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Beatriz Menendez

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SCIENZE E MATERIALI DEL PATRIMONIO CULTURALE

## CULTURAL HERITAGE FROM POLLUTION TO CLIMATE CHANGE

Edited by  
**Roger-Alexandre Lefèvre and Cristina Sabbioni**

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## Salt Climatology applied to Built Cultural Heritage

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### Abstract

The concept of “salt climatology” has been introduced by Grossi *et al.* (2011) and deals with the knowledge of environmental parameters conditioning salt weathering of cultural (built) heritage. In this paper we compiled a review of the different parameters involved in salt weathering as well as the acting mechanisms. These parameters and mechanisms are well known but the way they act and their relative importance is still under discussion. We calculated the future variations of salt weathering for two cities located in NW of France, Rouen and Caen. This estimation is derived from the future climate data for both cities given by the Arpege Global Climate model of Météo-France. Finally we establish different “salt weathering areas” for France. These calculations are based on previous results for Rouen and Caen and data of 44 meteorological stations uniformly distributed in France. This data base was also provided by Météo-France.

### Résumé

Le terme “climatologie des sels” a été établi par Grossi *et al.* (2011) et concerne l'étude des paramètres météorologiques qui conditionnent l'altération du patrimoine bâti par les sels. Dans cet article nous passons en revue les différents paramètres et mécanismes qui interviennent dans la dégradation des pierres par les sels. Ces mécanismes et paramètres sont connus de longue date mais leur importance relative est encore discutée. Nous avons calculé la variation de la dégradation future par les sels au cours du siècle présent pour deux villes du NO de la France, Rouen et Caen. Nous avons comparé la dégradation par les sels calculée pour le passé avec celle calculée pour le futur à partir de données du modèle climatique Arpege de Météo-France. Les résultats obtenus nous ont permis d'établir des zones d'altération par les sels en France métropolitaine. Nous avons calculé cette dégradation à partir des données de 44 stations météorologiques distribuées uniformément en France. Ces données nous ont également été fournies par Météo-France.

**Key-words:** salt weathering, building stone, climate change, climate model.

### 1. Introduction

Scientists have shown their interest on built cultural heritage conservation from the beginning of 18<sup>th</sup> century. Salt crystallization is accepted to be one of the most important agents in stone weathering. Field observations of salt rock weathering on natural environments have been published by Darwin, 1839; Futterer, 1902; Walther, 1924.

In 1968, A. Kieslinger published an extensive bibliographic compilation about the main factors of building stones weathering. This review covers mainly the period between thirties and sixties and pointed out the main degradation factors accepted nowadays: humidity, salts dissolved in water, pollution, temperature changes, freezing, fire, biological organisms, mechanical stresses, and human activity. So, most of the parameters we will

study in this paper were already identified as stone weathering factors at the beginning of the 20<sup>th</sup> century.

Salt weathering in monumental stones has been described by Hirschwald, 1912; von Moos & de Quervain, 1948, Knetsch, 1952, Winkler, 1965, Kwaad, 1970. This last author pointed out the fact that salt crystals are present in the rock pores and exert a pressure on their walls, which can exceed the tensile strength of the rock. According to Correns, 1949, Barth *et al.*, 1960 and Louis 1968, Kwaad listed four causes of salt volume expansion:

- a) Crystallization of supersaturated solutions results in a mixture of crystals and solutions occupying a volume bigger than the original solution;
- b) Thermal expansion of crystallized salts;
- c) Adsorption of water to create hydrate salts;
- d) Crystal growth.

Salts in building stone come by capillary water or atmospheric pollution. The sources can be natural (soils, sea spray) or anthropogenic (fertilizer, de-icing salt, pollution, interactions between building materials) (Price, 1996; Ruedrich & Siegesmund, 2007). The most common cations in building stones are  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ , and the most common anions are  $\text{CO}_3^{2-}$ ,  $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ .

Salts in buildings are not uniformly distributed (Charola, 2000). On a wall salts crystallize at different heights depending on their solubility. It is generally accepted the distribution established by Arnold (1982) with four different zones: the first one close to the ground shows less damage, it is where the less soluble salts are found (gypsum and calcite); the second one shows the higher deterioration degree and it contains potassium nitrate as well as magnesium and sodium sulphates. The third one is the darker one with the most soluble salts like sodium nitrate and chloride; finally the fourth and upper one is the sound wall. Steiger *et al.* (1993) precisely characterized the distribution of salt on a northern façade on a building in Bavaria. They found that the maximum concentration of salts corresponds to the capillary rise height, and is located around 2-3m. This height will depend on rock characteristics, mainly on its pore size distribution that control capillarity properties.

Our planet has been subjected to thermal cycles all throughout its history. During the last 1000 years shorter cycles were observed within the overall cycle. Combined to these cycles is superimposed, in the last 100 years, the impact of human activity. The “Intergovernmental Panel on Climate Change” highlights an average increase of temperature during the last century. There is strong evidence that warming occurred during the past 50 years is due to human activity (Viles, 2002).

Climate change is a challenge for the scientific community as well as for the society, with a particular interest in areas such as agriculture, water, industry, energy, transport and health. While the effects of climate change on human health and ecosystems have been extensively studied, the effects on cultural heritage are not mentioned among the indicators that should

be considered to identify adaptation strategies and remediation options. This is particularly important when considering the cultural heritage as a non-renewable resource that must be preserved (Sabbioni *et al.*, 2004). For example, the European Environment Agency (EEA) report “*Climate change, impacts and vulnerability in Europe 2012. An indicator-based report*” does not consider cultural heritage among the socio-economic impacts nor in the vulnerability of cities and urban areas.

During the next hundreds of years, climate change must have important direct and indirect effects on the natural environment and materials, including the built heritage environment (Sabbioni *et al.*, 2006). Some weathering processes on buildings could be accelerated while others could be slowed down. This change in environmental conditions could involve new degradation processes/intensities and therefore different methods of conservation and restoration.

The 20th century showed a profound change in the nature of air pollution. The increase in the use of the automobile has had the effect of increasing the concentration of volatile organic compounds in urban air. At the same time the replacement of coal by gas and electricity had the opposite effect. The reduction of air pollution in large cities, even if it was originally as a health policy has had a beneficial effect on the rocks of construction (Brimblecombe *et al.*, 2006), in particular through the reduction of acid gases and production of gypsum (Brimblecombe, 2000).

## 2. Salt climatology concept

The term “building climatology” deals with concepts as comfort, and indoor environments and has been introduced in the seventies. In 1979, A. Sealey (the Commonwealth Association of Architects) published the “Introduction to Building Climatology”. Heritage climatology deals with the long term weathering of monuments. P. Brimblecombe in 2010 set down the basis of Heritage climatology, based on work done on the Noah’s Ark project. There are factors relating weather to damage. Weathering parameters such as mean temperature are not always the best to

explain damage induced on stones. In many cases cyclic phenomena will create more damage than stable parameters. For example in the damage induced by frost, the number of freeze-thaw cycles is much more important than the mean temperature. A constant very low temperature will induce less damage than a temperature around 0°C with daily changes between negative and positive temperatures. The heritage climatology parameters are different from the climate parameters.

