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Study of the effects of salt crystallization on degradation of limestone rocks

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Abstract

Salt crystallization is widely recognized as a cause of deterioration of porous building materials. In particular, the crystallization pressure of salt crystals growing in confined pores is found to be the main cause for damage. The aim of this study is to better understand the degradation of porous rocks induced by salt crystallization and correlate such processes with the intrinsic characteristics of materials. With this intent, an experimental salt weathering simulation was carried out on two limestones widely used in the Baroque architecture of eastern Sicily. A systematic approach, including petrographic, porosimetric and colorimetric analyses, was used to evaluate the correlation among salt crystallization, microstructural and chromatic variations of limestones. Results showed a quite different resistance of the two limestones to salt damage, and this was found to be strongly dependent on their pore structure and textural characteristics.

Key words: Degradation; limestone; salt crystallization pressure; microstructure.

Introduction

Much of the world's architectural heritage is mainly made up of carbonate rocks. Unfortunately, such monuments are often affected by different alteration and degradation processes

mostly attributable to salt crystallization phenomena (e.g. La Russa et al., 2008; Belfiore et al., 2012), which is considered to be one of the most powerful weathering agents in porous materials, particularly limestone rocks. From a macroscopic viewpoint, such a kind of

degradation process produces extremely aggressive damages such as erosion, loss of material, flaking, exfoliation and, in some cases, even the complete disaggregation of the material.

When a salt-rich solution penetrates into the pore structure of a material, in specific supersaturating and thermodynamic conditions, the salt crystallization takes place and nucleation and growth of salt crystals within the pore spaces can induce alteration and degradation of the stone (Angeli et al., 2004; Benavente et al., 2007). The damage of the material depends on the shape of crystals, the supersaturation of the salt, the pore size and the force of repulsion between the salt and the walls of pores (Scherer, 2004). Porosity represents a crucial parameter in the salt crystallization process, since it regulates the fluid mobility within the material. The pressure exerted by salt crystals on the capillary wall, namely the linear pressure, is directly proportional to salt concentration and crystal size, and inversely proportional to the radius of the pore (Everett, 1961; Fitzner and Sneath, 1982).

Among the most aggressive salts, sodium sulphate (Na_2SO_4) plays a major role. Its formation, in many cases, is due to the reaction between sodium chloride, coming from the sea spray, and sulphur oxides mainly coming from anthropogenic activities. Although degradation mechanisms induced by sodium sulphate are extensively studied in literature, their full understanding is still ambiguous (Rodríguez-Navarro et al., 2000; Flatt, 2002; Tsui et al., 2003; Benavente et al., 2004; Scherer, 2004; Steiger, 2005).

Sodium sulphate can crystallize both as mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4), depending on the temperature and humidity conditions (Flatt, 2002; Benavente et al., 1999). Thenardite is the anhydrous phase which is reported to precipitate directly from solutions at temperatures above 32.4 °C. Below this temperature, the stable phase is mirabilite,

which rapidly dehydrates at relative humidity (RH) below 71% (20 °C) to form thenardite. The latter will rehydrate to mirabilite if the humidity rises over 71% (Rodríguez-Navarro et al., 2000). However, sodium sulphate may also undergo various polymorphic transitions as the temperature changes (Rodríguez-Navarro et al., 2000; Steiger and Asmussen, 2008). Several studies attribute the decay to the crystallization pressure of mirabilite, rather than thenardite (Benavente et al., 2004; Scherer, 2004; Flatt, 2002; Rodríguez-Navarro et al., 2000; Steiger, 2005). This damage depends on several factors, such as the type and quantity of salt in the stone, the characteristics of the pore network and the environmental conditions (Angeli et al., 2007).

Many studies in the literature have addressed the calculation of the crystallization pressure (Steiger, 2005; Benavente, 1999). However, only few papers focused on the relations between the crystallization pressures of salts (and the consequent degradation of the rock) and the intrinsic characteristics of stones. As an example, Benavente et al. (2007) carried out an experimental study on five different types of porous stones (whose origin was not specified), founding that the mechanical properties of rocks have a predominant statistical weight in the prediction of salt weathering, with a minor contribution of water transport and pore structure parameters.

This work aims at correlating the degradation processes due to the crystallization of sodium sulphate with the pore structure and textural features of two different limestones, which are widely used in the eastern Sicilian Baroque architecture (La Russa et al., 2008; Anania et al., 2012).

For this, an experimental salt weathering simulation was carried out, along with mercury intrusion porosimetry to observe the gradual variation of porosity of both materials. In addition, the examined stones have been characterised from a petrographic viewpoint

through a thin section analysis in order to define their mineralogical and textural characteristics. Finally, colorimetric measurements have been performed, since chromatic variations represent another important issue associated with salt crystallization.

Materials and methods

Limestones analysed here have been taken out from two different extraction sites in the province of Syracuse, an historical quarry, located in Cassibile (in the Noto Valley), and a recent quarry, located in Carlentini, near Noto (Figure 1). Both lithotypes have been widely used as building stone materials in the Baroque monuments of the Val di Noto (La Russa et al., 2008; Anania et al., 2012; Punturo et al., 2006), an area in south-eastern Sicily which has been recently included in the UNESCO's World Heritage List.

