

# Climate change and land subsidence in the frame of “Venezia 2021” project: the deterioration of architectural stone materials

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**Abstract** – The overflowing of the canals and the flooding of the pedestrian walkways are the consequences of the well-known periodic large water inflow into the Venetian lagoon (high water or *acqua alta*). These phenomena lead the strong degradation of the stone buildings over time. With the aim to better understand the effects of high water and support the best actions and practices for preserving the cultural heritage of Venice by Municipality and Superintendences, thirty samples of five varieties of carbonate lithotypes were exposed to natural weathering in different Venetian areas and on Torcello island. The specimens were periodically monitored and compared with samples made of the same lithologies subjected to accelerated artificial aging tests. The results concerning the main deterioration morphologies observed on all the samples after three years of exposure are here presented and commented.\*

## I. INTRODUCTION

“Acqua alta” (high water) is the term used for the exceptional tide peaks that periodically occur in northern Adriatic Sea reaching their maximum in the Venetian lagoon. This natural phenomenon takes place in autumn and springtime due to the combination of astronomical tide, strong south wind (*scirocco*) and seiche. The consequence of these events is the flooding of the city of Venice caused by the overflowing of the canals. This represents a critical issue because of the interaction between water and buildings leads to severe deterioration effects over time (i.e. mechanical damages, cracks, erosions, efflorescences, chromatic alterations and biological colonizations). Moreover, high tides frequency has been increasing in Venice in the last 60 years. Since 2010, the situation became dramatic, as the number of high tides events exponentially increased. Particularly, twenty-six high tides ( $\geq 1.10$  m) were recorded between November and December 2019. On 12 November 2019,

the city was hit by the highest tide in more than 50 years, with an intense high water peaked at 1.87 meters. Therefore, the climate changes of the recent decades and the last exceptional high water events, urgently require the implementation of new strategies for the preservation of monuments [1-4].

This study aims to better understand the effects of high water on Venetian historical buildings and to develop strategies for their preservation. For this purpose, six different building sites in Venice and Torcello island were selected to place five of the most common carbonate rocks of the Venetian architecture in order to evaluate the weathering effects caused by high tide. These sites were chosen according to both their different altimetry with respect to the mareographic zero and their different exposure to marine aerosol, winds and wave motion. The selected dimension stones are five (more or less) pure limestones, with different porosity and texture and one crystalline marble. An integrated multi-analytical approach was established to identify and map the chemical-physical deterioration and their related macro- and micro-morphologies due to high tide events. The stones’ decay was evaluated during ten monitoring periods by means of different tests and analyses, such as dry weight loss, ultrasound P-waves velocity, colorimetric measures, X-Ray Fluorescence, stereomicroscope observations and recognitions of biological patinas. The samples were exposed to natural ageing for three years. Preliminary results after three months of natural weathering were presented in a previous work [5]. The data collected after three years of exposure show how, even if in slight entity, the main deterioration patterns (e.g. bleaching and discoloration, efflorescences, increase of porosity, loss of material, etc.), are already recognizable after a short time of exposure to exogenous agents. The elaboration of the collected data tries to highlight how and to what extent the microclimate, the intrinsic characteristics of the building stones and above all the trends of the high tides influence the development of the deterioration phenomena and the

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timing of their development, suggesting in some cases a hypothesis of long-term prediction of the evolution of the decay.

In order to define the deterioration morphologies under extreme conditions, some specimens of the same lithology were subjected to artificial aging tests in laboratory.

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## II. MATERIALS AND METHODS

### A. MATERIALS

Five stone varieties were selected based on their widespread use in the stone facings of the historic Venetian downtown [6-7]: *Aurisina Fiorita Stone*, *White Carrara Marble*, *Istrian Stone*, *Ammonitico Rosso* from Verona, and *Vicenza Soft Stone* (Fig. 1). The specimens ( $5 \times 5 \times 2 \text{ cm}^3$ ) were placed in six historical buildings chosen on the basis of both altimetry and exposure to marine aerosol: *Ca' Foscari*; the former slaughterhouse of *San Giobbe*, today economic campus of the *Ca' Foscari* University; *Palazzo Badoer*; *Ca' Tron*; *Palazzo Malipiero*; and the small church dedicated to St. Mark on the Torcello island (Fig. 2). At each site, specimens were placed at two different elevations above ground level: the first corresponding to the walking surface, the second at 110 cm above tidal zero, considered as the level at which the MoSE mobile bulkheads were put into operation.



