HERITAGE 2018

Proceedings of the 6th International Conference on Heritage and Sustainable Development

10th Anniversary Edition

VOLUME 2

Edited by

Rogério Amoêda
Sérgio Lira
Cristina Pinheiro
Juan M. Santiago Zaragoza
Julio Calvo Serrano
Fabián García Carrillo

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In Memoriam
Professor Gregory Ashworth

(1941-2016)

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Foreword

Heritage 2018 - 6th International Conference on Heritage and Sustainable Development celebrates the 10th anniversary of Heritage Conferences. As the previous editions *HERITAGE 2018* aimed at maintaining a state of the art event regarding the relationships between forms and kinds of heritage and the framework of sustainable development concepts, namely the framework of the 2030 Agenda for Sustainable Development.

However, the four dimensions of sustainable development (environment, economics, society and culture) are, as in the past, the pillars of this event defining an approach on how to deal with the specific subject of heritage sustainability. Furthermore, beyond the traditional aspects of heritage preservation and safeguarding the relevance and significance of the sustainable development concept was to be discussed and scrutinised by some of the most eminent worldwide experts.

For a long time now, heritage is no longer considered as a mere memory or a cultural reference, or even a place or an object. As the previous editions of “Heritage” (2008, 2010, 2012, 2014 and 2016) have proven, heritage is moving towards broader and wider scenarios, where it often becomes the driven forces for commerce, business, leisure and politics. The Proceedings of the previous editions of this conference are the "living" proof of this trend.

As stated by some the Sustainable Development Goals of the 2030 Agenda, the role of cultural and social issues keeps enlarging the statement where environment and economics had initial the main role. The environmentalist approach (conceiving the world as an ecological system) enhanced the idea of a globalised world, where different geographic dimensions of actions, both local and global, emerged as the main relationships between producers, consumers and cultural specificities of peoples, philosophies and religions. In such a global context heritage became one of the key aspects for the enlargement of sustainable development concepts. Heritage is often seen through its cultural definition and no further discussion seams to be appropriate. However, sustainable development brings heritage concepts to another dimension, as it establishes profound relationships with economics, environment, and social aspects.

Nowadays, heritage preservation and safeguarding is constantly facing new and complex problems. Degradation of Heritage sites is not any more just a result of materials ageing or environmental actions. Factors such as global and local pollution, climate change, poverty, religion, tourism, commodification, ideologies and war (among others) are now in the cutting edge for the emerging of new approaches, concerns and visions about heritage. Recent events in the Middle-East and other parts of the World are saddling proving the rightness of these assertions and deserve our attention.

Thus, *HERITAGE 2018 - 6th International Conference on Heritage and Sustainable Development* proposed a global view on how heritage is being contextualised in relation with the four dimensions of sustainable development. What is being done in terms of research, future directions, methodologies, working tools and other significant aspects of both theoretical and fieldwork approaches were the aims of this International Conference. Furthermore, heritage governance, and education were brought into discussion as key factors for enlightenment of future global strategies for heritage preservation and safeguarding.

A special chapter on Preservation of Muslim heritage was included in this edition because of its singular and utmost significance and because the Venue of this edition was the city of Granada, one of the most extraordinary places to understand and feel the merging of cultures, arts and traditions. When religious and cultural issues are raising significant misunderstandings Heritage 2018 aimed at contributing to a valid, peaceful and fruitful discussion under the broad umbrella of sustainable development goals.

Authors submitting papers to Heritage 2018 were encouraged to address one of the topics of the Conference by providing evidence on past experience and ongoing research work. As a result, Heritage 2018 welcomed a significant number of papers and presentations addressing field work and case studies but also theoretical approaches on a diversity of thematic. As in the previous editions Early Stage Researchers were welcome to share the results of their research projects, namely post-graduation projects and doctoral projects, among others.

The Organising Committee also expresses its gratitude to all Members of the Scientific Committee who reviewed the papers and made suggestions that improved the quality of individual work and the over-all quality of the event.

The editors would like to express their gratefulness to all the partners and sponsors of this edition of Heritage who joined the effort to make a significant Conference. Our special word or recognition to the University of Granada that joined efforts with Green Lines Institute to make this event. Also to the Municipality of Granada, to the Bureau of Tourism of Granada and to the Council of the Alhambra and Generalife our recognition for their participation.