A further step drove to the definition of “salt climatology” which was defined by Grossi *et al.* (2011) as an example of heritage climatology: the study of the climate parameters that affect monuments, materials and sites. In this paper they studied the effect of climate on salt damage in specific places of Western Europe: Caen, Rouen and Paris in France and Peninsular Spain.

### 3. Salt weathering: mechanisms and environmental factors

Two main mechanisms of salt weathering in building materials are traditionally considered: crystallization and phase transitions of hydrated salts. Kwaad in 1970 has established the base of the actual crystal growth theory including, crystal pressure, hydration pressure, etc.

Crystallization/dissolution processes occur under precise environmental conditions, temperature and relative humidity. For non-hydrated salt, as sodium chloride, these conditions are quite constant over the usual temperature range. For more complex systems, as sodium or magnesium sulphate, the phase diagram is more complex with salts presenting different number of water molecules stable at different temperature-relative humidity conditions.

It should not be neglected that rocks could have a different mechanical behaviour if they have salt filling their pore space. Differences in thermal expansion between rock forming minerals and salt can be very high (Winkler, 1994), so thermal cycles will have a much larger effect on rocks contaminated by salt than on salt-free rocks.

Crystallisation takes place in supersaturated solutions. Supersaturation can be reached by evaporation or by temperature decrease. In order

to generate a crystallisation pressure against the pore wall a supersaturated solution film between the crystal and the pore surface should be present (Taber, 1916). Different ways of calculating this crystallisation pressure can be found in the literature as described in Ruedrich and Siegesmund (2007).

Crystallisation mechanisms are influenced by the properties of the salt in solution, the properties of the crystals, the properties of the rock and the environmental conditions (Ruedrich & Siegesmund, 2007).

Some salts present different degrees of hydration, in this case hydration/dehydration reactions can generate hydration pressures. Even if the concept of hydration pressure was first introduced by Mortensen (1933) nowadays it is still questionable which process, crystallization or hydration, may cause higher damage in stones (Ruedrich & Siegesmund, 2007).

#### 3.1 Salt composition / atmospheric pollution

Most common salts found in buildings are carbonates, sulphates, chlorides and nitrates of sodium, magnesium, calcium, and potassium (Arnold, 1984). Some of these salts can be present in different hydrated degrees. The origin is different but we can consider that in cities most of the salt comes from interactions between building materials (stones, bricks, cements) and atmosphere, mainly pollution.

Pollution should be taken into account when studying decay processes. As it is well known the nature of pollutants has changed in the last decades with a decrease in acid air pollution but an increase of photochemical oxidants, carbon monoxide and fine particles from diesel use (Grossi *et al.* 2008). Cultrone *et al.* (2008) studied the sulfation of lime mortars and found that diesel particles enhanced the formation of magnesium sulphates, one of the most destructive salt (Goudie & Viles, 1997; Julinget *et al.*, 2004).

Even if the pollution has changed in the past and will change in the future, Monna *et al.* (2008) suggested that pollutants will stay on the stone surface for years. Atmospheric SO<sub>2</sub> has been greatly reduced during the past decades but we should consider that it can still influence stone

weathering during subsequent periods (Searle & Mitchell, 2006)

Mona *et al.* (2008) sampled surface material from 4 different façades of the Carnot College in the centre of Dijon (France). The Carnot College has been built in 1883 in a Bathonian/Callovianoolitic and oobioclastic limestone. They concluded that “lithogenic and anthropogenic elements have been deposited, and retained by surface of the façades to some extent”. “Building façades therefore conserve traces of atmospheric memory” even if surface particles are subjected to a competition between deposition/precipitation and cleaning by rain. This conclusion has a great importance in our studies. Even if no more (or little) SO<sub>2</sub> is present in atmosphere nowadays, sulphates (Na, Mg, Ca) are still found in monuments and continue to contribute to stone weathering. For example, gypsum present in the stone surface increases its roughness and facilitates the mechanical deposition of particles.

Another weathering factor related to air pollution, recession, will stay more or less constant during this century (Brimblecombe & Grossi, 2009) due to an average initial decrease of sulphur and nitrogen oxides (first quarter of century) followed by a constant concentration (Brimblecombe & Grossi, 2010).

Some climate models predict more extreme rains in the future and consequently a higher flood risk. During flood periods a big number of substances dissolved in the water can reach the base of buildings and rise to the wall by capillarity. A lot of salts are present not only in sea water but also in river water, which can get into the building stone and stay for long periods.

An important parameter controlling salt rock weathering is brine composition. Shahidzadeh-Bonn *et al.* (2010) explained why different salts do not have the same “damage capacity”. They realised experiments on saline solution of NaCl and Na<sub>2</sub>SO<sub>4</sub>. And found why sodium sulphate is much more destructive than sodium chloride. They studied the crystallisation/dissolution/recrystallisation processes of sodium sulphate and sodium chloride. For sodium sulphate first crystallisation occurs at a growth speed of 0.022µm/s, at a supersaturation of 0.018mol/l that generates a crystallization pressure of 0.12

MPa. In the second cycle speed crystallisation is much higher, growth speed is 0.26µm/s, at a supersaturation of 0.21 mol/l that generates a crystallization pressure of 1.4 MPa.

Sodium chloride crystallisation at first and second cycles follows the same patterns, with a supersaturation of 0.018mol/l producing a crystallization pressure of 0.3 MPa. This crystallisation pressure is much higher than those of the first cycle of sodium sulphate but much lower than the one generated during the next cycles. This experimental work explains the fact that crystallisation / dissolution / recrystallisation history of the stones has a great incidence on their susceptibility to damage.

Traditional salt crystallization tests have been described in the thirties (Schaffer *et al.*, 1929; Schaffer, 1932) and have progressed with time until actual normalized tests, even if for research purposes non standard tests are used. To compare the effect of brine temperature and concentration, Angeli *et al.*, 2010, compared artificial weathering processes in Lutetian limestone at different cooling temperatures. They used temperature cycles consisting in 2h of capillary imbibition in brines of different concentration followed by a 16h drying at 105°C and a cooling period of 6h at 5°C, 25°C and 50°C. In Table I we can observe the different experimental conditions.

In Fig. 1 we can observe where these solutions are located on the temperature-concentration phase diagram. All correspond to non saturated conditions. The authors observed that independently of the saturation conditions at 50°C no damage has been observed after 15 cycles. But at 5°C and 25°C at the end of the 15 cycles samples were very weathered. The weathering patterns change slightly at 5°C where the samples suffer superficial degradation (crumbling), but at 25°C degradation concentrates above the surface with contour scaling (Fig. 2).

Concentration	5°C	25°C	50°C
5%in weight	0.85	0.25	0.17
12% in weight		0.60	0.40
25% in weight			0.83

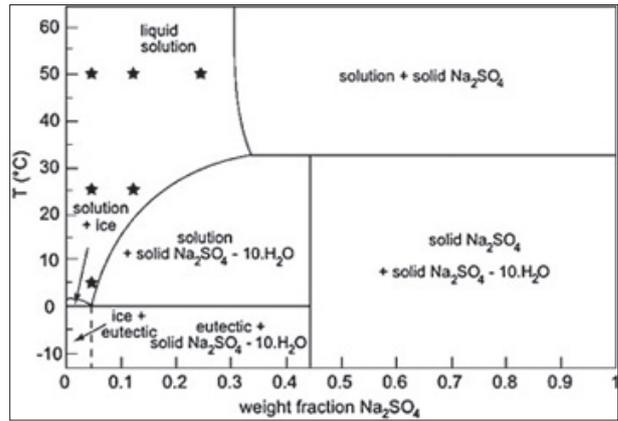
Tab. I - Details of the experimental conditions of artificial weathering of Lutetian limestone. Values correspond to the saturation in Na<sub>2</sub>SO<sub>4</sub> of brine (Angeli *et al.*, 2010).

