Protection and Restoration of the Environment XI

EFFECT OF ENVIRONMENTAL FACTORS TO THE DETERIORATION OF STONE MONUMENTS IN THE ARCHAEOLOGICAL SITE OF DION (MACEDONIA, GREECE)

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ABSTRACT

The aim of this paper is the study of the effect of the environmental factors to the deterioration of stone monuments in the archaeological site of Dion. The main building materials of Demeter and Asklepios sanctuaries in Dion are mainly limestones and conglomerates, consisting mainly of calcite and/or dolomite. The deteriorated surfaces contain also gypsum, secondary and recrystallized calcite and dolomite, various inorganic compounds, fluoroapatite, microorganisms and other organic compounds. The most proper approach to select effective methods for the structural and surface consolidation, the cleaning, the protection and the overall conservation of these structures is the knowledge of the processes contributing to their deterioration.
The influence of specific weathering agents and factors to the behavior of the materials was examined. The particular environmental conditions in Dion combine increased moisture and rain fall, insolation and great temperature differences, abundance of intensive surface and underground water bodies in the surrounding area, an area full of plants and trees, therefore, they can cause extensive chemical, biological and mechanical decay of the monuments. The following physical characteristics of the building materials have been studied: bulk density, open porosity, water absorption and desorption, capillary absorption and desorption. The chemical composition of bulk precipitation, surface and underground water was investigated. The salts presence and crystallization was examined. The growth of microorganisms, bacteria, plants and lichens was observed and determined. The growth of lichens and bryophytes was observed and the species were determined.
The existence of water in the bulk of the materials due to capillary penetration, the increased moisture absorption and the growth of lichens on the surface of the materials, correlated with the intensive surface and underground water presence in the surrounding area, led to loss of the structural cohesion and the surface instability of the building materials.

Keywords
Stone building materials; deterioration; rainwater; underground water; biodeterioration; physical characteristics

1. INTRODUCTION

Deterioration of historical monuments is the result of chemical reactions of polluted air, soil and water with the stone building materials. The crystallization and hydration of weathering products result in their expansion causing the degradation of dolomite, limestone, marble, sandstone and other building materials. In most cases the stone surfaces are gradually covered by salts and black crusts containing calcium, magnesium, sodium, potassium sulphates, nitrates and other constituents. Also the water can easily penetrate and remain into the building stone materials, resulting in a destructive influence due to the absorption and evaporation of the moisture that affects their volume and causes cracks leading to the deterioration of the structure (Young 2008). Under these conditions, the stone surfaces disintegrate into powder and the building materials gradually lose their mechanical strength and their artistic form (Price, 1996; Winkler, 1997; Lan et al., 2005; Skoulikidis, 2000; Moreno et al., 2006). In the case of marbles the main mechanism of deterioration is the sulphation of their surfaces, leading to the formation of gypsum layers on the stone surface, due to the solid state diffusion of Ca^{2+} (Camuffo et al., 1982; 1983; Del Monte et al., 1984; Rodriguez-Navarro et al., 1996; Keatings, 2007; Simao et al., 2006; Sharma et al., 2007).

The lichens and bryophytes are resistant organisms, suffering long periods of moisture without being destroyed. They absorb, store and desorb rapidly humidity, depending on the environmental conditions. They do not have a root system, but they have strong mechanisms for snapping in the substrate. These properties make them the most dynamic colonists of the building materials of the monuments. The porous surface is more favourable in the colonization. The effect of lichens and bryophytes on the monument depends on the specie, the nature and chemical composition of the substrate. Many lichen or bryophyte species retain humidity in the snapping area, causing physical and chemical alterations of the substrate. Many lichens secrete oxalic acid, produce organic acids (by-products of metabolism) and carbon dioxide, leading to chemical corrosion and deterioration of the material (Ahmadian et al., 1983; Ascaso et al., 1994; Sawidis et al., 1995; Scagel et al., 1965).

The aim of the present work is the study of the effect of the environmental factors to the deterioration of stone monuments of Demeter and Asklepios sanctuaries in Dion archaeological site (Figure 1), one of the most important religious centers of ancient Greeks in central Macedonia. In earlier works (Papanikolaou et al., 2010; 2011) we studied the main building materials of the monuments which are limestones and conglomerates, although sandstones, marbles and ceramic plinths were also used. These materials consist mainly of calcite and/or dolomite, whereas the deteriorated surfaces contain also gypsum, secondary and recrystallized calcite and dolomite, various inorganic compounds, fluoroapatite, microorganisms and other organic compounds. The purpose of this investigation is the analysis of the environmental conditions in the area of the archaeological site and the examination of their contribution to the deterioration of the building materials, in correlation with the decay characteristics of the monuments.