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Influence of several metabolites excreted by microorganisms on building stone deterioration

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ABSTRACT: One of the most important weathering factors of building stone, besides the meteorological phenomena (rain, snow, drought, hail…) is the biodeterioration produced by micro-organisms. In situations of water stress or extreme temperatures, microorganisms respond with the excretion of several metabolites that can affect stone. The effect of some metabolites (citric acid, ascorbic acid, oxalic acid, glucose and glycerol) has been evaluated on two types of stone with dissimilar porosity, limestone and Macael marble. The samples have been subjected to several cycles of exposure to metabolites, followed by freezing and desiccation as well as other cycles without exposure. The deterioration of the stones has been quantitatively evaluated by physical properties (bulk density, porosity, absorption and capillary water absorption). This study has concluded that deterioration depends on the nature of the stone, the presence or absence of metabolite and its chemical nature. The control of microorganisms present on building stone is essential for its conservation.

1 INTRODUCTION

Stones used in building construction and ornamental elements get damaged over time as a result of weather effects, air pollution and growth of organisms on them (Warscheid & Braams, 2000). Biodeterioration generated by microorganisms, such as algae or cyanobacteria, has attracted considerable attention, especially when it is produced in artistic and historical heritage buildings (Griffin, et al., 1991).The harsh weather conditions (frosts, rain and drought) are mostly mechanical in nature and give rise to physical dissolution. The effect caused by environmental pollution has a physical-chemical nature and also can be related to adverse environments, like sea breezes that carry substantial amounts of salt suspended particles (Chabas & Jeannette, 2001). In addition to the above, biodeterioration should be taken into account because of its mechanical nature as well as the chemical action of organic material deposited by higher beings (droppings), like metabolites originated by microorganisms. The aesthetic deterioration can either be accompanied by the deterioration or improvement of certain stone characteristic parameters.

There is a vast literature concerning the topic of biodeterioration and it involves numerous facets, such as artistic, biological, ecological or environmental aspects, and so on. Typically, the biodeterioration is addressed through case studies covering buildings and ornamental elements, like fountains and ponds (Bolívar & Sánchez, 1997; Sarró, et al., 2006; DePriest & Charola, 2017;), and rarely happens in a controlled manner. Many different types of excreted metabolites are widely known, and possible scenarios about their effect over stones in this case studies are proposed (Centeno, et al., 2016; Wase et al., 2017). However, little is known about their performance under controlled laboratory conditions.

Simulation of natural phenomena in the laboratory is not an easy task, particularly if they develop over a period of many years or even centuries. Despite that, it is possible to carry out some tests using climatic chambers, in which factors like temperature, moisture or action of chemical substances are accelerated. This enables us to achieve an intense action in a short period of time, which is equivalent to a smooth action over a long span of time (up to centuries).

Annual cycles can be simulated in a few hours, exposing the materials to abrupt and intense changes in environmental conditions. Regarding durability tests on materials, it is common to cause strong freezing, in the presence of high moisture, and then lead the material to a strong and fast desiccation at elevated temperature. If, apart from that, the material is exposed to the activity of several substances, it is possible to evaluate their relative effect upon these annual cycles in an accelerated way (Taghipour et al., 2015; Vázquez et al., 2013).

The aim of this study is to clarify the action of a selected group of metabolites, usually excreted by microorganisms, after freeze-thaw-drying-washing intense cycles on stones that are commonly used in historical and artistic heritage.

2 MATERIALS AND METHODS

2.1 *Stones*

Two types of stone have been chosen: Macael marble and limestone, both were supplied by Tino Natural Stone (Marbella, Spain). They share similar chemical composition (>98% of $CaCO_3$) but have very different porosity. The most interesting properties for this study are shown in Table 1. The different value of porosity implies that limestone has lower apparent density, higher water absorption and higher capillarity than marble.

Table 1. Stone's specifications.

Stone	Length	Width	Thickness	Apparent density	Absorption	Capillarity
	cm	cm	Cm	$kg \cdot m^3$	%	$g \cdot m^{-2} \cdot s^{-0.5}$
Macael Marble	10.0	5.0	2.0	2.7	0.1	0.316
Limestone	10.0	5.0	2.0	2.2	5.5	85.2

2.2 *Metabolites and other reagents*

Amongst the huge variety of metabolites that are excreted by cyanobacteria and algae, two groups have been chosen because of their representativeness and availability: one of them entailing low-molecular weight organic acids and the other one entailing polyhydroxy compounds. As a comparison, trials with hydrochloric acid and distilled water have been performed as well. The Table 2 shows the specifications of these reagents.

Table 2. Reagent's specifications.

