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1 "Effect of mixed vs single brine composition on salt weathering in porous carbonate building stones  
2 for different environmental conditions"

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8 **Key words:** salt weathering, limestone, environmental conditions, sodium chloride, sodium sulphate,  
9 calcium sulphate, salt mixture

10

## 11 **Abstract**

12 The influence of different factors, brine composition, environmental conditions and pore structure, on  
13 salt weathering of porous carbonate building stones is investigated. The main goal of this study is to  
14 highlight the differences in weathering between single salts and a mixture of different salts. Two kinds  
15 of weathering mechanism are studied, the crystallization pressure and the  
16 deliquescence/recrystallization process. To achieve this purpose wetting and drying cycles and cycles  
17 varying relative humidity on samples containing salts were performed. The effect of total salt content  
18 with different salts and mixtures is simulated by weathering tests with solution of different  
19 compositions (NaCl, 6% in weight,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , 6% in weight,  $\text{CaSO}_4$  at saturation, and a mixture  
20 of them at total concentration of 6.2%). Weathering tests were performed at room temperature and  
21 50°C and under low and high relative humidity.

22 The results show that the final weathering depends on a complex combination of three parameters: (i)  
23 environmental conditions, (ii) salt composition and (iii) petrophysical properties of stones, and general  
24 conclusions on the impact of each parameter can be drawn. An important result is that salt mixtures  
25 have a lesser impact on weathering during crystallization cycles: single salt brines, especially sodium

26 sulphate, produce more weathering than complex brine compositions during wetting and drying  
27 cycles. Conversely during variations on RH, samples with salt mixtures suffer more damage than  
28 samples weathered with a brine of single salt composition.

29

## 30 **1. Introduction**

31 Salt crystallization is one of the most dangerous weathering agents in monumental stones. Salts are  
32 always present in any environment, natural or anthropogenic and under any climatic conditions. The  
33 composition of these salt is very variable (Goudie and Viles, 1997) and depends on many different  
34 factors such as proximity to sea; actual and historical air, soil and water pollution; mineralogical and  
35 chemical composition of affected materials, i.e. not only the studied material but also other materials  
36 such as mortars, cements, metals, etc. in contact with it. The behaviour of salts depends very much on  
37 the environmental conditions, mainly temperature and relative humidity (RH) that control the stability  
38 of phases present in the stone. For example, natural cycles of RH variations can cross the equilibrium  
39 curve between thenardite (anhydrous sodium sulphate) and mirabilite (sodium sulphate decahydrate)  
40 which is probably one of the most important causes of damage in natural rocks or in building materials  
41 (Steiger and Asmussen, 2008). Other salts such as gypsum can dehydrate to less hydrate or anhydrous  
42 salts but this reaction occurs on a geological time scale and therefore, phase changes of this species do  
43 not contribute to building stone weathering. Nevertheless, the importance of gypsum as a deterioration  
44 factor over time is recognised (Charola et al., 2007).

45 Material properties are also important, not all stones react in the same way under the action of one  
46 weathering agent. Benavente et al (2007) summarized the factors controlling salt weathering in porous  
47 materials as pore size and porosity, nature of the salt, transport properties of the solution in pores and  
48 strength and the material's resistance to crystallisation pressure.

49 Laboratory studies in salt crystallization impact on construction materials began more than a century  
50 ago. In 1824 the "Annales des Mines" published a note about the work done by M. Brard to determine  
51 if construction materials are vulnerable to frost action. To simulate the effect of water solidification,

52 stones, bricks and other materials were saturated with different salt solutions and it was found that the  
53 Glauber salt (sodium sulphate) produced the “best” results. Research concerning monumental stone  
54 durability began in the 1920s and 1930s to identify the role played by soluble salts on the degradation  
55 of building materials (West, 2000).

56 The most studied salt is sodium sulphate even if other salts have been tested as well. An extended  
57 bibliographic review of crystallization tests with sodium sulphate can be found in Steiger and  
58 Asmussen (2008). Other salts used in laboratory tests are sodium chloride (Rodriguez-Navarro and  
59 Doehne, 1999; Desarnaud, 2014), magnesium sulphate (Espinosa-Marzal and Scherer, 2013; Ruiz-Agudo,  
60 2007), gypsum (Menéndez and David, 2013), etc. In nature and monuments a combination of different  
61 salts is usually present.

62 The weathering caused by salt crystallization in nature is a complex process also involving the action  
63 of different aqueous salt mixtures together with frost. McGreevy (1982) performed frost cycles in  
64 samples saturated by saline solutions of sodium chloride, sodium sulphate and magnesium sulphate  
65 and found that freezing of NaCl solutions is more destructive than freezing of sodium sulphate  
66 solutions.

67 Only recently has the behaviour of salt mixtures been investigated in laboratory. Sawdy and Heritage  
68 (2007) studied crystallization of binary salt mixtures in non-porous media. The authors combined  
69 nitromagnesite ( $\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ) and halite (NaCl) with nitratite ( $\text{NaNO}_3$ ), niter ( $\text{KNO}_3$ ) and gypsum  
70 ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The obtained salt mixtures were exposed to different relative humidity, below and  
71 above their equilibrium RH at room temperature, and the mass variation was registered. After 2 hours  
72 under RH above the equilibrium, all samples had undergone some degree of deliquescence but none  
73 were completely dissolved. They concluded that in comparison to single salts  
74 deliquescence/dissolution rate increases, deliquescence began when the RH was above the lowest  
75 individual equilibrium RH of salts in the mixture and the evaporation rate decreases.

76 Lopez-Acevedo et al (1997) investigated the salt weathering of two calcareous stones with different  
77 salts and salt mixture compositions: sodium, potassium and magnesium sulphates. Their experiment

78 consisted in a continuous capillarity rise of salt brines without any control of environmental  
79 conditions. They observed differences in the weathering patterns as a function of the employed salt  
80 with efflorescences for sodium and magnesium sulphates and subflorescences and crusts for potassium  
81 sulphate.

82 Cardell et al (2008) carried out capillary rise crystallization tests with different sulphate solutions (Ca,  
83 Mg, Na, K) and with binary mixtures of them in a limestone. They observed differences in the  
84 weathering pattern depending on the salt composition. Calcium sulphate did not produce any apparent  
85 weathering, magnesium sulphate caused a hard crust on the lower part of the wet stone, potassium  
86 sulphate created a hard film on the surface of the sample and sodium sulphate caused granular  
87 disintegration and efflorescences. Mixed solutions only produced a thin crust on the surface. They  
88 found that single salt solutions cause more damage than do mixed brines.

89 De Clercq et al (2013) performed crystallization experiments in two limestones with two different  
90 brine compositions, a first one composed of sodium sulphate and nitrate and a second one composed  
91 of sodium and potassium sulphate. The RH conditions were sustained at 50% and 85%. They found  
92 different mineralogical compositions of efflorescences depending not only on the nature of the  
93 solution but also on the type of stone, mainly on their porosity and evaporation rate. They concluded  
94 that crystallization behaviour of mixed salt solutions in porous materials is more complicated than in  
95 bulk solutions.

96 Lindstrom et al (2015) studied the behaviour of salt mixtures of  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  in sandstones  
97 with comparison to simple salt behaviours. Samples previously saturated with salts were exposed to  
98 wetting and drying cycles with pure water. Among many other results they found that  $\text{NaNO}_3$  is the  
99 least damaging salt and  $\text{Na}_2\text{SO}_4$  the most damaging one. Tests with salt mixture were not in accord  
100 with previously obtained results in solution droplets. The authors suggested that more research should  
101 be done.

102 Investigation of the behaviour of salt mixtures equilibrium models provides an extremely useful tool  
103 for predicting crystallization behaviour as a function of brine composition and environmental

104 conditions. The results can contribute to define the safe ranges of climatic conditions for the optimal  
105 conservation of objects (Steiger and Heritage, 2012).

106 To summarize it has been recognized that salt crystallization weathering on stone with salt mixtures is  
107 different from weathering when only one salt is concerned. Cardell et al, 2008 reported that salt  
108 mixture produces less damage than single salts. To test the effect of salt mixture versus single salt on  
109 salt crystallization weathering a mixture of three salts: NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub> was used to perform  
110 accelerated ageing tests. The obtained results were compared to those obtained for the same kind of  
111 experiments but performed with a single salt. Other parameters considered in this paper are the  
112 temperature and relative humidity. Salt cycles were performed under two different RH conditions  
113 (high and low) and two different temperatures (20°C and 50°C). Low relative humidity values are  
114 different for the two temperatures due to experimental limits, 45% at room temperature corresponding  
115 to the room RH and 5% at 50°C, relative humidity in the oven.

116 The two principal mechanisms of salt weathering are crystallization pressure and phase transitions.  
117 Crystallization pressure plays an important role during brine evaporation and precipitation of salts. To  
118 test this mechanism wetting and drying cycles were performed under environmental conditions given  
119 above. To test the effect of salt phase transitions RH variation cycles were performed at 50°C and  
120 room temperature. The brine concentrations for all the tests were always around 6%, except for  
121 calcium sulphate (0.2%). The obtained results allow a better understanding of salt weathering  
122 phenomena under real conditions where salt mixtures are present.

## 123 **2. Materials**

124 Three different calcareous stones used in the construction of monuments in the NW of France, but also  
125 in other regions and countries were tested in this study. The selected stones are Lutetian limestone  
126 (“roche fine” variety), Vernon chalk and Caen limestone (“demi-ferme” variety). These stones were  
127 chosen due to their similar mineralogical composition (calcite) with different microstructure and pore  
128 size distribution.

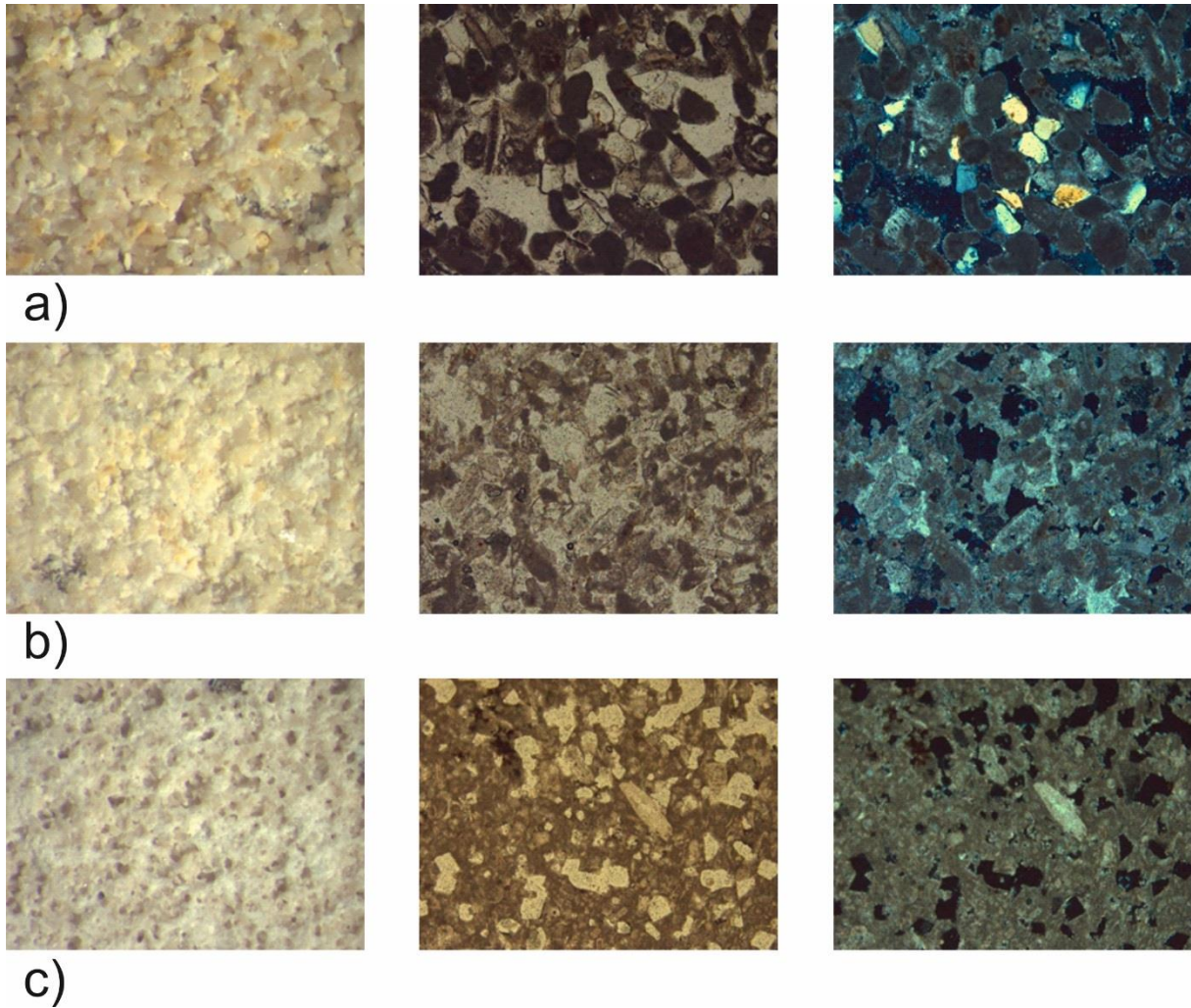
129 Lutetian limestone (Fig. 1a) used in this study is a middle Lutetian limestone from the Saint Maximin  
130 quarry (Rocamat company) known as “Roche Fine”. The Lutetian formation has different  
131 stratigraphic levels with very different properties [Angeli et al, 2007; Fronteau et al, 2010; Vazquez et  
132 al, 2015). The selected variety is a homogenous yellowish limestone without macroscopic fossils and  
133 with brownish spots (ferruginous oxides). It is a detritic limestone formed by accumulation of calcite  
134 grains and foraminifers (Moreau, 2008). Macroscopically, numerous small pores can be observed  
135 (Noel, 1970).

