

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

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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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Key words: salt weathering, limestone, environmental conditions, sodium chloride, sodium sulphate,
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, $Na_2SO_4 \cdot 10H_2O$, 6% in weight, $CaSO_4$ at saturation, and a mixture

20 of them at total concentration of 6.2%). Weathering tests were performed at room temperature and

 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)

environmental conditions, (ii) salt composition and (iii) petrophysical properties of stones, and general

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

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

29

30 1. Introduction

Salt crystallization is one of the most dangerous weathering agents in monumental stones. Salts are 31 32 always present in any environment, natural or anthropogenic and under any climatic conditions. The composition of these salt is very variable (Goudie and Viles, 1997) and depends on many different 33 34 factors such as proximity to sea; actual and historical air, soil and water pollution; mineralogical and chemical composition of affected materials, i.e. not only the studied material but also other materials 35 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.

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

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

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

The weathering caused by salt crystallization in nature is a complex process also involving the action of different aqueous salt mixtures together with frost. McGreevy (1982) performed frost cycles in samples saturated by saline solutions of sodium chloride, sodium sulphate and magnesium sulphate and found that freezing of NaCl solutions is more destructive than freezing of sodium sulphate 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 ($Mg(NO_3)_2 - H_2O$) and halite (NaCl) with nitratite (NaNO₃), niter (KNO₃) and gypsum 70 (CaSO $_4$ ·2H $_2$ 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 were completely dissolved. They concluded that in comparison to single salts 73 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

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 potassium81 sulphate.

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

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

Lindstrom et al (2015) studied the behaviour of salt mixtures of NaNO₃ and Na₂SO₄ in sandstones
with comparison to simple salt behaviours. Samples previously saturated with salts were exposed to
wetting and drying cycles with pure water. Among many other results they found that NaNO₃ is the
least damaging salt and Na₂SO₄ the most damaging one. Tests with salt mixture were not in accord
with previously obtained results in solution droplets. The authors suggested that more research should
be done.

Investigation of the behaviour of salt mixtures equilibrium models provides an extremely useful tool
 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 optimal105 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 mixture produces less damage than single salts. To test the effect of salt mixture versus single salt on 108 109 salt crystallization weathering a mixture of three salts: NaCl, Na₂SO₄ and CaSO₄ 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 (high and low) and two different temperatures (20°C and 50°C). Low relative humidity values are 113 different for the two temperatures due to experimental limits, 45% at room temperature corresponding 114 to the room RH and 5% at 50°C, relative humidity in the oven. 115

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

123 **2.** Materials

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

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

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

142

Caen stone (Fig. 1c) samples come from the Cintheaux quarry (Societe des Carrieres de la Plaine de
Caen) and correspond to the "demi-ferme" variety. It is a middle Bathonian light yellow limestone
composed of lime sand (bioclasts and pellets) with calcite cement (Blows et al, 2003). Small pyrite
crystals are locally present, producing an oxidation halo of rusty staining (Palmer , 2008).
Mineralogical analysis obtained by X-ray diffraction showed that the main mineral is calcite for the all

148 three rocks with some quartz ($\sim 10\%$) in the Lutetian limestone.



150 Fig. 1. Studied stones: a) Lutetian Limestone, b) Caen Limestone and c) Vernon chalk. Left magnified

151 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).

154	Porosity of the	studied rocks i	s given in	Table 1,	with mean,	maximum	and minimum	values a	is 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
- 157 varies very much from one sample to another. This variability can be explained by the presence of flint
- 158 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

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 μ m. Moreover, it contains the largest
168	amount of pores in the range from 0.1 to 1 μ m. Vernon stone has an asymmetric pore size distribution
169	with a maximum at 7.3 μ 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 I	Mercury	porosimetry	pore size	distribution	parameters
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Stone	Mean	Median	Mode	Standard	Skewness	Kurtosis
				deviation	(Pearson coef)	(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

Capillary properties of stones play an important role in salt weathering studies because salt brine
usually gets into the building by capillary forces. Standard capillary tests were done on cubes of size
4x4x4cm. Furthermore, 4 vertical faces were monitored in order to obtain the evolution of water front
in time. Capillary coefficients (C, in kg/(m²s^{1/2})) are very different for each stone: Lutetian limestone
has an extremely high C of 1.15, Caen stone has a C equal to 0.097. These two stones are quite
homogeneous and curves for different samples are very similar. In Vernon stone two different trends

can be observed, the majority of samples have mean C equal to 0.61 whereas one sample presents a 184 185 capillary imbibition lower than the others, with a mean C equal to 0.022. Looking in detail, two different slopes were found in all the samples of Vernon chalk (V0, V1 and V2). The mean C can be 186 187 decomposed into two different coefficients (C1 and C2) because during the first 30 min the imbibition is faster (C1 is equal to 0.073 for V0 and V2 and to 0.031 for V1) whereas the rate of further 188 imbibition decreases and C2 is equal to 0.035 for V0 and V1 samples and to 0.017 for V2 sample. 189 190 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 that the capillary front in Vernon is quite irregular, capillary rise significantly varies between different 193 194 faces of one sample.

