

To the Editor of the journal *Journal of Cultural Heritage*

Dear Editor,

please find attached the manuscript entitled: “Effects of different coatings applied on *Pietra di Lecce* limestone: a neutronographic study” by Luciana Randazzo, Valentina Venuti, Vincenza Crupi, Domenico Majolino, Frédéric Ott, Michela Ricca, Natalia Rovella, Mauro Francesco La Russa and myself, submitted for publication in the journal *Journal of Cultural Heritage*.

We declare that the manuscript is not under consideration for publication and has not been published elsewhere in any medium including electronic journals and computer databases of a public nature.

In this work a neutronographic investigation was carried out on a type of limestone, known as *Pietra di Lecce* stone, widely used in Italian Baroque as construction material. The limestone was treated with two different commercially-available coatings, namely nanosilica and nanolime, and artificially aged by temperature/relative humidity and salt crystallization. The aim was to provide an experimental evidence of the effectiveness of such protective coatings by looking at the water absorption process occurring inside the pore network of the analyzed stones. The analysis of the wetting front position revealed significant variations in the water absorption kinetics among the investigated samples, suggesting different mechanisms of interaction between the protective layer and the underlying bulk stone. Finally, a quantitative evaluation of the best effectiveness of the two products was addressed, particularly useful in view of an appropriate choice of restoration procedures to be applied to building materials.

The contents of this manuscript could appeal to the broad readership of the journal *Journal of Cultural Heritage* because of the strong interdisciplinary nature of the argument.

We are looking forward to hearing from you.

Thank you for your consideration.

Yours sincerely,

Giuseppe Paladini (on behalf of all authors)

CORRESPONDING AUTHOR: Giuseppe Paladini

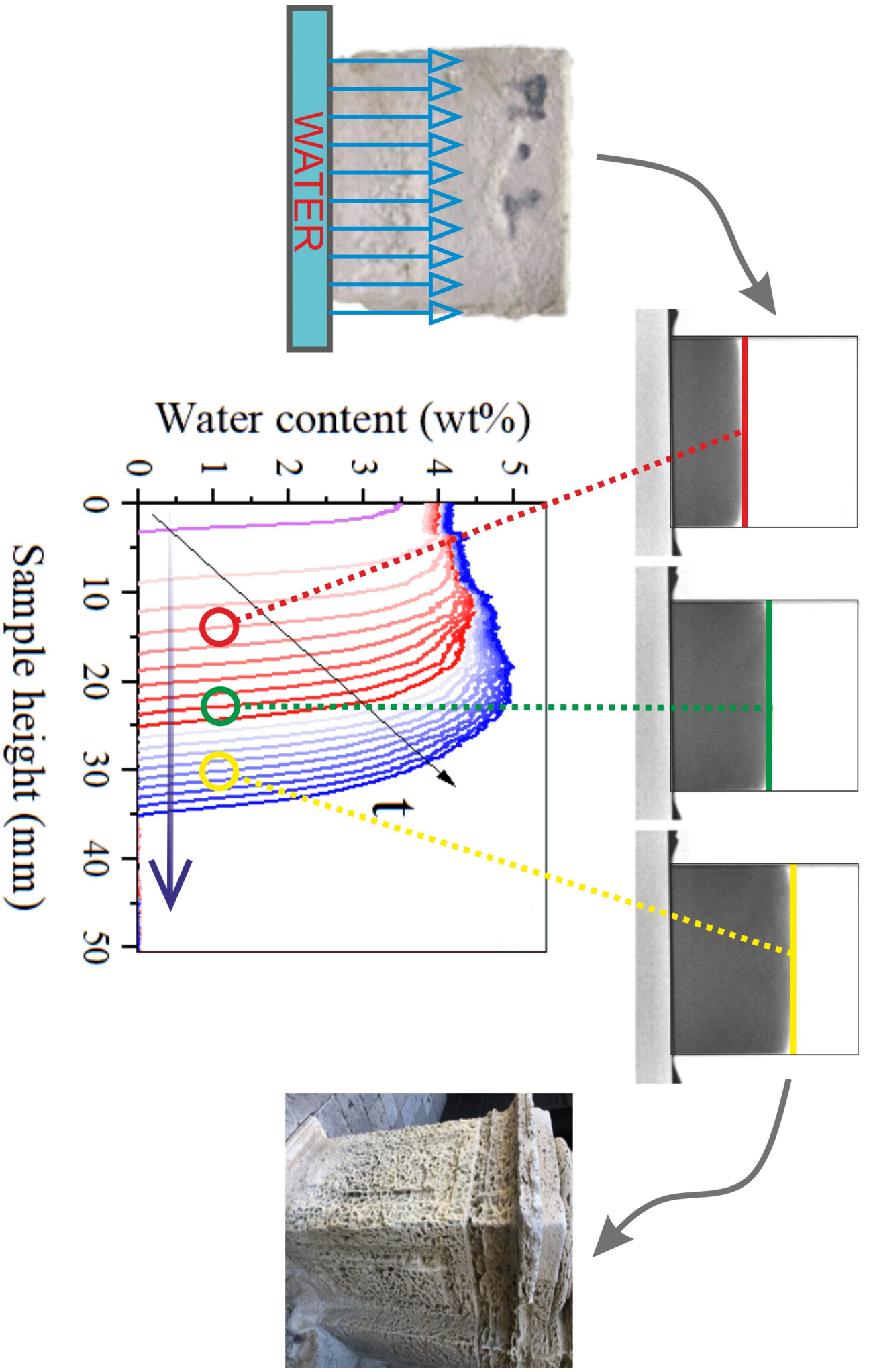
AUTHOR'S PHONE NUMBER: +39 090 6765299

AUTHOR'S EMAIL: gpaladini@unime.it

AUTHOR'S POSTAL ADDRESS: Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Viale Ferdinando Stagno D'Alcontres 31, 98166 Messina, Italy.

Highlights

- Neutronography was employed for the non-invasive investigation of the interaction between consolidants (i.e. nanosilica and nanolime) and *Pietra di Lecce* limestone.
- Water motion inside the investigated limestones was visualized.
- The effectiveness of the two consolidants as protective agents against several artificial weathering tests was demonstrated.
- A better performance of nanosilica with respect to nanolime was revealed.
- The data could represent methodological proposal scheme in view of a proper restoration/conservation procedure.



Effects of different coatings applied on *Pietra di Lecce* limestone: a neutronographic study

Luciana Randazzo^{a,1}, Valentina Venuti^{b,1}, Giuseppe Paladini^{b,*}, Vincenza Crupi^c,
Domenico Majolino^b, Frédéric Ott^d, Michela Ricca^a, Natalia Rovella^a, Mauro
Francesco La Russa^a

^a*Department of Biology, Ecology and Earth Science, University of Calabria, via Pietro Bucci cubo 12B piano 2, 87036, Arcavacata di Rende (CS), Italy.*

^b*Department of Mathematical and Computer Sciences, Physical Sciences and Earth Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres 31, 98166 Messina, Italy.*

^c*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres 31, 98166 Messina, Italy.*

^d*Laboratoire Léon Brillouin, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France.*

¹These Authors contributed equally to this study.

*Corresponding author. E-mail address: gpaladini@unime.it (G.Paladini).

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^a*Department of Biology, Ecology and Earth Science, University of Calabria, via Pietro Bucci cubo 12B piano 2, 87036, Arcavacata di Rende (CS), Italy.*

^b*Department of Mathematical and Computer Sciences, Physical Sciences and Earth Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres 31, 98166 Messina, Italy.*

^c*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres 31, 98166 Messina, Italy.*

^d*Laboratoire Léon Brillouin, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France.*

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*Corresponding author. E-mail address: gpaladini@unime.it (G.Paladini).

