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# A NEW PREVENTIVE COATING FOR BUILDING STONES MIXING A WATER REPELLENT AND AN ECO-FRIENDLY BIOCIDES

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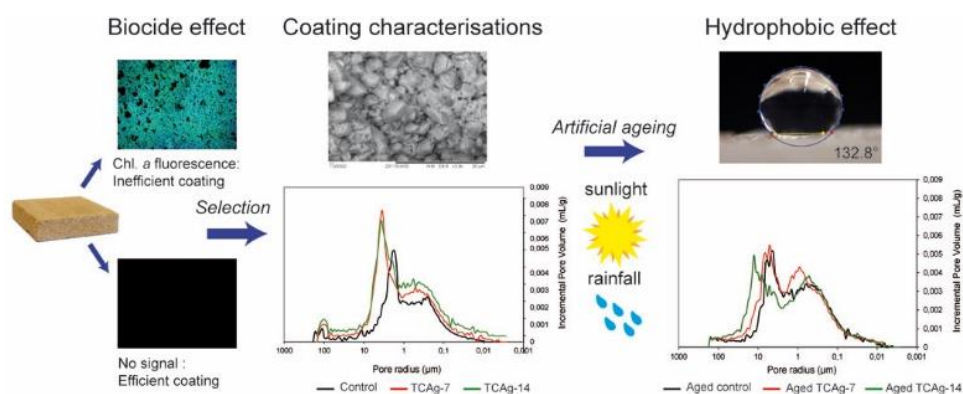
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## Graphical abstract



## Abstract

The durability of stone monuments is a constant problem as their decay through weathering is irremediable and endless. Fortunately, coatings are becoming more and more efficient and tailored to specific alterations of the stone material. This study aimed at developing an eco-friendly coating with both hydrophobic and biocide properties based on a silane/siloxane emulsion as a water repellent combined with chitosan and silver nitrate as biocides. Chitosan was first added at different concentrations to the water repellent and its efficacy was tested in laboratory conditions by the inoculation of axenic suspension of the green algae *Chlorella vulgaris* on a building porous limestone. Chlorophyll *a* fluorescence analysis displayed the chitosan acted on the photosystem of algae and limited their development but its effect was not optimal and higher dose modified the aspect of the stone. Low concentration of silver nitrate achieved a good performance thanks to the combination with the chitosan and the water repellent. The properties of coated stones and the efficacy of the formulation were assessed at two different doses of coating. The results showed that the lowest dose gathered all requirements to both preserve the stone monument with a weak colour change over time and to reach optimal biocide effect and a good hydrophobicity.

## 43 1. Introduction

44  
45 For centuries, stone has been considered to be the perfect building material thanks to its durability.  
46 It imparted nobility and demonstrated the power and wealth of the building owners. The choice of stones  
47 was often dictated more by their aesthetics and availability rather than by their physical and mechanical  
48 properties. Now, the historical and cultural significance of many monuments calls to their preservation.  
49 The first effects of weathering are aesthetic but eventually lead to disintegration. Preserving stone in  
50 Cultural Heritage is a more effective way to assist in conservation than operating on altered stones by  
51 consolidation and substitution, processes that are more expensive and difficult since many quarries are  
52 now closed.

53 Weathering is mainly caused by climatic and anthropic conditions modulated by the intrinsic properties  
54 of stone linked to the fabric elements [1,2]. Water is the main natural factor of weathering which  
55 penetrates inside the stone directly by rainfall or by capillary rise. It causes damage through its chemistry  
56 laden with salts or pollutants and its mechanical stress induced by the changing states with temperature  
57 variations [3–5]. Protective layers, in the form of natural coatings, have been applied for a long time to  
58 prevent stone alteration. Some of them are still under study like oxalate salts for the protection of marble  
59 and limestone against chemical weathering [6]. Nevertheless, the development of water repellents based  
60 on synthetic inorganic and organic polymers substantially increased their efficiency and durability [7].  
61 Hybrid coatings developed since the 1980s are mixed organic and inorganic components in mild  
62 synthetic conditions such as sol-gel process using metallo-organic precursors [8–10]. They have a good  
63 hydrophobic function that can still be improved to reach a superhydrophobicity with the silica  
64 nanoparticles embedded at various concentrations [11–13]. Avoiding the ingress of water could be the  
65 key to stop all the deleterious effects that alter stone monuments, but environmental factors like wall  
66 orientation, stone position and shape could favour biological degradation despite the application of a  
67 water repellent [14]. The intrinsic properties of building materials such as roughness, porosity and  
68 mineral composition also provide an appropriate environment for biological adhesion [15–17], thus  
69 compromising the efficiency of water repellents [18]. Furthermore, biocides used to remove biofouling  
70 inhibit the efficiency of water repellent if applied later [19]. Nowadays biocides are specifically  
71 developed for a preventive effect. Thanks to sol-gel process, many hybrid coatings are easily  
72 functionalised by the incorporation of metals as Ag, Cu, Zn, widespread for their antimicrobial  
73 properties and used in many fields for a long time [20]. In Cultural Heritage, they are still being  
74 investigated thanks to the emergence of nanoparticles (NPs – CuNPs, CuONPs, AgNPs, ZnONPs...),  
75 whose the performance has been assessed [21–24]. For many years, great interest has been devoted to  
76 the photocatalytic activity of the  $\text{TiO}_2$ , but many drawbacks persisted, e.g. its dependence on the wall  
77 exposition to sunlight, on the formation of soluble salts, on the dissolution of  $\text{TiO}_2$  by rainfall and on its  
78 superhydrophilicity [25]. The best solution to reduce the penetration of water into the stone whilst  
79 keeping a biocide effect seemed to mix a water repellent and a biocidal or self-cleaning coating. Many  
80 studies demonstrated the effectiveness and the interaction of different components [13,26–28].

81 The present study aims at developing a new protective coating combining hydrophobic and biocide  
82 effects. Because many biocides have been banned due to their negative impact on the environment and  
83 human health, this research looked for an eco-friendly alternative. The chitosan, a polysaccharide  
84 derived from the chitin of crustaceans, exhibits an antibacterial activity despite its low toxicity towards  
85 mammalian cells [29,30].

86 In a previous study [31], the biocide effects of coatings based on tetraethoxysilane functionalised with  
87 hydrophobic silica as the water repellent were tested through chlorophyll *a* fluorescence with different  
88  $\text{AgNO}_3$  concentrations as the biocide. The lowest concentration of  $\text{AgNO}_3$ , when combined with  
89 chitosan and hydrophobic silica achieved an optimal biocide impact. Therefore, the addition of chitosan  
90 allowed reducing the use of  $\text{AgNO}_3$ , which is environmentally desirable. Moreover, the previous study  
91 used hydrophobic silica as the water repellent, which dispersed heterogeneously on the stone. The  
92 hydrophobic effect was also improved in the present study by the use of a hybrid silane/siloxane  
93 polymer. So the present study aimed at finding the best coating with chitosan as the only biocide or the  
94 best mixing of chitosan, silver nitrate and water repellent. It was designed to first validate the biocide  
95 effect with a biofouling test in laboratory conditions using the green alga *Chlorella vulgaris*. In a second  
96 step, coatings whose biocide impact was validated were further assessed for their influence on the aspect

97 and microstructural properties of the stone. Finally, the hydrophobic performance and the durability  
98 were evaluated by artificial ageing procedure simulating sunlight and rainfall.

