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Article

WEATHERING AND DETERIORATION OF CARBONATE STONES FROM HISTORICAL MONUMENTS: A REVIEW

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Abstract: *The degradation of historical monuments due to atmospheric and anthropogenic factors is a frequently encountered phenomenon on all continents, being intensively investigated to understand the type and degree of damage and to choose an appropriate restoration method. Based on extensive bibliographic documentation, this study presents a comprehensive review of the physical, chemical, and biological weathering processes induced by extrinsic factors (atmospheric, biological, and anthropic) that lead to the deterioration of limestone and marble, the most common construction materials found in historic buildings of humanity's architectural heritage.*

Keywords: heritage building, historical monuments, limestone, marble, weathering, deterioration, extrinsic factors

1. INTRODUCTION

Historical monuments constitute the architectural heritage of each country and include thousands of history years. They are present in a wide range of architectural styles and have an important economic, touristic, and cultural role for humanity (Kanani and Zandi, 2011). Practically, historical heritage represents the identity and pride of each country and contributes to maintaining the culture and tradition of the respective country. Unfortunately, world heritage buildings and monuments were not built to withstand the aggressive action of today's air pollutants and, since many of them are located in or near industrial cities, they have developed considerable damage over time (Fistos et al., 2022). Therefore, the accurate diagnosis of the building's materials' deterioration together whit choosing the appropriate methods for reconditioning process of the historical monuments are important nowadays aspects. Atmospheric weathering of building materials (i.e. stone) is defined by Vergès-Belmin et al. as "the result of natural atmospheric phenomena on the surface" while deterioration is "any chemical or physical change in intrinsic properties that lead to a loss of value or use" (Vergès-Belmin and Siedel, 2005). Atmospheric weathering and deterioration processes led to building materials degradation and the decay of the monuments. Over time, historic building materials such as natural stones, bricks, mortars, and concrete, etc. have been weathered as a result of daily and seasonal changes in temperature and humidity, wind, snow, and rain, transported soluble salts of water, air pollutants, bacteria, plants, and plant roots, etc. (Cardell et al., 2008; Fistos et al., 2022; Oguchi and Yu, 2021; Saltık, 2018; Sena da Fonseca et al., 2020). Natural factors have acted on heritage buildings since their construction. Even Herodotus mentioned in his History that the stone materials of the pyramids from Egypt were already damaged when he saw them in the 5th century BC

(Oguchi and Yu, 2021). Starting with the industrial revolution, the world's built heritage developed significant deteriorations induced by the increasing concentration of some pollutants in the atmosphere (i.e. SO_2, NO_2, material particles, PM, etc.) (Mascaro et al., 2022; Olaru et al., 2010; Reyes-Trujeque et al., 2016; Saltık, 2018; Vidal et al., 2019).

To create a sustainable urban and non-urban environment with an appropriate managerial development plan, it is important to study the degradation degree of heritage monuments determined by atmospheric pollutants and climate changes. This is valid both for the correct planning of their restoration and conservation process, and for the monitoring of the pollution sources themselves (Bogdan et al., 2022; Fistos et al., 2022). Atmospheric pollution is a main challenge for urban and sub-urban areas both in terms of development policies and traffic efficiency strategies connected with aspects related to the protection of cultural heritage. The change in climatic factors (e.g. precipitation, wind circulation, large temperature variations, etc.), caused by the increase in the level of pollution, generates a series of negative effects that determine the accelerated decay of historical monuments that are part of the UNESCO cultural heritage (Bogdan et al., 2022; Sesana et al., 2021; Vyshkvarkova and Sukhonos, 2023).

Rainwater, combined with gaseous air pollutants (i.e. SO_2, NO_2), leads to the formation of acid precipitations, and the formed sulphurous, sulphuric, and nitric acids can react with the calcite ($CaCO_3$) from limestone, marble, concrete, mortar, etc. causing the surfaces' destruction in the exposed areas of the monuments. Additionally, acid precipitations can dissolve limestone by direct contact. (Basu et al., 2020; Battista and de Lieto Vollaro, 2017; Vidal et al., 2019). Dry and wet acidic deposits together with water, moulds, and lichens are the main degradation factors causing irreversible structural damage and aesthetic problems to the buildings and statues (Comite et al., 2020b; Hall and Hall, 1996; Mascaro et al., 2022).

A recent study by Spezzano P. in 2020 provided an estimate of the air pollution effects on the cultural sites included in the UNESCO World Heritage throughout Europe. In this study, the potential risk for UNESCO heritage monuments in the EU was evaluated based on exceeding the tolerable degradation thresholds recommended for each type of construction material (Spezzano, 2021). The results highlighted that, despite the improvements in the air quality at the European level noticed in the last decades, air pollution is still significant and continues to play an important role in the processes of cultural heritage degradation, especially in densely populated urban and sub-urban areas with intense traffic and polluting industrial activities (Spezzano, 2021; Török et al., 2011).

According to Kanani and Zandi, the factors that lead to the deterioration of historical monuments can be classified as follows: natural factors with instantaneous function (i.e. earthquakes, lightning, natural fires, floods, etc.); natural factors with gradual function; physical factors (wind, sunlight, changes in humidity, temperature changes, etc.); chemical and electrochemical factors (atmospheric pollutants and acid rain that lead to dry and wet acid deposition); plant destructive factors (plants and micro-plants); biological and microbiological factors; complex factors; social factors due to profit or negligence and defective management (Kanani and Zandi, 2011). These extrinsic factors act synergistically with intrinsic factors of the building materials (i.e. mineralogy, chemical composition, porosity, permeability, strength, fractures, etc.) causing decay of the historic heritage by various weathering and deterioration processes such as salts crystallization and dissolution, freeze-thaw, Krast effect, efflorescence and sub-florescence, black crust depositions, etc., (Kryza et al., 2009; Livingston, 2016; Pappalardo et al., 2022; Vidal et al., 2019) as can be seen in **Figure 1.**

The weathering and deterioration processes of building materials can occur on the entire surface of monuments and buildings or only in certain more exposed and reactive areas (Aucouturier and Darque-Ceretti, 2007; Badouna et al., 2020; Bogdan et al., 2022; Cardell et al., 2008; Kanani and Zandi, 2011; Kryza et al., 2009; Livingston, 2016; Olaru et al., 2010; Vidal et al., 2019).

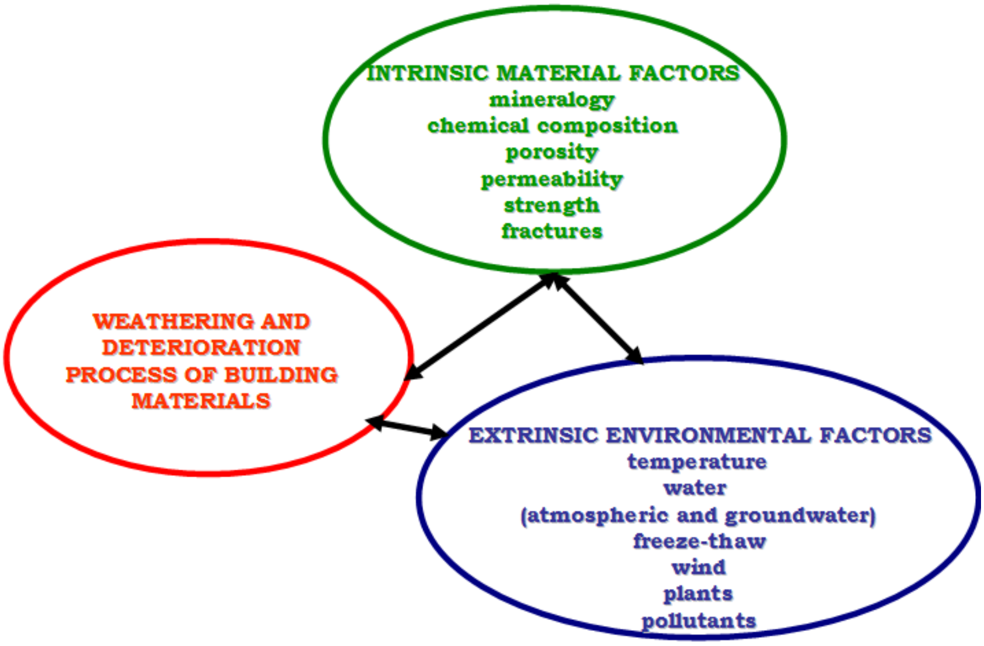


Figure 1. Synergistically interaction of extrinsic and intrinsic factors leads to weathering/ degradation processes of heritage materials

The paper aims to present a comprehensive review of the most important weathering and deterioration (degradation) processes induced by extrinsic factors (atmospheric, biological, and anthropic) and their effect on the carbonic stones materials (limestone and marble) from historical monuments. For this purpose, 74 articles published in indexed specialized journals were selected, of which ~40% are recent studies published in the 2019-2023 period.

2. NATURAL STONES AS BUILDINGS MATERIALS FOR THE HERITAGE STRUCTURES

One of the oldest natural materials used for buildings, monuments, and statues is stone. In general, the stone has a porous structure and the chemical composition consists of different minerals such as carbonates, silicates, and alumino-silicates (Bogdan et al., 2022).

Natural stones that have been used over time as building materials can be classified as follows:

- inclusive rocks (granite, gabbro, anorthosite, etc.);
- extrusive rocks (basalt, andesite, etc.);
- sedimentary rocks (sandstone, limestone, dolomite, diatomite, etc.);
- metamorphic rocks (marble, travertine, etc.).

