PRELIMINARY OBSERVATIONS ON THE BUILDING MATERIALS AND THE DETERIORATION PROBLEMS OF THE MONUMENTS OF DEMETER AND ASKLEPIOS SANCTUARIES IN THE ARCHAEOLOGICAL SITE OF DION

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ABSTRACT

Dion sits among the eastern foothills of Mount Olympus, at the southern end of the Pierian plain. The ancient city was built on a site commanding the road from Thessaly into Macedonia. In antiquity it was just 1.5 km. from the coast of the Thermaikos Gulf.
The Dion archaeological site covers roughly 100 hectares. Excavation of the ancient city has brought to light the enhance of the fortified walls and an urban core laid out on a grid plan. Within its regular urban blocks the remains of public buildings, shops, workshops and luxurious dwellings have been brought to light. The excavations finds from this area are Hellenistic, Roman and Early Christian. Outside the walls, archaeologists have unearthed the sanctuaries of a number of gods, a Hellenistic and a Roman theatre, a stadium and extensive burial grounds. The sanctuary of Demeter is the most important and more ancient saved sanctuary in the whole area of the northern Greece.
The building materials of the sanctuaries of Demeter and Asklepios are porous limestone, sandstone, conglomerate and marble.
Condition 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 composition and properties of the materials as well the processes contributing to their deterioration.
A study of the mineralogical and chemical composition was carried out as well as preliminary results on the physical and mechanical properties and characteristics related to the weathering resistance of the materials were obtained: bulk density, water adsorption, point load index, uniaxial compressive strength, ultrasonic velosity, Young's modulus.
From the preliminary macroscopic examination follows that the materials show serious problems of corrosion and deterioration caused mainly by the atmospheric environment, the rain water and the presence on these of various kinds of pollutants, the capillary penetration of water in the bulk of the materials due to intensive surface and underground water presence in the whole surrounding area, the vegetation, the great temperature differences between day and night and in the various seasons. These factors lead to loss of the structural cohesion and the surface stability of the materials, the deterioration and the formation of various corrosion products in the materials surface (layers of various color and kind of crusts, biological patina, growth of microorganisms, gypsum formation).

INTRODUCTION

Deterioration of historical monuments is the result of chemical reactions of polluted air, soil and water with the stone material. The crystallization and hydration of corrosion products results in their expansion causing the degradation of dolomite, limestone, marble, sandstone and other building materials. The stone surface is gradually covered with salts and black crusts containing calcium, magnesium, sodium, potassium sulphates, nitrates and others. After that stone surface disintegrates into powder and the object gradually loses its mechanical strength and artistic form. These processes have been observed on all unique ancient monuments of 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 [1-4]. The water can easy penetrate and remain into the material, resulting in a destructive influence due to the absorption and evaporation of the moisture that causes changes in the volume and cracks in the bulk and the surface of the structure, leading to deterioration. In the case of marbles the main mechanism of deterioration is the sulfation of their surfaces, leading to the formation of gypsum layers, due to the solid state diffusion of Ca^{2+} [1, 5-6].
Various destructive or non-destructive methods are used for the study of the decay of the building stone materials of the monuments, being part of the conservation [7-9]. Conservation may be defined as the dynamic management of change in order to reduce the rate of decay at the building materials of ancient monuments. The monuments must be conserved as authentic documents and interventions should be limited to actions strictly necessary to insure the techniques and materials used should not impede future treatment or examinations. In order to select an effective preservation method against the deterioration of the stone materials we have to identify the mineralogical composition, the petrographical features and the physical-mechanical properties, as well the processes contributing to the decay of their structures.
The aim of the present study is to investigate the stone building materials of two ancient sanctuaries in Dion, one of the most important religious centers of ancient Greeks in central Macedonia. These sanctuaries were dedicated to goddess Demeter and to god Asklepios respectively and their condition is rather critical due to the advanced erosion of their building materials. The purpose of the investigation is to demonstrate the mineralogical composition along with the petrographical characteristics and to determine their physical and mechanical properties, in order to compose special reactants for their rehabilitation and conservation.

