Deterioration Problems of the Building Materials from Demeter and Asklepios Sanctuaries in the Archaeological Site of Dion, Greece

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ABSTRACT

The main building materials of Demeter and Asklepios sanctuaries in Dion archaeological site are limestones and conglomerates. Travertines, marbles, sandstones and ceramic plinths were also used. A detailed mineralogical and petrographic study of these materials showed that they consist mainly of calcite and/or dolomite, whereas the deteriorated surfaces contain also gypsum, recrystallized calcite and dolomite, various inorganic compounds, fluoroapatite, microorganisms and other organic compounds. The influence of the water presence to the behavior of the materials was examined by in situ ultrasonic velocity and infrared thermographic measurements. Cracks and holes were carefully observed in various parts of the stones. Ultrasonic velocity values were not depended neither on the distance from the ground level, nor from the orientation of the wall. In contrast, temperature values increased from the lower to the upper parts of the building stones and they significantly depend on the orientation of the walls. These results indicated the existence of water in the bulk of the materials due to the capillary penetration, from the underground water which is present in shallow levels at the surrounding area. These conditions led to loss of the structural cohesion and the surface stability of the material and to the formation of various layers on the material surfaces (crusts of recrystallized calcite/dolomite, sediments, biological patina, growth of microorganisms, gypsum).

Keywords: stone, deterioration, mineralogical composition, water influence, non destructive techniques

INTRODUCTION

Deterioration of historical monuments is the result of chemical reactions of polluted air, soil and water with the building stone materials. The crystallization and hydration of corrosion products results 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. Under these conditions, the stone surfaces disintegrate into powder and the building materials gradually lose their mechanical strength and their artistic form. These processes have been observed in most of the ancient monuments in Greece.

The main causes of deterioration of the stone materials, in addition to their nature, composition and properties, are the low stability of the material due to the repeated periods of absorption-adsorption of water and evaporation of moisture, the crystallization of soluble salts at or near the surface and the destructive action of rainwater and groundwater (Keatings 2007), (Lan et al. 2005), (Skoulikidis 2000), (Moreno et al. 2006). 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. In the case of marbles the main mechanism of deterioration is the

sulfation of their surfaces, leading to the formation of gypsum layers on the stone surface, due to the solid state diffusion of Ca^{2+} (Keatings 2007), (Simao et al. 2006), (Sharma et al. 2007).
Various destructive or non-destructive methods are used for the study of the corrosion of the building stone materials of the monuments, being part of their conservation (Moropoulou et al. 2000), (Moropoulou et al. 2002), (Christaras 1998). Conservation may be defined as the dynamic management of change in order to reduce the rate of decay of the building materials in ancient monuments. In order to select an effective preservation method against the deterioration of the stone materials we have to identify the mineralogical composition, the petrographic features and the physical-mechanical properties, as well the processes contributing to the decay of their structure.
The aim of the present work is the study of the building materials and the processes contributing to the deterioration of Demeter and Asklepios sanctuaries in Dion archaeological site, one of the most important religious centers of ancient Greeks in central Macedonia. The purpose of the investigation is to demonstrate the mineralogical composition and the petrographic characteristics of the bulk and the deteriorated surfaces of the materials and to examine the influence of the water presence to their behavior, in order to compose special reactants for their rehabilitation and conservation.