Reagent	Specifications	Supplier	Reference
1. Hydrochloric acid	37.20 %	PanReac AppliChem	871020
2. Citric acid anhydrous	99.5 % - 100.5 %	PanReac AppliChem	141808
3. Oxalic acid 2-hydrate pure	99 %	PanReac AppliChem	141041
4. L(+)-Ascorbic acid	99.0 - 100.5 %	PanReac AppliChem	141013
5. Glycerol	> 98 %	Faisa	
6. D(+)-Glucose anhydrous	97.5 % - 102.0 %	PanReac AppliChem	141341
7. Desionized water	18.2 MΩ·cm	Millipore	

2.3 *Equipment*

Thermostatic chambers (CLN 32 STD INOX/G model) were used to simulate elevated temperature and drought conditions. Freezer (CNP3803 Index 20B/088 model) to simulate low temperature and freezing conditions. To simulate stable temperature and moisture conditions, thermostatic chambers (ST 2/2 COMF model) were employed.

Mass variations were estimated using a balance with accuracy of ± 0.01g (Precisa BJ 1000C model), and the variation of dimensions were measured using a caliber with an accuracy of ± 0.01mm (GT-DC-01 model). The pH of the different solutions was measured by means of pH-meter (Crison mi-cropH2000 model).

2.4 *Experimental procedure*

In order to simulate the biodeterioration in the laboratory, 10 cycles have been carried out. Each one involves contact between metabolites and stones, followed by freeze-thaw-drying intense stages, exposure to elevated temperature, and finally, washing-drying stages to start a new cycle.

Each cycle consists of:

1. Immersion of stones in solutions of each metabolite (concentration of 0.1 mol/l; 300 ml) for 30 minutes. The target is to simulate the effect by direct contact of metabolites that microorganisms generally excrete.
2. Freezing of stones at -32ºC for 1h 30 minutes (samples surface is previously dried). This is because, after that time and at that temperature, freezing at 0ºC in the middle of the stone is ensured as soon as possible. Thus, frosts effect is simulated.
3. Heating of stones at 70ºC for 1h 30 minutes. This time ensures heating at 40ºC reach the middle of the stone. In such a way, high temperatures during summertime with direct sun are simulated.
4. Immersion of stones in running water with a flow rate of 0.002l/s approximately, for 20h to ensure samples washing. In this step, superficial washing effect due to the rain is simulated.
5. Drying of stones at 70ºC for 4h. This step enables accurate dry weight measures to evaluate weight losses in each cycle. Weighing of samples is carried out with an accuracy of 0.01g.

In cycle 0 and 10, stones masses were measured in different moisture conditions for the later calculation of hydric tests. Between cycles, stones were kept at ambient temperature (25ºC) in thermostatic chambers.

Figure 1 shows the studied stones in cycle 0 and cycle 10 (before step 4).

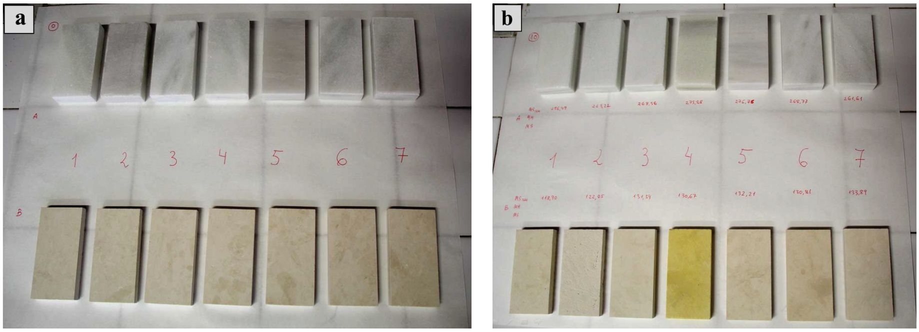

Figure 1. Studied stones, marbles (above) and limestones (below), in cycle 0 (a) and after 10 cycles of treatment (b).

2.5 *Hydric tests*

Absorption has been calculated in accordance with UNE-EN 13755 standard. This test allows us to determine the water addition within the stone.

The capillary rise test was carried out according to the UNE-EN 1925 standard. This test allows us to determine the capillary absorption coefficient (C).

2.6 *Calculation of stone's dimensions*

For each dimension (length, width and thickness), 5 measurements were taken. The average values have been those considered to analyse their variations and to calculate volume, perimeter area and specimen surface area submerged in water.

3 RESULTS AND DISCUSSION

3.1 *pH of solutions*

The pH in aqueous solutions 0.1M of metabolites and other reagents where stones were immersed are shown in Table 3.