Despite the unique properties of stones, environmental pollutants can damage them (Vidal et al., 2019). The stone's surface may undergo structural changes as a result of the interaction with various physical, chemical, and biological factors. According to Aucouturier and Darque-Ceretti the stone's deterioration surface is “a superficial thin layer with a different composition from the stone's bulk and unique characteristics due to the disturbances that have taken place such as roughness, colouration, black crust, etc.” (Aucouturier and Darque-Ceretti, 2007)

The attack of atmospheric pollutants, the dissolution and crystallization of salts in water, and the neutralization of rain acidity are the main physicochemical processes that cause the deterioration of the stone surface. An important role is also played by biological factors such as cyanobacteria, mosses, lichens, algae, etc. which cause bio-deterioration processes (Schiavon, 2002).

Frequently found in nature, limestone is a rock with a soft structure, being composed of calcite and aragonite ($CaCO_3$) or sometimes, of dolomite (double carbonate of calcium and magnesium, [$CaMg(CO_3)_2$]). Limestone was formed either by biological processes (i.e. accumulation of coral and shell fossils, etc.) or by non-biological processes such as precipitation of minerals from water containing dissolved calcium (Corvo et al., 2010; Schiavon et al., 2004; Wahab et al., 2019). Limestone often contains fossils, as can be seen in **Figure 2,** which provide interesting information on ancient environments and the evolution of life.

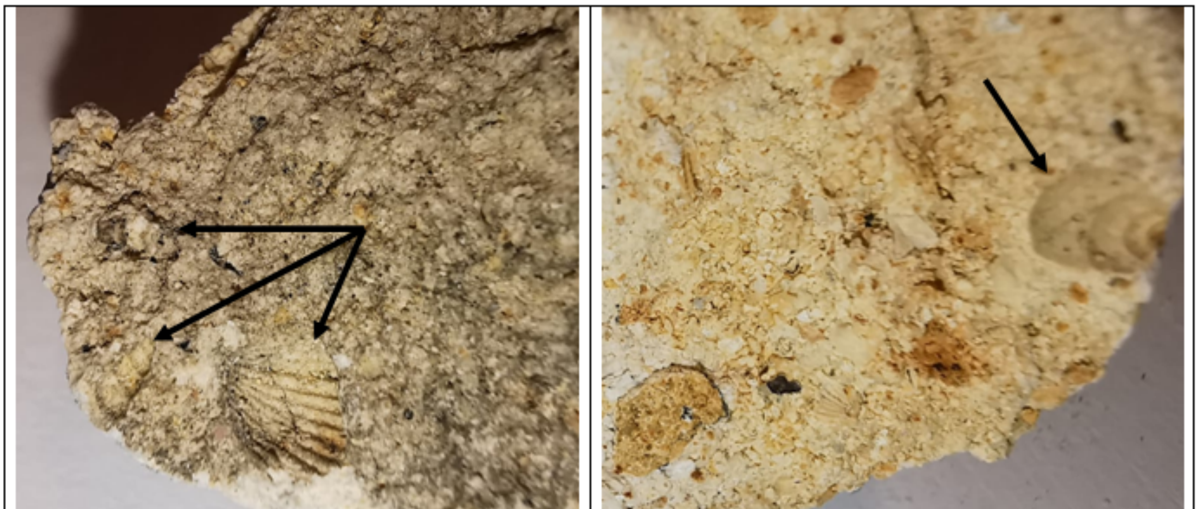
Major geological events caused some natural limestone deposits to undergo a series of metamorphic changes that led to calcite re-crystallization in the form of marble (Amer Khalil, 2020).

Travertine, a carbonate non-foliated stone, is a form of terrestrial limestone that occurs around mineral or thermal springs by rapid precipitation of $CaCO_3$ dissolved in water. Usually, travertine has a fibrous or concentric appearance, but there are also varieties of white, brown, cream, and even rust, depending on the metal oxides present (i.e.Fe_2O_3). It is the most frequently encountered variant of limestone in caves where it can form stalactites, stalagmites, and other speleothems. Since ancient times, limestone and marble have been widely used in architectural applications for buildings, walls, ornamental-decorative details, and statues (Amer Khalil, 2020). Many of the monuments included in the UNESCO world heritage were built from limestone and marble, some of the most famous ones being shown in **Figure 3**.

Due to their structure and chemical composition, calcareous stones are vulnerable to weathering and deterioration processes, many studies reported the results related to the effect of natural factors and acidic atmospheric pollutants on these materials (Basu et al., 2020; Comite et al., 2020b; Fistos et al., 2022; Ivaskova et al., 2015; Kanani and Zandi, 2011; Mascaro et al., 2022; Vidal et al., 2019; Vyshkvarkova and Sukhonos, 2023; Wahab et al., 2019).

3. DETERIORATION OF CARBONATE STONES

In the following paragraphs, we will briefly present the most important natural and anthropogenic factors involved in the degradation of carbonate stone materials, emphasizing the weathering and deterioration processes generated by these factors. The deterioration types of the carbonate stones are schematically presented in **Figure 4**.



Limestone with seashell and snail fossils
Samples taken from Limestone street wall, Eternitatea Cemetery, Arad, Romania
photo by D.R.C.