ARCHAEOLOGICAL BACKGROUND

Dion in Pieria of Macedonia was one of the most important religious centers of the ancient Greeks. Built at the eastern foothill of Mount Olympus, it was on the road leading from Thessaly to Macedonia. In antiquity it was just 1.5 km from the coast of the Thermaikos Gulf. Vaphyras, a navigable river passing to the east of the ancient city, provided a link to the sea, through the extensive marshlands and shallow lagoons of its estuary. Dion was directly connected with the worship of ancient gods and fairly described as the religious center of Macedonia. The flash and fame of Dion continued after the conquest by the Romans, who retained the worship of Zeus and other gods of the ancient Greeks. The rich and unique architecture dominates throughout the area both public and private buildings with very mosaics, famous sculptures, marble, columns.
During these many years of archaeological excavations important works of art made of white marble, dating from the Hellenistic period, Roman period and the early Christian era, were

uncovered. These marble implements were constructed by high quality raw materials from famous ancient quarries, such as those from Thasos and Penteli of Attica [10].
The site of Dion was identified in 1806 (Leake) and this identification was confirmed in 1855 (Heuzey). The excavations at Dion (Fig. 1) was launched in 1928 by the Rector of the University of Thessaloniki, G. Sotiriadis, and stopped in 1931. After stopping 30 years, research has continued by G. Bakalakis, Professor of Archeology at the Aristotle University of Thessaloniki. The third excavation season was inaugurated in 1973 by D. Pandermalis, Professor of Archaeology at the Aristotle University of Thessaloniki. The excavations continued until today under his direction [11-20].

Figure 1: Representation of the sanctuaries and the city of Dion [11].

The sanctuary of Demeter (Fig. 2) is the most important and more ancient saved sanctuary in the whole area of the northern Greece. The sanctuary of Asklepios was built after the middle of the 4th century BC.

(a) (b)

Figure 2: General view of the sanctuaries of a) Asklepios, b) Demeter [21].

The sanctuary of Demeter at Dion is one of the oldest sites sacred to the gooddess in Northern Greece. The temples within it were built at different periods, from the Late Archaic to the Imperial age. The earlier finds from the sanctuary were found in the enclosure with the wells, where libations were performed. The two fine Doric temples, were built in the late 4th century, replacing the Late Archaic megara. Within the sanctuary there were also smaller, single-room buildings, where offerings were made to divinities associated with fruitfulness and fertility, such as Aphrodite, Baubo and Kourotrofos. In front of the temples stood a raw of altars for sacrifices and libations to the underground deities. By the Late Imperial period, the sanctuary had been reduced to its northern section, while in Late Antiquity pottery kilns were set up in the area.
By the 4th century B.C. the cult of Asklepios was well established and flourishing at Dion. The sanctuary of the god (the Asklepieion) stood to the south of the sanctuary of Demeter. One of the reasons for the choice of this location was the presence of springs of pure water, which were an essential component of his cult and necessary for the cures that were effected in his temples. Excavation of the sacred precinct has already brought to light a temple, in which were found scattered fragments of inscriptions, pedestals and statues. In the Roman era a small public latrine was built to the north of the sanctuary, for the convenience of the many supplicants who came to seek healing there and who in all likelihood would spend the night in the temple, hoping for a miraculous cure for their ills.
The main excavated and saved constructions in the area of Asklepios sanctuary include a temple (with dimensions 10.70m x6.90m), an aqueduct (which was feed from a spring) and foundations of walls of 110m length, perhaps of a stoa. It was founded in the 4th or the beginning of the 3rd century B.C.

We have collected samples from the following buildings and monuments of the excavated area of Demeter sanctuary:

1) a temple of the Late 4th century B.C. (Southern Hellenistic Temple),
2) a temple of the Late archaic – classical period (Southern Classical Temple, with dimensions 6x4m),
3) an altar of the 4th – 3rd century B.C. (dimensions 4.10x2.60m and their foundations walls 4.40x3.10m),
4) a building of the 3rd century B.C. (Southern-East Building, 4.20x4.12m),
5) a stoa of the 4th – 3rd century B.C. (4.90m width and 30m length),
6) an enclosure of the 1st B.C.-1st A.C. century, 70m length,
7) a marble base of a statue of priestess Verenike of the 3rd century B.C.,
8) a roman temple (3rd Roman Temple, 6x4.50m) [1-10].

The main building materials of the structures are limestone, porous stone, conglomerate, marble, sandstone, ceramic plinth.