EXPERIMENTAL

A series of thirteen samples were collected from different locations. The samples DA1-DA4 are from the Asklepios sanctuary and the samples DD1-DD9 are from the Demeter sanctuary. The accurate sampling sites were previously mentioned and presented (Papanikolaou 2010).
The samples used for the mineralogical and petrographic study of the building materials had a weight from 10 to 200 gr each, and were obtained very carefully, using a hammer and a small chisel, from already broken or damaged surfaces, which were free of any anthropogenic traces.
Thirteen thin sections of the rock samples were studied mineralogically by optical microscopy using a Leitz Laborlux 11 POL S microscope at the Department of Mineralogy-Petrology-Economic Geology of the Aristotle University of Thessaloniki (AUTh), Greece. Microscopy was employed both to evidence the geometrical relationships among the mineral constituents, with particular reference to calcite and/or dolomite, as well as to detect the accessory grains. The mineralogical composition, the textural features and the general characteristics of the rocks were identified in details.
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) at the Faculty of Science of AUTh.
In addition, powders of the samples were processed by X-ray diffraction (XRD) in order to distinguish calcite from dolomite and aragonite and to verify the related abundances in each sample. XRD analyses were performed at the Department of Mineralogy-Petrology-Economic Geology of AUTh, using a Phillips type diffractometer with Ni-filtered $CuK_{á}$ radiation. The powders of the samples were scanned over the interval 3-63° of 2θ with count rate of 10^3/sec and at a scanning speed of 1°/min.
Ultrasonic velocity is a good index characteristic not only for determining the physico-mechanical behaviour but also for evaluating the weathering degree of the rocks. For this purpose a PUNDIT Portable Ultrasonic Nondestructive Digital Indicating Tester Surfer Ultrasonic Detector UK1401 was used. Measurements were applied along the axis of the rocks and the travel time of the 54-KHz source pulse was measured. Tests were made using the indirect method. The indirect method, used especially on in-situ measurements, as in this case, refers to arrangement of the transducers on the same surface of the stone ((Christaras 1998), (Kantiranis et al. 2001), (Vascongelos et al. 2008), (Christaras 2009).
Infrared thermographic in situ measurements were carried out by a portable infrared laser thermometer (Center 358, Infrared thermometer, Range:-18^{o} C~ 315^{o} C). The environment temperature during the measurements was ~ 22^{o} C. In this study, infrared thermography was used in the assessment of moisture in porous stones. Due to the difference between the thermal

diffusivities of moist and the dry stones, infrared thermography is capable of showing qualitative variations in respiration behaviour (i.e. moisture impact), appearing as surface temperature fluctuations (Avdelidis et al. 2003), (Avdelidis et al. 2004).

RESULTS AND DISCUSSION

The main rock types used as building materials in the studied monuments of Dion were limestone and conglomerate (Fig. 1-3). In some cases travertine, sandstone, and marble were used, whereas ceramic plinths were rarely used. In the deteriorated surfaces apart from the primary minerals (calcite and dolomite, Fig 4-5), gypsum, kaolinite, illite, sericite. recrystallized calcite and dolomite, Fe-oxides, chromite, rutile, fluoroapatite, microorganisms and other organic compounds were also found (Tab 1-2).

The sample DD1 is characterized as a fossiliferous limestone and consists mainly of calcite with traces of dolomite and quartz. The greatest part of the rock consists of micritic calcite and organic matter. Kaolinite and Fe-oxides were found on the deteriorated surface.

The samples DD2 and DA1 are calcitic conglomerates (Fig. 1) and consist of rounded limestone cobbles which are composed mainly of calcite, with minor dolomite and traces of white mica, quartz and fragments of fossils. Kaolinite, gypsum, illite, dolomite, Fe oxides, chromite and organic matter were detected on the deteriorated surfaces.

The samples DD3 and DA2 are dolomitic limestones displaying a characteristic layering (Fig. 2 and 5). The mineralogical composition of the limestones is dolomite with traces of calcite, aragonite, quartz, white mica or albite. White mica, illite, albite, rutile, Fe-oxides, dolomite, quartz and hematite were found on the deteriorated surfaces.

In the sample DD4 which is a white coarse-grained marble, the main mineral is dolomite, with traces of calcite and albite. Kaolinite and illite were detected on the deteriorated surface.

The samples DD5 and DD9 are coarse-grained marbles which consist mainly of calcite with traces of quartz or dolomite (Fig. 3). Kaolinite, illite, albite, fluoroapatite and Fe-oxides were found on the deteriorated surfaces.

The sample DD6 is characterized as a travertine and consists mainly of fine-grained calcite with traces of aragonite, dolomite and quartz (Fig. 3,4). Fragments of fossils are also observed whereas the main part of the rock consists of organic matter. Kaolinite, dolomite, chromite, illite, rutile and Fe-oxides were found on the deteriorated surface.

