Characterization and Weathering of the Building Materials of Sanctuaries in the Archaeological Site of Dion, Greece

Spathis P.[1], Papanikolaou E.[2], Melfos V.[2], Samara C.[1], Christaras B.[2], Katsiotis N.[3]

[1]School of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece,
[2]School of Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece,
[3]School of Chemical Engineering, National Technical University of Athens, 15780 Athens, Greece
Correspondence: Spathis P. (spathis@chem.auth.gr)

Abstract The sanctuaries of Demeter and Asklepios are part of the Dion archaeological site that sits among the eastern foothills of Mount Olympus. The main building materials are limestones and conglomerates. Sandstones, marbles, and ceramic plinths were also used. The materials consist mainly of calcite and/or dolomite, whereas the deteriorated surfaces contain also secondary and recrystallized calcite and dolomite, gypsum, various inorganic compounds, fluoroapatite, microorganisms and other organic compounds. Cracks and holes were observed in various parts of the stones. 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, pore size distribution, 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 influence of the water presence to the behavior of the materials was examined by in situ IR thermometer measurements. Temperature values increased from the lower to the upper parts of the building stones and they significantly depend on the orientation of the walls. The results indicate the existence of water in the bulk of the materials due to capillary penetration. The existence of water in the bulk of the materials due to capillary penetration, the cycles of wet-dry conditions, correlated with the intensive surface and underground water presence in the whole surrounding area, lead to partial dissolution-recrystallization of the carbonate material and loss of the structural cohesion and the surface stability.

Keywords: : stone, deterioration, physical characteristics, capillary rise, IR thermometry.

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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[1]. Under these conditions, the stone surfaces disintegrate into powder and the building materials gradually lose their mechanical strength and their artistic form[2-6]. 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+} [7-13]. Various destructive or non-destructive methods are used for the study of the weathering of the building stone materials of the monuments, being part of their conservation[14-16].

The aim of the present work is the study of the effect of the environmental factors and the deterioration problems 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[17-20] it was found that the main building materials of the monuments are limestones and conglomerates. Sandstones, marbles and ceramic plinths were also used. The materials consist mainly of calcite and/or dolomite. 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. The presence of crusts of various inorganic/organic compounds, such as illite, kaolinite, sericite, rutile, Fe-oxides, Mn-oxides, fluoroapatite, fragments of fossils, is related to various sediments that covered the primary materials. No significant amounts of salts were found on the surface or inside the pore of the materials. The purpose of this investigation is the analysis of the environmental conditions in the area of the archaeological site, the examination of their contribution to the deterioration of the building materials and the study of the influence of the water presence to the behavior of the materials by in situ IR thermometer measurements and laboratory measurements of their physical characteristics.

Materials And 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[17]. The in situ measurements were focused in two monuments, Asklepios Temple, Altar in Demeter sanctuary (Figure 1).

Figure 1 General view of the sanctuaries of a) Asklepios, b) Demeter.

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 an Energy Dispenser Spectrometer - EDS - (LINK, AN 10/55S). The physical properties of the materials were studied according standard methods[21].

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.

Two series of IR thermometer in situ measurements, in conditions of sunny or wet weather, were carried out by a portable infrared laser thermometer (Center 358, Infrared thermometer, Range:-18^o C~ 315^o C). The question was to determine the high of the capillary water at the base of building stones, at the contact with the soil, given that the aquifer is very high, quite near to the foundation level of the monument. The idea was to use an infrared thermometer, because the inside temperature of the wet part of a stone is different than the next dry part, of the same stone, for the same time and weather conditions. The environment temperature during the measurements was ~ 28^o C (sunny conditions) or ~ 9^o C (wet conditions). In this study, infrared thermometer measurements were used in the assessment of moisture in porous stones. Due to the difference between the thermal diffusivities of moist and the dry stones, IR thermometer measurements are capable of showing qualitative variations in respiration behaviour (i.e. moisture impact), appearing as surface temperature fluctuations[22-23].

Results and Discussion

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.

From these results it is evident 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.

