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Evaluating the Effects of High Tide on Venetian Stone Buildings: A Multi-Analytical Approach

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***Abstract* – "*Acqua alta*" (high water) is a natural phenomenon that generally occurs in the city of Venice (Italy) in autumn and springtime, when a combination of astronomical tide, strong south wind (*scirocco*) and seiche can cause a large water inflow into the Venetian lagoon. The consequences of these events are the overflowing of the canals and flooding of the pedestrian walkways, leading to the degradation of the stone buildings over time.**

With the aim to better understand the effects of high water and how to take action for preserving the cultural heritage of Venice, thirty samples of five varieties of carbonate lithotypes exposed to natural weathering were monitored in different areas of Venice and the island of Torcello. The present work shows the preliminary results obtained through a multi-analytical approach, evaluating the chemical-physical alteration and the morphological variations through systematic monitoring every three months.

I. INTRODUCTION

In the last years flood episodes are increasingly frequent in the city of Venice. The phenomenon, named by the Venetians "*acqua alta*", that means high water, refers to the occurrence of water levels of the Venetian lagoon higher than normal during high tide, which cause the overflowing of the canals and flooding of the pedestrian walkways.

The need to limit the deterioration effects of cultural heritage in the lagoon environment started after the high tide occurred in November 1966: this unprecedented exceptional event led devastating repercussions in all the lagoon settlements. Since then, numerous studies have been conducted to systematically recognize and define the deterioration effects of lagoon water on the lithotypes of Venetian architecture. However, effective solutions are still a challenge. On November 12th, 2019, the town was hit by the highest tide in more than 50 years, with an intense high water peaked at 1.87 metres. Therefore, the climate changes of the recent decades and the last episodes of exceptional high water recorded in Venice between November and December 2019 urgently require the implementation of new strategies for the preservation of monuments [1-3].

In this context, the present research is part of the project "*Venezia 2021- Programma di ricerca scientifica per una laguna regolata*", financed by the *Provveditorato alle OO. PP. del Triveneto* through *Consorzio Venezia Nuova* and coordinated by CORILA Consortium.* The study aims to better understand the effects of high water on Venetian historical buildings and to propose strategies for preserving them. In particular, an integrated multi-analytical approach was established to identify and map chemical-physical decay and morphological alterations to which the stones of the historical Venetian buildings are subjected due to high tide episodes.

For this purpose, thirty samples including five of the most common carbonate rocks of the Venetian architecture were located in different areas of both Venice and the island of Torcello to evaluate the weathering effects caused by high tide. The present work shows the preliminary results of the research and emphasizes the negative effects of high water on the conservation of the Venetian buildings.

II. EXPERIMENTAL SECTION

A. Materials

The selection of the stone materials to be tested was made considering the most common lithotypes used in historical Venetian building. Five different stone varieties of carbonate nature (four limestones and one pure marble, respectively) were chosen: *calcare rosso di Verona* (Ammonitico rosso from Verona), *pietra d'Istria* (Istrian stone), *pietra di Vicenza* (Vicenza stone), *pietra di Aurisina Fiorita* (the Aurisina stone variety with grey background and macroscopic fossil patterns) and white *Carrara* marble. The samples, each measuring 5x5x2 cm^3, have been housed in a polymeric sample holder (Fig. 1). Five pairs of sample holders were placed in different locations in the historic center of Venice and one in the island of Torcello. The sites were selected according to their different altimetry with respect to the mareographic zero and their different exposure to marine aerosol: (1) *Palazzo Ca' Foscari* (Dorsoduro); (2) the San Giobbe campus (Cannaregio); (3) *Palazzo Badoer* (San Polo); (4) *Palazzo Ca' Tron* (Santa Croce); (5) *Palazzo Malipiero* (San Marco); (6) the remains of the church of St. Mark the Evangelist in Torcello island. The sample holders were positioned directly on the original brick walls of the selected buildings at two different altitudes with respect to the mareographic zero: the first one corresponds to the ground level (referred as "*position 1*"), while the second one just over 110 cm (referred as "*position 2*"), the tidal reference level for the activation of the MOSE mobile bulkheads (Fig.1). The selection of sites characterized by a different altimetry with respect to the mareographic zero allows the comparison of the effects of high waters depending on the different areas of Venice.