Figure 2. Natural limestone formed by biological processes

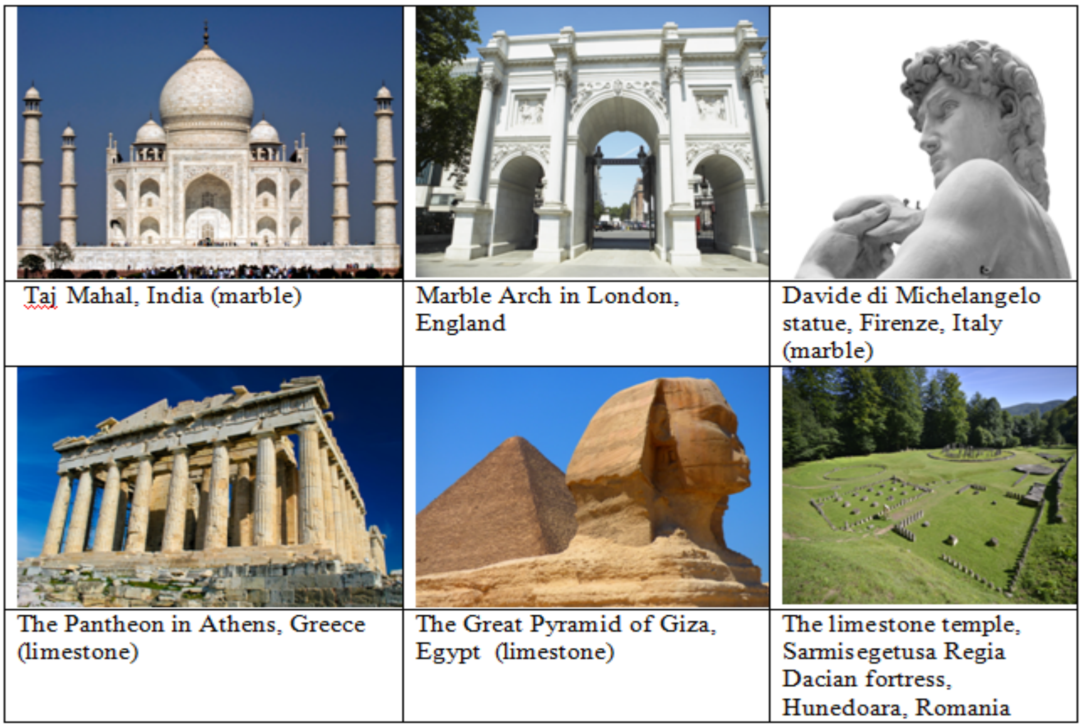


Figure 3. World heritage monuments and statues from carbonate stones

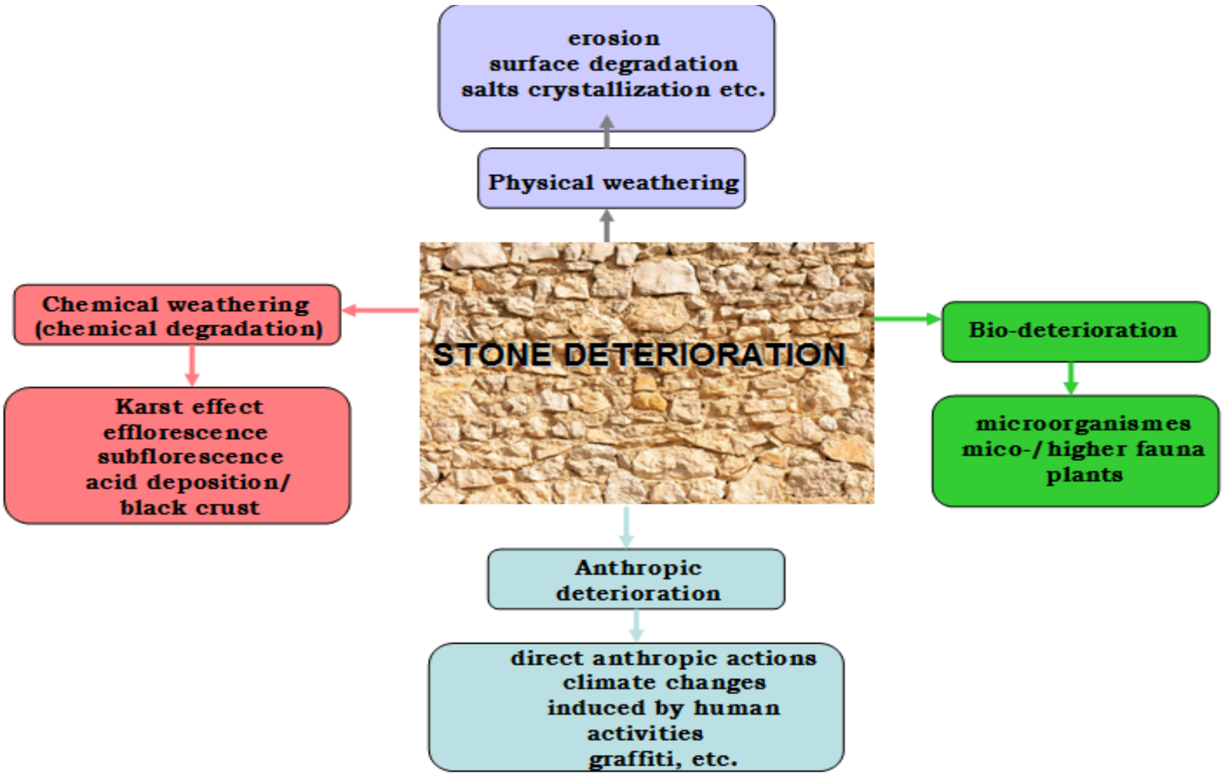


Figure 4. Deterioration types of the carbonate stones

3.1. Physical weathering

Physical weathering is a natural process for most types of stone materials, but it is predominant in the case of carbonate stones. This damage type is caused by some natural factors such as winds, temperature variations, humidity, etc. (Reyes-Trujeque et al., 2016; Saltık, 2018). In the presence of abrasive particles, the winds lead over time to the erosion of the carbonate materials' surfaces. Water from the atmosphere (precipitation, atmospheric humidity) or underground (phreatic water) plays an important role in the physical weathering of limestone and marble.

The presence of water can lead to the degradation of the stone's surface through expansion/contraction phenomena or freeze/thaw cycles, generating cracks, exfoliation, spalling, delamination, or descaling of the contour (Fistos et al., 2022; Pappalardo et al., 2022; Vidal et al., 2019). In **Figure 5**, some heritage structures degraded by physical weathering processes are exemplified.

Another predominant mechanism that causes physical weathering is the salts' crystallization induced by humidity and temperature variations. A decrease in the relative humidity inside the stones causes an increase in the concentration of some salts (in a dissolved state) in the material's pores. These salts, which come from the chemical structure of stone, masonry, and finishing mortars, the capillary migration of ions from the soil, agricultural works, de-icing solutions, metabolites of micro-organisms, etc. can finally crystallize inside the pores.

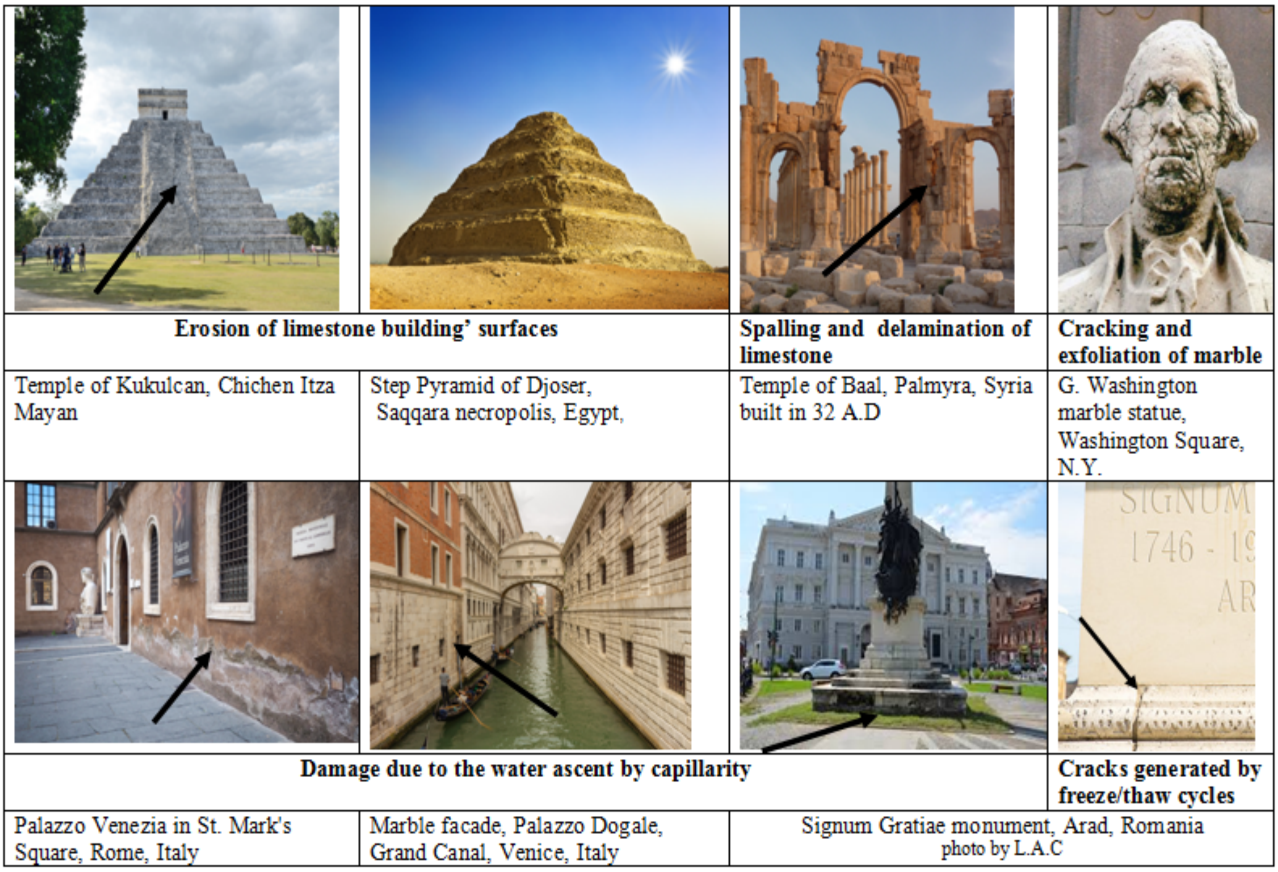


Figure 5. Heritages' deterioration due to physical weathering processes

As the relative humidity increases, the crystals are rehydrated/ dissolved, and thus repeated crystallization/rehydration cycles can create significant mechanical stress on the stones, thereby causing physical weathering (also called "salts weathering") (Cardell et al., 2008; Comite et al., 2020b; Fistos et al., 2022; Oguchi and Yu, 2021; Vidal et al., 2019).

According to Pappalardo et al., the pressures generated by salts' crystallization in the pores of carbonate rocks (resulting from the percolation of supersaturated solutions through the rock) are a major cause of the alveolar structures formation called "honeycombs". (Pappalardo et al., 2022). Many studies have shown that weathered carbonate stones from historical constructions widely present visible cavities (alveoli) variable in shape and size (Frank-Kamenetskaya et al., 2009; Gulotta et al., 2013; Oguchi and Yu, 2021; Reyes-Trujeque et al., 2016; Saltık, 2018). This phenomenon is amplified by the abrasive effect of the incoherent rocks, which are taken over by the turbulent air currents, thus contributing to the increase in the size of the cavities where salt crystallization takes place (Cardell et al., 2008; Oguchi and Yu, 2021; Weththimuni et al., 2022), as can be seen in **Figure 6.**

Computer modeling of experimental results together with a pragmatic case analysis has contributed to the improvement of the practical methods used to limit the building's materials damage due to the "salt weathering" phenomenon (Weththimuni et al., 2022).

The damage caused by the development of some plants or plant roots (**Figure 7.**) in the existing cracks of the constructions can also be considered physical weathering (Mascaro et al., 2022).

Earthquakes, landslides, or massive floods play an important role in the physical damage to buildings and monuments.

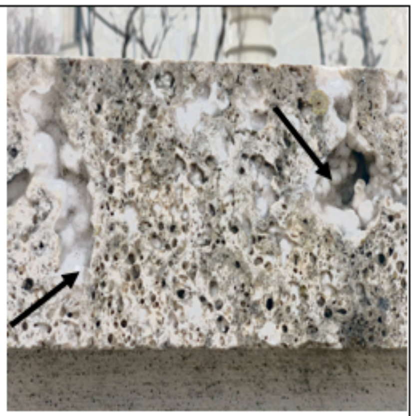
		
"Honeycombs weathering"	**Visible cavities (alveoli)**	**Salt crystals grown in the pores of the calcareous material**
Signum Gratiae monument, Arad, Romania photo by L.A.C	Limestone street wall, Eternitatea Cemetery, Arad, Romania photo by L.A.C	Limestone street wall, Holy Trinity Cathedral, Arad, Romania photo by L.A.C

Figure 6. The "salts weathering" of the limestone material

		
The Leshan Giant Buddha, China	The Franciscan Church inside the Arad Fortress, Arad, Romania photo by L.A.C	Şoimoş Fortress, Arad, Romania photo by L.A.C

Figure 7. Plants growing between stones of historic buildings

3.2. Chemical weathering

The chemical weathering, also called "chemical degradation", of stone materials represents the change in stone composition caused by several chemical processes and leads to the surface's deterioration.