Abstract

In this work a neutronographic investigation was carried out on a type of limestone, known as *Pietra di Lecce* stone, widely used in Italian Baroque as construction material. The limestone was treated with two different commercially-available coatings, namely nanosilica and nanolime, and artificially aged by temperature/relative humidity and salt crystallization. The aim was to provide an experimental evidence of the effectiveness of such protective coatings by looking at the water absorption process occurring inside the pore network of the analyzed stones. The analysis of the wetting front position revealed significant variations in the water absorption kinetics among the investigated samples, suggesting different mechanisms of interaction between the protective layer and the underlying bulk stone. Finally, a quantitative evaluation of the best effectiveness of the two products was addressed, particularly useful in view of an appropriate choice of restoration procedures to be applied to building materials.

Keywords: Limestone; Neutronography; Consolidants; Sorptivity; Water kinetics.

1. Introduction

One of the most relevant conservation principles in the field of cultural heritage states that historic objects or structures must be restored and preserved. Limestones represent the main type of stone materials around the world to be the subject of cultural heritage programs. Unfortunately, this kind of substrates undergo to different degradation and alteration processes, such as salts crystallization, erosion, dissolution, biological attack, etc. [1,2]. For this reason, in the last years, various consolidant and hydrophobic products have been widely used in the treatment of building materials of historical monuments, in view of consolidation and conservation of such structures [3-5]. To guarantee compatibility with the porous substrates, added products must be characterized by a suitable penetration depth with negligible or minimum alteration due to water permeability, and be stable along long times. Therefore, porosity and pore size distribution represent crucial parameters in conservation process, since they regulate the fluid mobility inside the material.

In particular, water dynamics in porous building materials represents a key tool for understanding the degradation processes due to both chemical and physical interactions between water and surrounding stone. As is well known, the rate of imbibitions, and hence the amount of water penetrating the porous material, can be considered simply proportional to the square root of the exposure time. Water diffusion into homogenous structures follows a classical behavior, although violation in the diffusion-like mechanism has often been achieved [6,7]. Such inconsistency must be associated to some kind of

54 processes occurring during the water suction, or to the presence of inhomogeneity within the inner
55 structure of the investigated sample. Application of consolidants strongly affects the water motion,
56 reducing the weathering effects to which buildings and monuments are continuously exposed.

57 The present study is part of a project having as goal the quantitative two- and three-dimensional
58 textural compositional analysis of a variety of rocks at different scales from the microscopic to the
59 macroscopic domain, aimed at the quantification of the fundamental properties such as porosity and
60 pore size distribution, geochemistry, crystalline abundance, degradation attitude, etc.. Neutron and X-
61 ray imaging techniques allow the analysis of different properties and processes including porosity,
62 degradation effects, fluid mobility and penetration depth of protective and consolidant products [8-
63 13]. In addition to diffraction and spectroscopic measurements, neutrons, beyond compositional and
64 textural features of rocks, can observe as well variations and damages induced by both the application
65 of different coatings and different aging tests in bulk samples, by static and dynamic neutron
66 radiography (NR).

67 In this framework, neutronography was employed in order to investigate, in a completely non-
68 invasive way, the interaction between two different protective/consolidant products, namely
69 nanosilica (nano-SiO₂, NS) and nanolime (Ca(OH)₂, NL), and a type of limestone widely used in
70 Italian Baroque buildings, i.e. *Pietra di Lecce* stone employed in Lecce city (Puglia, Southern Italy).
71 Limestones under investigation were already characterized by mineralogical-petrographic and
72 geochemical techniques [14-16]. Treated samples also underwent to different aging tests, such as
73 temperature/relative humidity jumps and salt crystallization. Aim of the present study was to visualize
74 the evolution of porosity, fracture network and rock disaggregation, also related to the texture
75 microstructure, texture of the rocks and type of products used for their conservation. In the case of
76 building stones, knowledge of these effects will help in elucidating their characteristics of durability
77 and variation over time. Finally, we remark that, in this topic, the effects of protective and consolidant
78 products are frequently limited to a qualitative description, whereas there are only few examples of
79 studies providing a quantitative view, as the one proposed here.

80 81 **2. Research Aim**

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83 In this work, neutronography was used to quantitatively and non-invasively study the variations of the
84 porous structure, as a consequence of the application of different coatings having both consolidant and
85 hydrophobic features, in a set of limestones cropping out in Lecce (Puglia, Southern Italy) and
86 employed as building materials in Baroque historical monuments, also submitted to different aging
87 tests. The performed research looks particularly promising in the field of Cultural Heritage, where the
88 characterization of effects of coatings on building materials is necessary before selecting the
89 appropriate restoration procedures.

90 91 **3. Materials and Methods**

92 93 *3.1. Materials and preparation of test specimens*

94
95 *Pietra di Lecce* (PL) stone is a fine-grained calcarenite, with a characteristic pale-yellow color. It is
96 widely used in the Baroque heritage of the Salento area, as well as in minor buildings (Fig. 1).
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Fig. 1. (a) Ancient quarry of *Pietra di Lecce* stone located in S. Cesario Street, Lecce; (b) Example of degradation forms suffered by *Pietra di Lecce* stone.

103 Petrographically, it is a wackestone [17], mainly composed of micritic fraction, mixed with fine clay
104 minerals and poor cryptocrystalline calcitic cement; it contains fine microfossil fragments, grains of
105 glauconite, sporadic quartz grains and phosphatic nodules [18,19]. The integral open porosity is
106 around 40%, with pore radius mainly between 4 e 0.5 microns. The rock has around 80% of calcium
107 carbonate and the insoluble residue is essentially made of clay minerals and glauconite. Before
108 proceeding with the salt crystallization tests (artificial decay process), the samples were treated with
109 two different consolidating products by brush application in order to verify their susceptibility to
110 degradation. In particular, the commercial products chosen for the experimentation are: a) nanosilica
111 suspension (Nano Estel®), and b) nanolime suspension (CaLoSiL®). The application of the
112 consolidants was carried out on the surface of the stone samples (~ 5 × 5 × 2 cm³) by brushing until
113 they were getting saturation. Throughout the experimental phase, an untreated sample was used for
114 subsequent comparison with the treated samples by subjecting it to the same procedure (see Table 1).
115

Sample Code	Products	Experimentation tests
PL1	Nano Estel®	Climatic chamber (T, RH) after 3 cycles of salt crystallization
PL2	Nano Estel®	Salt weathering (15 cycles)
PL3	Nano Estel®	Consolidated
PL4	CaLoSiL®	Climatic chamber (T, RH) after 3 cycles of salt crystallization
PL5	CaLoSiL®	Salt weathering (15 cycles)
PL6	CaLoSiL®	Consolidated
PL-TQ	Untreated	Not aged

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Table 1. List of specimens and details about products and experimentation tests.