## 99 2. Material and Methods

### 100 2.1. Substrate: Dom Stone

101  
102 Experiments were performed on a stone used in buildings and monuments in northern France and  
103 southern Belgium [32]. It is a limestone called the Dom stone dated from the Bajocian (180 Ma). For  
104 this study, fresh stone blocks were collected from the underground quarry located in the Dom-le-Mesnil  
105 village of the French Ardennes.

106 Dom stone is a russet bioclastic stone including iron oxide content (0.5 %) and made of calcitic debris  
107 (85 %): numerous echinoderm ossicles (25 %) in a syntactic cement (35 %), shell fragments (10 %),  
108 micritic grains (10 %) and with only few quartz grains (5 %) scattered in the rock [33]. It was chosen  
109 for its interesting petrophysical properties. Mercury (Hg) porosity value is about at 21.4 %. The pore-  
110 size distribution is bimodal with a major pore access radius at 1.8  $\mu\text{m}$  and a second one at 0.25  $\mu\text{m}$ .  
111 More precisely, 51.6 % of pore access radii are larger than 1  $\mu\text{m}$ , 41 % are between 1 and 0.1  $\mu\text{m}$  and  
112 7.4 % are between 0.1 and 0.01  $\mu\text{m}$ . The capillary coefficient  $C_1$  relative to the weight increase per  
113 surface and per square root of time unit is 146  $\text{g}\cdot\text{m}^2\cdot\text{s}^{-1/2}$  [34] and implies good connectivity in the  
114 intergranular macroporosity. Such characteristics make the stone particularly sensitive to weathering  
115 like heterogeneous disintegration [35] and mainly favour a bioreceptivity that results in a significant  
116 greening of the stone [36].

### 117 118 2.2. Composition and application of coatings

119  
120 The protective coatings presented in this study have as a basis a formulation named Tegosivin<sup>®</sup> HE 328  
121 developed by Evonik Industries AG. It is an emulsion concentrate based on organo-modified siloxanes  
122 and alkoxy-functional silanes. The polymerisation of this material is achieved at room temperature  
123 through a sol-gel process. This chemistry involves the evolution of nanoparticles in colloidal solution in  
124 a polymer network by gelation using Silicon as a precursor. Tegosivin<sup>®</sup> HE 328 was designed for the  
125 impregnation of building materials such as brick, stone and concrete, and is often used as a protective  
126 coating for porous stones in monuments [37,38]. It is diluted in water whereas many hybrid  
127 nanocomposite materials are diluted in organic solvents that promote the penetration of the treatment  
128 [39,40] but are less environmental friendly and pose health problem to the person applying the treatment.  
129 Moreover, Tegosivin<sup>®</sup> HE 328 was used here both as the precursor for the polymerisation of coatings  
130 and for its hydrophobic property.

131 Dom stone blocks were cut in prismatic slabs (5 x 5 x 1 cm) dried at 70°C in a forced-air oven. They  
132 were weighed every day until the weight was stable. Products were sprayed on stone at a distance of  
133 about 20 cm in a single-step application with an airbrush tool which provides an air pressure of 8 bar  
134 and 25 L/min. Many procedures of coating application were investigated and the spraying procedure  
135 was used to match with the use of restoration workers and to limit the loss of product. They were applied  
136 on triplicate stone slabs. Table 1 gives an overview of the seven coatings investigated with their  
137 respective concentrations, their consumption and dry weight on samples. All tested coatings were based  
138 on 97 g/L of Tegosivin<sup>®</sup> HE 328 diluted in distilled water. Two biocide agents, commercially acquired  
139 from Sigma-Aldrich, were added. Chitosan is a poly-glucosamine polymer commonly obtained by de-  
140 acetylating chitin from crustacean waste. It is currently used in the food-processing industry because of  
141 its bacteriostatic activity [30,41]. Chitosan was dissolved in lactic acid and mixed to the water repellent.  
142 It was tested at three different concentrations spanning one order of magnitude (TC-7 samples). Silver  
143 nitrate was added in low concentration to chitosan in order to improve the biocidal impact (HY samples).  
144 Silver is a component well-known for its antibacterial efficiency and is widely used in many fields  
145 (cosmetics, medicine, food industry) and notably against green algae [23,42,43]. Silver nitrate was  
146 chosen rather than silver nanoparticles (AgNPs). The relative toxicity of  $\text{AgNO}_3$  and AgNPs is still being  
147 discussed, with studies reporting that  $\text{AgNO}_3$  is more toxic than AgNPs [44,45], while other studies led  
148 to the opposite conclusion [21]. Moreover, AgNPs could release  $\text{Ag}^+$  in the environment [46] as  $\text{AgNO}_3$   
149 does. Hence, we consider that both compounds have an equivalent toxicity.

Coating name	Test	Function	Applied product quantity (L.m <sup>-2</sup> )	Equivalent dry weight (g.m <sup>-2</sup> )	Chitosan (g/L)	Silver nitrate (g/L)
TC-7	Biofouling	WR + biocide	0.2	7	1.5	
TC <sup>+</sup> -7	Biofouling	WR + biocide	0.2	7	10.1	
TC <sup>++</sup> -7	Biofouling	WR + biocide	0.2	7	13.6	
TCAg-7	Ageing + biofouling	WR + biocide	0.2	7	1.5	0.9
TCAg-14	Ageing + biofouling	WR + biocide	0.4	14	1.5	0.9
T-7	Ageing	WR	0.2	7		
T-14	Ageing	WR	0.4	14		

WR: Water Repellent

151

152 Table 1

153 Coating names with the test used for their efficacy, their function, the applied product quantity, the equivalent dry weight and  
 154 the concentration of components (Tegosivin® HE 328 concentration is not mentioned as it is 97 g/L in all coatings).

155

### 156 2.3. Experimental design

157

#### 158 2.3.1. Accelerated biofouling test

159

160 An accelerated biocolonisation test was set up on triplicates of control samples (i.e. uncoated stones)  
 161 and samples coated with the water repellent and biocides (TC-7 and TCAg samples; Table 1). It  
 162 consisted of inoculating slabs with a suspension of *Chlorella vulgaris* culture. *Chlorella vulgaris* fo.  
 163 Viridis (Chodat) was purchased from the Culture Collection of Algae and Protozoa (Dunstaffnage  
 164 Marine Laboratory, Scotland; strain reference CCAP 211/12). Algae were first grown in a liquid culture  
 165 medium composed of distilled water with BG11 (a medium from Sigma-Aldrich concentrated 50 times).  
 166 It was diluted to get a similar algal concentration for every test corresponding to  $574 \pm 58$  algae cells  
 167 per mm<sup>3</sup>, as measured by the chlorophyll *a* absorbance control at 665 nm and 653 nm using  
 168 spectrophotometry. Stone slabs were placed in Plexiglass cups. The cups were filled to the top with algal  
 169 suspension, 5 mm above the stone surface. Gravitational settling of the algae was achieved by letting  
 170 the slabs stand for 24 hours to obtain a homogeneous seeding. Then the broth was removed and distilled  
 171 water was added up to 0.5 cm from the bottom of each sample. Water was added regularly over the  
 172 entire incubation period to ensure that the stones were continually kept wet by means of capillary  
 173 absorption. The biofouling test was carried out under neon lights (Sylvania Gro-Lux) for four weeks at  
 174 room temperature (20°C). Colour and chlorophyll *a* fluorescence were measured weekly.