Table 3. pH of the solutions where stones were immersed.

Solution	pH
1. Hydrochloric acid	1.39
2. Citric acid anhydrous	2.18
3. Oxalic acid 2-hydrate pure	1.60
4. L(+)-Ascorbic acid	2.05
5. Glycerol	5.99
6. D(+)-Glucose anhydrous	5.40
7. Deionized water	6.52

3.2 *Relative change of dimensions and anisotropy*

After 10 accelerated ageing cycles, stone's dimensions (length, width and thickness) were measured and differences between initial and final dimensions were calculated (Figs 2-3). It is noticeable that limestone is the most affected material, while Macael marble resists better the metabolites action. As could be expected, hydrochloric acid generates the most severe attack and, for this reason, represents the greater intensity reference. Water also produces changes in stone's dimensions, and represents the reference action of meteorological agents in the absence of metabolites.

Surprisingly, citric acid (a weak organic acid) caused corrosion in materials almost as intense as hydrochloric acid. As shown in Table 3, citric acid has a higher pH than ascorbic acid (vitamin C) but the first one is more aggressive for stones than the second one, as well as oxalic acid. This is due to the fact that citric acid, apart from acting as an acid breaking down carbonate ion into CO_2, acts as a sequestering agent for calcium ion. Therefore, the combination of both factors result in a much stronger attack on stones.

$$CaCO_{3(s)} + H_3Cit_{(aq)} \rightarrow CO_2\uparrow + CaHCit_{(aq)} + H_2O$$

In the same way, it is observed that oxalic acid, although it is almost as acid as hydrochloric acid (pH=1.60), had scarcely changed the stone's dimensions, and even a slight increase in thickness can be seen. This can be justified because of the exchange of carbonate ion (released as CO_2) for a larger oxalate ion with greater weight, giving rise to very insoluble calcium oxalate, which is deposited on the surface.

$$CaCO_{3(s)} + H_2Oxa_{(aq)} \rightarrow CO_2\uparrow + CaOxa_{(s)}\downarrow + H_2O$$

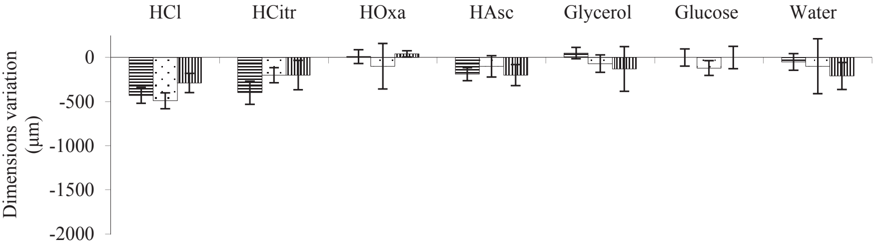

Figure 2. Change of Macael marble stone's dimensions after 10 accelerated ageing cycles. Length (▤), width (☐) and thickness (▥).

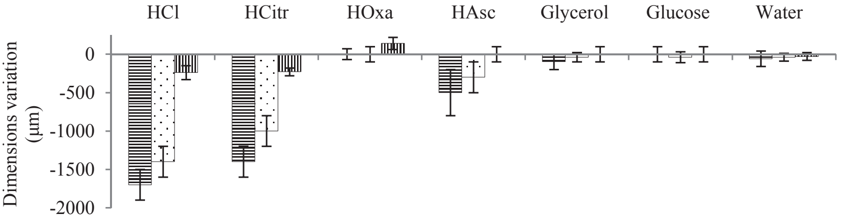

Figure 3. Change of limestone stone's dimensions after 10 accelerated ageing cycles. Length (▤), width (☐) and thickness (▥).

Water, as shown in figures, also produces a loss in stone's dimensions, less intense but significant enough, due to a well-known phenomenon. This phenomenon is produced by the increase in ice crystals volume by the time of freezing, which cause the stone weathering as a result of the mechanical action in their fissures and pores. Despite the fact that Macael marble stones are less porous than limestone stones, this phenomenon is stronger over marble stones. This might be justified on the assumption that marble is more crystalline, and therefore, more brittle and susceptible to mechanical action of ice crystals.

Glycerol and glucose metabolites are neither acids nor sequestering agents. Furthermore, they have very interesting colligative properties. Owing to the freezing-point depression, a well-known physical phenomenon, glycerol and glucose solutions only freeze at temperatures below 0ºC. In addition, when freezing, ice crystals formed are much smaller than those of the pure water. This leads to, as shown in figures, a lessened weathering when these metabolites are present, compared to water effect. Glycerol and glucose, and by extension, similar polyhydroxy compounds, have a freezing-point depression effect, already known to many diverse technological applications. Regarding weathering, microorganisms that excrete this kind of substances could produce, consequently, a certain bioprotector effect on stones.

