DECAY AND TREATMENT OF MACAEL WHITE MARBLE

M. A. Bello, L. Martin and A. Martin

Abstract—This paper reports the process of deterioration of the white marble used in the Alhambra of Granada, and its consequences. Variations in mineralogical composition, microscopic topology, hardness, compressive strength, propagation of ultrasonic waves, absorption and diffusion of water and properties related to the pore structure were studied. The relationships between these factors, the visible deterioration and possible mechanisms are discussed. A preliminary evaluation of some protective treatments was carried out. The results can also be applied to white Macael marble used in other monuments in an environment with wide fluctuations in temperature and relative humidity.

1 Introduction

White marble has been traditionally used as a quality building material. In Spain, especially in the south, the most important material is that from the Macael quarries (Almería). This is a marble of excellent technical and artistic qualities, which has frequently been compared with marble from Carrara, Italy.

The Alhambra of Granada is one of many monuments where the white marble from Macael has been profusely employed. All the columns, the pavement and the ornamental elements of the numerous fountains are made from this marble. Where the marble is located in exterior zones or in fountains, it is in an advanced state of deterioration.

The factors involved in the mechanism of alteration and the stages in the alteration process have been established previously [1]; variations in temperature and relative humidity, which are considerable in the city of Granada, are of special importance as will be seen later. The environmental conditions and the main visual indicators of alteration are described, followed by the characterization of the materials. The main commercial products used in conservation have been applied to artificially aged marble and to aged material from the Alhambra with the aim of evaluating their performance. The results should enable us to establish the most suitable treatments for the Macael marble used in various monuments and especially in the Alhambra of Granada.

1.1 Environmental conditions

The city of Granada, 664 metres above sea level, lies in the continental extreme subregion [2] which is characterized by cold winters and very warm summers; the high number of days per year with temperatures lower than 0°C and the great thermal variations are important. The relative humidity ranges between 30% in July and 90% in January; variations of as much as 40% in the relative humidity have been recorded within one day [3]. In a study carried out on the Alhambra during 1988 and 1989 [4], temperature variations of 30°C in a day were recorded. The environmental conditions in the area surrounding the monument rule out the action of gaseous and particulate atmospheric pollutants on the stone.

1.2 Macroscopic indicators of alteration

The most characteristic macroscopic morphology of alteration of the white marble from the Alhambra of Granada consists of intergranular loss of cohesion, which in many cases includes crumbling and grain separation (Figure 1). Where there are a lot of visitors, the damage they cause is visible: scoring, scratches, scrapes and chips (Figure 2). The fact that Granada is located within an area of high seismic activity accounts for the many cracks and fissures. The high temperature variations together with the anisotropic crystallization of the marble have given rise to distortion and bending in some places. Table 1 shows the relationship between factors, mechanisms and macroscopic indicators of deterioration for the material in this study.

Received 19 February 1991
Received in revised form 10 January 1992

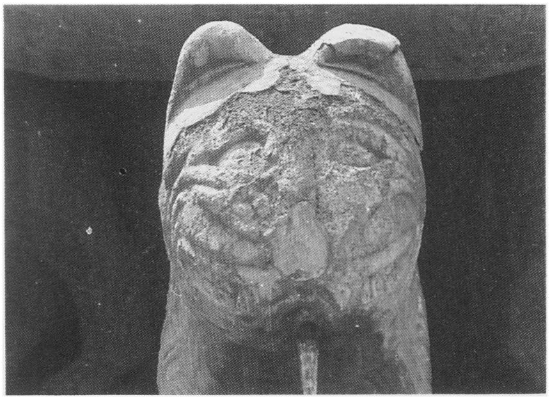

Figure 1 *Altered, disaggregated Macael white marble (Patio de los Leones, Alhambra, Granada).*

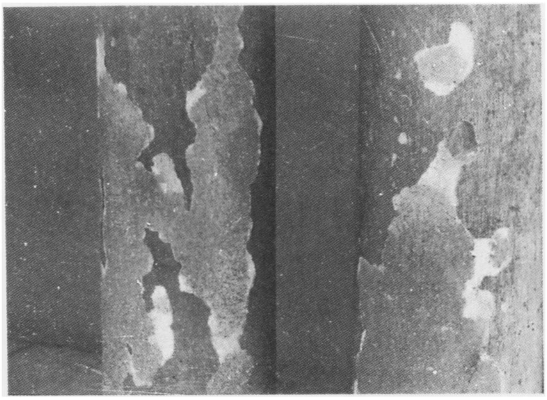

Figure 2 *Altered column of Macael white marble.*

The condition of the marble in the different areas of the Alhambra is described below:

'Patio de los Leones'

In this completely open patio, it is necessary to distinguish between the columns which surround the patio and the ornamental elements of the central fountain, the well-known lions.