119 Both before and after treatments, some physical properties have been measured through the following
120 techniques: colorimetric tests, scotch tape test and water absorption coefficient by capillarity [20].
121 Colorimetric test (CT) was performed by means of a CM-2600d Konica Minolta spectrophotometer,
122 to evaluate chromatic variations induced by the treatment according to Normal 43/93. Chromatic
123 values are expressed in the CIE L*a*b* space, L* being the lightness/darkness coordinate, a* the
124 red/green coordinate (+a* indicating red and -a* green) and b* the yellow/blue coordinate (+b*
125 indicating yellow and -b* blue). Scotch tape test (STT) is a method for making a quantified appraisal
126 of the adhesion of a surface or a near to-surface layer to a substrate. According to [21], a pressure-
127 sensitive tape was applied to the examined area and then removed. After each tape removal on the
128 same area (for a total of 5 times), the weight of material detached from the surface was measured.
129 Measurements were carried out on three samples for each treatment. The amount of materials
130 removed from the surface of the stone should reflect the cohesion characteristics of the substrate.
131 Therefore, an evaluation of the consolidation effects (after restoration procedures) as well as the
132 surface degradation was achieved by using this test. After the consolidation of the stone and the

133 evaluation about the formulation's properties, the water absorption coefficient by capillarity was
 134 measured following the normative on three specimens for each treatment [20]. Then, untreated and
 135 treated specimens (three for each treatment) have undergone salt crystallization test to evaluate the
 136 weathering resistance of rock materials [22,23]. As far as salt crystallization is concerned, the
 137 procedure adopted is the one described in the existing standard [24], modified according to Benavente
 138 et al., 2001 [23]. Specifically, specimens underwent several crystallization cycles consisting of: a) 2 h
 139 of immersion in a supersaturated solution of sodium sulfate (14% w/w at 20 °C) for 10 % of their
 140 height, b) 8 h of drying in an oven at 45 °C, and c) 16 h of cooling at room temperature. The initial
 141 weight of each test sample was measured as well as the weight after each cycle; the resulting weight
 142 loss was therefore determined. Lastly, aging test by means of a climatic chamber has been carried out
 143 on specimens subjected to 3 cycles of salt crystallization test. The specimens held inside this
 144 temperature/humidity-controlled environment for 1500 hours, with a temperature variation between
 145 20 °C and 45 °C and relative humidity from 40 to 80%. For laboratory experimentation, specimens of
 146 *Pietra di Lecce* stone were collected from quarries located in Salento area (Cursi-Lecce).

147

148 3.2. Neutron radiography and image processing

149

150 Neutron radiography measurements were carried out at the cold neutron imaging spectrometer
 151 IMAGINE of the Laboratoire Léon Brillouin (LLB) at the Orphée Reactor, in Saclay (F). Resolution
 152 was optimized by varying the L/D ratio, being L the distance between the entrance aperture of the
 153 neutron beam and the image plane, and D the diameter of the collimator aperture. Absorption
 154 contrast values with a resolution of 0.1% were achieved by increasing the L/D ratio up to 400, that
 155 guaranteed a spatial resolution of $\sim 250 \mu\text{m}$. The initial neutron flux was of about 2×10^7 neutrons \times
 156 $\text{cm}^{-2} \times \text{s}^{-1}$, that included a large spectrum of cold neutrons with wavelength ranging from 3 to 20 Å.
 157 Detection of the transmitted beam was achieved by using a sCMOS ANDOR NEO camera coupled to
 158 a Canon EFS 60mm F/2.8 Macro USM.

159 The acquired images allowed us to easily follow the water content profile because the key elements of
 160 the investigated limestones (Ca, C, O, etc.) are characterized by a cross section two orders of
 161 magnitude lower than hydrogen atoms in water. This means that even for low amount of penetrated
 162 water a good “contrast” between water and stone can be achieved.

163 First of all, dark field ($I_{(df)}$) and open beam ($I_{(ob)}$) images were acquired and used for further
 164 corrections. Limestones treated with the two coatings were placed one by one on a stack of filter
 165 paper within an aluminum container so that the whole stone specimen could be scanned. After the
 166 positioning, the water absorption dynamics by capillarity was recorded by manually adding water into
 167 the aluminum basement which ensured the saturation of the 10 mm thickness filter paper pack
 168 (obtained from Kaltek S.r.l. Padova Italy). Scans were acquired until full saturation of the specimen,
 169 with an exposure time of 10 s for all the investigated stones except than PL1, for which an exposure
 170 time of 40 s was used.

171 The images were pre- and post-processed using a homemade macro at the IMAGINE beamline.
 172 Accordingly, raw images of the dry ($I_{(dry)}$) and wet ($I_{(wet)}$) limestones were properly corrected with
 173 respect to both dark field ($I_{(df)}$) and open beam ($I_{(ob)}$) images using the following relations:

174

$$175 \quad I_{(wet,corr)} = C \frac{I_{(wet)} - I_{(df)}}{I_{(ob)} - I_{(df)}} \quad (1)$$

176

177 and

178

$$179 \quad I_{(dry,corr)} = C \frac{I_{(dry)} - I_{(df)}}{I_{(ob)} - I_{(df)}}, \quad (2)$$

180

181 where C is a rescaling factor which takes into account the neutron beam fluctuations. After that,
 182 images were uncounted using a median filter in order to remove unwanted bright pixels mainly due
 183 to scattered γ -rays. Absolute transmission images of the samples were obtained with an absolute
 184 precision in the 1% range. The water absorption analysis was conducted by normalizing hydrated
 185 samples with respect to the steady-state dry images taken prior to the water absorption, in order to get
 186 images in which the contribution of the stone is removed and the measured transmission is directly
 187 related to the amount of water in the sample [25]. The same procedure was applied on a staircase-like
 188 sample holder containing twelve different water contents with standardized thickness, varying from
 189 0.09 mm up to 5.00 mm. A plot of the neutron transmission vs. water thickness was created and used
 190 as a calibration curve for the water content of the water absorption images. The aforementioned
 191 procedure became necessary in the case of high values of water content, i.e. for equivalent thickness
 192 higher than 2.00 mm, where Beer-Lambert law is no more satisfied.
 193 Pre-processing and image analysis were performed by using Fiji ImageJ (Fiji Is Just ImageJ - Image
 194 Processing and Analysis in Java, open source) [26].
 195 Finally, the water content distribution inside the stones was quantified according to Kim et al. [27].
 196 By dividing the obtained wet image ($I_{(wet,corr)}$) to the corresponding dry one ($I_{(dry,corr)}$), the 2D
 197 distribution of the water thickness ($\delta_w(x, y)$) can be written as:

$$198 \quad \delta_w(x, y) = - \frac{\ln \left[\frac{I_{(wet,corr)}(x, y)}{I_{(dry,corr)}(x, y)} \right]}{\mu_w} \quad (3)$$

200 In the above expression, $I_{(dry,corr)}(x, y) = I_0(x, y)e^{-\mu_s \delta_s}$ and $I_{(wet,corr)}(x, y) = I_0(x, y)e^{-(\mu_s \delta_s + \mu_w \delta_w)}$
 201 respectively, being $I_0(x, y)$ the intensity of the incoming beam, μ_s and μ_w the stone and water
 202 attenuation coefficients, δ_s and δ_w the measured thickness of the stone and the equivalent water
 203 thickness.
 204 Being the thickness of the stone known, the mean moisture content (MC) was first of all calculated
 205 by:
 206
 207

$$208 \quad MC = \frac{\delta_w \cdot \rho_w}{\delta_s} \quad (4)$$

209 being ρ_w the density of water.

210 After that, the water content (WC), expressed in weight percentage, was determined as:

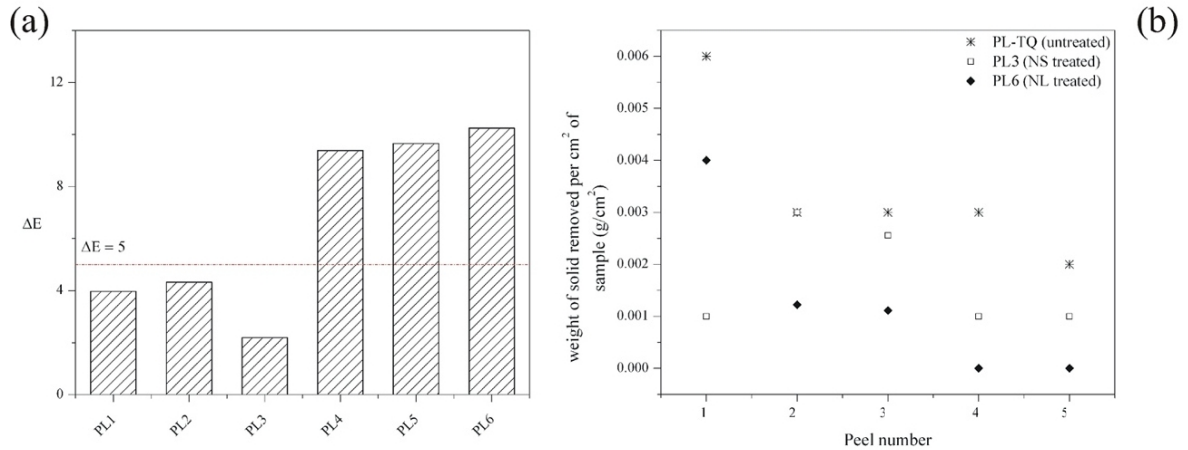
$$211 \quad WC = \frac{MC}{\rho_s} \quad (5)$$

212 with ρ_s , the density of the stone, taken almost equal to 2.71 g/cm³, being the stone mostly made up of
 213 calcite (90% of CaCO₃).