According to Pappalardo et al., chemical weathering of the stone is a spontaneous and irreversible degradation process that leads the affected material to a more stable state under given temperature and pressure conditions (Pappalardo et al., 2022).

3.2.1. Karst effect

The Karst effect is one of the most frequent weathering processes that particularly affects limestone and refers to the natural dissolution of calcareous stones in the presence of clean water (pH ~ 5.6) (Cardell et al., 2008; Fistos et al., 2022; Vidal et al., 2019). The fact that calcite is naturally soluble in pure water leads to a natural dissolution of stone by rain. In the presence of atmospheric CO_2 and humidity, the carbonation reaction takes place on the carbonate stone surface.

The Karst effect represents the chemical transformation of calcium carbonate ($CaCO_3$) into calcium bicarbonate ($Ca(HCO_3)_2$) in the presence of dissolved carbon dioxide (CO_2) in rainwater (H_2O) according to eq.1.

$$CO_{2(g)}+H_2O_{(l)}+CaCO_{3(s)} \Leftrightarrow Ca(HCO_3)_{2(aq)} \quad (1)$$

insoluble soluble

Fistos and col. showed that, the Karst effect is amplified by the increase in CO_2 concentration due to anthropogenic pollution and can cause an increase in the stone pH through the carbonic acid formation and subsequent processes which are necessary to restore the chemical equilibrium (Fistos et al., 2022). The aggressive CO_2 action is more intense in urban areas than in rural, where, it is known that the CO_2 concentration is higher and the precipitations' pH is lower (acid rain).

According to Fassina, the action of acid precipitation on limestone and marble surfaces can cause the re-crystallization of water-soluble calcium bicarbonate (Fassina, 1988). Carbon dioxide dissolved in water tends to evaporate when the solution temperature increases and, consequently, the following reaction (eq.2) takes place:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \quad (2)$$

The calcium carbonate formed has larger crystals and a more porous structure than the original calcite (from the carbonate rock), which is microcrystalline and non-porous. The increase of stone's surface porosity due to the re-crystallization process of calcium bicarbonate is a harmful phenomenon because it allows acid precipitations containing sulfuric acid and soluble salts (e.g. sulfates and chlorides) to penetrate deeper into the stone and accelerate its degradation.

3.2.2. Efflorescence and Subflorescence

Efflorescence is caused by salts crystallization (e.g. sulfates, nitrates, chlorides, and carbonates of sodium, potassium, and calcium, etc.) and their deposition on the stone' surface (Pappalardo et al., 2022), as can be seen in **Figure 8**. Efflorescence (also called "white crust" or "white deposit") is considered a chemical weathering process, and its presence has been observed in the last decades on the surfaces of many heritage monuments (Benavente et al., 2021; La Russa et al., 2015; Oguchi and Yu, 2021; Pappalardo et al., 2022; Přikryl et al., 2007). Salts can act both as a physical force and saline solutions which increases the dissolution rates of minerals into rocks (Benavente et al., 2021). Since this process involves the presence of water, the appearance of white deposits suggests the existence of water infiltration phenomena through the rock and the related consequences, previously presented. It has been observed that the efflorescence caused by salts can lead to haloclastic ruptures of the materials, being a serious problem for construction (Benavente et al., 2021; Pappalardo et al., 2022; Vergès-Belmin and Siedel, 2005). In the case of natural carbonate stones, the overpressure generated by the salt crystals causes them to exfoliate through a progressive detachment of the shallower portions.

According to Pappalardo et al., the results of crystallization and precipitation of salts below the building material surface causing spalling and/or flaking are recognized as sub-florescence (Pappalardo et al., 2022). If efflorescence is relatively easy to remove, sub-florescence is difficult to remove because it forms below the rock surface (Mineo et al., 2022; Pappalardo et al., 2020). Studies have shown that porous calcite formed by the re-crystallization process of calcium bicarbonate plays an important role in efflorescence and sub-florescence formation (Oguchi and Yu, 2021; Pappalardo et al., 2022; Pappalardo et al., 2020).

3.2.3. Black crust

The black crust, also called "black patina", is an indicator of the chemical weathering/degradation of heritage monuments due to atmospheric pollution and defines "accumulation areas of the resulting compounds from the chemical alteration of carbonate rocks and of the atmospheric particle depositions" (Rodrigues, 2015; Sabbioni et al., 2001). The black crust is a superficial layer with a porous structure composed mainly of gypsum crystals ($CaSO_4.2H_2O$) in which atmospheric dust, materials particle, organic compounds, metals, etc. can be entrapped or some microorganisms can develop.

The primary atmospheric pollutants causing black crust formation on the carbonate stone surface are sulphur dioxide (SO_2), nitrogen dioxide (NO_2), and particulate matter (PM). Interaction mechanisms between acid atmospheric gases and building carbonate materials occur via dry and wet depositions (Bogdan et al., 2022; Kryza et al., 2009; Olaru et al., 2010). The dry and wet acid depositions can react with the $CaCO_3$ to generate $CaSO_4.2H_2O$, as is shown in the following equations (eq.3., eq.4., eq.5.):

(i) wet deposition reactions:

$$SO_2 \xrightarrow{+H_2O\ from\ atmpsphere} SO_2 \cdot H_2O \xrightarrow{catalytic\ oxidation} H_2SO_4(droplets) \xrightarrow{+CaCO_3/-(H_2O+CO_2)} CaSO_4 \quad (3)$$

$$SO_2 \xrightarrow{+1/2O_2\ c\ catalytic\ oxidation} SO_3(aerosol) \xrightarrow{+H_2O} H_2SO_4(droplets) \xrightarrow{+CaCO_3/-(H_2O+CO_2)} CaSO_4 \quad (4)$$

(ii) dry deposition reactions:

$$CaCO_3 + SO_2 \xrightarrow{H_2O/-CO_2} \left\{ \begin{matrix} CaSO_3 \cdot 1/2H_2O \\ CaSO_3 \cdot 2H_2O \end{matrix} \right\} \xrightarrow{+1/2O_2\ and\ H_2O(atmosphere)} CaSO_4 \cdot 2H_2O \quad (5)$$

Because gypsum is more water soluble than calcite (2.4 g/L at 25°C), the majority of it can precipitate on the carbonate stone surfaces that are not washed directly by rain leading to the black crust formation (Comite et al., 2020b; Pozo-Antonio et al., 2022; Searle and Mitchell, 2006).

In areas subjected to rainwater washing, a fraction of gypsum is removed from the limestone surface by dissolving. This phenomenon leads to the loss of calcareous material and damage to the details of the monuments/statues. Additionally, new calcite layers are exposed to the acidic actions, and additional gypsum is formed (Comite et al., 2020b; Pozo-Antonio et al., 2022).

The development of the superficial gypsum layer on the limestone surface is a relatively rapid process and can be catalyzed by a series of metals and metal oxides (McAlister et al., 2008).

During the formation of the gypsum layer, some aerosol particles, carbon particles from the air, or particles originating from anthropogenic activities (e.g. fuel burning, transport, construction, industrial activities, agriculture, etc.) can be trapped in the crystal matrix of gypsum and calcite and the formed layer may darken over time resulting the black crust (Searle and Mitchell, 2006; Urosevic et al., 2012) Black crust is considered to be one of the most dangerous deterioration forms of building materials caused by anthropogenic air pollution (Battista and de Lieto Vollaro, 2017; Comite et al., 2020a). Based on the stratographic studies carried out by Ivaskova et. al. and Schiavon et al. it was discovered that the black crusts grow both inwards and outwards to the original surface of the stone (Ivaskova et al., 2015; Schiavon, 2002; Schiavon et al., 2004).

Nitrogen dioxides (NO_2) are also important atmospheric pollutants with acidifying effects on limestone and marble. Along with H_2SO_4, nitric acid plays an important role in wet and dry acid depositions. Although HNO_3 can react with calcium carbonate in limestone leading to calcium nitrate [$Ca(NO_3)_2$] formation, still, its role in the deterioration process of carbonate stone is not very clear (Reyes-Trujeque et al., 2010).

Even if marble is more compact than limestone, it is affected by dry and wet acid depositions and forms superficial layers of black crusts but at a lower rate (Christodoulakis et al., 2017; Ruffolo et al., 2015). Bugini et al., studying the kinetics of the black crust formation process on the surface of two Carrara marble monuments, showed that the amount of gypsum formed per surface unit was 5-13 mg/cm^2, and the formation rate of gypsum in the black crust was about 0.2 mg/cm^2 per year (Bugini et al., 2000).

Studies on the chemical composition of black crusts have shown that, in addition to gypsum crystals, they may contain traces of iron oxides, heavy metals, elements of the stone substrate such as quartz and calcite, organic compounds, elementary carbon, alkaline chlorides, dust, etc. In some cases, even traces of calcium oxalate resulting from the partial oxidation of organic carbon were found. (La Russa et al., 2018; La Russa et al., 2017; McAlister et al., 2008; Pozo-Antonio et al., 2022; Vidal et al., 2019).

The formation of black crusts is a complex process that is sometimes correlated with the growth of bacteria, algae, lichens, and fungi (Li et al., 2018; Ortega-Morales et al., 2019; Pinheiro et al., 2018; Schiavon, 2002). **Figure 8** shows some limestone and marble monuments affected by chemical weathering processes.

