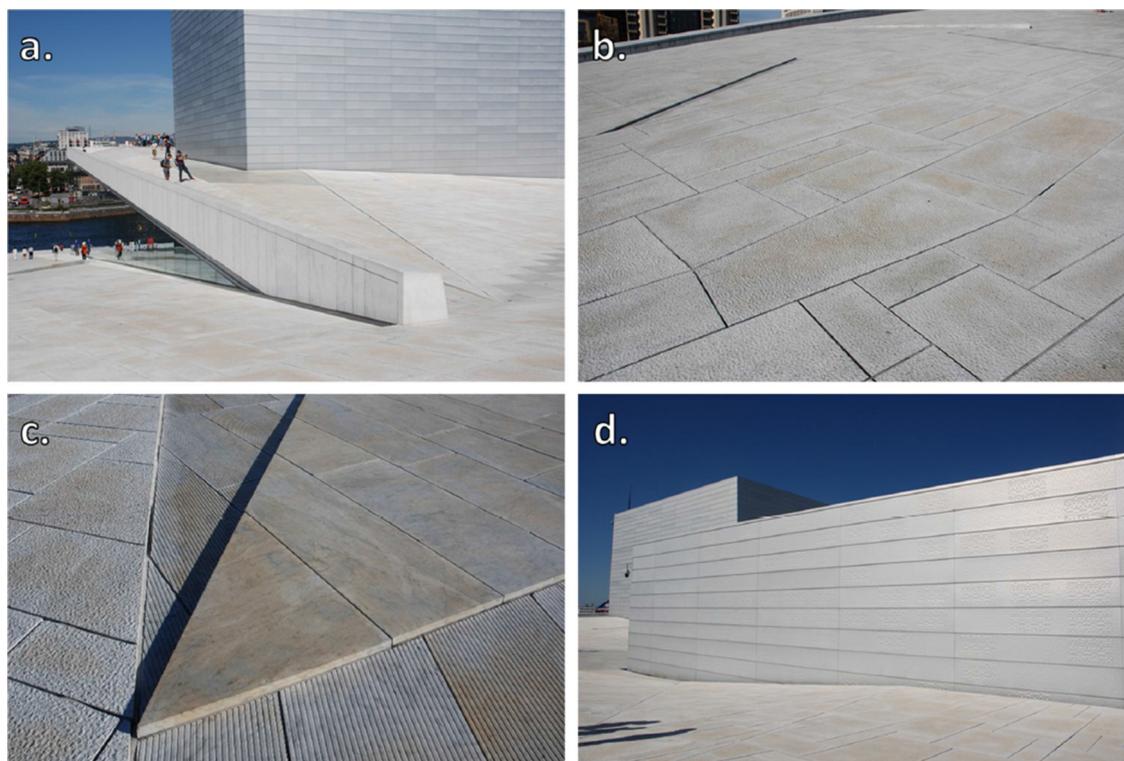


Fig. 1. The Oslo Opera House: a) vertical surface cladding and b) ornamental pavement slabs made of Carrara marble, characterized by c) different surface finishings; d) vertical surface cladding made of aluminum sheets.

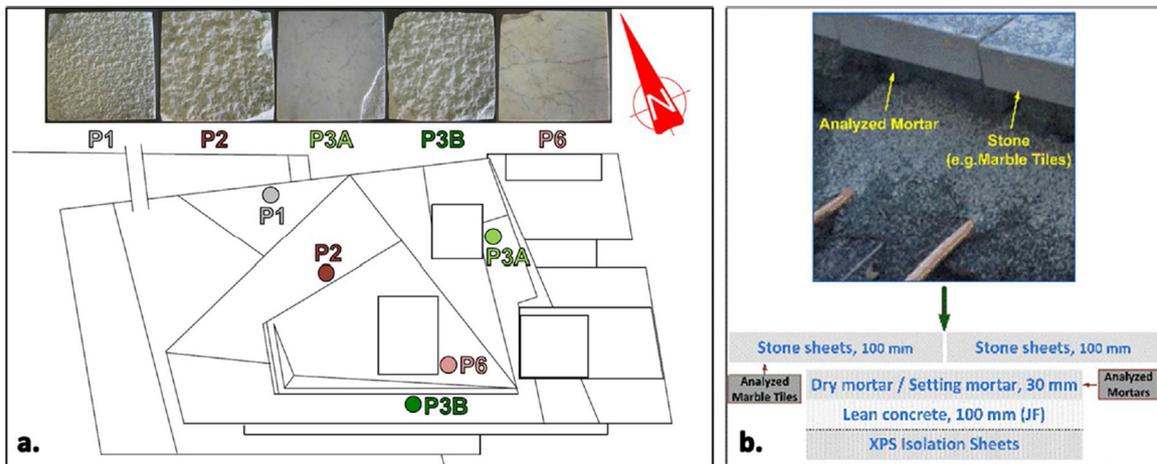


Fig. 2. Location and surface characteristics of the sampled marble slabs. a: P1, P2, P3A, P3B and P6 areas and their localization in the building plan; b: marble slabs mounting during construction and cladding technology and materials. Courtesy of Statsbygg [9].

more visible, compromising the aesthetical features of large areas especially on the roof terrace, on the staircase before the entrance and on the south front towards the sea [9]. As here reported, the yellowing is not only a surface phenomenon but it penetrates about 20 mm in the microstructure of the marble. The maintenance procedures were then revised, and different cleaning attempts were carried out without success.

This paper accounts for the results of the diagnostic campaign that was set-up and carried out to understand the causes of this alteration and to assess the state of conservation of contemporary marble slabs in the context of Oslo's fjord and after the above mentioned treatments. This investigation constitutes the basis to set-up new guidelines for maintenance (cleaning and protection) of the white marble of the Oslo Opera House. This paper aims also to draw the attention on the safeguard of high value contemporary architecture and the development of strict regulations about their conservation.

3. Materials and Methods

3.1. Marble and mortar samples

The marble used in the building (Bianco Carrara La Facciata) is a calcitic marble that shows flexural strength value of 17.2 N/mm² measured on a sawed sample with 300 × 50 × 50 mm size. In addition, the marble exhibits 0.11% by weight of water absorption [10]. Carrara marble slabs (100 mm thick) from Oslo Opera House were demounted from the floor in different areas of the building (P1, P2, P3A, P3B and P6), as reported in Fig. 2. Small marble slabs from the slabs with dimensions of 200 × 200 × 100 mm, 150 × 150 × 100 mm and 150 × 150 × 80 mm were cut and sent to the laboratories in Italy and Greece. According to the data available from Snøhetta Architectural Studio which conceived the building, the slabs are characterized by different surface finishing: P1 slab has a “heavy bush hammered” finishing, P2 and P3B slabs have a “rough bush hammered” finishing and P3A and P6 slabs have a “sawn” finishing (Table 1 and Fig. 2a). Some polished slabs were cut from the internal part of a Carrara marble slab “not exposed” on the roof of the building but conserved in the backyard of the Oslo Opera House, as not-deteriorated material. From the bulk of this slab, more than 3 cm under the surface, some small prisms representative of the internal morphology of the marble were cut and examined and considered as reference sample for the unaltered material (labelled as Reference). Moreover, mortars used as bedding materials for the Carrara slabs were also collected from the same areas. The mortars

Table 1

Surface finishing and location of the sampled marble slabs.

