WEATHERING OF MONUMENTAL ISLAMIC MARBLE IN EGYPT: A CONTRIBUTION TO HERITAGE STUDIES

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1. Introduction

Artists and builders considered colored marble as one of the everlasting and most beautiful stones for casing the outer surfaces and lower parts of walls in historical buildings, especially churches and mosques built during the 14th-16th centuries in Cairo, the capital city of the Mamluks. Mecca and Medina (in the Hejaz region) were the two holy cities of Islam and were annexed to the Mamluk Sultanate, so that the Mamluks would gain prestige as being responsible for the two holy mosques there. However, the buildings and their marble works were not all exquisitely decorated [1]. As Egyptian marble is not considered to be of the best quality, valuable decorative marble was imported from different countries such as Italy, Cyprus and Turkey to embellish the structures. As a result, the unique historical buildings in Cairo form a historic town center of extraordinary value because they were built from more than one type of stone. Indeed, marble has been used since prehistoric times in the SE Mediterranean region for many purposes in architecture and sculpture [2-5].

The study of the structural and decorative stones in these buildings bears witness to extraordinary technical and artistic achievements. The variable and beautiful colors of the marble made it a precious stone in human civilization, and it was well known that, as a quality, color is one of the most characteristic and visible aspects in building aesthetics and decorative stones. Color may be due to the presence of so called idiochromatic minerals or natural pigments present in the colored marble [6-7]; marble has variable colors which range from white to red-yellow, brown, gray and pink, as well as different shades of black and green. Blue calcite is very rare in marble and may be the

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result of physical defects in the calcite which occurred during the mechanism of metamorphism. Natural polished limestone is sometimes called marble, but usually marbles containing >90% calcite and dolomite are considered true marbles.

Various techniques are applied to investigate the deterioration of marble and appropriate methods are then used for conservation purposes; they can include a classification system using ultrasonic means [8], physio-chemical studies using analytical techniques such as Fourier transform infrared, X-ray diffraction and scanning electron microscopy [9], the cleaning of marbles with laser [10], and characterization studies [11-13].

The marbles used in the construction or decoration of the historical buildings is exposed to different deterioration and weathering factors (mechanical or physio-chemical and biological) and has caused a serious decline in the state of conservation. The deterioration phenomena vary greatly in the marbles present in these buildings, because atmospheric conditions, mainly air temperature and relative humidity, differ greatly in the interior and exterior. Weathered stones usually exhibit an increase in porosity and water absorption, as well as a decrease in mechanical properties [14]. These aging processes can also manifest themselves as films and external deposits. Their color varies from black to grey, and brown to orange, and can derive from many substances (fly-ash or other dust, biominerals formed by microbiological activity, Fe content of such minerals, organic pigments like melanins, melaninoids, humic substances, rusty decay products of chlorophyll) [15]. It has been mentioned in many scientific investigations that atmospheric conditions, or the environment itself, exert a wide range of pressure on building materials and that serious physio-chemical changes take place in the structure and mineral constituents of these building materials due to the severe action of environmental conditions, in addition to other deterioration factors.

Formation of a thick compact surficial crust is commonly observed on some archeological stones resulting from the precipitation of calcite dissolved from marble and limestone due to the attack of acidic and saline moisture [16-18].

For ancient stone monuments, the mechanisms of deterioration at archaeological sites differ for stones buried in the soil and those that remain unburied [19-21]. Deterioration of building stones buried in soil varies, depending on the temperature of the different soil layers, soluble salts, dissolved carbon dioxide, organic matter content of the soil, its pH value, vegetation cover, drainage conditions, hydrological status, climate, and soil structure. In poor surroundings and depending on the length of time in the atmosphere, especially during winds and/or storms, the wetting/drying process may result in advanced adsorption of water molecules into the grains of the marble surfaces and may cause a reduction in strength. It also leads to the growth and opening of joints (caused by stress, fatigue, hydration, drying, freezing, and thawing) and degradation of the rock materials, as a result of water saturation (leading to dissolution, chemical change, physical decomposition through salt crystallization) [22].

Another type of weathering is salt crystallization and recrystallization, as well as the presence of colonies of microorganisms forming a black encrustation on the main facades of the historical buildings as a result of the attack of extensive air pollutants present in the atmosphere, especially in Cairo. Indeed, deterioration phenomena due to atmospheric events are examined under the main headings of freeze-thaw [23-27], thermal shock [28-31], wetting-drying [32-34], and salt crystallization [35-37]. Biological effects represent the direct and indirect contribution of plants, lichens, fungi, bacteria, and algae to the physical and chemical disintegration of rocks [38-40]. Anthropogenic effects refer to the destruction caused by mechanical interventions to building stones and the wear caused by direct human contact [41,42].

The aim of the study is to identify and characterize the environmental parameters causing significant variable forms of weathering in the building stones, especially marble taken from different sites, such as the architectural group of Sultan Qalawun in Al-Muizz Al-Deen Allah Street in Cairo, and the investigation of weathered marble samples taken from marble columns inside the 14th century Qalawun mausoleum in Cairo. This is due to the interaction of their intrinsic properties and mineral constituents with external atmospheric conditions and the surrounding environment [43]. The objective is to increase the awareness of decision makers about conservation actions for these historic heritage monuments, whether the one in Cairo or similar ones in the two holy cities in Saudi Arabia.

2. Petrographic characteristics of marble

Marble is considered to be a very popular metamorphic rock and highly valued due to its exotic composition and complex fabric. Metamorphism has many definitions. Winkler [44] has stated that metamorphism is the process which is responsible for changes in the mineralogical and/or structural and/or chemical composition of rocks in a solid state. But literally, metamorphism means the transformation of mineral constituents and rock fabric under certain circumstances, without chemical changes to the principal minerals, with the exception of introducing H_2O and CO_2 during the metamorphic mechanism.

