CHARACTERIZATION AND CAUSES OF BUILDING STONE DECAY AT THE ARTEMIS TEMPLE, BRAURON, E. ATTICA, GREECE

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Abstract

At Brauron (Vraona or Vravrona) area, E. Attica, near the Brauron bay, by the Erasinos river there is an ancient monument of 415 B.C., dedicated to Artemis. The building material used for the construction of the monument is sandstone originated from Neogene sedimentary deposits. The ancient quarries are located 500m away from the monument and traces of quarrring are still visible. Monument ruins had been buried under the mud load curried by Erasinos river for many centuries. During the restoration works of the Temple of Artemis besides the stone found in situ, new material provided by the same formation was as well, used. The restored monument stones display intensive deterioration.

The purpose of this paper is to study of the decay forms and investigate the decay causes of the building stone in the monument. The decay forms result from intrinsic (endogenic) and environmental factors. The main endogenic factors of decay of the sandstone used as building material, are: a) the high porosity, and the pore size distribution, b) the calcite cement of the stone c) the mineralogical composition, especially the presence of swelling clay minerals. The main environmental factors of decay that result to the calcite and salt crystallization are a) the burial of the ancient building stones, in the brackish water-mud, for centuries b) the frequent floods and possible pollution of the nearby Erasinos river c) the acid rain and aerosol attack d) the bioteterioration. The conclusions of this case study may have application on other monuments of historical interest, in similar environment.

Key words: sandstone, endogenic, environment, salts, bioteterioration.
1. Introduction

Stone decay of engineering structures and monuments is closely related to the geologic process of rock weathering. Water is an important weathering factor for building stones, since many chemical reactions take place only in the presence of water. Water can reach a building material through capillary rise of ground moisture, rain, and condensation of air humidity.

The transport, crystallization, and hydration of salts is also controlled by water. Salt weathering is a process of rock disintegration that takes place in a variety of environments and affects many kinds of rocks (Lewin 1981). It is a well-known and widespread geomorphic process (Pye and Mottershead 1995) and one of the principal causes of deterioration of stonework and masonry used in ancient monuments or architectural heritage all over the world (Zezza 1996, Benavente et al. 2001). Building stones of monuments at coastal sites or near sea, as Brauron, are salt affected. Additionally, the Braurion area was a wetland system and stone ruins had been buried for centuries, so, salt-attack caused severe stone deterioration, as mechanical action of salt crystallization processes can exert pressures capable of destroying even the most resistant stone (La Iglesia et al. 1994, Theoulakis and Moropoulou 1997).

In addition, atmospheric precipitation or air humidity carry pollutants into building materials, leading to their deterioration, and salt deposition in buildings is mainly by marine aerosol (Zezza and Macri 1995, Moropoulou and Theodoulakis 1991, Moropoulou et al. 1995). Biological development can occur only in the presence of water and biodeterioration is an important factor of decay. Mineral breakdown and neo-formation by microbial activities are major influences on stone durability (Pochon et al. 1964, Gorbushina et al. 2000, Castanier et al. 1999).

The durability of Brauron sandstone depends on its own intrinsic properties (e.g. mineralogy, texture and structure) and on the environment to which it is exposed (e.g. air pollution, marine environment, humidity etc.). The combination of these factors can lead to different deterioration patterns (Fitner et al. 1995). The evaluation of the endogenic causes of the decay include petrographic analysis, since, stone characteristic as texture, pore size, porosity, not to mention mineralogy, are controlled by sedimentary and diagenetic processes.

