



## Investigations on Stone Weathering of Ottoman Architecture: A Kırklareli Hizirbey Kulliyesi Case Study

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### ABSTRACT

*Weathering has been recognized as a problem needing a legislative solution for centuries. Not only the primary cause of weathering is from the combustion of the hydrocarbon fuels but also in historical areas the dense population has had very grave decay effects on cultural heritage. Studies on properties and weathering behavior of the stones were carried out by in situ investigation of many historical monuments. A recent study provides a framework from which to consider the future conservation of Ottoman Architecture. The different forms of weathering is presented of the building materials used in the Hizirbey Kulliyesi of Kırklareli in Turkey, with the aim of establishing the cause and mechanisms of this decay. Samples of this limestone were subjected to a detailed investigation, using an optical microscopy and XRD powder diffraction method. The object of these tests was to determine the mineralogical and microstructural parameters that affect the durability of the investigated stone, whose main mineral component is calcite, although aragonite and quartz are also present.*

**Keywords :** limestone, stone decay, weathering damage, damage diagnosis, weathering progression, urban environments

### Introduction

Weathering causes significant damage to ancient monuments and conservation of weathered stone heritage is one of the most important problems in historical areas. Much outdoors stonework, in a good state of conservation for centuries, has suffered a quickly increasing deterioration in the recent years. The stone weathering was assessed with respect to weathering forms and weathering products. Many historical stone monuments in the Kırklareli are seriously threatened by damage and are in need of intervention. Results from our own observations and characterization, documentation, quantitative evaluation and rating of weathering damage were combined to provide a reliable basis on which to evaluate weathering factors and processes.

The high historical importance of the Hizirbey Complex (Kulliyesi) as one of the fine examples of Islamic Ottoman Architecture in the historical center of Kırklareli province has been taken into account. A characterization is to be had of the building materials used in the Hizirbey Kulliyesi<sup>1</sup>, as well as of the different forms of deterioration, with the aim of establishing the origin and mechanism of this decay. The Hizirbey Kulliyesi was built with limestone from upper Miocene. The different types of limestone on the building were located and characterized, and their state of decay mapped / observed. The aim of this paper is to observe the urban decay processes of limestones used on Hizirbey Kulliyesi, which have been extensively used as building stones in Kırklareli in the 14<sup>th</sup> and early 17<sup>th</sup> century. The original buildings of the Hizirbey Complex (Kulliyesi) dates from 1383, with various extensions in the fourteenth and fifteenth centuries in the traditional Ottoman Architecture style, which was located at the center of the city (Fig. 1). This Kulliyesi consists of the mosque, bath and arasta (Bazaar). The Complex was destroyed by a powerful earthquake in 1824 and restored. Still used today, the final praying place and garden walls of the mosque were built afterwards.



**Figure 1.** Exterior of the Hizirbey Kulliyesi viewed from the East and the environmental situation of the kulliyesi and surround area.

The research generally focuses on the description of processes and decay products of limestone used at Hizirbey Kulliyesi. The characterization, quantification and prognosis of weathering progression are important concerns of scientific damage diagnosis. Precise diagnosis is required for characterization, interpretation, rating and prediction of the weathering damages at stone monuments and is vital for remedy of stone

damages and sustainable monument preservation.

Limestone buildings located in polluted urban environments show considerable signs of decay. The rate of deterioration depends on the textural properties of the carbonates, on the contamination fluxes and on the environmental situation (air pollution, meteorological and micro-climatic conditions). The limestone shows several types of decay phenomena and takes many forms, from dissolution of calcite and granular disintegration through blistering and catastrophic decay (Robinson & Moses 2002). Mechanical breakdown, alteration and deposition were identified among others. The most frequent stone decay feature is crust formation. Crusts can be classified according to their colours and morphology. Dark coloured crust such as laminar black crust, globular black crust and dust crust develop on limestone types. White weathering crust is only found on limestone.