Examined materials consist of 19 samples from Cassibile and 19 from Carlentini. Samples chosen from both quarries were collected by taking into account their macroscopic homogeneity, in order to avoid the effects of textural heterogeneities (such as bioturbation, granulometric variability, etc...).

From a geological point of view, the first quarry belongs to the Palazzolo Formation (Serravallian-Tortonian), which consists of two members (Di Grande, 1982): (1) the lowermost Gaetani Member is formed of alternating decimetric yellowish calcareous and marly layers; (2) the uppermost Buscemi Member is constituted by decametric stratified calcarenites. The historical quarry of Cassibile belongs to the Buscemi Member. Samples taken out for the experimental study are homogeneously finely grained, whitish in colour and display a compact texture.

The second quarry belongs to the Carlentini Formation (Tortonian) (Grasso et al., 1982), consisting of volcanoclastic levels, mixed with

sedimentary carbonate material (mainly calcarenites) and subordinate basaltic lava flows. Biohermal levels with coral associations of Porites, *Tarbellastraea*, *Favites* and *Borelis melo melo*, also occur. Samples taken from this quarry are yellowish-white in colour and show a compacted and cemented texture.

Petrographic features of stones were analysed using a Zeiss Axiolab polarizing optical microscope. The physical characterization was performed using the following analytical methodologies:

a) salt crystallization tests were carried out for both lithotypes on specimens of cubic shape (4 cm), in order to experimentally study their resistance to decay and determine the forms of decay generated during tests. The procedure followed for salt crystallization is that described in the EN 12370 norm (EN 12370, 2001). Specifically, specimens underwent 15 cycles consisting of: i) 2 h of immersion in a supersaturated solution of sodium sulphate (14% w/w at 20 °C); ii) 16 h of drying in an oven, at 105 °C; iii) 6 h of cooling at room temperature.

The weight of each test sample was determined before measurements and after each cycle, and the resulting weight loss was determined for each lithotype.

b) the chromatic variations induced by salt crystallization were assessed through colorimetric tests, using a CM-2600d Konica Minolta spectrophotometer. Chromatic values were expressed in the CIE $L^*a^*b^*$ space, where L^* is the lightness/darkness coordinate, a^* the red/green coordinate ($+a^*$ indicating red and $-a^*$ green) and b^* the yellow/blue coordinate ($+b^*$ indicating yellow and $-b^*$ blue) (La Russa et al., 2011; Ruffolo et al., 2010; La Russa et al., 2012). The colour modification on the surface (ΔE) was calculated using the following relation: $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL^* , Δa^* and Δb^* represent the difference between the value of a specific chromatic coordinate after each aging cycle and the value in fresh sample.