214 4. Results and Discussion

215 4.1. Colorimetric test, scotch tape test, water absorption coefficient by capillarity and salt 216 crystallization test

224 Chromatic variations were evaluated to verify if a significant difference in color is present among
 225 treated and untreated samples, based on the normative [28]. Colorimetric tests results (Fig. 2(a))
 226 indicate that the color change (ΔE) is mostly around 3-4 for samples treated with NS and these
 227 values may be considered satisfactory [29]. For samples treated with NL, becoming lighter, greener
 228 and bluer, the color differences are more enhanced. The scotch tape test (SST), carried out on PL-TQ,
 229 PL3 and PL6 stones as examples, furnished evidences on the superficial cohesion of the stone. The
 230 obtained results are shown in Fig. 2(b). The comparison between the mechanical features of treated
 231 samples with untreated ones highlighted an improvement in superficial cohesion of treated specimens
 232 that show a diminishing in released material. More specifically, specimen treated with NL gives a
 233 better result, showing an enhanced efficacy as far as increased cohesion properties are concerned.
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 237 **Fig. 2.** (a) Colorimetric test results of treated samples; (b) Scotch tape test results of treated and untreated
 238 samples.
 239

240 To get further information about the improvements that the NS/NL-protective layer exerts on
 241 limestone specimens, the water absorption coefficient (W_{ac}) for samples PL-TQ, PL3 and PL6 was
 242 also calculated, according to the UNI 10859 standard procedure [20]. The choice of these samples is
 243 justified by the occurrence that they are the only specimens for which the water absorption coefficient
 244 can be considered reliable. In fact, in the case of artificially aged samples, the presence of salts and/or
 245 humidity leads to visible alteration of the sample weights mostly due to the growth of salt crystals
 246 within the porous structure, instead of the presence of water.

247 Before the absorption test, weights of the dry samples were measured. Being the surface A of the
 248 sample in contact with water known, the amount of absorbed water per unit area Q_i at a time t_i can be
 249 calculated as:
 250

$$251 \quad Q_i = \frac{m_i - m_0}{A} \times 1000, \quad (6)$$

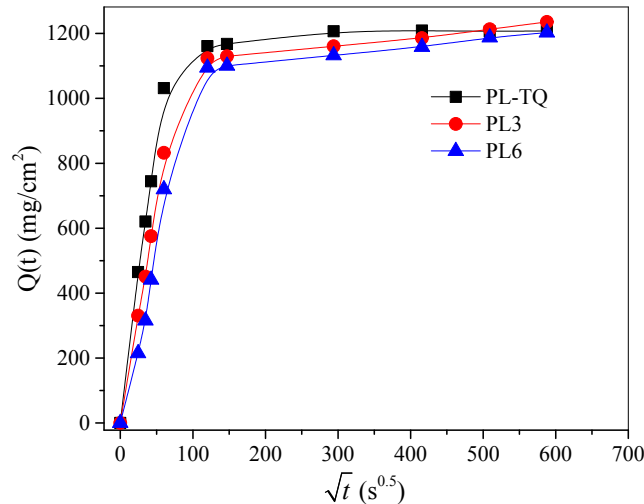
252
 253 with m_i and m_0 equal to the mass (in grams) of the wet (measured at a time t_i after the water
 254 contact) and dry sample, respectively.

255 The amount of water absorbed per unit area by a porous solid, after the period of immersion t , can be
 256 considered simply proportional to the square root of time:
 257

$$258 \quad Q(t) = W_{ac} \sqrt{t}, \quad (7)$$

259
 260 with W_{ac} equal to the aforementioned water absorption coefficient ($\text{g}/(\text{m}^2\text{s}^{0.5})$).

261 The plot of $Q(t)$ vs. \sqrt{t} for samples PL-TQ, PL3 and PL6 is reported in Fig. 3. All the curves show
 262 an initial linear trend (below 150 s^{0.5}), immediately followed by an asymptotic behavior, accounting
 263 for the full saturation of the specimen. The overall trend indicates a capillary network, dimensionally
 264 homogeneous and continuous or, in general, characterized by a good connection of the pores.
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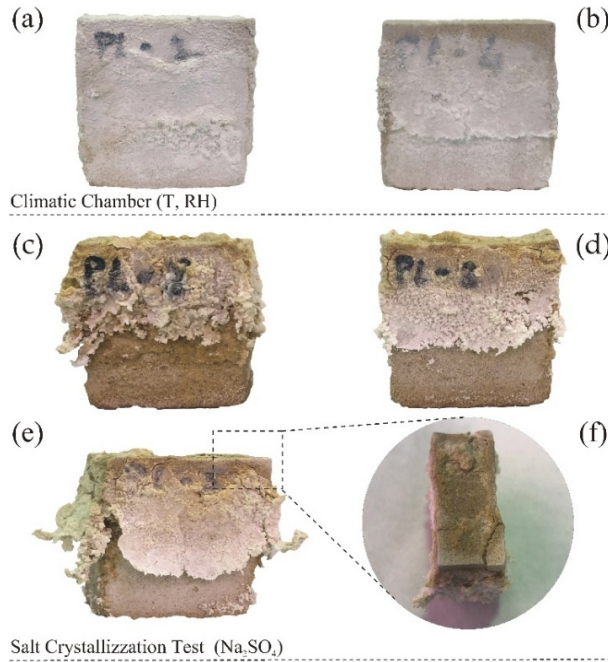


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268 **Fig. 3** $Q(t)$ vs. \sqrt{t} plot for samples PL-TQ, PL3 and PL6. Continuous lines are guides for eyes.
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270 According to Eq. 7, water absorption coefficients were evaluated from the slope of the linear part of
 271 curves displayed in Fig. 3, taking into account measurements up to 30 minutes, in agreement with the
 272 UNI 10859 standard procedure. The obtained values are 176.31 g/(m²s^{0.5}) for the reference sample
 273 (PL-TQ), 133.95 g/(m²s^{0.5}) for the sample treated with NS (PL3) and 100.31 g/(m²s^{0.5}) for the sample
 274 treated with NL (PL6). A slight decrease in the slope was experienced in both consolidated
 275 specimens, indicating a relative difficulty of water penetration, which can be attributed to a weak
 276 connection of the capillary pores or to heterogeneity in the distribution and/or dimensional variability
 277 of the porous network induced by both treatments.