EXPERIMENTAL

A series of thirteen samples were collected from different locations. The sam[les DA1-DA4 are from the Asklepios sanctuary and the samples DD1-DD9 are from the Demeter sanctuary. The accurate sampling sites are shown in Figures 3-4.

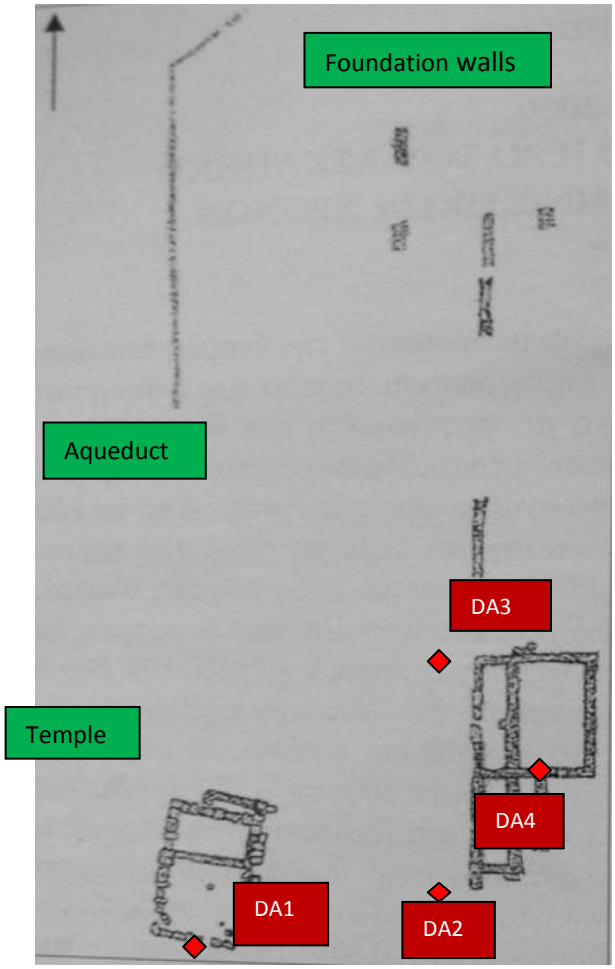


Figure 3: Ground plan of Asklepios sanctuary with the locations of samples DA1 conglomerate, DA2 limestone, DA3 ceramic plinth, DA4 sandstone

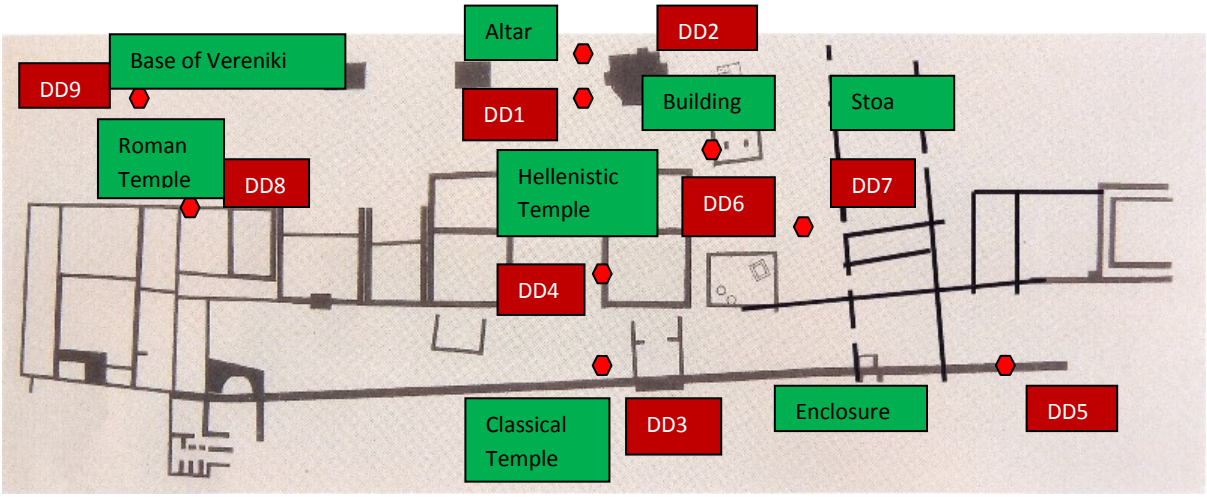


Figure 4: Ground plan of Demeter sanctuary with the locations of samples. DD1 porous stone, DD2 conglomerate, DD3 limestone, DD4 marble, DD5 marble, DD6 porous stone, DD7 sandstone, DD8 ceramic plinth, DD9 marble.