On the *columns* the main visual indicators of deterioration are fissures and cracks. However, we must distinguish between the sunny zone where the stone is subjected to great temperature variations, in which the columns show decay and a serious loss of material, and the shady zone where there is little decay.

The *lions* suffer important losses of material by disaggregation. The high humidity to which these structures are submitted, the cyclic variations during the day due to the water being cut off, the poor state of preservation of the water pipes in the interior of the ornamental figures and diverse modifications throughout history have led to the simultaneous action of other alteration mechanisms, principally freeze/thaw cycles, salt crystallization, wetting/drying cycles and microbiological action.

Rooms adjoining the 'Patio de los Leones'

These are interior rooms and consequently the thermohygrometric variations are less important than on the exterior; therefore, only a few cracks and fissures are found.

Arrayanes Palace

In this area of the monument loss of material is common due to the fact that most of it is exposed. There are many cracks and fissures. Where the stone is protected towards the interior of the building there is less deterioration.

Table 1 *Relationship between factors, mechanisms and visual indicators of alteration for Macael white marble from the Alhambra of Granada*

Factors	*Mechanisms*	*Visual indicators*
Thermohygrometric conditions	Temperature gradient Freeze/thaw cycle	Decohesion
Liquid water (splashes, gushes, leaks, etc.)	Freeze/thaw cycle	Decohesion
Salts (from mortars)	Mechanical action	Pulverization
Public	Mechanical action	Scrapes, scoring, scratches
Seismicity	Rupture	Cracks and fissures

Studies in Conservation **37** (1992) 193–200

Lindaraja
On the columns of this part of the monument macroscopic indicators of deterioration such as cracks, fissures and loss of material have been observed but they are less important than in the Arrayanes Palace.

2 Experimental

2.1 Sampling
For this study, some samples have been taken from the remains of ancient restoration and others were taken in the 'Patio de los Leones' during a previous investigation [4]. The number of samples used for each test method is shown in the results of the corresponding tests. The availability of samples from only some parts of the Alhambra explains why a study could not be carried out on the whole monument; however, we consider that the samples taken show the general situation.

2.2 Methods
The petrographic study was carried out by optical microscopic examination of polished thin-sections.

X-ray powder diffraction patterns (XRD) were obtained with a Philips PW-1710 diffractometer using CuKα radiation and a Ni filter.

For the micromorphological observations, a ISI-SS40 scanning electron microscope fitted with a Kevex energy dispersive X-ray spectrometer (EDX) was used. The samples were gold-plated for examination.

The changes in mechanical properties were studied by various techniques: the superficial hardness was tested with a Martens tester (conical tip and 1500g load) and with a Schmidt hammer rebound tester (Controls®) for hard stone; for changes in the compressive strength [5] an Ibertest DF-12000 universal test press was used on 5cm^3 specimens.

The degree of compaction was tested with a Controls E46 ultrasonic tester.

To evaluate the influence of the deterioration in the stone on the transport of liquid water, the most significant parameters were determined according to the RILEM proposal [6], using 5cm^3 samples. For water absorption at constant hydrostatic pressure, an adaptation of the Tiano method [7] was employed. To detect the position of the water front electrically, two 5mm-diameter holes were bored to a depth of 45mm, on the opposite face to that where the pipette was applied, and the electrodes of a Gann HT-95 digital hygrometer were fitted.

Mercury intrusion porosimetry measurements were performed with a Carlo Erba porosimeter. The marble samples were broken into pieces approximately 2–3mm in size prior to measurement. The pore structure was assumed to consist of cylindrical open pores. The pore size range covered was approximately 0·3–200μm.

3 Results and discussion

3.1 Petrography of Macael white marble
The unaltered material from the quarries shows a grain-blastic texture (the large crystals are cemented by very small ones) with tangential to sutured contact between grains (contact between crystals through large zones which look as if the crystals are inserted through one another). The material is heterogeneous with no pronounced anisotropy.