Rodriguez-Navarro & Doehne (1999) demonstrated that under the same environmental conditions halite may show efflorescences and crystallization of thenardite takes place in the pore space.

In figure 3 we can see samples of Vernon limestone (chalk) artificially weathered by sodium chloride(a) and sodium sulphate (b). In both cases samples did not show any decay after several cycles but sample weathered by NaCl sample shows efflorescences.

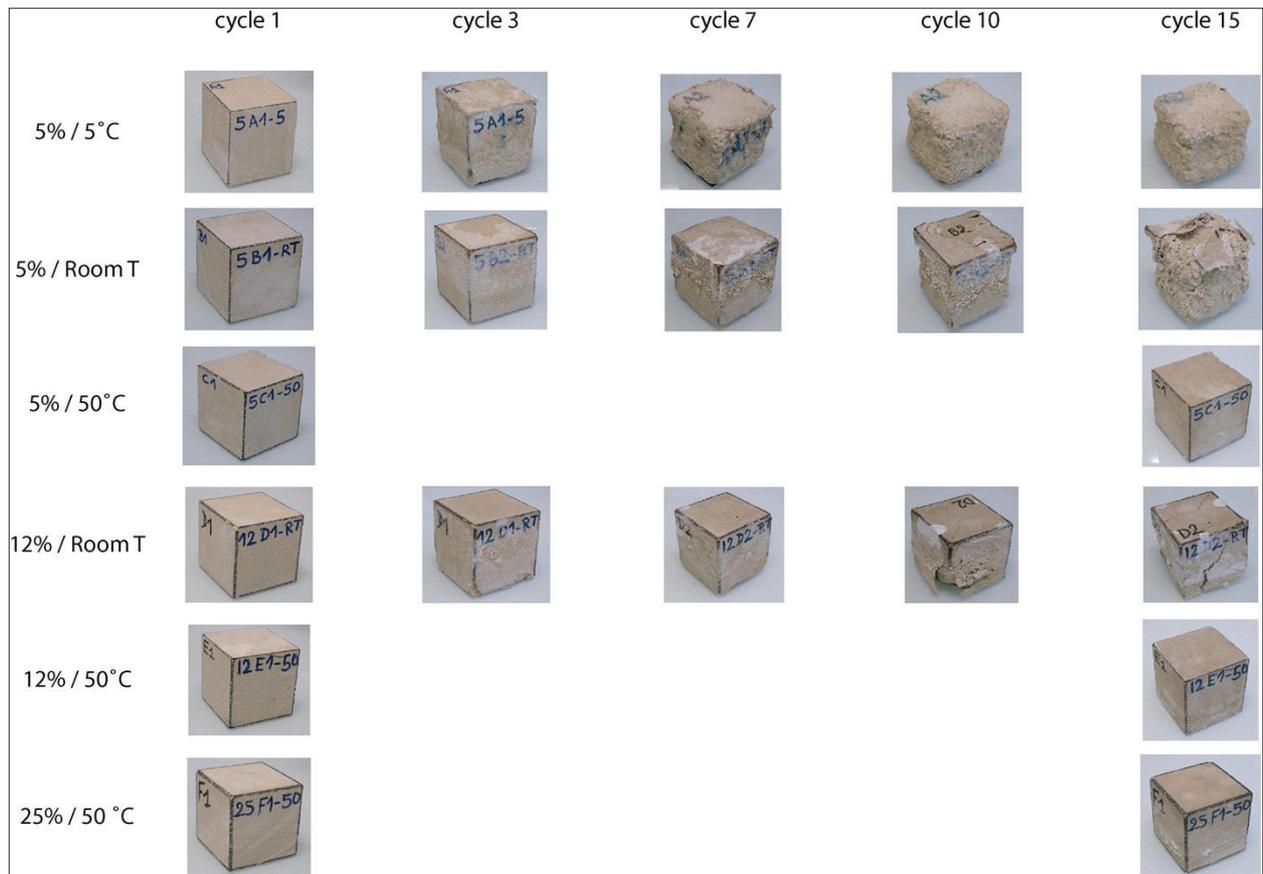
### 3.2 Effect of temperature

Concerning the climate parameters we will focus on temperature and moisture (water). The origin of materials decay can be generally related to variations in environmental conditions (Camuffo, 1983). It is important to consider the variation of climate parameters (temperature and relative humidity) between the surface and the inner part of stones.

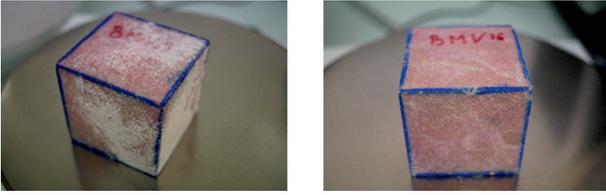


1. - Phase diagram of sodium sulphate. Stars represent the brine concentration and temperature in the salt crystallization tests (Angeli *et al.*, 2010).

Findlay (1911) found that during night, anhydrous salts (or lower hydrated) may transform into higher hydrated phases by absorption of water vapour from the atmosphere when the atmospheric aqueous vapour reaches the dissociation pressure of the hydrated salt. Some salts have transition temperatures over which only the anhydrous



2. - Different weathering degrees and patterns can be observed as a function of brine temperature and concentration. (Angeli *et al.*, 2010).



3. - Vernon chalk artificially weathered by (a) sodium chloride and (b) sodium sulphate.

phase is stable (Kwaad, 1970). External weather conditions have also an incidence on the indoor conditions and therefore on the degradation in the inner part of buildings. Martínez-Garrido *et al.* (2014) monitored the variation of the indoor temperature and relative humidity as well as the in-wall conditions as a function of external weather in the San Juan Bautista Church at Talama de Jarama (Madrid, Spain). They found that outdoor weathering conditions impact the temperature and relative humidity inside the building. Concerning the walls they found that solar radiation and rain are the factors that induce the more important changes.

It is also important to know how these parameters change with time. The rate of temperature change determines the evaporation time of salt solutions and so, where precipitation can take place (Smith *et al.*, 2005). For example, rapid heating can dry the surface layer more rapidly than moisture can migrate from the inner part to the surface and therefore salt will accumulate on the inner part of the rock producing scaling breakdown (Smith & McGreevy, 1988). Conversely, during slow drying solutions can migrate to the surface and salts precipitate close to the surface, producing surface flaking and granular disaggregation (Smith *et al.*, 1987). Heating, and associated relative humidity, variations may produce different weathering patterns and degrees in different façades orientation. For example Paradise (2002) found that east and west facing walls in Petra are more weathered than others. All these observations confirm the importance of microclimate conditions on the degradation of buildings. Gomez-Heras (2006) showed that in the case of sodium chloride, very common in coastal areas, the heat from solar radiation promotes the formation of sub-efflorescence, which led to a major presence of breakouts phenomena in sunny areas.