175

#### 176 2.3.2. Artificial ageing test

177 The test was performed on triplicates of (1) control slabs as new uncoated stones, (2) slabs coated with  
 178 Tegosivin® HE 328 (TG samples) and (3) slabs with the coatings that showed the best efficacy during  
 179 the biofouling test (HY samples - Table 1). The performance of every coating was tested after one  
 180 month of artificial ageing with the climatic chamber Suntest XXL+ from Atlas. The device is equipped  
 181 with three 1700 W air-cooled Xenon Lamps to simulate daylight with measurement and control of  
 182 irradiance 300-400 nm, chamber temperature (CHT) and black standard (BST). Rain was simulated by  
 183 spray system with two nozzles (Schlick nozzle 11-90° = 420 ml/nozzle/min). One cycle lasted 4 hours  
 184 and consisted of: 2 min of spray and 238 min of daylight fixed at 50 W.m<sup>-2</sup>, with CHT at 40°C and BST  
 185 at 60°C. The total artificial ageing procedure was 168 cycles corresponding to one month of experiment.  
 186 According to the information providing by Atlas, based only on sunlight radiation, one month of  
 187 artificial ageing corresponds to five months of real exposure in southern France. Static contact angles  
 188 and colour changes were measured after 42, 84, 126 and 168 cycles.

189

190

191

192

### 193 2.4. Evaluation of coated stone properties and performance

194

#### 195 2.4.1. Colourimetry

196

197 The colour of stone samples was measured by using a Chroma Meter CR-400 from Konica-Minolta with  
198 a light projection tube CR-A33c of 11 mm diameter (corresponding to the measurement zone).  
199 Calibrations were performed with a white ceramic plate CR-A43. Values are given in the CIELAB  
200 colour space [47]. Three parameters determine the colour location in colour space:  $L^*$  indicates lightness  
201 (0 = absolute black, 100 = absolute white), and  $a^*$  and  $b^*$  are the chromaticity coordinates.  $a^*$  is the  
202 position between green ( $a^* < 0$ ) and red/magenta ( $a^* > 0$ );  $b^*$  is the position between blue ( $b^* < 0$ ) and  
203 yellow ( $b^* > 0$ ).  $h_{ab}$ , corresponding to the hue angle, is calculated from the  $a^*$  and  $b^*$  parameters:  $h_{ab} =$   
204  $\arctan(b^*/a^*)$ .

205 For colour analysis, each stone surface was measured 9 times and the mean was calculated for every  
206 triplicate. Measurements were taken before and after coating and at every stage of tests (see section 2.3).  
207 The CIELAB lightness and chroma differences were calculated:  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ , and  $\Delta h_{ab}$  correspond to  
208 the differences between different surface conditions. The global colour variation ( $\Delta E^*_{ab}$ ) was calculated  
209 as follows:

$$210 \Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

211 First, colour was measured on the coated stones before testing and compared to the natural stone colour  
212 (control). Then, the  $\Delta a^*$  parameter was used to follow the greening of stones by *Chlorella vulgaris*  
213 during the accelerated biofouling test. The calculation represents the difference between  $a^*$  after 24 hours  
214 of inoculation of slabs by algae ( $T = 0$ ) and each week for one month of incubation. Finally, colour  
215 parameters were used during the artificial ageing test where parameters of colour variation ( $\Delta E^*_{ab}$ ,  $\Delta L^*$ ,  
216  $\Delta h_{ab}$ ) were defined as the difference between colour of coated surface before test ( $T = 0$ ) and after each  
217 test week corresponding to 42, 84, 126 and 168 cycles.

#### 218 2.4.2. Chlorophyll *a* fluorescence

219

220 The fluorescence arising from chlorophyll (chl.) is almost exclusively from photosystem II (PSII). The  
221 sensitivity of the PSII to the environmental variations reflects a stress that the chl. *a* fluorescence can  
222 detect [48]. The chl. *a* fluorescence of algae was quantified directly on the stone slabs with an  
223 IMAGING-PAM Chlorophyll Fluorometer (Walz, Effeltrich, Germany) after every incubation week  
224 during four weeks.

225 The measuring system uses an array of blue light-emitting diodes (LEDs) (peak wavelength = 470 nm)  
226 for saturating light pulses. The frequency of the pulses was adjusted to 10 Hz. Measurements were  
227 carried out at a distance of 4 cm between the camera and the slab's surface, corresponding to a  $34 \times$   
228  $25$  mm area. The image captured by the CCD camera was composed of  $640 \times 480$  pixels.

229 During the experiment, the measurements were performed on the central part of the slabs, which were  
230 pre-conditioned in the dark. The initial fluorescence ( $F_0$ ) was obtained after 30 minutes of dark  
231 adaptation. Maximal fluorescence ( $F_m$ ) was obtained with a saturating flash (1 s,  $1000 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ).  
232 The ratio of variable to maximal fluorescence ( $F_v/F_m = (F_m - F_0)/F_m$ ) was calculated. The protocol for  
233 fluorescence measurement was similar to the one described by [49]. The relative quantum yield of PSII  
234 ( $\Phi_{\text{PSII}}$ ) at steady state is defined as  $(F_m' - F_s)/F_m'$ , where  $F_s$  and  $F_m'$  are, respectively, steady-state  
235 fluorescence and maximum fluorescence in the light ( $\text{PAR} = 120 \mu\text{mol photon}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ).  $\Phi_{\text{PSII}}$  represented  
236 the number of electrons transported by a PSII reaction centre per mole of quanta absorbed by PSII. Both  
237 photochemical ( $q_p$ ) and non-photochemical quenching ( $q_n$ ) were calculated according to [50].

238

#### 239 2.4.3. Water vapour permeability

240

241 The diffusion of water vapour through stone is one of the properties of hydrophobic coatings. The  
242 Standard NF EN 15803 [51] details its measurement on coated stone discs 50 mm in diameter and 1.6  
243 mm thick. Discs were sealed in a glass cup containing water and placed in a dry keeper with a relative  
244 humidity around 53 % with a saturated solution of magnesium nitrate at  $20 \pm 2^\circ\text{C}$ . Triplicates for natural  
245 stones (control) and coated stones are used and the apparatus of disc in glass cup are weighted before  
246 and every 24 h until stabilisation of the weight. The water vapour permeability ( $\delta_p$ ) was calculated with  
247 the following formula and the mean was computed from the three measurements of control and coated  
248 stones:

249  $\delta_p = \frac{G}{A \cdot \Delta p_v} \cdot D$  (kg.m<sup>-1</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>)

250 with  $G = \Delta m / \Delta t$  (kg.s<sup>-1</sup>): the slope of the linear part of the curve corresponding to the mass variation  
251 in function of the time

252 A: surface of the disc (m<sup>2</sup>)

253  $\Delta p_v$ : variation of water vapour pressure on both sides of the cup (Pa)

254 D: thickness of the disc (m)

255

256 Then the reduction of the water vapour permeability ( $\delta_{p \text{ red}}$ ) was calculated from the Standard NF EN  
257 16581 [52], according to the formula:

258  $\delta_{p \text{ red}} (\%) = \frac{\delta_{p n} - \delta_{p c}}{\delta_{p c}} \cdot 100$

259 with :  $\delta_{p n}$  water vapour permeability of natural stone (kg.m<sup>-1</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>)

260  $\delta_{p c}$  water vapour permeability of coated stone (kg.m<sup>-1</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>)

261

262 *2.4.4. Static contact angles*

263

264 The wettability of the stone surface was monitored by the measurements of static contact angles ( $\theta$ ),  
265 often used to assess the hydrophobic effect of coatings. They were performed on the coated surfaces  
266 before and after each step of ageing test (42, 84, 126 and 168 cycles).

