**12th International Congress on the Deterioration and Conservation of Stone**
**Columbia University, New York, 2012**

# BIOPROTECTIVE ROLE OF LICHENS ON OOLITIC LIMESTONE BUILDINGS

Nicolas Concha-Lozano[1], Jacques Pages[2], Gisel de Billerbeck[3],
Pierre Gaudon[1] and Dominique Lafon[1]

[1] *CMGD, Ecole des Mines d'Alès, 6 avenue de Clavières, 30319 Alès, France*
[2] *Mousses et lichens du Haut-Languedoc, Hameau-La-Gineste, 34610 Rosis, France*
[3] *Laboratoire Elios, 2, rue Crébillon, 30900 Nîmes, France*

## Abstract

Some monuments of the central city of Nîmes (France) are well preserved while others are severely degraded despite of their similar environmental conditions. The main objective of this study is to further understand the weathering paths divergences, focusing particularly on the bioprotective role of lichens.

This study presents characterizations of weathering forms of the same oolitic limestone from four quarries and eight monuments exposed on various environmental conditions focusing on the waterproofing effect of endolithic organic matter. The *Bois des Lens* oolitic limestone was analyzed by capillarity coefficient through weathered and unweathered sides, gypsum content and porous network morphology by epoxy resin moulding.

The observations of weathering forms on old quarries show that lichens colonization can modify and fill the superficial porous network with a dense network of lichenised fungal hyphae. Capillary coefficient measurement on natural and on calcined samples showed that endolithic organic matter can waterproof the stone and could act as a sulphate contamination barrier. Similar endolithic organic layer due to ancient lichens growth are found on some antique monuments of the central city of Nîmes and could explain their well preserved state, unlike decayed 19th century churches that were never colonized by lichens.



**Keywords:** stone, durability, bioprotection, lichens, patina, capillary, gypsum

## 1. Introduction

This study focuses on a recurring debate about the development of patinas and their role in the protection or acceleration of buildings deterioration. It is commonly accepted that weathered forms - or patinas - depend on environmental factors around the exposed surfaces, such as water and aerosols exposure. Paradoxically, in the central city of Nîmes some monuments built with the same oolitic limestone are well preserved while others are severely degraded despite of their similar environmental conditions. Two types of weathering are observed. On one hand, several monuments (e.g. nineteenth century churches) are remarkably damaged, suffering blistering, yellowing and granular disintegration. On the other hand, monuments even much older (e.g. the roman temple *Maison Carrée*) and located in the same neighbourhood, do not exhibit such severe degradations. The main objective of this study is to further understand these observed weathering paths divergences, focusing particularly on the bioprotective role of lichens. For this, microstructure, composition and water transfer properties of patinas were studied on Bois des Lens oolitic limestone samples collected on 12 different sites. In this study, the patina is defined as the layer affected by irreversible aging that cannot be removed by conventional cleaning processes such as laser or sandblasting.

Decrease of erosion rate due to protective microorganism interface between the stone and its environment is an example of the bioprotection concept. According to Carter [Carter 2005], bioprotection is a little know-earth surface processes in comparison with the vast literature on lichen biodeterioration. Although deterioration mechanisms by lichens are well known [Warscheid 2000], it is unclear whether the weathering rate would be lower without them, especially in a polluted urban environment. Recent field studies gave evidence of the protective effect of lichens [Garcia-Vallès 1998] highlighting that biodeterioration is slower than physicochemical process. The main bioprotection mechanism is often called “umbrella effect” illustrating that lichens thallus forms a barrier layer that reduces the amount of runoff water in contact with stones [Corenblit 2011], but also protects the surface from wind erosion and reduces thermoclastic damaging due to intermittent solar radiation. This study focuses on a second type of bioprotection mechanism, due to the presence of organic matter entrapped beneath the surface of the stone, even after complete removal of epilithic biological colonization by cleaning.

## 2. The bois des Lens stone

Bois des Lens stone is a white and fine-grained oolitic limestone commonly used for building and sculpture over twenty centuries in southern France. Its exploitation and use as a building stone started in about the 4th BC century and its dissemination in the antic architecture extends over a large part of French Mediterranean coast [Bessac 1996].