In commercial terms, the term marble refers to a flexible and versatile material that can include rocks, such as calcium and/ or magnesium carbonate, and is called calcite marble if it contains low levels of magnesium carbonate, which is less than 5% of its components. Dolomitic marble is characterized by containing high levels of magnesium carbonate, between 5% to 40% of its composition; so is ordinary limestone which, when polished, is classified as marble. The term is often extended to include stones such as alabaster, serpentine and other soft rocks. The quality of the marble also varies according to the density of granules per cubic millimeter and we find that the higher the granularity, the higher the number per cubic millimeter; therefore the marble becomes less porous and more resistant to water absorption, but on the other hand, if the number of crystal particles per cubic millimeter decreases, the marble's porosity rises and its ability to absorb water increases and the marble becomes less solid, so the marble surface can easily crumble when exposed to humid or acidic environments [45].

Metamorphic rocks are natural rocks existing in/ or on the Earth's crust and make up about 15-18 vol % of this crust; some of these rocks are named according to their mineral constituents, such as marble. Some marbles are considered true marble where the calcite or dolomite is > 90% quartz, garnet, feldspar, tremolite, talc, graphite, magnetite, etc., commonly found in these marbles.

Marbles are characterized by different colors according to the minerals in them, which are responsible for their pigmentation. The most famous colors range from white, yellowish gray-beige, different shades of pink, red to brown, and greens of different hues [46]. Carrara has a gray field or background with light gray veins and can also have a blue-gray color.

Scientific research reveals that there is a direct relationship between the physical properties of stones and their internal material elements, the latter being responsible for their physio-chemical weathering. The physical, chemical, and mechanical properties of marbles vary greatly according to their mineral constituents, structure and the nature of the metamorphic process.

In the renovation of the facade of some archaeological sites and cathedrals in Cairo, Carrara marble of a light grey was used to a large extent in many parts of the building. The marble is characterized by its composition of mainly dolomite (80-90% in volume), minor calcite (10-15% in volume) and trace minerals such as quartz, white mica, and rutile apatite which are opaque minerals. The marble ranges from a homogeneous grain to a heterogeneous grain (average grain size 0.10 - 0.15 mm). The texture is grano-plastic with a three-point structure; the single crystal appears lobed with irregular edges; the composition and formation of this mineral compound indicates high pressure (low temperatures and metamorphic conditions) [47]. The most common marble is Carrara, named after the region from which it comes. The special fame of perfect white Carrara marble is due to the perfect combination of geology, location, topography, history and human creative effort, resulting in an outstanding production over thousands of years, which has provided some of the finest works of art and architectural achievements in history [48].

The present research focuses on Carrara marble which was widely used in Cairo for the construction and decoration of historical buildings. Tables 1 and 2 show that the density and porosity values of Carrara marble are variable. One of the most important physical properties of marble as a material is its density, which ranges from 2.6 to 2.8 g/cm3, and its compressive strength, which is typically from 50 to 100 MPa. Hardness on the Mohs scale ranges from 3 for calcite to nearly 4 for dolomite. However, this covers the inherent variability in grain size, the degree of crystal interlocking, and imperfections that can significantly affect cutting, carving and polishing. Certain impurities of a very different hardness, such as emery, quartz (e.g. grains of sand, nodules or veins of chert) and concentrations of silicate layer minerals (clay and mica), may also affect the usability and selectable range of work production. Kaolinite is a clay mineral produced by the chemical weathering of aluminum silicate minerals. Clay minerals with kaolinite are formed by the weathering or hydrothermal change of feldspars, aluminum silicates, fine-grained elastic metamorphic rocks [49]. When feldspar is broken down by chemical weathering, it goes through a process called hydrolysis. During hydrolysis, the feldspar reacts with water. This causes a chemical change in the feldspar. The new substance that is produced as a result of this chemical change is called kaolinite.

Table 1. Modal analysis (vol. %), densities, mean atomic weight (M), and cations packing index (K- values) (Carrara marble).

Modal Analysis (vol. %)	Mean Matrix Density g (cm^3)	Balk Density g (cm^3)	Mean Atomic Weight (M)	K-Value
96.8 cal , 3.2dol	2.72	2.71	20.04	5.40

Value is defined by the ratio of the pore volume (e.g. pores, open cracks) to the volume of the whole stone sample.

Table 2. Values of porosity, water uptake and degree of saturation (Carrara marble).

Porosity%	Mean pore radius (μm)	Water uptake (weight %)	Saturation degree (%)
0.42	0.06	0.02	0.90

Tables 1 and 2 show the results obtained on Carrara marble in previous studies by Guideti (2000), Said, T. et al (2005) and Widhalm, C., et al (1996) [22,50,51]. A recent study of Earth sciences as applied to cultural heritage highlights how the study of the genesis and properties of the stones used in antiquities is essentially the study of the geology of the material [52]. The documentation of these materials requires petrographic studies to know their source and state of preservation in order to choose the application of appropriate strategies for conservation purposes [47]. This type of study needs to consider buildings and artefacts made of marble – a valuable, widely used and traded material in ancient times – together with the use of a variety of analytical methods [53], such as optical and scanning electron microscopy. Classifying research on ancient marble objects is not only a subject of great archaeological importance, but also significant due to the different aspects of conservation that need to be examined.