267 For each measurement, a water droplet (5  $\mu$ l) was deposited on the surface of the stone at room  
268 temperature [53]. The angle made by the water droplet on the stone surface was defined geometrically  
269 as the angle formed by the liquid at the three-phase boundary where liquid, gas and solid intersect. It  
270 was calculated by computer analysis with the software See System (Advex Instruments) of digital  
271 images from the picture of the droplet on the surface after 10 min. Sixteen measurements were  
272 performed on each sample, averaging the results. We underline that Dom stone has a high surface  
273 roughness that could induce a non-ideal flat basis for the calculation of the angles, which could result in  
274 high standard deviations (Supplementary Table S11).

275

276 *2.4.5. Scanning Electron Microscopy (SEM) combined to energy dispersive spectroscopy*  
277 *(EDS)*

278

279 Environmental SEM-EDS was used in order to observe the coating on the surface stone and to  
280 evaluate the effect of the aging on the morphology of coated stones and control. The apparatus was a  
281 SEM Hitachi TM-3030 plus Tabletop Microscope with an energy-dispersive X-ray spectrometer  
282 (Swifted-TM Energy Dispersive XRay). Samples introduced in the microscope had a dimension of 2 cm  
283 x 1 cm x 0.5 cm and were placed on a double-sided adhesive carbon tape. The accelerating voltage was  
284 15 kV for imaging. The working distance was 6 mm. All images were acquired in the back-scattered  
285 electron mode.

286

287 *2.4.6. Porosity and pore access radii*

288

289 The microstructural characteristics of uncoated and coated stones were assessed through the mercury  
290 (Hg) intrusion measurements to evaluate the modification of the porous network involved by the  
291 application of coatings on the stone surface.

292 Data were obtained with a mercury intrusion porosimeter (Micromeritics Autopore IV 9500), reaching  
293 a pressure of 247 MPa and measuring pore radii sizes from 0.003 to 178  $\mu$ m. One sample (1 x 1 cm) of  
294 control (uncoated stone), TCAg-7 and TCAg-14 coated stone was analysed before and at the end of the  
295 artificial ageing.

296

297

298 *2.5. Statistics*

299

300 The open-source software R [54] has been used to compute statistics and to produce all graphics,  
301 with the following packages: ggplot2 [55], R. utils [56], doBy [57], readxl [58] and devEMF [59].  
302

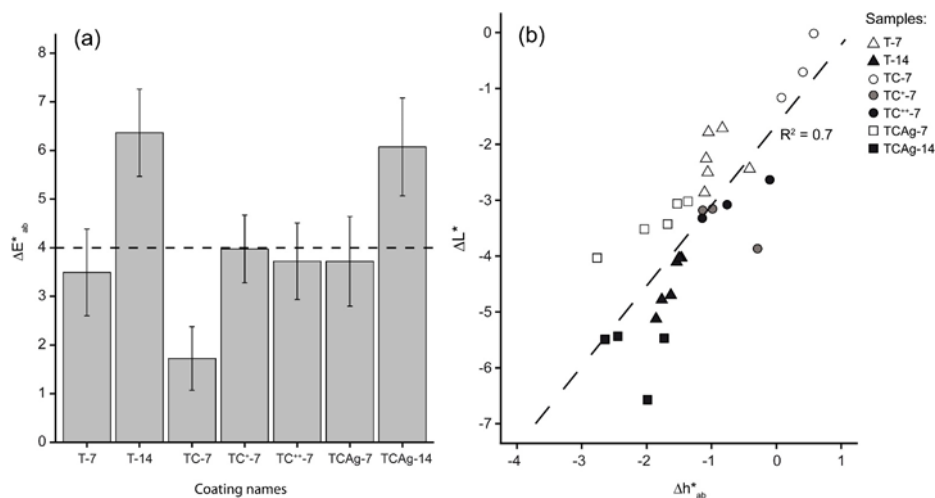
### 303 3. Results and discussion

#### 304 3.1. Colour change after coating

305  
306  
307 The colour change of stone involved after the application of coatings is as important as the performance  
308 of the coating itself. The generally accepted requirement is that no colour change can be visually noticed  
309 [60]. This depends on the stone; it ranges from  $\Delta E^*_{ab} \leq 3$  [6,61] to  $\Delta E^*_{ab} < 6$  [62]. For the Dom stone,  
310 the threshold for no visual colour change was set to  $\Delta E^*_{ab} \leq 4$  (Fig. 1a). A global trend of increasing  $\Delta L^*$   
311 with  $\Delta h^*_{ab}$  could be observed ( $R^2 = 0.7$ ,  $p < 0.001$ ; Fig. 1b). Therefore, the global colour change resulted  
312 from the darkening and reddening of stones.

313 The colour change was most significant with the highest quantity of water repellent (T-14 and TCAg-  
314 14). Chitosan mixed with the water repellent (TC-7, TC<sup>+</sup>-7 and TC<sup>++</sup>-7) changed colour below the  
315 required threshold ( $\Delta E^*_{ab} \leq 4$ ), as did the low dose of water repellent (T-7 and TCAg-7).

316 When AgNO<sub>3</sub> was added (TCAg-7),  $\Delta E^*_{ab}$  was most similar to that of T-7 (no biocide). However,  $\Delta L^*$   
317 and  $\Delta h^*_{ab}$  were lower, suggesting that the addition of AgNO<sub>3</sub> to the water repellent (with or without  
318 chitosan) does darken and redden the stone. Furthermore, an increase in the dose of water repellent in  
319 T-14, as compared to T-7, increased dramatically the global stone colour to 6.4 due to an important  
320 darkening ( $\Delta L^* = -4.5$ ). The addition of biocides to T-14 (i.e. TCAg-14) amplified the darkening and  
321 shifted the hue to even redder colours. Accordingly, the least amount of colour change was observed for  
322 the coating with the lowest dose of chitosan and water repellent (TC-7).  
323