The sample DD7 is characterized as a sandstone. Mineralogical examination revealed that it consists of calcite and dolomite with traces of quartz, opaque minerals (mainly sulfides) and Fe-oxides (Fig. 3). The sandstone is cemented with carbonates and occasionally with organic matter. Illite and gypsum were detected on the deteriorated surface.

The samples DD8 and DA3 are ceramic plinths consisting of angular grains of various minerals, such as quartz, calcite, dolomite, white mica, amphibole, epidote and K-feldspar which are dispersed in the fired clay (Fig. 3). Illite gypsum, Fe-oxides and chromite were detected on the deteriorated surface.

Finally the sample DA4 is sandstone consisting mainly of dolomite with minor calcite and traces of quartz. Kaolinite, illite and Fe-oxides were detected on the deteriorated surface.

From the above results it is evident that the surfaces of the building materials are partially covered by the weathering products of the primary minerals such as gypsum, recrystallized calcite and dolomite, illite, kaolinite, sericite rutile, Fe-oxides and Mn-oxides. The presence of crusts of various inorganic/organic compounds, such as Fe-oxides, Mn-oxides, fluoroapatite, fragments of fossils, is related to various sediments that covered the primary materials. The different micro-organisms and other organic compounds were generated on the surface of the building materials mainly after the excavation of the monuments.

In addition to the weathering products the deterioration of the building materials was increased by the numerous cracks and holes observed in various parts of the stones. For evaluating the weathering degree of the building materials, ultrasonic velocity measurements were applied and the travel time was measured. The measurements were applied along the horizontal axis of the walls of the temple of Asklepios sanctuary, in different distances from the ground and on the external or the upper sides of the plinths (Fig. 6).

Table 1. Mineralogical composition of the various building materials and the deteriorated surfaces from the Demeter sanctuary (samples DD1-9) and the Asklepios sanctuary (samples DA1-4). Data from microscopy and XRD.

Sample	Rock type	Primary minerals			Deteriorated surfaces - Secondary minerals
		Main minerals	Minor minerals	Trace minerals	
DD1	Limestone	Calcite	-	Dolomite + quartz	Kaolinite + Fe-oxides + organic matter
DD2-DA1	Conglomerate	Calcite	Dolomite	Quartz + white mica	Kaolinite + gypsum + illite + chromite + Fe-oxides + organic matter
DD3-DA2	Limestone	Dolomite	±Calcite + aragonite	Quartz + white mica + albite	Illite + rutile + Fe-oxides + quartz + hematite
DD4	Marble	Dolomite	-	Calcite + white mica + albite	Kaolinite + illite
DD5-DD9	Marble	Calcite	±Dolomite	quartz	Kaolinite + illite + albite + fluoroapatite+ Fe oxides
DD6	Travertine	Calcite	-	Dolomite + quartz + albite	Kaolinite + dolomite + Chromite + illite + rutile + Fe-oxides
DD7	Sandstone	Calcite	Dolomite	Quartz + opaque + Fe-oxides	Kaolinite + Illite + rutile + gypsum
DD8-DA3	Ceramic plinth	Quartz, dolomite, ±Calcite	White mica	amphibole, epidote, K-feldspar, albite	Kaolinite + illite + sericite + gypsum + chromite + Mn-oxides
DA4	Sandstone	Dolomite	Calcite	-	Kaolinite + illite + Fe-oxides

Table 2. Chemical composition of the primary and secondary minerals

Primary minerals	Secondary minerals
Calcite: $CaCO_3$	Kaolinite: $Al_2Si_2O_5(OH)_4$
Dolomite: $CaMg(CO_3)_2$	Illite: $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Aragonite: $CaCO_3$	Gypsum: $CaSO_4 \bullet 2(H_2O)$
Quartz: SiO_2	Rutile: TiO_2
White mica and sericite: $KAl_2(Si_3Al)O_{10}(OH,F)_2$	Hematite: Fe_2O_3
Albite: $NaAlSi_3O_8$	Fluoroapatite: $Ca_5(PO_4)_3F$
Amphibole: $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	
Epidote: $Ca_2(FeAl)_3(SiO_4)_3(OH)$	
K-feldspar: $KAlSi_3O_8$	