136 Vernon stone (Fig. 1b) is a hard white Santonian chalk, probably equivalent to the Newhaven  
137 Formation in Great Britain. The selected samples correspond to the “Gros lien” level and come from  
138 the Vernon quarry (TERH company) in Vernon. It is a white stone with small black dots (manganese  
139 oxides) and flint nodules. The flint nodules can reach several tens of centimetres but in the studied  
140 samples their maximum size was only few centimetres. This stone underwent a complex diagenetic  
141 history through a dolomitization and dedolomitization process (Blanc, 1990).

142

143 Caen stone (Fig. 1c) samples come from the Cintheaux quarry (Societe des Carrieres de la Plaine de  
144 Caen) and correspond to the “demi-ferme” variety. It is a middle Bathonian light yellow limestone  
145 composed of lime sand (bioclasts and pellets) with calcite cement (Blows et al, 2003). Small pyrite  
146 crystals are locally present, producing an oxidation halo of rusty staining (Palmer , 2008).

147 Mineralogical analysis obtained by X-ray diffraction showed that the main mineral is calcite for the all  
148 three rocks with some quartz (~10%) in the Lutetian limestone.



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Fig. 1. Studied stones: a) Lutetian Limestone, b) Caen Limestone and c) Vernon chalk. Left magnified lens image (width of the images is 3.5 mm). Centre and right optical polarized light microscope images, parallel and crossed nicols (width of the images is 0.9 mm).

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Porosity of the studied rocks is given in Table 1, with mean, maximum and minimum values as well as standard deviation for 16 samples. It can be seen that Lutetian limestone has the highest porosity which is quite uniform for all the samples. Vernon Chalk has an average porosity of 25% but porosity varies very much from one sample to another. This variability can be explained by the presence of flint nodules. Caen limestone has the lower porosity with an intermediate variability compared to the other investigated rocks.

160  
161



162 Table 1.  
163 Open porosity of studied limestones

Stone	Mean (%)	Standard deviation	Maximum	Minimum
Lutetian	42.0	0.61	43.8	41.0
Caen	23.1	1.06	24.2	20.9
Vernon	25.0	2.89	30.9	20.5

164

165 The three stone have different pore size distributions. Lutetian limestone has the largest pores with a  
166 quite unimodal distribution around 12 $\mu$ m and a tail towards the smaller sizes (Table 2). In contrast,  
167 Caen limestone has the smaller pores with a maximum of 1.6  $\mu$ m. Moreover, it contains the largest  
168 amount of pores in the range from 0.1 to 1  $\mu$ m. Vernon stone has an asymmetric pore size distribution  
169 with a maximum at 7.3  $\mu$ m and a slightly higher content of bigger pores. One of the samples of  
170 Vernon stone presented a different distribution with a bimodal pore size distribution with maxima at  
171 0.02  $\mu$ m and 1.6 $\mu$ m. This sample has a porosity of 17%- lower than the mean porosity of the Vernon  
172 chalk. Since specimens for mercury porosimetry are small, it can be assumed that this sample may  
173 contain a small flint nodule and has not been considered in Table 2.

174  
175 Table 2.  
176 Mercury porosimetry pore size distribution parameters

Stone	Mean	Median	Mode	Standard deviation	Skewness (Pearson coef)	Kurtosis (Fisher coef)
Caen	2.94	0.77	1.54	13.85	0.11	-0.78
Lutetian	11.04	9.34	12.66	18.50	-0.09	-1.33
Vernon	8.22	6.20	7.27	14.78	0.06	-1.58

177

178 Capillary properties of stones play an important role in salt weathering studies because salt brine  
179 usually gets into the building by capillary forces. Standard capillary tests were done on cubes of size  
180 4x4x4cm. Furthermore, 4 vertical faces were monitored in order to obtain the evolution of water front  
181 in time. Capillary coefficients (C, in kg/(m<sup>2</sup>s<sup>1/2</sup>)) are very different for each stone: Lutetian limestone  
182 has an extremely high C of 1.15, Caen stone has a C equal to 0.097. These two stones are quite  
183 homogeneous and curves for different samples are very similar. In Vernon stone two different trends

184 can be observed, the majority of samples have mean C equal to 0.61 whereas one sample presents a  
185 capillary imbibition lower than the others, with a mean C equal to 0.022. Looking in detail, two  
186 different slopes were found in all the samples of Vernon chalk (V0, V1 and V2). The mean C can be  
187 decomposed into two different coefficients (C1 and C2) because during the first 30 min the imbibition  
188 is faster (C1 is equal to 0.073 for V0 and V2 and to 0.031 for V1) whereas the rate of further  
189 imbibition decreases and C2 is equal to 0.035 for V0 and V1 samples and to 0.017 for V2 sample.

190 In order to quantify the capillary rise anisotropy the height of the different faces was measured on  
191 recorded images. The water front was white flat and regular for Lutetian and Caen limestones. Based  
192 on the results it can be pointed out that Lutetian stone takes all the water in less than 2 minutes and  
193 that the capillary front in Vernon is quite irregular, capillary rise significantly varies between different  
194 faces of one sample.

195

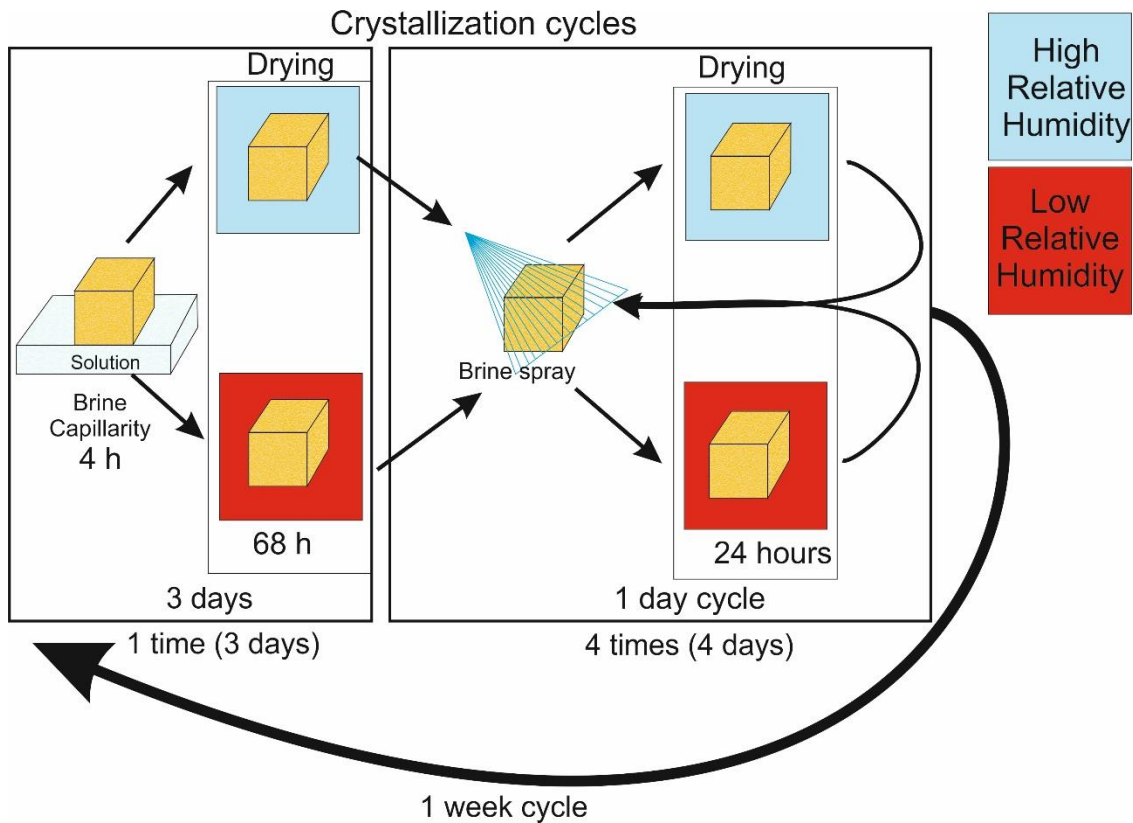
### 196 **3. Methods**

#### 197 *3.1 Crystallization cycles*

198 Nonstandard salt crystallization tests were performed to investigate the influence of brine composition  
199 and environmental conditions on salt weathering. Special interest was paid to the differences between  
200 single salt and salt mixtures behaviour during salt crystallization in porous media.

201 To simulate as closely as possible real conditions non classical cycles were used. Different samples  
202 were tested at different experimental temperature and relative humidity conditions. For some samples  
203 cycles were performed at room temperature and for others at 50°C and at both temperatures, for some  
204 samples RH was kept low and for others high. Cycles (Fig. 2) were the same for all the samples with  
205 two levels of cycles, cycles of one week and inside these, one-day cycles. At the beginning of the one  
206 week cycles, samples were wetted with brine by capillary imbibition for four hours. After this  
207 procedure samples were dried for three days. Everyday from day 4 to 7, after a cooling period of two  
208 hours for samples dried at 50°C, they were vaporized with brine. Tests at room temperature were  
209 performed inside vacuum bells, opened for low RH and closed with water on the bottom for high RH.  
210 Temperature and RH were continuously recorded as they were not precisely controlled. Both

211 parameters are quite constant during cycles without significant fluctuations. For tests performed at  
 212 50°C samples were placed into a climatic chamber for high RH and into a cooling oven for low RH.  
 213 Table 3 shows the environmental conditions for all the samples. To avoid thermal shocks before and  
 214 after imbibition at 50°C, temperature was decreased and increased slowly. The cooling oven  
 215 unfortunately does not control temperature very precisely and 5°C fluctuations around fixed  
 216 temperatures were observed.