Fig. 1. The five different carbonate lithologies located at two different elevations. From the left to the right and from up to down: *Istrian Stone*; *Aurisina fiorita*, *Verona Ammonitico Rosso*, *Vicenza Soft Stone*; *Carrara marble*.

### B. METHODS

Diagnostic investigations, useful for the mineralogical-petrographic, chemical-physical, and morphological characterization, were carried out on each stone sample before its outdoor exposition. 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 in order to allow a systematic characterization of the state of conservation of the samples every three months, for ten monitoring sessions.

Before carrying out the monitoring analyses, the samples were placed in an oven at  $50^\circ\text{C}$  for 24 hours and then in a dryer for 3 hours.

X-Ray Fluorescence (XRF) spectra were collected – using a Bruker M4 Tornado  $\mu$ -XRF apparatus – with the aim to study the nature of any deposits and spots on samples surface. For elemental mapping, a current of 200  $\mu\text{A}$  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  $1 \text{ cm}^2$  with a step size of  $20 \mu\text{m}$ . The  $\mu$ -XRF analyses were performed without any further preparation of the samples.

Colorimetric analyses were executed 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 ( $\Delta E^*$ ) was calculated as:

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

Color data were acquired with a CM-2600d Konica Minolta portable spectrophotometer with a D65 illuminant and  $10^\circ$  standard observer, according to the NORMAL 43/93 (EN 15886:2010 standard) [8]. 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.

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) [9].

In order to define the deterioration morphologies under extreme conditions, a specimen of each selected lithology was subjected to four artificial aging simulations conducted in laboratory:

- Thermal shock;
- Freeze-thaw;
- Salt crystallization;
- Thermal cycling.

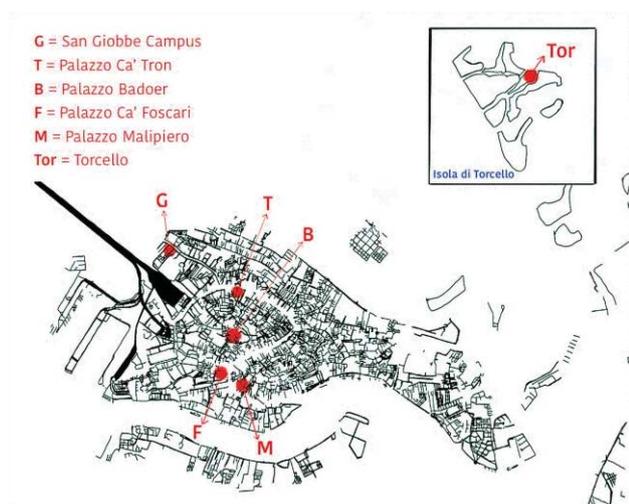


Fig. 2. Specimen exposure sites

### III. RESULTS

General considerations on each form of deterioration identified are summarised below.

#### A. Natural weathering

##### *Salt crystallization*

The variation and distribution of superficial salts were estimated by elemental XRF analysis. All lithotypes located at *Ca' Tron* site where significantly affected by the crystallization of NaCl, especially in the case of *Aurisina Fiorita Stone* and *Vicenza Stone*. The environment in which these samples are placed is closed, without ventilation, near to a water gate, and without heating/cooling or dehumidification system, consequently, the results can be considered in line with the type of exposure. In this way, the soluble salts, originally present in the stone or derived from several external sources, can be transported through the material as aqueous solution. The climate conditions directly influence the precipitation of the salts. The crystallization occurs on the surface and efflorescences are formed when the migration rate of the solution to the surface is higher than that of the water evaporation [10-12].

The development of subefflorescence was particularly observed in the case of *Ammonitico Rosso from Verona*, with the formation of well-limited, orange-colored, microscopically raised surface areas increasing over time. This phenomenon was observed for the specimens exposed not only at *Ca' Tron* but also at *San Giobbe* and

*Palazzo Malipiero* sites.