324  
325

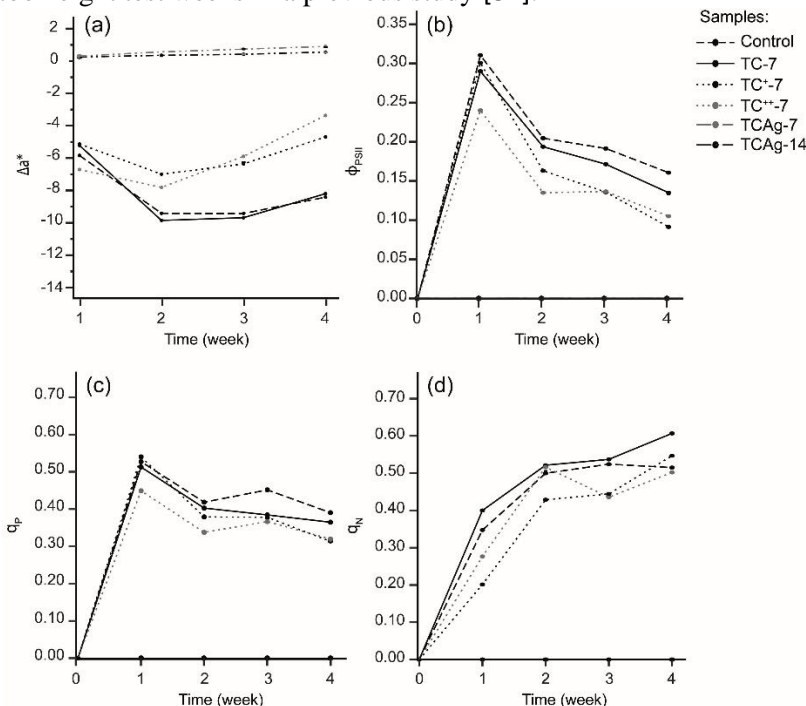
#### 326 3.2. Biocide effect

327  
328 The accelerated biofouling allowed the testing of the biocide effect of coatings containing different  
329 concentrations of chitosan, combined or not with silver nitrate. The colour parameter  $\Delta a^*$  was used to  
330 follow the development of *Chlorella vulgaris* over time [63,64]. The other calculated colour parameters  
331 were also analysed but their results (not shown) were similar to  $\Delta a^*$ , except for  $\Delta b^*$ , which mirrored far  
332 less the algae development.

333 Control samples displayed negative  $\Delta a^*$  which decreased progressively over time, although they  
334 increased slightly in the last week (Fig. 2a). This is mirrored by an algal development on stone surfaces.  
335  $F_v/F_m$ ,  $\phi_{PSII}$ ,  $q_N$  and  $q_P$  data of control indicated that the highest photosynthetic activity occurred during  
336 the first test week, implying an early algae settlement on stone. The fast decrease of  $\phi_{PSII}$  during the  
337 second week represented a lower effective photosynthetic activity of PSII (Fig.2b). This can be  
338 explained by the decrease of  $q_P$  (Fig. 2c) and thus by a decrease in the electron transfer from the PSII to  
339 the PSI. Nevertheless,  $q_N$  continued to increase during the second week and then became stagnant during



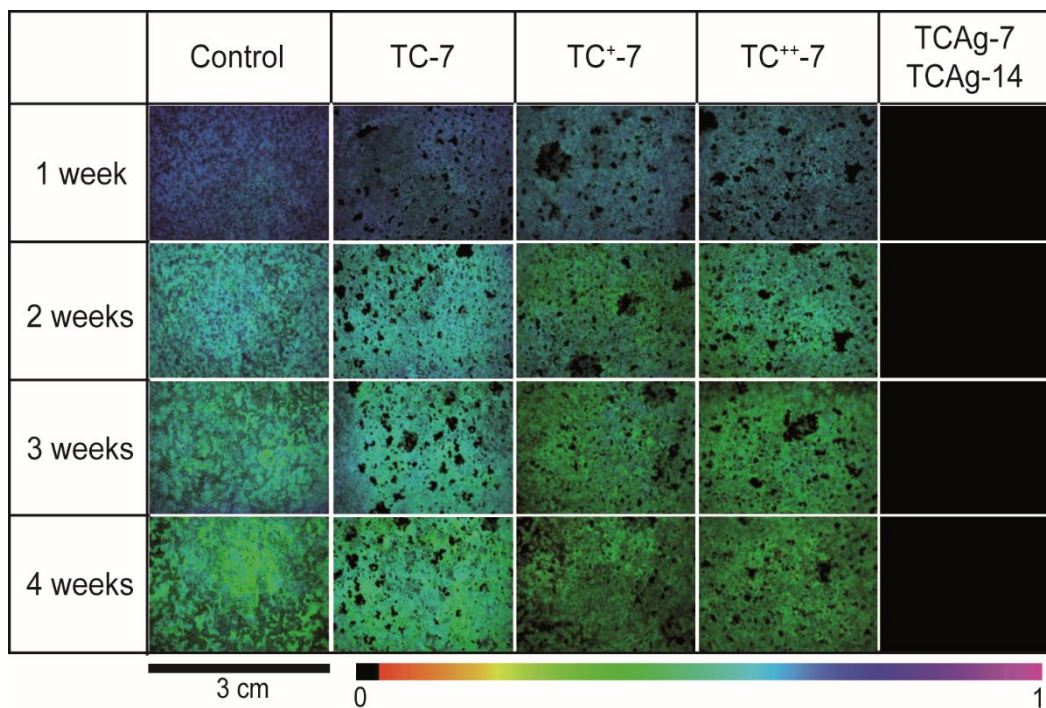
340 the last two weeks (Fig.2d). These results represented heat dissipation and corresponded to a regulation  
 341 of an excess of electrons and to an adaptation of the algal population. The progressive decrease of the  
 342 photosynthetic activity was therefore due to the senescence of the first algae and to the adaptation to the  
 343 substrate, which took eight test weeks in a previous study [31].



344  
 345  
 346 Fig. 2. Mean of  $\Delta a^*$  of triplicates calculated from measurements before incubation and after 1, 2, 3 and 4 weeks of incubation  
 347 (a). Evolution of Chl *a* fluorescence parameters of PSII ( $\phi_{PSII}$ , the effective quantum yield) in *Chlorella vulgaris* in triplicates  
 348 of control and coated stones after 1, 2, 3 and 4 weeks of incubation (b),  $q_P$  (the photo-chemical quenching) (c),  $q_N$  (the non  
 349 photo-chemical quenching that is the heat dissipation) (d). See Supplementary Tables S3–S6 for means and standard deviations.  
 350

351 Three response patterns could be observed from the biofouling analysis of the coated stones. The first  
 352 one, displayed by TC-7, was very similar to that of the control (Figs. 2-3), proving the same algae  
 353 development and the lack of biocide efficacy. The concentration of chitosan was apparently not  
 354 sufficient to avoid the algal development. The second pattern grouped TC<sup>+</sup>-7 and TC<sup>++</sup>-7 coatings.  $\Delta a^*$   
 355 was negative throughout the test, corresponding to a greening on stones. Nonetheless  $\Delta a^*$  was less  
 356 negative than control and increased after the second week, suggesting a decrease in the greening.  $F_v/F_m$   
 357 showed a decline of the maximal PSII quantum yield by a shift from a blue colour in the first week to a  
 358 green one the next weeks (Fig.3). Moreover,  $\phi_{PSII}$  and  $q_P$  values were lower than control and more so for  
 359 TC<sup>++</sup>-7. Thus, the effective activity of the PSII decreased and both coatings acted on the algal  
 360 development by limiting the electron transfer in the photosynthetic chain.  $q_N$  highlighted a heat  
 361 dissipation lower than in the control slabs, pointing out that the algae did not manage to regulate as well  
 362 the excess of electrons by heat dissipation. Accordingly, TC<sup>+</sup>-7 and TC<sup>++</sup>-7 had a biocide effect and  
 363 acted on the vital functions of algae but they could not fully avoid their development. An increase of  
 364 chitosan doses should improve even further its efficacy but that would likely induce a colour change of  
 365 stone too strong to be acceptable.