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: $CaSO_4$•$2(H_2O)$ Secondary carbonate (calcite-dolomite) precipitated from water solutions Recrystallized calcite-dolomite crystals

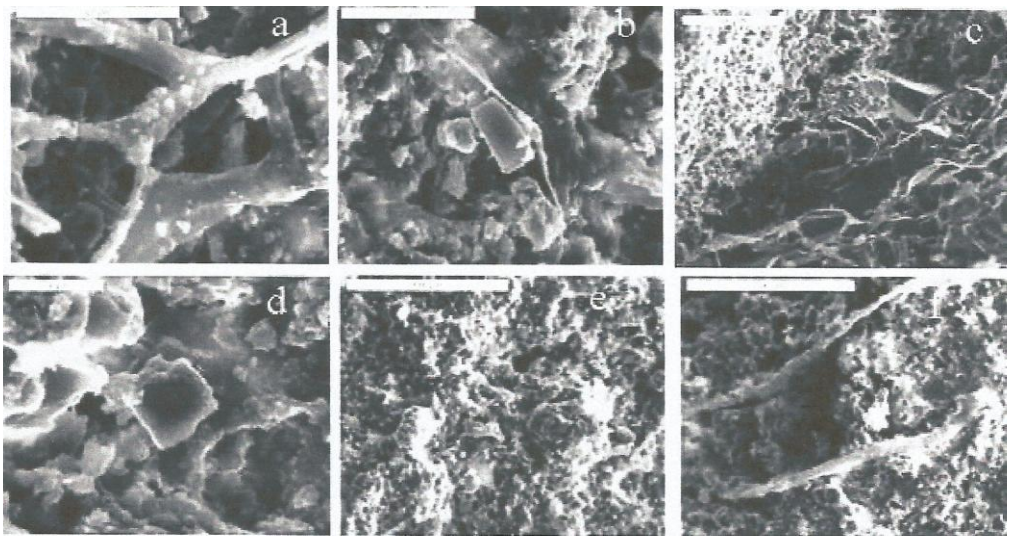

Figure 2 Photomicrographs of calcite limestone (a-d) and dolomitic limestone (e-f), secondary mineralogical composition of the deteriorated surface, a) Secondary carbonate (calcite-dolomite) precipitated from water solutions, SEM, b) secondary calcite-dolomite crystals, SEM, c) recrystallized calcite-dolomite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

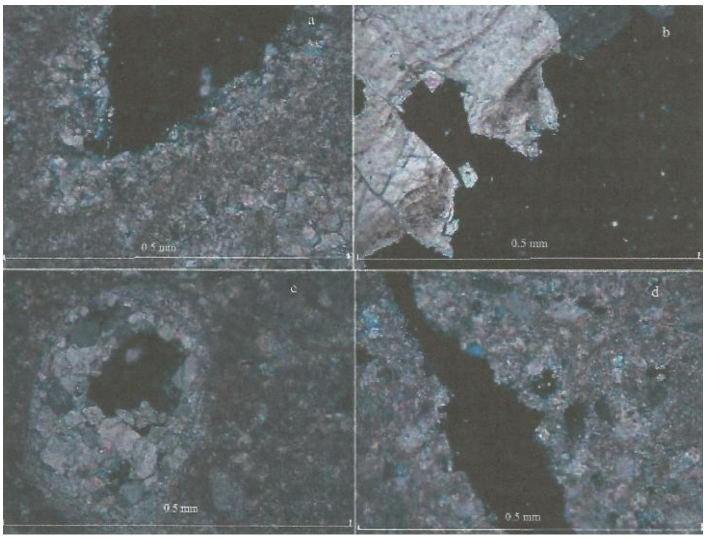

Figure 3 Recrystallization inside the pores of calcite limestone (a, b,), calcite sandstone (c, d)

The results of the study of the physical properties and characteristic pores of the materials are shown in Tables 2 and 3 and Figure 4.

These results show that exist great differences 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 waters 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 observed main weathering products, secondary and recrystallized calcite and dolomite, follow that the main deterioration problem of the materials is the moisture presence due to capillary action. The cycles of wet-dry conditions lead to partial dissolution-recrystallization of the carbonate material and loss of the structural cohesion and the surface stability.