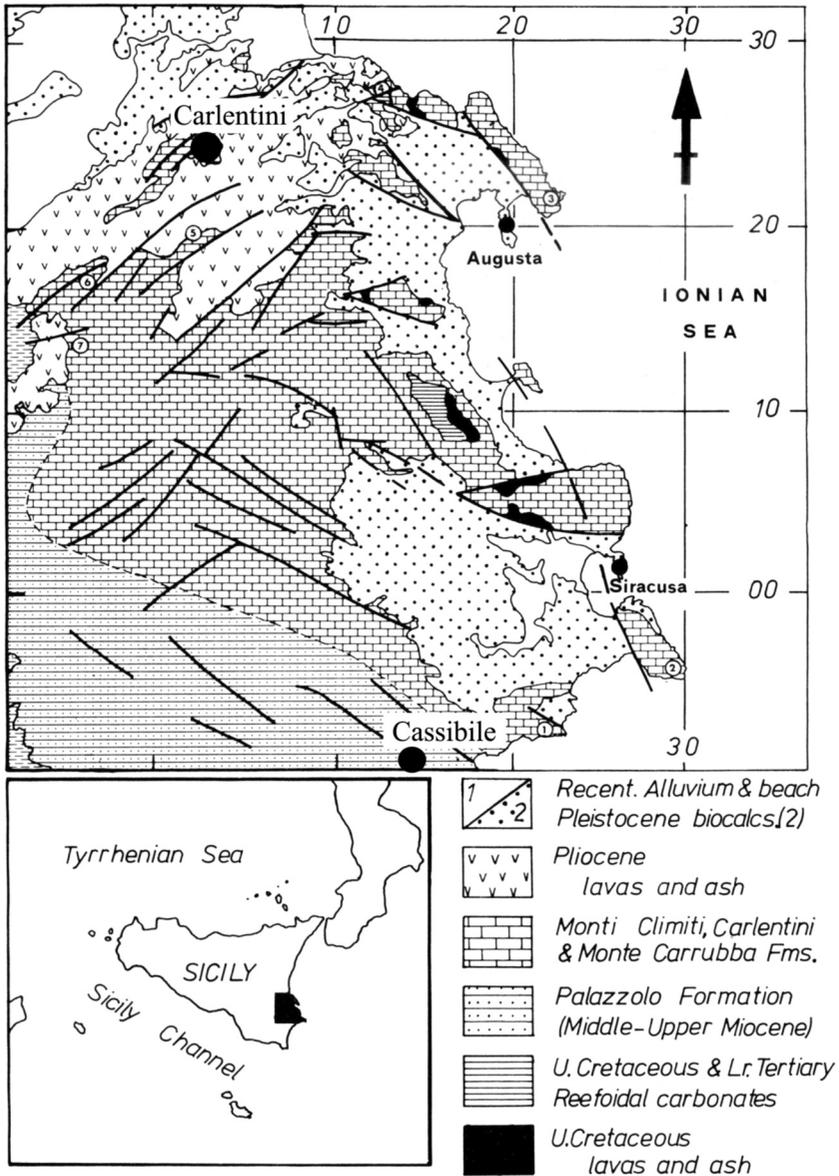


Figure 1. Geological sketch-map of south-eastern Sicily, from Grasso et al. (1982), showing the location of the two quarries in Cassibile and Carlentini.

According to Italian guidelines (NORMAL, 43/93), the ΔE value must be < 5 .

c) porosity and pore size distribution were

determined by mercury intrusion porosimeter (MIP) (Micromeritics Autopore IV), with maximum pressure of 400,000 kPa.

Measurements were performed on samples with the same weight (1.5 g) to standardize testing and minimize errors.

Results and discussion

Petrographic analysis

The microscopic analysis revealed some differences between stones from the two quarries. In particular, samples from the historical quarry of Cassibile have a mud-supported texture and an allochemical content of about 20-25% consisting of foraminifera, worms tube, fragments of echinoderms and peloids. A micritic matrix is present, while sparry cement (10%) occurs only within foraminifera. The intergranular porosity is about 20% (Figure 2a,

b). According to Folk (1962) and Dunham (1962), the stone can be classified as biomicrite and wackestone, respectively.

Conversely, the limestone from Carlentini, shows a grain-supported texture. The allochemical content of about 60% consists of foraminifera, fragments of algae, echinoderms and recrystallised shells. The matrix is sparitic. The intergranular porosity is about 30% (Figure 2c,d). According to Folk (1962) the stone can be classified as a biosparite, whilst according to Dunham (1962) it is a grainstone.

Salt crystallization test

Salt crystallization test is considered to be the best one for the characterisation of stone materials in terms of durability since it represents the main

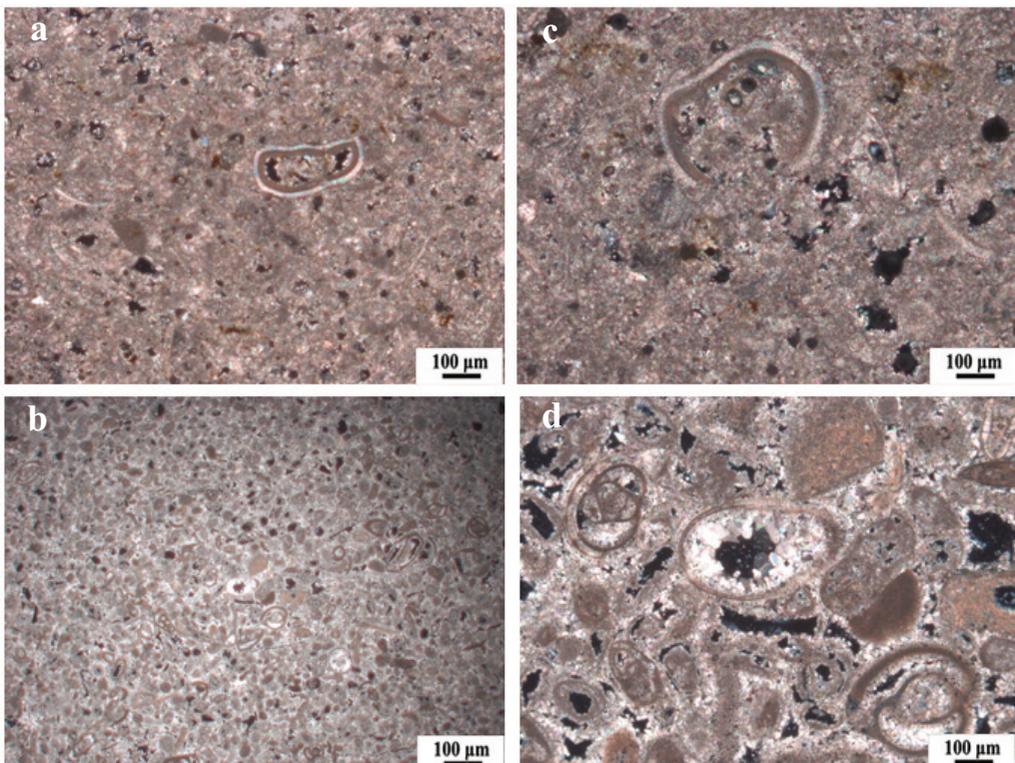


Figure 2. Photomicrographs (crossed polars light) representative of calcarenites from Cassibile (a,b) and Carlentini (c,d).

Table 1. Degradation forms observed in the Cassibile and Carlentini specimens during the fifteen aging cycles and weight loss at the end of test.