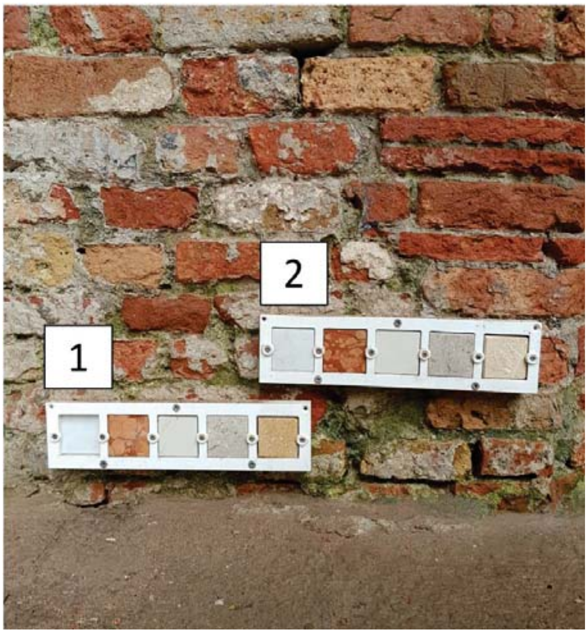

Fig. 1. Samples placed in Palazzo Badoer (Venice) in position 1 and 2.

B. Characterization

Before the outdoor exposure, diagnostic investigations useful for the mineralogical-petrographic, chemical-physical, and morphological characterization were carried out on each stone sample. These data represent a benchmark (at zero time = t_0) to be used as reference for the comparison of all the data collected during the subsequent monitoring steps. The monitoring was planned to allow a systematic characterization of the sate of conservation of the samples every three months, from June 2019 up to September 2021, for a total of ten monitoring sessions.

Before carrying out the monitoring analyses, the samples were placed in an oven at 50°C for 24 hours and then in a dryer for 3 hours.

In order to study the nature of any deposits and spots on samples surface, X-Ray Fluorescence (XRF) spectra were collected using a Bruker M4 Tornado µ-XRF apparatus. For elemental mapping, a current of 200 µA and a voltage of 50 kV were used. The chamber pressure was set at 20 mbar. The elemental maps were collected over an area of 1 cm^2 with a step size of 20 µm. The µ-XRF analyses were performed without any further preparation of the samples.

Colorimetric analyses were performed aiming at evaluating chromatic variations of the samples during the outdoor exposure. The color measurements were made in the CIE L*a*b* color space, where L* is the lightness (positive and negative values), while a* and b* are the chromaticity coordinates (the red-green and the yellow-blue direction, respectively).

The total color variation (ΔE^*) was calculated as:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (1)$$

According to the NORMAL 43/93 (EN 15886:2010 standard) [4], color data were acquired with a CM-2600d Konica Minolta portable spectrophotometer with a D65 illuminant and 10° standard observer. This instrument has a 5 mm diameter measurement area and it was set to quantify the potential specular component included (SCI) color variations. In order to obtain reliable and reproducible measurements, an average of 5 points with 3 scans each was considered for each specimen [5].

The investigations of possible alterations or formations of surface patinas of organic and/or inorganic nature were carried out through morphological observations using a Leica F12I stereomicroscope.

The recognition of biological patinas was made through the observation of freshly prepared slides by means of a Leitz LABORLUX 12 POL S microscope (UNI 10923: 2001) [6].

III. RESULTS AND DISCUSSIONS

From the results obtained after the first three monitoring, differences were found not only between the samples exposed at the five sites - due to their different exposure and altimetry - but also among the samples of the same site placed in positions 1 and 2.

A. Morphological Observations

In some samples placed at the ground level, the formation of a greenish patina was observed. In particular, this patina was found on the samples at *Palazzo Malipiero* after 6 months of outdoor exposure (Fig. 2). Through stereomicroscopic observations and subsequent study of freshly prepared slides, the patina was confirmed to be green algae (Fig. 3) [8]. The formation of these patinas can be explained by considering the position of the samples. In fact, they are located close to a water gate being subject to frequent waves and floods caused by the marine traffic. *Pietra di Vicenza* shows the greatest biological and algal surface colonization with respect to the other selected lithotypes due to its higher porosity [8-10]. Conversely, the samples exposed in position 2 did not show any organic patina.