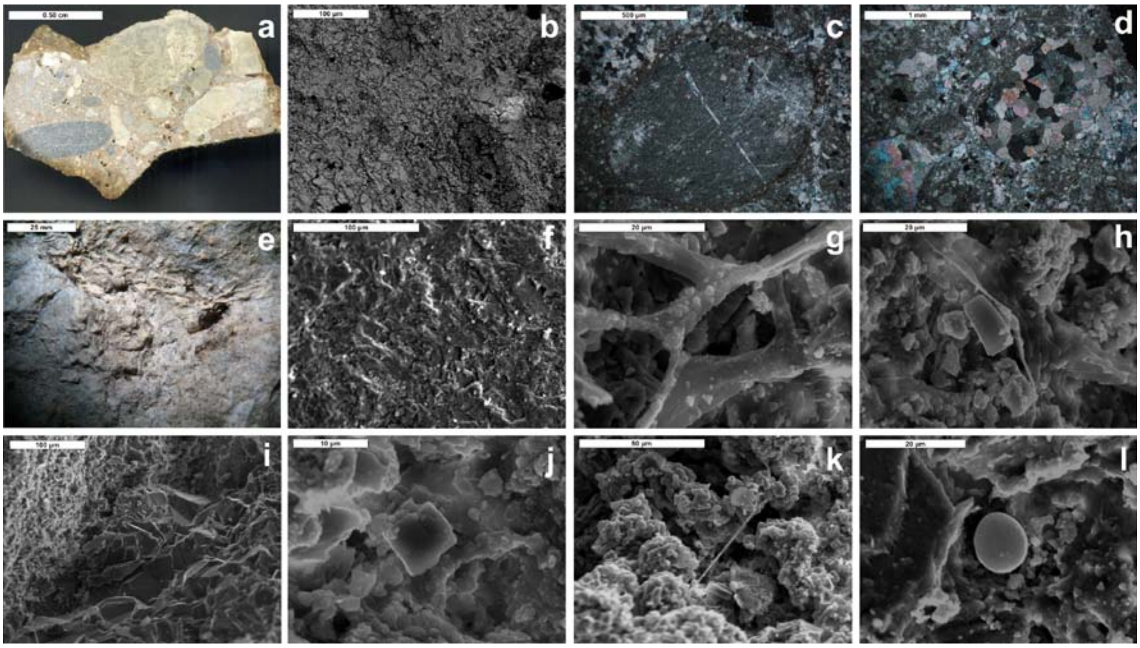

Fig.1. Photomicrographs of calcitic conglomerate (DD2 and DA1 samples). a-d: primary mineralogical composition. a) cross-sectione, b) general view of the surface, dark=dolomite, light=calcite, SEM, c) A cobble of fine-grained limestone in medium-grained dolomite-calcite, optical microscopy, d) A cobble of coarse-grained limestone in medium-grained dolomite-calcite, optical microscopy. e-l: secondary mineralogical composition of the deteriorated surface. e) surface, stereomicroscope, f) general view, g) Secondary carbonate (calcite-dolomite) precipitated from water solutions, SEM, h) secondary calcite-dolomite crystals, SEM, i) recrystallized calcite-dolomite crystals, SEM, j) gypsum crystal, SEM, k) illite and calcite-dolomite crystals and an organic fiber, SEM, l) An organism, SEM