2. Archaeological site of Brauron (Vraona)

Brauron area is located at east Attica, 10 km southeast of Venizelos airport. The Sanctuary of the Braurion Artemis is one of the earliest and most revered of the sanctuaries of Attica. An important settlement was established at the inner end of the bay of Brauron during the Neolithic period. It flourished particularly from Middle Helladic to early Mycenaean times (2000-1600 B.C.). As priestess of Artemis, Ifigeneia dies and is buried in Brauron where she too is honoured as a goddess of childbirth. Systematic excavation of the sanctuary began in 1948 under the
direction of I. Papadimitriou. Restoration of the Stoa was carried out during the years 1950-60 by Prof. Ch. Bouras. The most notable monuments of the site are: The big lodge (stoa) of Doric style with a Greek P (Π)-shaped ground plan. It was built between 425 and 415 B.C. and it framed the big closed interior courtyard, which opened toward the temple of Aphrodite, (Figs 1, 2). The temple of Artemis. A doric prostyle temple with a tripartite cella and deep adyton, built on the site of an earlier archaic temple. It dates to the first half of the 5th century B.C. The temple or heroon of Iphigeneia. (Fig. 4). It was built at the site of the Sacred Cave which was connected with the tomb and the worship of Iphigeneia, when the roof of the cave collapsed. The earliest Cult evidence goes back to the 8th century B.C. It is important to notice that since the 3 century BC the Temple was deserted and gradually the ruins were buried by the flood and brackish deposits of the Erasinos river delta (Figs 2, 3).

3. Geological setting

The archaeological site is situated by the delta of Erasinos river near the Brauron bay. As the area is flat and almost at sea level a wetland system was developed at the delta river consisted by lagoons and swaps, (Maroukian et al. 2002), (Fig. 5). This wetland system was partly preserved according to Geographical Military Service maps until 1987-89, being drained during the restoration works of the monument.

The archaeological site, as well as the regional area, is consisted by the following formations:
The substrate is marble. The monument is founded on it. Marbles outcrop in the surrounding area of the Temple, they are grey white massive to thickly bedded, locally karstified. They belong to the lower marble series of Attica of Jurassic age, (IGME, sheet Koropi-Plaka 2003).

They are overlaid by green phyllites (Jacobshagen et al. 1976) and whitish to grey bedded limestone (IGMR, sheet Koropi-Plaka), that outcrop southeast Vrarona bay, up to the beach.

On these formations upper-Miocene layers are located, that are consisted by shales, marls, siltstones, sandstones, conglomerates, and travertines, (Metots 1992, Papadeas 2002).

They outcrop along the Brauron to Loutsa local road. See section by Mettos (1992) (Fig. 7).

The sandstone quarried from this formation seem to has been used as the main building material in the monument.

4. Materials and Methods

The studied samples are derived

- From the building stones used for the construction of a. the Π shaped Portico b. the connected rooms and c. the sacred house, the alter and the tomb of Iphigeneia, (Fig. 4).
- From the sandstone layers of the above-mentioned upper-Miocene formation where the ancient quarries were (figure 4). They are located in a near by hill 500m away from the temple, at northeast and the quarry traces are well preserved, (Buras 1967)

Physical parameters as apparent and absolute density, compaction index and water absorption, were laboratory measured. Also porosimetry was estimated by a microscope (Motic) connected to PC using the Motic Images Plus version 2.0 ML software.

The sample slides were observed under the polaroid microscope. SEM and microprobe analysis were performed on slides as well as on natural samples using the SEM JEOL JSM-5600 equipped with EDX OXFORD LINK™ ISIS TM 300.

The samples were also mineralogical analyzed by powder-XRD using the Siemens 5005 diffractometer with Ni-filtered CuKα radiation on randomly oriented samples.
5. Results and discussion

5.1. Lithotypes of the building stones

The endogenic decay factors are controlled by sedimentary and diagenetic processes and are reflected by the petrographic characteristics. Three lithotypes were recognized by the microscopic study and mineralogical analysis:

Type I. Whitish-grey cohesive, coarse-grained sandstone (calcareous litherenite) that has been used in the construction of the columns and the capitals of the portico (stoa), (Table 2). It is characterized by good to moderate grain sorting. It consists of quartz, alkali feldspars, muscovite, chlorite, clay minerals and significant amount of rock fragments cemented by calcite. Also locally bioclasts were found.

Mineralogical analysis: the main constituents are calcite, quartz, albite, and the minor constituents are chlorite, smectite muscovite, illite, kaolinite.