3.2.4. Analytical techniques for characterizing the limestone chemical weathering

Various investigative techniques have been employed to characterize the stone materials from historic buildings or monuments as well as the composition of the black crust. Thus, techniques such as optical microscopy (OM), polarized light optical microscopy (PLOM), and fluorescence optical microscopy (FLOM) were used in petrographic and topographic analysis both to determine the textural characteristics of carbonate stone and to evaluate the morphology and the growth rate of black crusts (Cardell et al., 2008; Comite et al., 2020b; Gulotta et al., 2013; La Russa et al., 2017; Pozo-Antonio et al., 2017).

X-ray powder diffraction (XRPD) and X-ray fluorescence (XRF) techniques were used to investigate the carbonate stone and black crusts' mineralogical composition (Comite et al., 2020a; Comite et al., 2020b; Graue et al., 2013; Wahab et al., 2019).

Electron microscopy technique (SEM) was specifically used to acquire images of carbonate stones and black crusts at high magnification (Comite et al., 2020a; Comite et al., 2020b; Graue et al., 2013; Pozo-Antonio et al., 2022; Wahab et al., 2019; Zhao et al., 2019), and coupled with energy dispersive X-ray spectrometry (EDX) was a useful technique for obtaining information about the micro-morphology and chemical composition, in terms of major elements, of the building materials and black crusts (La Russa et al., 2018; La Russa et al., 2017; Livingston, 2016; Vyshkvarkova and Sukhonos, 2023; Zoghlami et al., 2019).

Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) was useful for geochemical composition analysis in terms of elements traces of the black crusts (Comite et al., 2020b; Pozo-Antonio et al., 2022; Ruffolo et al., 2015).

Atomic force microscopy (AFM) provided real three-dimensional topographies that showed the surface properties of the carbonate stones (Pozo-Antonio et al., 2022; Zhao et al., 2019).

Fourier transform infrared spectroscopy coupled with attenuated total reflectance (FTIR-ATR) was performed to identify the mineralogical phases of the carbonate building materials and also identify the presence of black crusts and entrapped organic and silicate compounds (La Russa et al., 2018; La Russa et al., 2017; McAlister et al., 2008; Ruffolo et al., 2015).

Thermogravimetric analysis (TGA/DTG) coupled with differential thermal analysis (DTA) was used to determine the content of moisture and calcium carbonate in calcareous materials, as well as to determine the content of elemental carbon (EC), inorganic carbon (AC) and organic (OC) from black crusts (Comite et al., 2020b).

Ion chromatography (IC) has been employed for quantification of the main ions from black crusts (Zhao et al., 2019).

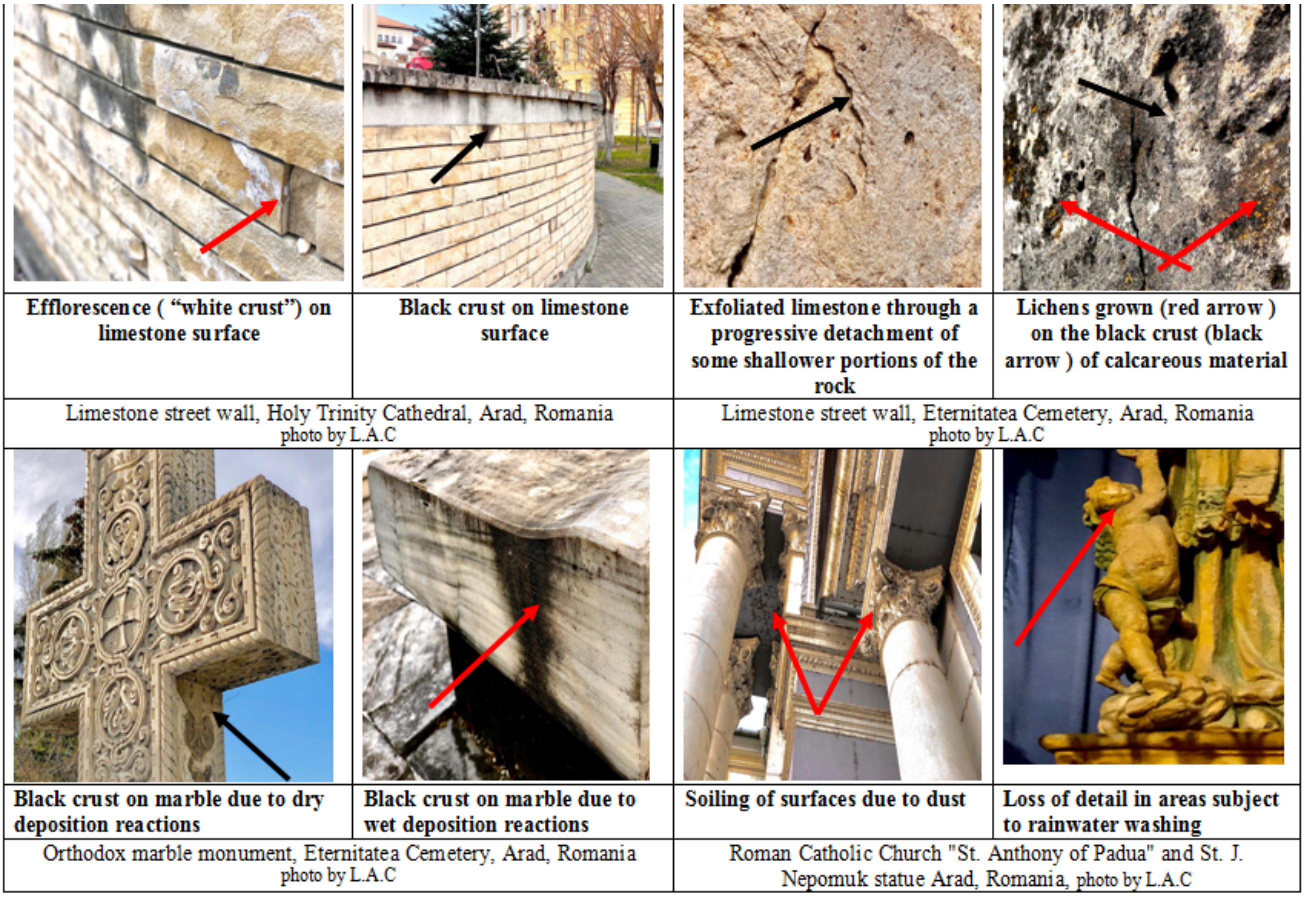


Figure 8. Chemical weathering (chemical degradation) of limestone and marble building materials

3.2.5. Soiling

Along with the black crust, the soiling phenomenon leads to the darkening of the heritage buildings' surfaces (**Figure 8**.- the case of the street facade at the entrance to the Roman Catholic Church "St. Anthony of

Padua", Arad, Romania). Although it is related to the formation of dark depositions, soiling is not a chemical degradation process because it represents an accumulation of dust particles on the non-reactive surfaces of buildings and statues. Unlike the black crusts consisting of gypsum and calcite crystals, the solid particles accumulated in the soiling layer can be easily removed by a washing treatment. The soiling phenomenon of the facades depends on several factors, such as meteorological factors, wind-rain interaction, porosity and roughness of the surfaces, the facade's setup, the inclination of the walls and windows, the existence of architectural edges, etc. (Urosevic et al., 2012; Vidal et al., 2019; Weththimuni et al., 2022). All these factors act synergistically leading to localized accumulations of dust and dirt particles. According to Grosii and Brimblecombe, the soiling process of the buildings and monuments is only an aesthetic problem, largely dependent on the degree of public acceptance (Grossi and Brimblecombe, 2004).

3.3. Bio-deterioration

The historical buildings' stones, due to the contained minerals, are ideal substrates for the growth and proliferation of various microorganisms such as cyanobacteria, algae, fungi, or some macroscopic organisms such as lichen mosses, plants (Li et al., 2018; Liu et al., 2022).

The microorganisms formed on the stones' surface so-called "biofilms" represent the microorganisms' growth communities. According to Mascaro et al., biofilms are complex mono- or multilayered systems of one or more species of microorganisms that can grow attached to any solid substrate and can excrete protective materials, usually proteins and sugar polymers, to produce extracellular exopolysaccharides matrix (EPS) in which phototrophic and heterotrophic organisms are incorporated. (Mascaro et al., 2022). From bacterial metabolism, a series of secondary acidic compounds (i.e. oxalic acid) can result that cause chemical degradation of stone materials. In addition, EPS accelerates the physical deterioration processes of materials, as the biofilm swells and shrinks in the stones pore network, which can cause micro-fractures (Skipper et al., 2016; Warscheid and Braams, 2000). The composition of the biofilm microbiota depends on various factors, such as environmental ecology, microbial biodiversity, climatic conditions, physico-chemical properties of the stone substrate, nutrient availability, etc (Ortega-Morales et al., 2019). The aspect and color of biofilm depend on microorganisms' growth level, microbiological formations thickness, surrounding environment characteristics, and type of biocenosis (Mascaro et al., 2022; Pinheiro et al., 2018).

The algal partner, also called photobiont, through the process of photosynthesis and CO_2 fixation produces polysaccharides that constitute food for the fungal partner (Liu et al., 2022). This helps the fungus survive in nutrient-poor conditions. On the other hand, algae take advantage of the fungus presence that protects them from the action of UV radiation and ensures the necessary humidity for their development. According to Warscheid and Braams, fungi form a dense crust around an inner layer, the latter being composed of loose hyphae associated with algal cells (Warscheid and Braams, 2000).