Number of cycle	Samples from Cassibile	Samples from Carlentini
1°	Superficial yellowing	Marked superficial yellowing
2°	No variation	
3°	Small superficial lesions	
4°	No variation	No variation
5°	No variation	
6°	Loss of material	
7°		
8°	Breakdown of material	Pulverulent appearance
9°		No variation
10°	No variation	Small loss of material
11°	No variation	
12°	Loss of shape and material	No variation
13°		
14°	No variation	Slight loss of shape
15°		
Final weight loss	-19,65%	-0.73%

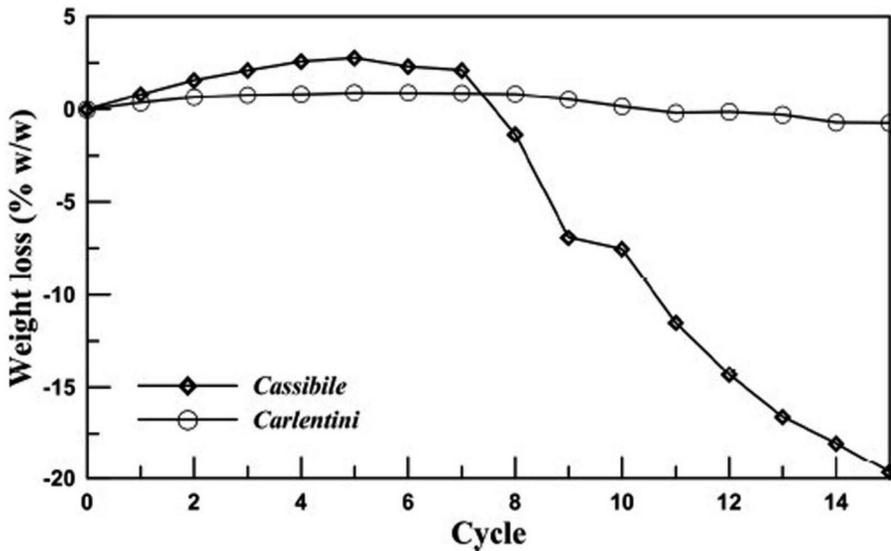


Figure 3. Weight loss of Cassibile and Carlentini stones during the fifteen aging cycles.

cause for its deterioration. The modifications suffered by the two investigated stones, along with their final weight loss, are listed in Table 1. The graph showing the trend of the weight loss in each cycle is shown in Figure 3.

Results display that the Cassibile calcarenite initially increases its weight (Figure 3), due to salt crystals inside the pore structure. It begins to degrade after the sixth cycle, showing loss of materials from the surface and several degradation forms such as cracks, rounding, erosion and flaking (Figure 4). At the end of the test, specimens show an average weight loss of about 20%.

Samples from Carlentini display a smaller increase in weight (Figure 3), thus meaning that a minor quantity of crystals formed within the pores. The stone does not undergo degradation and, only after the thirteenth cycle, small detachments and a surface yellowing are observed (Figure 4). The final average weight loss is less than 1%.

Accelerated aging tests show that the investigated calcarenites behave in a different

way, specifically the Carlentini limestone is more durable than the Cassibile one. By correlating the behaviour of stones under degrading condition with their textural characteristics, it is evident that the Cassibile stone tends to suffer more the salt crystallization because of its micritic matrix. On the contrary, the Carlentini stone, having a sparitic matrix, displays greater resistance. Therefore, textural features play a very important role in the context of degradation phenomena caused by the action of soluble salts. For this reason, a mineralogical-petrographic study of the material can roughly predict its behaviour.

In this respect, it must be underlined that in this work we have not taken into consideration the textural heterogeneities existing within each lithotype, which certainly would produce additional degradation effects related to salt crystallization. However, this choice does not affect the obtained results.

Colorimetric analysis

Colorimetric measures were performed to assess colour variations of the surface of

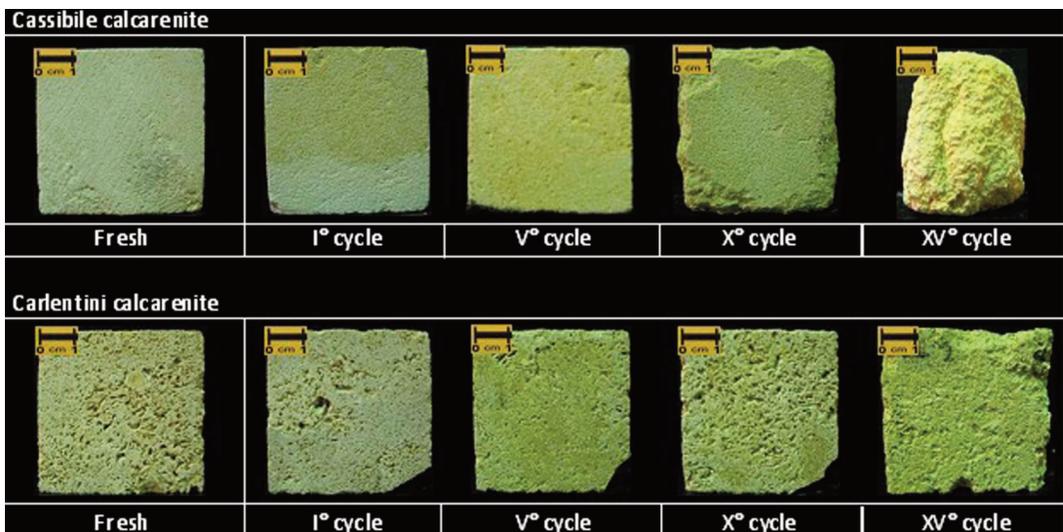


Figure 4. Degradation of Cassibile and Carlentini specimens during the most representative aging cycles.