This Early Cretaceous sedimentary rock is extracted from massive outcrops that allow blocs size up to several meters. At the macroscopic scale the stone has a smooth feel, bright uniform color and invisible bedding. Due to its isotropic mechanical properties the stone is appreciated for ornamental architecture and sculpture. Its relatively high porosity (13-17 %) does not allow a glossy polish but a fine softened surface. The peculiarity of this stone is that its patina extends up to several millimeters in depth, which is the cause of a great diversity of appearance in terms of color and texture after aging.

## 3. Physicochemical and biological characterisation

As the stone is composed of almost pure calcium carbonate, a moulding of porosity was performed by resin impregnation and calcite crystals dissolution. Dried samples were impregnated with epoxy resin under vacuum (around $10^{-2}$ Pa). After resin polymerization, samples were finely polished and then immersed in a 30 % HCl solution. Once the dissolution reaction was completed, the samples were extensively washed in pure water and then dried in open air. Total dissolution of calcite was confirmed by EDX calcium quantification performed on moulded samples. Gypsum content (wt %) was estimated from electric conductivity of unsaturated solution of powdered first 4 mm patinas in deionized water using a calibration curve. Lichen genus was identified by binocular microscopy on hymenial layer extracted from mature fungal fructification. Fruiting bodies were extracted from patinas using a pin and then cut in half by a razor blade. The presence or not of the waterprofing endolithic hyphae network was also observed by scanning electron microscopy.

## 4. Water transfer properties

Tested samples were cut into cuboids with one weathered side. Two samples were sandblasted (quartz sand under 4 bar pressure) in order to remove the superficial biological colonization (on sample RD-2, Table 1) or any traces of lime whitewash that could be applied during previous restoration work (on sample MC1-2). Capillary coefficients were measured four times for each sample with deionised water: first on weathered and unweathered faces and then after calcination on both sides. Calcination was performed in an oven at 500 °C for 20 min in order to remove the intraporous organic matter. Standard capillary measurement protocols (e.g. EN 1925:1999) were not suitable for measurement through thin stratified materials like patinas (<1 mm) due to the fact that contact between the sample and the free water must be precisely controlled to prevent absorption of water through the unweathered sample sides. So, an automatic monitoring soaked volume apparatus was used (KSV INSTRUMENT LPR 902) whose scheme is shown in Figure 1. Capillarity coefficient C [$g.m^{-2}.s^{-0.5}$] was calculated using:

$$C = \frac{V_{t_1} - V_{t_0}}{S.\sqrt[2]{t_1 - t_0}} \quad (1)$$

With $V_t$ the volume soaked at the time *t* through the surface *S*. Imbibitions duration was 30 min with an acquisition frequency of 1 Hz. Sample were dried in an oven at 60 °C for 12 h before each capillarity measurement. To reach a comparable initial saturation index, calcinated samples were previously immersed in water and dried under the same conditions than non calcinated samples. A waterproofing index $W_{INDEX}$ (%) can be calculated in function of the capillary coefficients of the unweathered $C_U$ and weathered $C_W$ sides:

$$W_{INDEX} = \frac{C_U - C_W}{C_U} \times 100 \quad (2)$$

An index close to 100, characterizes a highly impermeable patina, while an index close to 0 means no waterproofing effect. A waterproofing index of 0 was assigned to deteriorated patinas since their low cohesion cannot provide any protective effect.