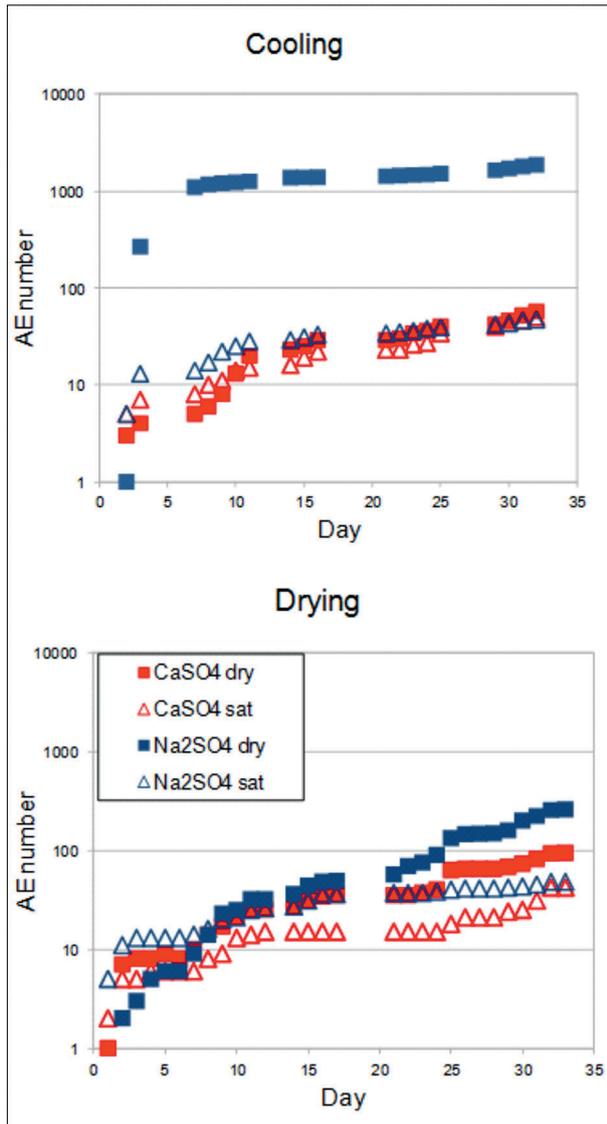
An important parameter controlling the building surface temperature is the rock colour,

especially albedo. Several authors measured the difference between air temperature and stone surface temperature. Warke & Smith (1998) measured air, surface and subsurface temperature in desert condition in four types of rocks with different albedo: Portland limestone (greyish white), Dunhouse sandstone (light gray/very pale brown), Antrim basalt (very dark grey) and Mourne granite (grey). They showed the results for two different temperature variations, one consisting in a relative slow temperature increase between 55°C and 65°C and the second in a rapid temperature decrease between 49°C and 30°C. During temperature increase, for light rocks the air temperature is higher than the surface temperature whereas for the dark ones the temperature at the surface is higher, around 8°C higher before the air temperature started to decrease. During temperature decrease the thermal inertia is different in each rock. In limestone temperature increase and decrease are slower than on the other rocks. The maximum temperature difference between surface rock and air is almost 0°C in the sandstone and limestone, around 6°C in the granite and 16°C in the basalt. In the sandstone and granite 3 hours after the temperature shut down, surface and air temperatures are quite close but in the basalt the difference is still of around 16°C. So we should take into account that considering air temperature (climate data) as rock temperature cannot be suitable as both temperatures can be, as we show, quite different depending mainly on the mineralogical composition of the rock.

### 3.3 Effect of relative humidity

Another important “climate” parameter controlling degradation of rocks is relative humidity (RH). Moisture reaches building stones by capillary absorption, condensation, rainwater infiltration or leaking pipes (Martínez-Garrido *et al.*, 2014).

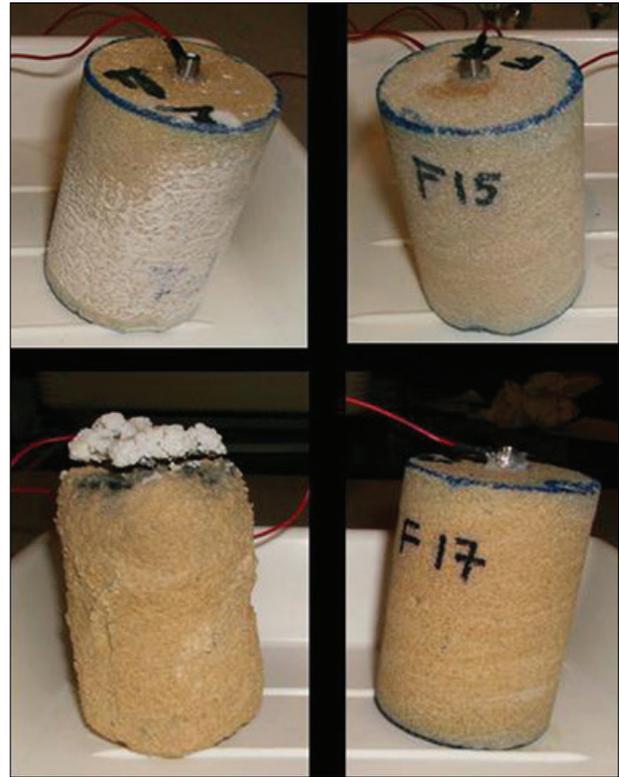
Following the methodology described in Menéndez & David (2012) we performed crystallisation cycles on a Lutetian limestone with two different brine compositions ( $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$ ) and under two different relative humidity conditions, 80% and 5%. In order to detect exactly when damage occurs we monitored the damage by the acoustic emission



4. - Cumulative number of acoustic emissions generated during the salt crystallisation tests.

(AE) technique. In this example we just take into account the number of acoustic emissions events generated during the crystallisation process. Each event can be assimilated to a “micro earthquake” generated in the sample by different phenomena: microcracking, crystallisation, grain motion, etc.

As shown in Fig. 4 the most important number of AE appears during the cooling period on the cycles with sodium sulphate under low relative humidity conditions. We should consider that for each cycle the drying period is much longer than the cooling one, 20 hours for drying and 2 hours for cooling. At the end of the tests (Fig.5) we can observe important differences between the samples. For example with calcium sulphate under



5. - Samples after weathering cycles with  $\text{CaSO}_4$  (up) and  $\text{Na}_2\text{SO}_4$  (bottom) under low relative humidity conditions (left) and high relative humidity (right).

low RH efflorescences appeared at the surface of the sample but not on the sample tested at high RH.

We can assume that under high RH precipitation occur in the inner part of the samples. For  $\text{Na}_2\text{SO}_4$  under high RH conditions no apparent damage is observed but under low RH conditions damage is important. This has been explained by the fact that under high RH conditions only the hydrated sodium sulphate crystallised with no hydration degree change during cycles. At low RH we will have hydration process during the cycles.