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

Material / Property	Conglo merate	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

Table 3 Pore size Distribution %

Material / Pore size(μm)	Conglo merate	Lime stone, calcite	Lime stone, dolom	Sand stone, calcite	Sand stone, dolom	Ceramic Plinth	Marble, calcite	Marble, dolom
100-200	23.87	30.49	73.17	23.34	49.63	22.28	46.18	71.82
200-300	76.13	20.71	-	53.15	34.70	45.68	18.21	15.48
300-500	-	21.96	21.26	12.11	11.85	12.29	0.76	0.89
500-700	-	11.76	5.05	8.64	3.54	13.68	19.31	8.54
>700	-	15.00	0.52	2.76	0.28	6.07	15.55	3.27

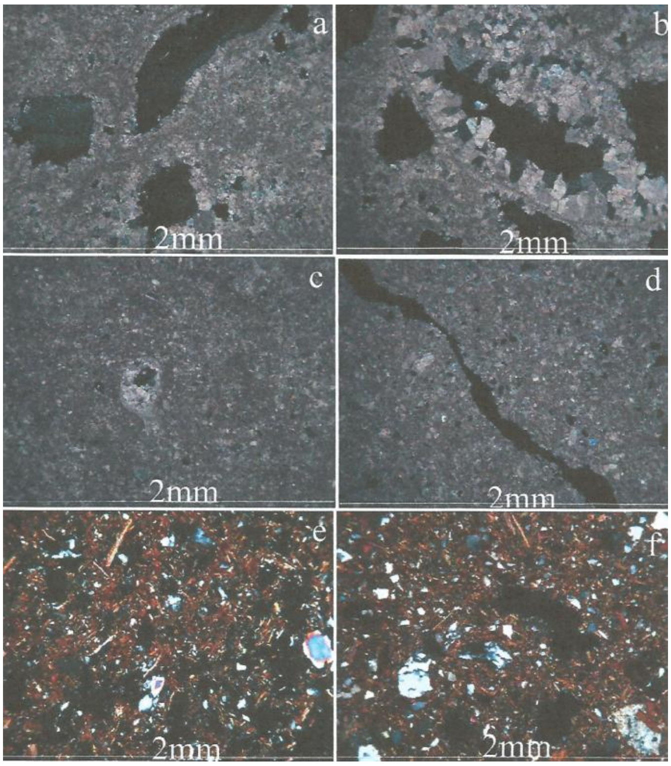

Figure 4 Photomicrographs of characteristic pores of calcite limestone (a, b,), calcite sandstone (c, d), ceramic plinth (e-f).

The results of the chemical analysis of bulk precipitation and surface water for major anions are shown in Figure 5.

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[24-25].

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})[26-27]. 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.

From these results 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).

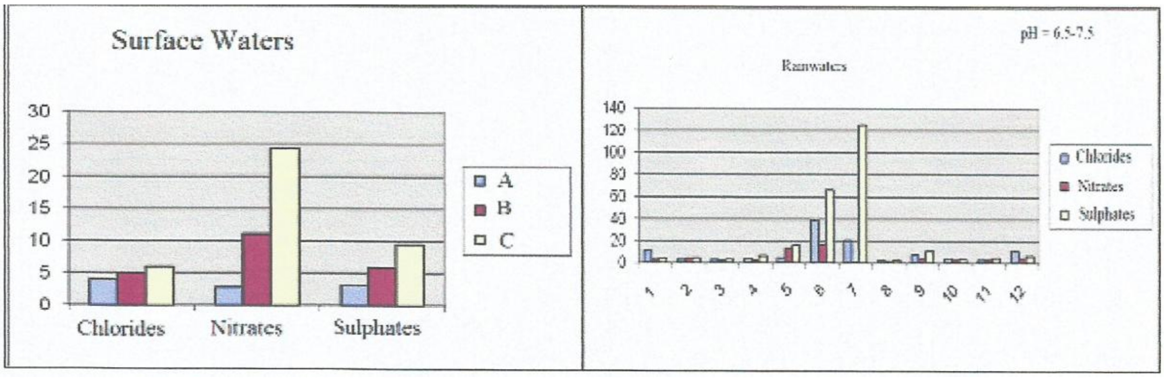

Figure 5 Concentrations (mgL^{-1}) of sulphates, nitrates and chlorides in surface waters (A: Rillet A, B: Rillet B, C: Vaphyras river) and rainwaters (1: Dec 2010, 2-12: Jan-Nov 2011)

The results of the IR thermometer in situ measurements are shown in Figures 6, 7 (sunny conditions) and Figures 8, 9 (wet conditions).