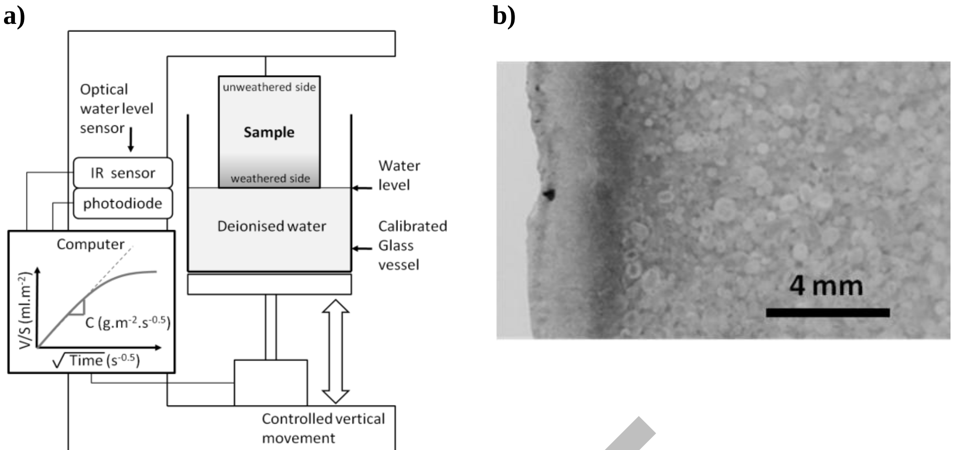


**Figure 1**. a) Scheme of the used automatic monitoring soaked volume for capillarity measurement. Here the sample is positioned for the weathered side capillary measurement. b) Microphotograph showing a colonised patina on sample MC1 (Roman temple Maison Carrée).

## 5. Results and Discussion

According to the waterproofing index (Table 1) the samples can be divided in two categories. On one hand, the patinas having low waterproofing index (< 60 %) with high gypsum content up to several centimetres deep, associated with blistering, disintegration, and yellowing. On the other hand, the patinas having high waterproofing index and containing endolithic organic matter such as MC1. These patinas do not present severe deterioration and some samples are not covered by a superficial biologic colonization.

The Maison Carrée is a characteristic example of a well preserved building. Its patina shows a low erosion rate and a good mechanical cohesion. The weathered form is composed of several layers beneath the stone surface (Figure 1b). The deepest layer located from 4 to 1 mm is a brownish or sometimes greenish layer. It’s boundary with unaltered rock is diffuse and is always associated with a dense hyphae network (Figure 2).

**Table 1**. Main characteristics of patinas

| *Samples* | *Sites* | *Years of exposition* | *Waterproofing Index (%)* | *Gypsum content of first 4 mm (%wt)* | *Endolithic hyphae layer* |
|---|---|---|---|---|---|
| MC1 | Maison Carrée | Ist Century | 92,5 | 4,0 | detected |
| MC1-2 | Maison Carrée | Ist Century | 88,4 (sanded) | 2.0 | detected |
| TD3 | Temple of Diana | Ist Century | 62 | 13,0 | detected |
| RQ2 | Roquet quarry | Roman | 88,8 | 0,0 | detected |
| PI3 | Pielles quarry | Roman - XVth | 96,8 | 0,0 | detected |
| ROA | Rocamat antique | Roman | 96,2 | 0,0 | detected |
| SG2 | Abbey of St Gilles | 12th Century | * | 15,0 | detected |
| EB3 | ST Baudile church | 1867 - 1877 | 0 | 23,0 | not detected |
| EPO | Pompignan church | 1850 | 0 | 16,0 | not detected |
| MMF | War memorial | 1920 | * | 0,0 | detected |
| EP2 | St Perpetue church | 1852 - 1862 | 0 | 20,0 | not detected |
| SP2 | St Paul church | 1835 - 1849 | 0 | 29,0 | not detected |
| RA | Rocamat quarry A | 2009 | 0,8 | 0,0 | not detected |
| RB | Rocamat quarry B | 1996 | 14,6 | 0,0 | not detected |
| RC | Rocamat quarry C | 1990 ± 2 | 87,7 | 0,0 | detected |
| RD | Rocamat quarry D | 1960 ± 10 | 92,7 | 0,0 | detected |
| RD-2 | Rocamat quarry D | 1960 ± 10 | 89,7 (sanded) | 0,0 | detected |

* Too small sample size for capillarity measurement

Analysis of the moulded porosity shows that the weathered zone is not a deposit or an encrustation but a superficial transformation since oolitic structure is visible from the unweathered area until the exposed surface (Figure 2). The moulded porosity shows a high density of micrometric tubes whose extent reaches about 1 mm in deep. This structural transformation of the rock could be the result of a dissolution/precipitation activity of endolithic lichen hyphae. However, a calcite structure is still visible even in the most invaded area and contributes to the mechanical cohesion of the patina. Nevertheless, this layer has lost its micro-porosity visible on the initial oolitic cortex. This implies that all the pores are filled with hyphae. Above the brownish layer, a thinner and lighter layer was observed which structure is petrographically nearly identical to that of the unweathered side. Although this superficial layer is thin (about 500 microns) it gives an unweathered appearance whereas the patina is deeply invaded by biological colonization.

Similar endolithic colonization was observed in stones aged in quarries due to growth of *Verrucaria nigrescens* and *Caloplaca aurantia* lichens [Concha-Lozano 2011].