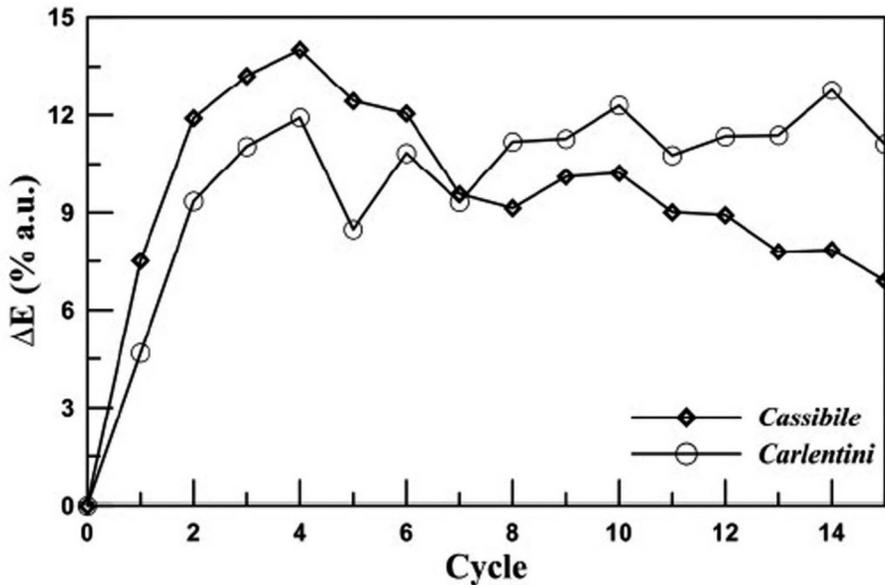


Figure 5. ΔE trends in Cassibile and Carlentini specimens.

specimens subjected to crystallization cycles. The results, shown in Figure 5, are reported in terms of ΔE values.

Both lithotypes show a dramatic increase of ΔE values until the fourth cycle. Such chromatic alterations can be macroscopically described as a yellowing and darkening of surfaces. This is due to the salt crystallization in proximity of surfaces that causes a “wetting effect”, since it produces a smoother surface similar to a water film. After the fourth cycle, under the same environmental conditions (light, humidity, ventilation, etc.), each stone behaves in a different way. In the case of the Cassibile stone, a decrease of ΔE values was observed up to the fifteenth cycle. This is due to the loss of material from the surface that leads to the formation of a new surface that is less affected by colour alteration. As regards the Carlentini limestone, ΔE values keep roughly constant, even if, after the fourth cycle, these seem to be affected by a greater noise. This can be probably ascribed to a

chromatic heterogeneity and non-planarity of the degraded surfaces. Obtained results suggest that chromatic alterations often detected on stone materials from buildings belonging to the eastern Sicilian Baroque (Belfiore et al., 2010), can be also attributable to salt crystallization.

Porosimetric analysis and crystallization pressure

Porosimetric analyses performed on both lithotypes, taking into account pores ranging from 0.003 μm to 50 μm in size, revealed a porosity of 18% for the Cassibile calcarenite and 16% for the Carlentini one. Pore size distributions were also calculated and reported in Figure 6. The Carlentini stone shows a higher amount of small pores ranging from 0,01 μm and 0.1 μm . Conversely, in the range 0.2 μm - 10 μm , the Cassibile calcarenite have the higher porosity. Pore size distribution measurements were repeated after each aging cycle in order to investigate modifications in the pore structures due to crystallization process. Of course, being

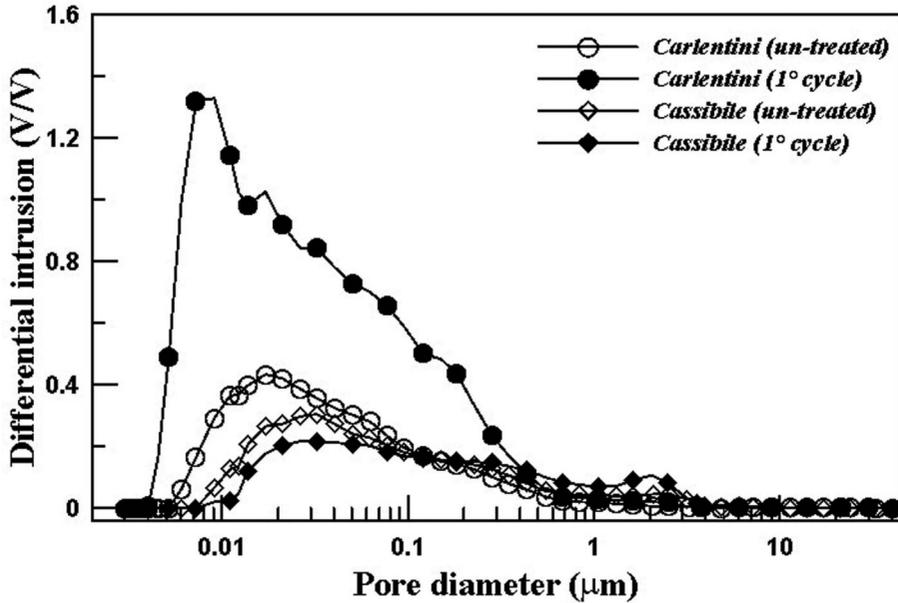


Figure 6. Pore size distribution in Cassibile and Carlentini specimens.