1. EXPERIMENTAL METHODS

A series of samples of the various building materials were collected from different locations of both monuments, Asklepios and Demeter. The accurate sampling sites were previously mentioned and presented (Papanikolaou et al., 2010).

Figure 1 General view of the sanctuaries of Asklepios (left), Demeter (right).

The mineralogical study of thin sections of the samples was carried out by optical microscopy using a Leitz Laborlux 11 POL S microscope. Scanning electron microscopy (SEM) was used to study the surface of samples. The SEM experiments were carried out with a JEOL, JSM-840 A scanning microscope, connected with a Energy Dispenser Spectrometer - EDS - (LINK, AN 10/55S). The physical properties of the materials were studied according standard methods (ICCROM 1999).

Twelve samples of bulk precipitation were collected on a monthly basis (December 2010 to November 2011) using a bulk precipitation collector located in the archaeological area for a period of one year. Three samples of surface waters were also collected from Vaphyras river and two rillets, all passing from the archaeological area. Upon receipt in the Laboratory, precipitation and surface water samples were filtered through 0.45 μm pore diameter cellulose membranes to remove particles. Chemical analysis for the determination of the chloride, nitrate and sulphate ions was carried out by Ion Chromatography.

2. RESULTS

The results of the mineralogical analysis of the deteriorated surfaces and inside the pores in the bulk of the materials are shown in Table 1 and Figures 2-3.

TABLE 1 Mineralogical composition of the deteriorated surfaces of the building materials of Asklepios and Demeter sanctuaries

Primary minerals	**Secondary minerals (sediments products)**	**Secondary minerals (deterioration products)**

Calcite: $CaCO_3$ Aragonite: $CaCO_3$ Dolomite: $CaMg(CO_3)_2$ Quartz: SiO_2 White mica and sericite: $KAl_2(Si_3Al)O_{10}(OH,F)_2$ Albite: $NaAlSi_3O_8$ Amphibole: $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ Epidote: $Ca_2(FeAl)_3(SiO_4)_3(OH)$ K-feldspar: $KAlSi_3O_8$	Kaolinite: $Al_2Si_2O_5(OH)_4$ Illite: $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ Mn-oxides Rutile: TiO_2 Hematite: Fe_2O_3 Fluoroapatite: $Ca_5(PO_4)_3F$ Chromite: $FeCr_2O_4$ Organic matter	Gypsum: $CaSO_4 \cdot 2(H_2O)$ Secondary carbonate (calcite-dolomite) precipitated from water solutions Recrystallized calcite-dolomite crystals