278 Finally, the salt crystallization test was performed by means of partial immersion [23], based on
 279 standardized EN 12370:2001 procedure [24]. After just 24 h, efflorescences are noticeable on the
 280 surface of untreated sample as an effect of the migration of the saline solution. Conversely, in the
 281 consolidated samples, the efflorescences begin to be noticed around the 5-6 cycle. This is reasonably
 282 due to the evaporation rate of the solution at the surface of the stone, that could have been affected by
 283 the presence of the consolidant [30]. During the various cycles, increases and losses in weight up to
 284 the 15 cycle are evident in all samples regardless of the type of treatment. This occurrence can be
 285 explained taking into account that the location of salt crystallization is controlled by the water flow
 286 and the substrate permeability, that allows the salt to move. In fact, the formation of salt crystals
 287 usually generates significant internal stress or pressure for volume expansion [31,32]. If, on one side,
 288 the liquid phase allows salt to be transported, evaporation, outside or inside the material (i.e.
 289 efflorescence or subefflorescence, respectively), makes, on the other side, its crystallization possible
 290 [33]. After 15 cycles, specimens appear rounded, and the loss of small fragments is evident, mainly at
 291 the edges. Based on the obtained results and in agreement with [33], the observed variations
 292 (increasing and decreasing) in weight are the result of two phenomena occurring simultaneously,
 293 namely the development of efflorescence and subefflorescence, and the loss of material, although
 294 minimal, observed along the edges of the samples. (Fig. 4).
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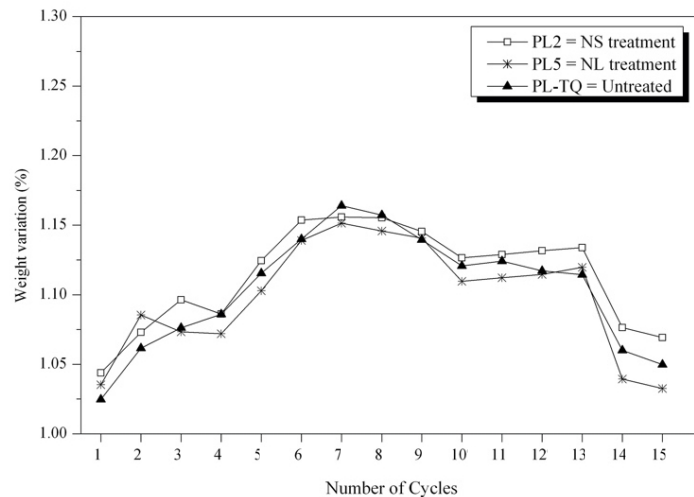


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Fig. 4. (a,b) Macroscopic appearance of specimens aged by temperature and relative humidity chamber; (c) untreated specimen after salt crystallization test (15 cycles); (d,e) NS and NL treated specimen after salt crystallization test (15 cycles); (f) detail of small fragment detachment at the edges of the specimen after salt crystallization test.

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Fig. 5 evidences, for all samples, an initial increase in weight (slightly greater for untreated sample), due to the entry of salt, prevailing over the loss by disintegration. After that, a relative progressive decrease in weight is detected, greater in the sample treated with NL [34,35]. This reduction in weight, although the efflorescences have been removed from the surface of the various specimens, does not allow the samples to reach the initial weight. This occurrence indicates that the observed increase is mainly due to the development of subefflorescences, and not to the loss of material or the presence of efflorescences.

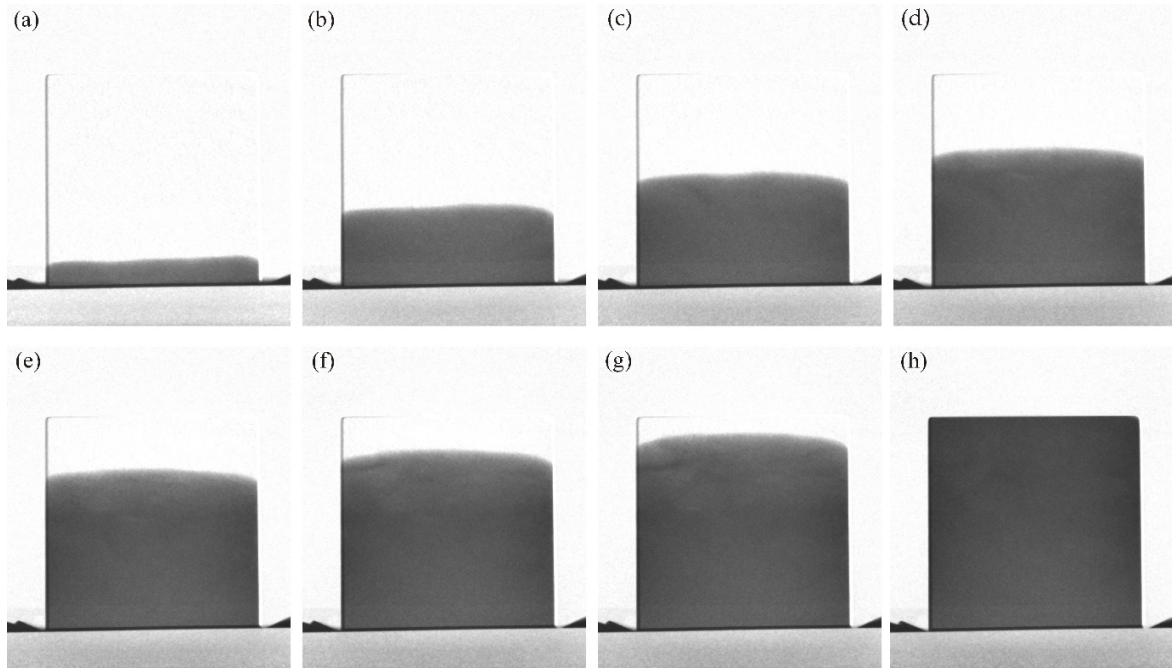


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Fig. 5. Weight variation (%) for specimens subjected to salt crystallization test.

4.2. Neutron Radiography

317 Neutron images collected for sample PL6 at different selected time-steps and with an integration time
318 of 10 s are displayed in Fig. 6, as example.
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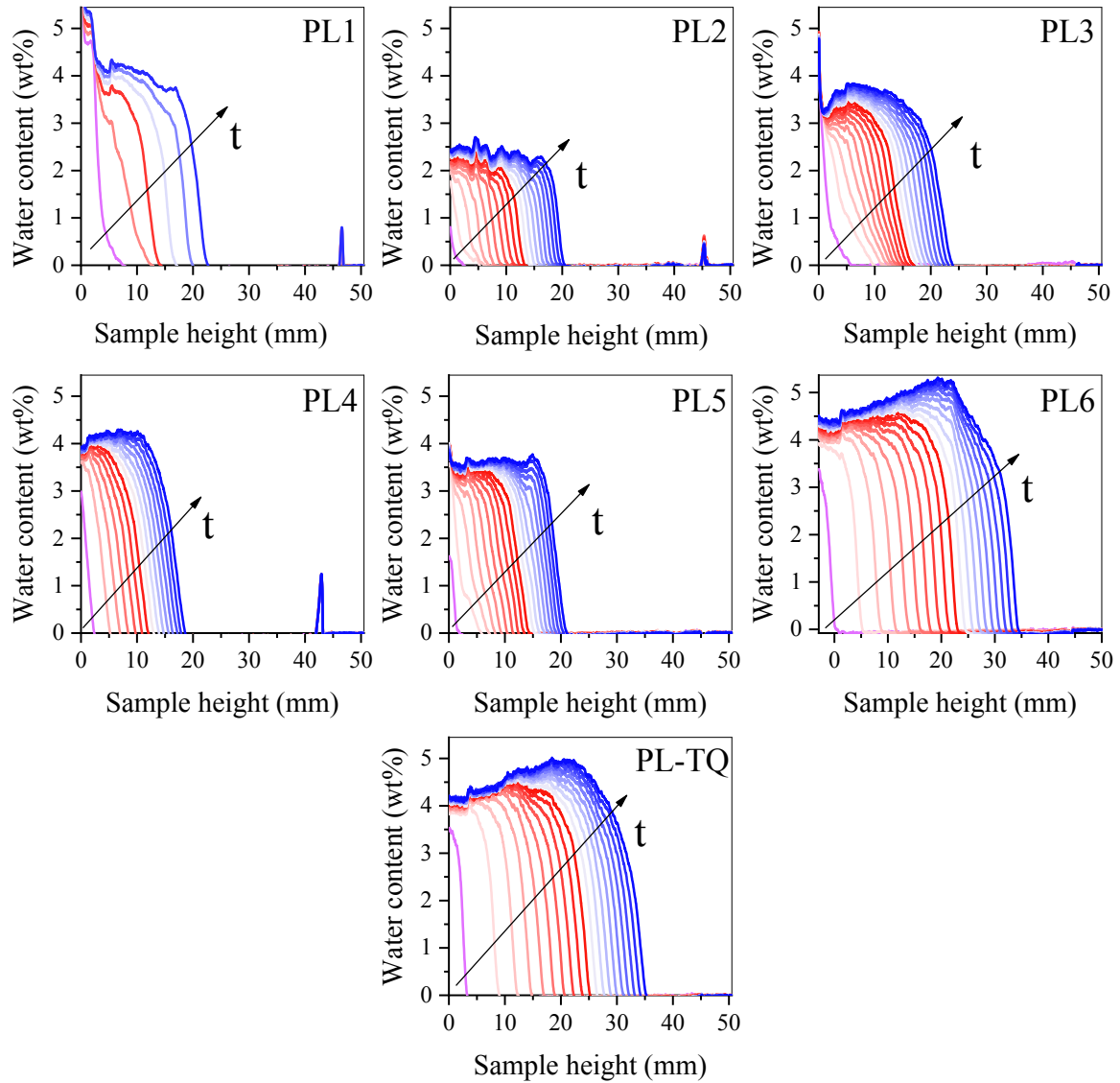