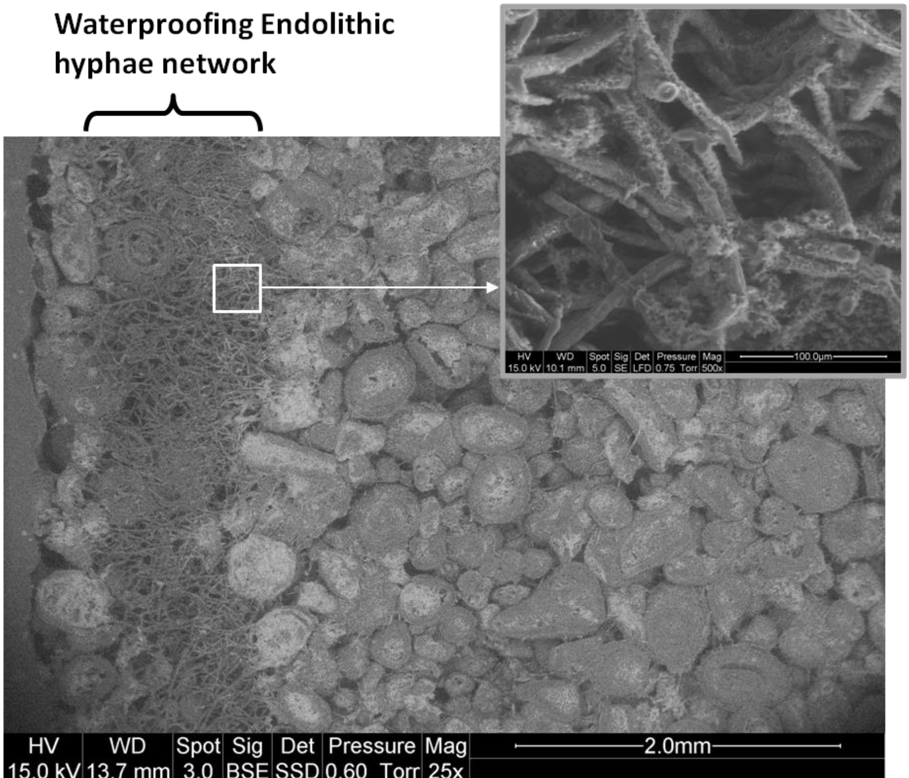


**Figure 2.** SEM of the moulded porous network showing a secondary porosity due to growth of endolithic lichen hyphae on sample MC1 (Roman temple Maison Carrée).

A link can be established between the gypsum content and the appearance of blisters and crumbling. All deteriorated buildings contain high load of gypsum upper than 15 %wt in their first 4 mm (sample EB3, EPO, and SP2, in Table 1). For these samples, the decrease of calcite ratio could explain the weakness, disintegration and swelling of the weathered layer. Below this gypsum content, the stones do not desquamate, and no erosion of their surface is visible (e.g. SG2, EPO, TD3 and MC1, in Table 1).

The waterproofing effect is mainly attributed to the entrapped organic matter that fills pores and leads to a hydraulic conductivity drop. This assumption is supported by the close capillarity coefficient value of unweathered and weathered-calcinated sides since organic matter was removed by the calcination treatment.

The low gypsum content of colonised samples suggests a protective effect due to the growth of lichens before the sulphur contamination. Conversely, the patinas of the 19th century Churches were deeply contaminated and not colonized by lichens. The water flow across stone surface during wetting and drying cycles is the main conveyor of soluble species such as sulphate or calcium ions. The waterproofing effect due to the lichens growth could reduce the mass of water flowing through the patina of the stone, and therefore, reduces soluble salts diffusion.