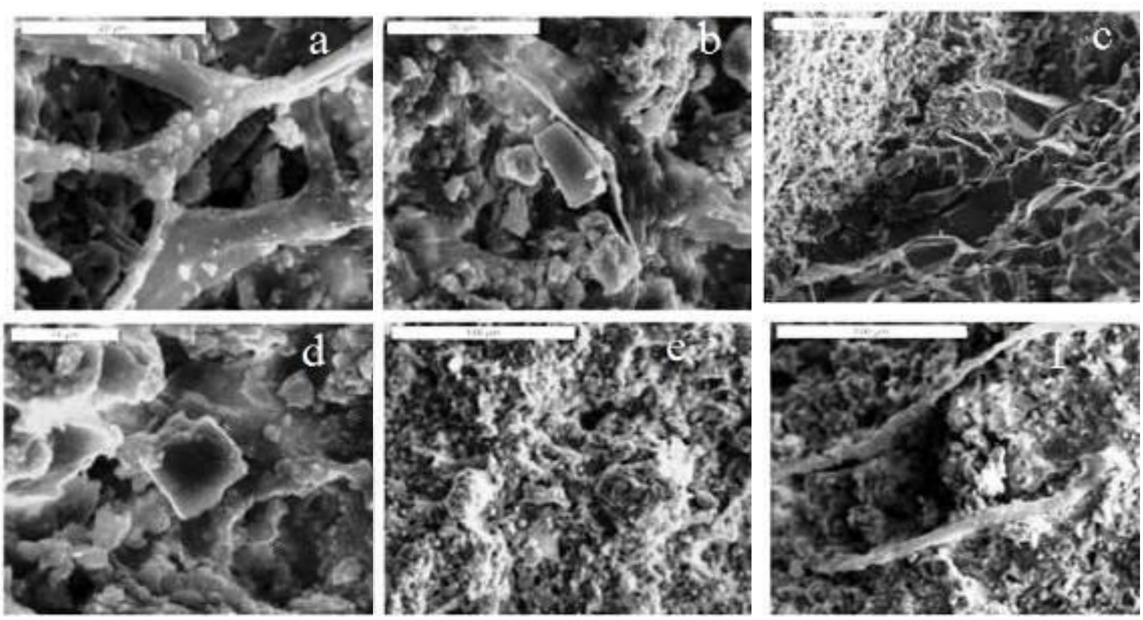
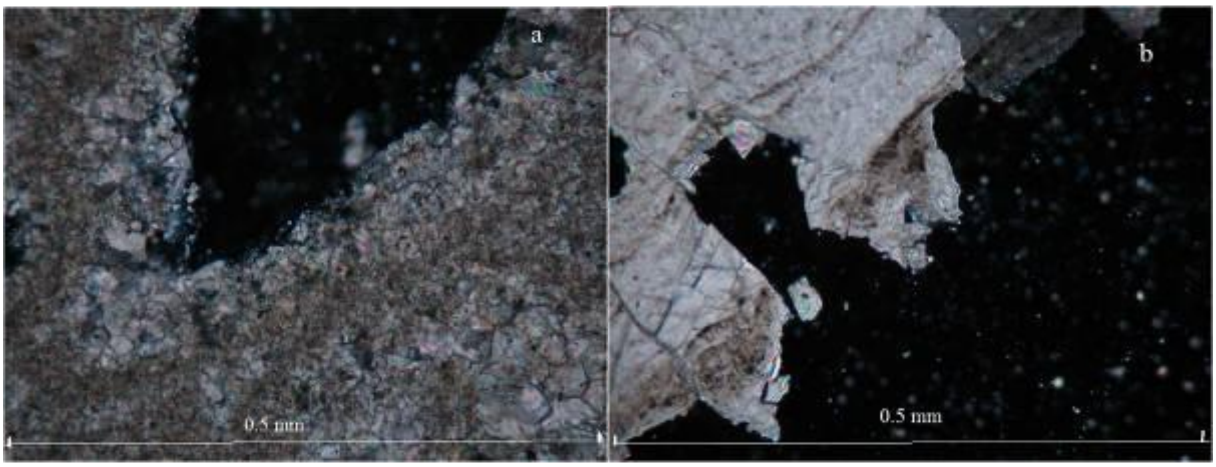


Figure 2 Photomicrographs of calcite limestone (a-d) and dolomitic limestone (e-f), secondary mineralogical composition of the deteriorated surface, a) Secondary carbonate (calcite-dolomite) precipitated from water solutions, SEM, b) secondary calcite-dolomite crystals, SEM, c) recrystallized calcite-dolomite crystals, SEM, d) gypsum crystal, SEM, e) secondary dolomite-calcite, SEM, f) carbonate (dolomite-calcite) precipitated from water solutions, SEM.