mercury intrusion porosimetry a destructive technique, measurements after each cycle were carried out on a single specimen and the salt crystallization test continued on the other ones. Results are summarized in Table 2.

As can be observed in Figure 6, the two lithotypes behave in a slightly different way. At the first cycle, the Cassibile stone shows a dramatic decrease in porosity, since salt crystals start occupying the pores. On the contrary, the Carlentini limestone displays an increase of porosity at the first cycle.

This can be due to the fact that this latter lithotype has a macroporosity, so once crystals have been grown into large pores, they can generate smaller pores that falls into the measured range. An alternative explanation is related to cracks and inaccessible pores. Some pores are unexplorable since they are not connected to the external surface, but salt crystallization could generate cracks within the material that create new pores and also

connections between blind pores and open pore structure. From the second cycle up to the last one, in both lithotypes a decrease of porosity is observed, because of the salt crystals that almost totally fill the stone cavities.

Pore size distribution data themselves are scarcely correlable with degradation trends. For this reason, a calculation of the crystallization pressure has been performed using pore sizes data. Within our system, samples suffer two types of pressure: 1) *hydration pressure*, due to the hydration of thenardite (already in pores) that becomes mirabilite when samples are put in a saturated solution (Hime et al., 2001; Thaulow and Sahu, 2004); 2) *crystallization pressure or linear pressure*, due to the crystallization of mirabilite, occurring when samples are picked up from the water (Everett, 1961; Fitzner and Snelthage, 1982). However, as shown by Steiger (2005), the supersaturation is the driving force in both cases, so the two types of pressures can be described by a single crystallization pressure equation.

Table 2. Mercury intrusion amounts [Vol (mL/g)] in the two lithotypes at each aging cycle.

Pore radius range (μm)	50-10	10-5	5-1	1-0.5	0.5-0.1	0.1-0.05	0.05-0.01	0.01-0.003
Cassibile specimens								
un-treated	0.0015	0.0039	0.0091	0.0192	0.0057	0.0043	0.0043	0.0001
1° cycle	0.0014	0.0037	0.0772	0.0144	0.0216	0.0048	0.0027	0.0000
2° cycle	0.0253	0.0558	0.0557	0.0092	0.0144	0.0030	0.0022	0.0000
3° cycle	0.0112	0.0720	0.0524	0.0114	0.0170	0.0039	0.0022	0.0000
4° cycle	0.0268	0.0517	0.0355	0.0081	0.0136	0.0038	0.0025	0.0000
5° cycle	0.0080	0.0627	0.0348	0.0079	0.0125	0.0033	0.0022	0.0000
6° cycle	0.0173	0.0636	0.0514	0.0120	0.0184	0.0043	0.0022	0.0037
7° cycle	0.0120	0.0999	0.0573	0.0096	0.0137	0.0033	0.0024	0.0000
8° cycle	0.0116	0.0638	0.0445	0.0092	0.0128	0.0029	0.0014	0.0000
9° cycle	0.0134	0.0908	0.0580	0.0108	0.0153	0.0034	0.0020	0.0000
10° cycle	0.0125	0.0673	0.0288	0.0073	0.0131	0.0038	0.0025	0.0000
11° cycle	0.0107	0.0505	0.0417	0.0093	0.0148	0.0041	0.0027	0.0001
12° cycle	0.0113	0.0735	0.0369	0.0115	0.0173	0.0036	0.0017	0.0000
13° cycle	0.0113	0.0721	0.0437	0.0097	0.0141	0.0033	0.0020	0.0000
14° cycle	0.0154	0.0656	0.0393	0.0088	0.0134	0.0034	0.0023	0.0000
15° cycle	0.0099	0.0528	0.0431	0.0107	0.0178	0.0042	0.0024	0.0000
Carlentini specimens								
un-treated	0.0174	0.0078	0.0051	0.0180	0.0072	0.0065	0.0065	0.0006
1° cycle	0.0139	0.0068	0.0196	0.0082	0.0445	0.0200	0.0153	0.0033
2° cycle	0.0142	0.0092	0.0196	0.0048	0.0161	0.0083	0.0069	0.0008
3° cycle	0.0191	0.0110	0.0118	0.0054	0.0145	0.0062	0.0042	0.0001
4° cycle	0.0211	0.0081	0.0089	0.0061	0.0145	0.0075	0.0066	0.0005
5° cycle	0.0159	0.0105	0.0106	0.0047	0.0115	0.0065	0.0060	0.0001
6° cycle	0.0270	0.0098	0.0077	0.0040	0.0146	0.0076	0.0066	0.0002
7° cycle	0.0110	0.0079	0.0087	0.0042	0.0166	0.0077	0.0058	0.0005
8° cycle	0.0141	0.0067	0.0076	0.0032	0.0168	0.0082	0.0063	0.0005
9° cycle	0.0123	0.0075	0.0095	0.0049	0.0144	0.0080	0.0075	0.0004
10° cycle	0.0162	0.0107	0.0120	0.0051	0.0142	0.0047	0.0038	0.0002
11° cycle	0.0211	0.0098	0.0111	0.0069	0.0191	0.0059	0.0044	0.0002
12° cycle	0.0189	0.0096	0.0096	0.0044	0.0100	0.0049	0.0046	0.0004
13° cycle	0.0147	0.0073	0.0093	0.0042	0.0090	0.0052	0.0048	0.0003
14° cycle	0.0123	0.0062	0.0083	0.0037	0.0117	0.0076	0.0077	0.0003
15° cycle	0.0170	0.0096	0.0100	0.0047	0.0156	0.0069	0.0052	0.0002

