

Review

Effects of Water on Natural Stone in the Built Environment— A Review

Carlos Alves ^{1,*}, Carlos A. M. Figueiredo ², Jorge Sanjurjo-Sánchez ³ and Ana C. Hernández ³

¹ LandS/Lab2PT-Landscapes, Heritage and Territory Laboratory (FCT-UIDB/04509/2020), Earth Sciences Department, School of Sciences, University of Minho, 4710-057 Braga, Portugal

² CERENA—Centre for Natural Resources and the Environment, FCT-UIDB/04028/2020, DECivil, Instituto Superior Técnico, University of Lisbon, 1049-001 Lisbon, Portugal; carlos.m.figueiredo@ist.utl.pt

³ University Institute of Geology, University of A Coruña, ESCI, Campus de Elviña, 15071 A Coruña, Spain; jorge.sanjurjo.sanchez@udc.es (J.S.-S.); ana.cristina.hernandez.santome@udc.es (A.C.H.)

* Correspondence: casaix@dct.uminho.pt

Abstract: The present work reviews studies with information on the effects of water by itself on stones of the built environment both to assess the impact of this substance and to discuss possible implications for conservation. The analysis concerns empirical results from previous publications dealing with the effects, on several rock types, of freeze–thaw, wetting, erosion by running water and substances resulting from the water–stone interaction. Laboratory studies have shown that water freezing can cause physical damage even in low porosity rocks. As far as we know, this is the first review that considers comparative laboratory studies of freeze–thaw and salt crystallization on the same rock specimens, and these point to lower erosive effects than salt weathering, as freeze–thaw can provoke catastrophic cracking. Wetting has shown strong damaging effects on some fine-grained clastic rocks. Erosive features have been reported for rain exposition and for some fountain settings albeit, in these field studies, it could be difficult to assess the contribution of pollutants transported by water (this assessment could have meaningful implications for stone conservation, especially in fountain settings). Water also interacts with stone constituents, namely sulfides and soluble salts, releasing substances that could impact those stones. Sulfides are a relatively frequent issue for slates and granites, and our observations suggest that for this last rock type, this issue is mostly associated with the presence of enclaves and, hence, avoiding the surface exposition of such enclaves could solve the problem.

Keywords: laboratory testing; stone decay; freeze–thaw; wetting-drying; fountains; oxidation stains



Citation: Alves, C.; Figueiredo, C.A.M.; Sanjurjo-Sánchez, J.; Hernández, A.C. Effects of Water on Natural Stone in the Built Environment— A Review. *Geosciences* **2021**, *11*, 459. <https://doi.org/10.3390/geosciences11110459>

Academic Editors: Piotr Migoń and Jesus Martinez-Frias

Received: 17 August 2021

Accepted: 3 November 2021

Published: 7 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Water is an important weathering agent in the Earth's crust, both at the surface and underground. Materials in the built environment are also exposed to the changing effects of water and this fluid is an important medium for the transport and alteration effects of other agents such as salts, biological agents and other diverse substances that can be deposited from water.

Our focus in this review will be on the effects of water by itself on natural stone, i.e., rock materials used in the built environment, giving special highlight to the different rock types used in testing. It is our contention that this kind of research will have at least two lines of interest for geoscientists: (a) in a more fundamental perspective, concerning the effects of this geological agent (water) on geological substances placed in a new context (the built environment); (b) in a more applied perspective, the assessment of the effects of pure water from those of water as a carrier of other agents can be relevant for the conservation strategies of built structures. The review will also include comparative studies considering both freeze–thaw and salt crystallization, which are considered two of the main erosive processes in the built environment. As far as we know, this is the first review considering these several perspectives related to the action of water on natural stone in the built environment.

The effects considered will encompass the effects of freeze–thaw, wetting–drying, and erosion by flowing water, and we will close our review considering the contribution of the interaction of water with stone constituents to generate pollutants that can affect the source–stone itself or those nearby. As is tradition in this cross disciplinary field of study, we attempt to use easy to understand and descriptive terms. Nonetheless, the interested reader could find further information on the terminology of stone decay features in a freely available ICOMOS glossary [1]. Readers could also find some further information on the basics of the processes considered in generalist works concerning stone decay such as the classic work by Winkler [2] and the more recent work on stone decay by Siegesmund and Snethlage [3].

2. Freeze–Thaw

Water freezing in pores has been frequently considered to have an important impact on stone decay, and its disruptive effects have been proposed for diverse types of rocks. A recent review of the involved mechanisms can be found in Deprez et al. [4], who also discuss the different field and laboratory techniques for assessment of the effects of this process. We will focus our review on studies that report observations of actual disruption in the specimens. There are several studies that propose equations attempting to relate the evolution of physical properties with freeze–thaw cycles and a summary of several of them can be found in the very recent publication of Jamshidi [5]. The alterations caused by freeze–thaw cycles on the rocks physical properties could also affect the performance of these materials in more demanding situations such as pavements, as is illustrated by the study by Özvan and Direk [6], where some pyroclastic rock types collapse in abrasion tests after freeze–thaw aging.

The total disintegration from freeze–thaw cycles has been observed in the study by Erguler and Shakoor [7] in specimens of clay-rich rocks such as claystones, mudrocks, siltstones and shales, albeit with wide variations of effects among the specimens in the last three types (some specimens of these rocks showed little degradation). The study of 17 rock types (mostly limestones but also a couple of sandstones, a marble, and a gabbro) by Ingham [8] found results that went from the absence of change even at the microscopic scale (in the marble and one of the sandstones) and some microscopic cracks (in gabbro and some limestones) to severe cracking and even complete disintegration for some limestones. This author highlighted that the patterns of breakdown did not resemble those usually observed in buildings and that some porous limestones, which presented good durability in the field, showed worse results than less durable ones, concluding that the conditions of the accelerated test did not reflect the field conditions.

The study by Martínez-Martínez et al. [9] reported specimen breaking and erosion in porous limestones while less porous limestones and a marble did not show visual deterioration. Lubera [10] studied six rock types (a fine-grained conglomerate, a dolostone breccia, a limestone, a sandstone, an amphibolite and two granites); the higher mass loss occurred in specimens of the dolostone breccia (around 6%) and the fine-grained conglomerate (around 4%) but other specimens of these rock types showed mass loss below 0.3% (for the other rock types, the higher mass loss was around 0.5% for a limestone). Korneeva et al. [11] found cracking of limestones specimens that were significant enough to stop the tests.

Rusin and Świercz [12] discuss the relationship between the effects of freeze conditions and water absorption. These authors noted degradation effects in gneiss, some limestones, some dolostones and two of the igneous rocks (a basalt and a diabase), while for other limestones, dolostones and igneous rocks (another diabase and a microgranite), mass variation and visual decay were minimal (in some cases, mass increase was observed).

There are studies of highly porous rocks with high values of water absorption showing low mass loss (below 1.4%) in freeze–thaw tests, as in the study of pyroclastic rocks by Koralay and Çelik [13]. However, these authors also report that some specimens suffered cracking and disintegration during the freeze–thaw tests. In another study in pyroclastic

rocks (tuffs), it was reported a mass loss of 5.55%, although the authors did not find visual evidence of damage on the surface of the specimens (Iucolano et al. [14]).