Turning to Figure 2 and Figure 3, it is observed that changes in stone's dimensions are not homogeneous according to spatial directions. Even though limestone and marble are different types of stone (sedimentary and metamorphic, respectively), both share a similar formation process which consists in sedimentation of insoluble calcium carbonate thin crystal layers as a result of decomposition of soluble carbonates calcareous solutions.

$$Ca(HCO_3)_{(aq)} \rightarrow CaCO_{3(s)}\downarrow + CO_2\uparrow + H_2O$$

Between layers, small remnants of silicates and other materials are usually present, thus both marble and limestone are anisotropic. Stonemasons, those who cut stones to apply them in building, tend to do so parallel to the layers. In that way, floors and plates become more resistant to pressure and abrasion. This is evidenced by the difference of changes in stone's dimensions, due to the metabolites action, according to the three spatial dimensions. In all samples, the decrease or increase, as the case may be, is more pronounced in stone's length or width, while in thickness, which is perpendicular to the layers, changes of stone's dimensions are much smaller.

3.3 *Mass and volume change of stones and its influence on bulk density*

Figure 4a shows mass change of Macael marble stones after 10 accelerated ageing cycles and volume change of stones is displayed on Figure 5a. Similarly, Figure 4b and 5b show mass and volume change of limestone stones. It is observed that:

- Changes produced by studied metabolites, especially those more aggressive, are much more intense on limestone than on marble stones. Thus, for example, the mass of Macael marble stone diminishes almost 2g with citric acid while those of limestone stone decreases almost 6 grams. Something similar occurs with volume: 1.5cm^3 of volume loss on marble and about 5cm^3 on limestone.
- Regardless of material type, hydrochloric acid (used as a reference) is the most aggressive substance and, predictably, causes the most acute reduction in mass and volume. Citric acid is a weak acid but, unexpectedly, its behavior is comparable to that of hydrochloric acid. Ascorbic acid (vitamin C) also shows noticeable effects of corrosion.
- However, oxalic acid generates slight increases of mass. It is probably due to the fact that calcium oxalate is insoluble. Thus, for each missing mol of calcium carbonate, one mol of calcium oxalate with higher molecular mass is deposited. In terms of volume, the oxalic acid behavior is similar to the mass increase.
- Glycerol, glucose and water (used as a reference substance) have scarcely changed mass or volume.
- For each type of stone and metabolite there is a correlation between mass variation and volume variation, irrespective of whether it is a decrease or an increase. So, bulk density hardly changes substantially.

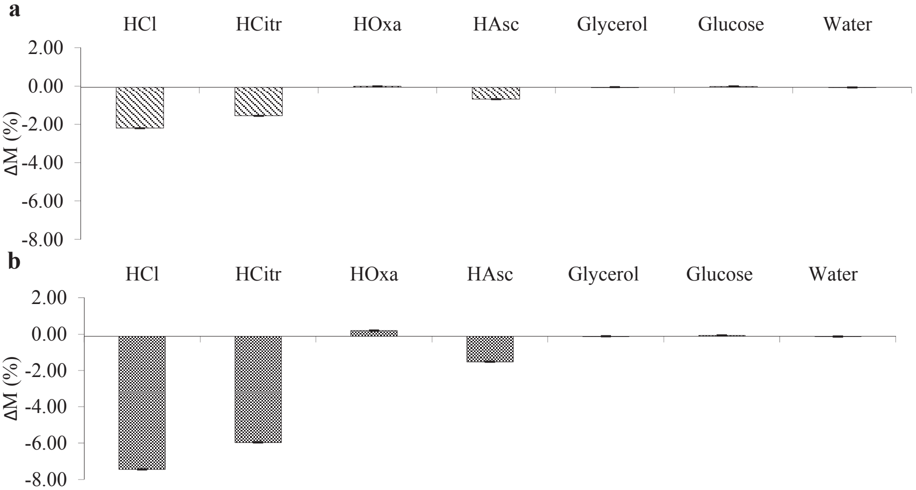

Figure 4. a. Change of Macael marble stone's mass after 10 accelerated ageing cycles; b. Change of limestone stone's mass after 10 accelerated ageing cycles.

Table 4 collect the bulk densities of stones calculated for all metabolites, before and after 10 accelerated ageing cycles. It can be seen that bulk density remains constant, which is compatible with the previous observations about mass and volume variation.