SEM analysis: most of the rock fragments are consisted mostly by clay minerals. Calcite cement is locally partly dissolute and showing different dissolution shape. Apatite and chromite were also observed in rock fragments. The porosity is estimated less than 10 %.

Type II. Beige semi-cohesive, fine-grained sandstone (calcareous litherenite) that has been used in the construction of the capitals and the rooms connected to the portico (Table 2). It is characterized by good grain sorting. It consists of quartz, plagioclasts, chlorite, alkali feldspars clay minerals, titanite, epidote, ferric oxide, and significant amount of rock fragments cemented by calcite. The porosity is estimated less than 15 %.
Mineralogical analysis: quartz, anorthite, albite, calcite, dolomite, smectite and mixed layers, chlorite and traces of staurolite (probably derived from metamorphic rock fragments). Calcite proportion seems to be lower than the other two types, but in the contrary the clay proportion is much higher.

SEM analysis: Initial coarse calcite cement crystals are locally dissolute and secondary recrystallized calcite is formed. The locally presence of germs was observed. They have developed between the grains were the cement is dissolute (Fig. 8) and are bound to the grains. Tiny salt (NaCl) are developed in voids and pores creating bridges between grains (Fig. 9). Zircon also was found as isolated grains or constituent in rock fragments.

Type III. Beige, non-cohesive, medium grained sandstone (calcareous litharenite) that has been used in the construction of the columns of the temple. It is characterized by good grain sorting. It consists of quartz, alkali feldspars chlorite, epidote, and significant amount of rock fragments cemented by calcite. The porosity is estimated more than 20%.

SEM analysis. Ferric oxide was found in proportion estimated less than 3%, as aggregates or as constituent in rock fragments.

Mineralogical analysis: the main constituents are calcite, quartz, albite, and the minor constituents are muscovite, chlorite, illite, and kaolinite.

The fist and the last types seem to display many similarities, especially in the mineralogical constituents.

In all types the porosity can be classified as intergranual to vuggy type, and a secondary origin seems to be dominating, with secondary calcite cement.

5.2. Physical characteristics of the building stones

The physical parameters of the three lithotypes that were measured are the porosity, the density (apparent and absolute), the compaction index and the water absorption. The compaction index reflex the cohesion of the rock and is defined as the ratio of apparent to absolute density (Tsirabidis 1996).

Also the pore size parameters were estimated and statistically analysed.

The results are show in Table 1. It is indicated that types I and II display almost similar parameters, while type III is more porous, of lower compaction index, of higher water absorption capacity. It is the same type that displays a wider range distribution of mean pore surface.

<table>
<thead>
<tr>
<th>Lithotype</th>
<th>Porosity %</th>
<th>Apparent density gr/cm³</th>
<th>Absolute density gr/cm³</th>
<th>Compaction index</th>
<th>Water absorption %</th>
<th>Mean pore surface mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>6</td>
<td>2.51</td>
<td>2.66</td>
<td>0.94</td>
<td>2</td>
<td>0.02-0.03</td>
</tr>
<tr>
<td>Type II</td>
<td>10</td>
<td>2.58</td>
<td>2.88</td>
<td>0.90</td>
<td>3</td>
<td>0.01-0.02</td>
</tr>
<tr>
<td>Type III</td>
<td>27</td>
<td>1.97</td>
<td>2.7</td>
<td>0.73</td>
<td>6</td>
<td>0.01-0.03</td>
</tr>
</tbody>
</table>

5.3. Description of the decay forms of the building stones

Thirteen columns of the portico have been restored. During the restoration of the monument, (1950-1960), besides the original parts found in situ and unburied from the marly alluvial sediments, new building stones were used, as well. These stones were quarried from the above-mentioned Neogene formation (Fig. 7), were ancient quarries had been found.