Usually, low porosity rocks like granite and marble are considered resistant to freeze–thaw. Nonetheless, in the study of Freire-Lista et al. [15], slight erosion and an increase in microcracks were observed in granites (highest porosity value = 1.7%). Tests with marble found mass loss that depended on the freezing temperature used (Luo et al. [16]). The mass loss results were presented in grams and were below 0.30 g, which for marble specimens with 50 mm diameter and 100 mm height would correspond to clearly below 0.5%. The more porous weathered varieties of granite (which, nonetheless, are usable as building stones) can show significant erosive effects under freeze–thaw as shown in the study by Martins et al. [17] in granites with porosities that are not higher than 4.6% (but these authors do not mention prominent cracks in the specimens). The study of Fahey [18] found that schists showed high resistance to freeze–thaw, but there was production of some measurable amount of debris. Lubera [10] refers to a study from 1987 by Evin indicating a little scale detachment and some sanding in a schist.

Some authors have proposed relationships between the effects of freeze–thaw and other characteristics of the pore space. The review by Deprez et al. [4] highlights unimodal and focused pore size distribution, which will improve frost resistance, the occurrence of small size pores, which will enhance freeze–thaw weathering and the presence of ink-bottle pore structures where large pores, draining water from smaller pores will reduce the impact of pressures arising from ice formation. The following recent examples also illustrate the relations between the characteristics of pore features and the impact of freeze–thaw processes. While their main focus was on the importance of porosity, Martínez-Martínez et al. [9] also discuss the impact of the presence of small pores in the affected rock types, as these small pores will increase the effectiveness of stresses due to freeze processes. In a study with two limestones and two volcanic rocks (a lavic and a pyroclastic), Uğur and Toklu [19] refer that the volcanic rocks presented more marked changes, with cracks that caused texture disintegration but did not lead to the specimens' rupture. These authors relate the higher susceptibility of these rocks to existing microcracks and pore space characteristics (open porosity and interconnected pores), with higher resistance for rocks with higher variation in pore size (this study also found chromatic changes in the volcanic rocks and in one of the limestones). The deleterious effects of micropores have been indicated for limestones (Fogue-Djombou et al. [20]) and tuffs (Germinario and Török [21]); although, in the latter case, the authors considered that porosity and strength variations had a bigger impact. Other authors have considered the convergent effects of several factors related to pore space and strength in lavic rocks (Dursun and Topal [22]) and limestones (Hashemi et al. [23]).

The effects of freeze–thaw can be related to other textural features (besides the characteristics of the pore space). Examples in limestones regarding the cracking and breaking along stylolites are presented by Heidari et al. [24,25], Fogue-Djombou et al. [20] and Torabi-Kaveh et al. [26]. Other examples include the effects of a wider distribution of clay minerals that can contribute to some lamination in limestones (Heidari et al. [27]), grain size variations in tuffs (Germinario and Török [21]), the contacts between grains in marbles (Mahmutoğlu [28]), sandstones (Sun et al. [29]) and volcanic rocks (Uğur and Toklu [19]), and between grains and cement in sandstones and limestones, with references to a potential higher durability for sparry cemented limestones (Montiel-Zafra et al. [30]).

An additional point of interest concerns the comparison of the effects of the action of water by freeze–thaw cycles with the impact of salt crystallization. This comparison is presented in Table 1 for sedimentary rocks and in Table 2 for volcanic rocks (most of them concern pyroclastic rocks). In the majority of cases, salt crystallization caused a higher erosive impact. Nonetheless, there are several results showing the impact of freeze–thaw, including instances where freeze–thaw caused catastrophic impact (with the breakage of the specimens).

Table 1. Analysis of comparative studies of salt crystallization (sodium sulfate unless indications otherwise) and freeze–thaw on sedimentary rocks.

Reference	Rock Type	Comparison
Cárdenes et al. [31]	Dolostone, limestone, sandstone	Freeze–thaw—straight fractures; salt crystallization—disaggregation. Results of an alteration index based on visual assessment of effects were generally similar or higher for freeze–thaw, but for three carbonate rocks, salt crystallization caused higher decay than freeze–thaw.
DiBenedetto et al. [32]	Limestone	Higher salt mass loss with salt crystallization (73%) than freeze–thaw (6%).
Ghobadi and Babazadeh [33]	Sandstone	Higher mass loss for salt crystallization (up to almost 50% but some specimens were destroyed before the 15th cycle) than for freeze–thaw (up to 4% but some of these specimens broke before the 30th cycle).
Molina et al. [34]	Sandstone	Mass gain in freeze–thaw and mass loss with salt crystallization (up to slightly over 40%).
Heidari et al. [25]	Limestone	Development of microcracks and fractures along stylolites in freeze–thaw. No mass loss assessment for freeze–thaw. Minor mass loss (up to 0.6%) for sodium sulfate with clear erosion and negligible for magnesium sulfate (up to 0.03%).
Benavente et al. [35]	Limestone	Some erosive effects and fractures for both but mass loss achieved higher values with salt crystallization (up to 2.4%) than with freeze tests (up to 1.7%).
Scrivano et al. [36]	Limestone	Under freeze–thaw, some blocks broke and had irregular mass variation but higher variation around 5%. Mass loss for salt crystallization around 30–35%.
Shekofteh et al. [37]	Limestone	Higher mass loss in salt crystallization tests (around 20%) than in freeze–thaw tests (lower than 3%).
Torabi-Kaveh et al. [26]	Limestone	Specimen broke under freeze–thaw (this was not observed in salt crystallization tests). No mass loss assessment for freeze–thaw. Negligible mass loss for salt crystallization tests with either magnesium sulfate or sodium sulfate (up to 0.1%).
Karakaş et al. [38]	Limestone	Mass loss under freeze–thaw was much higher than with calcium chloride or sodium sulfate but even so very low (0.1%).

Table 2. Analysis of comparative studies of freeze–thaw tests and salt crystallization tests (sodium sulfate unless indications otherwise) on volcanic rocks.

Reference	Rock Type	Comparison
DiBenedetto et al. [32]	Pyroclastic rocks.	Disintegration with salt crystallization (at 9th cycle) and breaking along cracks for freeze–thaw (at 20th cycle).
Bozdağ et al. [39]	Pyroclastic rocks	Specimen breaking for freeze–thaw and for salt crystallization (generally higher erosion for salt crystallization, which achieved considerable breakage of the specimens). Freeze–thaw: spalling and flaking at the edges for the massive type; granular surface for the vesicular type.
Dursun and Topal [22]	Lavic rocks	Salt crystallization (magnesium sulfate): flaking and chipping off along specimens' edges, which are smoothed off, surface cavities and breakage along rock structural discontinuities in the massive type; flaking, spongy appearance and total disintegrated for the vesicular type.
Germinario and Török [21]	Pyroclastic rocks	Freeze–thaw tests were stopped after 8 cycles due to physical degradation for two types (but mass loss < 5%) while the other two types did not show major changes after 90 cycles. Mass loss was higher (for any type) with salt crystallization tests.
Çelik and Sert [40]	Lavic rock	Low mass loss in each case (below 1.0%) but results for sodium sulfate were around 8 times higher.