Air pollution is often viewed as a dominant factor in causing stone damage, particularly in the case of outdoor exposition. Sulfur dioxide has long been recognized as the primary gaseous component of human-polluted air. Sulfur dioxide ( $\text{SO}_2$ ) with nitrogen oxides ( $\text{NO}_x$ ) is the most harmful one for stone materials and are the major source of soluble salts, mainly sulfates and nitrates. Additionally the salts may be carried into building from the basement, rising by capillarity from the soil itself, or from the soil containing deicing or other chemicals, or as aerosols brought by winds. In urban atmosphere, oxidation of SO to sulfate is catalyzed by metals emitted from power plants.

The current damage in the Hizirbey Kulliyi is the result of humidity and acid rains, which are relatively common processes in other historic buildings in Kırklareli. The Hizirbey baths have even been overwhelmed by the new buildings surrounding them, and seem lost among them.

## Materials and Methods

### Lithotypes and their petrographical properties

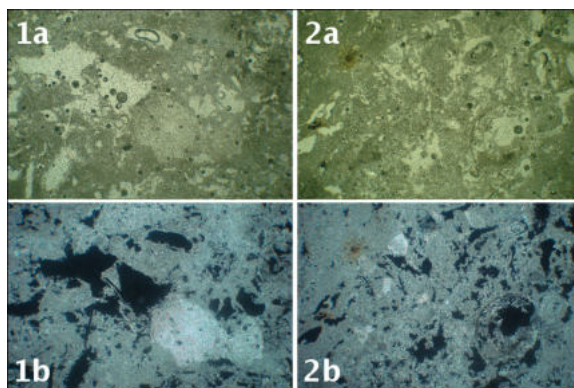
The petrographic examination on the prepared thin sections was carried out using the polarized light microscope (PLM). The results showed that the limestone types in the area are microsparry calcite embedded in a micrite matrix rich in fossils and grains of quartz.

The mineralogy of the samples from the Hizirbey Kulliyi building stones is studied by Polarizing Microscope (PM) and by XRD analyses in the Department of Geology, İTÜ (İstanbul, Turkey). A Philips Diffractometer and  $\text{CuK}\alpha$  radiation were used for all XRD analysis. The samples are ground and sieved to less than 44 mm and then analyzed at  $1^\circ 2\theta$  per min. through the angular range of  $2\text{--}60^\circ 2\theta$ .

The Hizirbey Kulliyi was mainly constructed from local limestones. Different kinds differ one from another in respect to chemistry, texture, and mineral content. In general, limestones can be classified into three major groups: organic, chemical, and detrital or clastic. The origin of limestones may be freshwater or marine, and usually indicate precipitation in a warm-water environment. Many of these rocks contain organic, detrital and chemically precipitated material in varying proportions. All limestones can be characterized as almost pure limestones. Calcite ( $\text{CaCO}_3$ ) represents the predominating carbonate mineral. Another common material, which is presented in modern limestone accumulations, is aragonite (orthorhombic  $\text{CaCO}_3$ ). These rocks form a part of widespread sedimentation, which began during the late Eocene-Early Miocene. The significant chemical characteristic of these rocks is enrichment in organic material. The organic material can be macroscopically and microscopically seen in the structure of these rocks.

The mineralogy of the samples is similar to other fossiliferous limestones formations found around Pınarhisar (Fig. 2). Calcite as main mineral is common in a large quantity in all the formations. Other members of the Pınarhisar mineral

assemblage are quartz and limonite in decreasing order of abundance. These minerals have only been noticed as accessory minerals in thin section. According to the microscope and XRD analyses, the samples contain no chemical weathering products.



**Figure 2. Photomicrograph showing fossiliferous limestone in plane-polarized light (above) and cross-polarized light (below). Generally, a large number of fossils and grains of quartz can be observed in the bedrock samples.**

The samples studied are a dense rock with brown-grey color and fine-medium grained and homogenous appearance. Secondary fractures are absent and alteration products are not found in rock surface and also in fractured particles. Brown color is probably due to the some minerals including iron. The porous structure of its surface is evident. According to the microscope study, the sample contains mainly micritic and recrystallize-coarse grained calcite and rarely quartz and limonite. Recrystallize-coarse grained calcites with 0,8 mm size show rhomboidal cleavages. High amounts of fossil shells formed secondary calcites are identified in the sample. Quartz are disseminated grains and generally 0,5 mm in size (Table 1).

