HONEYCOMB WEATHERING OF LIMESTONE BUILDINGS IN THE ARCHAEOLOGICAL SITES OF LEPTIS MAGNA (LIBYA): CAUSES, PROCESSES AND DAMAGES

Nabil. A. ABD EL-TAWAB BADER*
Conservation department, South Valley University, Qena, Egypt

Abstract

Honeycomb weathering is a common surface phenomenon affecting a variety of rocks in a range of environments. The processes involve the appearance of closely spaced cavities which are generally small, with an average width of a few millimeters to several centimeters in diameter. Honeycomb weathering is also known as fretting, cavernous weathering, alveoli/alveolar weathering, stone lattice, stone lace or miniature tafoni weathering. Incipient honeycomb weathering in a homogeneous limestone has been experimentally reproduced by wind exposure and salt crystallization. It is a type of salt weathering common on coastal and semi-arid limestone. Honeycomb weathering occurs in many populated region and must have been noted in archaeological sites at Leptis Magna (Libya). Leptis Magna is a World Heritage site on the Mediterranean coast of North Africa in the Tripolitania region of Libya. In order to create an appropriated conservation concept, it was necessary to investigate the damage processes. For this purpose we used X-ray powder diffraction (XRD), optical and scanning electron microscope (SEM) coupled with EDX, Stereo microscope, polarizing microscopes (PM). Biodeterioration problems in the site were analyzed by taking into account their impact on the substrate and their relationship with environmental factors. Chemical analysis and field observations indicated that honeycomb weathering in coastal exposures of limestone in the archaeological sites of Leptis Magna resulted from the evaporation of salt water deposited by waves from the Mediterranean Sea. Microscopic examination of weathered samples showed that erosion resulted from the disaggregation of mineral grains, rather than from chemical decomposition. Thin walls separating adjacent cavities seem to be the result of the protective effects of organic coatings produced by microscopic algae inhabiting the rock surface.

Keywords: Honeycomb; Leptis Magna; Limestone; Environmental factors, Salts; Biodeterioration

Introduction

The stone blocks of Leptis Magna/Libya, limestone from the Lower Cretaceous age, display extensive honeycomb weathering features. The spatial variations in the degree of weathering, together with geochemical evidence, suggest that marine salt played a key role in the development of the honeycomb patterns. Leptis Magna is a World Heritage site on the Mediterranean coast of North Africa in the Tripolitania region of Libya. Its ruins are located

* Corresponding author: drnabil_bader@yahoo.com, Tel. (+2)01113464493
3km west of AlKhums, 12km west of Villa Sileen, 80km southeast of Misrata, 130km East of Tripoli, on the coast where Wadi Lebda meets the sea (Fig.1a and b). The site is one of the most spectacular and unspoiled Roman ruin in the Mediterranean. It is called Lpqy, Neapolis, Lebida or Lebda by the modern-day residents of Libya. Leptis Magna was added to the UNESCO World Heritage List, together with 5 other places in Libya. Originally founded by the Phoenicians in the 10th century BC, it survived the actions of Spartan colonists, became a Punic city and eventually part of the new Roman province of Africa, around 23 BC. Although it provided a source of building materials to various pillagers throughout history, it was not excavated until 1920. The number of great monuments in Leptis Magna makes it a bit difficult to point out highlights, but the theatre is clearly one and it has a splendid view from its upper tiers [1].

![Fig.1. Map of the main archaeological sites in Leptis Magna,](wikipedia.org/wiki/2010)

The dryness of this location, given its latitude and its maritime character, is typical of a Mediterranean climate. The temperature is moderate, with a yearly average of 16°C; the extreme monthly averages are 22°C (July) and 8°C (January). Nevertheless, a maximum value of 46°C and a minimum of 14°C have been recorded. The average annual precipitation is 600 mm and the average yearly relative humidity is 68%. There are 2350–2680h of sunshine per year and no more than 12 frost days (tab.1). The dominant wind directions are NW and SW (from the Mediterranean). Winds favor evaporation from stone surfaces and the release of marine aerosols. According to Auger (1987) the marine influence on the alteration of monuments in this region extends as far as 100km inland [2].