195

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 cycles were performed at room temperature and for others at 50°C and at both temperatures, for some 203 204 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

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



218 Fig. 2. Schematic representation of salt weathering cycles

219

217

220 Table 3.

221 Environmental conditions for crystallization cycles and duration of the cycles.

	Room ter	nperature	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	

3.2 Brine composition

225 Different brines were used for capillarity imbibition and vaporization. For the experiments corresponding columns a to d of Table 3, each sample was wetted by a different brine composition 226 227 (always the same for the same sample), NaCl, Na₂SO₄·10H₂O, CaSO₄ or a mixture of the three salts. 228 The concentration of the $CaSO_4$ brine was kept constant at saturation ($CaSO_4$ 0.01 mol/kg), whereas 229 NaCl and Na₂SO₄·10H₂O concentrations were increased during cycles, from 1.5% in weight during the first week, to 3% the second week and finally to 6% (NaCl 1.03 mol/kg; Na₂SO₄ 0.19 mol/kg) for the 230 231 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 room temperature and under low and high RH as explained before. 234

235 *3.3 Relative humidity cycles*

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

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

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

248 **4. Result**

Two kinds of results were obtained, mass evolution during cycles and visual observation of weathering. 249 250 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 due to the amount of different possibilities (3 stone types $2 RH^4$ brine composition = 24 samples). At 253 254 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 for 50°C) and finally the RH conditions (D, dry, for low humidity and W, wet, for high humidity 257 condition). Samples were weighed before and after imbibition or spray (vaporization). 258

259 *4.1 Drying and wetting cycles at room temperature*

The variation of weight with crystallization cycles can be observed in Fig. 3 during the twelve oneweek cycles that were performed. The traditional measure of mass increment over original mass was substituted by mass increment over volume of the sample and it was multiplied by 100. The reason for this choice is that with weight/weight calculations for samples of low density, as in this case Lutetian limestone with 1530 kg/m³, values are magnified with respect to samples with higher densities such as Caen, 2060 kg/m³, and Vernon 2000 kg/m³. Several observations are summarized below:

266 For all stones and salts, samples dried under low humidity conditions (room RH) had lower weight

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

than at low RH. For Caen Limestone and Vernon stone the variation is the opposite, higher for low RH

than for high RH.

For samples "dried" under wet conditions, samples imbibed by CaSO₄ brine show fluctuations higher
than samples wetted just by water. Under dry conditions these fluctuations were very small, except for
Lutetian stone.

For tests done with NaCl the only sample that shows a decrease in weight is the Vernon sample under
dry conditions. All the others show a slight mass increment. Na₂SO₄ crystallization cycles at high
humidity do not produce any apparent change on samples after the initial mass increase produced
during the first imbibition by capillarity. Under dry conditions Lutetian limestone showed a slight loss
of mass at the end and Caen and Vernon stones suffer clear weight decrease. The most affected sample
was Caen limestone. Cycles with CaSO₄ just produced an accumulation of gypsum on samples dried at
low RH, especially on the Lutetian limestone.

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



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

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 limestone showed efflorescences not uniformly distributed on the sample, they were mainly located in 314 315 the upper part of the sample and also concentrated on the flint concretion surfaces.

a) NaCl



- Fig. 4. Samples weathered by a) sodium chloride b) sodium sulphate and c) salt mixture at roomtemperature and low relative humidity conditions.
- 320

317

321 *4.2 Drying and wetting cycles at* 50°

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

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

It was also observed that samples wetted by NaCl did not show any mass decrease but mass continued to increase until the end of the test. This increase was more important on samples dried at high RH condition than on samples dried at low RH. Samples contaminated by sodium sulphate showed an initial mass increase smaller than samples tested with sodium chloride and after three one-week cycles started to lose mass. The most affected samples were Caen limestone but Lutetian samples revealed also an important beginning of mass loss. Samples tested with CaSO₄ did not show any significant change in weight.