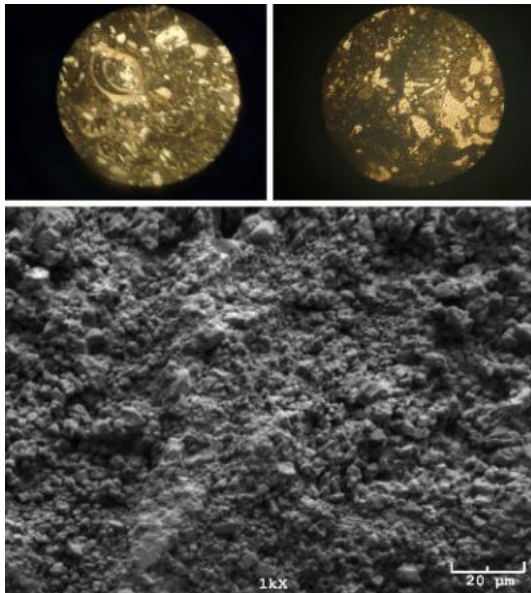
**Table 1. Mineralogical Composition of the sample taken from the building**

Mineral / Component	Ratio (%)
Calcite (Primary, micritic)	85,2
Calcite (Secondary)	12,5
Quartz	1,3
Opaque minerals (Limonite)	1,0

Thin sections of the limestone indicate that this limestone is formed biomicrite / packstone (Folk, 1962; Dunham, 1962). This limestone includes fragments and complete fossil shell. These carbonate fragment are bonded by brown colored microcrystalline calcite or micritic matrix. Second limestone also has similar properties with first one. It consists of fossil fragments and some calcite grains (possible formed from the transition of micrite to calcite cement under the effect of mineral transformation during diagenesis). This rock may be classified as biomicrite-biosparite / packstone-grainstone (Folk, 1962 / Dunham, 1962). Electron microscopic view shows the equant microcrystalline calcite crystal development possibly belongs to micrite parts of the limestone (Fig. 3).

The mineralogy of samples from building stones was studied by optical microscopy and X-ray powder diffraction method. Generally, XRD analyses were performed to determine the mineralogy of the carbonates, but the mineralogy of the building stones was determined in thin sections by transmitted light and in polished section, respectively. The limestone used on Hizirbey Kulliyi shows low content quartz and the clay (illite) minerals; concern totally the carbonate components micrite (microcrystalline carbonate). The relatively simple mineral

assemblage of the limestone samples include calcite (95-98 modal %), quartz (1-2 %) and opaque minerals (1 %) and minor amounts of illite. Quartz and opaque minerals are seen in all of the samples. Opaque minerals are essentially hematite and limonite. Calcite, a common mineral in the samples, is seen as massive, relatively prismatic and granular grains. It includes no alteration in thin sections taken from the center of the samples.



**Figure 3.** Thin section of Hizir Bey limestones textures (upper) and SEM photo of oolitic limestone clay concentrated along bedding planes.

Eocene outcrops in the area of Turkish Thrace predominantly provided the limestones for the construction of the historical monuments in this region. Vize-Pinarhisar area were quarried for the Ottoman Architecture in Kırklareli province. They are still being used for stone replacement or restoration works at the monuments as well as for modern buildings. Most of the limestones used on historical monuments in Kırklareli are related to the Sogucak formation of middle Eocene. Sogucak formation is characterized by a complex deposition of the reefal and coastal carbonates on shelf during transgression ranging from middle Eocene to early Oligocene. It is consequently developed as time-transgressive, and its deposition period is not unique. Also, coastal morphology, hydrology and sea-level changes caused formation of various reefal types and coastal depositions during the long-stage transgression (Dal, 2008).