**Building materials of Leptis Magna**

Settlers from the Greek and Roman periods built cities of native limestone blocks excavated and cut to size. This is evident in the remains of cities such as Leptis-Magna,
following this period of active building on a grand scale [3]. The building materials for Leptis Magna are mainly local limestone from the surrounding area. "Building was made considerably easier by the existence nearby (at Wadi Zennad as well as Lebda itself) of excellent quarries for stone and for a grey limestone that acquires a fine yellow patina with time. This quarry belonged to the Al-Khumus formation. The Al-Khumus formation was established by Mann for a sequence of about 70km of shallow marine limestone exposed near Al-Khumus. The Al-Khumus formation consists of a basal unit of Gypiferous marls with pelecypods, followed by siliceous, saccharoidal and marly limestone and calcareous clays. An acalcarene layer overlain by a conglomerate of disintegrated limestone pebbles marks the middle of the formation. The upper part contains fine grained algal and oolitic limestone and contains a marine fauna of foraminifera, gastropods, and ostracods, which indicate a Langhian age Don [4].

In the Leptis Magna site, the honeycomb weathering is found on steep surfaces in the salt spray zone, above the average high tide level. The cavity development is initiated by salt weathering. In the intertidal zone, cavity shapes and sizes are primarily determined by the wetting/drying cycles and the rate of development greatly diminishes when cavities reach a critical size where the amount of seawater left by receding tides is so great that evaporation no longer occurs[5, 6]. Honeycomb weathering commonly occurs in homogeneous sediments and massive crystalline rocks [7]. Honeycomb weathering is extensively developed on coastal buildings, although its distribution shows some variation according to local conditions. Honeycomb weathering cavities can be found on buildings dispersed through the intertidal zone, where they commonly consist of rather shallow circular depressions, inhabited by a variety of marine organisms. The most spectacular occurrences of honeycomb weathering appear above the high tide line and they occur approximately 2.5m above average tide level. Honeycomb weathering is most prominent in the zone extending 3m above the high tide line, with a cavity width of 5 to 10cm, although individual cavities sometimes reach a diameter of more than 30cm. The diameter commonly exceeds their depth, which is seldom more than 10cm (Fig. 2). Shallow cavities are generally in the form of simple depressions, while deeper cavities typically widen toward the interior. Cavities generally occur within a very restricted vertical range and lithologically identical units at higher elevations do not contain honeycomb textures. In order to explain the observed differences in physical deterioration, samples of alveolar weathered limestone were taken and analyzed from several locations of the archaeological sites at Leptis Magna (Fig. 3). The aim of our investigation was to understand the weathering processes, as a requirement for an appropriate conservation and restoration concept.

Fig. 2. Honeycomb weathering at the Leptis Magna: A and B - honeycomb weathering developed along inclined bedding in limestone; C - honeycomb weathering in homogenous limestone
Fig. 2. Pockets, carvings and cavities resulted from the weathering of limestone at Leptis Magna:
A – Shallow circular depressions inhabited by a variety of marine organisms; B - growth of plants which made cavities; C - shadow cavities and black rust; D - most prominent extend honeycomb weathering; E, F – salt spray zone

Materials and methods

Several samples were taken from the archaeological sites in Leptis Magna. The following analytical techniques and scientific methods were used to investigate all intrinsic and extrinsic factors that affected the archaeological sites, in order to define their deterioration mechanisms. Thin sections from the studied samples were prepared. The samples were first observed by using a Carl Zeiss Light Optical Microscope (LOM) and then examined by using a polarized transmitted microscope (Olympus BX41) with digital camera attached, at 40-60X magnification, in plane-polarized and cross polarized-light. The samples were also investigated by Scanning Electron Microscope (SEM, JEOL, Jsm-5500 LV, Japan) equipped with an Oxford energy Dispersive X-ray Microanalyzer (EDX) system, with link Isis software and a model 6587 X-ray detector, (Oxford, England). Various samples had been coated with gold (20nm). Stone samples and salt efflorescences were analyzed from back-weathered expositions by using X-ray diffraction with a diffractometer (Philips, PW 1840) with Ni-filtered Cu Kα radiation, at operating, conditions of 40KV/25 am and a scan speed of 2° (2θ)/min. [8].