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





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

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

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

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

Na₂SO₄



L50D





C50W

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

364

361

365 Comparing samples altered at 20°C and 50°C it can be observed that only weathering produced by 366 Na_2SO_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 at room temperature after four one-week cycles, only Caen samples under dry conditions presented 369 370 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

Lutetian samples tested at 20°C and 50°C can be explained by the low evaporation rate in this stone. 374

At 20°C after the drying period most of the solution was still in the samples whereas at 50°C the 375

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

4.3 Relative humidity cycles

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



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



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

390

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

weathered by salt mixture (Fig. 8). Fig. 9 shows the visual variation before and after the RH cycles for

samples dried at 50°C. RH cycles produced granular disaggregation in all samples weathered by pure

400 NaCl solution and the appearance of surface efflorencence. 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.



humidity cycles.

- 4.4 Salt mass variation
- In order to interpret damage, the salt content added to the samples during each cycle should be
- determined. Mass increment, after capillary imbibition and after spray was measured for this purpose.
- The evolution of mass increase during capillary imbibition cycles in samples tested at 20°C is given in
- Table 4.

414 Table 4

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

Stone and	Brine						Cycle					
conditions	composition	1	2	3	4	5	6	7	8	9	10	11
	NaCl	18.88	14.38	10.96	6.88	4.52	2.81	7.71	5.98	2.39	2.75	4.86
	CaSO4	18.74	2.92	3.24	2.01	1.45	1.42	2.81	2.47	0.69	1.10	0.61
LZOD	All	17.64	17.05	12.80	11.24	12.93	7.69	13.20	12.71	7.10	8.19	6.20
	Na2SO4	21.13	3.57	3.29	3.93	3.77	6.15	5.83	5.67	5.42	4.84	13.89
	NaCl	19.81	19.06	11.92	9.59	5.74	5.29	4.15	4.10	2.48	1.57	4.52
12014/	CaSO4	21.41	7.98	4.79	2.91	3.09	0.47	3.47	1.98	1.86	0.33	1.77
LZUVV	All	19.27	15.85	12.34	7.69	6.22	4.21	10.97	6.80	5.43	7.40	7.38
	Na2SO4	19.22	8.47	3.52	4.29		5.77	5.33	2.79	3.37	3.36	9.40
	NaCl	11.58	5.04	4.79	2.83	2.06	1.18	1.27	1.15	0.57	0.48	0.39
C20D	CaSO4	11.69	5.36	4.28	9.16	9.45	8.38	7.57	6.80	3.95	3.16	4.77
C20D	All	11.76	8.34	7.21	4.90	2.87	0.99	1.88	1.22	1.04	0.44	1.21
	Na2SO4	10.57	7.49	5.98	7.43	6.43	5.64	5.51	4.07	5.45	3.66	
	NaCl	11.86	11.65	10.68	8.49	7.33	6.56	6.27	4.62	3.18	2.57	2.89
C2014/	CaSO4	11.17	11.62	11.34	11.61	11.57	10.66	11.50	11.38	11.22	11.18	11.13
C20W	All	11.88	12.27	11.15	9.88	7.98	6.89	5.70	5.87	3.79	2.35	3.80
	Na2SO4	9.63	12.16	11.65	11.64	11.8	9.61	12.42	11.10	10.06	10.70	10.85
	NaCl	7.88	5.59	4.48	2.61	1.98	1.48	1.42	1.61	1.06	1.12	0.52
	CaSO4	6.69	6.06	6.69	7.44	7.50	7.81	7.56	7.51	7.66	7.27	8.05
V20D	All	4.48	6.80	4.73	3.9	2.39	0.67	1.52	1.75	1.43	0.80	2.31
	Na2SO4	7.60	8.23	7.39	8.12	7.86	8.39	8.24	6.90	8.16	5.80	9.20
	NaCl	4.59	8.14	7.57	6.53	6.26	6.41	7.53	5.87	5.22	4.24	5.26
1/2014/	CaSO4	6.21	7.65	7.14	7.14	7.05	6.87	7.24	7.16	7.50	7.50	7.29
V 20 VV	All	11.96	12.25	11.71	11.65	10.28	10.01	10.04	10.23	8.94	5.74	9.04
	Na2SO4	4.76	7.98	7.08	7.23	6.85	6.78	8.20	7.37	7.38	7.43	7.77

⁴¹⁶

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 (Na₂SO₄ and CaSO₄) 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

⁴¹⁷

426 constant. Sodium chloride probably inhibits capillary absorption more than sodium and calcium427 sulphates.