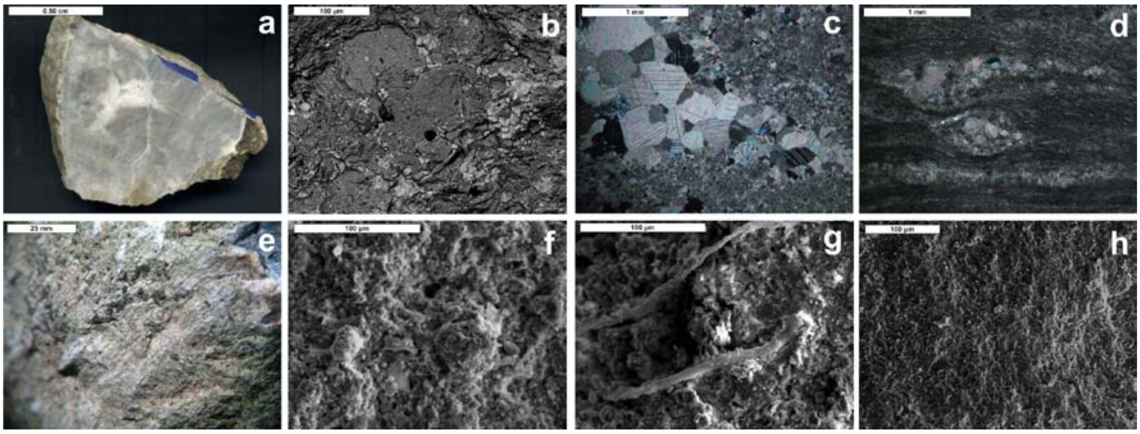

Fig. 2. Photomicrographs of dolomitic limestone (DD3 and DA2 samples). a-d: primary mineralogical composition. a) cross-section, dark=fine-grained dolomite, light= coarse-grained dolomite, b) Dolomite (dark) and calcite (light) crystals on the surface, SEM, c) Coarse-grained and fine-grained dolomite-calcite, optical microscopy, d)) Coarse-grained dolomite lenses in fine-grained dolomite-calcite, optical microscopy. e-i: secondary mineralogical composition of the deteriorated surface. e) surface, stereomicroscope, f) Secondary dolomite-calcite, SEM, g) and h) Carbonate (dolomite-calcite) precipitated from water solutions, SEM, i) Secondary dolomite and illite precipitated on the surface, SEM

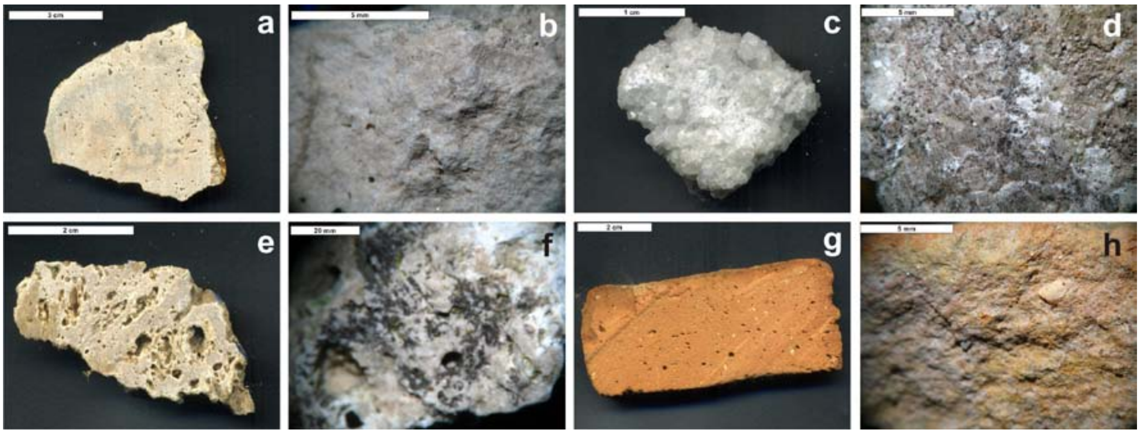

Fig. 3. Cross-sections and deteriorated surfaces of selected samples: a) and b) Sandstone (sample DD7), c) and d) Marble (sample DD5), e) and f) Travertine (sample DD6), g) and h) Ceramic plinth (sample DA3)