The samples used for the petrographic and mineralogical study of the building materials were 10 to 200 gr each and were obtained very carefully, using a hammer and a small chisel, from broken or damaged surfaces, which were free of any anthropogenic traces.
Thirteen thin and polished-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, 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.
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 in the Department of Mineralogy, Petrology, Economic Geology of the Aristotle University of Thessaloniki, using a Phillips type diffractometer with Ni-filtered $CuK_{\acute{a}}$ 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.
Preliminary experiments on the follow physical and mechanical characteristics were carried out, [9, 22-23]: bulk density, water adsorption, point load index, uniaxial compressive strength, ultrasonic velosity, Young's modulus.

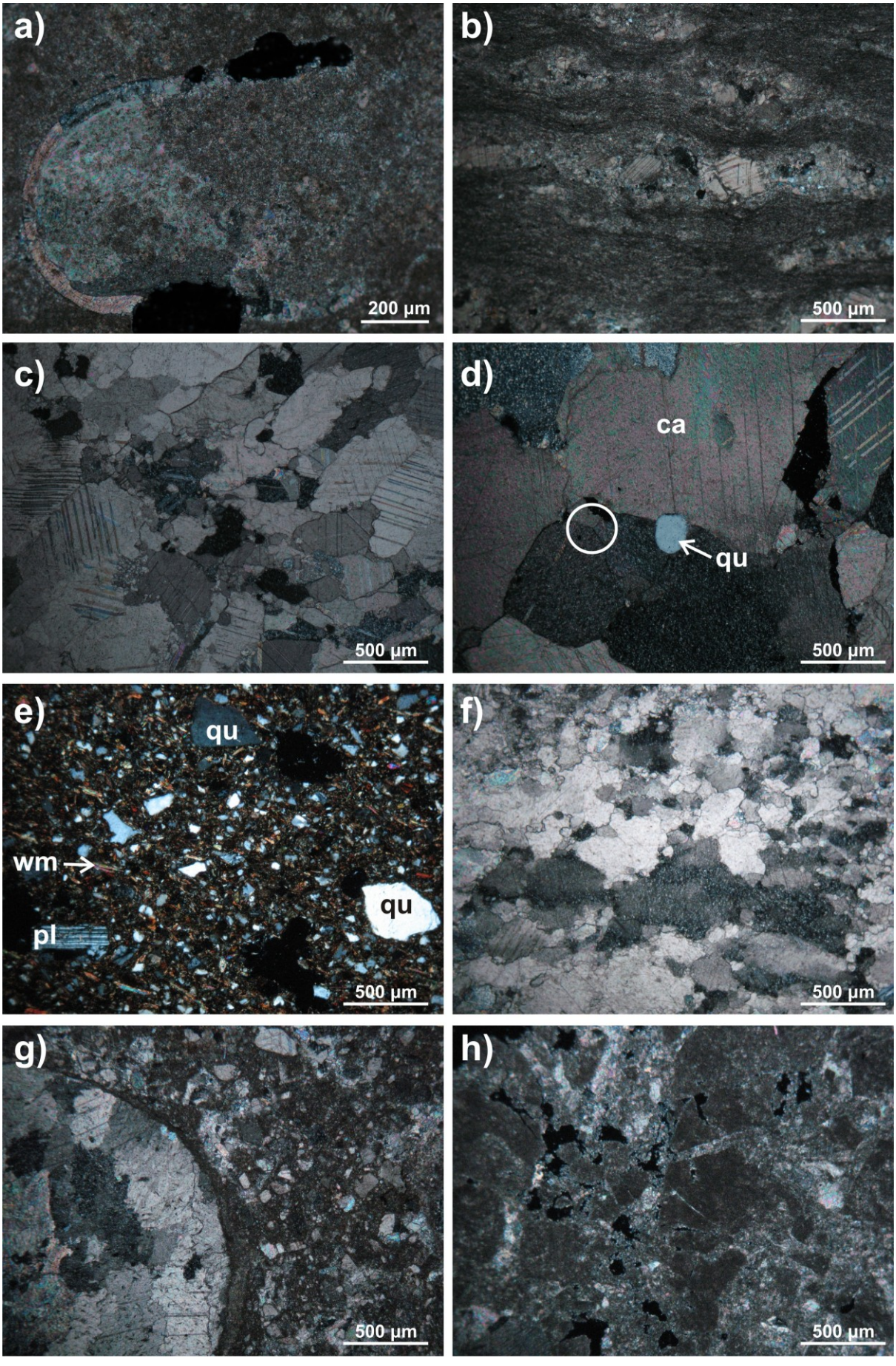
RESULTS AND DISCUSSION

The rock types which were used as building materials in the studied monuments of Dion were clay, limestone, travertine, porous stone, sandstone, conglomerate and marble (Tab. 1) , whereas ceramic plinths were rarely used. The provenance of these raw materials, except marble and plinths, is of local sources, mainly from the broader area of Dion at the slopes of Olympos mountain. Marble and ceramic plinths were in second use, obtained from older implements or architectural parts.
The sample DD1 is characterized as a fossiliferous limestone (Fig. 5a) and consists mainly of calcite with traces of dolomite and quartz (Fig. 6a). The calcite is fine-grained and the greatest part of the rock (>70%) consists of organic matter. In few cases the carbonate matrix contains fragments of fossils, mainly bivalve shell remnants and gastropods.
The sample DD2 is a calcitic conglomerate which consists of rounded limestone cobbles with a size reaching 5 cm. The cobbles are composed mainly of calcite, with minor dolomite and traces of white mica and quartz. The cobbles are filled and cemented by a fine-grained matrix of calcium carbonate which rarely contains fragments of fossils.
The sample DD3 is a dolomitic limestone displaying a characteristic layering (Fig. 5b). The mineralogical composition of the limestone is dolomite with traces of calcite, aragonite, quartz and white mica. The greatest part of the rock (>70%) consists of organic matter.