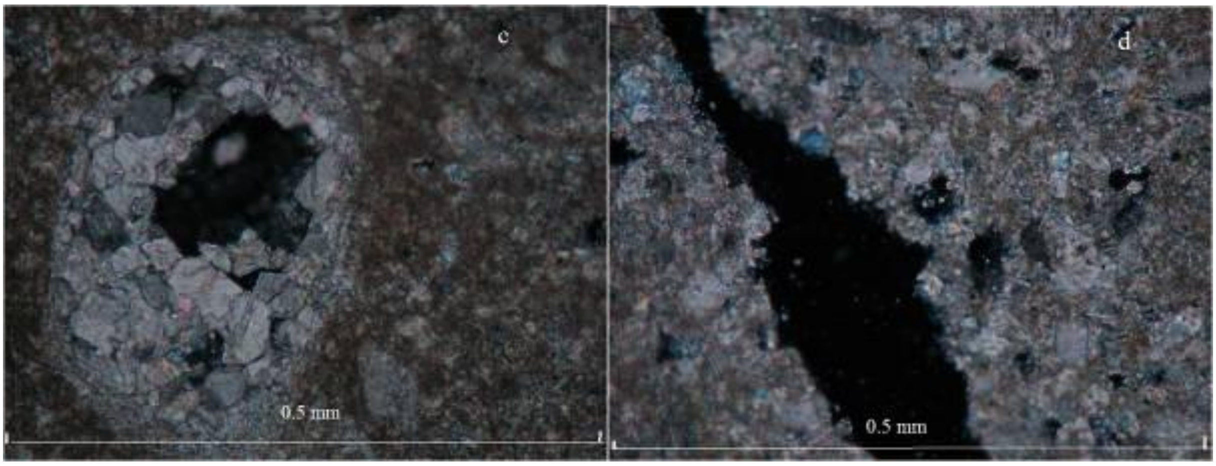


Figure 3 Recrystallization inside the pores of calcite limestone (a, b,), calcite sandstone (c, d)

The results of the study of the physical properties of the materials are shown in Table 2.

TABLE 2 Physical properties of the building materials of Asklepios and Demeter sanctuaries

Material / Property	Conglomerate	Lime stone - calcite	Lime stone - dolomite	Sand stone - calcite	Sandstone - dolomite	Ceramic Plinth	Marble - calcite	Marble - dolomite
Bulk density, γ, (gr/cm^3)	2.56	2.42	2.81	4.04	1.84	1.82	1.99	1.61
Dry bulk density, γ(d) (gr/cm^3)	2.72	2.59	2.84	5.41	1.93	2.78	2.01	1.62
Porosity Open, Pop, %	5.69	6.45	0.99	25.46	4.61	33.67	1.15	0.86
Water absorption, Wab, %	2.24	3.69	0.47	9.31	3.42	18.41	0.98	0.65
Water desorption Wde, %	2.21	3.65	0.44	9.13	3.36	17.05	0.92	0.62
Capillary absorption Cab, %	1.80	3.40	0.43	7.72	2.90	17.00	0.86	0.61
Capillary desorption Cab, %	1.78	3.37	0.41	7.57	2.83	15.69	0.81	0.59
Remained % of capillary absorbed-environmental conditions	1.02	0.89	5.03	1.85	2.61	7.73	5.53	3.21
Remained % of capillary absorbed	0.31	0.37	0.79	1.12	1.85	0.29	2.35	1.14

The results of the chemical analysis of bulk precipitation and surface water for major anions are shown in Figure 4.

In all surface water samples, ionic concentrations followed the order nitrates>sulphates>chlorides while the highest values were found in Vaphyras river. In all samples, ionic concentrations were within the range of values found in the river systems of Macedonia, northern Greece (Kouimtzis et al., 1994; Voutsa et al., 2001).
All bulk precipitation samples exhibited alkaline pH (6.5-7.5) suggesting neutralization of rainwater with alkaline reagents, such as gaseous ammonia and calcareous dust particles. Expectedly, bulk precipitation samplers, which are continuously open, also sample gases and particles deposited on the collection surface. With the exception of May and June samples, that exhibited extremely high sulphate content, concentrations ranged between 4.1 and 16 mgL^{-1} in agreement with the range of values found in wet-only precipitation samples in Thessaloniki (2.5-30 mgL^{-1}, Samara et al., 1992; Samara and Tsitouridou, 2000). Nitrate concentrations were highest in April and May (13 and 17 mgL^{-1}, respectively), but in most months they were below 4.4 mgL^{-1}, similarly to previous data. Finally, chlorides exhibited somewhat elevated concentrations (2.4-39 mgL^{-1}) with highest values in May and June suggesting possible transport of marine aerosol.