The equation for calculating the crystallization pressure was developed from a thermodynamic model proposed by Wellman and Wilson (Wellman and Wilson, 1968; Arnold and Zehnder, 1989). The model predicts that crystallization will originate in larger pores, as observed by Arnold and Zehnder, and that porous materials with larger capillaries connected to smaller ones are the most susceptible to damage (Arnold and Zehnder, 1989). The pressure that builds up between two such connected pores, once crystallization takes place, is given by the equation proposed, assuming spherical geometry, by Everett (1961): $\Delta P = 2\gamma(1/r - 1/R)$, where ΔP = crystallization pressure (dyne/cm²); γ = crystal-solution surface tension (dyne/cm); r = smaller pore radius (cm); R = larger pore radius. The calculation of theoretical crystallization pressures in the porous network of “Cassibile” and “Carlentini” limestones was carried out by using a surface tension of 80 dyne/cm, as suggested by Fitzner and Snethlage (1982), which corresponds to the surface tension of halite crystals, supposed to be suitable for our system. The calculation has

been done following the method employed by Rossi-Manaresi and Tucci (1991). For this aim, the pores < 10 microns were grouped according to radii (expressed in micron) into seven classes in the following ranges: class I ($r < 0.01$); class II, $0.01 < r < 0.05$; class III, $0.05 < r < 0.1$; class IV, $0.1 < r < 0.5$; class V, $0.5 < r < 1$; class VI, $1 < r < 5$; class VII, $5 < r < 10$). The median radii of pore classes I to VII are: 0.005, 0.03, 0.075, 0.3, 0.75, 3, and 7.5 respectively. To calculate the effective pressure that can arise in the stones, it is necessary to consider the volume percent of the pores of each class V_r which should be related to the volume percent of coarse pores V_R . Multiplying the factor V_r/V_R for the theoretical pressure of each class permits calculation of the effective pressure value, which is the sum of the effective pressure of each pore class. In Figure 7, the values of crystallization pressure as function of aging cycles have been reported for both stones. At the second cycle, both curves reach their maximum, after that a dramatic decrease of pressure occurs. A relative maximum can be also observed at the seventh cycle for the Cassibile

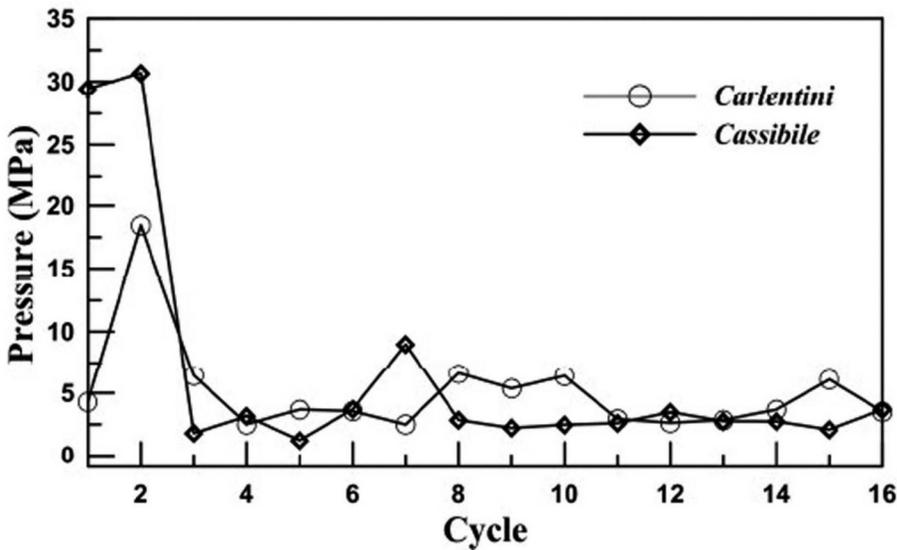


Figure 7. Trend of crystallization pressure in Cassibile and Carlentini specimens during the aging cycle.