Mass gain in Caen limestone at room temperature decreased also with increasing number of cycles.
The depletion was more significant in samples dried at low RH as well as in samples impregnated with
NaCl solution at high and low RH conditions. At 50°C the behaviour was similar to that in Lutetian
samples with a mass gain almost constant for all samples that decreased after cycle 2 for samples
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 Salt Mass = $(\sum \Delta m(capillarity)) + n \times 4 \times \overline{\Delta m(vaporization)}$ (1)

442 where *Salt Mass* indicates the final total mass of salt, Δm (*capillarity*)*is* the mass increment during

443 capillarity, *n* the number of one week cycles, and $\overline{\Delta m(vaporization)}$ the mean mass increase during 444 spray.

		Lutetian	Caen	Vernon		Lutetian	Caen	Vernon		
RH	Salt	Roon	n tempera	ature	-	50°C				
D	NaCl	6.42	1.55	1.39	-	3.23	1.59	1.48		
D	Na_2SO_4	9.06	1.63	1.67		3.75	1.85	1.52		
D	$CaSO_4$	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_2SO_4	2.48	1.06	1.33		3.76	1.44	1.63		
W	$CaSO_4$	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		

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

449

Total mass gain after all cycles for samples wetted with solutions at equal concentration are listed in 450 Table 6. The Total mass column for mirabilite (Na₂SO₄ 10H₂O) represents mass gain without water

- 451
- 452 molecules.
- 453 Table 6.
- Total salt mass gain during crystallization cycles for samples dried at room temperature and 50°C. 454

Solution	Sample	Total mass (g)	Sample	Total mass (g)	Sample	Total mass (g)
NaCl	L20D	21.87	C20D	5.97	V20D	5.46
Na ₂ SO ₄ 10H ₂ O	L20D	11.54	C20D	3.87	V20D	4.06
CaSO ₄	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 ₂ SO ₄ 10H ₂ O	L20W	4.21	C20W	4.53	V20W	3.63
CaSO ₄	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 ₂ SO ₄ 10H ₂ O	L50D	3.68	C50D	1.96	V50D	1.56
$CaSO_4$	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 ₂ SO ₄ 10H ₂ O	L50W	3.62	C50W	1.79	V50W	1.31
CaSO ₄ All	L50W L50W	1.39 14.58	C50W C50W	0.74 6.44	V50W V50W	0.56 5.88

455

4.5 Salt volume model 456

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

corresponding to experimental cycles. The obtained results with ECOS RUNSALT are depicted in 460 Fig. 10 for each environmental condition. Drying corresponds to crystallization process after wetting 461 462 phases. Just after saturation it can 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 composition of salts without considering their hydration degree. For example changes occurring 464 around RH 77% in the Na₂SO₄ curve at room temperature correspond to mirabilite-thenardite 465 466 transitions. In the simulation of tests performed at 50°C two different environmental changes were 467 considered, drying and cooling. For tests done at room temperature no cooling period was necessary. To simulate what happen in a particular sample, the obtained amount of substances can be multiplied 468 by the total amount of salt present in this sample. Taking into account these results it seems that the 469 470 most important volume increases correspond to salt mixture under low RH conditions. The final composition of the precipitated salts given by the ECOS-RUNSALT model is Thenardite (~2.25cm³), 471 halite (~2 cm³) and Glauberite (Na₂SO₄·CaSO₄) (~0.75 cm³). X-ray qualitative mineralogical analysis 472 was performed at the end of the cycles on samples weathered at 50°C and dry conditions and only 473 474 single salts, halite, thenardite and gypsum, were found.



477 Fig. 10. ECOS RUNSALT simulations with the employed brines and during the period of change in478 environmental conditions.

4.6 Microscopic studies on weathered samples

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



- 490 Fig. 11. Scanning electron microscopy images of the surface of weathered samples at 50°C and under
- dry conditions: a) Vernon limestone V50D with NaCl, b) Caen limestone C50D with Na₂SO₄, c)
- 492 Lutetian limestone L50D with CaSO₄, d) Caen limestone C50D with salt mixture of NaCL, Na₂SO₄
- and $CaSO_4$. On the right the semi-quantitative element analysis of areas 1, 2 and 3 on d) image.