Another kind of comparative study consists of performing freeze–thaw cycles after imbibition with solutions with different compositions, where imbibition with water will correspond to the basic freeze–thaw tests while the others represent the contribution,

furthermore, of the presence of other pollutants in solution. These studies could represent field situations where freeze–thaw cycles affect stones already contaminated by those other pollutants. The results of the few studies using this comparative approach that we were able to find are reviewed in Table 3 and they seem to point to a higher impact caused by the presence of salts (in comparison with pure water). We can include in this kind of test the performing of freeze–thaw tests in rock specimens coupled with cements (as it will be expected that the cement contributes with salt pollution) as in the study developed by Török and Szemerey-Kiss [41] using specimens of two limestones coupled with different types of cement. Results show significant erosive features in one of the limestone types, but there seem to be variable erosive features in the limestones for different types of coupled cement (which can be seen as reinforcing the idea of the different salt contributions of the cement).

Table 3. Analysis of comparative studies of freeze–thaw tests with water and other solutions.

Reference	Rock Type	Other Solutions	Comparison
Williams and Robinson [42]	Sandstone	Ammonium alum, aluminum alum, calcium sulfate, potassium alum, sodium chloride, a mixture of ammonium alum and ammonium alum, mixtures of calcium sulfate with each of the alum salts and also ammonium potassium alum, a mixture of calcium sulfate and sodium chloride.	Most salt solutions caused a higher mass loss (highest value for sodium chloride that achieved around 94%) than pure water (mean mass loss of around 3.6%) but calcium sulfate caused a similar mean mass loss and some salt solutions (aluminum alum and a mixture of aluminum alum with calcium sulfate) achieved less mass loss than the tests with water.
Zhang et al. [43]	Sandstone	Sodium chloride, sodium hydroxide, sulphuric acid.	Higher mass loss using solutions of sodium hydroxide (around 7%) and sodium chloride (4%) than with sulphuric acid (almost 1%) and water (which caused almost no variation). All specimens showed mass loss and increasing roughness but those with magnesium sulfate suffered higher variations (but mass loss was not higher than 2.4%).
Sun et al. [29]	Sandstone	Magnesium sulfate (with two concentrations).	

3. Wetting

Moisture variations (due to wetting–drying) have been indicated as a potential alteration agent of natural stone. There is the obvious chromatic effect (wetter materials are darker), but physical disruption with consequent erosion has also been ascribed to wetting–drying cycles. Several publications have attempted to relate the evolution of rocks' properties to wetting–drying cycles, and a recent review can be found in Zhang et al. [44].

There are several examples of laboratory studies on the effects of wetting–drying and, perhaps, the type of natural stone that has been more studied in this regard has been sandstone. The deleterious effects of wetting–drying have been associated with the presence of clay minerals (Jiménez-González et al. [45]; Tiennot et al. [46]), and with variations of physical properties, micro-crack patterns and surface roughness (Zhou et al. [47]; Tiennot et al. [46]). Sumner and Loubser [48], in a study with sandstones, found mass loss, as granular particles, around three times higher than the control specimen (used to assess the error of mass measurement). According to Zhou et al. [47], wetting–drying affected the cement between grains in sandstones. The effect of clays under wet–dry cycles might be enhanced by the presence of soluble salts such as sodium chloride, according to a study by Sebastián et al. [49] based on swelling behavior of the specimens (and field observations). Decay due to moisture variations has also been linked with the relation between water and the pore system, according to laboratory swelling studies (Ruedrich et al. [50]). An et al. [51] observed increasing roughness (albeit at the micrometric scale) and microcracking that the authors attributed to feldspar hydrolysis, clay swelling and mineral dissolution.

However, the effects of wetting–drying have also been mentioned for other rock types. Hall and Hall [52] mention the loss of splinters from sandstones and a dolerite, with one of the sandstones achieving a mass loss around 5%. According to Trenhaile [53], the downwearing of specimen surface was higher in an argillite, followed by a sandstone (between around an eighth and less than half of the argillite reduction) and a basalt (which was almost negligible; between around a tenth and around half of the reduction observed in the sandstone). The concentration of clay minerals in stylolites of limestones has been proposed to explain cracking along these features (besides changes in physical properties) under wetting–dry tests (Aly et al. [54]). Studies on schists have observed a slight mass loss (Mottershead [55]) and fracturing and splitting (Wells et al. [56]). Swelling and strength decrease have been related to the presence of clay minerals for limestones (Aly et al. [57]) and for tuffs (Pötzl et al. [58]), a process also reported for other igneous rocks such as kersantite, affecting cracking patterns (Tiennot et al. [59]). Also in tuffs, the effects of wetting–drying were ascribed to the interaction between water and pore characteristics and zeolites (Lubelli et al. [60]). In another study with tuffs, which were subject to cycles simulating sunlight and condensation, a mass loss of 1.5% was found (Iucolano et al. [14]). Tests with two basalt types reported mass loss up to 1% (Dursun and Topal [22]). Noor-E-Khuda and Albermani [61] performed wetting–drying tests with tap water on two gabbroic rocks and a granite that showed very slight mass loss (around 0.1%) for one of the gabbroic rocks and mass gains in the other rock types studied (the mass gain results could reflect added mass from the tapwater, a situation that could also affect the results of the rock showing mass loss). According to Pozo-Antonio and Alonso-Villar [62], a slight mass loss was observed for two granite types (0.25% for one type and 0.1% for the other) as well as a reduction in surface lightness (L^* parameter from CIELAB). There is even a study on a peculiar rock resulting from debris from a meteoritic impact on the decrease in strength on the wet state, which implied higher susceptibility (Heap et al. [63]).

Extreme results have been obtained under wet-drying cycles for fine-grained clastic rocks. Erguler and Shakoor [7] report intense degradation by wetting–drying cycles on claystones, mudrocks, siltstones and shales (albeit in the last three types some specimens were little affected). Studies with mudstones have shown intense degradation (Hu et al. [64]; Sakai and Nakano [65]; Zeng Ling et al. [66]).

An example of significative mass redistribution was observed by Beck and Al-Mukhtar [67] with the formation by wetting–drying cycles of a calcite patine in limestone. Tests with alabaster (gypsum-rich material) performed by Bustamante et al. [68] attained a mass loss slightly below 14% in conditions of immersion and shaking, using water with “natural” pH (i.e., the pH of water in equilibrium with atmospheric CO₂ without human contributions; pH = 5.6), which was prepared by mixing tap water (pH around 7) and distilled water (pH = 4.5). Visual observations in this last study showed some noticeable dissolution with clay-filled fissures developing a positive relief. The development of fractures on siltstones was observed in wetting–drying tests, mostly at the surface in the beginning and henceforth propagating to the rest of the specimen (vertically and horizontally) with further cycles, developing a fracture network (Zeng et al. [69]).

We will also include here information from studies of rock immersion such as the jar slake test, which does not involve mechanical abrasion (given that our focus here is on the behavior of stone). These studies have shown the degradation effect of immersing in water specimens of shales (Vallejo et al. [70]; Santi [71]; Santi and Higgins [72]), with Vallejo et al. [70] linking the effect to pore size distribution. Linked to our discussion above concerning wetting–drying, a study with several clay-rich types (shales and a marl) obtained results suggesting that air drying time before immersion lead to increasing degradation (Youn and Tonon [73]). Similar results have been reported for mudrocks (Venter [74]) and siltstones (Phien-Wej et al. [75]). This kind of test (by immersion in water) has been used in the specific context of cultural heritage, as in the study of the Taya caves in Japan, showing that the siltstone material could suffer total disintegration by immersion in water (Germinario et al. [76]).