Table 2 displays the distribution of the three sandstone types in different architectural parts of the monument.
Table 2 - Distribution of building stone type in the monument

<table>
<thead>
<tr>
<th>Building stone</th>
<th>columns</th>
<th>capitals</th>
<th>rooms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type II</td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Type III</td>
<td>+</td>
<td></td>
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</tr>
</tbody>
</table>

The more intense decay problems appear on the portico columns, (Figs 12, 13, 14, 15). The sandstone of the columns seems to be strongly deteriorated. The different types of decay can be summarized

1. Pitting corrosion to cavitation erosion of graduated degree: the presence of vugs and cavities, large enough, approximately of 1-4 cm mean diameter, is very extensive, (Figs 12, 13, 16, 17, 18, 19). These vugs that were observed on many different pieces of the columns, seem to have diminished not only the durability, but also the good appearance of the monument, (Figs 13, 14, 15). When the cavities are getting enlarged they are connected by “bridges” (narrow areas of rock), (figure 13). Eventually bigger pieces are loosening and the result is a complete alteration of the original grooves and progressively of the shape of the column pieces (Figs 12, 13).

The construction materials used for the capitals during the restoration works are:

a whitish-grey sandstone found in situ and b: beige (light brown) sandstone cut from the nearby quarry. These two stone materials show different degree of corrosion. The former (Figs 14, 16) displays strong cavity corrosion and colour alteration (calcareous crust), while the latter displays pit and cavity corrosion of a lower degree (Figs 14, 17).

2. Strong colour alteration- calcareous crust formation: observed in many column pieces having deep grey colour, instead of whitish-grey to beige colour of the new column pieces, used at the restoration, (Figs 1, 3, 14)

Calcareous crust was also observed on the column pieces, which were in contact to the capital, constructed of white Penteli marble, (Figs 13, 14).

A close inspection of the building stones indicates that in the restored monument pieces of stone found in situ and other new pieces display different degree of decay. For example in figure 12, the lower part of the column, characterized by great material loose was found in situ, whereas the upper part is a new piece. The different stage of deterioration between the weathered source rock and the decayed building stone is quite obvious in figures 22, 23, 24 and 25. In the pair of figures 22-23 and 24-25 under the same magnification, rock samples from the quarries and samples of the building stones that correspond to the same lithotype, I and III, are compared. The degree of decay of the building stones is obvious. The calcareous cement is been partly dissolute. Pits, pores and vugs have developed. Progressive dissolution of cement leads to the formation of bigger pores and cavities. These cavities may be connected by narrow areas as “bridges” (Fig. 13), which progressively will be diminished. That gradually results to grain loose and material removal. The concave surfaces occupied previously by grains are obvious (Fig. 25).

5.4. Main decay factors

5.4.1. Endogenic factors of decay

The endogenic decay factors coincide with petrographic features and are controlled by sedimentary, as well as diageneric processes. The high porosity, the pore size distribution, the multy mineral composition, the presence of swelling clay minerals, the cement composition, seem to be the main endogenic factors, that have impact in the decay process.
Figure 12 - Honeycomb decay of bottom column piece of type I sandstone, and shape alteration

Figure 13 - Severe decay of bottom column piece constructed of type III sandstone and shape alteration

Figure 14 - Different degree of decay on capitals and Calcareous crust development

Figure 15 - Different degree of decay on column pieces

Figure 16 - Capital constructed by lithotype I illustrating high vuggy decay, shape alteration- material loss and crust development

Figure 17 - capital constructed by lithotype II illustrating vuggy decay and color alteration

Figure 18 - Intence decay form on sandstone type III

Figure 19 - decay form on sandstone type I
Porosity and pore size distribution

Rock properties controlling the effects of acid rainwater or/and pore water include mineralogical composition and permeability. The later is again controlled by porosity, more particularly by pore size distribution. The three sandstone types display mean to high porosity. On this basis they are considered of poor quality for building material. The role of pore size distribution is clearly indicated in the decay patterns of sandstone type III, which displays the most intense decay problems compared to the other two types, while its mineralogical composition is similar to that of type I. With increasing porosity the attacking solution waters are able to penetrate deep into the rock. During dry periods of evaporation the salt solution are drawn by capillary action toward the surface, where precipitation may cause the development of a resistant crust over the deteriorated interior, (Figs 13, 15, 16).