217  
 218 Fig. 2. Schematic representation of salt weathering cycles

219

220 Table 3.  
 221 Environmental conditions for crystallization cycles and duration of the cycles.

	Room temperature		50°C	
	a) High RH	b) Low RH	c) High RH	d) Low RH
Temperature (°C)	20	20	50	50
Relative humidity (%)	90	45	90	5
Number of 1 week cycles	12	12	4	4

222

223

### 224 *3.2 Brine composition*

225 Different brines were used for capillarity imbibition and vaporization. For the experiments  
226 corresponding columns a to d of Table 3, each sample was wetted by a different brine composition  
227 (always the same for the same sample), NaCl, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, CaSO<sub>4</sub> or a mixture of the three salts.  
228 The concentration of the CaSO<sub>4</sub> brine was kept constant at saturation (CaSO<sub>4</sub> 0.01 mol/kg), whereas  
229 NaCl and Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O concentrations were increased during cycles, from 1.5% in weight during the  
230 first week, to 3% the second week and finally to 6% (NaCl 1.03 mol/kg; Na<sub>2</sub>SO<sub>4</sub> 0.19 mol/kg) for the  
231 rest of the cycles. For the brine with all three salts, the total concentration in weight is almost the same  
232 as the one of the single salt brines (6.2%). The low concentration of sodium sulphate in relation to NaCl  
233 was chosen due to their known differences in weathering capacities. Samples were tested at 50°C and  
234 room temperature and under low and high RH as explained before.

### 235 *3.3 Relative humidity cycles*

236 At the end of the series of one-week cycles with brine supply by capillarity imbibition and  
237 vaporisation all the samples followed new cycles where only RH conditions varied between low and  
238 high, first 15 two-days cycles (one day high RH, one day low RH) followed by 20 two-week cycles  
239 (one week low RH, one week high RH). Two-day cycles were not enough to allow real weight  
240 differences. For samples at 50°C during the initial two-week the high RH was set to 80%, after that it  
241 was raised to 90% as 80% was not enough to produce significant changes on the samples.

### 242 *3.4 measurements*

243 During the crystallization cycles samples were weighed at different times, before and after capillarity  
244 imbibition and before and after vaporization. The employed balance has a precision of 0.01g. During  
245 relative humidity cycles samples were weighed at every change of RH conditions. One to several  
246 pictures of every sample were taken before every wetting (capillarity or vaporization) for the  
247 crystallization cycles and every time RH conditions changed for the relative humidity cycles.

## 248 **4. Result**

249 Two kinds of results were obtained, mass evolution during cycles and visual observation of weathering.  
250 Investigation of salt distribution in tested stones was performed in scanning electron microscope  
251 equipped with X-ray detector enabling determination of different phases. For tests at room temperature  
252 (columns a and b of Table 3) one sample was always used for each humidity condition/brine composition  
253 due to the amount of different possibilities (3 stone types\*2 RH\*4 brine composition = 24 samples). At  
254 50°C (columns c and d of Table 3) two samples per humidity condition/composition were tested. The  
255 samples were named according to the following code, the first capital letter corresponds to the stone (C,  
256 Caen; L, Lutetian, V, Vernon), after that the temperature is indicated (20 for room temperature and 50  
257 for 50°C) and finally the RH conditions (D, dry, for low humidity and W, wet, for high humidity  
258 condition). Samples were weighed before and after imbibition or spray (vaporization).

#### 259 *4.1 Drying and wetting cycles at room temperature*

260 The variation of weight with crystallization cycles can be observed in Fig. 3 during the twelve one-  
261 week cycles that were performed. The traditional measure of mass increment over original mass was  
262 substituted by mass increment over volume of the sample and it was multiplied by 100. The reason for  
263 this choice is that with weight/weight calculations for samples of low density, as in this case Lutetian  
264 limestone with 1530 kg/m<sup>3</sup>, values are magnified with respect to samples with higher densities such as  
265 Caen, 2060 kg/m<sup>3</sup>, and Vernon 2000 kg/m<sup>3</sup>. Several observations are summarized below:

266 For all stones and salts, samples dried under low humidity conditions (room RH) had lower weight  
267 variation than samples “dried” at high humidity. High RH prevents the samples from completely  
268 drying even if inside the one-week cycles fluctuations of mass increase are observed. These  
269 fluctuations are quite similar for both sulphates and are less important for NaCl and for salt mixture.

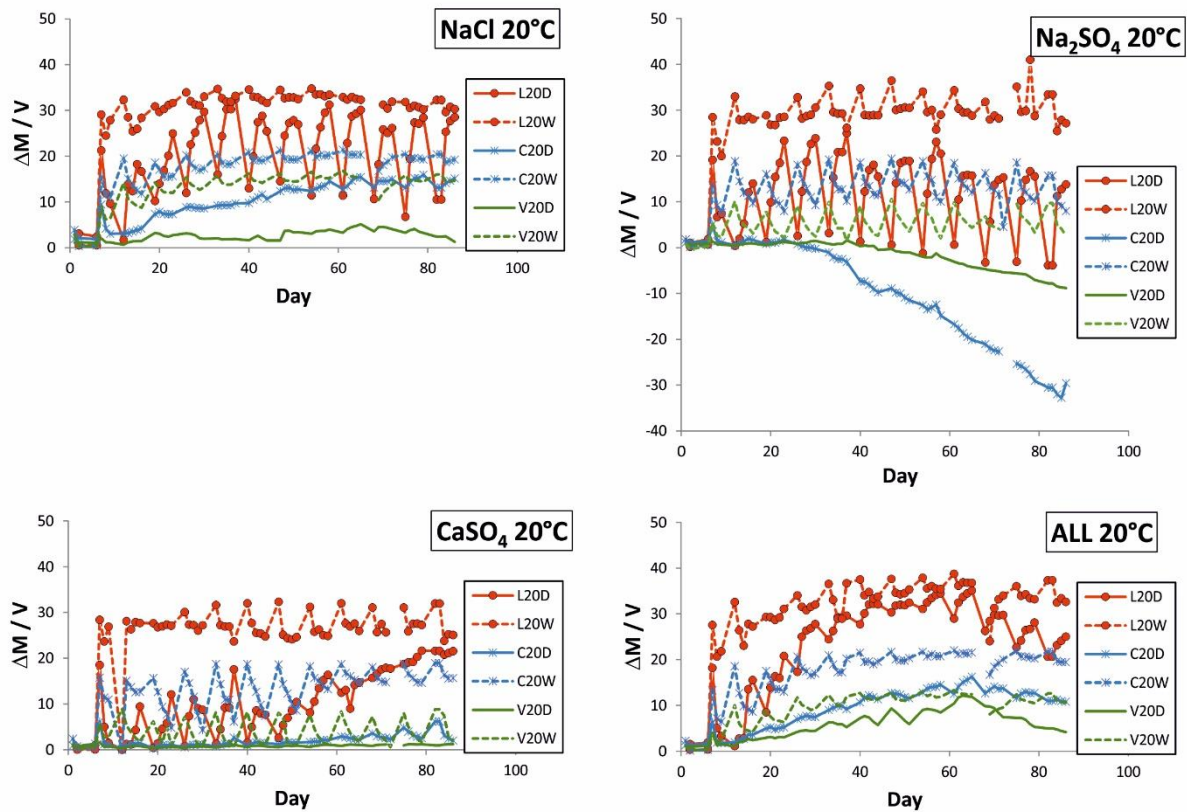
270 It can be seen that for the Lutetian limestone the amplitude of these fluctuations is higher at high RH  
271 than at low RH. For Caen Limestone and Vernon stone the variation is the opposite, higher for low RH  
272 than for high RH.

273 For samples “dried” under wet conditions, samples imbibed by  $\text{CaSO}_4$  brine show fluctuations higher  
274 than samples wetted just by water. Under dry conditions these fluctuations were very small, except for  
275 Lutetian stone.

276 For tests done with  $\text{NaCl}$  the only sample that shows a decrease in weight is the Vernon sample under  
277 dry conditions. All the others show a slight mass increment.  $\text{Na}_2\text{SO}_4$  crystallization cycles at high  
278 humidity do not produce any apparent change on samples after the initial mass increase produced  
279 during the first imbibition by capillarity. Under dry conditions Lutetian limestone showed a slight loss  
280 of mass at the end and Caen and Vernon stones suffer clear weight decrease. The most affected sample  
281 was Caen limestone. Cycles with  $\text{CaSO}_4$  just produced an accumulation of gypsum on samples dried at  
282 low RH, especially on the Lutetian limestone.

283 During cycles done with a salt mixture the differences between samples dried at high and low RH  
284 seemed less important than in cycles with simple solutions. All the samples dried at low RH showed a  
285 beginning in loss of weight. The initial mass increase was more important than for any of the single  
286 salt solutions, even if the concentration was almost the same (~6% weight) for all the solutions. For  
287 example in Lutetian limestone, the maximum increment of mass was 23% for the complex brine, 15%  
288 for gypsum, 16% for sodium sulphate and 20% for halite. On samples dried at high RH no apparent  
289 changes were observed.

290



291

292 Fig. 3. Mass variation in percentage over sample volume evolution with cycles for samples dried at  
 293 room temperature and with different brine composition (equal total concentration of 6% except for  
 294 gypsum solution, 0.2%).

295

296 Cycles with NaCl only produced superficial efflorescences on Lutetian stones but a loss of material  
 297 was observed in Caen and Vernon samples. This loss was more important for Vernon sample than for  
 298 Caen sample (Fig. 4a). On the weight curves a loss of mass was only observed for Vernon, no  
 299 apparent mass loss for Caen sample. No significant change was observed on any sample at high RH.

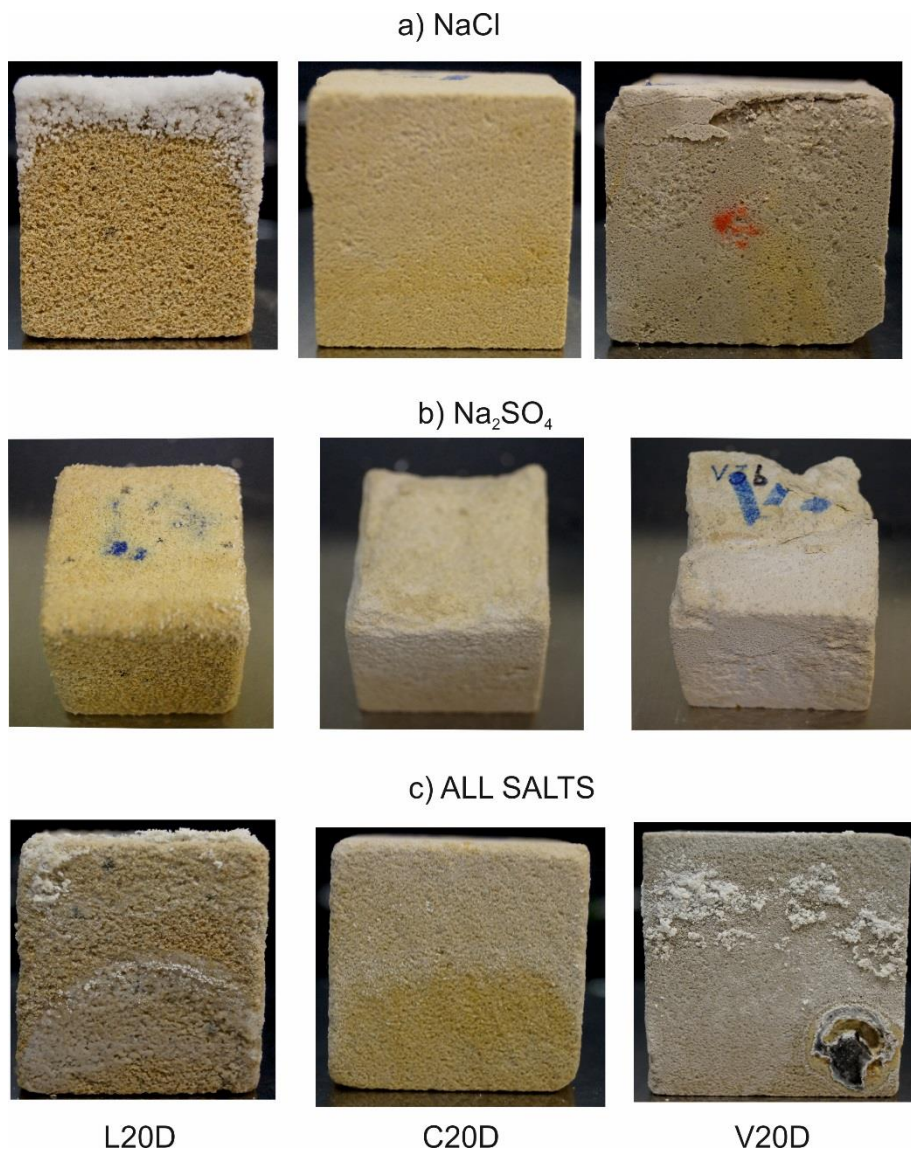
300 After cycles with sodium sulphate samples presented quite different behaviour as a function of  
 301 lithology (Fig. 4b), Lutetian samples only showed a slight superficial granular disintegration, Caen  
 302 limestone presented a more important granular disintegration on the upper face of the sample and  
 303 Vernon limestone presented irregular behaviour with significant degradation in some areas. Mass loss  
 304 was more important in Caen samples than in Vernon samples. At high RH Caen and Vernon samples  
 305 presented efflorescences mainly in the upper side of samples.