### Methodology

This study commenced with detailed of the Monument: survey, classification and registration of the weathered forms (Fitzner et al. 1995; Fitzner, Heinrichs 2002). General photographs of all the walls were taken in order to get a general idea of their conservation state. Close-up photos of the different alterations were taken for documentation and monitoring purposes. Different types of alteration were documented in terms of their morphology (texture and colour). Each alteration was described and photographed by taking one or more close-ups. This exercise was proved to be useful as a first step to understand the types of alteration presented on the surface of the building complex. The damage categories are photographed and evaluated quantitatively. With respect to monument maintenance, damage categories are very appropriate indicators for need and importance of interventions.

All weathering forms of the monument were located according to a morphological criteria on a mm–cm scale and weathering rates (in mm) were determined for all particular areas of the building under investigation and then were illustrated in maps. The type, intensity, damage category and distribution of weathering forms were evaluated as indicators of weather-

ing processes and environmental influences. As a first step, damage categories were determined for each group of weathering forms. In the next step, schemes were developed for origin of final damage categories considering all groups of weathering forms.

### Result

Several types of weathering form were identified on limestone Hizirbey Kulliyi in Kırklareli. The forms were classified according to Fitzner et al. (1995). Limestone complexes display various forms of surface alteration and deposition.

### Weathering cause

The decay of limestones is a complex process in which physical and chemical mechanisms are usually considered to be the main factors; it generally starts with alteration processes due to the synergetic action of rain, wind, and sunlight and freezing/thawing cycles. Air pollution is often viewed as a dominant factor in causing stone damage in Kırklareli, particularly in the case of outdoor exposition. Sulfur dioxide ( $\text{SO}_2$ ) has long been recognized as the primary gaseous component of human-polluted air.  $\text{SO}_2$  with nitrogen oxides ( $\text{NO}_x$ ) are the most harmful ones for stone materials and are the major source of soluble salts, mainly sulfates and nitrates. The deposition of atmospheric pollutants on stones is one of the most important causes of the deterioration, which affects the facades of Hizirbey Complex.

Thrace Region constitutes the European part of Turkey and the study province Kırklareli is located on the west coast of the Black Sea. The Black Sea coast receives the greatest amount of rainfall and is the only region of Turkey that receives rainfall throughout the year. The climatic parameters recorded in Kırklareli showed that relative humidity was always above 70% while temperature ranged seasonally between  $-1^\circ\text{C}$  and  $30^\circ\text{C}$  (average  $13.1^\circ\text{C}$ ). The summers are generally hot (average temperature  $27^\circ\text{C}$ ) and receiving high precipitation. Total annual rainfall is 772,8 mm. The winters are cold (average temperature  $4^\circ\text{C}$ ) and rainy, especially inland areas experience heavy snow and freezing temperatures below  $0^\circ\text{C}$ . The absolute minimum temperature measured in Kırklareli was  $-2^\circ\text{C}$ , while the absolute maximum temperature was  $35^\circ\text{C}$ .

Climatic changes together with weathering and atmospheric effects such as rain; fog, wind and snow cause deterioration on the surface of historic buildings in Kırklareli. Green house gases ( $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{CH}_4$ ) which are effective in the form of sulphurs, carbonates, nitrates, over the normal values and humidity play an active role in deterioration of the surface of stone building materials (Kucukkaya 1998). The dissolution of stones and the formation of black crusts as a consequence of the way the stone is washed out or simply wetted by meteoric water (Camuffo 1995). The widespread development of black patinas on Hizirbey Complex is a decay feature that predominates in urban atmosphere (Fig. 4).



**Figure 4.** Black crusts that have formed in upper part of



walls where rainwater wets but unable to remove the deposit by means of running-off and the color change due to air pollution and sunlight effects on the wall surfaces of east side of kulliyeh.

#### Weathering damage

Weathering forms are visible results of weathering process, which are initiated, and controlled by interacting weathering factors. Weathering forms such as soiling, black crusts and white crusts are very characteristic for the limestone monuments in Kırklareli. Several forms of mechanical breakdown, alteration and deposition were identified on this oolitic limestone of Hizirbey Kulliyeh (Fig. 5).