Detailed examination is required to obtain reliable information about this white marble to understand whether it is from the original building or whether new Carrara marble was used to replace the old, etc. This is because in some historical buildings, the marble is not the original at the time of construction. The marble is characterized by dolomite (Dol 80–90% in vol) and minor quantities of calcite (10–15% in vol) with some additional minerals such as quartz, white mica, apatite, and opaque minerals [10-12]. This is especially important because, over the past few years, studies have exposed many works of art thought to be made of Carrara marble to be of Asian origin. Hence, the provenance of many white marble artefacts has (or may have) been incorrectly attributed to Göktepe and Carrara marble. Identification must involve more than just a personal visual assessment; therefore, complex analyses are essential in order to accurately study the objects and materials. Documentation on nero antico Göktepe stone and new data on white marble sculptures of Göktepe stone, which were frequently thought to relate to Carrara, need more than macroscopic identification based on personal eye assessments to obtain accurate information. A series of complex analyses on the stone quarried at Göktepe are essential to study the objects correctly [54].

A comparison between the two marbles highlights that Göktepe white is a pure calcitic marble, as is evident from its practically mono-mineral character; no accessory minerals were noticed by optical microscopy; a minimum amount of quartz was exposed by XRD. The grain size of Carrara marble appears on average coarser than that of Göktepe marble, although MGS estimates of Göktepe white marble are frequently similar to those for Carrara [55-57]. A multi-method approach, using a series of 11 diagnostic tests, based on petrography, stable isotope information and electron spin resonance spectroscopy was used to understand the source of the white marbles and to obtain data on the sample colour and its homogeneity, according to Attanasio, D., et.al [55]. The results contained the quantitative measurement of the sample colour and its homogeneity and on this basis, we tried to differentiate the three main quarrying basins of the Carrara district, that is, Torano, Miseglia and Colonnata. This distinction, if based on single techniques is indefinite, but may be completed with suitable confidence using a properly selected subset of six petrographic, isotopic and spectroscopic variables that provide additional data. One study [57] looks at the organization of a database for rock and isotope data banks, based on hundreds of analyses relating to marble from both major quarries and small quarries. These new data allow the statistical significance of the whole database to be upgraded and new global reference isotopic diagrams related to maximum grain size (MGS) of the different marbles to be drawn, proving very useful in better determining the provenance of a given archaeological marble object. It was on this basis that we differentiated the three main excavation sites in the Carrara area, Torano, Miseglia and Colonnat.

Investigation of the grain size distribution is another reliable technique for distinguishing Carrara marble and comparing it with others. When discussing Carrara marble, the public often imagines only one variety of stone. However, from a commercial point of view, the term Carrara marble can often be too general and misleading. It has frequently, and mistakenly, been used to describe a huge variety of different marbles (more than 150 commercial varieties) which, with their marketable diffusion, can create misunderstandings, since the one name – Carrara Marble –, is given to almost any commercial variation of the marble. It would, therefore, be more correct to use the term Marmo Bianco Carrara (white Carrara marble), also named "Ordinary White". It is typically homogeneous, and of a white ground color made up of shiny grains mixed with grey veins which run through the stone in irregular patterns, despite the Italian adjective *bianco* meaning white [58].

3. Results of experimental marble samples

Table 3 shows the water absorption value obtained in the weathered marble sample, which is 0.02 minimum and 0.40 maximum in weight % and was investigated by the Housing & Building National Research Center (HBRC), an Egyptian agency. With results obtained from previous studies and after conducting tests for different types of Egyptian marble, by comparing them with our study of Carrara Marble, we came to the following conclusions: from the results of previous studies on some Egyptian marble it was observed that the samples of sunny marble (the commercial name for marble that comes from El sheikh Fadl, Minya, Egypt) have reduced physical and mechanical properties and the lowest compressive strength value (52.7 Mpa); these samples also have the highest value of porosity (5.46), hence water absorption is high (2.12%). Also, Teriesta marble (the commercial name for marble that comes from Wadi Wata, South Sina, Egypt) [45], displays decent physical and mechanical properties. It has a higher compressive strength value (79.8Mpa) with low levels of porosity (2.05), hence, water absorption is low (0.8%).

Carrara marble samples show decent physical and mechanical properties (Table 4). It has a high compressive strength value (Mpa) (80.2 Mpa) with the highest value of tensile strength (5.8 Mpa) and abrasion strength ($cm^3/50\ cm^3$) (22.9). Also, these samples exhibit the highest resistance to abrasion due to the presence of a higher ratio of silica in this rock (0.72%).

Samples were tested under uniaxial compression. The uniaxial compression test was carried out by using a computerized compression machine. The compressive strength was obtained from the recorded value of the force divided by the cross-sectional zone of the sampling [59].

The physical properties of marble, according to Reda [60], are apparent porosity, bulk density and water absorption. Abrasion resistance was examined. The specimens were mounted on a rotating abrasion testing machine with a rate of rotation at 38 p.m. The loss in weight was determined after 352 revolutions. The Egyptian marble specimens (sunny and Teriesta marble) were placed under a pressure of 600 gm/cm^2 using sand (25-36 mesh) as an abrasive material. There was a loss in thickness (abrasion) in the sunny marble and Teriesta marble. All tests were carried out at the Housing & Building National Research Center (HBRC) in Egypt, Cairo and the results for Carrara marble are shown in Tables1-4.

Initial porosity seriously increased due to the effects of deterioration factors and was about 0.54٪ facilitating the penetration of moisture into the marble columns at Qalawun, of which a sample was examined, leading to the dissolution of crystalline salts present in the marble. It was shown that marbles, even those that are dolomitic, are sensitive to temperature impacts. For rocks with clay minerals, the effect of temperature may be responsible for shrinking [61-62]. Mineralogical studies were done by XRD revealing that the main mineral composition of the marble was calcite, and the additional minerals were quartz and dolomite. As regards the thermal expansion of Carrara marble Siegsmund and Durast [61-62] stated that the average value of thermal expansion is around 11x10-6 K-1 and this expansion can be classified in all categories:(a) isotropic thermal expansion without residual strain; (b) isotropic thermal expansion with residual strain; (c) and anisotropic thermal expansion with residual strain. Compressive, tensile and abrasion values are shown in Table 4.

Table 3. Water absorption value in the weathered Carrara marble sample (weight %).