Sample	Surface finishing	Location in the building
P1	Heavy bush hammered	Floor slab, sloping roof
P2	Rough bush hammered	Floor slab, sloping roof
P3A	Sawn	Floor slab, roof
P3B	Rough bush hammered	Floor slab, sloping roof
P6	Sawn	Floor slab, roof

were cut in dimensions of 80 × 80 × 20 mm and send to the Labs (Fig. 2b). These samples were analysed in order to assess a possible migration of staining compounds from inward towards the exposed Carrara marble surface. The marble mortars were named as P(number of area)MR and analysed from the surface part close to Carrara marble slabs (0 mm) to a depth of 20 mm from the surface.

3.2. Color investigation

VIS spectrophotometric measurements were carried out on the surface of each sample slab with a Konica Minolta CM-600D instrument with a D65 illuminant at 8°, wavelength range between 360 nm and 740 nm. Measurements were, then, elaborated according to the CIE L*a*b* standard color system. Hundred and eighty measurements were performed on each area (200 × 200 mm) of exposed and unexposed marble slabs. The average results of L*a*b* were used to calculate the color difference ΔE^* ($\Delta E^* = [(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2]^{1/2}$) between the exposed and the reference marble slabs.

3.3. Morphological observation of samples

From each slab, different micro-samples were collected from the surface. They were observed with a Leica M205 C stereomicroscope equipped with a Leica DFC 290 video camera. Then, the morphology of the stone specimens was analysed by Environmental Scanning Electron Microscopy (ESEM) and EDX analyses (Zeiss EVO 50 EP ESEM, equipped with an Oxford INCA 200 – Pentafet LZ4 spectrometer). The exposed surface, fresh fractured surface and the polished cross-section of the samples were investigated.

3.4. Characterization of the marble slabs surface material

In order to identify the protective treatments applied to the surface of both the unexposed and exposed marble slabs, a small amount of powder was collected from the surface by a scalpel

Table 2
Colorimetric coordinates L^* , a^* and b^* obtained from the exposed marble slabs (P1, P2, P3A, P3B and P6) and the unexposed one (Reference) and ΔL^* , Δa^* , Δb^* and ΔE^* values measured compared to the Reference.

	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Reference	85.0 ± 2.0	-0.74 ± 0.09	0.8 ± 0.3	–	–	–	–
P1	73.0 ± 1.0	0.6 ± 0.2	10.0 ± 1.0	–12.0	1.3	9.0	15.0
P2	71.0 ± 2.0	1.3 ± 0.4	13.0 ± 1.0	–14.0	2.0	12.0	19.0
P3A	79.0 ± 2.0	0.0 ± 0.3	7.0 ± 1.0	–6.0	0.7	6.0	9.0
P3B	74.0 ± 1.0	0.3 ± 0.2	8.1 ± 0.8	–11.0	1.0	7.3	13.0
P6	72.0 ± 2.0	1.1 ± 0.4	13.0 ± 2.0	–13.0	1.8	12.0	18.0

and a solvent extraction was carried out using the following solvents or combination of solvents: hexane, acetone, chloroform, methanol (Sigma–Aldrich) and white spirits (CTS srl). The liquid extracts were deposited on KBr window and then analysed by Fourier-Transform Infrared Spectroscopy (FTIR), using a Nicolet 6700 spectrophotometer equipped with a DTGS detector (acquired between 4000 and 400 cm^{-1} with 128 scans and 4 cm^{-1} resolution), after solvent evaporation. For comparison, two surface coatings applied for the protection of the marble slabs (Faceal Oleo HD and PSS 20, PSS Interservice AG, Switzerland) were analysed by FTIR in the same conditions. In addition, from each sample slab under stereomicroscopy, surface residues of extraneous materials were collected with a pin and analysed by a Nicolet Continuum FTIR microscope equipped with a MCT detector (acquired between 4000 and 600 cm^{-1} with 128 scans and 4 cm^{-1} resolution) using a micro-compression diamond cell accessory.

DTA-TG simultaneous measurements were carried out in dry nitrogen atmosphere (100 mL min^{-1}) within the temperature range of 25 – $1000\text{ }^\circ\text{C}$ using a Setaram thermobalance with temperature and weight precision of $0.1\text{ }^\circ\text{C}$ and $0.1\text{ }\mu\text{g}$, respectively. Approximately 15 mg of finely pulverized sample, dried in oven at $70\text{ }^\circ\text{C}$ for at least 48 h , weighed on aluminium oxide crucibles, was heated in a nitrogen atmosphere flow adopting a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were carried out on 2 sets of Carrara marble samples ($50 \times 5 \times 5\text{ mm}$) cut from the P6 slab, collected at different depths from the surface: 5 mm , 10 mm , 15 mm , 20 mm and 25 mm . The marble samples were mineralized with nitric acid and analysed with a Perkin Elmer Optima 8300 ICP-OES. P6 sample was selected because representative of intense yellow discoloration both on the surface and in depth of the matrix (about 20 mm).

3.5. Characterization of mortar samples

The mortar samples were examined by infrared spectroscopy (FTIR, Perkin Elmer system 1000). The samples were homogenized with KBr and pressed to obtain a pellet with the aid of a vacuum hydraulic press. The spectra were recorded with a spectral resolution of 4 cm^{-1} and 100 consecutive scans were added and averaged before Fourier-transform, in order to obtain good signal-to-noise ratio. All spectra were collected in the absorbance mode. As background, the spectrum of the KBr pellet was used.

The Energy Dispersive X-Rays Fluorescence (EDXRF) with 109Cd and 55Fe radioactive sources, Si(Li) semiconductor detector (resolution 150 eV at 5.9 keV), TC-244 Spectroscopy Amplifier, PCA-II Nucleus Multichannel card, AXIL (RN) computer program analysis was employed for qualitative and quantitative analyses of the samples. The mortar samples were prepared by collecting powder from the upper and lower surface of the supplied specimens with the aid of a scalpel in order to cover the whole surface. For the quantitative analysis of samples, the most appropriate quantification was applied and checked on standard samples [13].