**Figure 5. Typical weathering forms on limestone monument Hizirbey Külliye in Kırklareli ; Differential weathering of the veneer stones of the wall (a); thick layer of dust (b); White crust (c); Cavernous hollows developing on a Limestone (d, e); Coloration to colored crust tracing the surface(f)**

The most frequent stone decay feature is crust formation. Crusts can be classified according to their colours and morphology (Fitzner et al. 1995). In the polluted environment of Kırklareli, two kinds of crusts develop on calcareous rocks, the so-called white and black crusts (Fig. 6). The deterioration of building stones of Hizirbey Complex by pollutants derived from urban and human activities, but microorganisms and biological activities also play a role in the whole process. Direct visual observation in situ has revealed that the various types of alteration have been distinguished.

The visual features of the crusts of limestone monuments are not only a function of the prevailing micrometeorological conditions near the monument, but also of the geometry of the surface and its exposure to rainwater (Camuffo 1995). Similar geometries induce similar patterns of crusts. The pattern of the 'white' and 'black' crusts found on monuments are caused by the meteoric water wets or washes the surface: where run-off dominates, dissolution and erosion occur and calcareous rocks form white areas. These areas are characterized by crystals of reprecipitated calcite that form when the rainwater with the dissolved stone evaporates; where the stone is wetted but not washed out, black gypsum crusts originate (Fig. 3), with embedded carbonaceous particles which play an important role in this process.

Direct visual observation in situ has revealed that the various types of alteration present could be divided into four main types: (1) Loss of stone material; (2) Discolouration / deposits; (3) Detachment; (4) Fissures. All facades of the building complex have suffered loss of stone material. By means of weathering forms the weathering state of stone surfaces can be described according to phenomenological-geometrical criteria at "mm" to "cm" scale (Fitzner et al. 2002).



**Figure 6. Blistering thin white crust and blackening in the joints.**

Light coloured crusts are formed on rain and wind exposed surfaces. Thick, hard white crusts are smooth and almost flat and occur on medium-grained oolitic limestones (Fig. 7). These crust range from a few millimeters to a centimeter in thickness. Two black crusts types on the walls of kulliyeh were documented: thick framboidal black crusts and thin laminar black crusts. Similar black crusts morphology is also known as dendritic black crusts (Camuffo 1995). These crusts form over heavily weathered stones with a maximum thickness of approximately 1 cm. The primary constituents of framboidal black crusts are gypsum, calcite and organic carbon. The mean gypsum and organic carbon concentrations show some variation depending on whether the crusts are formed in the city centre. The host rock below the crusts is always calcite-rich but in every case also contained some gypsum.



**Figure 7. Example of a "white area" in a zone over which rainwater runs-off. The surface has been worn away and rainwater runs-off. The surface has been worn away and covered by reprecipitated crystals of spatic calcite. The pitting is due to the biocorrosion of microflora in the past.**

Grey dust forms an approximately millimeter thick unconsolidated layer on the stone surface that can be removed without affecting the underlying stone surface. It is found on dry stone surfaces on the walls of kulliyeh. These grey dust layers are rich in organic carbon and in other minerals (mostly quartz). Studies on the composition of the black crusts have revealed particularly the presence of fly-ashes (porous carbon particles, smooth and porous glass spheres, iron oxides) and gypsum. The contaminated atmosphere, water and organisms bring about chemical melting on stones, and usually the thin dust layer gets thick by forming a dirty layer on the stones and affects the whole structures of the limestones.

Biodeterioration is the physical or chemical damage caused by biological agents on structural materials and occurs through the formation of biofilms and has been considered to be a secondary degradation process following the initial deteriorating effects of inorganic agents. Various lower plants, lichens, fungi, moss, bacteria and algae have been found to be involved in the degradation of stones at the lower part of

the walls (Fig. 8).