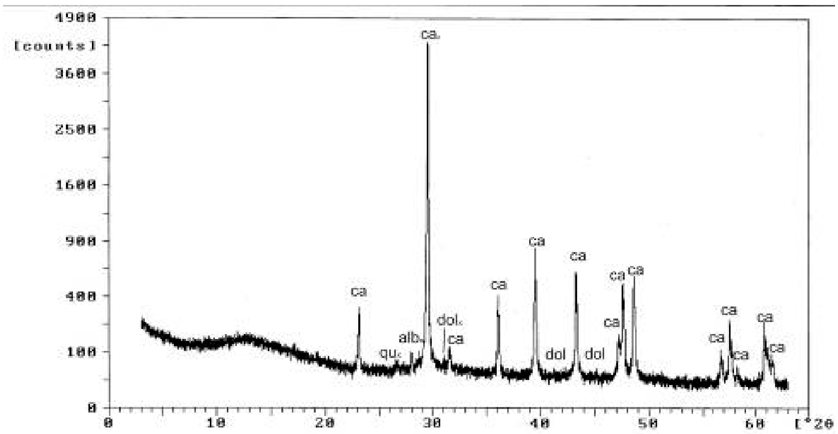

Fig. 4. X-ray diffraction diagram of the sample DD6 from the Demeter sanctuary in Dion. ca: calcite, dol: dolomite, qu: quartz, alb: albite.

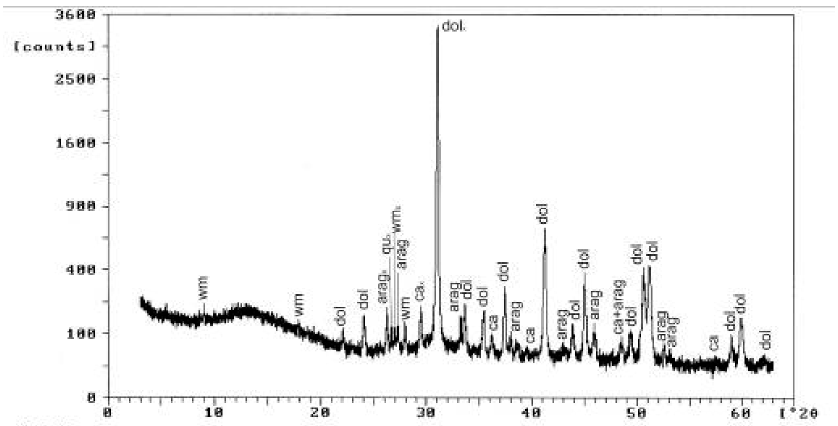

Fig. 5. X-ray diffraction diagram of the sample DD3 from the Demeter sanctuary in Dion. dol: dolomite, ca: calcite, arag: aragonite, wm: white mica

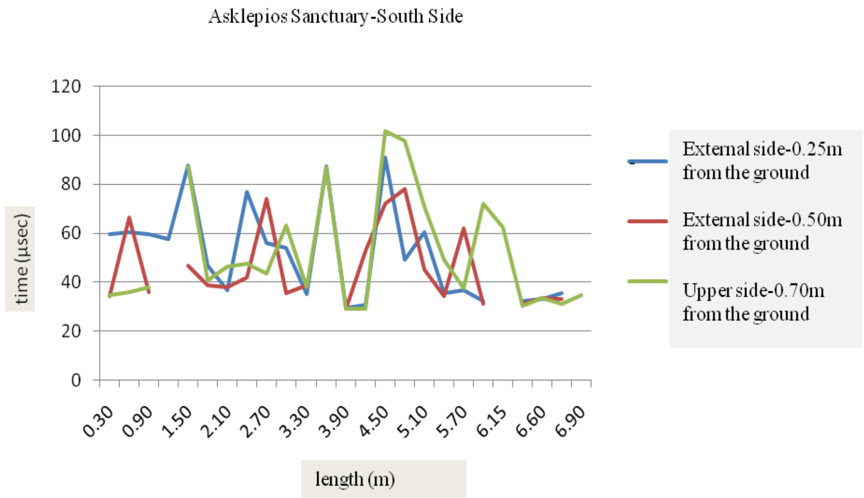

Fig. 6. Ultrasonic velocity measurements, travel time vs length (horizontal axis), on the surfaces of the external or the upper side of the plinths of the south wall of the temple of Asklepios sanctuary.