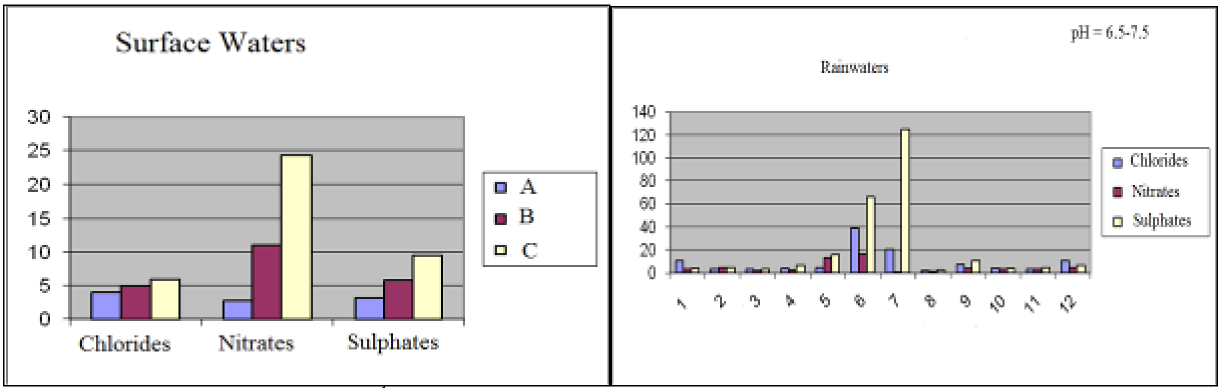


Fig. 4. Concentrations (mgL^{-1}) of sulphates, nitrates and chlorides in surface waters (A: Rillet A, B: Rillet B, C: Vaphyras river) and rainwaters (1: Dec 2010, 2-12: Jan-Nov 2011)

The kinds of lichens and vria found on the surfaces of the stone or in contact with it and the corresponding photo images are shown in Table 3 and Figure 5.

TABLE 3 Identification of lichens and bryophyta found in Asklepios and Demeter sanctuaries areas.

Lichens	Growth Form	Color	Bryophyta	
Candelariela aurella	Crust.	Yellow	*Aloina aloides*	*Rhynchostegium megapolitanum* **
Caloplaca citrina	Crust.	Yellow	*Ceratodon purpureus*	*Scorpiurum circinatum*
Collema tenax	Gelat.	Black	*Cratoneuron filicinum*	*Syntrichia Montana* Nees
Lecanora albescens	Crust.	white	*Didymodon luridus*	*Tortula intermedia*
Lecanora dispersa	Crust.	pale gray	*Didymodon vinealis*	*Tortula muralis*
Lecanora muralis	Placod.	Gray-green	*Fissidens bryoides*	*Pleurochaeta squarrosa*
Verrucaria nigrescens	Endol.	Dark olive-green	*Grimmia pulvinata*	
Xanthoria saxicola	Fol.	Orange	*Kindbergia praelonga* ***	
Rinodina calcarea	Crust.	gray	*Lunularia cruciata*	