Table 4. Bulk density values, g/cm^3, of Macael Marble and limestone stones.

	Macael Marble		Limestone	
Metabolites	Cycle 0	Cycle 10	Cycle 0	Cycle 10
1. Hydrochloric Acid	2.67 ± 0.01	2.692 ± 0.009	2.188 ± 0.009	2.17 ± 0.01
2. Citric Acid	2.68 ± 0.02	2.683 ± 0.002	2.175 ± 0.004	2.16 ± 0.01
3. Oxalic Acid	2.706 ± 0.006	2.704 ± 0.007	2.204 ± 0.006	2.182 ± 0.009
4. Ascorbic Acid	2.69 ± 0.01	2.702 ± 0.006	2.22 ± 0.01	2.221 ± 0.006
5. Glycerol	2.69 ± 0.03	2.709 ± 0.008	2.22 ± 0.02	2.214 ± 0.006
6. Glucose	2.711 ± 0.009	2.720 ± 0.008	2.188 ± 0.009	2.18 ± 0.01
7. Water	2.67 ± 0.02	2.70± 0.01	2.262 ± 0.008	2.268 ± 0.003

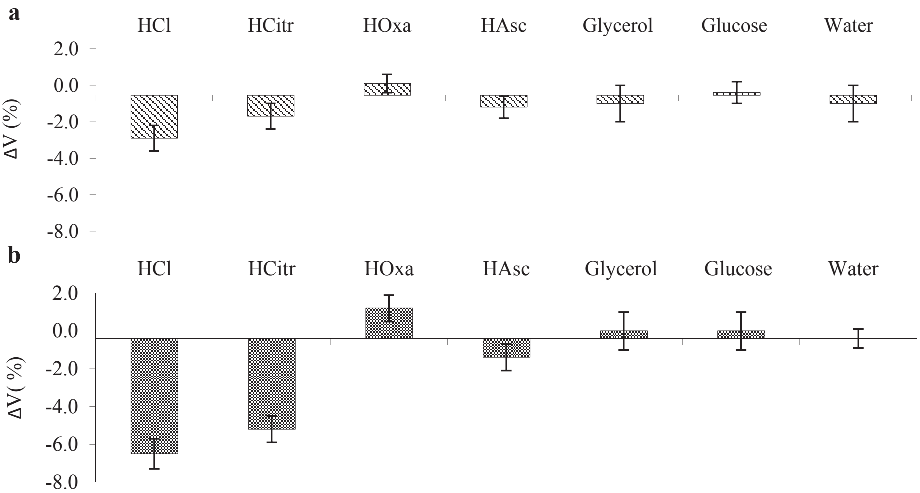

Figure 5. a. Change of Macael marble stone's volume after 10 accelerated ageing cycles; b. Change of limestone stone's volume after 10 accelerated ageing cycles.

Consequently, losses in mass and volume associated with relatively constant bulk densities means that corrosion of stones by metabolites is essentially a superficial phenomenon. This is in particular relevant for limestone. Despite being very absorbent, limestone suffers corrosion preferably on the surface, rather than within stone. This is because kinetics of chemical reactions between metabolites and calcium carbonate is much faster than kinetics of absorption. Therefore, metabolites react with the stones surface and no more corrosion is produced by the time metabolite is absorbed.

3.4 *Changes in water absorption and capillarity*

Table 5 shows initial and final absorption values after 10 cycles for both stone types and all studied metabolites. Following the action of metabolites, water absorption must be checked to ensure that no substantial changes are produced. This is in line with the constant bulk density previously analysed. Hence, internal corrosion is not generated and no new holes are created. So, holes are not big enough to increase absorption values significantly.

Table 5. Water absorption values, %, of Macael Marble and limestone stones.

	Macael Marble		Limestone	
Metabolites	Cycle 0	Cycle 10	Cycle 0	Cycle 10
1. Hydrochloric Acid	0.130 ± 0.008	0.117 ± 0.008	6.39 ± 0.02	6.59 ± 0.02
2. Citric Acid	0.131 ± 0.007	0.171 ± 0.008	6.48 ± 0.02	6.36 ± 0.02
3. Oxalic Acid	0.108 ± 0.007	0.108 ± 0.007	6.18 ± 0.02	6.03 ± 0.02
4. Ascorbic Acid	0.058 ± 0.007	0.091 ± 0.007	5.93 ± 0.02	6.11 ± 0.02
5. Glycerol	0.072 ± 0.007	0.098 ± 0.007	5.99 ± 0.02	5.80 ± 0.02
6. Glucose	0.112 ± 0.007	0.108 ± 0.007	6.31 ± 0.02	6.20 ± 0.02
7. Water	0.118 ± 0.008	0.092 ± 0.008	5.01± 0.02	5.06 ± 0.02

While absorption indicates how much water can be absorbed by stones, capillarity is related with water absorption velocity per unit area from the wet bottom to upper dry zones. Capillarity is connected with pore size and stone "microchannels" as well as physical properties of absorbed liquid. However, capillarity is not necessarily related to the high amount of free holes.