4. Erosion by Flowing Water

Some examples of the erosive effects of running water can be mentioned. Winkler [2] observed that columns of carbonate rocks (marble and limestones) often present patterns according to exposition, with the side exposed to rain presenting marked erosion while on the protected side the finishing is preserved. This is the symmetrical pattern of what would be expected if the erosion features were related to salt crystallization since the sheltered portion will promote salt crystallization. Bonazza et al. [77] present another study based on the exposure of marbles and review several other studies, proposing that rain can have an erosive effect, especially in low porosity carbonate rocks, even in the cases of low pollution (hence mostly related to the effect of water). Some more recent examples include the preferential leaching of magnesium from the structure of minerals in a serpentinite, with discoloration and small scaling of these stones (Gulotta et al. [78]). Gulotta et al. [79] present a case of marble erosion in exposed portions attributed to meteoric waters. A study on sandstones pillars by Waragai and Hiki [80] related depth values for hollows in these stone elements to rainfall.

Stones in fountains are in continuous contact with running water, which has been related to erosion in fountains of carbonate rocks (Bello et al. [81]; Sarró et al. [82]; Sanjurjo-Sánchez and Alves [83]), with observations of calcitic marbles being more affected than dolomitic marbles (deAzcona Fraile et al. [84]) and dolostone showing higher resistance than limestone (Freire-Lista and Fort [85]).

However, one must be aware of the limitations in the constraining of variables involved in field studies. It will be difficult to assess whether the effects related are linked only to the passage of water or are influenced by the presence of other pollutants in a decisive way, by which we mean that the results observed will not develop in the presence of water alone and in the absence of those other pollutants. In the effects of other pollutants, we include agents such as soluble salts but also the presence of acidic or basic ions that fundamentally change the pH or ionic force of the passing “waters”. For example, in a case study of a fountain built with marbles, López de Azcona et al. [86] report on how the water in the closed circuit, due to atmospheric pollutants, tends to increase its acidity with time (as well as other chemical contents), which then impacts the stones.

There are other situations where erosive features are associated with water-rich environments such as fountains but that present distribution patterns that do not seem related to water flow. One such situation is illustrated in Figure 1, with several scales in a granitic fountain in places located away from the water flow (the role of water will not be clear in this case).

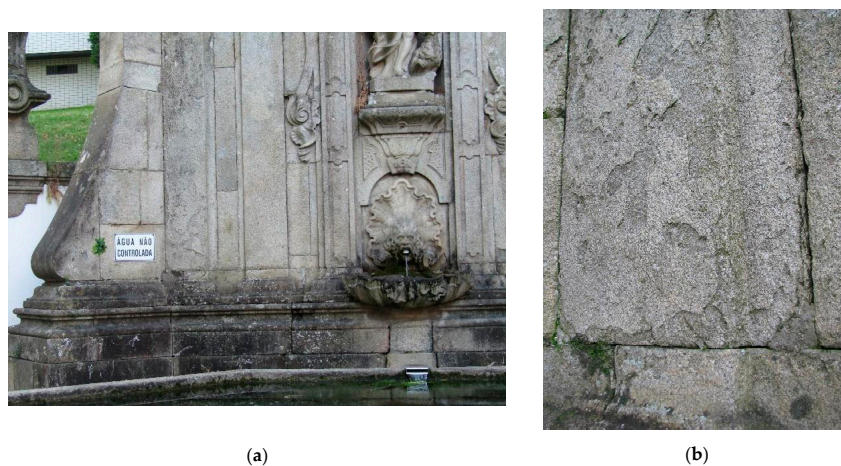


Figure 1. Example of erosive features on granite stones in a water fountain of Braga (NW Portugal): (a) general view showing the position of the eroded portions in relation to the water flow (to the left, near the warning in Portuguese—“ÁGUA NÃO CONTROLADA”); (b) detail of the erosive features.

5. Water as Releaser of Pollutants from Stones

As stated in the introduction, we do not focus here on water as a promoter of the action of other agents. Nonetheless, we will consider situations where water releases pollutants from the stone, which then contribute to the alteration of those stones or others.

The passing water can react with the rock constituents and promote the release of substances that will be deposited further along (according to the water flowpaths). A relatively recent example is the field study of a fountain by Ďoubal [87] linking the dissolution of limestones by acid rain to the formation of gypsum in sandstones below those limestones. However, as in the examples discussed above, the effects of the solutions involved could be significantly related to the presence of other pollutants in water.

Sulfides are constituents that are particularly sensitive to oxidation, which can lead to unseemly stains and sometimes be associated with local erosion (albeit it is unclear whether the erosion resulted directly from the oxidation of sulfides or from the action of salts resulting from it). We have observed the effects of sulfide oxidation in marbles, slates, and granites (an example from the latter in a contemporary structure is presented in Figure 2), but there are examples from other rock types such as limestones (Dreesen et al. [88]). The presence of sulfides is one of the points explicitly addressed by standards about technical specifications of slates (Cárdenes et al. [89]). According to a survey developed by Cárdenes et al. [90], oxidation stains account for around 86% of the costs associated with litigations related to slate pathologies for a company. Commercial reclamations related to oxidation stains in the application of granite slabs have also been relayed to the first author by a former student. In the case of granites, the observations we have made show these limited stains associated with enclaves. Other minerals with iron have been mentioned as sources for the development of stains and coatings such as kutnohorite (Zha et al. [91]) and biotite and other iron-bearing minerals in trachytes (Germinario et al. [92]).

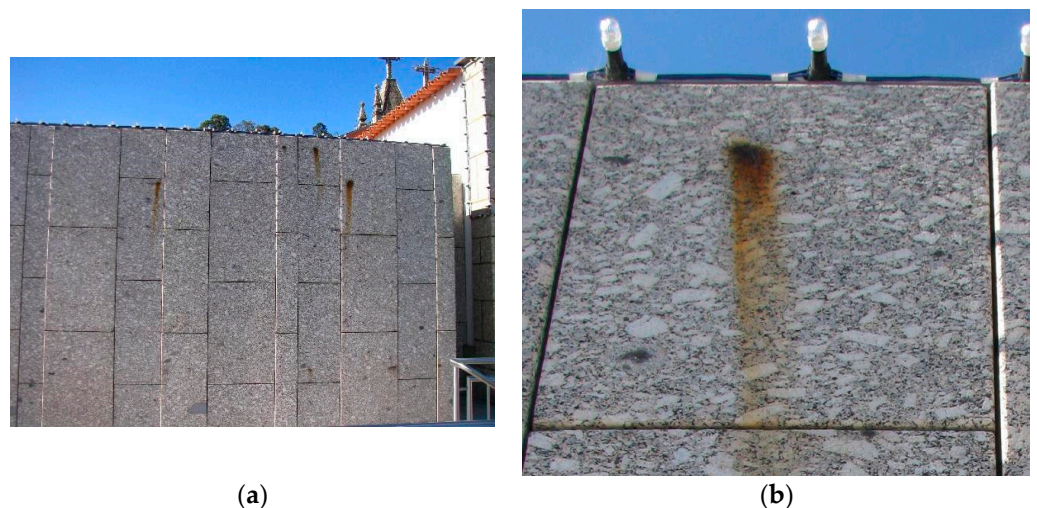


Figure 2. Oxidation stain associated with the presence of iron sulfides in granite stones on the wall of a contemporary structure: (a) general view showing several stains; (b) detail of one of the stains showing the stain crossing the boundary between two stones.