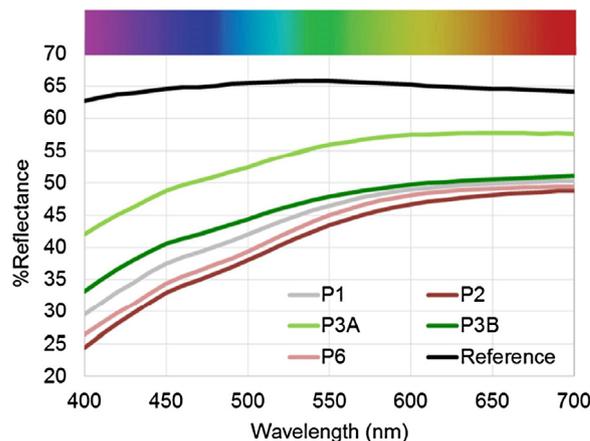


Fig. 3. Reflectance spectra obtained from Vis spectrophotometric measurements on unexposed (Reference) and exposed (P1, P2, P3A, P3B and P6) slabs.

4. Results and discussion

4.1. Investigation of the color of marble surfaces

VIS reflectance measurements of both unexposed and exposed surfaces of marble samples provide a quantitative basis to the visual perception of the alteration of color. Compared to the reference sample, P1–P6 slabs exhibit a remarkable decrease in L^* , that accounts for a loss of brightness, and an increase in b^* values which represents the saturation of the yellow component in the CIE $L^*a^*b^*$ system (Table 2). Reflectance curves (Fig. 3) display a general decrease in reflectance values as compared to the white reference marble slab and a marked decrease at wavelengths lower than 500 nm with shoulder peaked at 450 and around 570 nm . Indeed, the former feature can be linked to the decrease of the observed L^* values while the two shoulders account for the general yellowing. Among them, P2 and P6 slabs are those showing a more intense discoloration with an increase of b^* coordinate of 12 units (Table 2 and Fig. 3).

4.2. Evaluation of the crystalline morphology of marble surface

The crystal structure of the unexposed reference slab is very compact and the boundaries of calcite grains are almost not visible (Fig. 4b and c). This morphology, which is peculiar of a sound Apuan marble microstructure, can be highlighted also in the cross-section observations (Fig. 6a). The surface of exposed slabs is rather different, as far as an intense decohesion of the crystal fabric can be detected [7,14]. The grain boundaries can be clearly perceived with rounded edges and detachment empty spaces creating a network of microfissures (Fig. 4e, f, h and i and Fig. 5b–f). Moreover, in the calcite crystals of hammered slabs (P1, P2, P3B), the cleavage planes are evidenced with the appearance of internal subparallel lines due to an ongoing intragranular corrosion phenomenon in the initial phase (Fig. 4f and Fig. 5b, c and e). Observing the cross-

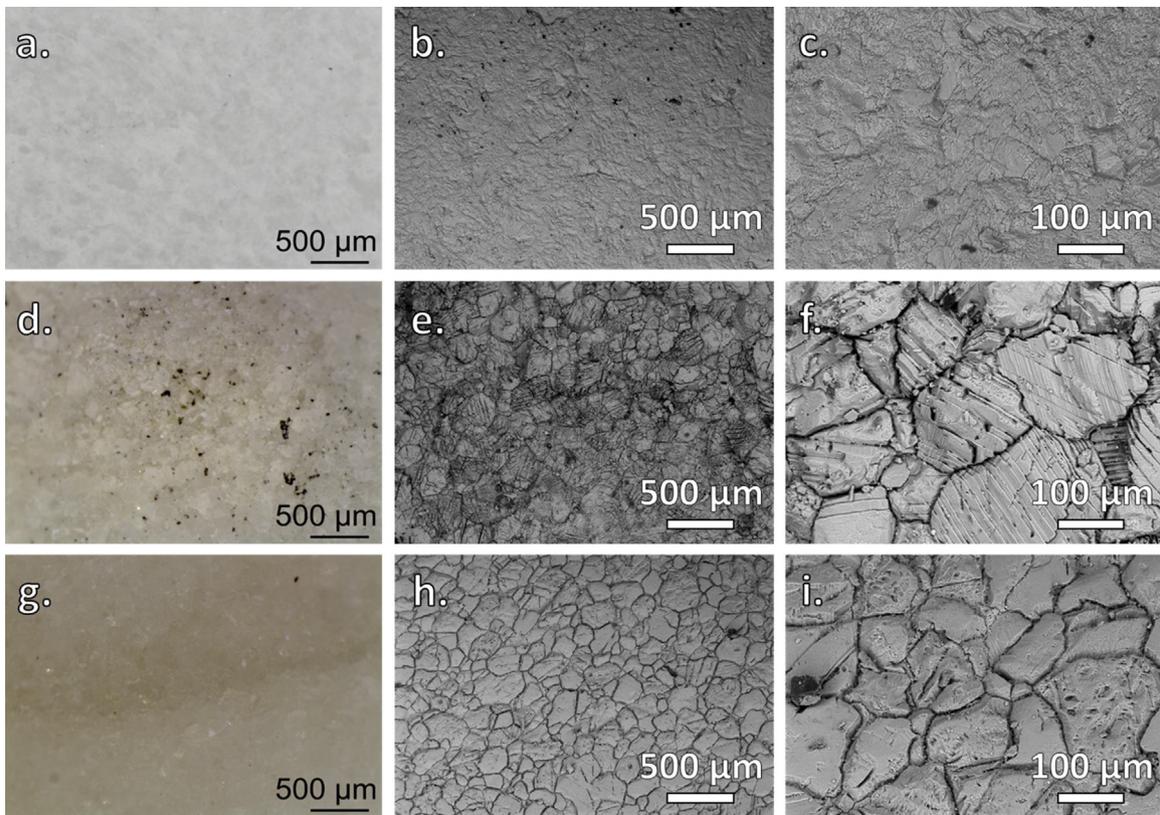


Fig. 4. Optical and BSE-ESEM images of surface of unexposed reference (a, b, c) and exposed P1 (d, e, f) and P6 (g, h, i) slabs.