##### *Sulfation*

Significant concentrations of sulfur were detected especially on the surface of the *Aurisina Fiorita Stone* and *Vicenza Stone* specimens placed at *Palazzo Badoer*, *Ca' Tron*, and *San Giobbe* sites. The most probable cause lies in the presence of pollutants related to vehicular traffic, which are diffused both in the atmosphere and in water and which, through the action of aerosols and the phenomenon of capillary rise, chemically react with carbonate matrices. The sulphur quantity recorded was much higher in downtown area than in Torcello island and it drastically decreased during lockdown period due to pandemic emergency of COVID-19.

##### *Superficial concretions*

Superficial carbonate (calcite) encrustations were observed on *Istrian Stone* samples exposed at *San Giobbe*, *Ca' Foscari*, *Ca' Tron* and *Torcello* sites. The deposition of secondary calcite as superficial concretions is a direct consequence of the environmental conditions to which specimens were subjected: the succession of humidity/drying cycles, in fact, leads to the dissolution of primary calcite and the subsequent re-precipitation of calcium carbonate in the superficial pores of the stone.

##### *Material loss*

*Ammonitico Rosso from Verona* and *Vicenza Soft Stone* specimens placed in position 2 at *Palazzo Malipiero*, showed consistent detachments near the stylolithic joints and structural discontinuities. These two lithologies are characterized by the presence of more or less abundant contents of clay minerals with expanding lattice. Consequently, the continuous expansion/contraction process and salt crystallization resulted in the physical decay of the samples.

##### *Decohesion*

In general, the total exposure time of the samples was sufficient to show significant physical deterioration of the specimens placed at "position 2", in particular, the decay is due to a loss of compactness, as measured by ultrasonic velocity trend. In fact, samples placed at the highest position were more susceptible to salt deposition due to the cycles of capillary absorption and subsequent drying of wall surfaces. Particularly significant is the ultrasonic velocity trend recorded for *Carrara Marble* in all the sites considered, where the stone resulted always characterised by a more or less accentuated intergranular decohesion as a result of cyclic temperature variations (*marmo cotto / baked marble*).

### Biological deterioration

The development of specific biodeteriogens were found to be characteristic of some lithotypes and exposure sites.

In particular, all the specimens exposed in “position 1” at *Palazzo Malipiero* generally showed colonization of the surfaces by green algae and cyanobacteria; this is due to the continuous wave motion and high tides to which the specimens were constantly subjected.

On the contrary, a wide presence of fungal hyphae – typical biodeteriogens that develop in very humid areas with little exposure to light – was observed in the case of the samples placed at *Palazzo Badoer*.

### B. Artificial aging

The objective of this study was to understand and define the deterioration forms and morphologies under extreme or limit conditions, considering the deterioration agents one by one.

Finally, based on the data collected during the period of outdoor exposure of the specimens, an algorithm was developed based on the MATLAB programming and numerical computing platform. Fig. 3 shows an example of the output provided by the prediction model for the *Vicenza Soft Stone*; in particular, it displays a plausible trend of the ultrasonic velocity range (i.e. the red vertical bar), as calculated for each specimen, on which the real experimental measurement taken during the last monitoring field was plotted.

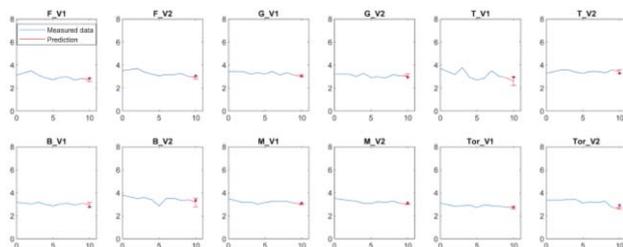


Fig. 3. Prediction of ultrasonic velocity change.

The data collected through the natural and accelerated aging tests were exploited for proposing a *deterioration and intervention index* (1). This index is linked to both the chromatic features (expressed as  $\Delta E^*$ , i.e. the total colour change) and ultrasonic velocity ( $V_p$ ) variations occurred to the specimens, as follows:

$$SDIi = \left( \frac{v_p}{v_{p_0}} \right)^{(v_{p_0} - v_p) \cdot \sqrt{\Delta E^*}} \quad (1)$$

## IV. CONCLUSIONS

The results obtained clearly indicate that the intrinsic minero-petrographic and physical properties of each

lithological variety tested have a significant influence over the development of specific deterioration morphologies; the latter are also appreciably influenced by the different conditions of exposure to the environmental forcings, which characterize each of the sites where the samples were placed.