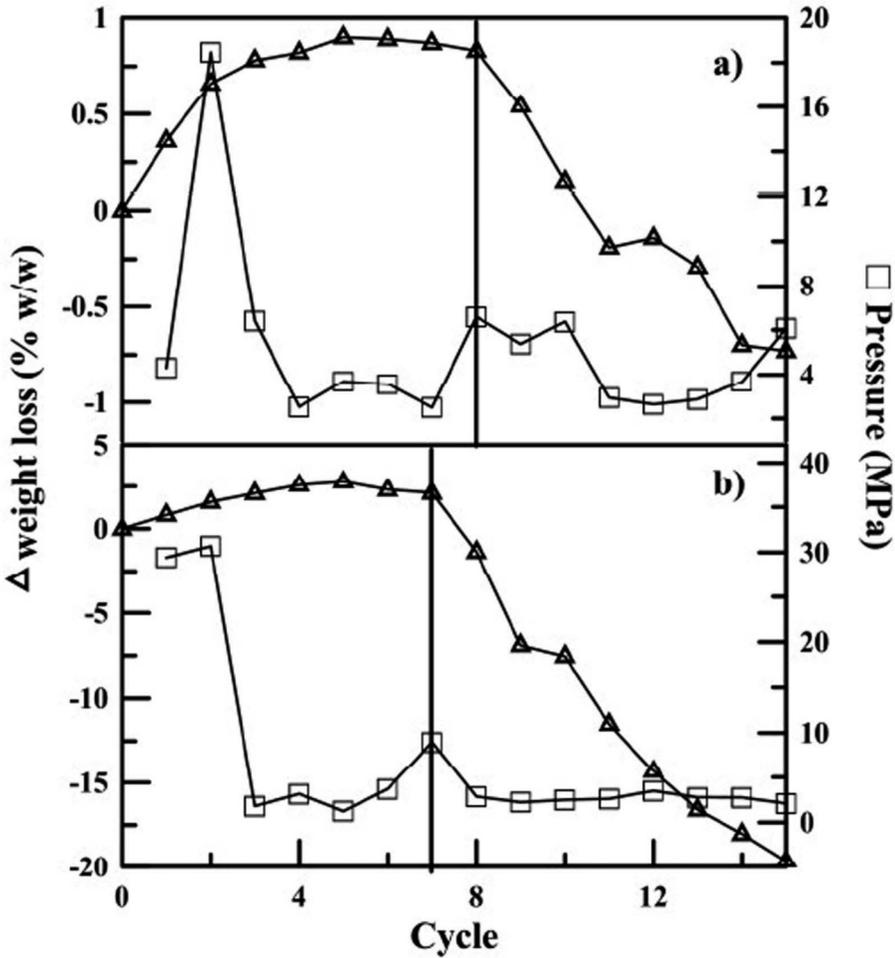


Figure 8. Comparison between weight loss and crystallization pressure in a) Carlentini and b) Cassibile specimens.

stone and at the eighth cycle for Carlentini. In order to deeply understand the correlation between stone decay and crystallization process, weight loss and crystallization pressure trends have been plotted together in Figure 8. It is worth noting that at the maximum of linear pressure do not correspond any weight loss, thus meaning that both limestones are still resistant to those pressures at the second cycle. After the

maximum, there is a sort of steady state since pressure does not increase and stones do not suffer any increase of stress. When in both materials a pressure enhancement takes place, an evident decay occurs and weights starts decreasing (Cassibile stone from the 7th cycle, Carlentini from the 8th).

Peak values of linear pressure are higher for the Cassibile specimens, this is in accordance

with the behaviour of this stone with respect to decay test. Its poor resistance to salt crystallization can be ascribed not only to textural features but also to an higher crystallization pressure.

Conclusions

In this work, a deeper knowledge of calcareous stone degradation due to salt crystallization, has been achieved. A comparative study between two different limestones widely used as building materials in the Baroque architecture of eastern Sicily, has been conducted through salt crystallization tests, petrographic and porosimetric analyses and colorimetric measurements. The latter have been carried out through the wetting of specimens in a sodium sulphate solution and their consequent drying in order to let crystals form within the stone pores. The test was repeated fifteen times, as prescribed in the EN 12370 norm (EN 12370, 2001).

From the results obtained, a correlation between stone degradation and textural features was found. In particular, referring to the two local stones (Cassibile and Carlentini), a sparitic matrix seems to confer to the stone a greater resistance to crystallization pressure. Moreover, salt precipitation within the pore structure of stone leads to a chromatic alteration of surfaces. This is due to the formation of crystals in proximity of surface that causes a “wetting effect” and consequently it results to be darkened and yellowed. This means that colour alteration often affecting the Sicilian Baroque buildings, can be caused not only by biological colonisation and/or organic protective coatings but also by salt crystallization.

In addition, for these lithotypes, an evident relationship between decay and pore structure was also found through the calculation of the crystallization pressure from the data of pore size distribution. Obtained results suggest that the higher is the pressure of crystallization and the

smaller is the pore size, the greater is the stone decay.

The pressure was calculated after each aging cycle in order to follow its evolution while the crystallization took place. The pressure trend in both the studied stones shows a maximum value which is reached after few aging cycles, however an evident stone decay takes place only in correspondence of a second maximum that occurs at different values for the two lithotypes. This reveals a precise correlation between the two lithotypes pore structure and their degradation.

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