366 The third response pattern was displayed by TCAg-7 and TCAg-14, which showed a weak positive  $\Delta a^*$ ,  
 367 meaning a lack of greening on stones. Chl. *a* fluorescence measurements stayed nil throughout the test,  
 368 which proved that no photosynthetic activity took place. Therefore, the addition of a weak concentration  
 369 of silver nitrate to chitosan and a silane/siloxane emulsion had a significant biocide impact. Even though  
 370 chitosan did not reach an optimal effect alone, a previous study [31] clearly displayed that the  
 371 combination of chitosan with low doses of  $AgNO_3$  and hydrophobic silica can have the same effect as  
 372 higher doses of  $AgNO_3$  alone or with hydrophobic silica. Achieving the same biocide effect with lower  
 373 doses of  $AgNO_3$  is a great improvement for the environmental implications.  
 374



375 Fig. 3. Fluorescence imaging of the dynamic evolution of chlorella vulgaris inoculated in control and coated stones. Samples  
 376 were dark-adapted for 30 min and submitted to saturation pulse. A photo of photosynthetic efficiency (Fv/Fm) was captured  
 377 every test week. The false colour code ranges from black (0.000) to pink (1.000). See Supplementary Table S7 for means and  
 378 standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version  
 379 of this article.)  
 380

### 381 3.3. Properties of coated stones in artificial ageing test

382 TCAg-7 and TCAg-14 coatings were selected for the ageing test because of their optimal biocide effect  
 383 during the accelerated biofouling test (see section 3.2). They were then tested for their durability,  
 384 hydrophobicity and changes in stone properties throughout an artificial ageing test.  
 385  
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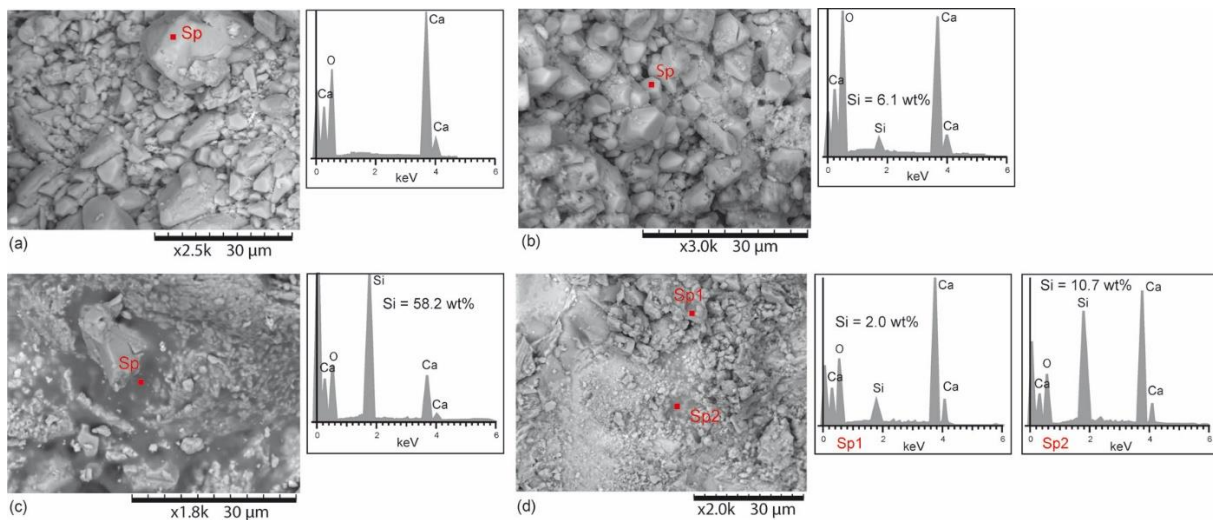
#### 388 3.3.1. Coatings integrity

389 The distribution of the coatings on the surface of the stone was observed by SEM and analysed by EDS.  
 390 Before the ageing test, the EDS analysis measured high peaks of calcium in uncoated stones, as expected  
 391 for a limestone (Fig 5a). On coated stones, the coating was not observed on the major stone surface at  
 392 this scale of observation. A small peak of Silicon (Si) allowed its detection on calcite grains that attested  
 393 the presence of the Si-O network in the whole stone surface (Fig 5b). The concentrations of Si on calcitic  
 394 grains were very variable as displayed by the means from six measured spots (Table 3) and depended  
 395 probably on the thickness of coatings. Nevertheless, the coating could be clearly observed as a coating  
 396 flooding grains and partially filling the porosity (Fig 5c). It was characterised by a higher proportion of  
 397 Si than on calcitic grains and a higher variability that depended on the thickness too.  
 398

399 The viscosity of HY is 3.20 mPa.s, which is common for other hybrid polymers with values around 2-  
 400 3.3 mPa.s [65]. The evaporation of the solvent probably happened too fast and limited the entire  
 401 penetration into the stone or there was a competition between the dissolution of stone (as showed Hg  
 402 measurements) and the polymerisation.

403 Partial glazing has already been observed with a nano-composite SiO<sub>2</sub>/CuONPs, which modified the  
 404 topography locally [24]. On stones coated with TCAg-14 (higher dose than TCAg-7), the glazing could  
 405 be observed in the roughest areas. TG-coatings, corresponding to the application of only the water  
 406 repellent, were observed for comparison (Fig. 5d). They showed the same result, suggesting that they  
 407 are related to the water repellent itself and not to the polysaccharide network of chitosan in HY. After  
 408 the ageing, SEM observations on coated stones showed local compact films were disrupted as patches

409 on the surface (Fig 6a) and cracks were locally observed in coatings (Fig 6b). They revealed the erosion  
 410 of the film in the face of the weathering simulation.  
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### 3.3.2. Colour change

417

418 The artificial ageing test was carried out on coatings TCAg-7 and TCAg-14 with both biocides and  
 419 water repellent, and compared to T-7 and T-14 coatings (water repellent only with different applied  
 420 quantities) (Table 1). The colour changes of stones induced by those coatings have been discussed in  
 421 section 3.1. The evolution of the stone colour along the ageing test was measured after 42, 84, 126 and  
 422 168 cycles.

423 Control slabs showed the highest global variations of colour (Fig. 7a). These variations corresponded to  
 424 a darkening of the stone throughout the ageing process, as reflected by the decrease of  $\Delta L^*$  while the  
 425 hue ( $\Delta h^*_{ab}$ ) stayed stable (Fig. 7b). The uncoated Dom stone is therefore influenced by the sunlight and  
 426 rain simulated in a climatic chamber. The colour variation over time depends on the type of stone: Luvidi  
 427 et al. [25] showed that the uncoated Lecce stone had  $\Delta E^*_{ab} > 15$ , whereas  $\Delta E^*_{ab} < 2$  for the uncoated  
 428 marble after an outdoor exposure.

429 In our study, all coated stones had lower colour changes than control ones and never exceeded 4 except  
 430 for TCAg-14 (highest value = 4.26). The lowest  $\Delta E^*_{ab}$  were measured for T-7 and for TCAg-7. Those  
 431 coatings had a stable colour over time. In details, the lightness of T-7 and TCAg-7 was stable over time  
 432 as well ( $\Delta L^*$  was around 1 for T-7 and close to 0 for TCAg-7). Nevertheless, the addition of chitosan  
 433 and silver nitrate to Tegosivin® (TCAg-7) increased the variation of the hue (3.4 instead of 0.9 for T-7)  
 434 which corresponded to a more yellowish stone. This trend increased throughout the ageing.