When the rocks surfaces are the stone materials, in the sense that the cultural information is recorded on them, the circulation of water through the rock formations can promote the genesis of agents with deleterious effects in the cultural information. Some examples can be found concerning the genesis of soluble salts in caves in siltstones (Germinario et al. [76]) and tuffs (Germinario and Oguchi [93]).

Sometimes the rocks are already enriched in soluble salts that are easily dissolved by passing water, as in the studies (all in sandstones) of Zehnder in 1982 and Blauer in 1987 (cited by Arnold and Zehnder [94]) and of Heiss et al. [95]. Similar considerations are pre-

sented by Wüst and Schlüchter [96], who discuss the contribution of salts present in marls rocks that caused the deterioration processes of the walls of some Egyptian monuments.

6. Conclusions

The studies reviewed here have shown that water *per se* can have some significant erosive effects, especially by freezing, which can cause some extensive breakage of stone specimens. Nonetheless, compared with salt weathering, freeze–thaw is frequently reported to produce lower mass loss, albeit the existing comparative studies are clearly biased towards limestones, sandstones, and pyroclastic rocks.

The simple contact with water (wetting, including cyclical moisture variations by wetting–drying) seems to cause lower damage, but some clastic rocks, especially finer-grained ones, can experience major disaggregation.

There are also observations of noticeable erosive features associated with running water such as rainwater and especially in fountains. However, in these observations related to field studies, it is not clear whether the effects can be ascribed to water alone or whether they are significantly promoted by the presence of other pollutants (namely those affecting the pH of the solutions). These two situations will imply different approaches to conservation, such as simply changing the water or to avoid the contact between water and the stone surfaces.

The effects of water on stone decay also include the release of substances from the stone that contribute to alteration features of this material (or others nearby). A particularly frequent situation concerns oxidation stains related to the presence of iron sulfides due to the widespread occurrence of these minerals (especially on slates and granites), which can affect historical and contemporary applications.

In the case of granites, our observations suggest that this is mostly associated with the presence of enclaves. This trend shows a potential path for solving the problem in principle, i.e., avoiding the use of stone surfaces with enclaves (albeit we are not assessing the economic cost involved in this option). Since the stains are essentially a surficial phenomenon, on many occasions this issue could be avoided just by exposing the face of the stone that does not present enclaves. The interaction between circulating water and constituents of rock materials could also lead to the genesis of other decay agents such as salts. This will be a particularly complex case in terms of conservation, as while water circulation could feed salt contamination, the removal of the moisture source could affect the erosive effects of the salts.

Author Contributions: All authors contributed to the conceptualization and writing of this manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This specific research received no external funding (but please see the acknowledgments).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The Lab2PT-Landscapes, Heritage and Territory laboratory—UIDB/04509/2020 is supported by the Portuguese FCT—“Fundação para a Ciência e a Tecnologia”. The authors also gratefully acknowledge the support of the CERENA (funded by a strategic project of the FCT-UIDB/04028/2020) and the LAMPIS of the DECivil, Instituto Superior Técnico, University of Lisbon, Portugal. The University Institute of Geology of the University of A Coruña (Spain) receives support from the Xunta de Galicia from the program “Consolidación y estructuración de unidades de investigación competitivas: Grupos de potencial de crecimiento” (ED431B 2018/47 and ED431B 2021/17). We also thank the IACOBUS Program from the European Strategic Group of Territorial Cooperation Galicia/North of Portugal for support for the last author in 2020.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. ICOMOS-ISCS—International Council on Monuments and Sites—International Scientific Committee for Stone Illustrated Glossary on Stone Deterioration Patterns. 2008. Available online: https://www.icomos.org/publications/monuments_and_sites/15/pdf/Monuments_and_Sites_15_ISCS_Glossary_Stone.pdf (accessed on 4 November 2021).
2. Winkler, E.M. *Stone in Architecture. Properties, Durability*; 3rd Completely rev. and extended Edition; Springer: New York, NY, USA, 1997; p. 313.
3. Siegesmund, S.; Snethlage, R. (Eds.) *Stone in Architecture*; Springer: Berlin/Heidelberg, Germany, 2014. [\[CrossRef\]](#)
4. Deprez, M.; De Kock, T.; De Schutter, G.; Cnudde, V. A review on freeze-thaw action and weathering of rocks. *Earth Sci. Rev.* **2020**, *203*, 103143. [\[CrossRef\]](#)
5. Jamshidi, A. Predicting the Strength of Granitic Stones after Freeze–Thaw Cycles: Considering the Petrographic Characteristics and a New Approach Using Petro-Mechanical Parameter. *Rock Mech. Rock Eng.* **2021**, *54*, 2829–2841. [\[CrossRef\]](#)
6. Özvan, A.; Direk, N. The relationships among different abrasion tests on deteriorated and undeteriorated rocks. *Bull. Int. Assoc. Eng. Geol.* **2021**, *80*, 1745–1756. [\[CrossRef\]](#)
7. Erguler, Z.; Shakoor, A. Relative contribution of various climatic processes in disintegration of clay-bearing rocks. *Eng. Geol.* **2009**, *108*, 36–42. [\[CrossRef\]](#)
8. Ingham, J. Predicting the frost resistance of building stone. *Q. J. Eng. Geol. Hydrogeol.* **2005**, *38*, 387–399. [\[CrossRef\]](#)
9. Martínez-Martínez, J.; Benavente, D.; Gomez-Heras, M.; Marco-Castaño, L.; Garcia-Del-Cura, M.A. Non-linear decay of building stones during freeze–thaw weathering processes. *Constr. Build. Mater.* **2013**, *38*, 443–454. [\[CrossRef\]](#)
10. Lubera, E. Frost weathering of selected rocks from the tatra mountains. *Quaest. Geogr.* **2014**, *33*, 75–88. [\[CrossRef\]](#)
11. Korneeva, E.; Vatin, N.; Dontsova, A. Mechanical properties of the Crimean limestone, treated with material based on silicic acids. *Mag. Civ. Eng.* **2019**, *85*, 59–70. [\[CrossRef\]](#)
12. Rusin, Z.; Świercz, P. Frost resistance of rock materials. *Constr. Build. Mater.* **2017**, *148*, 704–714. [\[CrossRef\]](#)
13. Koralay, T.; Çelik, S.B. Minero-petrographical, physical, and mechanical properties of moderately welded ignimbrite as a traditional building stone from Uşak Region (SW Turkey). *Arab. J. Geosci.* **2019**, *12*, 732. [\[CrossRef\]](#)
14. Iucolano, F.; Colella, A.; Liguori, B.; Calcaterra, D. Suitability of silica nanoparticles for tuff consolidation. *Constr. Build. Mater.* **2019**, *202*, 73–81. [\[CrossRef\]](#)
15. Freire-Lista, D.; Fort, R.; Varas-Muriel, M. Freeze–thaw fracturing in building granites. *Cold Reg. Sci. Technol.* **2015**, *113*, 40–51. [\[CrossRef\]](#)
16. Luo, X.; Zhou, S.; Huang, B.; Jiang, N.; Xiong, M. Effect of Freeze–Thaw Temperature and Number of Cycles on the Physical and Mechanical Properties of Marble. *Geotech. Geol. Eng.* **2021**, *39*, 567–582. [\[CrossRef\]](#)
17. Martins, L.; Vasconcelos, G.; Lourenco, P.; Palha, C. Influence of the Freeze–Thaw Cycles on the Physical and Mechanical Properties of Granites. *J. Mater. Civ. Eng.* **2016**, *28*, 04015201. [\[CrossRef\]](#)
18. Fahey, B.D. Frost action and hydration as rock weathering mechanisms on schist: A laboratory study. *Earth Surf. Process. Landf.* **1983**, *8*, 535–545. [\[CrossRef\]](#)
19. Uğur, I.; Toklu, H. Özer Effect of multi-cycle freeze-thaw tests on the physico-mechanical and thermal properties of some highly porous natural stones. *Bull. Int. Assoc. Eng. Geol.* **2019**, *79*, 255–267. [\[CrossRef\]](#)
20. Fogue-Djombou, Y.I.; Corn, S.; Clerc, L.; Salze, D.; Garcia-Diaz, E. Freeze-thaw resistance of limestone roofing tiles assessed through impulse vibration monitoring and finite element modeling in relation to their microstructure. *Constr. Build. Mater.* **2019**, *205*, 656–667. [\[CrossRef\]](#)
21. Germinario, L.; Török, Á. Variability of technical properties and durability in volcanic tuffs from the same quarry region—Examples from Northern Hungary. *Eng. Geol.* **2019**, *262*, 105319. [\[CrossRef\]](#)
22. Dursun, F.; Topal, T. Durability assessment of the basalts used in the Diyarbakır City Walls, Turkey. *Environ. Earth Sci.* **2019**, *78*, 1–24. [\[CrossRef\]](#)
23. Hashemi, M.; Goudarzi, M.B.; Jamshidi, A. Experimental investigation on the performance of Schmidt hammer test in durability assessment of carbonate building stones against freeze–thaw weathering. *Environ. Earth Sci.* **2018**, *77*, 684. [\[CrossRef\]](#)
24. Heidari, M.; Chastre, C.; Torabi-Kaveh, M.; Ludovico-Marques, M.; Mohseni, H. Application of fuzzy inference system for determining weathering degree of some monument stones in Iran. *J. Cult. Herit.* **2017**, *25*, 41–55. [\[CrossRef\]](#)
25. Heidari, M.; Torabi-Kaveh, M.; Mohseni, H. Assessment of the Effects of Freeze–Thaw and Salt Crystallization Ageing Tests on Anahita Temple Stone, Kangavar, West of Iran. *Geotech. Geol. Eng.* **2016**, *35*, 121–136. [\[CrossRef\]](#)
26. Torabi-Kaveh, M.; Heidari, M.; Mohseni, H.; Ménendez, B. Role of petrography in durability of limestone used in construction of Persepolis complex subjected to artificial accelerated ageing tests. *Environ. Earth Sci.* **2019**, *78*, 297. [\[CrossRef\]](#)
27. Heidari, M.; Torabi-Kaveh, M.; Chastre, C.; Ludovico-Marques, M.; Mohseni, H.; Akefi, H. Determination of weathering degree of the Persepolis stone under laboratory and natural conditions using fuzzy inference system. *Constr. Build. Mater.* **2017**, *145*, 28–41. [\[CrossRef\]](#)
28. Mahmutoğlu, Y. Prediction of weathering by thermal degradation of a coarse-grained marble using ultrasonic pulse velocity. *Environ. Earth Sci.* **2017**, *76*, 435. [\[CrossRef\]](#)
29. Sun, Q.; Dong, Z.; Jia, H. Decay of sandstone subjected to a combined action of repeated freezing–thawing and salt crystallization. *Bull. Int. Assoc. Eng. Geol.* **2019**, *78*, 5951–5964. [\[CrossRef\]](#)