In the sample DD4 which is a white coarse-grained marble, the main mineral is dolomite, with traces of calcite and albite (Fig. 6b). The dolomite crystals are flattened and elongated parallel to the foliation plane (Fig. 5c) and their maximum grain size (MGS) is 1.5 mm.
The sample DD5 is a coarse-grained marble which consists mainly of calcite with traces of quartz. The maximum grain size (MGS) is 3 mm. It is a well recrystallized marble resulting in triple-grain junctions of the calcite crystals meeting at about 120° angles (Fig. 5d).
The sample DD6 is characterized as porous stone and consists mainly of fine-grained calcite with traces of aragonite, dolomite and quartz. Fragments of fossils are also observed whereas the main part of the rock (>60%) consists of organic matter.

The sample DD7 is characterized as a sandstone. Mineralogical examination revealed that it consists of calcite and dolomite with traces of quartz, opaque minerals (sulfides) and Fe-oxides. Most of the grains have an anhedral subangular shape and their size reaches up to 200 μm. The sandstone is cemented with carbonates and occasionally with organic matter.
The sample DD8 is a ceramic plinth consisting of angular grains of various minerals which are dispersed in the fired clay. The grains have a diameter up to 1 mm and their mineralogical composition is quartz, calcite, white mica, amphibole, epidote, plagioclases and K-feldspar (Fig. 5e).
The sample DD9 is a marble which consists mainly of calcite with traces of dolomite and quartz. It exhibits a heteroblastic texture (Fig. 5f).
The sample DA1 is a conglomerate, similar to the sample DD2. It consists of rounded limestone cobbles (Fig. 5g) composed mainly of calcite and dolomite, with traces of quartz. The cobbles are filled and cemented by a fine-grained matrix of carbonate and Fe-oxides which rarely contains fragments of fossils.
The sample DA2 is a limestone which consists mainly of dolomite with traces of albite. The greatest part of the rock (>70%) consists of organic matter.
The sample DA3 is a ceramic plinth which consists of angular grains of various minerals, such as quartz, calcite, white mica, microcline, epidote and plagioclases.
Finally the sample DA4 is a sandstone, consisting mainly of dolomite with minor calcite and traces of quartz (Fig. 5h).