A study of the biodeterioration of the Leptis Magna has been performed, in order to characterize the kinds of bacteria and fungi. For each collected sample, 1g was diluted with 9mL of sterilized saline solution. Samples were shaken vigorously to form a uniform solution of 10-1 concentration [8]. The decimal serial dilutions (10-1 to 10-5) were prepared by using the method of N. Okafor and M.A.N. Ejiofor [9] for the isolation of fungi. The plate count method of K.B. Raper and D.I. Fennell [10] was used as follows: a known volume of the diluted sample, from sample serial dilutions, was used to inoculate the used medium in plates. The plates contained Czapek’s agar medium. That was melted and kept at 45°C. According to N.R Smith and V.I. Dawson [11] the plates were incubated at 28°C for 5-7 days, during which the developing fungi colonies were identified. The method of K.H. Domsch et al. [12] was used for the isolation of bacteria, by using a nutrient agar medium.

Results

Petrographic Study

The microscopic examination of the polished thin section of sample (W1) indicated that the sample was composed of fossil fragments, micro spars, interaclasis embedded in a micritic
matrix and micro spary calcite cement, stained by iron oxide (Fig. 4). According to a classification from 1962 [13], the rock was named packstone. The microscopic examination of sample (W2) (Fig. 5) indicated that the limestone sample consists essentially of bioclasts (fossil fragments), pellets, and intera clasts embedded in micro spars and sparite cement with a biogenic texture. According to Dunham, the rock is named grainstone. The thin section of sample (W3) revealed that the rock consisted of mainly quartz, fossils, rock fragments and feldspars embedded in calcareous cement, as shown in (Fig. 6). The rock is packstone to grainstone, according to Dunham’s classification.

Fig. 4. Petrographic view of limestone sample (W1) shows the components are fossil fragments, micro spar, micrite (low percent), intera clasts and iron oxide (25X): A – Fossil fragments, B – fossil fragments and micro spars, C - Triloculina.

Fig. 5. Petrographic view of limestone sample (W2) shows the weathered stone heterogeneous pore system contains, A- ferric oxides and hydroxides (black spots) B- fossil fragments and structural less Peloids (SLP), C- quartz grains, structure peloids (SP) and iron oxide (25X)

Fig. 6. Petrographic view of limestone sample (W3): A, B and C - its mineralogy is quartz, fossil fragments, rock fragments and feldspars; D, E and F - show fungal remains and minor inertinite. Sporomorphs include aunqueloculua sp., milislida (foraminifera), shell fragments (pelecypoda).
**SEM-EDX Techniques**

SEM has been used for studying the morphological features of the same samples. The images we recorded showed that there was a wide range of deterioration features as shown in (Fig. 7), such as micro exfoliation and micro pitting which were clearly visible. Decayed limestone samples show etching features in some calcite and quartz grains, indicating micro-dissolution processes (chemical weathering). Carbonate cement dissolution and subsequent calcite re-crystallization were also observed. Drusy calcite sparite crystals are noticeable. Dissolution of cements occurs in the limestone, which leads to an increasing porosity and the loss of the cohesion of the stone. Crystal outlines are poorly defined, as a consequence of leaching. Disintegration of calcite crystals is seen clearly and most of the ooides are removed due to the effect of soluble salts (Fig. 8). Our observations revealed significant quantities of shell and shell fragments. Evidence of biophysical damage was observed in the samples colonized by cyanobacterial and microalgal biofilms. Cyanobacterial filaments were observed to grow inside pores of the stone. Microalgae adhered closely to particles of the substratum and they grew inside preexisting pores and cracks (figure 9). Certain fungi are capable, through a range of etching and chelating processes, to bore and burrow their way into mineral surfaces, producing distinctive borehole pits and channels. Anhedral and subhedral halite crystals were found in the stones.

The EDX results (Fig. 10) show that Quartz grains formed secondary components, because the limestone in Laptis Magna is sandy limestone. Moreover, the decayed samples contained K, Ti, Mg, and Sr. The higher concentration of these elements was caused by the presence of clay minerals and iron oxyhydroxides that made up the Curia micrite. E. Gavish and G.M. Friedman, in 1969 [14], mentioned that magnesium, strontium and iron have to be analyzed, because of their ability to substitute calcium in the limestone and their expected variability with mineralogical changes by the weathering. The study showed the presence of Cl and high percentage of S. Those elements are considered to form halite and gypsum.