			(L.) *	

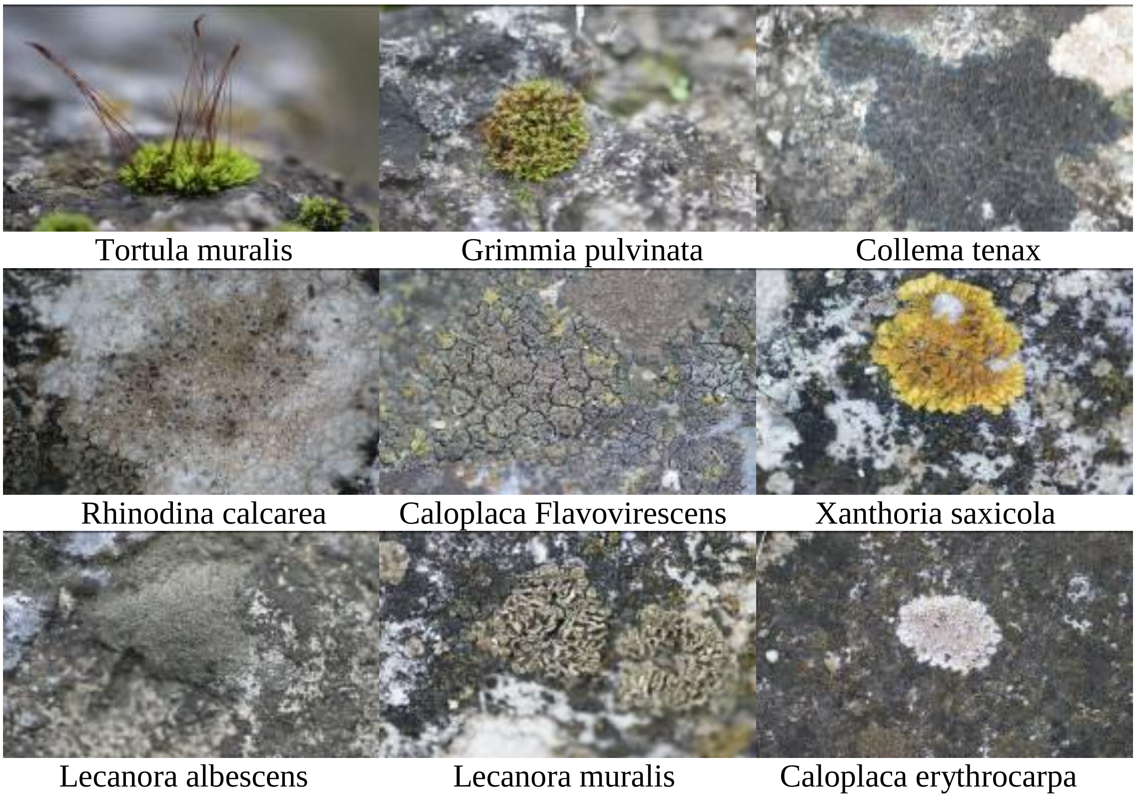


Figure 5 Lichens and bryophyta found in Asklepios and Demeter sanctuaries areas.

3. DISCUSSION

It is evident (Table 1 and Figures 2, 3) that the surfaces of the building materials are partially covered by the weathering products of the primary minerals such as secondary carbonate (calcite-dolomite) precipitated from water solutions, recrystallized calcite and dolomite and in some cases gypsum. An intense presence of lichens and bryophyte is observed. The presence of crusts of various inorganic/organic compounds, such as illite, kaolinite, sericite, rutile, chromite, Fe-oxides, Mn-oxides, fluoroapatite, fragments of fossils, is related to various sediments that covered the primary materials.

From the results of the chemical analysis of the rain and surface waters (Figure 4) it is evident that there are not significant amounts of various ions such as chlorides, nitrates or sulphates (except a period of two months of rain water samples). This observation is in accordance with the mentioned absence of crystallized salts on the surface or inside the pores of the materials (only limited gypsum was observed).

The results of the study of the physical properties of the materials (Table 2) show significant variances in the values of open porosity, water and capillary absorption between the various building materials. Despite this, it is observed that in all cases of materials the values of capillary absorption are close to the corresponding values of total water absorption indicating that capillary absorption is enough for the materials to reach moisture saturation conditions. It is also shown that a significant amount of the capillary absorbed water remains in the material after desorption in environmental conditions. In the specific conditions of the archaeological area a permanent intensive presence of surface and underground water for all periods of the year and high temperature values in the dry periods of summer are observed, leading in repeated cycles of wet-dry conditions of the materials. From these results and observations, in correlation with the examined weathering products, mainly secondary and recrystallized calcite and dolomite, it is confirmed that the main deterioration problem of the materials is the moisture attributed to the capillary action. The cycles of wet-dry conditions lead to partial dissolution-recrystallization of the carbonate materials and loss of the structural cohesion and the surface stability.

The intensive presence and growth of various lichen and bryophyte species on the surface of the materials is also a result of the environmental conditions. Especially species such as *Lunularia cruciata*, *Rhynchostegium megapolitanum*, *Kindbergia praelonga*, *Scorpiurum circinatum* require the existence of high moisture contents for their growth, whereas *Tortula, Syntrichia, Grimmia* are proof against intensive dry conditions, growing on sunny surfaces. The inward growth of bryophyte rhizoids via fissures leads to physical damage of the stonework, which could promote disaggregation. The penetration of the lichens in the substrate and the rapid absorption and desorption of water cause mechanical stress, consistently reducing the cohesion of the material. These actions undoubtedly lead to mechanical damage to stonework yielding a significant disaggregation and fragmentation of the substrate immediately below the lichen thallus (Gazzano et al. 2009, De los Rios et al. 2009). Combined with the chemical breakdown of substrata by lichen metabolic products it is clear that all these biogeophysical processe are of great importance. Colour alteration is also induced in the material due to the adsorption of the pigments contained in lichens.

4. CONCLUSIONS

1. The surface of the building materials are partially covered by the weathering products of the primary minerals such as secondary calcite and dolomite precipitated from water solutions, and recrystallized calcite and dolomite.
2. Limited presence of crystallized salts on the surface or inside the pores of the materials is observed.
3. Absence of significant amounts of various ions such as chlorides, nitrates or sulphates is observed in the rain and surface waters.
4. Lichens colonization is observed in various parts of the surface of the materials.
5. The existence of water in the bulk of the materials due to capillary penetration, the increased moisture absorption and the growth of lichens on the surface of the materials, correlated with the intensive surface and underground water presence in the whole surrounding area, led to loss of the structural cohesion and the surface instability of the building materials.

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