#### 4. Future salt weathering predictions

In order to estimate future weathering of rocks, several authors established different dose/response or damage functions. These functions express the quantitative relationship between meteorological parameters, pollutant concentration and material change. Bonazza *et al.* (2009) did a review of the proposed models and functions to calculate the surface recession of limestone under different environmental conditions. They pay

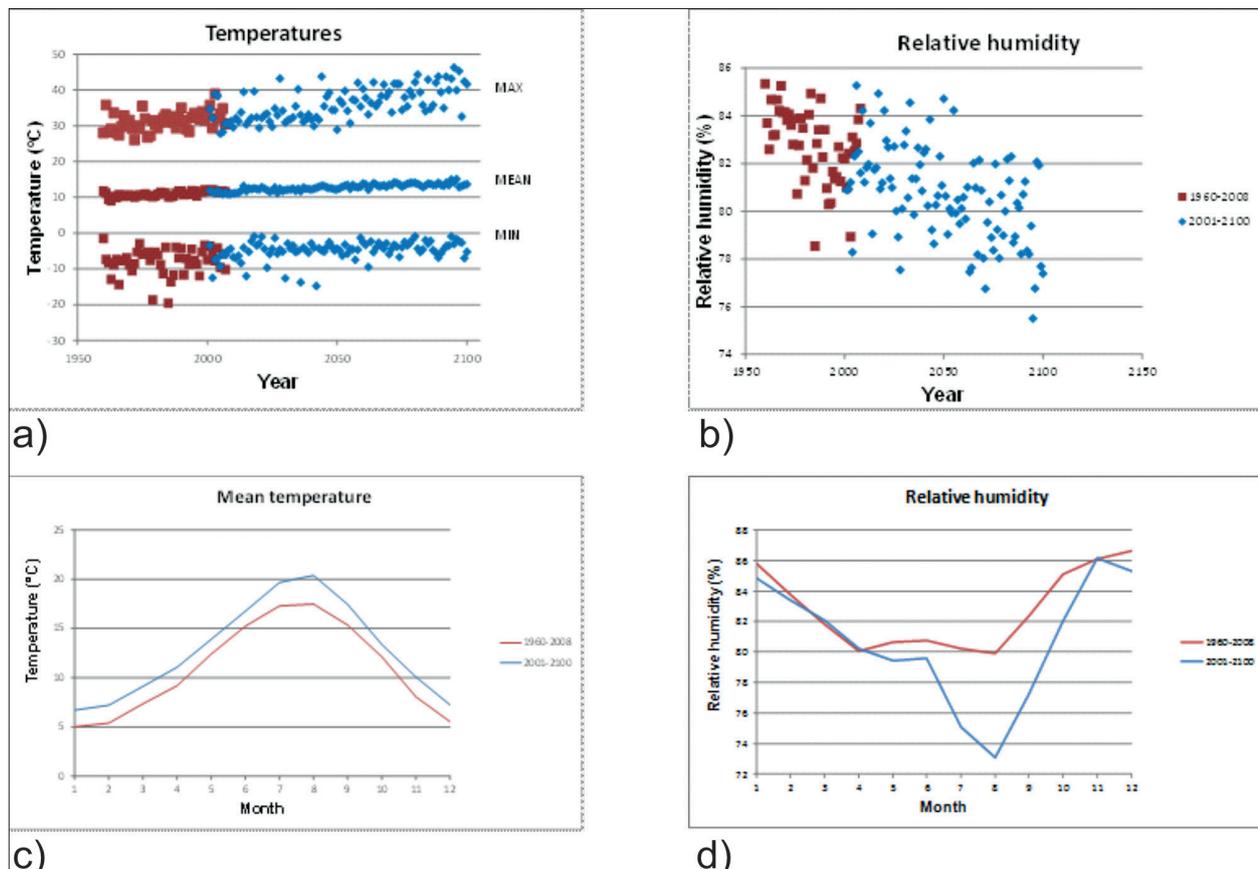
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special attention to the Lipfert function (Lipfert, 1989), which takes into account the effect of the dissolution of calcite by clean rain (Karst Effect), acid rain and dry deposition. Other reviewed functions are the dose-response function proposed by Tidblad *et al.* (1992, 1998), the method of Livingston (1992), the function of Webb *et al.* (1992), the dose-response function of Baedecker *et al.* (1992) and the dose-response function of Kucera *et al.* (2007) for multipollutant situation.

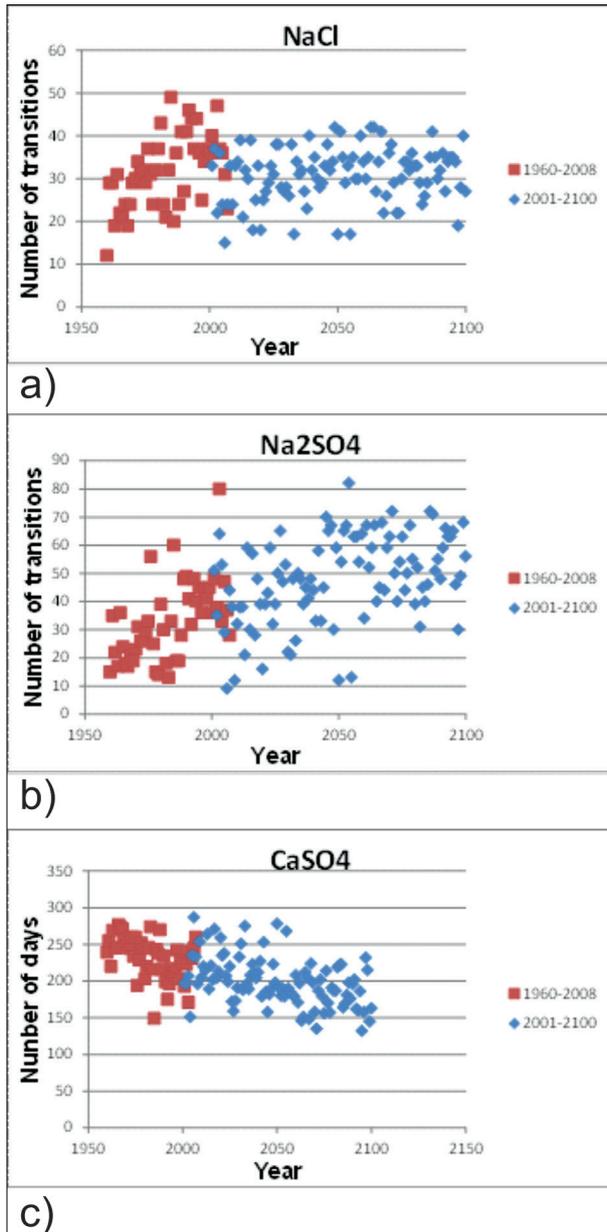
Grossi *et al.* (2008) compared three of these functions: Lipfert, ICP (Kucera *et al.*, 2007) or the MULTI-ASSESS (Kucera *et al.*, 2007). They calculated the monthly linear recession for the city of Oviedo (Northern Spain) for the period 2001-2005. Recession simulation for Prague, Paris and Oviedo were obtained for the period 1981-2099 based on Hadley HadCM3 climate model. As the functions used are empirical laws obtained during past pollution conditions, they concluded that more theoretical and robust laws should be established to extrapolate to low pollution conditions.