Min	Max	Median
0.02	0.40	0.15

Table 4. Compressive, tensile and abrasion values of Carrara marble.

Compressive strength (Mpa)	Tensile strength (Mpa)	Abrasion strength (cm3/50 cm3)
80.2 (16.5)	5.8 (19.1)	(5.6)

4. Weathering effects

Although metamorphic stones, especially marbles, are considered more durable than other building materials, marbles are seriously affected by weathering factors such as atmospheric factors and microorganisms which cause serious damage to the mineral constituents of these stones and lead to the collapse of their physical structures. Weathering refers to the transformation and degradation of archaeological materials due to the action of the weather and regional climate; the microclimate, and humidity and air pollution, have a crucial environmental impact in our context [63]. Moreover, discoloration is a problem in buildings, as they damage the beautiful appearance of the stone. Previous research has found that a sample of uniformly white Carrara marble changed into a uniformly yellow-orange color when preserved with an alkaline solution. The discoloration depended directly on the oxidation of pyrite and hematite minerals dispersed in the marble. Although the oxidation of pyrite crystals is a natural process, basic aqueous solutions increased the rate of oxidation [64].

Weathering is a complex mechanism because it may result from different deterioration factors (e.g. physio-chemical and biological). For this reason, a single type of stone can have different deterioration patterns and the resistance of stones to different deterioration factors vary greatly from one stone to another, depending on its nature and durability. The most important weathering agents include air temperature, light, air humidity, air pollution and ground moisture as well as wind, man-made deterioration factors and acid rain [65].

4.1. Natural thermal weathering

Natural thermal weathering of marble is considered a very common deterioration phenomenon resulting from a variation in air temperature which eventually leads to dimensional changes (mechanical damage). Coarse grained marble may have significant differences in expansion between different varieties of the same rock type. Table 5 shows the thermal expansion coefficient of marble (10^{-6} x k^{-1}).

Table 5. The thermal expansion coefficient of marble (10-6 x k^{-1}).

Average	Max	Min
11	15	8

Calcite, dolomite and quartz which are considered very common minerals in marble have different expansion coefficients (Table 6).

Table 6. The thermal expansion coefficient of calcite, dolomite and quartz

Parallel to c axis	Perpendicular to c axis	Temp. Degree
Calcite25.1x10^{-6}	5.6 x10^{-6}	0-85
Dolomite25.8 x10^{-6}	6.2 x10^{-6}	24-700
Quartz 7.7 x10^{-6}	13.3 x10^{-6}	0-80

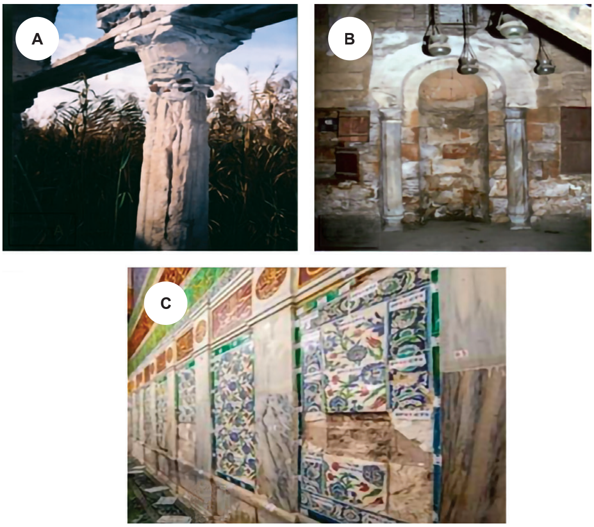

Figure 1. (A) Spalling and fracturing of marble column inside the courtyard of Omar Ibn Al-Aas Mosque, Damietta, Egypt; (B) infiltration of large amounts of ground water and crystallization of salts in historical mihrab (niche), Qalawun Mosque; (C) part of the restoration of Ottoman marble on the southern wall of the Prophet’s Mosque in Medina.

Changes in volume occur in marbles exposed to continuous variations in air temperature in their surroundings; in this case, the marbles tend to suffer from spalling, fracturing and separation of grains and layers (Figure 1A). These aspects of deterioration subsequently lead to an increase in porosity (called artificial porosity). The marble elements are already exposed to temperatures of around 45- 50°C in the summer season, but even when there are small variations in temperature, frequent heating and cooling of the stone will finally lead to deterioration over time [66,67].

4.2. Moisture

Moisture content in the air (relative humidity, rainwater) and ground water are very harmful deterioration factors that can cause serious damage to carbonate stones such as marble. Humidity accelerates the occurrence of damage in most building materials [68] and it is also one of the most important physicochemical factors that causes damage to the surfaces of stone monuments [69].

It can be observed that the marble slabs used for casing the lower parts of the walls inside Qalawun (254 AH corresponding to 868 AD) tend to bow and separate from the walls due to the penetration of large amounts of saline ground water and the crystallization of salts between these slabs and the walls. The rate of deterioration has seriously increased in the last decades due to the infiltration of ground moisture in large amounts as well as the thermal cycling (daily and seasonally) of the marble (Figure 1B).

4.3. Relative humidity

Relative humidity is commonly high inside Cairo's historical buildings because of the lack of openings. It is more than 80% in the case of the Qalawun buildings. When this degree of relative humidity is reached inside, marble surfaces become wet due to the penetration of this humidity, which in turn leads to the recrystallization of salts on or below the surface. An interesting phenomenon was noticed in the marble slabs, which exhibited a tendency towards concave bowing. Several studies have tried to clarify the phenomenon [50]. Past experiments have proved that permanent elongation can be produced by uniformly heating marble slabs. The bowing phenomenon, however, could only be partially reproduced [44] and stresses the fact that moisture is needed for marble slabs to buckle. Calcitic marble is more sensitive to thermal expansion than dolomitic marble, since calcite crystals, when heated, show a positive expansion coefficient on their c-axis, and a negative one perpendicular to it (Figure 1C) [70].