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322 **Fig. 6.** Water penetration images of samples PL6, in which it's possible to follow the water front position as
323 function of time: (a) 40 s; (b) 410 s; (c) 810 s; (d) 1210 s; (e) 1810 s; (f) 2040 s; (g) 2240 s; (h) saturation
324 condition.
325

326 Thanks to the high quality of the obtained radiographs, the water penetration into the porous calcite-
327 based materials can be clearly observed with high spatial and temporal resolution. The penetrating
328 water front becomes visible for almost all the investigated samples after a contact time of 10 - 40 s,
329 and goes towards the top of the stone with a regular rise until the full saturation of the specimen.

330 Going from the bottom to the top of the material, the water content decreases giving evidence of the
331 presence of two distinct phases (water/stone) within the inner structure of the limestone during the
332 imbibition. Furthermore, the formation of a well-defined boundary between the two aforementioned
333 phases, as evidenced by the regularity of the water front at different contact times, experimentally
334 supports the existence of a rather uniform microstructure without internal inhomogeneities, as already
335 reported [17-19]. Finally, water is observed to flows up into the limestone specimen without any
336 distortion of the path, testifying the absence of macroscopic (having size of the order of mm)
337 watertight zones, that would be clearly visible in the NR images as light spots within the investigated
338 ROI.

339 In Fig. 7 we report typical plots of water content (WC) as a function of the sample height for treated
340 and untreated PL samples, as obtained for different contact times by scans performed in the first 30
341 min of exposure.
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Fig. 7. Water content (WC) profiles as a function of the sample height for all investigated specimens. Plots are obtained for different contact times by scans performed in the first 30 min of exposure.

348 For all the investigated samples, the distance between two consecutive curves diminishes by
349 increasing the contact time, indicating an accelerated water penetration rate in the first minutes of
350 water absorption. This can be explained by taking into account both the initial available space for
351 water inside the stone material and the porosity. In particular, even if the stone under investigation can
352 be considered rather homogeneous [17-19], the observed diminishing could be justified in terms of a
353 “skin” effect, widely reported in literature [36], according to which the outer layer of the stone
354 appears significantly different from the inner ones (bulk) in terms of pore size distributions. Being the
355 porosity much higher close to the surface of the stone, we shall expect more pronounced water suction
356 by capillarity in the proximity of the outer shell, which slowly will tend to a plateau for long contact
357 time, accounting the full saturation of the specimen. Furthermore, it is worth remarking that,
358 according to the Young-Laplace equation [37], the capillary stresses are proportional to the inverse of
359 the effective pore radius. Accordingly, a faster filling of small pores was expected, since larger
360 cavities do not exert pressure enough to let the water flow up during the initial stage of contact.

361 Going on, it should be noticed that the obtained values for the water content and the height of water in
362 the case of treated specimens, both artificially aged or not, are always lower than those of the
363 untreated sample (PL-TQ), that were found to be ~ 5 wt% and ~ 35 mm, respectively. This occurrence

364 represents and experimental evidence of the consolidating action of both the used products. More in
 365 detail, the comparison of the wetting profiles of PL-TQ specimen with those calculated for the surface
 366 impregnated limestones not subjected to any artificial weathering test (PL3 and PL6) suggests that, in
 367 the early steps of the absorption test, the presence of nano-SiO₂ as consolidant clearly affects the
 368 water kinetics more than nanolime. In fact, after 30 min the suction motion into PL6, which was
 369 brushed with a ~ 2 mm thick layer of nanolime, turned out to be characterized by very similar values
 370 of WC and height of water. On the contrary, the water absorption for PL3 is more hindered of ~
 371 66.7%, reaching a maximum height of ~ 21 mm after 30 min. These preliminary results indicate that
 372 the use of nanosilica as a consolidating agent visibly affects the water uptake within the crystalline
 373 structure, presumably by occluding pores to a greater extent than nanolime. Concerning samples
 374 exposed to 15 cycles of salt crystallization, namely PL2 and PL5, a substantial reduction in the
 375 absorbed water can be observed. In particular, in the case of PL2 the water content turned out to be ~
 376 2.5 wt% after 30 min, reaching approximately ~ 18 mm of height in the sample, whereas a slight
 377 increase in the water content can be detected in PL5, reaching a value of ~ 3.5 wt% after the same
 378 time, and a penetration depth of ~ 20 mm. These results suggest that that the rising of water is more
 379 hindered in PL2 than in PL5 of ~ 28.6%, confirming the effectiveness of nanosilica as protective film
 380 in increasing the structural properties and hydrophobicity of the investigated limestone. Variations
 381 induced by thermal and RH treatment have also a measurable impact on the water absorption kinetics
 382 in PL limestones. In fact, in the case of PL1 and PL4 specimens, both consolidants seem to partially
 383 obstruct the water motion, as can be seen by the relatively low mean penetration depth reached by
 384 water in these two samples, with respect to PL-TQ. This can be reasonably due to an enlargement of
 385 the inner cavities induced by thenardite-mirabilite transition occurring as a consequence of changes in
 386 humidity and temperature [38]. In particular, the stone damage due to sodium sulfate is strictly related
 387 to the presence of these two different phases: because of the fluctuations in microclimatic conditions,
 388 the transition from thenardite to mirabilite is favored, and it is accompanied by the development of
 389 high crystallization pressures [22,39].