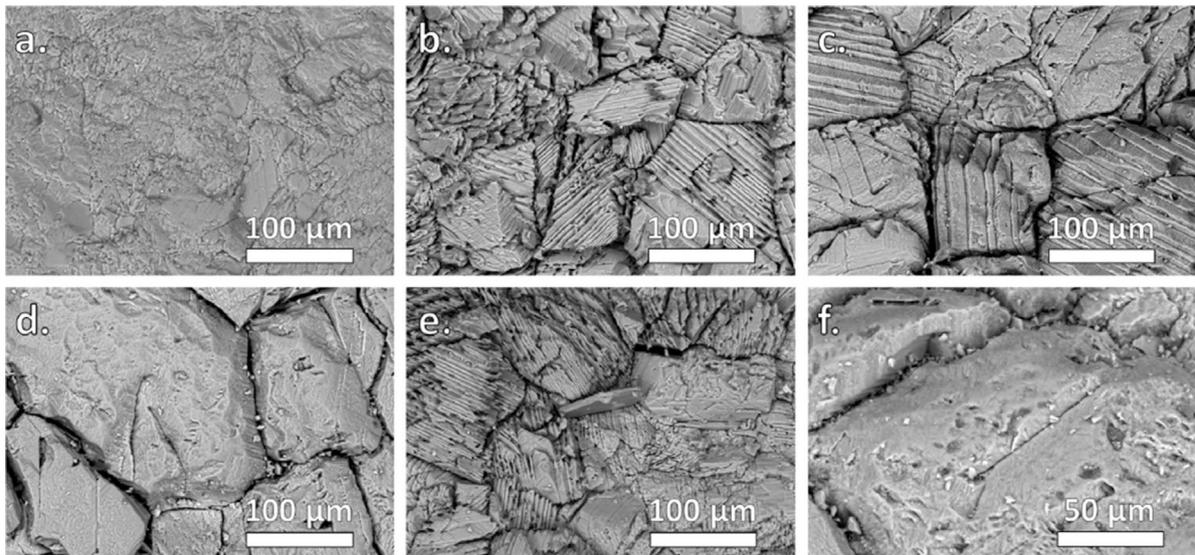


Fig. 5. BSE-ESEM images of surface of unexposed reference (a) and exposed P1 (b), P2 (c), P3A (d), P3B (e) and P6 (f) slabs.

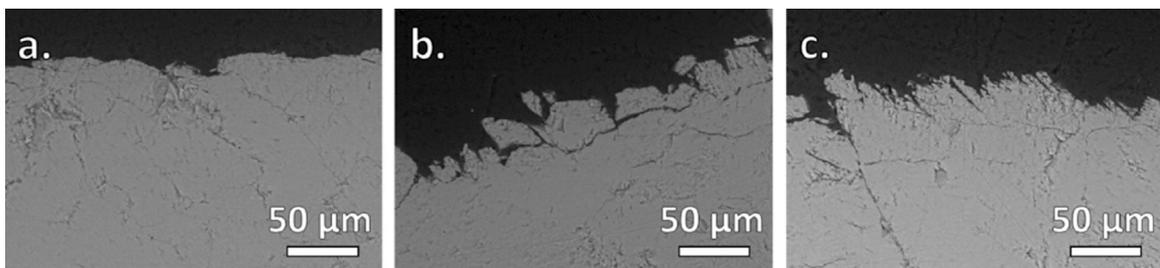


Fig. 6. BSE-ESEM images of cross-sections of unexposed reference (a) and exposed P2 (b) and P6 (c) slabs.

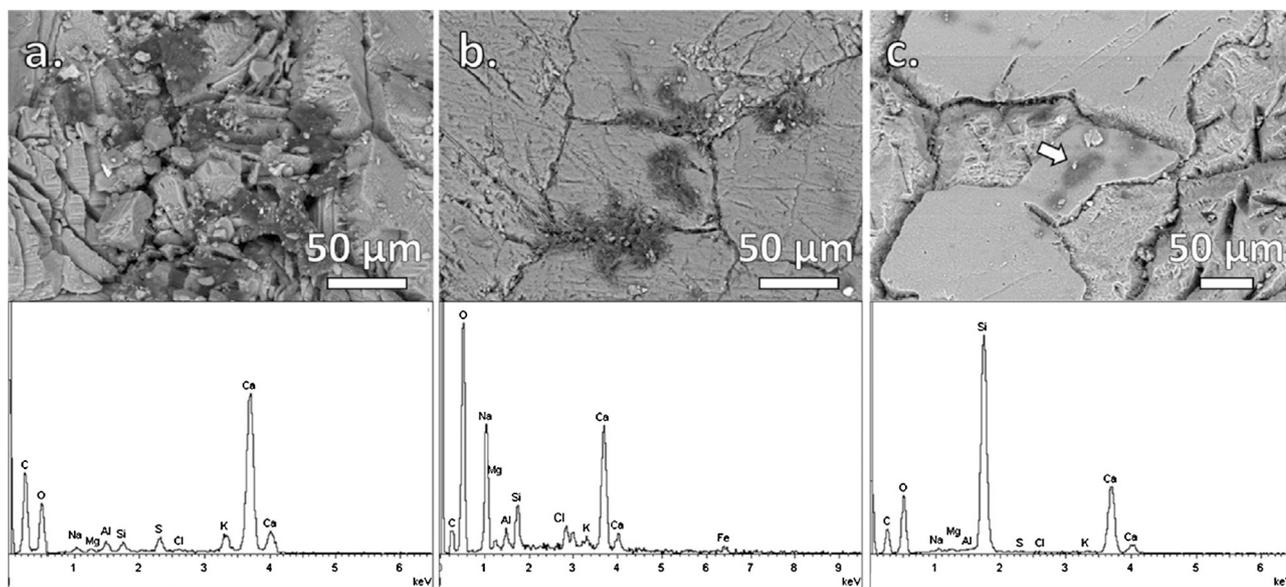


Fig. 7. ESEM-EDX images of deposits on the surface of exposed P3B (a and b) and P6 (c) slabs and elemental composition of the deposits.

sections of P1, P2, P3B slabs the surface is characterized by the network of microfractures (more than 200 μm inside the bulk of the material) and the incipient detachment of corroded surface grains (Fig. 6). Slabs with a “sawn” finishing exhibit a crystalline microstructure with the same intergranular decohesion, whereas the single grain shows a better preservation of the internal crystalline microstructure (Fig. 4h and i). Only some isolated crystals are deteriorated and corroded, with microfractures that can be noticed on the surface at higher magnification (Fig. 4i and Fig. 5d and f). By observing the cross-section of the samples collected from P6 slab, one of the most altered in color, high granular decohesion can be observed not only on the surface (Fig. 6c), where the grains are detached, but also inside the sample till about 2 mm. It is well evident that the different finishing surface working determine a different reaction of calcite grains towards environmental corrosion. The degradation phenomenon of the crystalline microstructure should be primarily ascribed to thermal excursions due to severe microclimatic condition in Oslo, subjected to frequent and long freezing-thawing cycles [7,14–16]. In addition, surface erosion phenomena caused by weather precipitations (rain and snow) and salt crystallization cycles due to Cl^- containing marine spray and therefore cyclic dissolution and re-crystallization of halite (NaCl) inside the surface porosity of the stone can play a significant role in the observed surface decay. The surface finishing of the marble slabs can have influenced their state of conservation, as the hammered ones evidenced a more intense corrosion and damage of the crystal grains.