**Figure 8. Microbiological colonization, biodeterioration and weathering effects, Mosses and weeds growing between blocks of supporting rocks**

### Discussion and Conclusions

The deterioration is a complex process that changes the mechanical properties and mineralogical composition of limestones. The Different types and extents of damage have been observed on Hizirbey buildings. There are numerous reasons for this, including intrinsic variables such as type of limestone used, as well as extrinsic variables such as microclimate (e.g., affected by location, orientation), and pollution (from coal-burning in the city, and traffic pollution). The difference between the surface strength and water absorption of unaltered rock, crusts and host rock varies if we compare various carbonate substrates.

Some stone types are susceptible to encrustation and blistering as well as flaking, spalling and affected through soiling (blackening). The canyon effect created by tall buildings at roadways acts to trap pollutants and concentrate them locally and impacts on microclimate. Building orientation could affect exposure to sunlight (e.g., a greater fluctuation in the number of total hours of bright sunshine [Figure 8c]), which would affect the thermal regime and expansion-contraction of stone fabric that drives physical weathering damage, such as flaking, scaling, and blowouts.

All of the buildings complexes of Hizirbey Kulliyi have been surveyed in this study (e.g. mosque, bath, arasta and fountains) it was found that the most common decay features included blistering (most common) and blowouts (found frequently), whereas other decay features (such as pitting, etching along bedding planes, and granular disintegration) were less common. Moreover, her research findings showed more than 25% of surface discolouration from a generally buff colouration to a light to medium grey stone colour. Most decay and discolouration of stonework occurred on groundfloor ashlar, which she attributed was less likely to be caused by traffic or road salt and more likely to reasons in the past (e.g., coal

use) because of her finding that blistering and blowouts appeared where there was no traffic today. Blistering was linked to orientation on south-facing walls. She concluded that building aspect (orientation), and management influence building stone decay. However, her statement that "nevertheless, the fact that newly restored facades are becoming rapidly discoloured and eroded where road traffic is busy suggests that pollution from vehicle exhaust is one increasingly important factor in the decay of limestone" does implicate air pollution in this problem.

Besides the type of limestone used, atmospheric pollution (from coal-sourced to traffic emissions) is still a major culprit in the weathering of limestone. Limestone, in particular, is susceptible to atmospheric turbidity and acidification. The precipitation indicates that acid rain could be enhanced with the wet deposition of pollutants. However, it should be noted that the available pollution record is recent and portrays only recent trends in the atmospheric loading of pollution. The weathering damage due to exposure (either from intrinsic factors such as rock type, or extrinsic environmental factors such as micro/climate and pollution) varies.

Hizirbey K lliye is contained in quadrangles, which enclose them and protect them from passing traffic (point-source pollution). Enclosure, however, does not protect the buildings from air-borne (diffuse) pollution that travels in the atmosphere through natural dispersion, wind currents, and in rainfall that can be concentrated and transmitted through urban corridors. For this reason, other than completely encasing the buildings, the City of K rklareli needs to continue with a stringent programme of clean air. By doing so, environmental pollution can be controlled to reduce soiling, encrustation, and dissolution features that develop even on cleaned and restored buildings. To continue controlling emissions and air pollution, particularly where the buildings are located, is in the interest of protecting heritage buildings and structures and promoting their sustainability. For the historical monuments in the centre of K rklareli the combined evaluation of weathering forms, weathering products and weathering profiles shows clear correlations between the development of weathering damage of the stones as a consequence of air pollution and rising humidity. They demonstrate the need and urgency for monument preservation measures.

The results of the diagnostic studies have provided quantitative, statistically reliable information on the characteristics of stone weathering and the current weathering damage on the Hizirbey K lliye. This diagnostic concept, well targeted to wards the objectives and aims of research and monument preservation practice, can also be recommended for the long-term monitoring of the monuments and as a basis for the quality control of preservation measures. The results enhance the planning and implementation of appropriate monument preservation measures. This concerns immediate safeguarding measures, measures for the reduction of causes of damage, measures for remedy of damage and preventive measures in the same way. The results provide information on need, urgency and type of preservation measures as well as on monument areas where to be applied.

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