390 In order to quantitatively determine the effect of the application of consolidants and artificial
 391 weathering tests on the water uptake process inside the analyzed stones, a classical theory of the water
 392 suction in porous materials has been taken into account [40,41]. Based on the model of “capillary
 393 transport” by J. R. Philip [42], widely reported in literature for a variety of homogeneous, porous
 394 materials including limestones [43,44], the wetted region obtained by neutron images was
 395 approximated to a fully saturated rectangular wet front. In our case, i.e. 1-phase flow and with
 396 constant air pressure, the mean penetration depth $x(t)$ can be predicted as a function of time using the
 397 following equation:

$$398 \quad x(t) = S\sqrt{t} + B_0t + B_1t^{3/2} + \dots, \quad (8)$$

400 being S the so-called sorptivity (m/s^{0.5}), considered as a measure of the tendency to absorb and
 401 transmit liquid through capillarity, and B_0 a dimensionless parameter known as *Bond number*,
 402 numerically equal to:

$$403 \quad B_0 = (\rho K / \sigma) \times g. \quad (9)$$

404
 405 In the above expression, ρ indicates the density of water (~ 1000 kg/m³), K the intrinsic
 406 permeability of the rock (for limestone, permeability values range between 1.3×10^{-16} and 4×10^{-16}
 407 m² [45]), σ the air-water interfacial tension (~ 0.0729 N/m at T = 20 °C) and g the gravitational
 408 acceleration (~ 9.8 m/s²). Based on these values, B_0 was found from Eq. 9 to be equal to ~ 1.34×10^{-11} .
 409 As a consequence, during the experiment the contribution of gravity can be neglected with respect
 410 to the active capillary forces [46]. In other words, for short time-steps the water suction can be
 411 considered only capillary-driven, being the effect of gravity too low at the initial stage to affect the
 412 water motion, and Eq. 8 reduces to:

415

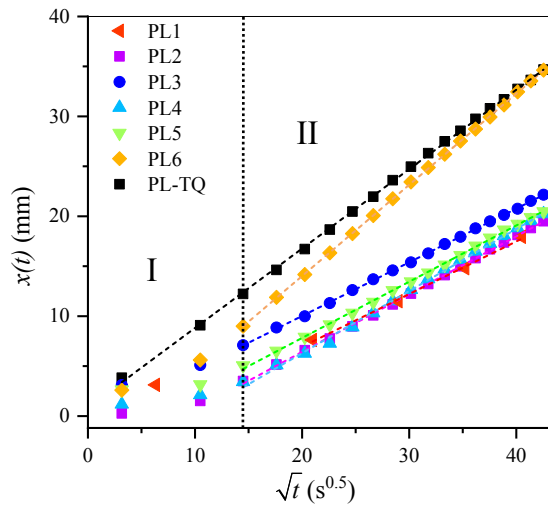
416

$$x(t) = S\sqrt{t}. \quad (10)$$

417

418 According to literature [47-49], $x(t)$ was experimentally obtained through NR by looking at the
 419 sample height corresponding to the inflexion points (IPs) of the decreasing curves shown in Fig. 7,
 420 accounting for the wetting front position (WFP). The IPs account for the transition between a water-
 421 saturated region and a dried one (grey and white areas within the stone shown in Fig. 6). For all the
 422 investigated samples, as can be seen from an inspection of Fig. 7, the inflexion points correspond to
 423 water content of about 1 - 2 wt%.

424 In Fig. 8 we display the $x(t)$ vs. \sqrt{t} plot for all the investigated PL samples at the initial stage of the
 425 water absorption process (first 30 min of exposure).
 426



427

428

429 **Fig. 8.** $x(t)$ vs. \sqrt{t} plot, as obtained from NR analysis, for all the investigated PL samples.
 430

431 First of all, it is worth of note that in the case of PL-TQ specimen, if compared to the treated PL
 432 samples, a favored water penetration is clearly observed. This can be due to the fact that since no
 433 protective coating is applied, an initial bottom swelling could occur, making the structure more
 434 susceptible to the presence of water, especially during the first minutes of exposure.

435 Based on Eq. 10, a linear dependence on $t^{0.5}$ was expected for the mean penetration depth, also
 436 according to what already reported in literature for uniform bricks, mortars and limestones [50-53].
 437 Actually, for all the investigated specimens, with the exception of PL-TQ for which a linear trend is

438 revealed, a non-linear dependence on $t^{0.5}$ can be observed during the first 4 minutes of exposure (\sqrt{t}
 439 $< \sim 15 \text{ s}^{0.5}$), followed by the expected linear trend. This occurrence suggests the presence of two
 440 regions characterized by different water suction kinetics, namely region I and region II. According to
 441 Küntz and Lavallée [54], a possible explanation for this different absorption behavior could be a
 442 deviation from the water flux gradient proportionality accounted by the Darcy's Law. Moreover, a not
 443 uniform capillary force during the water absorption, due to an intrinsic anisotropy of the stone, may
 444 also contribute to deviation from the theoretical model [55,56]. In our case, for treated samples it is
 445 reasonable to assume that, at the initial stage of the water absorption process (region I), the crossing of
 446 the NS/NL-protective layers by water after the initial contact can be responsible of the observed
 447 deviation from the theoretical model. In fact, the presence of consolidants brushed onto the limestone
 448 surface tends to change the chemical-mechanical properties of the stone outer layers, leading to
 449 significant variations in the effective pores' distribution. This leads the system towards a less
 450 homogeneous conformation characterized by two types of porosity, the first one associated to the
 451 stone + consolidant system (limited to the impregnated thickness) and the second one related to the

452 rest of the stone. As a consequence, the assumption at the basis of the model, consisting in dealing
 453 with homogenous, porous materials, is not valid any more. However, after a short period of time, the
 454 observed variation in the water absorption tendency, accounted by the residual linear-dependent part
 455 of the calculated depth profiles vs. $t^{0.5}$ (region II), can be associated to the presence of a greater pore
 456 volume made up of air bubbles of $\sim 0.5 - 4 \mu\text{m}$ available for the water flow inside the inner stone
 457 microstructure [57].

458 In order to quantitatively evaluate the susceptibility to weathering of the investigated materials, the
 459 sorptivity S was evaluated by linear fit (according to Eq. 10) of the WFPs in region II, as reported in
 460 Fig. 8.

461 The obtained S values in PL samples are reported in Table 2. As can be seen, they range from $9.13 \times$
 462 $10^{-4} \text{ m/s}^{0.5}$ (PL6) to $5.27 \times 10^{-4} \text{ m/s}^{0.5}$ (PL1), that corresponds to a relative variation of $\sim 73.2\%$.

463

Sample	$S \text{ (m/s}^{0.5}\text{)}$
PL1	5.27×10^{-4}
PL2	5.78×10^{-4}
PL3	5.37×10^{-4}
PL4	6.21×10^{-4}
PL5	5.63×10^{-4}
PL6	9.13×10^{-4}
PL-TQ	8.03×10^{-4}

464

465 **Table 2.** Sorptivity values calculated for all the investigated specimens through linear fit of the water front
 466 position as a function of the square root of time.

467

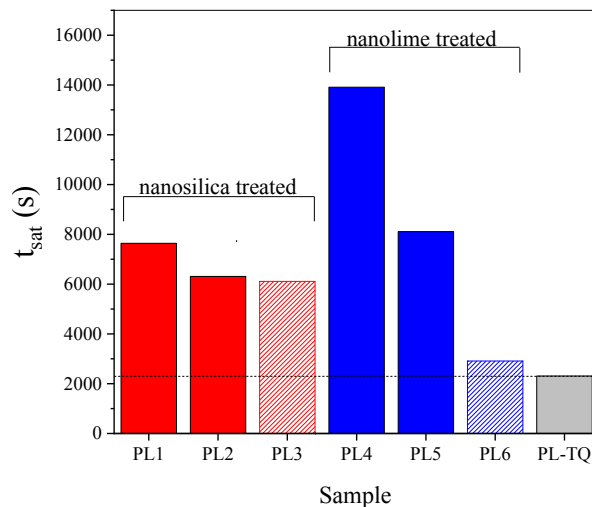
468 Such a difference can be attributed to several factors, including distribution of pores inside the stone
 469 matrix and artificial ageing treatments. Let's focus first of all the attention on values obtained for PL-
 470 TQ specimen, and for samples consolidated but not artificially aged, namely PL3 (consolidated with
 471 NS) and PL6 (consolidated with NL). In the case of PL-TQ limestone, the tendency to absorb and
 472 transmit water by capillary suction is expressed by an S -value of $8.03 \times 10^{-4} \text{ m/s}^{0.5}$, which is higher
 473 than, or at least equal to, the values obtained for the specimens treated with the two protective layers.
 474 In particular, the value of S for PL6 ($9.13 \times 10^{-4} \text{ m/s}^{0.5}$) appears almost comparable to that of PL-TQ,
 475 which means that during the initial stage of the water uptake the presence of nanolime brushed onto
 476 the surface does not affect almost at all the water absorption tendency. This can be explained
 477 considering the possible effect that NL exerts on the 3D microstructure of the investigated stone. As a
 478 matter of fact, it can reasonably hypothesized that the use of NL increases the water fluidity. This
 479 because this product does not occlude pores but rather reinforces them. As a consequence, the rise of
 480 the water front is not significantly hindered, being the microstructure close the surface almost "open"
 481 for the capillary suction process. Moreover, as evidenced by Al-Omary et. al. [58], the variation of the
 482 pores distribution induced by nanolime in limestone specimens is almost negligible, and hence the
 483 water absorption cannot be considerably affected by a different porosity. Finally, the limited impact of
 484 NL can be also ascribed to a relatively low penetration depth of such consolidant into the limestone
 485 structure.