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

Sample	**Rock type**	**calcite**	**dolomite**	**quartz**	**White mica**	**aragonite**	**albite**	**opaque**	**Fe-oxide**
DD1	Limestone	Main	Minor	Minor	-	-	-	-	-
DD2	Conglomerate	Main	Minor	Traces	Traces	-	-	-	-
DD3	Limestone	Minor	Main	Traces	Traces	Minor	-	-	-
DD4	Marble	Minor	Main	-	-	-	Minor	-	-
DD5	Marble	Main	-	Traces	-	-	-	-	-
DD6	Porous stone	Main	Traces	Traces	-	Traces	-	-	-
DD7	Sandstone	Main	Main	Traces	-	-	-	Traces	Traces
DD8	Ceramic plinth	Calcite, quartz, white mica, amphibole, epidote, K-feldspar, plagioclase							
DD9	Marble	Main	Minor	Traces	-	-	-	-	-
DA1	Conglomerate	Main	Main	Traces	-	-	-	-	-
DA2	Limestone	-	Main	-	-	-	Traces	-	-
DA3	Ceramic plinth	Calcite, quartz, white mica, microcline, epidote, plagioclase							
DA4	Sandstone	Minor	Main	-	-	-	-	-	-


a)
200 µm
b)
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c)
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ca
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500 µm
f)
500 µm
g)
500 µm
h)
500 µm

Figure 5: Photomicrographs (+N) of the studied rocks showing textural features. a) Limestone: a fossil in the fine-grained calcite (sample DD1). b) Limestone: "lenses" of recrystallized dolomite, parallel to the layering of the limestone (sample DD3). c) Dolomitic marble: heteroblastic texture and dolomite crystals showing a slight elongation (sample DD4). d) Marble: quartz (qu) and twinned calcite grains (ca) with triple-grain junctions at 120° angles - in the circle (sample DD5). e) Ceramic plinth: disseminated grains of quartz (qu), white mica (wm) and plagioclase (plag) in the fired clay (sample DD8). f) Marble: heteroblastic texture and elongated calcite crystals (sample DD9). g) Conglomerate: rounded limestone cobble consisting of coarse-grained calcite, in the carbonate cement (sample DA1). h) Sandstone: clastic angular grains of calcite and dolomite and fine-grained carbonate cement (sample DA4).