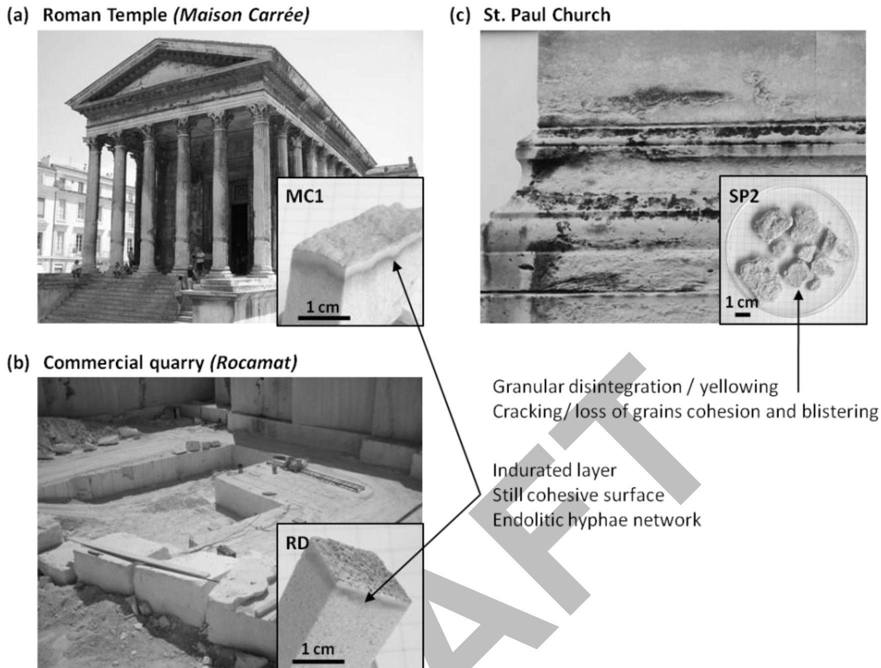


**Figure 5.** Photographs showing three different patinated samples of Bois des Lens stone. (a) The façade of a Roman temple dating from the 1st century after JC in Nimes downtown (Maison Carrée) and detail of a patinated sample (MC1). (b) Stone quarry currently in operation and details of a sample taken from a 50 years working face (RD). (c) Front of St Paul's Church showing blistering, yellowing and granular disintegration.



## 6. Conclusions

This study consists in providing some explanations on the weathering differences of the Nîmes downtown monuments built with the same stone focusing on the protective role of organic matter trapped beneath the stone surface. Petrophysical characterization of patinas sampled on monuments located in the same neighbourhood leads to a classification into two main categories: Yellowish patinas that become blistered and disintegrated and on the other hand patina of well preserved monuments that maintain a mechanical cohesion. The main pathology of decayed monuments is a loss of mechanical cohesion due to deep gypsum content, especially on the 19th century churches. Regarding the well preserved monuments, a layer of entrapped organic matter was detected below the surface. Morphological analysis of the porous network by resin moulding showed the existence of a secondary porosity filled by lichen hyphae. The protective role of entrapped organic matter is supported by capillarity measurement that showed a significant pore-sealing waterproofing. Moreover, the waterproofing effect appears to slow down the sulphate diffusion through the stone surface. There is evidence that lichen growth in a previous era is enough to explain the good preservation of some antique monuments of Nîmes.

**Acknowledgments**

This research was funded by the civil engineering laboratory of the Ecole des Mines d'Alès. The authors gratefully acknowledge the contribution of E. Garcia-Diaz and L. Tibiletti for their helpful comments. Thank also to J. M. Taulemesse and A. Diaz for their technical support.

**References**

Bessac JC, Aucher MR, Blanc A, Blanc P. 1996. La pierre en Gaule Narbonnaise et les carrières du Bois des Lens (Nîmes): histoire, archéologie, ethnographie et techniques. *Journal of Roman archeology*, supplementary series number sixteen.

Carter NEA,Viles HA. 2005. Bioprotection explored: the story of a little known earth surface process. *Geomorphology*. 67(3-4) 273-281.

Concha-Lozano N, Gaudon P, Pages J, de Billerbeck G, Lafon D, Eterradossi O. 2012. Protective effect of endolithic fungal hyphae on oolitic limestone buildings. *Journal of Cultural Heritage*. 13(2):120–7

Corenblit D, Baas ACW, Bornette G, et al. 2011. Feedbacks between geomorphology and biota controlling Earth surface processes and landforms: A review of foundation concepts and current understandings. *Earth-Science Reviews*.

Garcia-Vallès M, Vendrell-Saz M, Molera J, Blazquez F. 1998. Interaction of rock and atmosphere: patinas on Mediterranean monuments. *Environmental Geology*. 36(1-2) 137-149.

Warscheid T, Braams J. 2000. Biodeterioration of stone: a review. *International Biodeterioration & Biodegradation*. 46(4) 343-368.