Analysis of the mineralogical composition reveals mainly calcite with an abundance of polysintetical macles (three or more crystals whose surfaces grow parallel) and few widely dispersed needle crystals of white mica, little quartz and some quantities of zircon, opaques (minerals dark to transmitted light), esfene (a variety of titanite), apatite and dolomite as accessories.

The altered materials from the monument show numerous holes and cracks within grains, a disaggregation process which provides an indication of the state of decay. The SEM photomicrographs (Figures 3 and 4) show the considerable disaggregation of the calcite crystals in the altered material which leads to an increase in the porosity and allows water to penetrate deep into the stone, accelerating the process of degradation.

XRD studies do not reveal the formation of any new substances; the absence of gypsum shows that there has been no sulphur dioxide (SO_2) chemical attack (the levels of SO_2 in the environment of the monument are not significant).

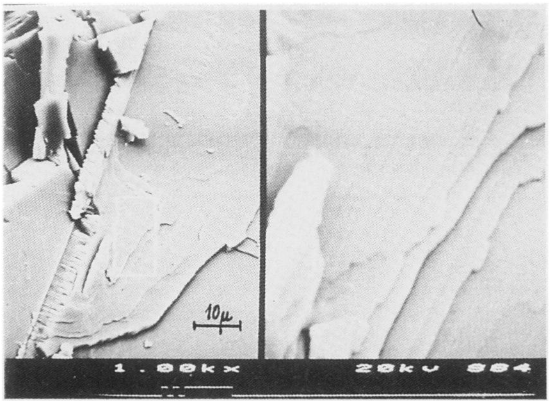

Figure 3 *SEM photomicrograph of unaltered Macael white marble (magnification on the right,* × *5).*

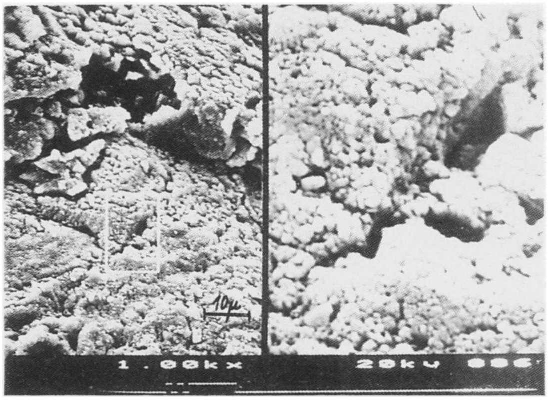

Figure 4 *SEM photomicrograph of altered Macael white marble (magnification on the right,* × *5).*

3.2 Mechanical properties

Unaltered material from the quarries (five samples) and an ancient remnant of pavement from the Arrayanes Palace (two samples), in an advanced state of alteration, which we can consider as representative of the last stage in the process of decay, have been submitted to the various tests considered; other samples cannot be taken for the tests due to the size needed. Table 2 shows the values for the different properties measured.

Table 2 *Mechanical properties of new (unaltered) and weathered (altered) Macael white marble*

Property	*Unaltered*	*Altered*
Hardness by Martens test		
—width of the mark (µm)	350	700
Hardness by Schmidt hammer rebound test		
—rebound value	60	14
—cube compressive strength (kgm^{-2})	825	70
Compressive strength		
—rupture load (kN)	269	98
—modulus of rupture (kgm^{-2})	1241	418

The considerable loss of cohesion observed corresponds to a loss of hardness in the Martens test; an increase of 100% in the width of the mark was observed. The great difference in the compressive strength and the modulus of rupture indicates that the altered material has almost completely lost its utility as a structural material; in this case the material studied is a pavement remnant, but a similar result can be expected for the decay on the columns.

3.3 Velocity of propagation of ultrasonic waves

Fresh stone from the quarries (more than 20 samples), together with samples from numerous columns and ornamental elements (more than 50 samples), have been checked by this technique and we can conclude from the results obtained that the decrease in the propagation velocity is directly related to the degree of degradation observed.

In the fresh stone from the quarries, the velocity of propagation varies between 5500 and 6000ms^{-1}; this velocity decreases with the loss of cohesion to values as low as 2000ms^{-1} in very decayed material, which indicates a considerable loss in the compaction and strength of the stone.