A pair of symbiotic organisms consisting of an alga (or cyanobacteria) in close spatial and physiological association with a fungus forms lichens with different thallus (e.g. foliose lichens form a coral-like thallus; fruticose lichens form a leaf-like thallus; squamulose lichen forms a flat thallus with small lobes at the top, etc.). The symbiotic relationship between fungus-algae/cyanobacteria favors the lichen's development on stones that are poor in nutrients and arid places (Matteucci et al., 2019). In the case of stones and rocks, crustose lichens are predominating and can strongly adhere to surfaces (Cozzolino et al., 2022; Santo et al., 2021).

The bio-deterioration or bio-degradation phenomena due to some organisms or microorganisms can occur on all types of stone substrates and in all climatic zones (Paiva et al., 2022; Zhang et al., 2023).

For instance, in environments with natural light and high humidity, the phototrophic subaerial biofilm consisting of epilithic organisms is growing (Mascaro et al., 2022; Skipper et al., 2016) while in arid and semi-arid areas, the biodeteriogens that develop on stones' surfaces are black rock fungi, also known as rock-inhabiting fungi or micro-colonial fungi (Gadd, 2017; Isola et al., 2022).

According to Isola et al., the black rock fungi are a polyphyletic poikilotolerant morpho-ecological group excellently adapted to extreme temperature changes, drought, starvation, osmotic stress, and high ultraviolet solar radiation (Isola et al., 2022). Anyway, fungi are considered the most important colonizers of stones, being omnipresent on the surfaces of monuments and buildings in all climatic zones. Fungi are heterotrophic organisms with a more versatile metabolism than other biodeteriogenic agents, which allows them to colonize a wide range of substrates (e.g. wood, metal, stone, etc.) (Gadd, 2017; Liu et al., 2022; Paiva et al., 2022).

Bio-deterioration is defined as "any unwanted modification of a material caused by the vital activities of organisms or microorganisms" and is a secondary phenomenon that frequently occurs on buildings' stone surfaces (Mascaro et al., 2022; Ortega-Morales et al., 2019). The bio-deterioration is influenced by the stone's bio-receptivity, which represents the availability of a material to be invaded by a living species. Each heritage monument is characterized by its bio-receptivity that depends on several factors such as the construction structure, petro-physical and chemical properties of the building materials, materials' pH and moisture quantity, chemical or physical degradation degree of the surfaces, preservation state, weathering conditions or surrounding atmosphere pollution, etc. (Fistos et al., 2022; Liu et al., 2022).

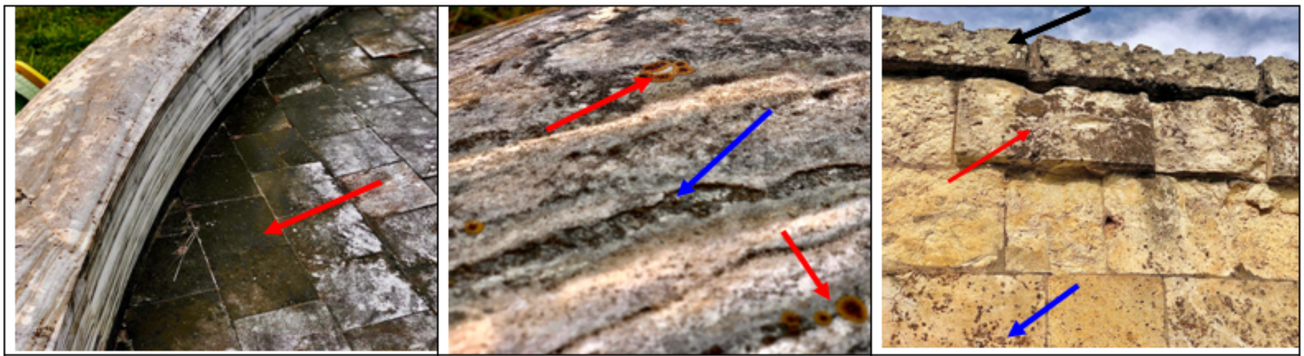
The interaction between the building material and the biodeteriogen is a complex one. Caneva and Ceschin proposed the "ecology of bio-deterioration" concept that highlights the close relationship between the colonization organisms of the stone materials and all the environmental factors that regulate their growth (Caneva and Ceschin, 2009). Calcareous substrates such as limestone and marble have a high intrinsic bio-receptivity being vulnerable materials to bio-deterioration. (Paiva et al., 2022; Pinheiro et al., 2018; Trovão et al., 2020).

Recent studies have shown that black fungi can penetrate and develop in deep areas within limestone and marble materials (Isola et al., 2022; Liu et al., 2022; Paiva et al., 2022; Vyshkvarkova and Sukhonos, 2023; Warscheid and Braams, 2000; Zhang et al., 2023).

In the case of historical monuments made of calcareous materials, the bio-deterioration produced both aesthetic damage and irreversible degradations due to the changes in the chemical composition of carbonate stones. For example, epilithic organisms such as cyanobacteria and green algae caused the marble's colour change, affecting the aesthetics of the monuments (Isola et al., 2022; Mascaro et al., 2022; Skipper et al., 2016). The accumulation of photosynthetic biomass over time facilitates the penetration of the microbial biofilm into the cracks and pores of the limestone and marble, thus intensifying the activity of the endolithic organisms that decomposed the stone material through various physico-chemical processes (Sterflinger and Piñar, 2013; Warscheid and Braams, 2000). Over time, fungi have led to the bio-deterioration of carbonate rocks in historical monuments through several physico-chemical mechanisms, often with synergistic action. These mechanisms resulted in the appearance of bio-pitting, the dislocation of minerals, the dissolution and re-precipitation of carbonic salts, etc. (Gautam et al., 2022; Paiva et al., 2022; Skipper et al., 2016; Warscheid and Braams, 2000).

Studies have shown that both epilithic and endolithic lichens are present in historic calcareous materials. In the case of epilithic lichens, their thallus is mostly on the materials' surface and only single hyphae (filaments) have penetrated the substrate. In the case of endolithic lichens, most of the thallus is inside the cracks and fissures of the substrate and only the fruiting bodies are visible on the surface (Mascaro et al., 2022; Matteucci et al., 2019; Pinheiro et al., 2018; Santo et al., 2021; Schiavon, 2002; Urosevic et al., 2012).

In addition, under favorable growth conditions, also vascular plants were able to colonize the calcareous materials contributing to their damage (Mascaro et al., 2022; Schiavon, 2002), as shown in **Figure 9**.



Algae developed on the marble surface	**Lichens developed on the marble surface** (red arrows: epilithic lichens; blue arrow: the marble' cracking and delamination due to bio-deterioration)	**Lichens developed on the limestone surface** (red arrow: epilithic ; black arrow: endolithic; blue arrow: bio-pitting)
Orthodox marble monument, Eternitatea Cemetery, Arad, Romania photo by L.A.C		Limestone street wall, Holy Trinity Cathedral, Arad, Romania photo by L.A.C

Figure 9. Bio-deteriorations of limestone and marble building materials

Studies have shown that both epilithic and endolithic lichens are present in historic calcareous materials. In the case of epilithic lichens, their thallus is mostly on the materials' surface and only single hyphae (filaments) have penetrated the substrate. In the case of endolithic lichens, most of the thallus is inside the cracks and fissures of the substrate and only the fruiting bodies are visible on the surface (Mascaro et al., 2022; Matteucci et al., 2019; Pinheiro et al., 2018; Santo et al., 2021; Schiavon, 2002; Urosevic et al., 2012).

3.4. Atrophic deterioration

Along with physical, chemical, and biological factors, some human actions can contribute to the degradation of heritage monuments. Thus, inefficient drain and sewerage systems or inadequate urban systematization or landscaping works can lead to an increase in humidity through capillarity inside the building materials (Fistos et al., 2022).

The gaseous emissions resulting from combustion processes at the domestic, industrial, or transport levels amplify climate changes and increase the aggressiveness of dry and wet acid deposits with the previously shown consequences on historical buildings (Sesana et al., 2021; Vyshkvarkova and Sukhonos, 2023).

Agricultural activities or those involving the enrichment with nitrates or chlorides of the soil in direct contact with the heritage monuments represent a real danger for them.

Conservation works and inappropriate restoration treatments play an important role in the deterioration of cultural heritage (Doehne and Price, 2011; Gulotta et al., 2013; Rodrigues, 2015).

Another frequently encountered damage factor in today's society is represented by graffiti, which can be considered an act of vandalism (Merrill, 2011). Present around us, graffiti affects historic monuments and it is particularly difficult to counteract because the materials associated with graffiti include a series of agents (i.e. paints, polyurethanes, varnishes, enamels, chalk, adhesives, etc.) that can induce several physico-chemical degradation processes with a damaging effect on the historical monuments. Additionally, graffiti removal works may involve the use of abrasive materials leading to further degradation (Fistos et al., 2022).

CONCLUSIONS

The protection and preservation of historical monuments, as part of the world's architectural heritage, plays an important role in the development of modern communities.

The intrinsic properties and structure of the stone materials that were used for the historical monuments were affected by the atmospheric environment since the construction moment. Several studies reviewed in this paper have shown that with the development of industrial activities and transport, buildings, and monuments of the world heritage have shown a series of significant damages induced by a significant increase in the concentrations of some atmospheric pollutants.