Artificial aging tests allowed, on one hand, to define the deterioration forms and morphologies developed under limit conditions and, on the other hand, to hypothesize some correlations with the decay occurred to the stone samples exposed outdoor:

- Bleaching of Carrara Marble was found in all the specimens subjected to artificial aging tests, as well as in those exposed to natural aging. In both cases, samples quickly underwent a marked process of superficial dissolution-precipitation of the carbonate minerals, essentially calcite. The superficial layers of secondary calcite, which is significantly more brittle than the primary one, predispose the stones to other possible forms of physical decay and chemical alteration.

- Ultrasonic velocity measurement showed that *Carrara Marble* specimens also undergo physical degradation by thermoclastism (“*marmo cotto*”/ “baked marble”, i.e. marble presenting an inter-crystalline dechoesion) in a fairly short time.

- Graying of the Verona Red Limestone samples was observed as the consequence of all the artificial aging simulation conducted in laboratory. This phenomenon can be compared to the decrease in tone that also occurred in specimens exposed to outdoor conditions, although in this case the chromatic alteration is less marked.

The developed “predicting algorithm” proved to be reliable with respect to the collected experimental measurements, and the results obtained through the prediction model appear to be useful in defining a possible “threshold limit value” of intervention and, more in general, in a conservation perspective. Indeed, the related deterioration and intervention index can help to provide an estimate of deterioration and an assessment of the need for intervention through targeted conservation and restoration actions. Moreover, such an algorithm is potentially open and further implementable with other parameters.

## REFERENCES

- [1] F.Trincardi, A.Barbanti, M.Bastianini, A.Benettazzo, L.Cavaleri, J.Chiggiato, A.Papa, A.Pomaro, M.Sclavo, L.Tosi, G.Ungiesser, “The 1966 flooding of Venice: what time taught us for the future estimating the uncertainty in the frequency domain characterization of digitizing waveform

- recorders”, *Oceanography*, vol. 29, n.4, 2016.
- [2] L.Cavaleri, “The oceanographic tower acqua alta activity and prediction of sea states at Venice. Automatic signal recognition for a flexible spectrum management”, *Coastal Engineering*, vol. 39, 2000, pp.29-70.
- [3] A.Cormerlati, M.Ferronato, G.Gambolati, M.Putti, P.Teatini, “Saving Venice by seawater”, *Journal of Geophysical Research*, vol. 109, 2004.
- [4] L.Randazzo, N.Rovella, S.Muto, F.Antonelli, E.Tesser, M.F.La Russa, “Environmental impact on historical monuments: The black crusts of the Venice lagoon”, *Proc. of 2020 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage*, 2020, pp. 472–476.
- [5] G. Zaccariello, E. Tesser, R. Piovesan, F. Antonelli “Evaluating the Effects of High Tide on Venetian Stone Buildings: A Multi-Analytical Approach”. *2020 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage*, 2020, pp. 27–31.
- [6] F. Antonelli, “The stones (of Venice) tell stories: how to read them | Le pietre (di Venezia) raccontano: come leggerle, *Vesper*, 2019, vol.1, pp. 196–203.
- [7] F.Antonelli, L.Lazzarini, S.Cancelliere, E.Tesser, “Study of the deterioration products, gilding, and polychromy of the stones of the Scuola Grande di San Marco's façade in Venice”, *Studies in Conservation*, 2016, 61(2), pp. 74–85.
- [8] EN 15886:2010. Conservation of cultural property - Test methods - Colour measurement of surfaces. UNI 10923:2001.
- [9] Cultural heritage - Natural and artificial stones - Preparation of biological specimens for the observation by light microscopy.
- [10] L. Lazzarini and M. Laurenzi Tabasso, *Il restauro della pietra*. 2010.
- [11] A. E. Charola, “Salts in the deterioration of porous materials: an overview,” *JAI*, vol. 39, pp. 327–343, 2000.
- [12] C. Alves, C. Figueiredo, A. Maurício, M. A. Sequeira Braga, and L. Aires-Barros, “Limestones under salt decay tests: assessment of pore network-dependent durability predictors,” *Env. Earth Sci*, vol. 63, pp. 1511–1527, 2011.