Compared to the unexposed slab (Fig. 4a), the exposed ones exhibit a general yellowing and brown/grey surface particulate deposit (Fig. 4d and g). In particular, the yellow discoloration penetrates in the marble for about 20 mm (Figure S1). At higher magnifications, solid materials with different morphologies can be observed (Fig. 6). The elemental compositions of the deposits show Na, Mg, Al, Si, S, Cl and K peaks related to environmental deposits and sea spray (Fig. 7a and b). It is important to highlight that on the yellowed surface of the exposed slabs, iron (Fe) was scarcely detected by EDX analyses, and only very few grains of pyrite can be observed, pertaining to the mineral composition of the marble. On the “sawn” slabs (P3A and P6) the surface deposits accumulate both on the surface and inside the micro-cavities of the grains. In particular, some darker areas in BSE can be evidenced with the accumulation of “drops” of organic materials (Fig. 7c). The elemen-

tal analysis of these areas exhibits high peaks of Si and C (Fig. 6c) that can be ascribed, therefore, to organosilicon treatments applied on the surface (these materials have been also investigated by micro-FTIR spectroscopy). Moreover, on the surface of some grains from the sample collected from P6 slab, a sporadic accumulation of organic deposit, characterized by the presence of F, C and Si in the EDX spectrum, was detected. As already reported in the introduction, the application of a fluorinated protective product, a “fluor acryl copolymer” was carried out just after cladding.

4.3. Chemical characterization of surface materials of marble slabs

The FTIR spectra (Fig. 8a) of the hexane extracts obtained from the surface of four different slabs (P1, P2, P3A, P6) show a pattern of absorption peaks at 1020 and 1090 cm^{-1} (Si-O-Si stretching), 1260 cm^{-1} (Si- CH_3 bending), 800 cm^{-1} (Si- CH_3 rocking) and from 2950–2850 cm^{-1} (C-H stretching). These signals indicate the presence of a polysiloxane macromolecule [17–20], as the comparison with the reference spectrum of one of the most common siloxanes, i.e. polydimethylsiloxane (PDMS), clarifies (Fig. 8a). The finding of such product is plausible, since, to the best of our knowledge, a siloxane-like product was most probably applied on marble slabs in 2012, yet the chemical composition of this coating remains unknown to us, hence it must be emphasized that the reported reference spectrum does not necessarily refer to the product actually applied few years ago on marble. Moreover, further signals can be observed in the spectra of the materials extracted with different organic solvents, which clearly point to the co-presence of other organic compounds. Indeed, the peak around 1740 cm^{-1} (C=O stretching of esters) and the multiple peaks in the range from 1650–1510 cm^{-1} (not readily interpretable but possibly comprising the COO^- stretching vibrations of carboxylate ions) suggest the presence of esters and carboxylates [21], while the wide band between 3800–3300 cm^{-1} (O-H stretching) is evidence of the presence of free hydroxyl groups. These signals were observed in the spectra of extracts up to several millimeters under the surface, extending as deeply as the yellowing of marble, whereas signals ascribable to the siloxane backbone were only detected on the marble surface. Their co-extension with the yellowing suggests that they may be degradation products, with a likely implication in the discoloration of marble, yet their source and formation mech-

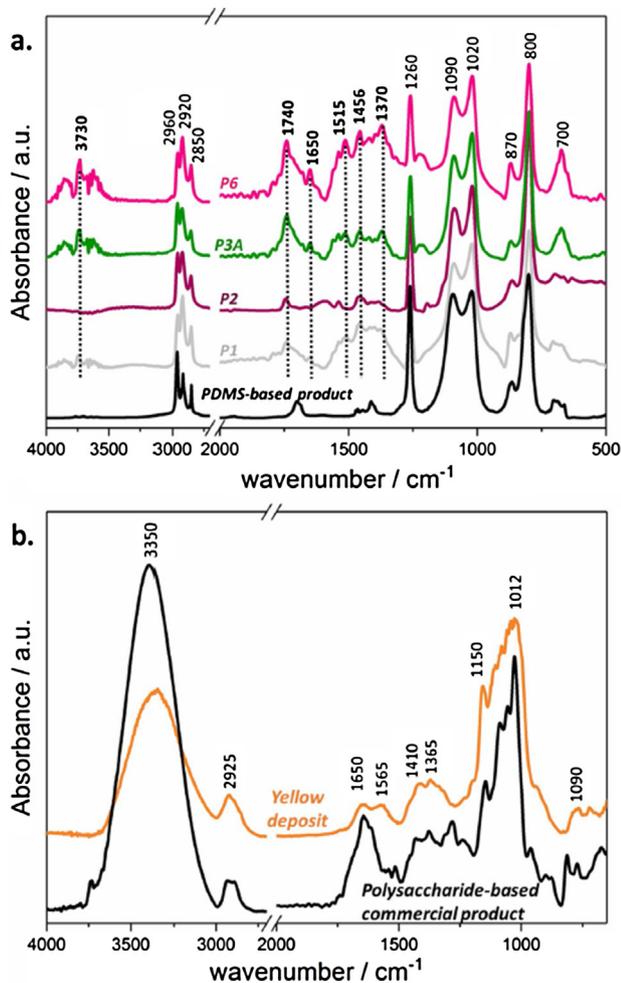


Fig. 8. a: FTIR spectra of the extract with hexane from surface powder of P1, P2, P3A and P6 slabs and the spectrum of a reference poly(dimethylsiloxane)-based product (PDMS); b: FTIR spectrum of a yellow deposit collected from P1 slab and the spectrum of the polysaccharide-based commercial product (PSS20).

anism are open to speculation and FTIR analysis does not provide any conclusive evidence thereon. Since the yellowing had already appeared on marble slabs when the polysiloxane coating was first applied, it might be speculated that the degradation process is related to one of the treatments applied earlier (2007–2008), i.e. Faceal Oleo HD (a fluorinated acrylic copolymer) and PSS20 (a polysaccharide based material). The cleaning procedure carried out with hot water, high pressure and with the addition of an alkaline cleaning product could have also played a role in the degradation of the protective treatments.