Another phase of deterioration is the black discoloration (formed by a thin black layer) of the marbles slabs due to the salty surface deposits mixed with soot; the crystalline salts, mainly gypsum, cause several deterioration patterns in these slabs such as granular disintegration, blistering, scaling and delamination. Water and moisture are very severe deterioration dynamics, since destructive chemical responses in archaeological materials cannot occur without water, as the salts cannot easily dissolve and pass into holes or pores without water (Figures 2A and B).

4.4. Acidic rainwater

Acidic rainwater causes severe chemical deterioration of the carbonate stones by dissolving the mineral constituents through a chemical reaction. In interaction with moisture, oxygen and calcium carbonate, the product of this sulfate process is the distillation of calcium sulfate (gypsum) which resembles scales on the surface. These sulfates can be dissolved by rainwater, or they can seep into the pores of the stone, so that a certain volume of calcium sulfate is higher than the volume of the calcium carbonate when recrystallized and can create enormous stress on the pore walls and an increase in volume with peeling, leading to the damage of the stone.

The H^+ – ion is responsible for the dissolution of carbonaceous materials as shown from the following chemical formulae (1).

$$Ca\ CO_3 + 2H^+Ca^{2+} + CO_2 + H_2O \qquad (1)$$

These minerals, such as calcite and dolomite, are considered highly soluble minerals compared with other minerals, such as quartz and feldspars.

The rate of the minerals' dissolution reaction depends on:

(a) the amount and contact time of liquid water available at the mineral's surface.
(b) The solubility of the minerals in question.
(c) The presence of acidity.

Although the mineral constituents of stones are soluble in fresh water due to the high acidity of rainwater in Cairo's atmosphere, these stones deteriorate as a result of the attack of carbonic acid and sulphuric acid present in this kind of water according to the following chemical formulae (2-5).

$$Ca\ CO_3 + CO_2 + H_{20} \leftrightarrows Ca^{2+} + 2\ HCO_3 \qquad (2)$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (3)$$

$$H_2SO_3 + Ca\ CO_3 \rightarrow Ca\ SO\ ½\ O + CO_2 + ½\ H_2O \qquad (4)$$

$$2\ Ca\ SO_3.\ ½\ H_2O + CO_2 + 3H_2O \rightarrow 2\ Ca\ SO_4\ 2\ H_2O \qquad (5)$$

4.5. Air pollution

Figure 2A. Damaged marble of the archaeological Mihrab, Ahmed Ibn Tulun Mosque, in Cairo, Egypt.

Air pollution is a chemical deterioration factor causing serious damage to carbonate stones. It is observed that the carbonate building or decorative stones used in Cairo's historical buildings have serious deterioration phenomena resulting from air pollutants. The deterioration of building stones depends largely on climate. Many experimental studies have shown that temperature changes, both increases and decreases, induce major deterioration [71]. Black particulate materials (carbon black and soot) and crusts are deposited on the surfaces of the historical buildings which spoil their appearance and cover the decorative elements present on their surfaces (Figure 2). These solid particulate materials also play an active part in the oxidation of gaseous pollutants such as sulfur dioxide, which is considered a very harmful gas that causes serious damage to carbonate building materials.

Figure 2B. A marble tombstone with kufic inscriptions engraved in 913 AD-1009 AD Egypt, in the Museum of the Faculty of Archeology, Cairo University. Despite its presence in the confined space, the accumulation of dust and dirt on the surface, which hides the writing, is evident.

Sulphur dioxide (SO_2) is an abundant gas in Cairo, and the holy city of Mecca's atmosphere is highly polluted by many sources, such as industries and heavy traffic, which produce large quantities of solid, liquid and gaseous pollutants.

Sulphation of carbonate stones is a very common phenomenon in historical buildings in Cairo and Mecca, where the external surfaces of these stones have layers of black encrustation which are considered layers rich in crystalline salts, mainly calcium sulphate (gypsum). Due to this phenomenon marble surfaces become sugary because their mineral constituents have been separated and the physical structure has become very weak due to salt weathering (Figures 3A, B and C).

Figure 3A. A marble column with a Corinthian crown on the entrance door illustrates the Qalawun Group, Cairo, with obvious damage to the marble surface.

Figure 3B. Inside Omar Ibn Al-Aas Mosque, Damietta. Salt weathering of marble.

Figure 3C. Marble column with kufic inscriptions in the Grand Mosque in Mecca.

4.6. Bio weathering

Cultural heritage monuments may be stained and degraded by the growth and activity of living organisms. As a result of the secretions of microorganisms, layers of biofilms form on stone surfaces, causing aesthetic and structural damage. Though the existence of biofilms on stone monuments exposed to outdoor environments is noticeable, thin films also occur on monuments under controllable indoor environmental conditions [72]. The organisms involved are bacteria, fungi, algae, and lichens [73]. Bio weathering of monumental stones is no less dangerous than other weathering factors where microorganisms, which are considered the most severe bio weathering factor, can cause serious damage to stone in all climates (Figure 4).

Figure 4. Bacterial colonies growing close to the marble columns of historical mosques; algae growth, and the spread of ground water inside the courtyard of Omar ibn Al-Aas Mosque, Damietta.

Decisive factors affecting the growth of microorganisms on or below the surface of monumental stones are:

1) Sources of moisture which penetrate to inside the stones; it was noticed moreover that wet stones can retain thick colonies of microorganisms more than dry stones.
2) Nutrients used by microorganisms for their continued survival.
3) Stones that contain carbonate compounds that microbes live on commonly have thick microbial growth. Microbiological colonization producing a dark-colored crust was observed on the surface of columns and covering the marble. Micro-organisms play a significant and considerable role in all change processes that occur in the stone.