435  $\Delta E^*_{ab}$  increased with higher quantities of Tegosivin® (T-14), especially from 84 cycles onwards, which  
 436 can be explained by a net lightening (Fig. 7b). Therefore, the colour of the water repellent changed with  
 437 the accelerated ageing and with increasing dose.

438 When both chitosan and silver nitrate were added to T-14 formulation (i.e. TCAg-14), the global colour  
 439 change was generally higher than TCAg-7. In details, the coating did not influence the lightness over  
 440 cycles and the colour shifted to yellow tones as for TCAg-7 but standard deviations of  $\Delta L^*$  and  $\Delta h^*_{ab}$   
 441 (Supplementary Tables S9-S10) are much higher than for TCAg-7 and displayed an heterogeneity of  
 442 TCAg-14 through time.

443 Accordingly, all coatings stabilised the stone colour despite the exposure to sunlight and rain in chamber,  
 444 as compared to the uncoated stone. Higher dose of water repellent changed the colour by fading. The  
 445 addition of biocides did not induce great global change ( $\Delta E < 5$ ). They stabilised the lightness but the  
 446 hue did increase, meaning that the stone colour evolved toward yellow tones for both HY coated stones.

447 Nonetheless, the best coating gathering hydrophobic and biocide effects seems to be TCAg-7 because  
448 it does not induce important colour changes over time either.

449

450

### 3.3.3. Porous network

451

452 The application of coatings, without artificial ageing, led to an increase in the Hg porosity of the stone  
453 (Table 2). It was reflected by a shift of the peak for the major pore access radius from 1.8  $\mu\text{m}$  in the  
454 control samples to 3.5  $\mu\text{m}$  for both TCAg-7 and TCAg-14 coated stones, while the pore size distribution  
455 stayed bimodal (Fig.4a). Moreover, the increase of the Hg intrusion for every class of the pore access  
456 radii for both coated stones (except for TCAg-7 in the 10-1  $\mu\text{m}$  class) evidenced the enlargement of pore  
457 size (Table 2). These results revealed a dissolution of pores probably induced by the slight acidity of  
458 Tegosivin<sup>®</sup> HE 328 which has pH = 6, but HY has pH = 4 due to the use of lactic acid to solubilize the  
459 chitosan powder which had not fully reacted. This could explain the dissolution of the stone that  
460 occurred during the application of the coating.

461 The porosity of the control was higher after the ageing test (28.6 % instead of 21.4 % before the ageing).  
462 The Hg intrusion increased for every class of pore access (Table 2), pointing to a development of the  
463 porous network. In details, there was a widening of the largest pore access radii from 1.8  $\mu\text{m}$  to 4-7  $\mu\text{m}$   
464 (Fig.4b) and an increase of the pore access radii between 1-0.1  $\mu\text{m}$  and 10-1  $\mu\text{m}$ . Therefore, artificial  
465 weathering dissolved the fresh uncoated stone.

466 The ageing on the coated stones also increased their porosity but the difference before and after ageing  
467 was weaker than for the non-coated stone. That was displayed by a significant development of the pore  
468 radii bigger than 10  $\mu\text{m}$  for TCAg-14 where the peak of the biggest pore radius shifted to 14  $\mu\text{m}$  (Fig.4c)  
469 and the Hg intrusion for this pore class increased from 0.011 to 0.038  $\text{mL.g}^{-1}$  (Table 2). For TCAg-7,  
470 the bigger pore radius reached 5  $\mu\text{m}$  and a second one 1  $\mu\text{m}$  (Fig.4c); there was an increase in Hg  
471 intrusion, and thus an increase of pores bigger than 10  $\mu\text{m}$  and between 10 and 1  $\mu\text{m}$  (Table 2).  
472 Consequently, the weathering enlarged all pore radius classes in the natural stone, whereas in the stone  
473 coated with TCAg-7, the enlargement was noticed in both bigger and medium classes and in the stone  
474 coated with TCAg-14 mainly in the bigger class. The coatings limited the enlargement of medium and  
475 smaller pores but the most significant impact occurred in the class of pores bigger than 10  $\mu\text{m}$  on stones  
476 with the highest dose of coating.

477

478

479

### 3.3.4. Performance of the hydrophobic effect

480

482 The two next tests are part of the NF EN 16581 Standard for the evaluation of the water repellency of  
483 coatings.

484

485

#### 3.3.4.1. Water vapour permeability

486

487 The water vapour transfer was measured only before the ageing test because the thin stone discs required  
488 could not be used in the climatic chamber where the water spray would blow and move them. It was  
489 measured from the inside of the coated stones toward the external surface.

490 The reduction of water vapour permeability ( $\delta_{p, \text{red}}$ ) of the coated stones could be explained by the  
491 widening of the porous network due to dissolution during the application of the coating combined with  
492 the hydrophobicity of the coating. Diffusion depends on tortuosity of the porous network, adsorption  
493 films and capillary condensation meniscus [66–69]. The widening of pore access radii in the coated  
494 stones limited the capillary condensation in the porous network as well the hydrophobicity of the grains  
495 and thus limited diffusion.  $\delta_{p, \text{red}}$  was below or close to the 20 % threshold (Table 4). This suggests that  
496 all coatings fit the requirement for hydrophobic coatings [60]. Moreover, all  $\delta_{p, \text{red}}$  were similar, implying  
497 that the adjunction of biocides or increasing the dose of water repellent did not greatly modify the  
498 properties of the water repellent.

499 Pia et al. [12] noted the low permeability of experimental nano-structured organic and inorganic coatings  
500 and used the transmission degree of water vapour (V) to test vapour permeability on hybrid coatings.

501 Three classes were used, class I with  $V > 150 \text{ g m}^{-2}\cdot\text{d}^{-1}$ , class II with  $15 < V < 150 \text{ g.m}^{-2}\cdot\text{d}^{-1}$  and class  
502 III with  $V < 15 \text{ g.m}^{-2}\cdot\text{d}^{-1}$ . Our four coatings had values ranging between 163 and  $177 \text{ g.m}^{-2}\cdot\text{d}^{-1}$  and thus  
503 all belong to class I, corresponding to a high transmission degree of water vapour. In comparison, the  
504 boehmite/siloxane-modified metacrylic coatings of Esposito et al. [70] achieved a transmission degree  
505 of water vapour on two carbonate stones of 17.3 and  $7.0 \text{ g.m}^{-2}\cdot\text{d}^{-1}$ . Accordingly, the coatings in the  
506 present study have a good performance in the transmission of water vapour through the stone.

#### 507 508 *3.3.4.2. Static contact angle* 509

510 The static contact angle was measured before and at every stage of the artificial ageing in order to  
511 confirm the efficacy of the water repellent and to define the possible interaction between the water  
512 repellent and the biocide components.

513 Directly after application, contact angles ranged between  $122.8^\circ$  and  $129.4^\circ$  (Fig.8), higher than the  
514 minimum requirement of  $90^\circ$  [60]. Thus, all coatings had a good hydrophobicity. T-14 coating had the  
515 highest value whereas TCAg-14 had the lowest one. The addition of biocides seemed to interfere with  
516 the performance of the water repellent; nonetheless, T-7 and TCAg-7 had the same contact angles.  
517 Hence, the interference appeared to occur only at higher concentrations of the water repellent. This  
518 warrants further investigation.