The FTIR spectra (Fig. 8b) of the localized yellow-brown deposits collected from the surface of marble slabs show the typical features of a polysaccharide compound. This is evident through the strong absorption bands around 3350 cm^{-1} and from $1000\text{--}1150\text{ cm}^{-1}$, which are typically the most intense signals in the spectra of polysaccharides, related to the O-H and C-C-O stretching vibrations, respectively [22]. Furthermore, a comparison with the spectrum (Fig. 8b) of PSS20, the commercial anti-graffiti product that was applied on marble slabs in 2007–2008 and is based on a natural polysaccharide, indicates with strong probability that the yellow-brown deposits are residuals of this treatment. Among the other signals, a peak at 1650 cm^{-1} can be noticed. This peak is difficult to assign univocally, but, according to one reasonable hypothesis, it may be related to the O-H bending vibration of adsorbed water, which can be found in variable content in the spectra of these com-

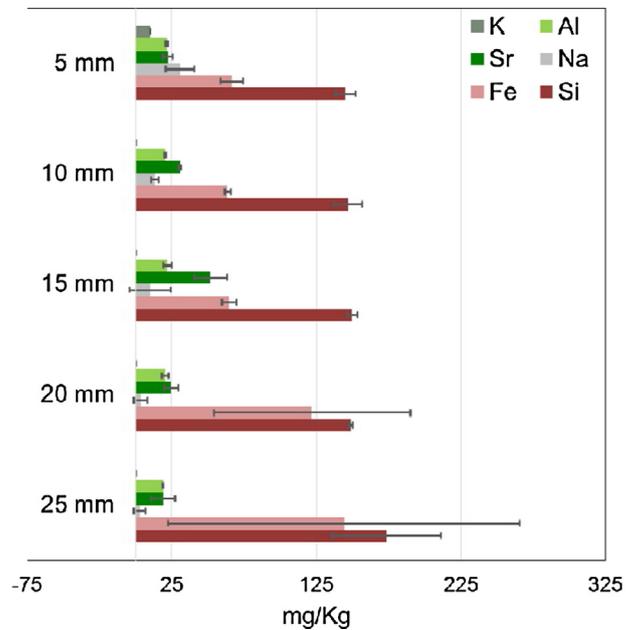


Fig. 9. Average elemental composition (mg/Kg, ppm) obtained by ICP-OES of 2 sets of samples collected from P6 slab at different depth from the external surface: 5, 10, 15, 20, 25 mm.

pounds [22]. It is important to underline that, despite of their color, these deposits do not represent the main origin of the extended yellow discoloration of the marble.

By observing the cross-section of the marble slab perpendicular to the external surface, it has been evidenced that the yellowing phenomenon affects a thickness of about 20 mm inside the stone material (Figure S1). Two sets of samples collected from the P6 marble slab were analyzed by ICP-OES, aiming at assessing the quantitative elemental composition at different depths from the surface. As far as the carbonatic matrix of the stone is concerned, the content of Ca and Mg is 39.6 (%w/w) and 0.46 (%w/w) respectively, for the examined samples at different depth, and this represents the calcite and dolomite content of the marble. The average elemental (Si, Fe, Na, Sr, Al and K) composition (mg/Kg, ppm) of the two sets of samples is reported in Fig. 9, whereas the contribution of Ti, Zn and Zr is not evidenced since their amount is below the detection limit ($<5\text{ mg/Kg}$). The concentration of Al, Si and Sr is rather constant at the different considered depths for both sets of samples (Fig. 9). The high Si content is related to the presence of quartz crystals in the marble. The Fe concentration in one set of samples is rather constant at the different depths, whereas it significantly increases at higher depths (20 and 25 mm) in the second one. This issue explains the high standard deviations of Fe concentration in samples collected at 20 and 25 mm from the surface (Fig. 9). These results clearly suggest that the surface yellowing should not be correlated to the accumulation of iron-based compounds (iron oxides or hydroxides) on the surface, up to the first 20 mm. The increase of iron content at a specific depth (25 mm) inside the second set of samples can be correlated to the presence of some pyrite crystals of veins in the collected powder that have been mineralized during the analysis. Finally, the concentration of Na and K is higher on the surface of both sets of samples, as a result of the accumulation of atmospheric salt deposits (marine spray) on the surface of the slab.

Figure S2 shows the DTA-TG thermographs of powders originating from the upper yellowed part of exposed rough and sawn slabs along with a reference unexposed Carrara slab, located in a sheltered place in the backyard storage of the building. The latter consists of calcium carbonate, as it becomes evident from the

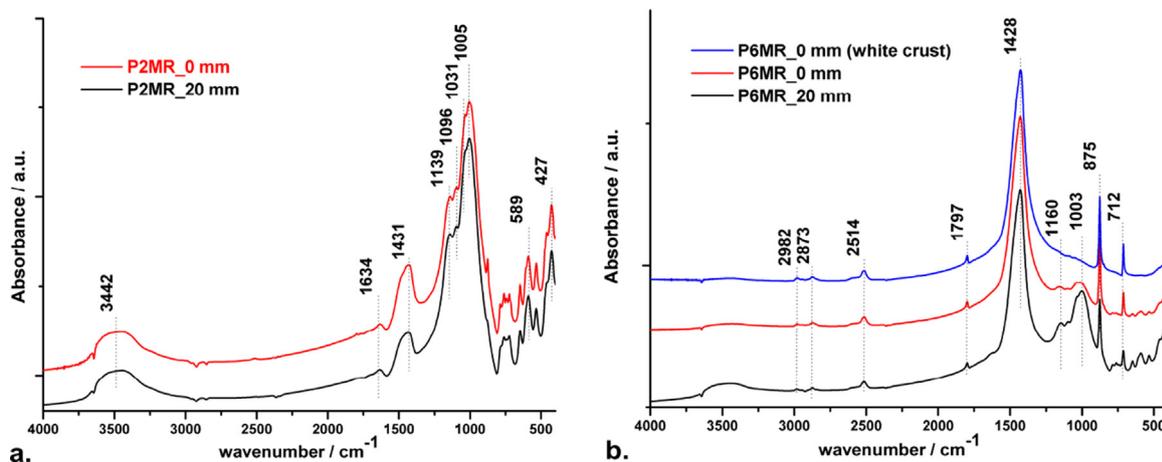


Fig. 10. FTIR spectra of both sides of P2MR (a) and P6MR (b) mortars.

endothermic peak in the temperature range from 700–900 °C and the corresponding weight loss in this area, that can be attributed to calcite only (Figure S2 a.) [23]. The other analysed samples (Figure S3 b. and c.) exhibit also weight losses in the temperature range 200–600 °C up to 1.5% (w/w) that should be ascribed to organic compounds. This can be inferred from the observed three exothermic peaks appeared at temperatures 302, 356 and 456 °C e.g. for the yellowed P2 (see Figure S3 b.), associated with the decomposition of organic substances [18,24,25]. The thermal decomposition of samples provides further support to the presence of organic substances on the yellowed marble slabs, as it has been already proved in the previously mentioned analytical results.

4.4. Chemical characterization and thermal analyses of bedding mortars

The mortars used as bedding material for marble slabs cladding were also analysed in order to examine a possible migration of organic compounds towards the exposed Carrara marble slab, which could contribute to yellowing. In Figure S3 the macroscopic characteristics of mortars (about 20 mm thick) are illustrated both for the upper part in contact with the Carrara marble slabs (0 mm) and for the opposite side, in contact with the concrete structure. In Figure S4 images of these samples obtained under the optical microscope are reported.