In this work we considered how salt weathering will vary in the future as a function of climate change in several places of the NW of France. We used future simulations provided by the Arpege model of Météo-France with the scenario A1B of IPCC. To illustrate the results obtained we present the simulations for Caen (France) and for three different salts: sodium chloride, sodium sulphate and calcium sulphate. We chose these salts based on mineralogical analysis performed on weathered material of the Saint Nicolas Church of Caen.

The methodology employed has been described in Grossi *et al.* (2011). We compare the estimated “weathering” for the past (1960-2008) to those obtained from climate model simulation from 2001 to 2100. For NaCl we estimate the number of times salt can crystallise from a solution. To do that we consider the number of times that daily relative humidity crosses the deliquescence value of 75.3%, from RH higher than 75.3% to RH lower than 75.3%, and for temperatures above 0°C.



6. - Evolution of maximum, average and minimum yearly (a) temperatures and (b) relative humidity for the selected area (Caen, France) between 2001 and 2100. Past data from 1960 to 2008 have been plotted for comparison; (c) Changes in seasonality of temperature and (d) relative humidity between 2001-2100 and 1968-2008.



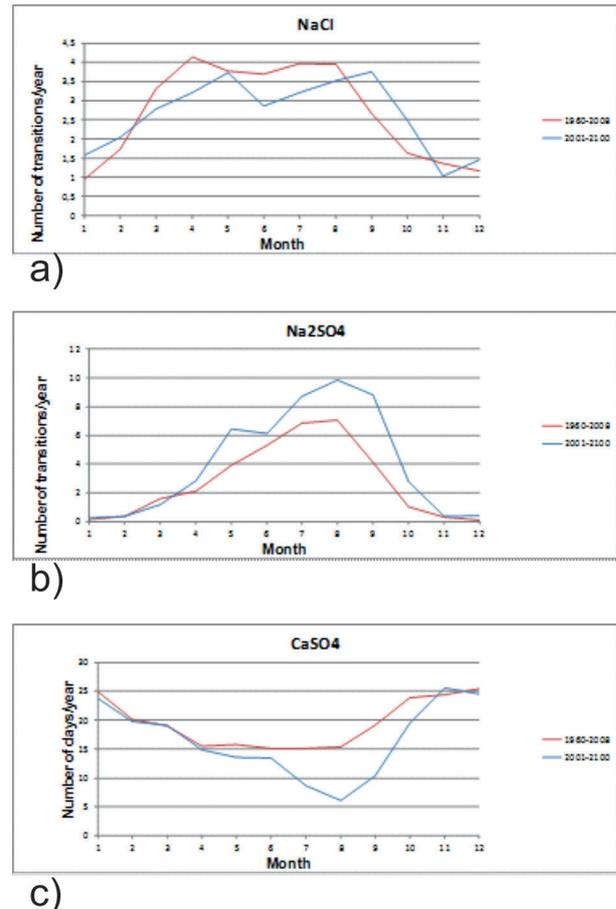
7. - Evolution of “salt weathering” with time. (a) Number of NaCl precipitation by decrease of the relative humidity. (b) Number of thenardite mirabilite transitions. (c) Number of days with relative humidity higher than 80% (for CaSO<sub>4</sub> crystallization).

To estimate the weathering produced by Na<sub>2</sub>SO<sub>4</sub> we count the number of times the equilibrium line between thenardite and mirabilite has been crossed. On the phase diagram temperature/relative humidity for Na<sub>2</sub>SO<sub>4</sub> we assume that the line between thenardite and mirabilite domains is a straightline for the temperature range between 0 and 35°. For every daily relative humidity value we calculate the corresponding equilibrium temperature. If this temperature is between the minimum and maximum temperature of this day

we consider that a thenardite/mirabilite transition has occurred. This estimator is different from the one used in Grossi *et al.* (2011).

Similar simulations for gypsum were performed using an estimator based on a paper of Lefèvre & Ausset (2002). These authors claimed that, when relative humidity is higher than 80%, gypsum will precipitate on the inner part of the rock inducing important damage, whereas it will precipitate on the surface when relative humidity is lower than 80%. Therefore the number of days with relative humidity higher than 80% has been considered as an estimator of gypsum weathering.

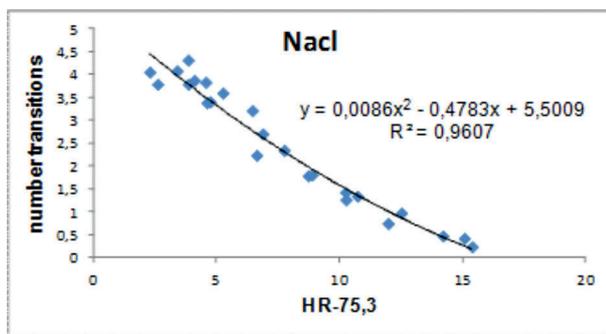
In Fig. 6 we can observe the evolution of temperature and relative humidity for the selected location according to the Arpege simulation. In fig. 6 (a) and (b) we plotted in blue the predicted future evolution of temperatures (maximum, mean and minimum) and relative humidity for the period 2000-2100 compared to the real data from 1960 to 2008, in red. In Fig.6 (c) and (d) we



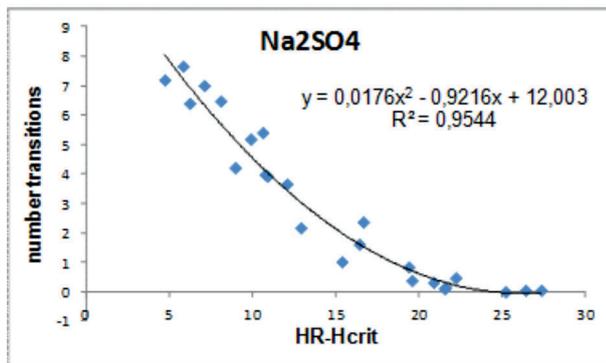
8. - Distribution of “salt weathering” during the year for the periods 1960-2008 and 2001-2100.

Class	Central object	NaCl (number of transitions)				Na <sub>2</sub> SO <sub>4</sub> (number of transitions)				CaSO <sub>4</sub> (number of days)			
		Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD
1	Loire	9,854	4,452	7,191	1,832	19,226	3,643	10,381	5,385	13,180	3,324	6,954	3,514
2	Maine et Loire	6,439	0,811	4,010	2,109	12,452	0,056	5,430	4,622	33,708	6,923	16,313	10,156
3	Calvados	3,160	0,991	2,198	0,808	5,105	0,338	2,426	1,830	31,972	17,866	23,496	5,251

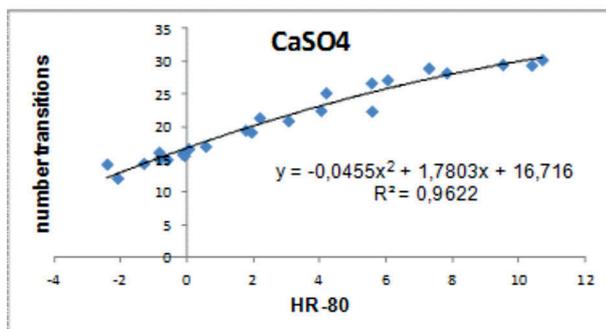
Tab. II. - Salt transitions data for the three barycentres resulting from the Ascending Hierarchical Classification method.



a)



b)



c)

9. - Average number of transitions per month calculated from observed data at Rouen and Caen versus the difference between relative humidity and equilibrium relative humidity for each salt system.

compared the variations of seasonality of mean temperature and relative humidity distribution between these two periods.