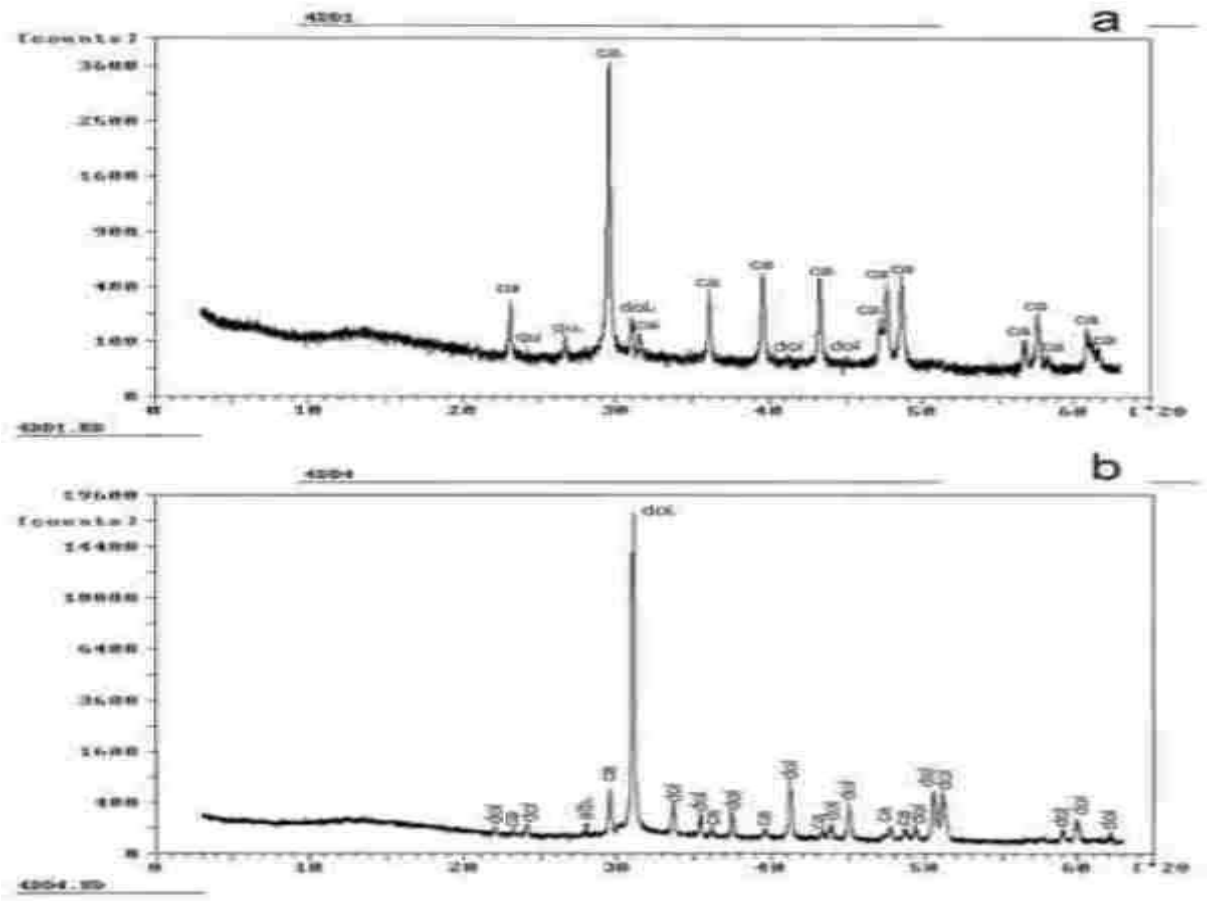

Fig. 6. X-ray diffraction diagrams of the samples DD1 (a) and DD4 (b) from the Demeter sanctuary in Dion. Ca: calcite, dol: dolomite, qu: quartz, alb: albite.

Indicative values of the physical and mechanical characteristics of the materials (bulk density, water adsorption, point load index, uniaxial compressive strength, ultrasonic velosity, Young's modulus) are shown in Table 2.

Table 2: Indicative values of the physical and mechanical characteristics of the materials

Material / Property	porous stone	conglomerate	limestone	marble	ceramic plinth	sandstone
Bulk density, γ (gr/cm^3)	2.31-2.55	2.49-2.63	2.72-2.91	1.61-2.81	1.72-1.92	1.84-4.04
Water adsorption (%)	2.21-3.17	1.61-2.86	0.33-0.37	0.48-0.56	16.09-20.55	2.54-6.53
Point load index, Is (MPa)	2.04-3.21	6.64-6.92	13.00-19.26	4.96-11.08	2.37-9.37	8.17-10.54
Uniaxial compressive strength, UCS (MPa)	44.88-67.73	146.08-152.24	292.50-423.72	109.12-221.60	53.33-196.77	171.57-221.34
Ultrasonic velosity, V (m/s)	4586.2 - 4881.35	4163.04 – 5719.29	6179.1 - 8068	3692.3 - 4301	1594.69 – 1980.58	3000 – 6277.77
Young's modulus E $(MPa).10^{-3}$	12.84-19.71	39.12-41.53	77.28-114.09	30.00-65.99	14.78-55.94	48.88-62.82

The above values are only indicative and there is no possibility to come to accurate conclusions from these. For this reason an analytical and systematic study, with experiments in the laboratory and in situ, is in progress to determine the physical and mechanical characteristics of the building materials in order to have a clear view of their decay state and the factors related to their weathering behaviour.

CONCLUSIONS

1. The main building materials of the constructions of Demeter and Asklepios sanctuaries in Dion archaeological area are limestone, porous stone, conglomerate, marble, sandstone, ceramic plinth.
2. The provenance of these raw materials, except marble and plinths, is of local sources, mainly from the broader area of Dion at the slopes of Olympos mountain. Marble and ceramic plinths were in second use, obtained from older implements or architectural parts.
3. The limestone and porous stone materials consist mainly of calcite or dolomite. The conglomerate materials consist of limestone and they are composed mainly of calcite. The marble is a white coarse-grained dolomite or a coarse-grained calcite. The sandstone materials consist mainly of calcite and dolomite. The ceramic plinths consist of angular grains of various minerals dispersed in the fired clay.
4. The materials show serious problems of corrosion and deterioration caused mainly by the atmospheric environment, the rain water and the presence on these of various kinds of pollutants, the capillary penetration of water in the bulk of the materials due to intensive surface and

underground water presence in the whole surrounding area, the vegetation, the great temperature differences between day and night and in the various seasons.

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