Fig. 2. Samples in position 1 placed at Palazzo Malipiero (Venice) after six months of exposure. From left: marmo di Carrara; rosso di Verona; pietra d'Istria, pietra di Aurisina and pietra di Vicenza. The latter is completely covered by an organic patina.

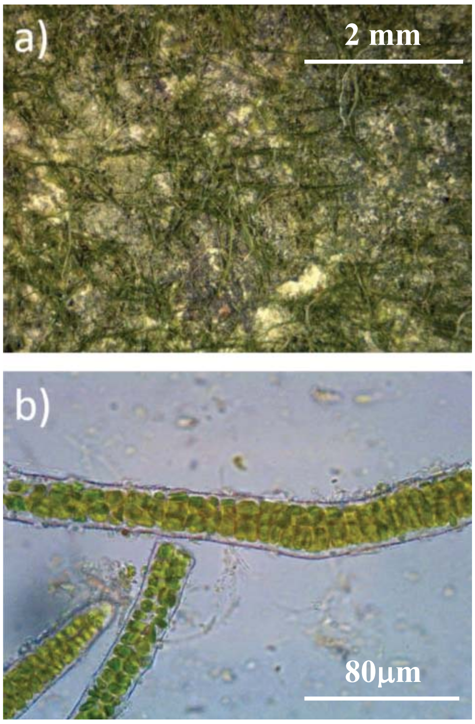

Fig. 3. Stereograph of green algae (a) and algae cell photomicrograph (b) on the surface of pietra di Vicenza sample exposed at Palazzo Malipiero (Venice) in position 1 after six months of exposure (#PM-V1_t_2).

A biological colonization by species of brown color with a branched structure was observed on some samples of *Palazzo Badoer*. These specimens, investigated through the stereomicroscope and the transmitted light optical microscope, showed the presence of meristematic *fungi* with characteristic brown colors, well-evident fungal hyphae and lichens (Fig. 4) [6]. The development of these micro-organisms is probably due to the context in which the samples are placed. *Palazzo Badoer*, indeed, is in a particularly low position that is frequently subjected to high water phenomena. Moreover, the samples are located in a mostly shady area, so the humid environment can facilitate the proliferation of this fungal species.

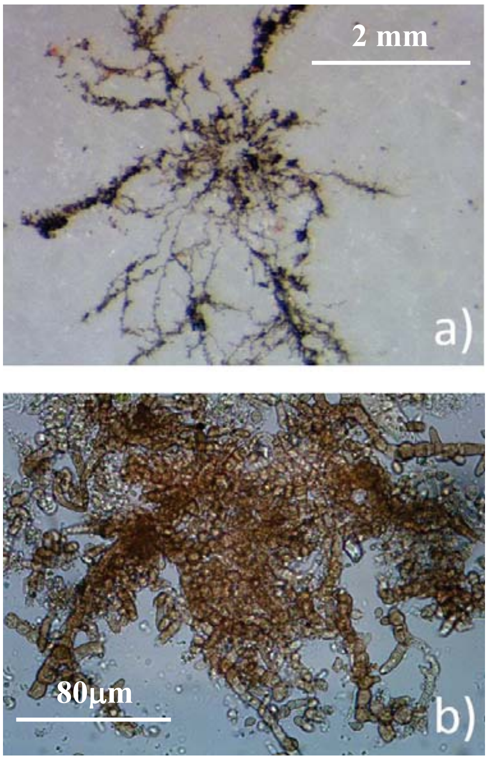

Fig. 4. Stereograph (a) and photomicrograph (b) of a fragment of lichen taken from marmo di Carrara sample placed at Palazzo Badoer in position 1 at t_2 (#PB-V1_t_2).

B. Colorimetric Analysis

Many samples have undergone significant chromatic alterations. In particular, the lithotype that presented the largest colorimetric variations is *pietra di Vicenza*, regardless of the location. Since this is the most porous lithotype among those under study, it can be assumed that it easily retains atmospheric particulates and deposits on its porous surface.

The significant influence of the altimetry and exposure conditions of each site is evident if we compare the behavior of the samples positioned at *Palazzo Badoer* with respect to those placed at *Palazzo Malipiero*. As already mentioned above, a humid and shady environment characterizes the samples in the first site, while the samples of the second one are positioned near a water gate, so they are frequently wet.