Following the aspects and examples presented in this paper, daily or seasonal temperature variations, the underground water and atmospheric humidity, the freeze-thaw cycles, the winds, snows, and rains, the repeated processes of dissolution/re-crystallization of water-soluble salts inside pores or on surfaces, the biological/micro-biological agents (cyanobacteria, algae, fungi, lichen mosses, etc.), the particulate matter and polluting gases with an acidifying action (i.e. CO_2, SO_2, NO_2, PM, etc., resulting from anthropogenic activities) are the most important extrinsic factors that have induced, over time, a series of physical, chemical or biological weathering and deterioration processes or aesthetic problems of the carbonate stones (limestone and marble) from heritage buildings.

Surface erosion, fissures, exfoliation, splitting, delamination or contour scaling, formation of alveolar structures (honeycombs), increase in cavity and pore size, and development of plants or plant roots in cracks are the physical weathering processes, while, the Karst effect, the efflorescence ("white crust")/sub-florescence appearance, and the black crust formation are the main chemical weathering processes leading to the deterioration of carbonate building stones.

The existence of biofilm and lichens and black rock fungi colonies on the calcareous stones surfaces is an indicator of bio-deterioration, which together with some anthropogenic actions (improper works, wrong reconditioning, graffiti, etc.) determines the physical, chemical, or aesthetic degradation of historical buildings.

REFERENCES

Amer Khalil, N., 2020. The possibility of using limestone rocks in sculpture as an alternative to marble: An empirical study. PalArch's Journal of Archaeology of Egypt / Egyptology 17, 15061-15069.

Aucouturier, M., Darque-Ceretti, E., 2007. The surface of cultural heritage artefacts: Physicochemical investigations for their knowledge and their conservation. Chemical Society reviews 36, 1605-1621.

Badouna, I., Koutsovitis, P., Karkalis, C., Laskaridis, K., Koukouzas, N., Tyrologou, P., Patronis, M., Papatrechas, C., Petrounias, P., 2020. Petrological and geochemical properties of greek carbonate stones associated with their physico-mechanical and aesthetic characteristics. Minerals 10, 507.

Basu, S., Orr, S.A., Aktas, Y.D., 2020. A geological perspective on climate change and building stone deterioration in London: Implications for urban stone-built heritage research and management. Atmosphere 11, 788.

Battista, G., de Lieto Vollaro, R., 2017. Correlation between air pollution and weather data in urban areas: Assessment of the city of Rome (Italy) as spatially and temporally independent regarding pollutants. Atmospheric Environment 165, 240-247.

Benavente, D., de Jongh, M., Cañaveras, J.C., 2021. Weathering Processes and Mechanisms Caused by Capillary Waters and Pigeon Droppings on Porous Limestones. Minerals 11, 18.

Bogdan, A., Chambre, D., Copolovici, D.M., Bungau, T., Bungau, C.C., Copolovici, L., 2022. Heritage building preservation in the process of sustainable urban development: The case of Brasov medieval city, Romania. Sustainability 14, 6959.

Bugini, R., Tabasso, M., Realini, M., 2000. Rate of formation of black crusts on marble. A case study. Journal of Cultural Heritage - J CULT HERIT 1, 111-116.

Caneva, G., Ceschin, S., 2009. Ecology of biodeterioration. Plant Biology for Cultural Heritage. Biodeterioration and Conservation, 35-58.

Cardell, C., Benavente, D., Rodríguez-Gordillo, J., 2008. Weathering of limestone building material by mixed sulfate solutions. Characterization of stone microstructure, reaction products and decay forms. Materials Characterization 59, 1371-1385.

Christodoulakis, J., Tzanis, C.G., Varotsos, C.A., Ferm, M., Tidblad, J., 2017. Impacts of air pollution and climate on materials in Athens, Greece. Atmospheric Chemistry and Physics 17, 439-448.

Comite, V., Pozo-Antonio, J.S., Cardell, C., Rivas, T., Randazzo, L., Russa, M.F.L., Fermo, P., 2020a. Environmental impact assessment on the Monza cathedral (Italy): a multi-analytical approach.

Comite, V., Ricca, M., Ruffolo, S.A., Graziano, S.F., Rovella, N., Rispoli, C., Gallo, C., Randazzo, L., Barca, D., Cappelletti, P., La Russa, M.F., 2020b. Multidisciplinary approach for evaluating the geochemical degradation of building stone related to pollution sources in the historical center of Naples (Italy). Applied Sciences 10, 4241.

Corvo, F., Reyes-Trujeque, J., Valdés, C., Villaseñor, F., Cuesta, O., Aguilar, D., Quintana, P., 2010. Influence of Air Pollution and Humidity on Limestone Materials Degradation in Historical Buildings Located in Cities Under Tropical Coastal Climates. Water Air and Soil Pollution 205, 359-375.

Cozzolino, A., Adamo, P., Bonanomi, G., Motti, R., 2022. The Role of Lichens, Mosses, and Vascular Plants in the Biodeterioration of Historic Buildings: A Review. Plants 11, 3429.

Doehne, E., Price, C., 2011. Stone Conservation: An Overview of Current Research.

Fassina, V., 1988. Environmental pollution in relation to stone decay. Durability of building materials 5, 317-358.

Fistos, T., Fierascu, I., Doni, M., Chican, I.E., Fierascu, R.C., 2022. A short overview of recent developments in the application of polymeric materials for the conservation of stone cultural heritage elements. Materials 15, 6294.

Frank-Kamenetskaya, O., Vlasov, D., Zelenskaya, M., Knauf, I., Timasheva, M., 2009. Decaying of the marble and limestone monuments in the urban environment. Case studies from Saint Petersburg, Russia. Studia Universitatis Babes-Bolyai, Geologia 54.

Gadd, G., 2017. Fungi, Rocks, and Minerals. Elements 13, 171-176.

Gautam, A., Verma, R., Avasthi, S., Sushma, Bohra, Y., Devadatha, B., M, N., Suwannarach, N., 2022. Current Insight into Traditional and Modern Methods in Fungal Diversity Estimates. Journal of Fungi 8, 226.

Graue, B., Siegesmund, S., Oyhantcabal, P., Naumann, R., Licha, T., Simon, K., 2013. The effect of air pollution on stone decay: The decay of the Drachenfels trachyte in industrial, urban, and rural environments-a case study of the Cologne, Altenberg and Xanten cathedrals. Environmental Earth Sciences 69.

Grossi, C., Brimblecombe, P., 2004. Aesthetics of Simulated Soiling Patterns on Architecture. Environmental science & technology 38, 3971-3976.

Gulotta, D., Bertoldi, M., Bortolotto, S., Fermo, P., Piazzalunga, A., Toniolo, L., 2013. The Angera stone: A challenging conservation issue in the polluted environment of Milan (Italy). Environ Earth Sci 69, 1085-1094.

Hall, K., Hall, A., 1996. Weathering by wetting and drying: Some experimental results. Earth Surface Processes and Landforms 21, 365-376.

Isola, D., Bartoli, F., Meloni, P., Caneva, G., Zucconi, L., 2022. Black Fungi and Stone Heritage Conservation: Ecological and Metabolic Assays for Evaluating Colonization Potential and Responses to Traditional Biocides. Applied Sciences 12, 2038.

Ivaskova, M., Kotes, P., Brodnan, M., 2015. Air pollution as an important factor in construction materials deterioration in Slovak Republic. Procedia Engineering 108, 131-138.

Kanani, S., Zandi, H., 2011. A Study of the Damages to Historical Monuments due to Climatic Factors and Air Pollution and Offering Solutions. World Academy of Science, Engineering and Technology, International Journal of Social, Behavioral, Educational, Economic, Business and Industrial Engineering 5, 1018-1021.

Kryza, R., Prell, M., Czechowski, F., Domaradzka, M., 2009. Acidic weathering of carbonate building stones: experimental assessment. Studia Universitatis Babes-Bolyai, Geologia 54, 33-36.

La Russa, M.F., Belfiore, C.M., Fichera, G.V., Maniscalco, R., Calabrò, C., Ruffolo, S.A., Pezzino, A., 2015. The behaviour to weathering of the Hyblean limestone in the Baroque architecture of the Val di Noto (SE Sicily): An experimental study on the “calcare a lumachella” stone. Construction and Building Materials 77, 7-19.

La Russa, M.F., Comite, V., Aly, N., Barca, D., Fermo, P., Rovella, N., Antonelli, F., Tesser, E., Aquino, M., Ruffolo, S.A., 2018. Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their composition. The European Physical Journal Plus 133, 370.

La Russa, M.F., Fermo, P., Comite, V., Belfiore, C.M., Barca, D., Cerioni, A., De Santis, M., Barbagallo, L.F., Ricca, M., Ruffolo, S.A., 2017. The Oceanus statue of the Fontana di Trevi (Rome): The analysis of black crust as a tool to investigate the urban air pollution and its impact on the stone degradation. Science of The Total Environment 593-594, 297-309.

Li, Q., Zhang, B., Yang, X., Ge, Q., 2018. Deterioration-Associated Microbiome of Stone Monuments: Structure, Variation, and Assembly. Appl Environ Microbiol 84, e02680-02617.

Liu, X., Qian, Y., Wu, F., Wang, Y., Wang, W., Gu, J.-D., 2022. Biofilms on stone monuments: biodeterioration or bioprotection? Trends in Microbiology 30, 816-819.

Livingston, R.A., 2016. Acid rain attack on outdoor sculpture in perspective. Atmospheric Environment 146, 332-345.