3.4 Water absorption

Table 3 shows the results for water absorption and diffusion. Figure 5 shows the capillary absorption curves and Figure 6 the curves of absorption and diffusion at constant hydro-

Table 3 Water absorption and diffusion for unaltered and altered marble

	Unaltered marble	*Altered marble*
Total immersion		
Water content (%)		
(atmospheric pressure)	0·07	0·34
Maximum water content (%)		
(20mmHg pressure)	0·15	0·55
Saturation coefficient (%)	52·00	61·40
Capillarity		
Water absorption coefficient ($kgm^{-2}s^{-1/2}$)	$8{\cdot}1 \times 10^{-4}$	$8{\cdot}4 \times 10^{-3}$
Constant hydrostatic pressure		
Velocity of water diffusion (ms^{-1})	$1{\cdot}7 \times 10^{-5}$	$5{\cdot}0 \times 10^{-4}$

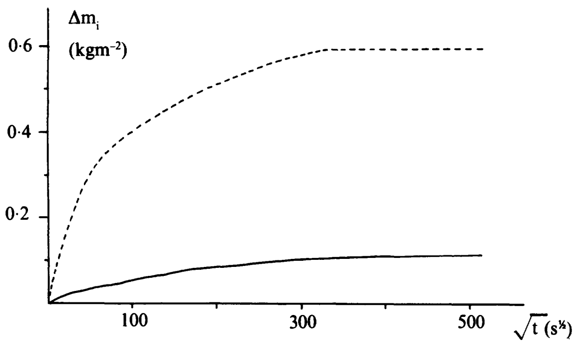

Figure 5 Curves for water absorption by capillarity test (——— unaltered marble, – – – altered marble).

static pressure for new Macael marble and for the ancient remnant of pavement from the Arrayanes Palace (section 3.2). All these tests were carried out on three samples of new marble and two of the deteriorated material.

The increase in the water absorption capacity and velocity is considerable. This suggests that acceleration of the decay in the weathered marble is possibly caused by the frequent freeze/thaw cycles in the winter.

3.5 Porosity and pore size distribution

Mercury intrusion porosimetry measurements were carried out on four samples of altered marble: samples A, B and C correspond to

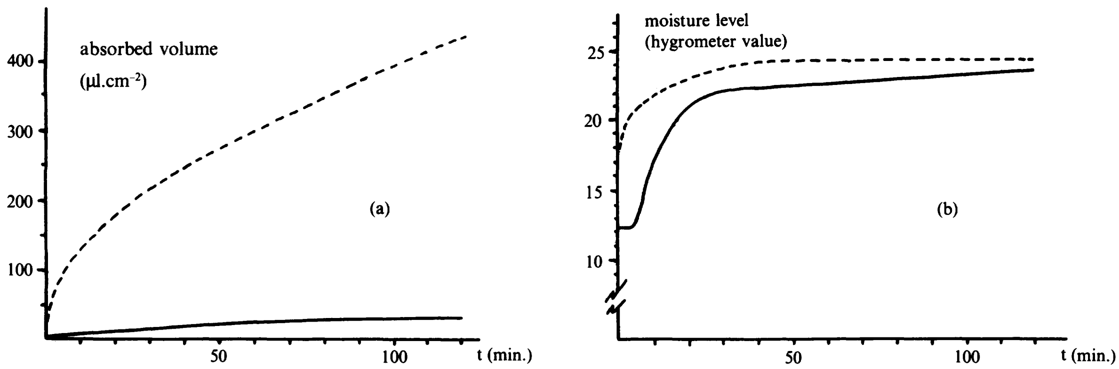

Figure 6 Water absorption (a) and diffusion (b) curves at constant hydrostatic pressure for unaltered (———) and altered (– – –) Macael white marble.

Table 4 Data from a mercury porosimetry study of Macael white marble samples

	Total porosity (% vol)	Intrusion volume (mlg^{-1})	Density (gcm^{-3})	Bulk density (gcm^{-3})	Median Pore radius (μm)	Total pore area (m^2g^{-1})
Unaltered	0·45	0·0111	2·75	2·63	0·0068	3·32
Sample A	4·51	0·0178	2·66	2·54	1·4970	3·60
Sample B	6·25	0·0249	2·68	2·51	7·2864	4·12
Sample C	6·46	0·0254	2·72	2·55	5·4222	5·04
Sample D	6·02	0·0234	2·74	2·58	0·0728	7·71

materials in an advanced state of alteration and sample D corresponds to material in the early stages of the process of alteration.