On these graphs we can observe that relative humidity data present much more dispersion than temperature data.

On figures 6 c and d we can see that changes in relative humidity seasonality are predicted to be more important than for temperature seasonality. A decrease in relative humidity is predicted for the months from April to November with a maximum drop of more than 6% during the summer. Temperature shows a uniform increase of 2°C except during the summer where this difference will be of 3°C.

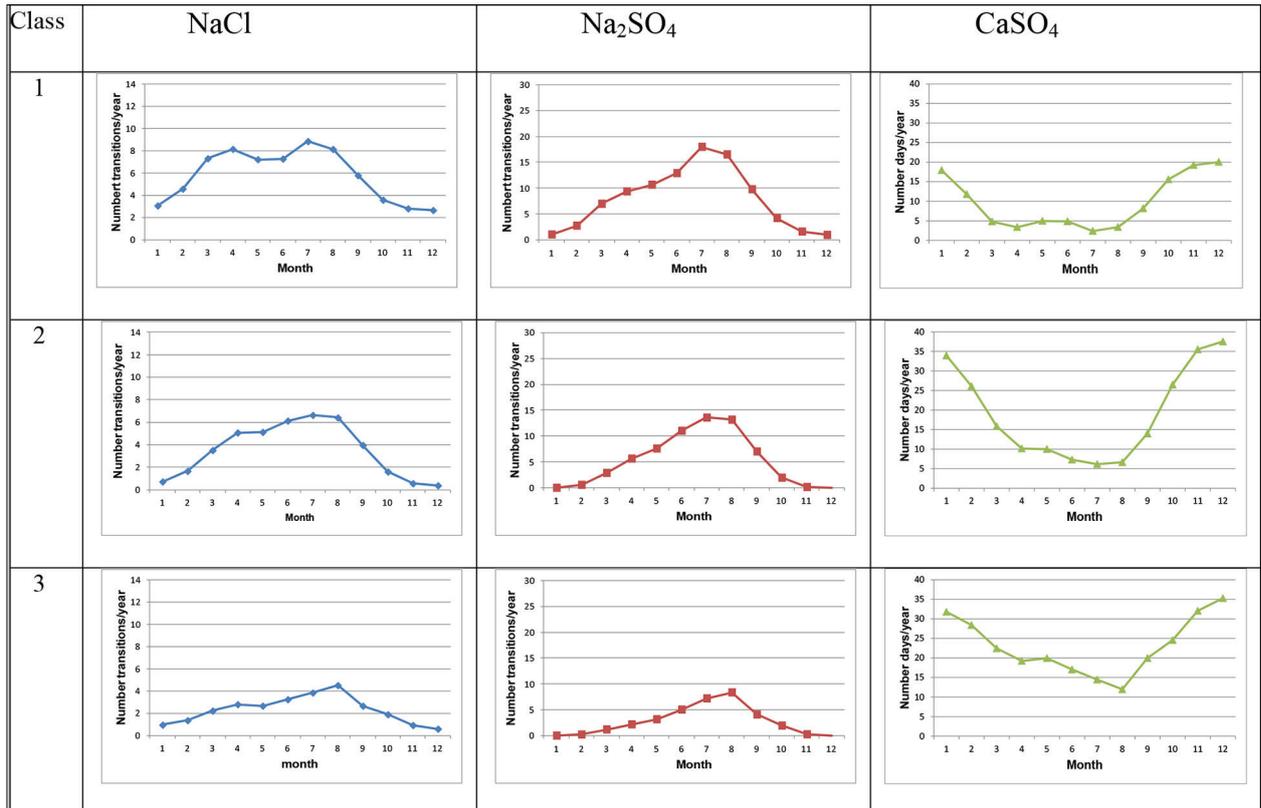
Based on this “climate” data we calculated the future salt weathering. Results are shown in figure 7.

As shown in Fig. 7 the model predicts that salt weathering by NaCl crystallization will remain constant in the future, whereas degradation by sodium sulphate is supposed to follow a slight increase and calcium sulphate will have less importance in the future.

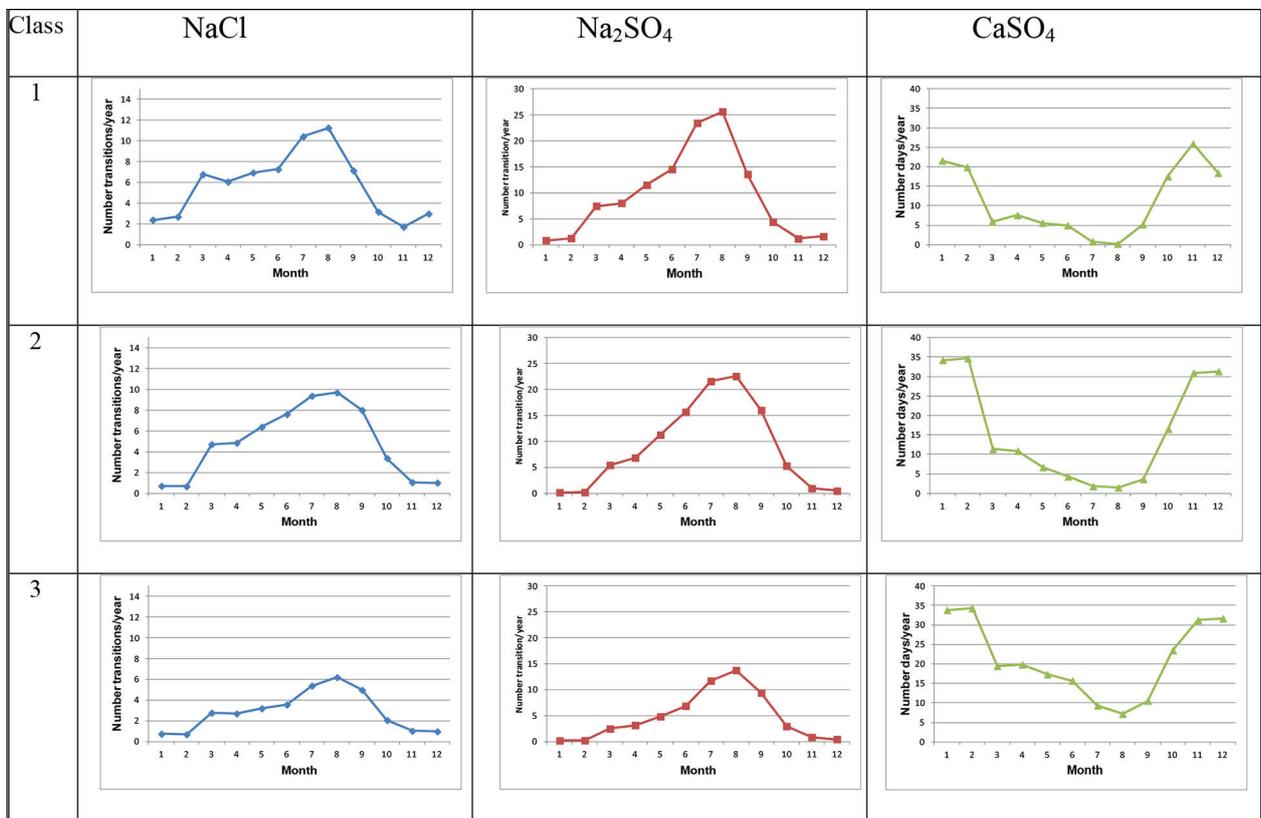
If we look at seasonality of salt weathering (fig. 8) we can observe that it changes more than annual values. We can observe that sodium chloride will be less aggressive during spring and summer but will increase its activity during autumn. Sodium sulphate transitions will be more frequent almost all over the year except the months of low temperatures, when the cross line between thenardite and mirabilite will be rarely reached. Concerning calcium sulphate we observe that the more important changes will occur during summer and beginning of autumn corresponding to an important decrease in relative humidity.