Figure 6 shows capillarity values for stones before and after 10 cycles of treatment. To achieve a better understanding of the impact on capillarity, the abscissa axes have been drawn referred to capillarity initial values (before treatment) for Macael marble and limestone, respectively. Increases in capillarity are plotted upward and decreases in capillarity are plotted downward. Macael marble capillarity is very low (0.3161g/($m^2s^{0.5}$), since marble is quite compact.

On the other hand, limestone capillarity (85.203g/$m^2s^{0.5}$) is appreciably greater.

Metabolites impact on marble capillarity after 10 accelerated ageing cycles is low, but considerably high compared to capillarity initial values (before accelerated ageing cycles). In all cases, capillarity increases, particularly citric acid followed by hydrochloric acid and water. Oxalic acid, ascorbic acid, glucose and glycerol capillarity show less increase than water capillarity. So, in moist environments these metabolites protect marble against adverse weather conditions.

Metabolites impact on limestone capillarity is very disparate. Glycerol and oxalic acid effect are particularly noteworthy since they lead to a marked capillarity reduction. Regarding oxalic acid, capillarity values shift from 85.203g/$m^2s^{0.5}$ to just 25.448g/$m^2s^{0.5}$; glycerol capillarity values achieve 70.81g/$m^2s^{0.5}$. This has really interesting implications, since this metabolites released by microorganisms diminish capillarity and, for instance, could protect walls from moisture. This would enable an improvement in heritage preservation and even these same microorganisms might be employed in bio-restoration of porous stones like limestone.

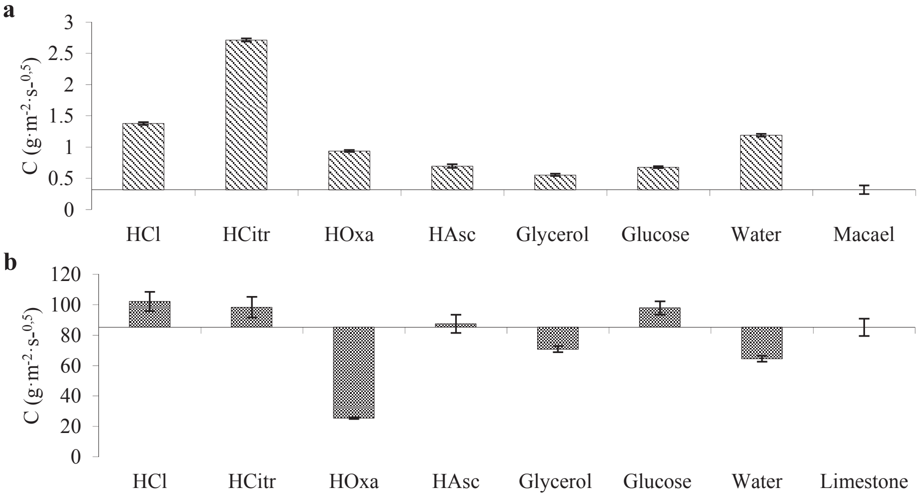

Figure 6. a. Capillarity of Macael marble stones after 10 accelerated ageing cycles; b. Capillarity of limestone stones after 10 accelerated ageing cycles.

3.5 *Aesthetic alterations: color and texture*

3.5.1 *Color*

The colors of stones have been recorded in dry conditions, using the notations for hue, value and chroma as given in the Munsell Soil Charts (Munsell, 2000). The Munsell notation for color consists of separate notations for hue (dominant spectral color), value (lightness/darkness of color) and chroma (strength of color), which are combined in that order to form the color designation. This notation is especially useful for international correlation, since no translation of color names is needed.

After 10 cycles, stones do not show significant changes in color, except the limestone that was treated with ascorbic acid: limestone without treatment: 10YR 8/1.5, a very pale brown-white; limestone after ascorbic treatment: 2.5Y 8/5, a yellow-pale yellow (Fig. 7a). Regarding marble stones, color is N 8.5/, a very light grey-white, before and after the treatment.