Both the macroscopic and microscopic images of all of the samples show the presence of a whitish residual layer on their surfaces, related to the carbonatic material of the Carrara slab remained adhered on the mortar during detachment [9]. In particular, a higher thickness of this residual white layer remained on P6MR mortar (Figure S3 i. and Figure S4 i.) than on the other mortar samples.

The mortars P2MR and P6MR at two different depths from the surface, along with the whitish crust of P6MR, were analysed by FTIR spectroscopy. P2MR mortar sample (Fig. 10a) consists of calcite (1431 cm^{-1}), hydrated aluminosilicate and siloxane components which exhibited absorption peaks in the spectral range 1000–1100 cm^{-1} (1005, 1031 and 1096 cm^{-1}). It is well established that the SiO_4^{4-} vibration of the CSH compounds of cement show infrared absorption bands in the range of 970–990 cm^{-1} [26]. The sharp peaks in the range 1000–1100 cm^{-1} shown in the Fig. 10a are attributed to the Si-O-Si due to siloxane admixtures in the mortars. The presence of hydrated sulphates is indicated by absorptions at 3442, 1634, 1139 and 589 cm^{-1} . The infrared spectrum of the whitish upper layer of P6MR mortar reported in Fig. 10b, showed absorption peaks of calcite with traces of absorptions in the range

1000–1100 cm^{-1} attributed to Si-O-Si bonds of CSH and siloxane components; the latter increase in the spectra of the internal part of the mortar sample (20 mm). The high content of calcite should be ascribed to the residual marble adhered to the cement bedding mortar and could be considered as an indication of no migration of the components of bedding mortar through the marble.

The diagram of Fig. 11a compares the concentration of Si and Ca (%w/w) identified in all the mortars. The lowest content of Si that was detected for P6MR.S sample can be correlated with the high Ca concentration due to the marble residue adhered to the mortar and it is in agreement with the FTIR results. Moreover, the considerable Na amount detected in the mortars is in good agreement with the Na quantity found in the lower side of the marble slab, which were in direct contact with the mortars. Finally, it is important to highlight that no Fe migration occurred from the mortars to the marble slabs. This becomes evident from the lowest Fe amount detected in the P6MR.0 mm sample (Fig. 11b), which reflects the residual marble adhered to the mortar.

5. Conclusions

The marble slabs of the Oslo Opera House showed some early surface alteration and deterioration that was noticed with some worries by the technical public management of the building and highlighted by the media. The paper accounts for the thorough campaign of scientific investigations that was carried out to understand the phenomena and their causes, at the aim of formulating guidelines for a suitable maintenance.

The yellowed surface areas showed a remarkable decrease of L^* and increase of b^* with a specific and constant alteration of the VIS reflectance curves. The study of the morphology of the altered marble surface revealed an ongoing phenomenon of calcite grains detachment, with inter- and intra-granular corrosion, surely correlated to the atmospheric conditions to which the marble slabs are exposed (wide range thermal excursions, strong solar irradiation, salt marine spray, particulate matter deposition, mechanical wear stress, dissolution). In the samples coming from the yellowed surface, the DTA-TG analysis allowed to detect clearly the presence of surface organic materials beyond the constituent calcite. Micro-FTIR spectroscopic examination pointed out the diffused presence of siloxanes and oxidized by-products (esters and carboxylates) of a mixture of treatments, applied just after the construction; the small yellow-brown residues, collected under the microscope among the surface calcite grains, were identified as residues of the anti-graffiti treatment based on polysaccharides used for the protection of the surface.

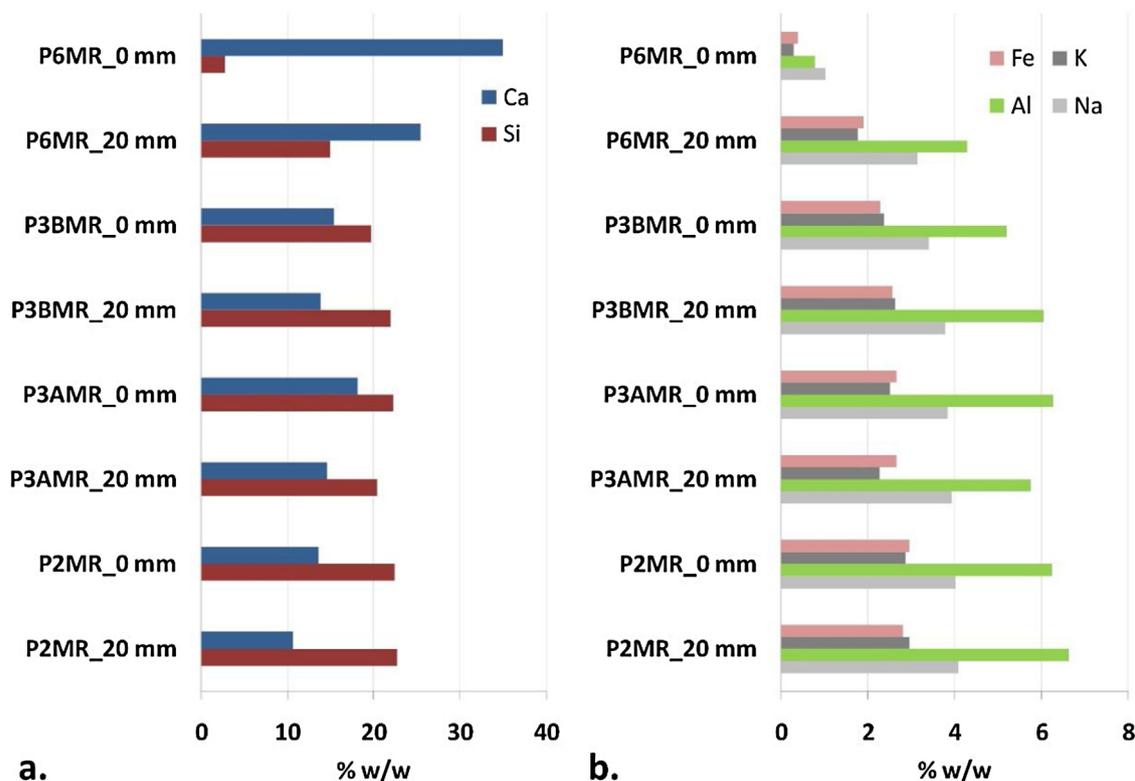


Fig. 11. EDXRF analysis on the surface and up to a depth of 20 mm of the studied mortars.

ICP-OES determination of the in depth (20 cm) elemental composition, demonstrated that there is not a correlation of yellowing with iron (Fe) ions concentration.

The analysis of several samples of the cementitious bedding mortars used for cladding, allowed to assess that no migration phenomena towards the surface occurred. The mortars consist of hydraulic aluminosilicates with siloxane as additive, while the high amount of calcite, identified in several mortars such as those coming from P6 level, is the result of the residual marble micro-fragments remained adhered to the mortar during sampling. There is no evidence of iron migration from the mortars to the marble slabs.