306 Cycles with gypsum did not produce apparent degradation on the samples. Only precipitation in the  
307 pores that could be observed as a sacaroid brightness and an intensification of colours. In samples of  
308 Vernon, oxides stains, which were not present at the beginning of the cycles were observed

309 Samples that followed cycles with the mixed brine did not show any apparent damage, only  
310 efflorescences and precipitation of salts on the surface could be seen (Fig. 4c). Caen limestone  
311 presented less efflorescences than Lutetian and Vernon stones. Lutetian samples showed two different  
312 kinds of efflorescences, one more attached to the surface and another one whiter, less compact and  
313 easier to take off. Caen samples presented efflorecence located in the upper half of the sample. Vernon  
314 limestone showed efflorescences not uniformly distributed on the sample, they were mainly located in  
315 the upper part of the sample and also concentrated on the flint concretion surfaces.

316





317  
 318 Fig. 4. Samples weathered by a) sodium chloride b) sodium sulphate and c) salt mixture at room  
 319 temperature and low relative humidity conditions.

320

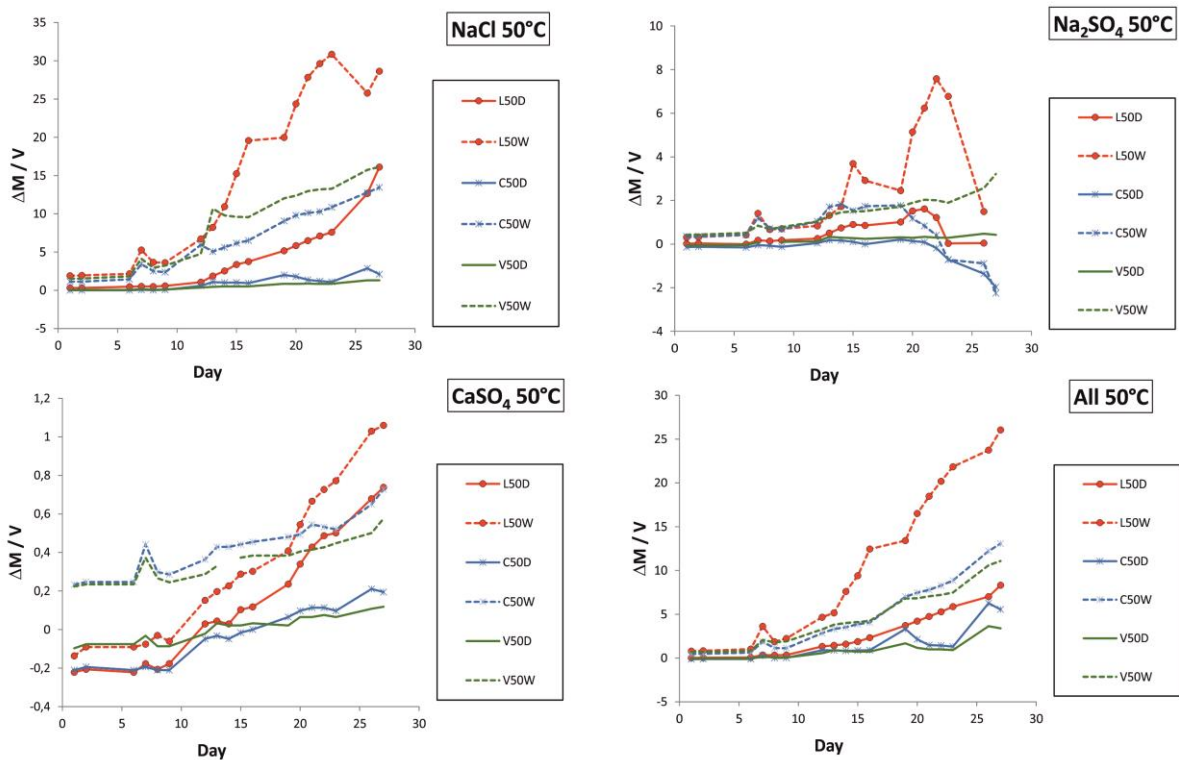
321 *4.2 Drying and wetting cycles at 50°*

322 Four cycles of one week were done at 50°C, the results of mass evolution with cycles are shown in  
 323 Fig. 5. Two samples of each stone were tested for each brine and environmental condition. It can be  
 324 observed that the two samples of the same stone and in the same conditions showed relatively  
 325 uniform behaviour in almost all the cases. Exceptions were some samples of Vernon limestone and  
 326 Caen stone weathered by sodium sulphate at high humidity conditions for which one of the samples

327 showed a large mass decrease on the 21<sup>st</sup> day. This day the sample lost a piece of stone, producing this  
328 marked change in the weight.

329 It was also observed that samples wetted by NaCl did not show any mass decrease but mass continued  
330 to increase until the end of the test. This increase was more important on samples dried at high RH  
331 condition than on samples dried at low RH. Samples contaminated by sodium sulphate showed an  
332 initial mass increase smaller than samples tested with sodium chloride and after three one-week cycles  
333 started to lose mass. The most affected samples were Caen limestone but Lutetian samples revealed  
334 also an important beginning of mass loss. Samples tested with CaSO<sub>4</sub> did not show any significant  
335 change in weight.

336 For the samples with the brine mixture only an increase of mass is observed. For all samples dried at  
337 high RH this increment was similar to the one of NaCl samples. On samples dried in low humidity  
338 conditions Lutetian stone got less salt with the mixture than with NaCl and Caen and Vernon increased  
339 their weight more with the complex brine than with halite.



340  
341 Fig. 5. Mass variation in percentage over sample volume evolution with cycles for samples dried at  
342 50°C and with different brine composition.

343

344 Generally samples dried at 50°C were more damaged than samples weathered at room temperature  
345 even if the number of cycles was much smaller at 50°C. In samples weathered with sodium chloride  
346 only efflorescences were observed and these efflorescences were more visible on samples dried at  
347 high RH than in samples dried at low RH. In samples wetted with sodium sulphate (Fig. 6) different  
348 patterns were found for Caen and Lutetian stones. In Lutetian samples weathering under low RH was  
349 more important than under high RH but on Caen stone high RH conditions induced more damage than  
350 low RH. Vernon chalk did not show any visible degradation.

351 At low RH Lutetian samples showed uniform degradation all over the surface with the formation of  
352 superficial detached layers and important efflorescences whereas Caen samples showed desegregation  
353 on the upper surface. At high RH the weathering patterns were different with a blistering phenomenon  
354 concentrated on the surface for Lutetian limestone and uniformly distributed desegregation all over the  
355 surface for Caen samples.

356 Samples weathered by calcium sulphate showed an accumulation of gypsum on pores at the surface of  
357 the samples. This accumulation was more evident on Lutetian limestone than in the others, especially  
358 on samples dried at low RH conditions. Samples weathered with the salt mixture did not show any  
359 visible degradation, even if the mass increase was similar to those of samples wetted by sodium  
360 chloride.



L50D

L50W



C50D

C50W

361  
362 Fig. 6. Details of samples weathered by sodium sulphate dried at 50°C at low (D) and high (W)  
363 relative humidity conditions.

364

365 Comparing samples altered at 20°C and 50°C it can be observed that only weathering produced by  
366  $\text{Na}_2\text{SO}_4$  seems enhanced by temperature increase. In samples weathered at 20 °C after the same  
367 number of cycles as samples weathered at 50°C (four one-week cycles) only efflorescences are  
368 observed on samples tested under dry conditions. Concerning samples weathered by sodium sulphate  
369 at room temperature after four one-week cycles, only Caen samples under dry conditions presented  
370 some degradation. On the samples weathered by gypsum or the salt mixture only a few efflorescences  
371 were observed at the end of cycles.

372 Lutetian samples looked more vulnerable to temperature than Caen and Vernon samples. At 50°C  
373 Vernon limestone did not suffer any apparent damage with any salt. Different behaviour between  
374 Lutetian samples tested at 20°C and 50°C can be explained by the low evaporation rate in this stone.  
375 At 20°C after the drying period most of the solution was still in the samples whereas at 50°C the

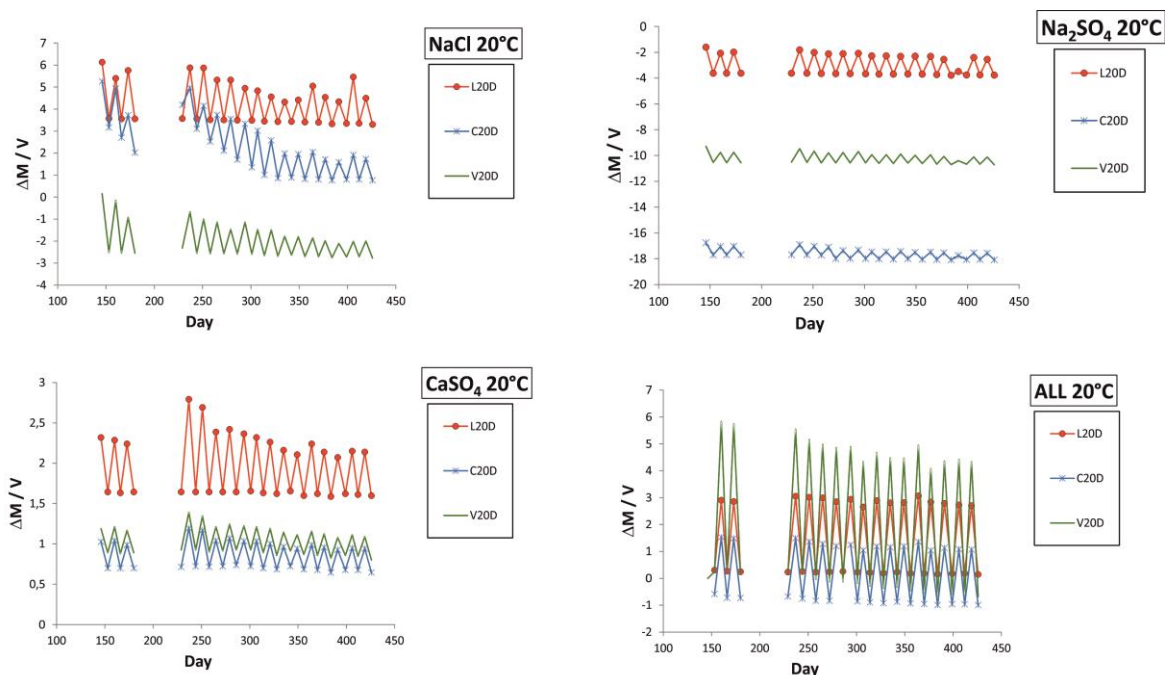
376 evaporation was accelerated. This was valid also for the Caen and Vernon samples. Nevertheless,  
377 higher evaporation conditions caused little differences among samples tested at both temperature  
378 conditions. .