Since a moist porous material presents emittance variations, moisture detection in porous stones by means of IR thermometer measurements is feasible. IR thermometry monitors the water movement in porous materials and detects its impact by recording temperature variations on the stones' surfaces. The presence of moisture (lower temperatures) that arises as a result of the capillary movement of water causes deterioration of the building material. In such cases, the optical properties are altered, the density, specific heat capacity and thermal conductivity are also affected and so any temperature changes are much slower in a moist area, as the energy required to raise the temperature of a moist area would be much greater than an area that is unaffected by water. In all cases of IR thermometer in situ measurements, the recorded temperatures on the side surfaces of the walls increase with the distance from the ground. The temperature differences depend mainly on the environmental conditions (sunny or wet), also on the kind of the material and the orientation of the wall, being greater in sunny and smaller in wet conditions. The IR thermometer measurements correlated with the water and capillary absorption and desorption results (Table 2) and also the permanent intensive presence of surface and underground waters indicate that the main deteriorating factor of the materials is the moisture penetration due to capillary action. In sunny conditions, moisture penetrates into the materials only by capillary absorption (greater temperature differences, Figures 6, 7), while in wet conditions rain water and environmental humidity contribute also to the total moisture absorption (smaller temperature differences, Figures 8, 9).

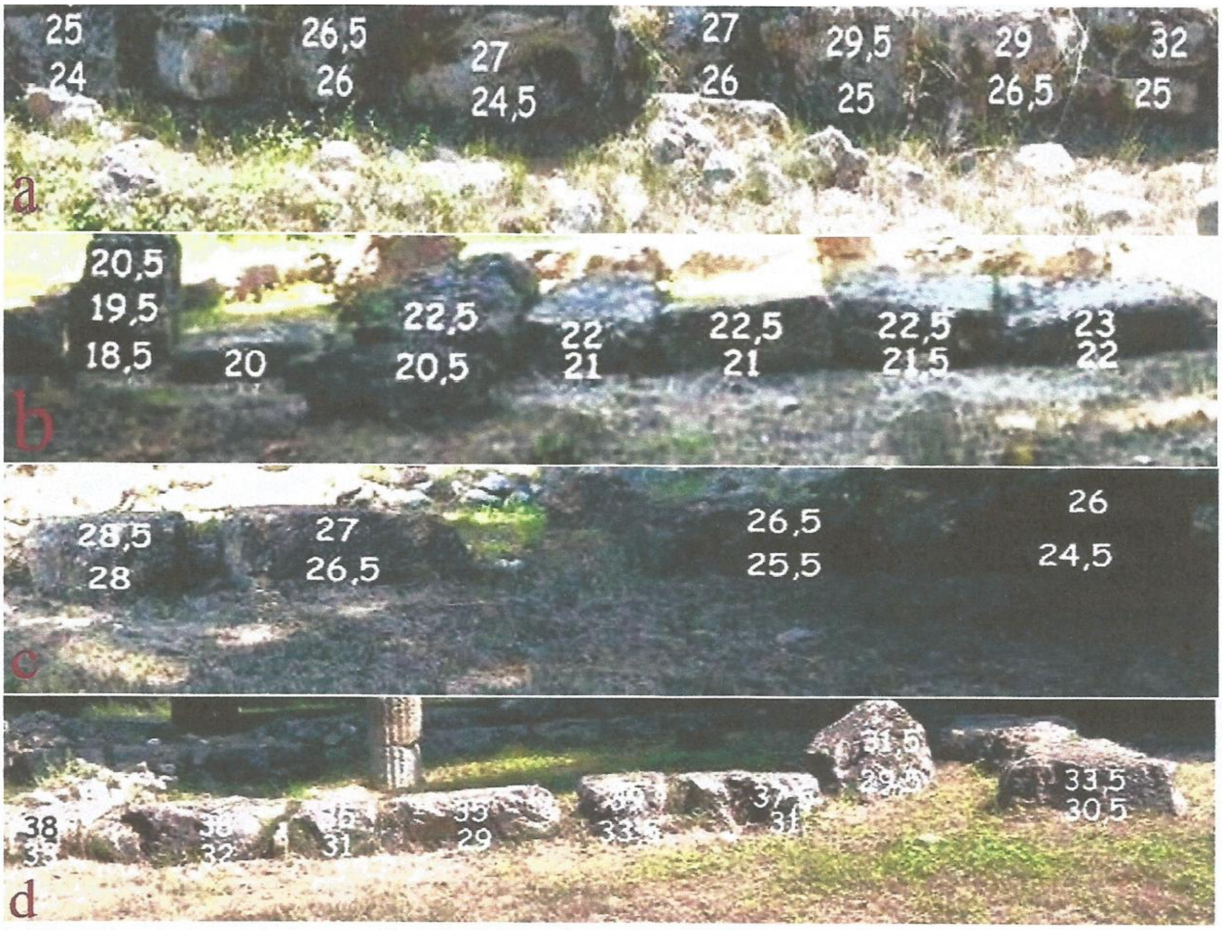

Figure 6 IR thermometer measurements, sunny conditions, Asklepios temple, a) north side, b) east side, c) south side, d) west side