From the results of ultrasonic velocity measurements (Fig. 6) and the examination of the possible influence of the orientation on the weathering degree of the materials we concluded that the travel times were not depended on the distance from the ground level and on the orientation of the walls. However, great differences and fluctuations of the measured time values along the horizontal axis were observed. This fact is probably due to the nature of the measured materials. The building materials of the walls of the temple of Asklepios sanctuary consist mainly of conglomerate and limestone, which are relatively porous materials with an anomalous and not stable structure. This suggestion was confirmed by the ultrasonic measurements that were carried out on the marble base of a statue of priestess Verenike, sited in the area of Demeter sanctuary. The measured times on the marble surface were very similar, with no fluctuations and the observed values (22-25 μsec) were obviously lower than the observed values on conglomerate and limestone (30-120 μsec), indicating greater ultrasonic velocities and so more stable and less weathered material.
The results of the infrared thermographic insitu measurements are shown in Fig. 7, where the recorded temperatures on the surfaces of the walls of the temple of Asklepios sanctuary and in various distances from the ground are also presented. The observed temperature variations indicated the presence of water within the stones.

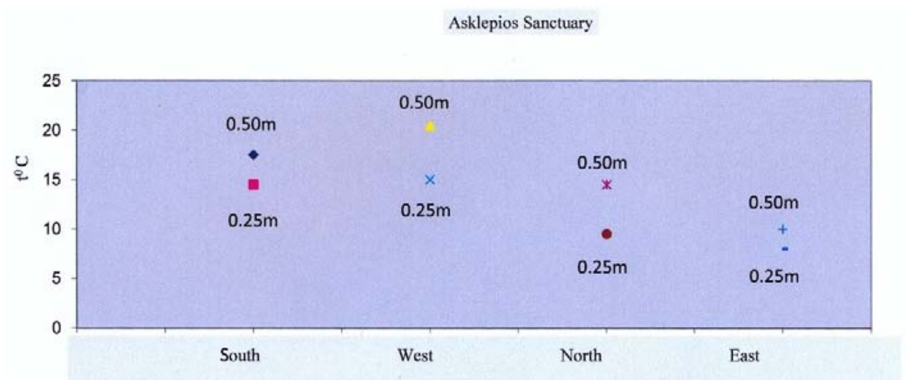

Fig. 7. Temperatures recorded on the surfaces of the walls of the temple of Asklepios sanctuary and in various distances from the ground.

Since a moist porous material presents emittance variations, moisture detection in porous stones by means of infrared thermography is feasible. Thermography provides visualisation of

moisture (water movement) in porous material; it 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 has caused deterioration of the building material. This is mainly because during water movement inside the pores there is also movement of salts. Since such porous materials have high porosity values and large amounts of large pores that trigger capillary action, water movement inside their porous systems occurs. 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.
The temperatures recorded on the surface of the marble base of the statue of priestess Verenike were 22-31.5 ºC in the areas near the ground and 27-36 ºC in the upper areas, indicating smaller water movement and deterioration of the material, in accordance with the above mentioned results of the ultrasonic measurements.

CONCLUSIONS

1. The main building materials of Demeter and Asklepios sanctuaries in Dion archaeological site are limestones and conglomerates. Travertine, marble, sandstone and ceramic plinths were also used in some cases.
2. The limestones and the travertines consist mainly of calcite and/or dolomite. The conglomerates are composed mainly of calcite and partly dolomite. The marbles consist of either white coarse-grained dolomite or coarse-grained calcite. The materials made of sandstone consist mainly of calcite and dolomite. The ceramic plinths contain angular grains of various minerals dispersed in the fired clay.
3. In the deteriorated surfaces of the building materials the presence of gypsum, recrystallized calcite and dolomite, illite, kaolinite, sericite rutile, Fe-oxides and Mn-oxides demonstrate the nature of the weathering products of the primary minerals. The crusts of various inorganic/organic compounds, such as Fe-oxides, Mn-oxides, fluoroapatite, fragments of fossils, originated from various sediments that covered the primary materials. The microorganisms and other organic compounds were generated on the surface of the building materials mainly after the excavation of the monuments. Cracks and holes are observed in various parts of the stones.
4. The existence of water in the bulk of the materials due to capillary penetration is indicated and is correlated with an intensive surface and underground water presence in the whole surrounding area. These factors led to loss of the structural cohesion and the surface unstability of the building materials.

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