379

### 380 4.3 Relative humidity cycles

381 In buildings and monuments deliquescence/dissolution cycles can occur on samples already  
382 contaminated with salts. To simulate similar conditions, RH cycles were performed on previous  
383 weathered samples. In this case phase transitions and deliquesce should be the principal ageing factor.  
384 Results of mass variations are depicted in Figs. 7 and 8 for the samples dried at room temperature and  
385 50°C. For the samples at 50°C high RH had been set at 80% for 8 two-week cycles and after it was  
386 raised to 90%.

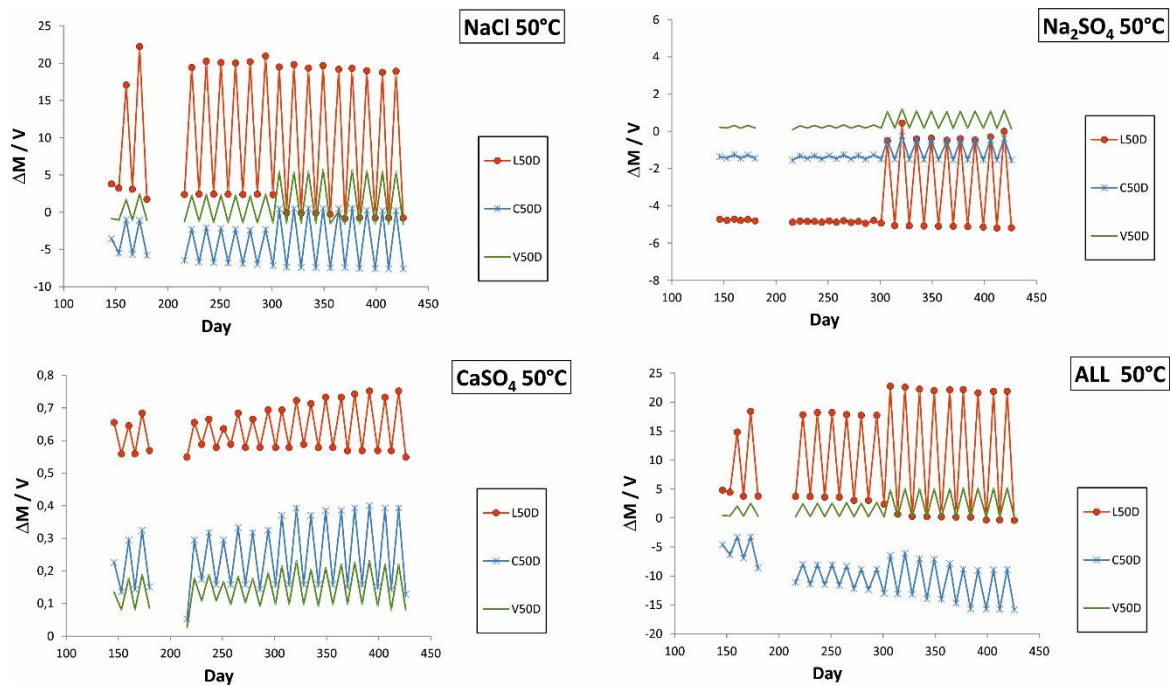
387



388

389 Fig. 7. Mass variation during relative humidity cycles for samples dried at room temperature.





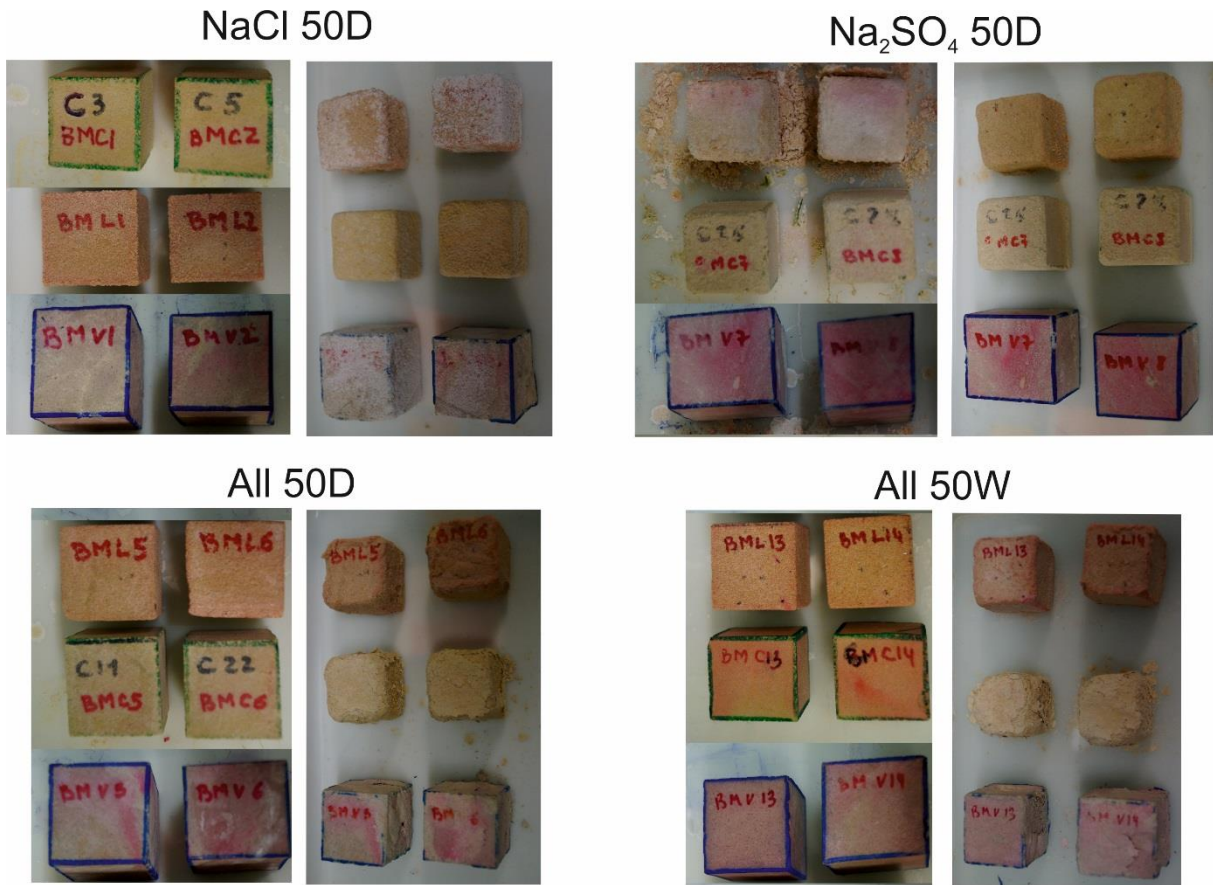
390

391 Fig. 8. Mass variation during relative humidity cycles for samples dried at 50°C.

392

393 Samples dried at room temperature continue to lose mass during the cycles (Fig. 7), especially in  
 394 samples weathered by sodium chloride. Visually the most common difference between before and  
 395 after RH cycles is the appearance of salt efflorescences at the surface of the samples and the  
 396 superficial degradation suffered by samples weathered with the salt mixture.

397 For samples dried at 50°C the most significant mass decrease was observed in Caen samples  
 398 weathered by salt mixture (Fig. 8). Fig. 9 shows the visual variation before and after the RH cycles for  
 399 samples dried at 50°C. RH cycles produced granular disaggregation in all samples weathered by pure  
 400 NaCl solution and the appearance of surface efflorescence. In contrast, samples weathered with  
 401 sodium sulphate, especially Lutetian limestone, lost superficial efflorescences after RH cycles. All  
 402 samples weathered with salt mixture suffered real degradation during the RH cycles. Caen limestone  
 403 seems to be the most affected one by RH cycles, especially with salt mixtures.



404

405 Fig. 9. Samples at 50°C tested with constant global concentration solutions before and after relative  
 406 humidity cycles.

407

408 *4.4 Salt mass variation*

409 In order to interpret damage, the salt content added to the samples during each cycle should be  
 410 determined. Mass increment, after capillary imbibition and after spray was measured for this purpose.

411 The evolution of mass increase during capillary imbibition cycles in samples tested at 20°C is given in  
 412 Table 4.

413

414 Table 4

415 Mas increase by capillarity absorption at each one week cycle for samples dried at room temperature.

Stone and conditions	Brine composition	Cycle										
		1	2	3	4	5	6	7	8	9	10	11
L20D	NaCl	18.88	14.38	10.96	6.88	4.52	2.81	7.71	5.98	2.39	2.75	4.86
	CaSO <sub>4</sub>	18.74	2.92	3.24	2.01	1.45	1.42	2.81	2.47	0.69	1.10	0.61
	All	17.64	17.05	12.80	11.24	12.93	7.69	13.20	12.71	7.10	8.19	6.20
	Na <sub>2</sub> SO <sub>4</sub>	21.13	3.57	3.29	3.93	3.77	6.15	5.83	5.67	5.42	4.84	13.89
L20W	NaCl	19.81	19.06	11.92	9.59	5.74	5.29	4.15	4.10	2.48	1.57	4.52
	CaSO <sub>4</sub>	21.41	7.98	4.79	2.91	3.09	0.47	3.47	1.98	1.86	0.33	1.77
	All	19.27	15.85	12.34	7.69	6.22	4.21	10.97	6.80	5.43	7.40	7.38
	Na <sub>2</sub> SO <sub>4</sub>	19.22	8.47	3.52	4.29		5.77	5.33	2.79	3.37	3.36	9.40
C20D	NaCl	11.58	5.04	4.79	2.83	2.06	1.18	1.27	1.15	0.57	0.48	0.39
	CaSO <sub>4</sub>	11.69	5.36	4.28	9.16	9.45	8.38	7.57	6.80	3.95	3.16	4.77
	All	11.76	8.34	7.21	4.90	2.87	0.99	1.88	1.22	1.04	0.44	1.21
	Na <sub>2</sub> SO <sub>4</sub>	10.57	7.49	5.98	7.43	6.43	5.64	5.51	4.07	5.45	3.66	
C20W	NaCl	11.86	11.65	10.68	8.49	7.33	6.56	6.27	4.62	3.18	2.57	2.89
	CaSO <sub>4</sub>	11.17	11.62	11.34	11.61	11.57	10.66	11.50	11.38	11.22	11.18	11.13
	All	11.88	12.27	11.15	9.88	7.98	6.89	5.70	5.87	3.79	2.35	3.80
	Na <sub>2</sub> SO <sub>4</sub>	9.63	12.16	11.65	11.64	11.8	9.61	12.42	11.10	10.06	10.70	10.85
V20D	NaCl	7.88	5.59	4.48	2.61	1.98	1.48	1.42	1.61	1.06	1.12	0.52
	CaSO <sub>4</sub>	6.69	6.06	6.69	7.44	7.50	7.81	7.56	7.51	7.66	7.27	8.05
	All	4.48	6.80	4.73	3.9	2.39	0.67	1.52	1.75	1.43	0.80	2.31
	Na <sub>2</sub> SO <sub>4</sub>	7.60	8.23	7.39	8.12	7.86	8.39	8.24	6.90	8.16	5.80	9.20
V20W	NaCl	4.59	8.14	7.57	6.53	6.26	6.41	7.53	5.87	5.22	4.24	5.26
	CaSO <sub>4</sub>	6.21	7.65	7.14	7.14	7.05	6.87	7.24	7.16	7.50	7.50	7.29
	All	11.96	12.25	11.71	11.65	10.28	10.01	10.04	10.23	8.94	5.74	9.04
	Na <sub>2</sub> SO <sub>4</sub>	4.76	7.98	7.08	7.23	6.85	6.78	8.20	7.37	7.38	7.43	7.77

416

417

418 Absorption of solution by capillarity in Lutetian stone tested at 20°C was the most significant at the  
419 beginning of experiment (cycle 1). Subsequent mass gain during following cycles gradually decreased  
420 up to cycle 4 (NaCl and mixture) or immediately dropped in cycle 2 (Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub>) and  
421 remained almost constant till the end of the experiment. The mass gain is quite similar among samples  
422 tested at low or high RH. At 50°C and low RH conditions mass gain was also similar for all the tested  
423 salt solutions and remained constant during the cycles. At high RH important differences were  
424 observed between solutions containing sodium chloride and other salts. In solutions containing NaCl  
425 mass gain considerably decreases after cycle 2 but for sodium and calcium sulphates it remains



426 constant. Sodium chloride probably inhibits capillary absorption more than sodium and calcium  
427 sulphates.