30. Montiel-Zafra, V.; Quesada, F.J.C.; Campos-Suñol, M.; Vera-Candeas, P.; Ruiz-Reyes, N. Monitoring the internal quality of ornamental stone using impact-echo testing. *Appl. Acoust.* **2019**, *155*, 180–189. [[CrossRef](#)]
31. Cárdenes, V.; Mateos, F.J.; Fernández-Lorenzo, S. Analysis of the correlations between freeze–thaw and salt crystallization tests. *Environ. Earth Sci.* **2014**, *71*, 1123–1134. [[CrossRef](#)]
32. Di Benedetto, C.; Cappelletti, P.; Favaro, M.; Graziano, S.F.; Langella, A.; Calcaterra, D.; Colella, A. Porosity as key factor in the durability of two historical building stones: Neapolitan Yellow Tuff and Vicenza Stone. *Eng. Geol.* **2015**, *193*, 310–319. [[CrossRef](#)]
33. Ghobadi, M.H.; Babazadeh, R. Experimental Studies on the Effects of Cyclic Freezing–Thawing, Salt Crystallization, and Thermal Shock on the Physical and Mechanical Characteristics of Selected Sandstones. *Rock Mech. Rock Eng.* **2015**, *48*, 1001–1016. [[CrossRef](#)]
34. Molina, E.; Benavente, D.; Sebastian, E.; Cultrone, G. The influence of rock fabric in the durability of two sandstones used in the Andalusian Architectural Heritage (Montoro and Ronda, Spain). *Eng. Geol.* **2015**, *197*, 67–81. [[CrossRef](#)]
35. Benavente, D.; Martínez-Martínez, J.; Cueto, N.; Ordóñez, S.; Garcia-Del-Cura, M.A. Impact of salt and frost weathering on the physical and durability properties of travertines and carbonate tufas used as building material. *Environ. Earth Sci.* **2018**, *77*, 147. [[CrossRef](#)]
36. Scrivano, S.; Gaggero, L.; Aguilar, J.G. An Experimental Investigation of the Effects of Grain Size and Pore Network on the Durability of Vicenza Stone. *Rock Mech. Rock Eng.* **2019**, *52*, 2935–2948. [[CrossRef](#)]
37. Shekofteh, A.; Molina, E.; Rueda-Quero, L.; Arizzi, A.; Cultrone, G. The efficiency of nanolime and dibasic ammonium phosphate in the consolidation of beige limestone from the Pasargadae World Heritage Site. *Archaeol. Anthr. Sci.* **2019**, *11*, 5065–5080. [[CrossRef](#)]
38. Karakaş, A.; Morali, G.; Coruk, Ö.; Bozkurtoğlu, E. Geomechanical, durability–hygrothermal and thermal shock properties of Kocaeli Kandira stone used as building stone in historical structures. *Environ. Earth Sci.* **2021**, *80*, 1–15. [[CrossRef](#)]
39. Bozdağ, A.; Bayram, A.F.; Ince, I.; Asan, K. The relationship between weathering and welding degree of pyroclastic rocks in the Kilistra ancient city, Konya (Central Anatolia, Turkey). *J. Afr. Earth Sci.* **2016**, *123*, 1–9. [[CrossRef](#)]
40. Çelik, M.Y.; Sert, M. Accelerated aging laboratory tests for the evaluation of the durability of hydrophobic treated and untreated andesite with respect to salt crystallization, freezing–thawing, and thermal shock. *Bull. Int. Assoc. Eng. Geol.* **2020**, *79*, 3751–3770. [[CrossRef](#)]
41. Török, Á.; Szemerey-Kiss, B. Freeze-thaw durability of repair mortars and porous limestone: Compatibility issues. *Prog. Earth Planet. Sci.* **2019**, *6*, 42. [[CrossRef](#)]
42. Williams, R.B.G.; Robinson, D.A. Experimental frost weathering of sandstone by various combinations of salts. *Earth Surf. Process. Landf.* **2001**, *26*, 811–818. [[CrossRef](#)]
43. Zhang, J.; Deng, H.; Taheri, A.; Ke, B.; Liu, C.; Yang, X. Degradation of physical and mechanical properties of sandstone subjected to freeze-thaw cycles and chemical erosion. *Cold Reg. Sci. Technol.* **2018**, *155*, 37–46. [[CrossRef](#)]
44. Zhang, Z.; Niu, Y.; Shang, X.; Ye, P.; Zhou, R.; Gao, F. Deterioration of Physical and Mechanical Properties of Rocks by Cyclic Drying and Wetting. *Geofluids* **2021**, *2021*, 1–15. [[CrossRef](#)]
45. Jiménez-González, I.; Rodríguez-Navarro, C.; Scherer, G.W. Role of clay minerals in the physicomaterial deterioration of sandstone. *J. Geophys. Res. Space Phys.* **2008**, *113*. [[CrossRef](#)]
46. Tiennot, M.; Mertz, J.-D.; Bourguès, A. Influence of Clay Minerals Nature on the Hydromechanical and Fracture Behaviour of Stones. *Rock Mech. Rock Eng.* **2019**, *52*, 1599–1611. [[CrossRef](#)]
47. Zhou, Z.; Cai, X.; Ma, D.; Chen, L.; Wang, S.; Tan, L. Dynamic tensile properties of sandstone subjected to wetting and drying cycles. *Constr. Build. Mater.* **2018**, *182*, 215–232. [[CrossRef](#)]
48. Sumner, P.D.; Loubser, M.J. Experimental sandstone weathering using different wetting and drying moisture amplitudes. *Earth Surf. Process. Landf.* **2008**, *33*, 985–990. [[CrossRef](#)]
49. Sebastián, E.; Cultrone, G.; Benavente, D.; Fernandez, L.L.; Elert, K.; Rodriguez-Navarro, C. Swelling damage in clay-rich sandstones used in the church of San Mateo in Tarifa (Spain). *J. Cult. Herit.* **2008**, *9*, 66–76. [[CrossRef](#)]
50. Ruedrich, J.; Bartelsen, T.; Dohrmann, R.; Siegesmund, S. Moisture expansion as a deterioration factor for sandstone used in buildings. *Environ. Earth Sci.* **2011**, *63*, 1545–1564. [[CrossRef](#)]
51. An, W.-B.; Wang, L.; Chen, H. Mechanical Properties of Weathered Feldspar Sandstone after Experiencing Dry-Wet Cycles. *Adv. Mater. Sci. Eng.* **2020**, *2020*, 1–15. [[CrossRef](#)]
52. Hall, K.; Hall, A. Weathering by wetting and drying: Some experimental results. *Earth Surf. Process. Landf.* **1996**, *21*, 365–376. [[CrossRef](#)]
53. Trenhaile, A. Tidal wetting and drying on shore platforms: An experimental study of surface expansion and contraction. *Geomorphology* **2006**, *76*, 316–331. [[CrossRef](#)]
54. Aly, N.; Wangler, T.; Török, Á. The effect of stylolites on the deterioration of limestone: Possible mechanisms of damage evolution. *Environ. Earth Sci.* **2018**, *77*, 565. [[CrossRef](#)]
55. Mottershead, D.N. Rapid weathering of greenschists by coastal salt spray, east Prawle, south Devon: A preliminary report. *Proc. Ussher Soc.* **1982**, *5*, 347–353.
56. Wells, T.; Binning, P.; Willgoose, G. The role of moisture cycling in the weathering of a quartz chlorite schist in a tropical environment: Findings of a laboratory simulation. *Earth Surf. Process. Landf.* **2005**, *30*, 413–428. [[CrossRef](#)]
57. Aly, N.; Hamed, A.; El-Al, A.A. The Impact of Hydric Swelling on the Mechanical Behavior of Egyptian Helwan Limestone. *Period. Polytech. Civ. Eng.* **2020**. [[CrossRef](#)]