Calcite cement, calcite and salt crystallization

The three sandstone lithotypes are cemented by calcite. This is a feeble characteristic since acid water attack results easily to calcite dissolution, (Fig. 20). Vulnerability of stone to certain decay forms, as soluble minerals, is highly controlled by microstructural and mechanical characteristics of the stone (Leith, et al. 1996). When the cementing material is loose through solution, the mechanical properties of the stone are diminished. That results in rapid disintegration of the clasts. The consequence is the development of honeycomb forms, which is a usual decay form of sandstones, (Fig. 12).

Calcium carbonate recrystallized as secondary cement. These recrystallized crystals formed under supersaturated conditions, of a solution, exert pressure against the pore walls, known as crystallization pressure (Moropoulou and Theoulakis 1991). Salt (NaCl) crystallization in pores increases physical stress and causes breakage of the stone (Cardell et al. 2003).

Mineralogical composition

The heterogenic mineralogical composition is another feeble characteristic of the stone, since each mineral displays different behavior to environmental changes and has different thermal dilatation factor. This leads to differential attack velocity by the aggressive solutions different microstructure of dissolution products and this facilitates the stone deterioration.

The presence of oxides indicates the alteration of primary minerals and possible volume inflates that cause physical stress. In addition the presence of clay minerals as illite, chlorite, kaolinite and especially swelling clays as smectite and mixed layers, facilitates the stone deterioration. When water enters the pore system, the clays expand primarily due to osmotic swelling and to a minor extend due to crystalline swelling, promoted by the presence of sodium ions from salts, (Rodriguez-Navaro et al. 1997). The alternating conditions of humidity–dryness periods is an aggravate factor.
5.4.2. Environmental factors of decay

Erasinos river (wetland and flood)

The monument is been constructed just aside the bed river that had a significant impact on the stones decay. The temple area is located in a shallow depression not far from the river mouth (Figs 5, 6). A wetland system of lagons and swaps had been developed (Fig. 5) and the monument ruins burried for centuries and had been corroded by the attack of sea water.

Although Erasinos is a small river, it is flooding after strong and intense rainfalls. (Figs 26, 27). Then the waters caring along mineral materials as bed load or in suspension, cover all the area of the monument, (Fig. 16), for considerable period, until the waters withdraw. The water drainage area of Erasinos is large enough including locations as Attica Road, Venizelos airport, Marcopoulo city. Rainwaters and Municipal wastewater treatment from the above areas are driven into the bedload of Erasinos. This might be a possible pollution source for the river waters that reinforce the ion and bio content. Running water picks up ions on its way downstream or loses ions by absorption to clay particles. The flow through stone pores and narrow channels gives the water enough time to reach near equilibrium condition quickly in the presence of calcium carbonate in the stones. The ion content of groundwater is subject to extreme variation depending on both the source rock and the length of travel; groundwater is generally high in Ca, Mg, SO₄, Cl, and Fe. Saline groundwater that usually indicates invasion of corrosive marine water cannot be excluded even in the present since distance from the shore is short and wetlands partly and periodically exist. Soluble salts are considered to be the key-deteriorating factor of building materials in the case of monuments and historic buildings (Arnold 1989). During salt crystallization pressure crystallization occurs within the pores of rocks, and degree of weathering is depends on the degree of salt saturation of the solution and the pore size (Benavente et al. 1999).
The corrosive action of the water is enforced by the presence of the suspension load, rich in clay minerals. When the stones are immersed in the water, the influence of the water affects also area above it, due to capillary action that is related to fine pores. These pores are sensitive to condensation under low humidity due to Kelvin model (Camuff 1983).

Unfortunately flood controls are not sufficient and the phenomenon goes on for centuries, increasing the stone decay by the river or/and seawaters. In addition, the columns side mainly of the new stones, facing toward northeast are affected by marine aerosol and display stronger decay degree due to salt crystallization. The rate of decay is at its greatest when the cycling of the crystallization–hydration cycles is relatively infrequent. It is the length of this ‘drying’ period that apparently has the greatest influence on the rate of decay and could explain the significant difference in the rate of decay between different stone pieces. (Colston et al. 2001).