428 Mass gain in Caen limestone at room temperature decreased also with increasing number of cycles.

429 The depletion was more significant in samples dried at low RH as well as in samples impregnated with

430 NaCl solution at high and low RH conditions. At 50°C the behaviour was similar to that in Lutetian

431 samples with a mass gain almost constant for all samples that decreased after cycle 2 for samples

432 wetted with solutions containing NaCl at high RH.

433 For Vernon samples tested at room temperature mass gain remained constant for samples wetted with

434 sulphates and gradually decreased with the number of cycles for samples wetted with NaCl and

435 mixture solution. This reduction of mass increment was more important in samples dried at low RH.

436 At 50°C all samples presented a similar behaviour, only slight diminution of mass was observed in the

437 samples containing NaCl solution dried at high RH.

438 The mass change in samples impregnated by spraying of salt solutions was also monitored. Mass

439 increments were quite constant during the experiment and the mean values for all cycles are listed in

440 Table 5. The final total mass of salt in each sample was calculated by equation (1)

$$441 \text{ Salt Mass} = (\sum \Delta m(\text{capillarity})) + n \times 4 \times \overline{\Delta m(\text{vaporization})} \quad (1)$$

442 where *Salt Mass* indicates the final total mass of salt,  $\Delta m(\text{capillarity})$  is the mass increment during

443 capillarity,  $n$  the number of one week cycles, and  $\overline{\Delta m(\text{vaporization})}$  the mean mass increase during

444 spray.

445

446

447 Table 5.

448 Mass increase before and after spray process for samples dried at room temperature and at 50°C.

RH	Salt	Lutetian	Caen	Vernon	Lutetian	Caen	Vernon
		Room temperature			50°C		
D	NaCl	6.42	1.55	1.39	3.23	1.59	1.48
D	Na <sub>2</sub> SO <sub>4</sub>	9.06	1.63	1.67	3.75	1.85	1.52
D	CaSO <sub>4</sub>	3.94	1.43	1.80	4.50	2.04	1.52
D	All	2.85	1.49	1.41	4.27	1.82	1.48
W	NaCl	1.55	0.65	0.69	2.83	1.18	1.44
W	Na <sub>2</sub> SO <sub>4</sub>	2.48	1.06	1.33	3.76	1.44	1.63
W	CaSO <sub>4</sub>	3.17	1.21	1.14	3.73	1.82	1.79
W	All	1.96	0.69	0.55	5.78	1.82	1.52

449

450 Total mass gain after all cycles for samples wetted with solutions at equal concentration are listed in  
 451 Table 6. The Total mass column for mirabilite (Na<sub>2</sub>SO<sub>4</sub> 10H<sub>2</sub>O) represents mass gain without water  
 452 molecules.

453 Table 6.

454 Total salt mass gain during crystallization cycles for samples dried at room temperature and 50°C.

Solution	Sample	Total mass (g)	Sample	Total mass (g)	Sample	Total mass (g)
NaCl	L20D	21.87	C20D	5.97	V20D	5.46
Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	L20D	11.54	C20D	3.87	V20D	4.06
CaSO <sub>4</sub>	L20D	3.00	C20D	1.05	V20D	1.10
All	L20D	19.24	C20D	12.50	V20D	14.01
NaCl	L20W	9.37	C20W	6.29	V20W	5.87
Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	L20W	4.21	C20W	4.53	V20W	3.63
CaSO <sub>4</sub>	L20W	2.43	C20W	1.35	V20W	1.62
All	L20W	14.40	C20W	14.41	V20W	9.77
NaCl	L50D	7.60	C50D	4.35	V50D	3.65
Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	L50D	3.68	C50D	1.96	V50D	1.56
CaSO <sub>4</sub>	L50D	1.53	C50D	0.78	V50D	0.48
All	L50D	14.55	C50D	7.40	V50D	5.39
NaCl	L50W	5.55	C50W	3.03	V50W	3.38
Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	L50W	3.62	C50W	1.79	V50W	1.31
CaSO <sub>4</sub>	L50W	1.39	C50W	0.74	V50W	0.56
All	L50W	14.58	C50W	6.44	V50W	5.88

455

456 *4.5 Salt volume model*

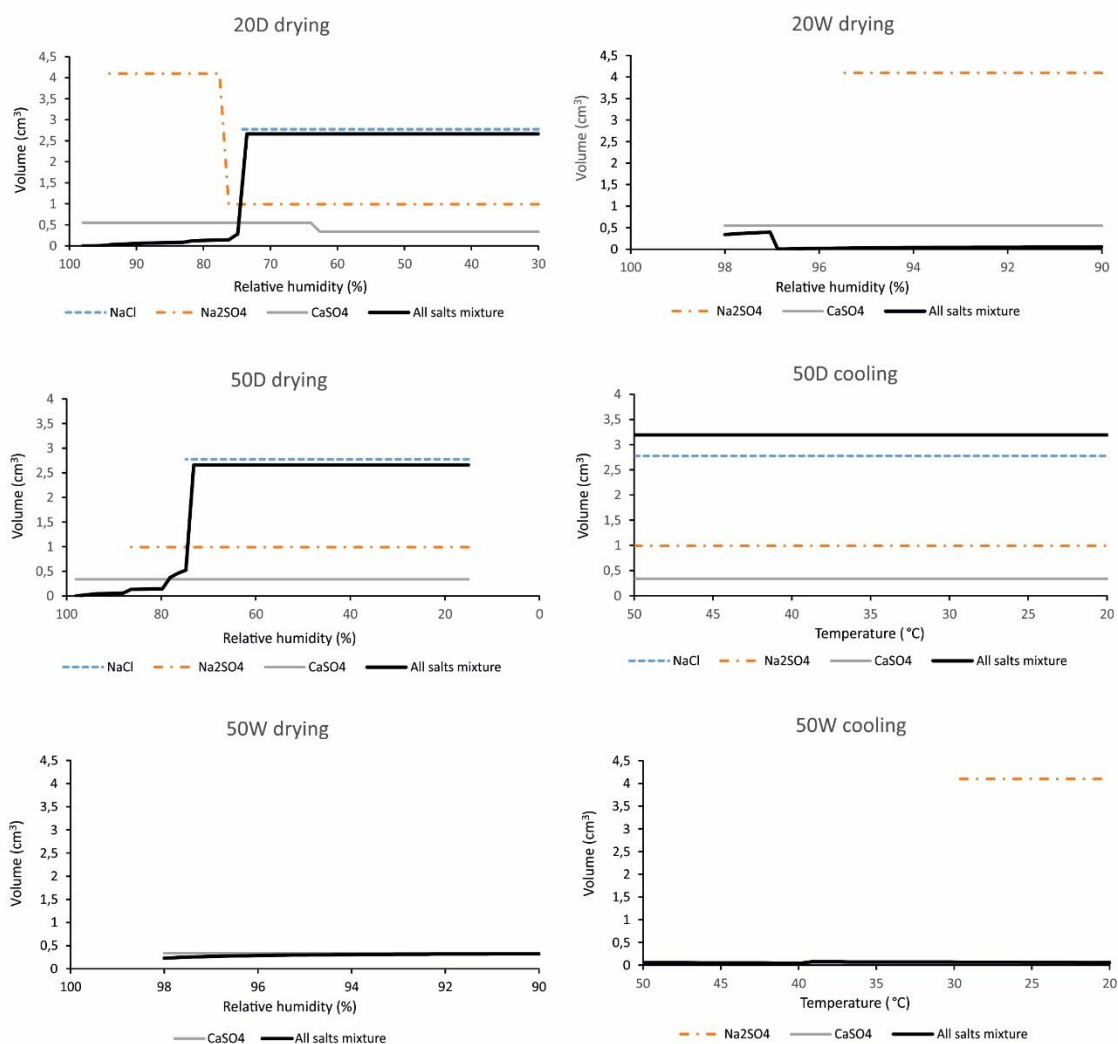
457 In order to estimate the volume of crystallized salt in the samples the ECOS-RUNSALT (Bionda,

458 2005; Price, 2010) thermodynamic model was used. Calculations were performed using 100ml of

459 standard solutions with the original brine compositions and the environmental variations

460 corresponding to experimental cycles. The obtained results with ECOS RUNSALT are depicted in  
461 Fig. 10 for each environmental condition. Drying corresponds to crystallization process after wetting  
462 phases. Just after saturation it can be considered that relative humidity in the pores is almost 100% and  
463 later it decreases to be in equilibrium with the environmental RH. Legends show the chemical  
464 composition of salts without considering their hydration degree. For example changes occurring  
465 around RH 77% in the  $\text{Na}_2\text{SO}_4$  curve at room temperature correspond to mirabilite-thenardite  
466 transitions. In the simulation of tests performed at  $50^\circ\text{C}$  two different environmental changes were  
467 considered, drying and cooling. For tests done at room temperature no cooling period was necessary.  
468 To simulate what happens in a particular sample, the obtained amount of substances can be multiplied  
469 by the total amount of salt present in this sample. Taking into account these results it seems that the  
470 most important volume increases correspond to salt mixture under low RH conditions. The final  
471 composition of the precipitated salts given by the ECOS-RUNSALT model is Thenardite ( $\sim 2.25\text{cm}^3$ ),  
472 halite ( $\sim 2\text{cm}^3$ ) and Glauberite ( $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ ) ( $\sim 0.75\text{cm}^3$ ). X-ray qualitative mineralogical analysis  
473 was performed at the end of the cycles on samples weathered at  $50^\circ\text{C}$  and dry conditions and only  
474 single salts, halite, thenardite and gypsum, were found.