The black fungi present on the marble surface also produce oxalic acid as a metabolic product, which could have added to the formation of such a thick crust [74]. The most effective microorganisms in the bio-weathering of monumental carbonate stones are: bacteria, algae, lichens, and fungi.

4.7. Bacterial species

Bacteria are single-cell organisms, their size ranging from 1 um up to 100 um in some bacterial species, which have the ability to exist in fissures, pores and on stone surfaces.

Chemoheterotrophic bacteria cause chromatic changes in the monumental stones because they produce different organic pigments, but chemolithotrophic bacteria are famous for producing sulfurous and sulphuric acids. The latter acid reacts with calcite (calcium carbonate), the principal mineral in marble and produces calcium sulphate (the organic source of calcium sulphate).

Cyanobacteria (phototrophic bacteria) are called blue-green algae; they also cause chromatic changes in the surface of the archaeological stones as a result of producing different pigments.

4.8. Fungal species

A fungal species such as *Aspergillus Niger, Alternaria* etc., can form colonies of different colors on or below the surface of archaeological stones and also are capable of producing severe acids which cause biodeterioration, especially for carbonate stones.

4.9. Lichens

Lichens cause pigmentation on the surface of archaeological stones; these surfaces will have spots of green, gray, yellow, black, orange and pink colors.

The microorganisms previously mentioned cause serious biodeterioration to the carbonate stones in many ways, including physio-chemical degradation of the mineral constituents; the catalytic effect of microbial metabolic activities can multiply reaction rates enormously, as well as changes in pH by producing organic acids which enhance mineral solubility.

5. Materials and Methods

About 40 specimens were collected from the most deteriorated parts of the marbles located inside and outside the selected historical buildings: The *Qalawun complex,* Cairo, and the *Omar ibn Al-Aas Mosque,* Damietta (see previous figures). The aim of this widespread sampling was to cover an extensive range of weathering forms present in these marbles. The specimens were then analyzed and investigated using the following techniques:

(1) X-ray diffraction (XRD): The identification of the mineral composition of the samples was made by X-ray diffraction patterns, using a Philips X-ray PW 1840 diffractometer.

(2) Scanning electron microscopy (SEM-EDX): The surface features of the damaged layers were examined by Scanning electron microscopy (SEM), (SEM JEOL JSM 6400) coupled with an energy dispersive X-ray spectrometer (EDS), to reveal details of the digenetic processes.

(3) Polarized light microscopy (PLM): The mineralogical appearance and texture of the marble samples were examined by using a polarized optical microscope. Petrographic thin sections were prepared and optically analyzed by using a Leitz polarizing microscope.
(4) Groundwater analysis was performed by atomic absorption.

5.1. Imaging methods

Image investigation is an efficient method for illustrating the physical structure and mineral constituents of the archaeological stone samples. Optical microscopy investigations were performed by polarized light microscope (PLM) to characterize the mineral constituents of the marble specimens with fine grains of calcite and dolomite as the principal minerals and the exfoliation of the sample structure, and calcite with cracks and micro cracks. Marble samples are carbonate rocks containing both calcite and dolomite in variable proportions, with important to moderate contents of quartz and orthoclase. There were very dissimilar textural features. Samples from all sections exhibited a more or less strong preparation of the shape of anisotropic grains. The surface rocks showed enormous structures. The image in Figure 5 displays an increase in porosity and the samples exposed more micro cracks within the thin sections. Rare crystals of quartz and orthoclase were detected. Contact metamorphism fossil fragments and iron oxide were also observed. Most of the calcite crystals were granoblastic, with equidimensional shapes (pseudo-hexagonal) and different sizes.

The investigated marble samples from the Qalawun Mosque showed the presence of calcite dolomite crystals as well as the exfoliation of the physical structure. Examination of the marble samples under polarized microscope (40X) shows the images seen in Figures 5A and B.

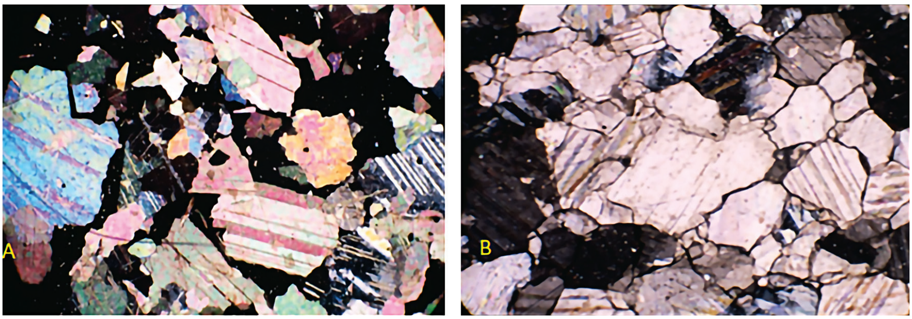

Figure 5. Fragment (sample 1) from the crown of a column in the courtyard of the Qalawun Mosque. A typical section in a marble rock under a polarizing microscope with magnification of X40 shows interlocking calcite grains in the mosaic texture. A) Calcite and dolomite as principal minerals and the exfoliation of the sample structure and B) calcite and cracks/ micro cracks.

Electron imaging was accomplished with SEM equipped with EDX to clarify the deterioration aspects in the marble sample from the Qalawun Mosque. The results prove that major deterioration is the result of the abundance of soluble salts in the rock. SEM micrographs revealed that salt deposits on the marble surface caused several changes, such as cracks and pores. The obtained results show that the crystalline salts played an active role in the deterioration of this sample. Moreover, the physical structure severely collapsed due to the sodium chloride and calcium sulphate. The analyses by EDX proved that the sample of the stone from the courtyard near the Qibla (Qalawun Mosque), consists of halite NaCl *(*sodium chloride) (Figures 6 and 7). Analysis of the sample shows the elemental composition of the marble sample (Table 7).