58. Pötzl, C.; Dohrmann, R.; Siegesmund, S. Clay swelling mechanism in tuff stones: An example of the Hilbersdorf Tuff from Chemnitz, Germany. *Environ. Earth Sci.* **2018**, *77*, 188. [[CrossRef](#)]
59. Tiennot, M.; Mertz, J.-D.; Bourguès, A. Sensitivity of kersantite toughness to moisture: Influence of the phyllosilicates. *Environ. Earth Sci.* **2018**, *77*, 483. [[CrossRef](#)]
60. Lubelli, B.; Nijland, T.G.; Tolboom, H.-J. Moisture induced weathering of volcanic tuffstone. *Constr. Build. Mater.* **2018**, *187*, 1134–1146. [[CrossRef](#)]
61. Noor-E-Khuda, S.; Albermani, F. Flexural strength of weathered granites under wetting–drying cycles: Implications to steel structures. *Adv. Steel Constr.* **2019**, *15*, 225–231. [[CrossRef](#)]
62. Pozo-Antonio, J.; Alonso-Villar, E. Article 6. Stone durability of a surfactant-synthesised alkoxysilane consolidant on granites with different mineralogy and texture. *Egypt. J. Archaeol. Restor. Stud.* **2020**, *10*, 11–12. [[CrossRef](#)]
63. Heap, M.J.; Gilg, H.A.; Hess, K.-U.; Mertens, L.; Pösges, G.; Reuschlé, T. Conservation and restoration of St. George’s church (Nördlingen, Germany), a 15th century Gothic church built using suevite from the Ries impact crater. *J. Cult. Herit.* **2020**, *41*, 256–263. [[CrossRef](#)]
64. Hu, M.; Liu, Y.; Song, L.; Zhang, Y. Constitutive Model and Damage Evolution of Mudstone under the Action of Dry-Wet Cycles. *Adv. Civ. Eng.* **2018**, *2018*, 1–10. [[CrossRef](#)]
65. Sakai, T.; Nakano, M. Effects of slaking and degree of compaction on the mechanical properties of mudstones with varying slaking properties. *Soils Found.* **2019**, *59*, 56–66. [[CrossRef](#)]
66. Zeng, L.; Luo, J.-T.; Liu, J.; Gao, Q.-F.; Bian, H.-B. Disintegration Characteristics and Mechanisms of Carbonaceous Mudstone Subjected to Load and Cyclic Drying–Wetting. *J. Mater. Civ. Eng.* **2021**, *33*, 04021195. [[CrossRef](#)]
67. Beck, K.; Almkhtar, M. Cyclic wetting–drying ageing test and patina formation on tuffeau limestone. *Environ. Earth Sci.* **2014**, *71*, 2361–2372. [[CrossRef](#)]
68. Bustamante, R.; Vázquez, P.; Rodríguez-Monteverde, P.; Monjo, J. Adapted ageing tests for the evaluation of alabaster used in the restoration of Bishop’s Palace of Tarazona. *Mater. De Construcción* **2020**, *70*, 219. [[CrossRef](#)]
69. Zeng, L.; Li, F.; Gao, Q.-F.; Yao, X.; Wang, G. Insight into the fracturing of silty mudstone in cyclic hydrothermal environments based on computed tomography. *Transp. Geotech.* **2021**, *26*, 100432. [[CrossRef](#)]
70. Vallejo, L.; Welsh, R.; Lovell, C.; Robinson, M. The Influence of Fabric and Composition on the Durability of Appalachian Shales. In *Rock for Erosion Control*; ASTM International: West Conshohocken, PA, USA, 2009; p. 15.
71. Santi, P.M. Improving the Jar Slake, Slake Index, and Slake Durability Tests for Shales. *Environ. Eng. Geosci.* **1998**, *IV*, 385–396. [[CrossRef](#)]
72. Chaney, R.; Demars, K.; Santi, P.; Higgins, J. Methods for Predicting Shale Durability in the Field. *Geotech. Test. J.* **1998**, *21*, 195. [[CrossRef](#)]
73. Youn, H.; Tonon, F. Effect of air-drying duration on the engineering properties of four clay-bearing rocks in Texas. *Eng. Geol.* **2010**, *115*, 58–67. [[CrossRef](#)]
74. Venter, J.P. Free-Swell Properties of Some South African Mudrocks. In Proceedings of the ISRM International Symposium, Tokyo, Japan, 21–24 September 1981. ISRM-IS-1981-040.
75. Phien-Wej, N.; Peiris, N.I.C.; Jinye, L. Slaking and Swelling Behaviour of Sedimentary Rocks of the Lam Ta Khong Pumped Storage Project, Thailand. In Proceedings of the 8th ISRM Congress, Tokyo, Japan, 25–29 September 1995. ISRM-8CONGRESS-1995-227.
76. Germinario, L.; Oguchi, C.T.; Tamura, Y.; Ahn, S.; Ogawa, M. Taya Caves, a Buddhist marvel hidden in underground Japan: Stone properties, deterioration, and environmental setting. *Herit. Sci.* **2020**, *8*, 1–20. [[CrossRef](#)]
77. Bonazza, A.; Vidornì, G.; Natali, I.; Ciantelli, C.; Giosuè, C.; Tittarelli, F. Durability assessment to environmental impact of nano-structured consolidants on Carrara marble by field exposure tests. *Sci. Total. Environ.* **2017**, *575*, 23–32. [[CrossRef](#)] [[PubMed](#)]
78. Gulotta, D.; Bontempi, E.; Bugini, R.; Goidanich, S.; Toniolo, L. The deterioration of metamorphic serpentinites used in historical architecture under atmospheric conditions. *Q. J. Eng. Geol. Hydrogeol.* **2017**, *50*, 402–411. [[CrossRef](#)]
79. Gulotta, D.; Villa, F.; Cappitelli, F.; Toniolo, L. Biofilm colonization of metamorphic lithotypes of a renaissance cathedral exposed to urban atmosphere. *Sci. Total. Environ.* **2018**, *639*, 1480–1490. [[CrossRef](#)] [[PubMed](#)]
80. Waragai, T.; Hiki, Y. Influence of microclimate on the directional dependence of sandstone pillar weathering in Angkor Wat temple, Cambodia. *Prog. Earth Planet. Sci.* **2019**, *6*, 10. [[CrossRef](#)]
81. Bello, M.A.; Martin, L.; Martin, A. Decay and treatment of Macael white marble. *Stud. Conserv.* **1992**, *37*, 193–200. [[CrossRef](#)]
82. Sarró, M.I.; Garcia, A.M.; Rivalta, V.M.; Moreno, D.A.; Arroyo, I. Biodeterioration of the Lions Fountain at the Alhambra Palace, Granada (Spain). *Build. Environ.* **2006**, *41*, 1811–1820. [[CrossRef](#)]
83. Sanjurjo-Sánchez, J.; Alves, C. Decay effects of pollutants on stony materials in the built environment. *Environ. Chem. Lett.* **2011**, *10*, 131–143. [[CrossRef](#)]
84. De Azcona Fraile, M.C.L.; González, R.F.; Martín, F.M. Conservation of the stone in Cibeles Fountain, Madrid (Spain). *Mater. De Construcción* **2002**, *265*, 65–76.
85. Freire-Lista, D.M.; Fort, R. Historical Quarries, Decay and Petrophysical Properties of Carbonate Stones Used in the Historical Center of Madrid (Spain). *AIMS Geosci.* **2017**, *3*, 284–303. [[CrossRef](#)]
86. De Azcona, M.C.L.; Gonzalez, R.F.; Martín, F.M. La conservación de los materiales pétreos en la Fuente de Cibeles, Madrid (España). *Mater. De Construcción* **2002**, *52*, 65–75. [[CrossRef](#)]