This analytical campaign brought to the attention of architects and conservators the necessity of providing a specific maintenance protocol to ensure the safeguard of the beautiful marble slabs, in the case of this outstanding contemporary building, with such a short life. The project has been continued and developed in two main directions: the first one was the set-up of a specific not harmful methodology for the cleaning of yellowed areas, the second the development of an affordable and effective protective treatment for the marble slabs.

Acknowledgements

This research was carried out in the framework of the competitive Project “The Oslo Opera House – Condition analysis and proposal for cleaning, protection and maintenance of exterior marble” funded by Statsbygg, Oslo (Norway). The Authors gratefully thank Dr. Adriana Eidsvik and all the Statsbygg staff for the constant support and advice during the work; they also thank the companies Betong Consult, NanoPhos and SPS for the collaboration in the Project.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://www.dx.doi.org/10.1016/j.culher.2018.06.008>.

References

- [1] R.d. Sousa Camposinhos, Cladding with Stone: Introduction. Stone Cladding Engineering, Springer, Netherlands, Dordrecht, 2014, pp. 1–8.
- [2] A. Silva, J.L. Dias, P.L. Gaspar, J. de Brito, Service life prediction models for exterior stone cladding, Building Research Information 39 (2011) 637–653.
- [3] A.J. Prieto, A. Silva, J.d. Brito, F.J. Alejandre, Functional and physical service life of natural stone claddings, J. Materials Civil Engineering 28 (2016) 04016150.
- [4] M. Franzini, Stones in monuments: natural and anthropogenic deterioration of marble artifacts, Eur. J. Mineralogy 7 (1995) 735–744.
- [5] S. Siegesmund, R. Snethlage, Stone in architecture: properties, durability, Springer Berlin Heidelberg, 2011.
- [6] C. Alves, J. Sanjurjo-Sánchez, Conservation of stony materials in the built environment, Environmental Chemistry Letters 13 (2015) 413–430.
- [7] G. Royer-Carfagni, Some considerations on the warping of marble façades: the example of Alvar Aalto’s Finland Hall in Helsinki, Construction Building Materials 13 (1999) 449–457.
- [8] <https://snohetta.com/project/42-norwegian-national-opera-and-ballet>, in.
- [9] V.V.A.A., The Oslo Opera House—Condition analysis and proposal for cleaning, protection and maintenance of exterior marble, Doc. N. doc 201501489 FDV.04.11.15, (Classification: Restricted), Statsbygg, Oslo, Norway, 2015.
- [10] L. Alnæs, O. Skjølvold, K. Lervik, E. Johansen, P. Nilssen, Technical properties/test results for marble and granite for new Opera House in Bjørnvika, Oslo. SINTEF Project 10395 New Opera House. H118 Testing of Natural Stone for Roofing and Cladding, Report (Classification: Restricted), SINTEF Civil and Environmental Engineering, Trondheim, Norway, 2004.
- [11] E. Doehne, C.A. Price, Stone conservation: an overview of current research, Getty Conservation Institute, 2011.
- [12] L. Toniolo, New trends and related problems in stone cleaning and conservation, in: M.P. Colombini, L. Tassi (Eds.), New Trends in analytical, environmental and cultural heritage chemistry, Transworld Research Network, 2008, pp. 257–276.
- [13] N. Kallithrakas-Kontos, S. Foteinis, K. Paigniotaki, M. Papadogiannakis, A robust X-ray fluorescence technique for multielemental analysis of solid samples, Environmental Monitoring Assessment 188 (2016) 120.
- [14] G.F. Royer-Carfagni, On the thermal degradation of marble, Int. J. Rock Mechanics Mining Sci. 36 (1999) 119–126.

- [15] S. Siegesmund, K. Ullemeyer, T. Weiss, E.K. Tschegg, Physical weathering of marbles caused by anisotropic thermal expansion, *Int. J. Earth Sci.* 89 (2000) 170–182.
- [16] T. Weiss, S. Siegesmund, E.R. Fuller, Thermal degradation of marble: indications from finite-element modelling, *Building Environment* 38 (2003) 1251–1260.
- [17] L. Téllez, J. Rubio, F. Rubio, E. Morales, J.L. Oteo, FT-IR study of the hydrolysis and polymerization of tetraethyl orthosilicate and polydimethyl siloxane in the presence of tetrabutyl orthotitanate, *Spectroscopy Letters* 37 (2004) 11–31.
- [18] C. Kapridaki, P. Maravelaki-Kalaitzaki, TiO₂-SiO₂-PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection, *Progress Organic Coatings* 76 (2013) 400–410.
- [19] P. Fermo, G. Cappelletti, N. Cozzi, G. Padeletti, S. Kaciulis, M. Brucale, M. Merlini, Hydrophobizing coatings for cultural heritage. A detailed study of resin/stone surface interaction, *Applied Physics A* 116 (2014) 341–348.
- [20] A. Hasan, L.M. Pandey, Kinetic studies of attachment and re-orientation of octyltriethoxysilane for formation of self-assembled monolayer on a silica substrate, *Materials Science and Engineering: C* 68 (2016) 423–429.
- [21] J.J. Hermans, K. Keune, A. van Loon, P.D. Iedema, An infrared spectroscopic study of the nature of zinc carboxylates in oil paintings, *J. Analytical Atomic Spectrometry* 30 (2015) 1600–1608.
- [22] S.Y. Oh, D.I. Yoo, Y. Shin, G. Seo, FTIR analysis of cellulose treated with sodium hydroxide and carbon dioxide, *Carbohydr. Res.* 340 (2005) 417–428.
- [23] V.S. Ramachandran, R.M. Paroli, J.J. Beaudoin, A.H. Delgado, *Handbook of thermal analysis of construction materials*, Elsevier Science, 2002.
- [24] C. Kapridaki, L. Pinho, M.J. Mosquera, P. Maravelaki-Kalaitzaki, Producing photoactive, transparent and hydrophobic SiO₂-crystalline TiO₂ nanocomposites at ambient conditions with application as self-cleaning coatings, *Applied Catalysis B: Environmental* 156–157 (2014) 416–427.
- [25] A. Verganelaki, C. Kapridaki, P. Maravelaki-Kalaitzaki, Modified tetraethoxysilane with nanocalcium oxalate in one-pot synthesis for protection of building materials, *Ind. Eng. Chem. Res.* 54 (2015) 7195–7206.
- [26] M. Chollet, M. Horgnies, Analyses of the surfaces of concrete by Raman and FT-IR spectroscopies: comparative study of hardened samples after demoulding and after organic post-treatment, *Surf. Interface Anal.* 43 (2011) 714–725.