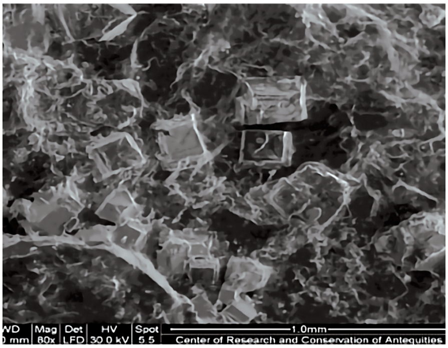

Figure 6. Sample 2 from the column in Qalawun Mosque shows the presence of crystalline sodium chloride inside the marble sample.

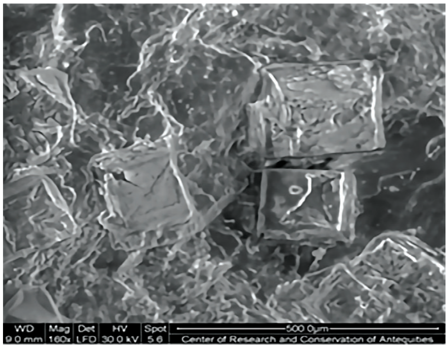

Figure 7. Sample 3 from the qibla (Qalawun Mosque); the crystalline shape shows the sodium chloride salt in its ideal form of cubic crystallization, indicating the stability of the salt state and lack of continuous moisture. SEM imaging shows the deterioration of the sample.

5.2. Groundwater analysis

Groundwater plays an active role in the deterioration of the building stones used in the historical buildings in Cairo. It is considered an aggressive deterioration factor because it contains Na, Cl and some other ions which cause serious damage (Table 8).

Table 7. The elemental composition of the investigated marble samples from the Qalawun Mosque.

No	Locality	Element	Weight%	Atomic	Compound	Compound Atomic%	Intensity	Line
1	Sample 1	Ca Na Mg Al K	32.20 4.22 1.06 1.06 0.16	16.68 3.18 0.91 0.82 0.25	$Ca\ Co_3$ $Na\ Cl$ $MgSO_4$ $Al._2O_2$ KSO_4	80.4 10.72 5.57 2.00 1.60	17.09 0.21 0.31 0.26 0.38	
2	Sample 2	Ca Na Ma Al K	34.0 2.29 1.28 1.24 0.41	17.36 2.04 1.08 0.94 0.22	$CaCO_3$ $NaCl$ $Mg\ SO_4$ Al_2O K_2O	48.99 5.68 6.34 2.34 0.50	30.75 0.18 0.26 0.99 0.59	K K K K K
3	Sample 3	Ca Na Ma Al K	33.34 2.28 1.44 1.25 0.36	17.12 2.52 1.10 1.06 0.19	$Ca\ CO_3$ $NaCl$ $Al\ _2O_3$ $MgSO_4$ K_2O	83.47 7.71 2.73 6.20 0.34	30.03 0. 22 0.58 0.26 0.50	K K K K K

Table 8. The elemental composition of the investigated marble samples from Qalawun Mosque.

Constituent %	Sample 1	Sample 2	Sample 3
Na^{+}	0.430	0.370	0.210
Ca^{+2}	1.510	1.710	1.300
Mg^{+2}	0.810	0.750	0.540
K^{+}	0.310	0.147	0.090
Fe^{+3}	0.057	0.102	0.021
Cl^{-}	0.190	0.210	0.085
HCO^{-3}	0.067	0.080	0.0305
SO_4^{-2}	0.570	0.910	0.0640
CO_3^{-2}	0.215	0.190	0.180
NO_3^{-}	0.160	0.185	0.170

5.3. X – ray diffraction (XRD)

Two deteriorated samples from Qalawun Mosque of red and black marble were analyzed by XRD. The obtained results show that calcite is the major mineral, but gypsum, manganese and hematite are trace minerals in the red marble sample, whereas calcite is the major mineral, and quartz and gypsum are trace minerals in the black marble sample (Figure 8).

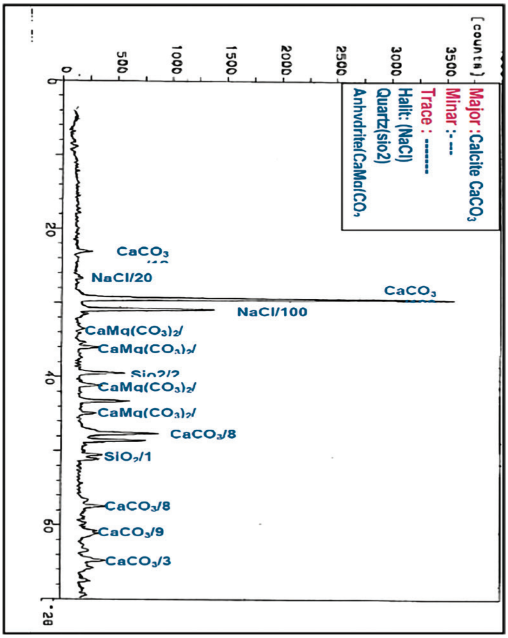

Figure 8. Marble sample from Qalawun Mosque, in which calcite is the major mineral and quartz and gypsum are trace minerals (black marble).

5.4. SEM with EDX

Another weathered marble sample (red and white) from the qibla in the Qalawun Mosque, was investigated by SEM equipped with EDX. The SEM image showed that the physical structure of this sample had seriously collapsed due to the serious effect of crystalline salts and fungi; the EDX showed the elemental composition of this sample.

Figure 9. SEM micrograph shows fungal growth inside the deteriorated marble sample.