Table 4 shows the values obtained from this study. The increase in porosity in the altered materials is important as is the increase in the total pore area. These, with the fall in density values, are the results to be expected, related to the loss of cohesion which is observed in the decayed stone.

Figure 7 shows the pore radius distribution of the materials referred to in Table 4. Unaltered material shows micro- and macroporosity. On the altered materials we can see a considerable loss in the microporosity which leads to the formation of macropores; sample D shows an intermediate stage of alteration with an almost regular distribution of pores over the whole range studied.

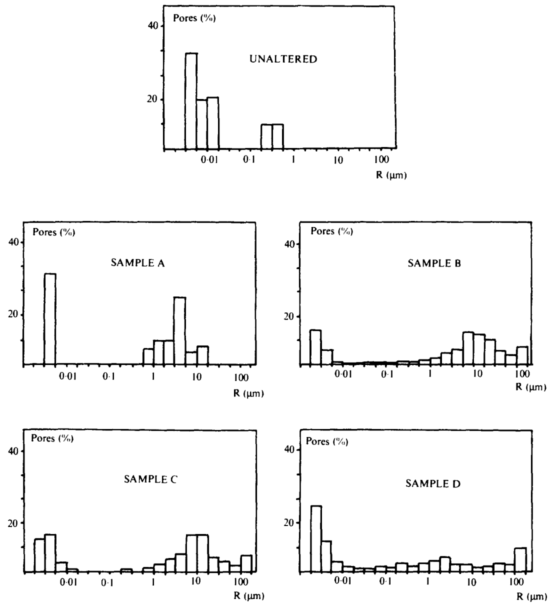

Figure 7 Pore radius distribution for unaltered and altered marble samples.

3.6 Preliminary evaluation of the water-proofing efficacy of protective treatments

Due to the importance of water as a factor in the deterioration, we considered it necessary to carry out a preliminary evaluation of the water-proofing effect of various products which have been used to treat stone.

Four commercial products were each tested on three samples of unaltered Macael marble: ARD 55.050 (Raccanello) acrylic silane; Paraloid B-72 (Rohm and Haas) acrylic polymer; Tegosivin HL100 (Th. Goldschmidt) silane; and Fomblin YR (Montefluos) perfluorine polyether. All the products were applied by immersing the marble for 10 minutes in a solution of the product in the solvent recommended by the manufacturer; the dilutions used were 1% (w/v) for Paraloid, 10% (w/v) for ARD 55.050 and Tegosivin and 70% (v/v) for Fomblin. After the treatment, a drying period of two months in laboratory conditions was allowed before any tests were carried out.

The extent of water-proofing achieved was measured by the test for water absorption at constant hydrostatic pressure described previously. The results obtained are shown in Figure 8 where water absorption and diffusion curves have been plotted against time. As can be seen, all the products give a decrease in water absorption and diffusion; the best results for water absorption were obtained with Fomblin and ARD 55.050, and for diffusion of water with Fomblin.

However, this is only a preliminary evaluation, for two reasons: the treatments were

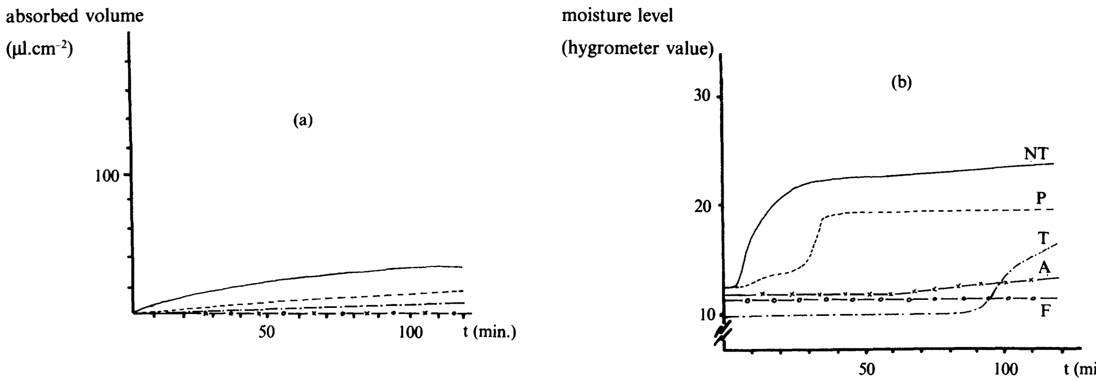

Figure 8 Water absorption (a) and diffusion (b) curves at constant hydrostatic pressure for Macael marble: untreated (NT), treated with Fomblin (F), ARD 55.050 (A), Tegosivin (T) and Paraloid B-72 (P).