475



476

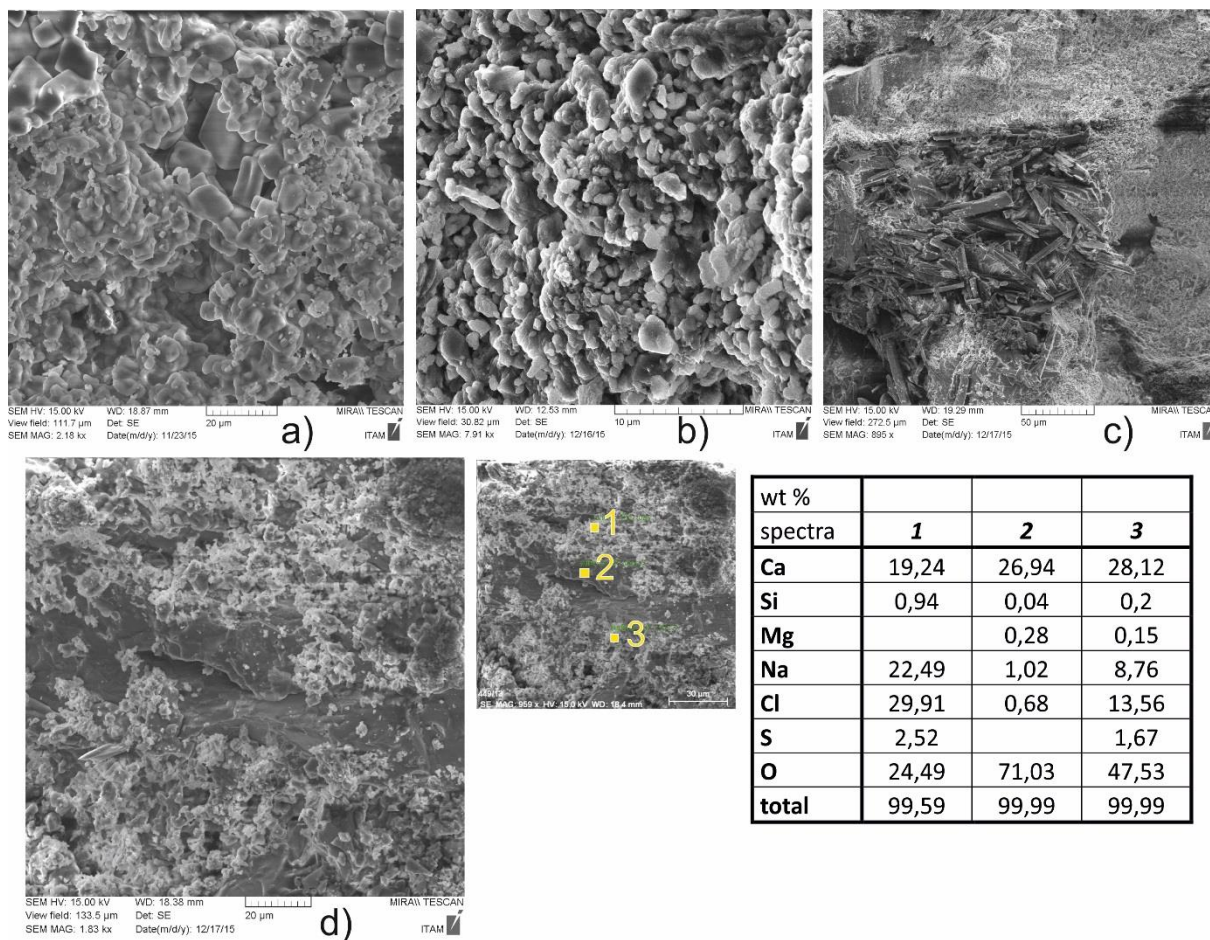
477 Fig. 10. ECOS RUNSALT simulations with the employed brines and during the period of change in  
 478 environmental conditions.

479

480 *4.6 Microscopic studies on weathered samples*

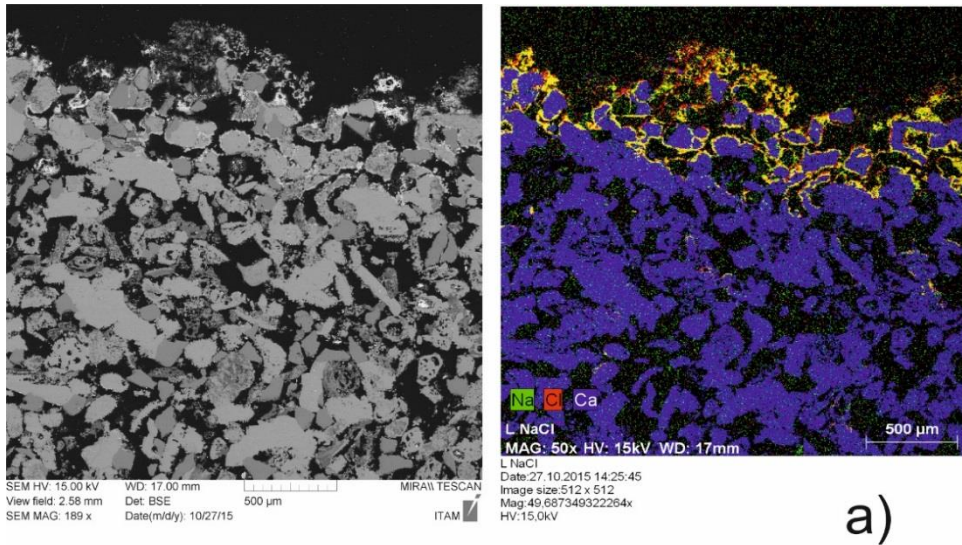
481 Investigation of salt distribution inside the stone was performed on samples of the series 50D in a  
 482 scanning electron microscope (SEM, MIRA II LMU, Tescan corp., Czech Republic) equipped with  
 483 energy dispersive X-ray detector (EDX, Bruker corp. Germany) enabling determination of chemical  
 484 composition. Several differences can be observed among samples weathered by different salts (Fig. 11  
 485 and 12). Sodium chloride crystals are bigger than sodium sulphate ones and are uniformly distributed  
 486 all over the surface (Fig. 11a et b). Calcium sulphate forms crystal aggregates with bigger crystals than

487 the other salts (Fig. 11c). On samples weathered by the complex brine a mixture of different salt  
 488 crystals covers the surface of the sample (Fig. 11d).

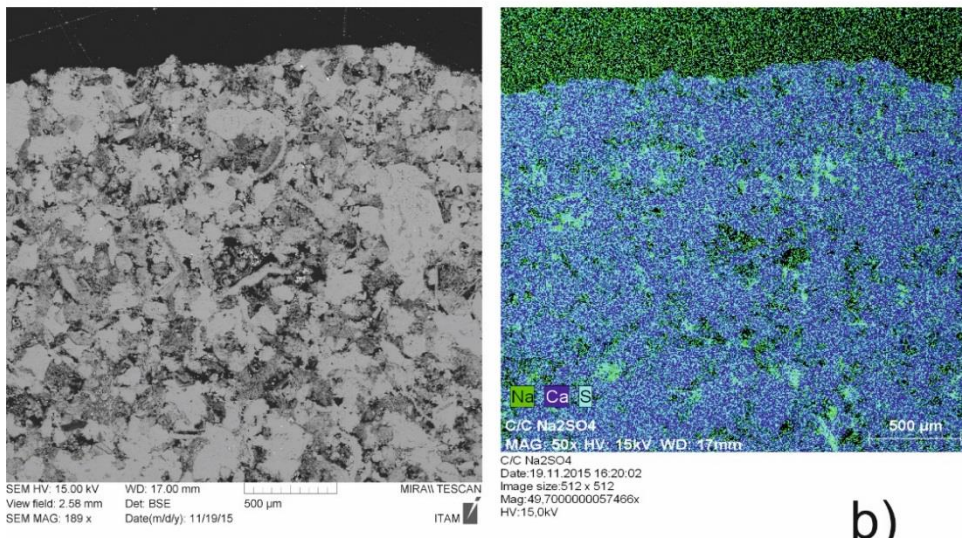


489  
 490 Fig. 11. Scanning electron microscopy images of the surface of weathered samples at 50°C and under  
 491 dry conditions: a) Vernon limestone V50D with NaCl, b) Caen limestone C50D with Na<sub>2</sub>SO<sub>4</sub>, c)  
 492 Lutetian limestone L50D with CaSO<sub>4</sub>, d) Caen limestone C50D with salt mixture of NaCl, Na<sub>2</sub>SO<sub>4</sub>  
 493 and CaSO<sub>4</sub>. On the right the semi-quantitative element analysis of areas 1, 2 and 3 on d) image.

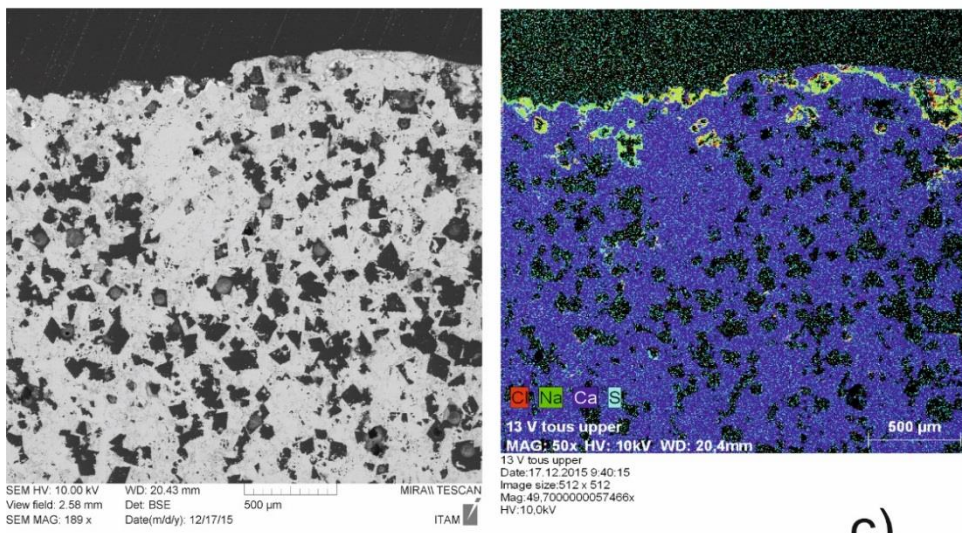




a)



b)



c)

494

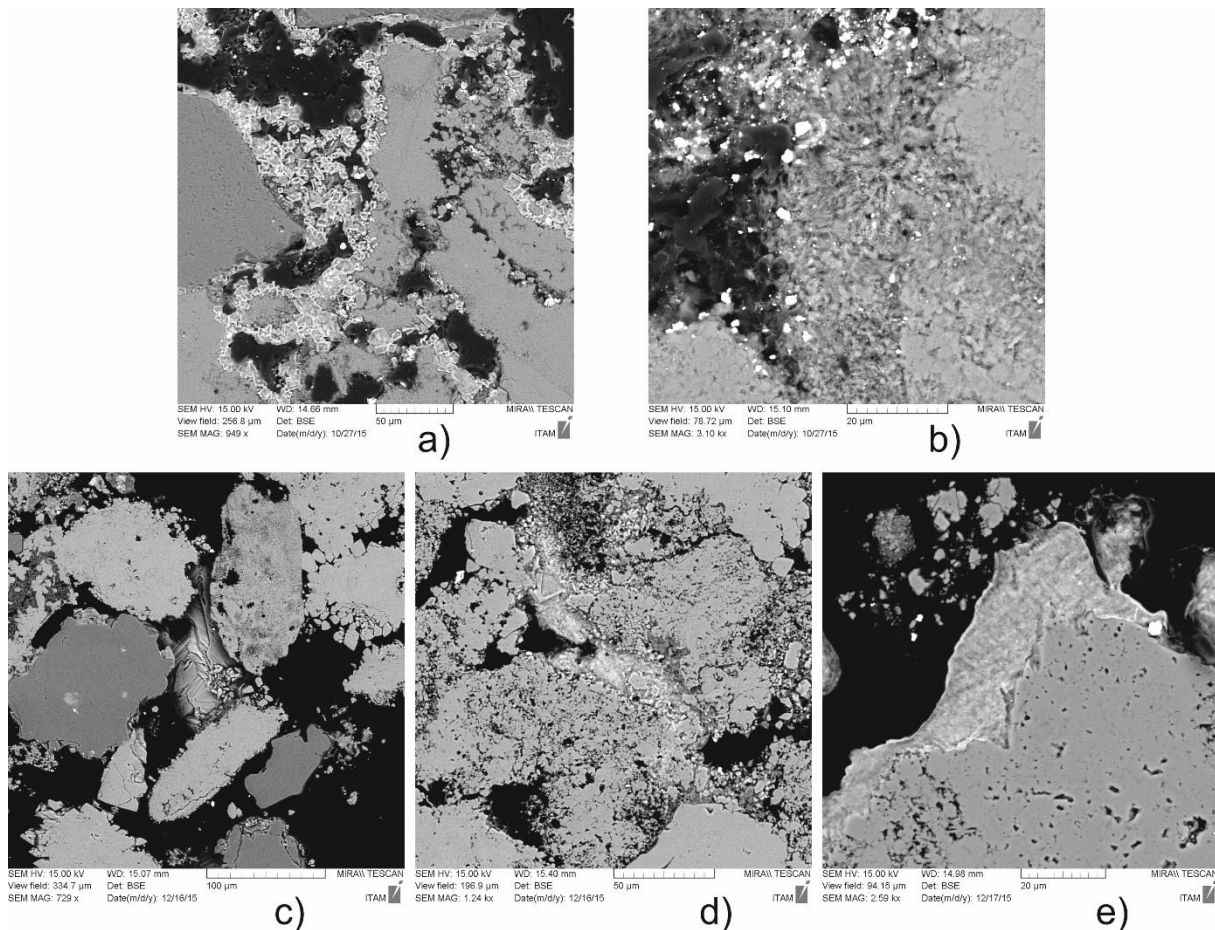
495 Fig. 12. Scanning electron microscopy images of weathered samples. a) Lutetian stone weathered by  
 496 NaCl, b) Caen stone weathered by sodium sulphate c) Vernon stone weathered by a salt mixture of  
 497 NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub>. The element mappings obtained by X ray are given on the righthand side of  
 498 these figures.