Mascaro, M.E., Pellegrino, G., Palermo, A.M., 2022. Analysis of Biodeteriogens on Architectural Heritage. An Approach of Applied Botany on a Gothic Building in Southern Italy. Sustainability 14, 34.

Matteucci, E., Scarcella, A.V., Croveri, P., Marengo, A., Borghi, A., Benelli, C., Hamdan, O., Favero-Longo, S.E., 2019. Lichens and other lithobionts on the carbonate rock surfaces of the heritage site of the tomb of Lazarus (Palestinian territories): diversity, biodeterioration, and control issues in a semi-arid environment. Annals of Microbiology 69, 1033-1046.

McAlister, J.J., Smith, B.J., Török, A., 2008. Transition metals and water-soluble ions in deposits on a building and their potential catalysis of stone decay. Atmospheric Environment 42, 7657-7668.

Merrill, S., 2011. Graffiti at Heritage Places: Vandalism as Cultural Significance or Conservation Sacrilege? Time and Mind: The Journal of Archaeology, Consciousness and Culture 4, 59-75.

Mineo, S., Caliò, D., Pappalardo, G., 2022. UAV-Based Photogrammetry and Infrared Thermography Applied to Rock Mass Survey for Geomechanical Purposes. Remote Sensing 14, 473.

Oguchi, C.T., Yu, S., 2021. A review of theoretical salt weathering studies for stone heritage. Progress in Earth and Planetary Science 8, 32.

Olaru, M., Aflori, M., Simionescu, B., Doroftei, F., Stratulat, L., 2010. Effect of SO2 Dry Deposition on Porous Dolomitic Limestones. Materials 3, 216-231.

Ortega-Morales, O., Montero-Munoz, J.L., Neto, J.A.B., Beech, I.B., Sunner, J., Gaylarde, C., 2019. Deterioration and microbial colonization of cultural heritage stone buildings in polluted and unpolluted tropical and subtropical climates: A meta-analysis. International Biodeterioration & Biodegradation 143.

Paiva, D.S., Fernandes, L., Trovão, J., Mesquita, N., Tiago, I., Portugal, A., 2022. Uncovering the Fungal Diversity Colonizing Limestone Walls of a Forgotten Monument in the Central Region of Portugal by High-Throughput Sequencing and Culture-Based Methods. Applied Sciences 12, 10650.

Pappalardo, G., Mineo, S., Caliò, D., Bognandi, A., 2022. Evaluation of Natural Stone Weathering in Heritage Building by Infrared Thermography. Heritage 5, 2594-2614.

Pappalardo, G., Mineo, S., Imposa, S., Grassi, S., Leotta, A., La Rosa, F., Salerno, D., 2020. A quick combined approach for the characterization of a cliff during a post-rockfall emergency. Landslides 17, 1063-1081.

Pinheiro, A., Mesquita, N., Trovão, J., Soares, F., Tiago, I., Coelho, C., Paiva de Carvalho, H., Gil, F., Catarino, L., Pinar, G., Portugal, A., 2018. Limestone biodeterioration: A review on the Portuguese cultural heritage scenario. Journal of Cultural Heritage 36.

Pozo-Antonio, J.S., Cardell, C., Comite, V., Fermo, P., 2022. Characterization of black crusts developed on historic stones with diverse mineralogy under different air quality environments. Environmental Science and Pollution Research 29, 29438-29454.

Pozo-Antonio, J.S., Pereira, M.F.C., Rocha, C.S.A., 2017. Microscopic characterisation of black crusts on different substrates. Science of The Total Environment 584-585, 291-306.

Přikryl, R., Melounová, L., Varilova, Z., Weishauptová, Z., 2007. Spatial relationships of salt distribution and related physical changes of underlying rocks on naturally weathered sandstone exposures (Bohemian Switzerland National Park, Czech Republic). Environmental Geology 52, 409-420.

Reyes-Trujeque, J., Perez, T., Castañeda, A., Corvo, F., 2010. Role of NOx in material corrosion and degradation. Revista CENIC. Ciencias Químicas 41, 1-10.

Reyes-Trujeque, J., Rivera, J., Owen, P., Bartolo, P., Pérez López, T., Casanova-González, E., Corvo, F., 2016. Weathering effects of an historic building in San Francisco de Campeche, Mexico. Intervención Revista Internacional de Conservación Restauración y Museología 7, 22-31.

Rodrigues, J., 2015. Defining, mapping and assessing deterioration patterns in stone conservation projects. Journal of Cultural Heritage 16, 267-275.

Ruffolo, S.A., Comite, V., La Russa, M.F., Belfiore, C.M., Barca, D., Bonazza, A., Crisci, G.M., Pezzino, A., Sabbioni, C., 2015. An analysis of the black crusts from the Seville Cathedral: A challenge to deepen the understanding of the relationships among microstructure, microchemical features and pollution sources. Science of The Total Environment 502, 157-166.

Sabbioni, C., Piccolo, D., Bonazza, A., Favoni, O., Zappia, G., 2001. Soluble and non water soluble sulphates in damage layers on hydraulic mortars. WIT Transactions on the Built Environment 55, 561-569.

Saltık, E., 2018. Atmospheric weathering of historic monuments and their related conservation issues. MATEC Web of Conferences 149, 01009.

Santo, A.P., Cuzman, O.A., Petrocchi, D., Pinna, D., Salvatici, T., Perito, B., 2021. Black on White: Microbial Growth Darkens the External Marble of Florence Cathedral. Applied Sciences 11, 6163.

Schiavon, N., 2002. Biodeterioration of calcareous and granitic building stones in urban environments. Geological Society, London, Special Publications 205, 195-205.

Schiavon, N., Chiavari, G., Fabbri, D., 2004. Soiling of limestone in an urban environment characterized by heavy vehicular exhaust emissions. Environmental Geology 46, 448-455.

Searle, D., Mitchell, D., 2006. The effect of coal and diesel particulates on the weathering loss of Portland Limestone in an urban environment. The Science of the total environment 370, 207-223.

Sena da Fonseca, B., Ferreira Pinto, A.P., Vaz Silva, D., 2020. Compositional and textural characterization of historical bedding mortars from rubble stone masonries: Contribution for the design of compatible repair mortars. Construction and Building Materials 247, 118627.

Sesana, E., Gagnon, A., Ciantelli, C., Cassar, J., Hughes, J., 2021. Climate change impacts on cultural heritage: A literature review. WIREs Climate Change 12.

Skipper, P., Schulze, H., Williams, D., Dixon, R., 2016. Biodeterioration of limestone built heritage: A multidisciplinary challenge.

Spezzano, P., 2021. Mapping the susceptibility of UNESCO World Cultural Heritage sites in Europe to ambient (outdoor) air pollution. Science of The Total Environment 754, 142345.

Sterflinger, K., Piñar, G., 2013. Microbial deterioration of cultural heritage and works of art--tilting at windmills? Applied microbiology and biotechnology 97, 9637-9646.

Török, Á., Licha, T., Simon, K., Siegesmund, S., 2011. Urban and rural limestone weathering; the contribution of dust to black crust formation. Environmental Earth Sciences 63, 675-693.

Trovão, J., Tiago, I., Catarino, L., Gil, F., Portugal, A., 2020. In vitro analyses of fungi and dolomitic limestone interactions: Bioreceptivity and biodeterioration assessment. International Biodeterioration & Biodegradation 155, 105107.

Urosevic, M., Yebra-Rodriguez, A., Sebastián, E., Cardell, C., 2012. Black soiling of an architectural limestone during two-year term exposure to urban air in the city of Granada (S Spain). The Science of the total environment 414, 564-575.

Vergès-Belmin, V., Siedel, H., 2005. Desalination of Masonries and Monumental Sculptures by Poulticing: A Review / Entsalzen von Mauerwerk und Steinfiguren mit Hilfe von Kompressen: Ein Überblick. Restoration of Buildings and Monuments 11.

Vidal, F., Vicente, R., Mendes Silva, J., 2019. Review of environmental and air pollution impacts on built heritage: 10 questions on corrosion and soiling effects for urban intervention. Journal of Cultural Heritage 37, 273-295.

Vyshkvarkova, E., Sukhonos, O., 2023. Climate Change Impact on the Cultural Heritage Sites in the European Part of Russia over the Past 60 Years. Climate 11, 50.

Wahab, G.M.A., Gouda, M., Ibrahim, G., 2019. Study of physical and mechanical properties for some of Eastern Desert dimension marble and granite utilized in building decoration. Ain Shams Engineering Journal 10, 907-915.

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

Weththimuni, M.L., Chobba, M.B., Sacchi, D., Messaoud, M., Licchelli, M., 2022. Durable Polymer Coatings: A Comparative Study of PDMS-Based Nanocomposites as Protective Coatings for Stone Materials. Chemistry 4, 60-76.

Zhang, Y., Su, M., Wu, F., Gu, J.-D., Li, J., He, D., Guo, Q., Cui, H., Zhang, Q., Feng, H., 2023. Diversity and Composition of Culturable Microorganisms and Their Biodeterioration Potentials in the Sandstone of Beishiku Temple, China. Microorganisms 11, 429.

Zhao, C., Zhang, Y., Hou, M., Li, A., 2019. Recent progress in instrumental techniques for architectural heritage materials. Heritage Science 7.

Zoghlami, K., López-Arce, P., Zornoza-Indart, A., 2019. Case Study Differential Stone Decay of the Spanish Tower Façade in Bizerte, Tunisia.

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