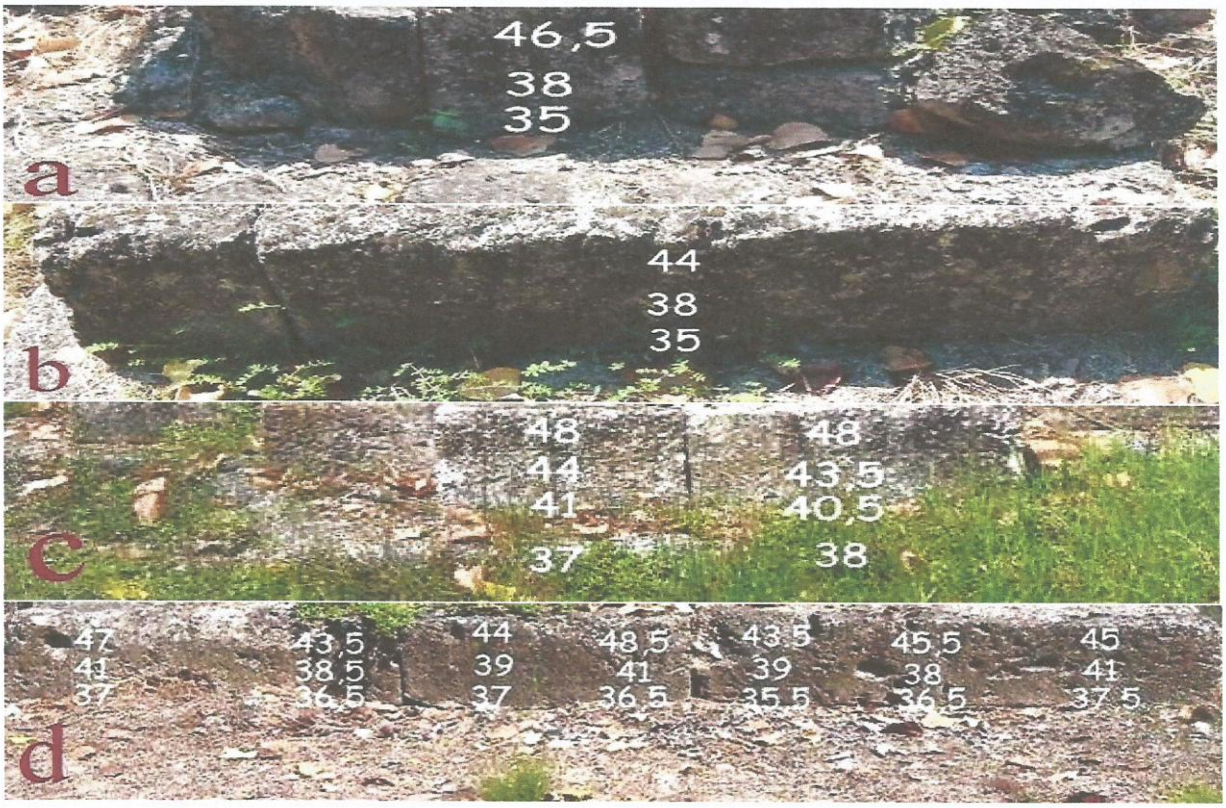

Figure 7 IR thermometer measurements, sunny conditions, Demeter sanctuary, Altar, a) north side, b) east side, c) south side, d) west side.