87. Ďoubal, J. The restoration of the Stone Fountain in Kutná Hora: An assessment of the contemporary intervention within the context of repairs throughout history. *Stud. Conserv.* **2017**, *62*, 371–383. [[CrossRef](#)]
88. Dreesen, R.; Nielsen, P.; Lagrou, D. The staining of blue stone limestones petrographically unraveled. *Mater. Charact.* **2007**, *58*, 1070–1081. [[CrossRef](#)]
89. Cárdenes, V.; Cnudde, J.P.; Wichert, J.; Large, D.; López-Mungira, A.; Cnudde, V. Roofing slate standards: A critical review. *Constr. Build. Mater.* **2016**, *115*, 93–104. [[CrossRef](#)]
90. Cárdenes, V.; Mateos, F.J.; Rubio-Ordoñez, A.; Monterroso, C. Ensayos normativos para la caracterización de patologías en pizarras para cubiertas. *Mater. De Construcción* **2011**, *62*, 251–268. [[CrossRef](#)]
91. Zha, J.; Wei, S.; Wang, C.; Li, Z.; Cai, Y.; Ma, Q. Weathering mechanism of red discolorations on Limestone object: A case study from Lingyan Temple, Jinan, Shandong Province, China. *Herit. Sci.* **2020**, *8*, 1–12. [[CrossRef](#)]
92. Germinario, L.; Siegesmund, S.; Maritan, L.; Simon, K.; Mazzoli, C. Trachyte weathering in the urban built environment related to air quality. *Herit. Sci.* **2017**, *5*, 85–93. [[CrossRef](#)]
93. Germinario, L.; Oguchi, C.T. Underground salt weathering of heritage stone: Lithological and environmental constraints on the formation of sulfate efflorescences and crusts. *J. Cult. Herit.* **2021**, *49*, 85–93. [[CrossRef](#)]
94. Arnold, A.; Zehnder, K. Monitoring wall paintings affected by soluble salts. In *The Conservation of Wall Paintings*; Getty Conservation Institute: Los Angeles, CA, USA, 1991; p. 103. Available online: <https://www.getty.edu/publications/virtuallibrary/089236162X.html> (accessed on 1 January 2011).
95. Heiss, K.; Skalli, M.; Zallmanzig, J. Diagnosis study of the St. Marienkirche, Lippstadt, a mediaeval greensandstone monument, for conservatory planning. In *Science, Technology and European Cultural Heritage*; Baer, N.S., Sabbioni, C., Sors, A.I., Eds.; Butterworth Heinemann: Oxford, UK, 1991; pp. 939–942.
96. Wüst, R.A.; Schlüchterb, C. The Origin of Soluble Salts in Rocks of the Thebes Mountains, Egypt: The Damage Potential to Ancient Egyptian Wall Art. *J. Archaeol. Sci.* **2000**, *27*, 1161–1172. [[CrossRef](#)]