Table 1 shows, as example, the colorimetric values of *pietra di Vicenza* sample located at *Palazzo Badoer* in position 1. Compared to the data collected at time zero (t_0), the total color variation shows a value of $\Delta E^*>5$, so the chromatic alteration is perceptible to naked eye [7]. In particular, there was a decrease in brightness, so that the surface is visibly darker than the original one at t_0. (Fig. 5).

Table 1. Colorimetric measurements of pietra di Vicenza sample exposed at Palazzo Badoer (Venice) in position 1 (#PB-V1). Comparison between the values collected at time 0 (t0), 1 (t1), 2 (t2) and 3 (t3), after 0, 3, 6 and 9 months of outdoor exposure, respectively.

Sample	L^*	a^*	b^*	ΔE^*
PB-V1/t_0	78.08	5.08	19.48	-
PB-V1/t_1	73.27	6.04	21.36	5.25
PB-V1/t_2	71.02	6.89	23.43	8.29
PB-V1/t_3	72.96	5.58	20.47	5.24

Table 2. Colorimetric measurements of pietra di Vicenza sample exposed at Palazzo Malipiero (Venice) in position 1 (#PM-V1). Comparison between the values collected at time 0 (t0), 1 (t1), 2 (t2) and 3 (t3), after 0, 3, 6 and 9 months of outdoor exposure, respectively.

Sample	L^*	a^*	b^*	ΔE^*
PM-V1/t_0	79.33	4.32	18.45	-
PM-V1/t_1	48.64	1.72	28.13	32.29
PM-V1/t_2	37.68	-2.76	15.98	42.32
PM-V1/t_3	64.11	6.05	24.49	16.5

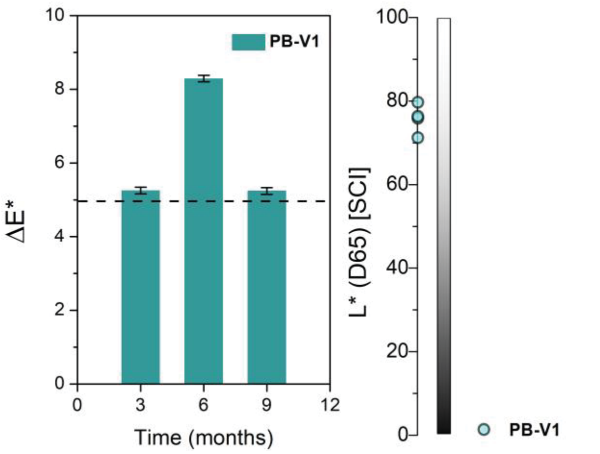

Fig. 5. Results of the colorimetric measurements of pietra di Vicenza sample exposed at Palazzo Badoer (Venice) in position 1 (#PM-V1). Comparison between the data collected at t_0 and those collected after 3, 6 and 9 months of exposure.

The strong impact of high water on stone samples was confirmed taking into account that the 1st and the 2nd monitoring (t_1 and t_2, respectively) were carried out in June and November, the typical periods in which the high tides occurred, while the 3rd monitoring (t_3) was conducted in March, just after a long period of exceptionally low tides, taken place between the months of January and February. As shown through the microscopic observations (Fig. 3), a substantial formation of green algae occurred on the stone surface on *pietra di Vicenza* sample at *Palazzo Malipiero*, as observed during the 1st and 2nd monitoring. However, after the 3rd one, the biological patina was no longer present due to dehydration. These results were confirmed also by means of the colorimetric measurements. In particular, the blue and red absorption features shown in the reflectance spectra are typical of a green material (Fig. 6a). Consequently, the L^*, a^* and b^* parameters showed strong variations and the total color difference is $\Delta E^*>15$ (Table 2 and Fig.6b).