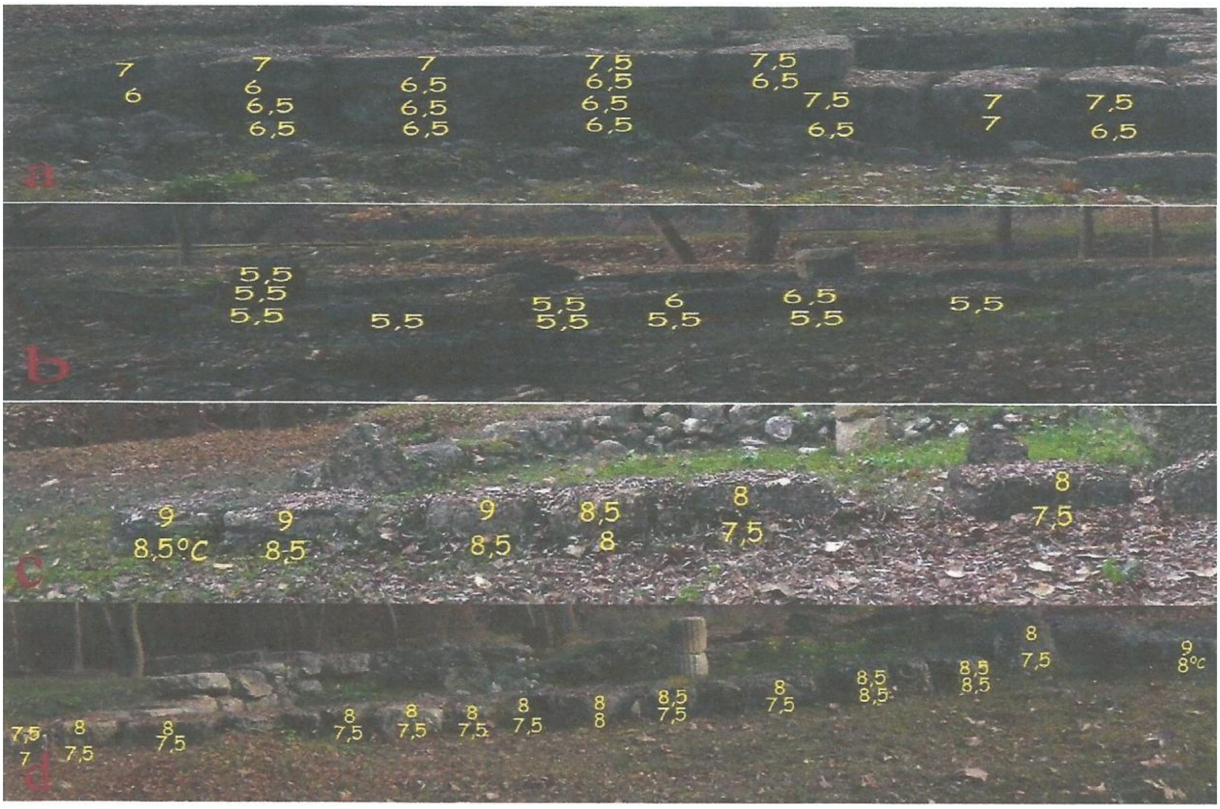

Figure 8 IR thermometer measurements, wet conditions, Asklepios temple, a) north side, b) east side, c) south side, d) west side