Det: BSE Date(m/d/y): 10/27/15 500 µn SEM M

C NaCl Date:27.10.2015 14:25:45 Image size:512 x 512 Mag:49,687349322264x HV:15,0kV





a)







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, Na₂SO₄ and CaSO₄. The element mappings obtained by X ray are given on the righthand side of 498 these figures.

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 CaSO₄ 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 surface of Lutetian and Vernon stones (Fig. 12c) although some salt was identified in the inner part. In 507 508 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 a) halite crystals covering the grain surface can be observed. Picture b) corresponds to sodium sulphate 512 crystal aggregates. Picture c) shows an aggregate of gypsum crystals in a pore. Pictures d) and e) 513

reflects a mixture of salts. No salt completely filling any pore was observed.



Fig. 13. Scanning electron microscopy images of polished cross sections of weathered samples at 50°C
and under dry conditions: a) Lutetian limestone V50D with NaCl, b) Lutetian limestone L50D with
Na₂SO₄, c) Lutetian limestone L50D with salt mixture of NaCl, Na₂SO₄ and CaSO₄, d) Caen limestone
C50D with salt mixture of NaCl, Na₂SO₄ and CaSO₄ e) Vernon limestone V50D with salt mixture of
NaCL, Na₂SO₄ and CaSO₄

515

522 **5.** Discussion

- 523 Degradation of porous stones is really a complex process depending not only on the nature of the salt
- 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
- 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
- solutions and more than during the crystallization cycles. Sawdy and Heritage (2007) stated that

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

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.

- 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.

			Crystallization	Relative
T (°C)	Brine	RH	Stone	Stone
20	NaCl	90	L20W	L20W
			C20W	C20W
			V20W	V20W
		45	L20D	L20D
			C20D	C20D
			V20D	V20D
	Na ₂ SO ₄ 10H ₂ 0	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
	NaCl	90	L50W	L50W
			C50W	C50W
			V50W	V50W
		5	L50D	L50D
50			C50D	C50D
			V50D	V50D
	Na ₂ SO ₄ 10H ₂ 0	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

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

553 The weathering pattern also change with brine. Efflorescences of sodium sulphate were concentrated

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

be seen on samples where Na₂SO₄ efflorescences under room temperature (slow evaporation) were

558 found on the upper surface of samples or following curved evaporation fronts.

The results show also that, whatever the salt solutions used in crystallization cycles, larger degradation
occurs in Caen and Vernon limestones than in Lutetian limestone. The only exception was Lutetian
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 $P = 2\sigma (1/r - 1/R)$ (2)

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

the crystallization pressure could be compared for the different stones. Tensile strength for the 575 576 different stones measured using Brazilian tests is 1.27 MPa for the Lutetian limestone, 2.35 MPa for Caen stone and 5.2 MPa for Vernon chalk. Estimated crystallization pressures, considering a mean σ 577 of 40 10⁻³ N/m, are 7 10⁻³ MPa for Lutetian, 100 10⁻³ MPa for Caen and 13.5 10⁻³ MPa for Vernon 578 stones. These values are smaller than the tensile strength and cannot explain the observed damage. To 579 580 have a crystallization pressure higher than the tensile strength, pore radius should be smaller than 581 0.08µm, 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 pressure differ by about 10x factor, which can explain, at least partially, the higher sensitivity of Caen 583 584 stone to salt weathering. The value of crystallization pressure estimated for Lutetian stone is the lowest 585 one. However, Lutetian stone was at 50°C more prone to salt weathering than Vernon stone. Other factors linked to its higher porosity (42%) and its lower tensile strength can explain this observation. 586 According to technical specifications uniaxial compression strength of Vernon stone varies between 587 588 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 0.12µm). This heterogeneity is probably caused by various flint

592 content that produces non-uniform weathering as was observed in the sample V20D.

Generally it can be said that cycles performed at low RH conditions produced more damage than those
at high RH. The only exceptions are samples weathered by sodium chloride at 50°C, in this case high
RH during drying induced more damage that low RH, especially in Lutetian samples.

596 Concerning the contrasting behaviour between room temperature and 50°C it is possible to state that

597 NaCl is more destructive at room temperature than at 50° C, and the opposite is true for Na₂SO₄ which

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

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
000	The obtained results commin previous studies concluding that offices composed of a mixture of
607	different salts, mainly NaCl and Na ₂ SO ₄ , 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_2SO_4 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

 $623 \qquad Na_2 SO_4, which can induce large errors.$

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635	
6 26	9 Deferrences
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