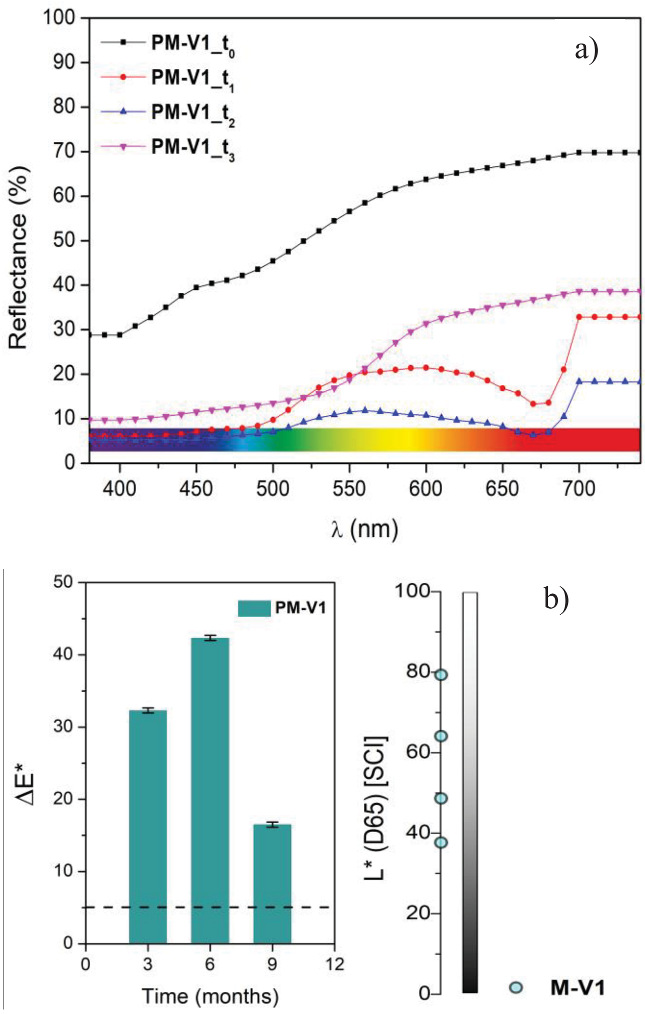

Fig. 6. Results of the colorimetric measurements of pietra di Vicenza sample exposed at Palazzo Malipiero (Venice) in position 1 (#PM-V1). (a) Comparison between the reflectance spectra *recorded after zero to three months of exposure. (b) Comparison between the ΔE*and L*data collected at zero time and those collected after three, six and nine months of exposure.*

C. µ-XRF Analysis

Several samples exhibited a superficial formation of dusty whitish deposits, as observed under the stereomicroscope and investigated by means of µ-XRF measurements, confirming the presence of salts on the samples surface. Fig. 6 shows a representative elemental mapping of a sample characterized by the presence of salts. The investigations revealed that these deposits are chlorine-based efflorescences (green areas in Fig. 7b).

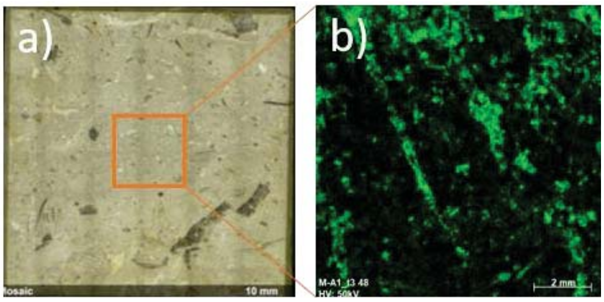

Fig. 7. Elemental µ-XRF mapping carried out on a sample of pietra di Aurisina Fiorita located in Palazzo Malipiero in position 1 (#PM-A1) at t_2.

IV. CONCLUSIONS

The data here presented are only preliminary results recorded after a short time of outdoor exposure and further series of *in situ* and in laboratory monitoring, still have to be conducted on the thirty samples placed in the historic center of Venice and on the island of Torcello. Nevertheless, after nine months of exposure to natural weather conditions, the samples revealed (i) significant colorimetric variations, (ii) development of biological patinas and (iii) significant presence of efflorescences. In particular, it is already evident that the different position of the samples with respect to the mareographic zero as well as the different exposure to the climate forcers directly impact on the sate of conservation of the selected stone materials also according to the intrinsic properties of the latter. The few monitoring cycles carried out so far are clearly not sufficient to obtain an exhaustive general picture of the behavior of the stone samples, nor to define evolutionary trends or reliable future scenarios. The monitoring and analytical tests that will be carried out in the next months (up to September 2021) will be essential to develop models, processes and strategies for the conservation of the Venetian cultural heritage.

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