3.5.2 *Texture*

Hydrochloric, citric and ascorbic acids, due to their aggressiveness, generate rough surface and local pitting corrosion. Because stones have a layered structure, between layers it is possible to notice fissures in some cases (e.g. ascorbic acid, Fig. 7b). By contrast, oxalic acid leads to a more compact structure; glycerol provides a smooth and slippery surface and glucose maintains initial texture.

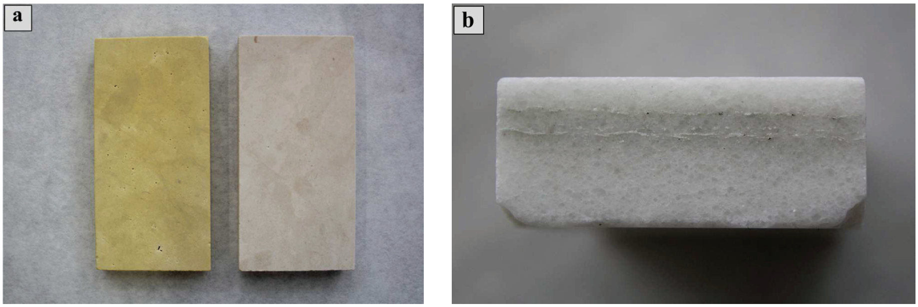

Figure 7. a) Limestone stone after (left) and before (right) treatment with ascorbic acid; b) Macael marble stone after treatment with ascorbic acid.

4 CONCLUSION

Accelerated ageing tests of stones in the presence of metabolites usually excreted by microorganisms, have made possible to predict their effect on stones in the long-term under controlled laboratory conditions. Throughout this preliminary approach performed with Macael marble and limestone (both made by calcium carbonate), a mechanism of interaction between metabolites and stones have been suggested.

Figure 8 shows a model of interaction between stones and metabolites together with reference substances employed. The main features of such model are:

a) Metabolites interaction is substantially superficial. It is produced on the outermost layers of stone. The hypothesis that can be made is that kinetics of interaction metabolite-stone is much faster than those of absorption.
b) Superficial interaction implies that mass and volume changes of stones are not conductive to substantial variations of bulk density.
c) Besides, superficial interaction implies that water absorption is not substantially modified owing to the absence of large empty holes within stones.
d) Acid metabolites react with calcium carbonate forming water soluble substances that lead to a superficial corrosion. Consequently, fine fissures were created and capillarity increased (for citric acid and ascorbic acid). Citric acid is especially

aggressive towards stones because of its acidic nature and high calcium sequestering power. In contrast, oxalic acid forms insoluble calcium oxalate. Therefore, fissures and pores get filled and capillarity did not decrease and even weight and volume of stones slightly increased.

e) Polyhydroxy metabolites, such as glucose or glycerol, do not produce corrosion since they are not acids. Moreover, they are able to inhibit adverse weather conditions effect. This can be justified by admitting these metabolites to act as cryoprotectants under freezing conditions.

To conclude, the impact of microorganisms on heritage stone buildings conservation can either be detrimental or beneficial, depending on the metabolites excreted. On one hand, citric acid and ascorbic acid (vitamin C) excretions are harmful, so microorganisms producing these metabolites should be removed. On the other hand, excretion of polyhydroxy compounds, like glycerol or glucose, provides a slight protector effect. Furthermore, oxalic acid excreted by microorganisms, or its direct application, can be beneficial to heritage marble or limestone stone buildings preservation and reinforcement.

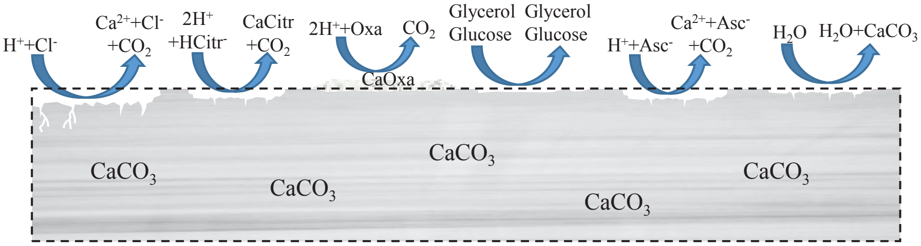

Figure 8. Model of metabolites attack on stones made by calcium carbonate, such as marble and limestone.

Nevertheless, further investigations should be done. For example: testing other types of metabolites, such as amino acids or proteins, at different concentrations and other types of stone.

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