A deteriorated white marble sample taken from behind the qibla and mihrab of Qalawun Mosque was also analyzed to illustrate its elemental composition; the obtained results are shown in Table 7. A white marble sample, deteriorated with microorganisms, was investigated by SEM in order to show the physio-chemical effects of these microorganisms. The obtained results show that fungi can penetrate deeply into marble and cause serious damage to its physical structure and mineral constituents (Figure 9).

6. Conclusion

Marble was used in large parts of the Islamic world especially in the city of Cairo and the two holy cities of Mecca and Medina during the Mamluk period. Across the centuries, the archaeological stones have therefore been susceptible to deterioration due to the attack of weathering processes and various other deterioration factors. The deterioration mechanism is complex because it is the result of different factors (physicochemical and biological factors), the most severe factors being air pollution, variations in air temperature and relative humidity, microorganisms and acidic rainwater. In order to assess the different deterioration factors affecting the archaeological marbles in Egypt and determine properties, various samples were collected from marble columns and decorative marble stones and investigated using different analytical methods. The obtained results showed that air temperature and relative humidity are considered vehicle factors causing serious physio-chemical damage in the marbles. Fracturing, spalling and fissuring are very common deterioration aspects resulting from variations in these atmospheric factors. Acidic rainwater is also responsible for the deterioration of carbonate stones in Cairo's historical buildings because it contains many acids which react with the stones causing damage to their mineral constituents.

Air pollution is also considered a very harmful deterioration factor. It plays a dominant role in deteriorating the previously mentioned stones on the facades of Cairo's historical buildings, which are covered with black layers of soot and grease as well as black encrustations; they also contain different kinds of salts, mainly calcium sulphate ($CaSO2*H2O$) and is an indicator of the high concentration of gaseous pollutants, mainly sulphur dioxide, in Cairo's atmosphere. Microorganisms and other deterioration factors such as plants, and animal and bird excrements are no less dangerous than the deterioration factors previously mentioned because they play a role in the bio weathering of carbonate stones. Most of the microbial species are responsible for alterations in the pigmentation (chromatic changes) of the original surface of the stones; moreover, these microorganisms, especially bacteria and lichens, are considered producers of acids such as oxalic, carbonic and sulphuric acids. Therefore, the crusts present on the surface of the carbonate stones contain crystalline salts such as calcium oxalate and calcium sulphate.

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Summary

Marble is a metamorphic rock widely used in historical buildings as a structural and decorative stone; also, it is commonly used for sculpture and as a building material; for example, the lower parts of many walls of Mamluk and Turkish buildings are covered with marble tiles of different colors (mainly, white, red, black) as well as many of the columns in these structures. Due to the severe effects of deterioration factors, such as, atmospheric parameters, air pollution, ground water, micro-organisms, the decorative marble slabs and columns are seriously deteriorated. Forty marble specimens were collected from the most deteriorated parts of marbles located inside and outside selected historical buildings, namely the Sultan Qalawun complex in Al-Muizz Al-Deen Allah Street in Cairo (1284 AD) an archaeological architectural group, built in the Mamluk style. The present work focuses on the identification of the mechanism of marble deterioration. In order to carry out this study, different samples were collected from the deteriorated historical marble of the Qalawun; the marble samples collected for study were not from a single building, but from the complex of the Sultan Qalawun Group or the Qalawun Mosque, and included a school and dome, and the Mosque. The mihrab of the dome is considered one of the most luxurious mihrabs of antiquity in Egypt. Each of its sides is surrounded by three marble columns, and its cavity has four layers of gilded recesses supported by marble columns. The marble samples were investigated by X-ray diffraction (XRD), X-ray fluorescence (XRF), polarized light microscope (PLM) and scanning electron microscope with energy dispersive x-ray spectroscopy (SEM-EDS). The obtained results showed that the mineral constituents of the investigated samples were seriously deteriorated, and the physical structure had collapsed.

Riassunto

Il marmo è una roccia metamorfica molto utilizzata negli edifici storici come pietra strutturale e decorativa; inoltre, è comunemente usato per la scultura e come materiale da costruzione: ad esempio, le parti inferiori di molte pareti di edifici mamelucchi e turchi sono ricoperte da piastrelle di marmo di diversi colori (principalmente bianco, rosso, nero) così come molte delle colonne di queste strutture. A causa dei gravi effetti dei fattori di degrado, quali parametri atmosferici, inquinamento atmosferico, acque sotterranee, microrganismi, le lastre e le colonne decorative in marmo sono gravemente deteriorate. Quaranta campioni di marmo sono stati raccolti dalle parti più deteriorate di marmi situati all’interno e all’esterno di edifici storici selezionati, in particolare il complesso Sultan Qalawun in Al-Muizz Al-Deen Allah Street al Cairo (1284 d.C.) un gruppo architettonico archeologico, costruito in stile mamelucco . Il presente lavoro si concentra sull’identificazione del meccanismo di deterioramento del marmo. Per realizzare questo studio sono stati prelevati diversi campioni dal marmo storico deteriorato del Qalawun; i campioni di marmo raccolti per lo studio non provenivano da un singolo edificio, ma dal complesso del Sultan Qalawun Group o dalla Moschea Qalawun, e comprendevano una scuola, una cupola e la Moschea. Il mihrab della cupola è considerato uno dei mihrab più lussuosi dell’antichità in Egitto. Ciascuno dei suoi lati è circondato da tre colonne di marmo e la sua cavità ha quattro strati di rientranze dorate sostenute da colonne di marmo. I campioni di marmo sono stati studiati mediante diffrazione di raggi X (XRD), fluorescenza a raggi X (XRF), microscopio a luce polarizzata (PLM) e microscopio elettronico a scansione con spettroscopia di raggi X a dispersione di energia (SEM-EDS). I risultati ottenuti hanno mostrato che i costituenti minerali dei campioni indagati erano gravemente deteriorati e la struttura fisica era crollata.