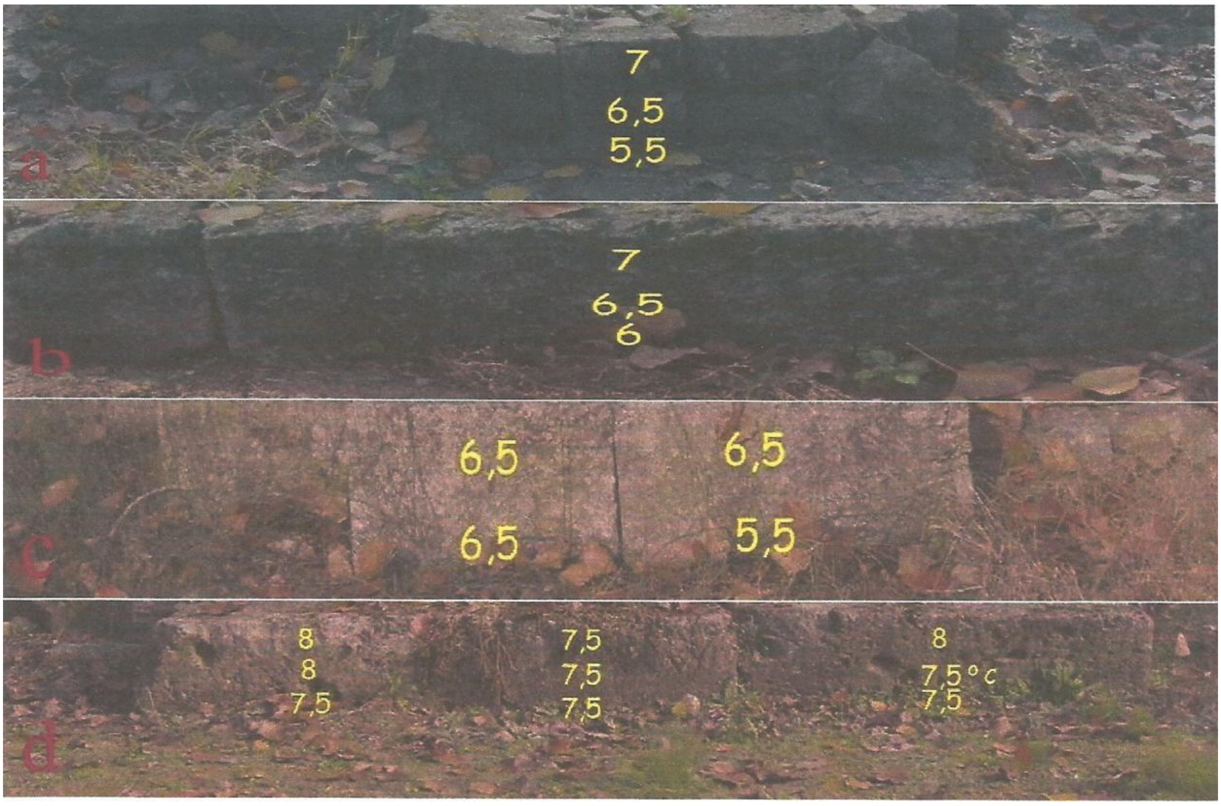

Figure 9 IR thermometer measurements, wet conditions, Demeter sanctuary, Altar, a) north side, b) east side, c) south side, d) west side.

Conclusions

From the combination of laboratory experiments and in situ IR thermometer measurements follow safe results about the deterioration problems of the materials.

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.

Limited presence of crystallized salts on the surface or inside the pores of the materials is observed.

Absence of significant amounts of various ions such as chlorides, nitrates or sulphates is observed in the rain and surface waters.

The main weathering factor of the materials is the moisture penetration due to capillary action.

In sunny conditions, moisture penetrates into the materials only by capillary absorption, while in wet conditions rain water and environmental humidity contribute also to the total moisture absorption.

The existence of water in the bulk of the materials due to capillary penetration correlated with an intensive surface and underground water presence in the whole surrounding area lead to loss of the structural cohesion and the surface instability of the building materials.

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