Rainwater

Generally rainwater increases the decay factors mentioned above. The effects of the acid rainwater on the rock material can be summarized as follows: Solution and washing away of the rock surface and possible formation of solution cavities, Alteration of minerals especially such as calcite and dolomite through the combination of sulphuric acid with calcium or magnesium carbonate. White calcite-rich crusts develop on rain-exposed surfaces and have a high surface strength that is combined with the weakening of substrate. (Skoulikidis 2000, Torok 2002). White calcite-rich crusts are formed as a result of run-off and dissolution with simultaneous formation of a thin recrystallized calcite layer, (Skoulikidis and Papakonstantinou-Zeotis 1981), (Figs 14, 15, 16, 17, 20). Figure 17 displays the development of calcareous crust on the part of the capital that is unprotected and more influenced by rain. Roofing and orientation display different degrees of decay as they partly protect the stone (Inigo and Vicente-Tavera 2001). The maximum salt concentration, and thus the maximum deterioration, is observed in a specific zones of the masonry, which depend on the type of the building material and on the micro-environmental conditions, (Cardell et al. 2003).

Bioteterioration

The physiological and ecological factors of organisms, creating etching bio deterioration and induced by a broad scope of microbial communities, have been the subject of many investigations and reviews, (Warscheid and Krumbein 1996, Dornieden et al. 2000).

Bacteria live in large quantities in soils performing different functions. The most important bacteria appear to be the nitrogen fixers which convert nitro-genous material into ammonia from both organic substance and from the atmosphere; another type of bacteria oxidizes ammonia to form nitrous and nitric acids which may attack rocks. Bacteria populations inhabit already weathered rock surfaces after Fungi have started growth on them. The bacteria break up silicates as quickly as Fungi do. Weathered rocks develop a large bacterial population along all surfaces as
well as along cracks, (Webley et al. 1963, Winnkler 1966). Since the stones have been covered by mud for a substantial period of time and are still influenced by the periodical presence of the water, the development of communities is expected (Michopoulos 2005), (Figs 20, 21) and has considerable impact on stone decay.

Mineral neo-formation by microbial activities is also, of major influence in the long-term stabilization and destabilization of surface of the physical heritage (Pochon et al. 1964, Krumbein and Jens 1981, Gorbushina et al. 1996, Castanier et al. 1999).

6. Conclusions

The decay condition of Brauron monument can be attributed to the endogenic factors (composition, texture, petrophysical properties) and environmental factors (characteristics of the site of the construction). The susceptibility of a porous stone as the studied sandstone to decay is a function of

A) The endogenic parameters that affect the stone durability. These are:

The eterogenic mineralogical composition. The presence of minerals that easily dissolve (calcite), products of oxidation, clay minerals (especially swelling).

The cementation of the sandstone by calcite. Dissolution of calcite cement leads to grain removal and material loose.

The high porosity, especially the pore size and the pore distribution.

B) Apart from the intrinsic characteristics of the construction material itself, the environmental conditions affect the stone durability:

The building stones had been in direct contact with seawater for centuries, since before the restoration works, the parts of the monument had been buried in the lagoon-river flood mud. So, salt-induced deterioration of Brauron stones is considered to be accelerated drastically in the marine environment.

The presence of Eratinos river near the monument area is critical, since the river waters might be polluted and often after rainfalls the area is flooded and immerged in the mud curried by the river.

The recrystallization of calcium carbonate besides salt crystallization and released free energy become critical agents of decay and destroy a non resistant stone as the Brauron sandstone. Crystal growth in pores is leading to disintegration through crystallization pressure, stones loose weight and surface deterioration is visible.

The influence of acid rain is minor but considerable. Last but not least the stones are affected by the development of microorganisms in them.

A deep knowledge of the state of conservation, of the building material characteristics and the interpretation of the environmental impact, can provide a substantial contribution to the preservation (and restoration) of the Brauron monument.

7. Acknowledgments

The authors acknowledge the archaeologists of the Third Archaeological Section for their assistance and historical information, expecting a further cooperation in regard to a more detailed study of the building stones of the monument.

8. References