499

500 Element mapping enables determination of salt distribution in the samples. In all the stones sodium  
501 chloride was concentrated mainly on the thin superficial part of the samples. Sodium sulphate  
502 occurred almost 10 mm in depth in Lutetian and 13 mm in Caen stone, in Vernon stone only a few  
503 crystals were detected close to the surface. Calcium sulphate crystals were detected in the inner part of  
504 Lutetian sample affected by mixed brine solution (Fig. 12c) and on the surface of the sample exposed  
505 to single  $\text{CaSO}_4$  solution, where massive crystals of gypsum were observed (Fig. 11c). In samples  
506 weathered by a complex brine, element mapping confirmed the presence of salt crystals mainly on the  
507 surface of Lutetian and Vernon stones (Fig. 12c) although some salt was identified in the inner part. In  
508 Caen stone no superficial deposition was detected by X ray analysis.

509 In general sodium chloride crystallizes along the surface of grains covering them, sodium sulphate  
510 forms more extended areas with smaller crystals than sodium chloride. Calcium sulphate forms bigger  
511 crystals than the other salts. Fig. 13 shows some details of salt crystals in polished sections. In picture  
512 a) halite crystals covering the grain surface can be observed. Picture b) corresponds to sodium sulphate  
513 crystal aggregates. Picture c) shows an aggregate of gypsum crystals in a pore. Pictures d) and e)  
514 reflects a mixture of salts. No salt completely filling any pore was observed.





515

516 Fig. 13. Scanning electron microscopy images of polished cross sections of weathered samples at 50°C  
 517 and under dry conditions: a) Lutetian limestone V50D with NaCl, b) Lutetian limestone L50D with  
 518 Na<sub>2</sub>SO<sub>4</sub>, c) Lutetian limestone L50D with salt mixture of NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub>, d) Caen limestone  
 519 C50D with salt mixture of NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub> e) Vernon limestone V50D with salt mixture of  
 520 NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub>

521

## 522 5. Discussion

523 Degradation of porous stones is really a complex process depending not only on the nature of the salt  
 524 and porous material but also on the environmental conditions and their variation. The main  
 525 observations and outputs of present research are discussed below:

526 It was observed that during crystallization cycles under identical environmental conditions, samples  
 527 tested with single brine compositions presented more damage than samples tested with a mixture of  
 528 salts. These differences cannot be explained by the ECOS-RUNSALT equilibrium model. During RH  
 529 cycles samples saturated by salt mixtures suffered more damage than those saturated by single  
 530 solutions and more than during the crystallization cycles. Sawdy and Heritage (2007) stated that



531 deliquescence/ dissolution rates in salt mixtures increased with respect to single solution, which can  
532 contribute to the more significant weathering observed during the RH variation cycles. This fact can  
533 also explain the larger amount of salt cumulated in samples wetted with complex brines than in  
534 samples dried with single salt solution (Table 6). According to Sawdy and Heritage (2007) the rate of  
535 evaporation of salt mixture solutions is slower than in single salt solutions, contributing to the smaller  
536 weathering observed during the imbibition/drying cycles in salt mixtures.

537 Table 7 allows one to compare apparent weathering between samples tested in the same conditions, for  
538 crystallization and relative humidity cycles. Samples tested at 50°C are more affected by salts than  
539 samples tested at 20°C. In the group of samples tested at 20°C those wetted with sodium sulphate are  
540 the most weathered and samples wetted by the salt mixture the least. Samples tested at low relative  
541 humidity present more apparent damage than samples tested at high RH. Lutetian limestone is the least  
542 affected by crystallization cycles followed by Caen and Vernon samples.

543

544 Table 7  
 545 Comparison of the apparent degree of weathering for samples tested in the same environmental  
 546 conditions. Red indicates the most degraded sample, orange intermediate, yellow the least degraded  
 547 and white no apparent weathering.

T (°C)	Brine	RH	Crystallization	Relative
			Stone	Stone
20	NaCl	90	L20W	L20W
			C20W	C20W
			V20W	V20W
		45	L20D	L20D
			C20D	C20D
			V20D	V20D
	Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	90	L20W	L20W
			C20W	C20W
			V20W	V20W
		45	L20D	L20D
			C20D	C20D
			V20D	V20D
	Mixture	90	L20W	L20W
			C20W	C20W
			V20W	V20W
45		L20D	L20D	
		C20D	C20D	
		V20D	V20D	
50	NaCl	90	L50W	L50W
			C50W	C50W
			V50W	V50W
		5	L50D	L50D
			C50D	C50D
			V50D	V50D
	Na <sub>2</sub> SO <sub>4</sub> 10H <sub>2</sub> O	90	L50W	L50W
			C50W	C50W
			V50W	V50W
		45	L50D	L50D
			C50D	C50D
			V50D	V50D
	Mixture	90	L50W	L50W
			C50W	C50W
			V50W	V50W
5		L50D	L50D	
		C50D	C50D	
		V50D	V50D	

548

549 The amount of solution absorbed by the samples during capillary imbibition or spraying depend on the  
550 composition of brine. Brines with sodium chloride were more susceptible to be absorbed than other  
551 brines. The volume of solution taken by capillarity decreased with increasing number of cycles, i.e.  
552 with increasing salt content in the samples.

553 The weathering pattern also change with brine. Efflorescences of sodium sulphate were concentrated  
554 in the zone of evaporation front. Sodium chloride mostly formed a surface crust more or less thick.  
555 This fact can be explained by different solubility, sodium sulphate has a solubility almost one order of  
556 magnitude lower than sodium chloride, and it precipitates before NaCl, on the evaporation front. It can  
557 be seen on samples where Na<sub>2</sub>SO<sub>4</sub> efflorescences under room temperature (slow evaporation) were  
558 found on the upper surface of samples or following curved evaporation fronts.

559 The results show also that, whatever the salt solutions used in crystallization cycles, larger degradation  
560 occurs in Caen and Vernon limestones than in Lutetian limestone. The only exception was Lutetian  
561 stone affected by sodium sulphate solution at 50°C.

562 During wetting and drying cycles it can be assumed that the more active damage process is  
563 precipitation with the associated crystallization pressure. The pressure can be estimated following the  
564 equation proposed by La Iglesia et al (1997) based on the assumption that in an interconnected pore  
565 structure with non-uniform distribution of pores, i.e. coarse pores are interconnected with finer pores,  
566 salt crystals grow preferentially in coarse pores until they are filled. Subsequent crystallization into  
567 finer pores and thus smaller pore entries can develop pressure on the pore wall expressed by equation  
568 (2):

$$569 \quad P = 2\sigma (1/r - 1/R) \quad (2)$$

570 where  $\sigma$  is the salt-solution interfacial tension,  $r$  radius of smaller pores and  $R$  radius of coarse pore. In  
571 this work  $r$  was obtained by mercury porosimetry and  $R$  was estimated from thin sections as the radius  
572 of the equivalent circle with the same area as the actual pore surface. The obtained values of  $r$  and  $R$   
573 are 9.37 $\mu$ m and 55 $\mu$ m for Lutetian limestone; 0.765 $\mu$ m and 40 $\mu$ m for Caen stone and 6.20 $\mu$ m and  
574 40 $\mu$ m for Vernon chalk. For each brine composition salt-solution interfacial tension was constant so

575 the crystallization pressure could be compared for the different stones. Tensile strength for the  
576 different stones measured using Brazilian tests is 1.27 MPa for the Lutetian limestone, 2.35 MPa for  
577 Caen stone and 5.2 MPa for Vernon chalk. Estimated crystallization pressures, considering a mean  $\sigma$   
578 of  $40 \cdot 10^{-3}$  N/m, are  $7 \cdot 10^{-3}$  MPa for Lutetian,  $100 \cdot 10^{-3}$  MPa for Caen and  $13.5 \cdot 10^{-3}$  MPa for Vernon  
579 stones. These values are smaller than the tensile strength and cannot explain the observed damage. To  
580 have a crystallization pressure higher than the tensile strength, pore radius should be smaller than  
581  $0.08 \mu\text{m}$ , which is close to the resolution limit of the employed mercury porosimeter. For samples with  
582 similar open porosity - Caen (23%) and Vernon (25%) stone, the estimated values of crystallization  
583 pressure differ by about 10x factor, which can explain, at least partially, the higher sensitivity of Caen  
584 stone to salt weathering. The value of crystallization pressure estimated for Lutetian stone is the lowest  
585 one. However, Lutetian stone was at  $50^\circ\text{C}$  more prone to salt weathering than Vernon stone. Other  
586 factors linked to its higher porosity (42%) and its lower tensile strength can explain this observation.  
587 According to technical specifications uniaxial compression strength of Vernon stone varies between  
588 35 MPa and 60MPa, Caen 25MPa and Lutetian 9MPa.

589 Caen and Lutetian limestones are quite homogeneous while Vernon chalk contains more compact  
590 zones, this fact was confirmed on the basis of both irregular capillary imbibition and mercury  
591 porosimetry data (pore radius of  $0.12 \mu\text{m}$ ). This heterogeneity is probably caused by various flint  
592 content that produces non-uniform weathering as was observed in the sample V20D.

593 Generally it can be said that cycles performed at low RH conditions produced more damage than those  
594 at high RH. The only exceptions are samples weathered by sodium chloride at  $50^\circ\text{C}$ , in this case high  
595 RH during drying induced more damage than low RH, especially in Lutetian samples.

596 Concerning the contrasting behaviour between room temperature and  $50^\circ\text{C}$  it is possible to state that  
597 NaCl is more destructive at room temperature than at  $50^\circ\text{C}$ , and the opposite is true for  $\text{Na}_2\text{SO}_4$  which  
598 is more damaging at high temperatures. This phenomenon can be explained by the phase equilibrium  
599 curve of sodium chloride, less dependent on temperature than sodium sulphate.

600

601

## 602       **6. Conclusions**

603   The presented data set reflects the complexity of salt crystallization in porous media and highlights the  
604   specific influence of various factors inducing degradation in different types of rock. The main  
605   conclusions obtained in this study are summarized below:

606   The obtained results confirm previous studies concluding that brines composed of a mixture of  
607   different salts, mainly NaCl and Na<sub>2</sub>SO<sub>4</sub>, produce less damage during crystallization cycles than single  
608   salt solutions. Particularly, it was shown that the presence of NaCl attenuate the damaging effect of  
609   sodium sulphate.

610   Crystallization cycles performed at high RH produced less damage than cycles done at low RH  
611   although in the case of samples dried at 50°C and wetted by sodium sulphate this fact was not always  
612   verified as Caen limestone showed more damage at high RH than at low RH.

613   Changes in RH can induce more damage in samples polluted with different salts mixtures than with  
614   single salts, contrary to what happen during crystallization cycles.

615   Different salts crystallize at different depths in sample, for example NaCl precipitates mainly on the  
616   surface and Na<sub>2</sub>SO<sub>4</sub> on the inner part. This observation can explain the different weathering patterns  
617   produced by different salts.

618   To better understand the complexity of salt weathering in real cases, more research is needed including  
619   salts with magnesium, sodium and nitrates in the salt mixtures to be closest to salt composition in  
620   monumental stones.

621   The results of this work can be used to predict salt weathering (past, present and future) from climatic  
622   data. Most of the work done until now considers only individual salt behaviour, mainly NaCl and  
623   Na<sub>2</sub>SO<sub>4</sub>, which can induce large errors.

624

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635

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