applied on new marble and the samples were not submitted to weathering. The degree of absorption of the product on the marble can change with the degree of degradation. It is also possible that the efficacy of the treatment is modified by various alteration processes, so that a product which is good in some conditions can behave badly in a different environment. For this reason we are going to attempt to obtain large quantities of artificially altered marble to use for testing treatment products. These treated samples will then be submitted to different weathering regimes to evaluate the behaviour of each treatment under various aggressive conditions. However, we consider that the preliminary tests are a good starting point.

4 Conclusions

Although the availability of samples did not permit a complete study to be carried out, it is possible to conclude that the alteration of the white marble used in the Alhambra of Granada is caused, fundamentally, by the great environmental thermohygrometric variations. This leads to changes in certain properties whose magnitude depends upon the degree of deterioration of the stone.

Weathering causes disaggregation of the material which leads to a serious loss in hardness and mechanical strength; this is of special importance where the material has been employed for structural elements. The decayed material is capable of absorbing a greater amount of water and so acceleration of the decay is possible, caused by freeze/thaw cycles which are frequent due to the winter environmental conditions. Weathering also causes a serious increase in the porosity and the median pore radius of the marble.

These results indicate that for the conservation of the Macael white marble in the Alhambra of Granada, it is necessary to consider maintaining the water pipes in the fountains in a good state of repair to eliminate the high moisture level in the stone; careful selection of materials for restoration, choosing those which do not cause tension due to different thermal expansion coefficients; treatments to give consolidation and water-repellency resistant to the high thermohygrometric variations and to UV radiation where the treated material is exposed to high levels of sunlight.

Preliminary evaluation of the water-proofing effect of some protective products has shown that the acrylic product is not suitable for this purpose. The other products tested gave good results in general, but it will be necessary to submit the samples of treated marble to accelerated weathering to evaluate their behaviour under different conditions.

For structural components, e.g. columns, it is important to check the mechanical properties and to reinforce or replace those which are in a poor condition and might not withstand the high seismic activity of the area.

Manufacturers of materials

ARD 55.050: ARD F.lli Raccanello SpA, Strada 1 Zona Industriale no.13, 35129 Padua, Italy.
Paraloid B-72: Rohm and Haas Company, Philadelphia, PA 19105, USA.
Tegosivin HL100: Th.Goldschmidt AG, Goldschmidtstrasse 100, 4300 Essen, Germany.
Fomblin YR: Montefluos SpA, Via Principe Eugenio 1/5, 20155 Milan, Italy.

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Résumé—Ce mémoire décrit le processus de dégradation du marbre blanc utilisé à la construction de l'Alhambra de Grenade, et ses conséquences. On a étudié les variations minéralogiques, la topologie microscopique, la dureté, la résistance à la compression, la propagation d'ondes ultrasonores, l'absorption et la diffusion de l'eau en relation avec la porosité. On discute de la relation entre ces différents facteurs, la détérioration visible et les mécanismes envisageables. On fait une première évaluation de quelques traitements protecteurs. Ces résultats ont été appliqués aussi au marbre blanc de Macael utilisé dans d'autres monuments et se trouvant dans un environnement où les températures et l'humidité relative peuvent être très variables.

Zusammenfassung—Der Beitrag beschreibt den Zerfall von weißem Marmor, der in der Alhambra von Granada verbaut wurde, und die sich daraus ergebenden Konsequenzen. Untersucht werden Variationen in der mineralogischen Zusammensetzung, dem Gefüge, der Härte, der Druckfestigkeit, der Fortpflanzung von Ultraschall, der Adsorption und Diffusion von Wasser und Eigenschaften, die mit dem Porengefüge zu tun haben. Der Beitrag diskutiert diese Faktoren, ihre Beziehung zueinander, den sichtbaren Zerfall und mögliche Mechanismen. Gleichzeitig trifft er eine erste Bewertung schützender Behandlungen, die durchgeführt wurden. Die Ergebnisse lassen sich auf weißen Macael Marmor übertragen, der für andere Baudenkmäler in einer Umgebung mit stark schwankenden Temperatur- und Feuchtigkeitswerten verwendet wurde.