519 Throughout the ageing, T-14 had the highest contact angles compared to the other coatings (Fig.8).  
520 Moreover, values were even higher at the end of the experiment. The enhancement of performance after  
521 an artificial ageing test was already noted with a coating based on silsesquioxane and aged in climatic  
522 chamber at  $40^\circ\text{C}$  [71]. The authors explained this result by the enhancement in the networking of the  
523 polymeric structure thanks to temperature during the ageing test.

524 T-7 and TCAg-14 showed a net decline of the contact angles after 42 cycles and until 126 cycles; the  
525 hydrophobicity then increased to reach  $117.2^\circ$  and  $119^\circ$ , respectively at the end of the ageing. Contact  
526 angles of TCAg-7 were stable until 84 cycles and decreased as the other coatings at 126 cycles but less  
527 drastically. At the end of the test, TCAg-7 had a hydrophobicity close to T-7 and TCAg-14.

528 This downward and then upward trend of the static contact angle has also been described with another  
529 organic-inorganic hybrid coating subjected to a UV and water-condensation weathering in climatic  
530 chamber. The contact angle decreased progressively from  $140^\circ$  to  $110^\circ$  during 120 days with a minimum  
531 of  $105^\circ$  [20]. Nonetheless, variability of our data increased at 126 and 168 cycles and reflected an  
532 increase in the heterogeneity of the hydrophobicity at the stone surface despite the contact angle staying  
533 close to  $90^\circ$ .

534 Comparison of both coatings with hydrophobic and biocide effects revealed that the best hydrophobicity  
535 was not achieved with the highest dose of water repellent when associated to biocides. TCAg-7, with its  
536 lower quantity of Tegosivin<sup>®</sup> HE 328, had an intermediate but stable efficacy over time.

#### 537 538 **4. Conclusions** 539

540 Different coatings were prepared in the goal of achieving a biocide and hydrophobic efficacy by means  
541 of sol-gel process and the combination of a hybrid polymer with a natural biocide as chitosan. This last  
542 component did not change the stone colour and a coating with 13.6 g/L of chitosan is enough to disturb  
543 the photosystem of algae. However, it could not fully stop their development and a higher concentration  
544 could probably reach an optimal impact but at the expense of a higher colour change. Nonetheless, this  
545 shortcoming was compensated by supplementing a weak dose of silver nitrate. This low concentration  
546 of silver nitrate was efficient only when associated to the chitosan and the water repellent. Two doses  
547 of this formulation were investigated. Their application on stone induced a low change of colour and a  
548 good hydrophobicity. The analyses showed that the coatings spread over the whole stone surface as a  
549 thin film and flooded grains in local zones as well. They invaded the open porosity but they increased  
550 the latter by enlarging the pores during their application due to the low pH of solution. In further work,  
551 the formulations should be improved by limiting the colour change and increasing the pH induced by  
552 the solubilisation of the chitosan. This would ultimately allow the use of chitosan only, at higher  
553 concentrations than tested in the present study.

554 The artificial ageing test revealed a moderate colour variation on coated stones, whereas the natural  
555 stone reached the highest colour change over time. The simulation of rainfall caused the enlargement of  
556 pores and eroded the films in patches but the hydrophobic effect was not inhibited.  
557 The best coating combining a weak dose of water repellent with chitosan and silver nitrate (TCAg- 7)  
558 had a good biocide and hydrophobic efficacy while preserving the natural aspect of the stone.  
559 Furthermore, using low doses of silver nitrate also limits the negative impacts of this compound on the  
560 environment and health. These results obtained in laboratory conditions must be confirmed in a long-  
561 term outdoor test to evaluate the durability of coatings in a real exposure to the environment with all  
562 existing variables.

563

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565

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571

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785

786 **List of tables and figures:**

787

788 Table 1

789 Coating names with the test used for their efficacy, their function, the applied product quantity, the  
790 equivalent dry weight and the concentration of components (Tegosivin® HE 328 concentration is not  
791 mentioned as it is 97 g/L in all coatings).

792

793 Table 2

794 Mercury intrusion porosimetry for control, TCAg-7 and TCAg-14 coated stones before and after the  
795 accelerated ageing test: percentage of Hg porosity (%) and Hg intrusion (mL.g<sup>-1</sup>) for the four classes of  
796 pore access radii.

797

798 Table 3

799 Concentration of Silicon in mass fraction (wt (%)) on the surface of calcitic grains and on compact  
800 films on stones coated by TCAg-7, TCAg-14, T-7 and T-14.

801

802 Table 4

803 Reduction of water vapour permeability ( $\delta_{p,red}$ ) and transmission degree of water vapour (V).

804

805

806 Figure 1.

807 Global colour variation  $\Delta E^*_{ab}$  represents the colour difference between the stone surface before the  
808 application of coatings and after in the CIELAB colour space. The threshold of the visual colour  
809 variation for the Dom stone is marked by the dotted line at  $\Delta E^*_{ab} = 4$  (a).  $\Delta h^*_{ab}$  and  $\Delta L^*$  correspond  
810 respectively to the variation of the hue and of the lightness of the stone surface before and after the  
811 application of coatings (b). See supplementary Tables S1-S2 for means and standard deviations.

812

813 Figure 2.

814 Mean of  $\Delta a^*$  of triplicates calculated from measurements before incubation and after 1, 2, 3 and 4 weeks  
815 of incubation (a). Evolution of Chl *a* fluorescence parameters of PSII ( $\phi_{PSII}$ , the effective quantum yield)  
816 in *Chlorella vulgaris* in triplicates of control and coated stones after 1, 2, 3 and 4 weeks of incubation  
817 (b),  $q_P$  (the photo-chemical quenching) (c),  $q_N$  (the non photo-chemical quenching that is the heat  
818 dissipation) (d). See supplementary Tables S3-S6 for means and standard deviations.

819

820 Figure 3.  
821 Fluorescence imaging of the dynamic evolution of *chlorella vulgaris* inoculated in control and coated  
822 stones. Samples were dark-adapted for 30 minutes and submitted to saturation pulse. A photo of  
823 photosynthetic efficiency ( $F_v/F_m$ ) was captured every test week. The false colour code ranges from black  
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825  
826 Figure 4.  
827 Incremental mercury intrusion in relation to the pore size. Comparison of the pore access radii  
828 distribution of: the fresh stone (control) and the TCAg-7 and TCAg-14 coated stones before the  
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831  
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833 SEM images and EDS analysis of Dom stone. Natural uncoated stone made of calcitic grains (high Ca  
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835 grains (b). The same coated stone with the coating flooding calcitic grains as a glazing showed by a high  
836 Si peak (c). Stone coated with T-7, EDS analysis showing a small peak of Si on stone grains and a higher  
837 peak on a glazing (d).  
838  
839 Figure 6.  
840 SEM images of coated stone. Cracking of the compact film in TCAg-7 after the ageing test (a).  
841 Remaining glazing of T-7 on the stone surface (b).  
842  
843 Figure 7.  
844 Stone colour variation in control and coated stones before the accelerated ageing test and after 42, 84,  
845 126 and 168 cycles. Evolution of the global colour variation  $\Delta E^*_{ab}$  (a). Evolution of  $\Delta h^*_{ab}$  versus  $\Delta L^*$   
846 (b). See supplementary Tables S8-10 for means and standard deviations.  
847  
848 Figure 8.  
849 Evolution of contact angles ( $\theta$ ) before the accelerated ageing test and after 42, 84, 126 and 168 cycles  
850 for every coated stone. See supplementary Table S11 for means and standard deviations.  
851