486 On the contrary, the sorptivity calculated in the case of PL3 ($5.37 \times 10^{-4} \text{ m/s}^{0.5}$) appears decreased by
 487 47.1% with respect to reference specimen, suggesting a partial occlusion of the outer layer pores
 488 caused by the presence of the consolidant. As a result, the water rise in the first 30 minutes of contact
 489 is strongly hindered, which confirms that the use of Nano Estel® (nano-SiO₂) as protective product
 490 against short-term weathering agents is much more convenient with respect to CaLoSiL® (nanolime).

491 Regarding the kinetics associated to the initial stage of water suction for artificially aged samples
 492 treated with nanosilica (PL1 and PL2) or nanolime (PL4 and PL5), we can state that the comparable
 493 S values obtained for, on one side, PL1 ($5.27 \times 10^{-4} \text{ m/s}^{0.5}$) and PL4 ($6.21 \times 10^{-4} \text{ m/s}^{0.5}$) and, on the
 494 other side, PL2 ($5.78 \times 10^{-4} \text{ m/s}^{0.5}$) and PL5 ($5.63 \times 10^{-4} \text{ m/s}^{0.5}$) suggest that the type of treatment do
 495 not significantly affect the water absorption tendency of stones subjected to thermal/RH stresses
 496 and/or 15 cycles of salt crystallization.

497 It is worth of note, however, that both solutions (NL and NS) seem to act as stabilizers against
 498 artificial aging, as revealed by the obtained lower values of sorptivity with respect to that calculated

499 for PL-TQ. This occurrence could be related both to the intrinsic heterogeneity of each specimen and
 500 to an increase, because of the treatment and the aging, in the volume of the pores with capillary
 501 activity at the expenses of the coarser pores. In other words, the treatment is supposed to produce a
 502 change in the pore size distribution, limited to the impregnated thickness. Depending on the quantity
 503 of product that enters the porous network, variations in the pores distribution can occur. At the same
 504 time, the connectivity degree of the pores can be changed following salt crystallization. The salt may,
 505 in fact, completely occlude the smaller pores (with greater capillary activity) and only partially the
 506 larger ones.
 507 For a better understanding of the effect that temperature/RH jumps and salt crystallization cycles
 508 induce into the NS- and NL-treated samples, the time t_{sat} needed to reach the water saturated
 509 condition was also accounted.
 510



511
 512

513 **Fig. 9.** t_{sat} values calculated for all the PL samples. More in detail, red and blue closed bars refer to the
 514 artificially aged samples treated with nanosilica (PL1 and PL2) and nanolime (PL4 and PL5), whereas red and
 515 blue hatched bars refer to the only-treated samples not subjected to any artificial weathering test (PL3 and PL6,
 516 consolidated by NS and NL respectively). Grey closed bar refers to PL-TQ, used as reference.
 517

518 As can be seen, the saturation times for PL3 and PL6 are higher than that of PL-TQ, which means that
 519 both NL and NS consolidants keep the system strongly hydrophobic.

520 As already stated, the use of nanosilica as hampering agent against water penetration seems to be
 521 more convenient with respect to nanolime. This is also reflected in the time needed to reach the
 522 saturation state, as reported in Fig. 9. In fact, in the case of sample PL3 t_{sat} was found to be higher (~
 523 6110 s) than that of PL6 (~ 2900 s), revealing a hindering in water absorption process also for longer
 524 exposure time. As far as PL6 and PL-TQ are concerned, the saturation times seem to be almost
 525 comparable, suggesting a similar water soaking tendency of the two samples, in agreement with what
 526 already revealed from the sorptivity analysis.

527 Going on, limestones subjected to thermal/RH stresses after 3 cycles of salt crystallization (PL1 and
 528 PL4) are characterized by higher saturation times with respect to those exposed to 15 cycles of salt
 529 crystallization (PL2 and PL5). This can be explained by considering that, in the latter case, artificial
 530 weathering will presumably lead to fractures, cracks and plane distortions to a greater extent than
 531 those caused by the thenardite-mirabilite transition induced by changes in humidity and temperature.
 532 These features can be considered as preferential pathways for liquid water, which means that water
 533 can now penetrate more efficiently within the stone network and reach the top of the specimen more
 534 quickly, regardless of the type of treatment used.

535 On the other side, thermal and/or RH stresses can probably give rise to an enlargement of the initial
 536 micro-cracks of the stone, causing an irreversible structural damage and reducing the intra-cavity

537 distances. This will imply, in agreement with the Young-Laplace equation [37], a delay in reaching
538 saturation conditions.

539 From the whole set of neutron radiography results, the use of nanosilica is found to partially hinder
540 the pores of the outer layers, without fulfill them, in a more efficient way with respect to nanolime.
541 Although the calculated water absorption coefficients do not seem to fully support this statement, this
542 small discrepancy can be explained considering that, first of all, the penetration of NL and NS may be
543 different during the laboratory and NR measurements. At the same time, the hampering effect of the
544 two treatments with respect to water may not be the same. Furthermore, assuming a proper inclusion
545 of the consolidants within the porous structure of the investigated stones, the penetration depth of the
546 two products may be different, giving rise to different water diffusion properties especially at the
547 initial stage of the water absorption process.

548 Finally, it is also worth remarking that an almost-open microstructure, as observed for nanolime
549 consolidated limestones, is anyway of relevance in material science, since in this case the elastic
550 modulus and the thermal expansion coefficient of the rock are not altered in substantial way, and
551 water transport by capillary suction is still possible.

552

553 **5. Conclusions**

554

555 In this work, a systematic neutron radiography investigation on *Pietra di Lecce* limestone, widely
556 employed as building material in Lecce city (Puglia, Southern Italy), was performed. The aim was to
557 provide an evidence of the effectiveness of two different commercially-available consolidants (i.e.
558 nanosilica and nanolime) as protective agents against several artificial weathering tests. The obtained
559 neutron radiographs allowed us to visualize, in a non-destructive way, the water motion inside the
560 investigated limestones, which was used as marker for the study of the water absorption/ petrophysical
561 properties. A close relationship between structure, texture and composition of the rock and its
562 behaviour, in terms of response to degradation, was demonstrated. The qualitative and quantitative
563 analysis of the maximum amount of absorbed water, wetting front position and saturation times,
564 revealed an overall better performance of nanosilica with respect to nanolime, even if slight changes
565 in the capillary transport kinetics of aqueous solutions were highlighted. The effects of artificial
566 weathering on the pores network were also evidenced, suggesting the formation of new channels,
567 plane distortions and cracks, associated to the strong crystallization pressure experienced by the
568 structure as a result of phase transitions induced by artificial microclimatic variations.

569 As final remark, we want to underlying that the results reported here can be used as a methodological
570 proposal scheme, to be defined from time to time, for selecting and designing the proper procedure to
571 be adopted in order to preserve and maintain buildings/objects of interest in the field of cultural
572 heritage and conservation science.

573

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575

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