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10. - Monthly distribution of transitions/numbers of days for the three barycentre points obtained by the Ascending Hierarchical Classification process of the data from the 44 French meteorological stations.



11. - Number of transitions for the central points of the current classification during the periods 2071-2100.

### 5. Current salt climatology in France

We present here an example of a “salt climatology” study for a whole country, France. In order to establish salt weathering behaviour in France we use the methodology presented in Grossiet *al.* (2011). To obtain a “simple” way to estimate salt transitions in different locations, we plotted salt transitions calculated for the period 1960-2008 in Caen and Rouen data as a function of the difference between relative humidity and the equilibrium relative humidity for each salt. For sodium chloride the relative humidity equilibrium is equal to 75.3% and it is independent of temperature, in the range 0 to 40°C. For sodium sulphate we obtain the equilibrium relative humidity for each temperature from the phase diagram. For calcium sulphate we consider the 80% relative humidity threshold. On Fig. 9 we plot the monthly transitions or number of days of relative humidity higher than 80% as a function of the difference between monthly relative humidity and the equilibrium one. We obtain very high correlated relationships between these two parameters which can be fitted by second order polynomial functions.

Next we estimate the salt weathering in 44 locations uniformly distributed in France, applying the obtained equations to meteorological data of the 44 stations. All the data come from Météo-France stations from 1971 to 2000. The final goal was to classify the different salt weathering behaviours in the different regions. For each station we calculate the mean, max, min and standard deviation of the number of transitions ( $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ ) or the number of days ( $\text{CaSO}_4$ ) obtained from the polynomial functions. After that we apply an Ascending Hierarchical Classification (AHC) to the statistical data to classify the different locations. The goal of AHC is to build a partition of the population into homogeneous clusters (low variability within each cluster) which are different one from the other (large variability between different clusters).

In Table II we can see the barycentre points of the three obtained classes given by the AHC analysis of the transitions data. These barycentre points correspond to the French «départements» called «Loire», «Maine et Loire» and «Calvados». Fig.

10 gives the salt transition monthly distribution for each central object of each class. On fig. 11 we show the spatial distribution of these classes in France.

In the three classes  $\text{NaCl}$  transitions present a bimodal distribution with maximums in July and April for classes 1 and 2, and in August and April for class 3. The maximum number of salt transitions decreases from class 1 (~9), to class 3 (~3).

For  $\text{Na}_2\text{SO}_4$  we can observe that the maximum occurs in July for class 1, July-August for class 2 and August for class 3. As for  $\text{NaCl}$  the maximum number of transitions decreases from class 1 (~19) to class 3 (~5). The more important difference concerns the spring season: from class 1 to 3 the number of transitions in this period decreases significantly, the distributions are most centred on the summer time.

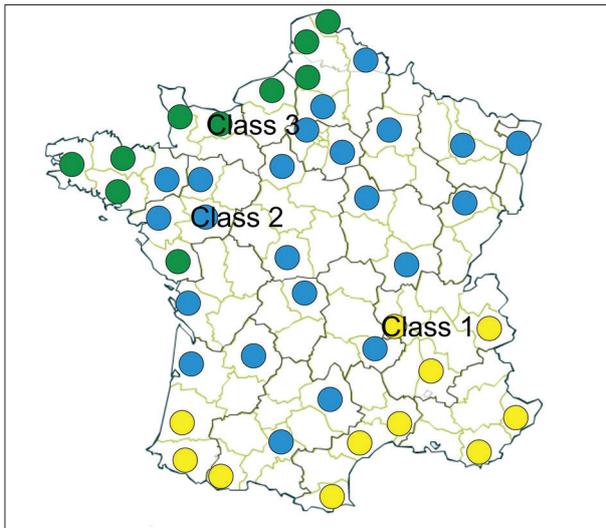
Concerning  $\text{CaSO}_4$  we can observe that the number of days with RH higher than 80% is less important in class 1 than for the others. In class 3 during more than half of the years the monthly number of days with  $\text{RH} > 80\%$  is higher than 20. In class 1 this number is never higher than 20 and in class 2 this number is less than 15 in more than half of the year.

In Fig. 11 we can see the expected salt weathering behaviour of these points during the period 2071-2100. To calculate these distributions we used the same procedure as for the current points: calculation of the number de transitions/number of days from the future data using the polynomial function. This data is also produced by the Arpege model and A1B IPCC scenario.

Fig. 12 shows the current spatial distribution of these classes in France. Class 1 corresponds to south-east regions with the higher average temperature (11.91°C, between 19.45°C in July-August and 5.21°C in January) and relative humidity (80.4%) intermediate between class 2 (74.8%) and 3 (80.05%).

Class 2 has the wider range in average temperatures, 19.5°C in July-August and 3.0°C in January and covers more area than the others, central region from South-West to North-East.

Class 3 presents the higher relative humidity and an average temperature range between



12. - Spatial distribution of “salt weathering classes” in France. The central point of each class corresponds to the location of the letter « C » of each Class.

17.35°C in July-August and 4.44°C in January. This class is present in the oceanic North-West of France, including the two specific points we studied: Rouen and Caen.

## 6. Conclusions

The term of salt climatology has been introduced by Grossi *et al.* (2011) based on previous concept of Cultural Heritage Climatology (Brimblecombe, 2010). In this paper we reviewed the different environmental parameters as well as salt composition and concentration governing salt weathering in rocks. We show that environmental conditions (mainly temperature and relative humidity) on stone building surface depend not only on meteorological parameters (mainly air temperature) but also on the characteristics of the rock, like colour. Some other parameters are important to consider like the dynamics of meteorological changes, i.e. temperature or relative humidity velocity changes can control where and how stone weathering occurs.

Wall orientation is also an important factor controlling rock weathering. Other parameters reviewed are brine composition, crystallization / dissolution cycles etc. We can conclude that salt weathering processes are very complex and in order to predict their future behaviour a deeper knowledge is necessary as shown by the large number of researchers working on this topic.

We apply the methodology presented by Grossi *et al.* (2001) to obtain a model of future salt weathering in two French cities (Caen and Rouen). The conclusion is that in these two cities salt weathering by sodium chloride will remain constant in the XXI<sup>st</sup> century, sodium sulphate weathering will slightly increase and degradation by calcium sulphate will decrease.

Based on an Ascending Hierarchical Classification (AHC) study of estimated salt weathering of 44 locations in France, three salt weathering types have been found and three different regions could be established.

Further work will be necessary to extrapolate the obtained results to future based on climate model data and on climate types.

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