![Fig. 7. SEM-EDX microanalysis and photograph of the limestone sample (W1): A - Shows the ooids of oolitic; B - the peeling of the calcite crystals; C - eroded pits; D - Clay minerals; E- fungi hyphate; F - needle crystals of salts](image-url)
Fig. 8. SEM-EDX microanalysis and photomograph of the limestone sample (W2):
A - fungi hyphate; B - eroded pits; C - halite crystals; D - clay minerals; E - eroded pits; F - Anhydral halite.

Fig. 9. SEM-EDX microanalysis and photograph of the limestone sample (W3):
A - Growth of mite (phylum: Arthropods); B - algal growth; C - Exfoliation and destroyed calcite ooids.

Fig. 10. SEM-EDX microanalysis of the limestone samples: A - EDX pattern of the sample (W1) revealed the presence of Ca as a major elements, Si as a minor and Al, Mg, K as traces; B - EDX microanalysis pattern of the sample (W2) revealed the presence of Ca & Si as a major elements, Al, Fe as a minor and S, Mg, Ag; C - EDX pattern of the sample (W3) revealed the presence of Ca & Si as a major elements, Al, Fe as a minor and Mg, P, Cl, Ti as traces.
Table 1. Composition of the samples

<table>
<thead>
<tr>
<th>Elements</th>
<th>W1 (%)</th>
<th>W2 (%)</th>
<th>W3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.5296</td>
<td>1.5431</td>
<td>0.6797</td>
</tr>
<tr>
<td>Al</td>
<td>1.1950</td>
<td>2.4488</td>
<td>3.3960</td>
</tr>
<tr>
<td>Si</td>
<td>3.3083</td>
<td>12.2038</td>
<td>1.2255</td>
</tr>
<tr>
<td>K</td>
<td>0.8772</td>
<td>1.2453</td>
<td>0.6567</td>
</tr>
<tr>
<td>Ca</td>
<td>92.8102</td>
<td>75.3832</td>
<td>75.3832</td>
</tr>
<tr>
<td>Fe</td>
<td>1.2797</td>
<td>2.0789</td>
<td>4.2069</td>
</tr>
</tbody>
</table>

XRD Study
Decayed stones have similar compositions in different monuments and buildings, with slight differences (Table 4 and Fig. 10). Calcite is the major mineral in the stones (90%) from a Doric temple, quartz is present in minor amounts, gypsum appears in crusts in efflorescences and in samples showing alveolar weathering, quartz is more abundant (15–30%). In the temple of Jupiter, the decayed samples contained gypsum (CaSO$_4$·2H$_2$O), halite (NaCl), biotite KMg$_3$(AlSi$_3$)O$_{10}$(OH)$_2$, forsterite (Mg$_2$SiO$_4$) and phyllosilicates (Si$_2$O$_5$). Curiously, halite was not detected in those monuments and gypsum was only found in the samples affected by flaking. The high content of sulphate was related to the atmosphere that was extremely polluted with SO$_2$.

Table 4. XRD analytical results of limestone samples from Leptis Magna

<table>
<thead>
<tr>
<th>Analytical results</th>
<th>Samples</th>
<th>Major minerals</th>
<th>Minor minerals</th>
<th>Traces minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td></td>
<td>Calcite (CaCO$_3$)</td>
<td>Quartz, Halite</td>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
</tr>
<tr>
<td>Sample B</td>
<td></td>
<td>Calcite (CaCO$_3$)</td>
<td>Quartz, Halite</td>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
</tr>
<tr>
<td>Sample C</td>
<td></td>
<td>Calcite (CaCO$_3$)</td>
<td>Quartz, Halite</td>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
</tr>
<tr>
<td>Sample D</td>
<td></td>
<td>Calcite (CaCO$_3$)</td>
<td>Quartz, Halite</td>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
</tr>
<tr>
<td>Sample E</td>
<td></td>
<td>Calcite and Quartz</td>
<td>Quartz, Forsterite</td>
<td>Biotite KMg$_3$(AlSi$<em>3$)O$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Sample F</td>
<td></td>
<td>Calcite</td>
<td>Quartz</td>
<td>Forsterite (Mg$_2$SiO$_4$)</td>
</tr>
<tr>
<td>Sample G</td>
<td></td>
<td>Calcite and Gypsum</td>
<td>Halite</td>
<td>Quartz</td>
</tr>
</tbody>
</table>

Fig. 11. XRD patterns of limestone samples from Leptis Magna
Light Optical Microscopes (LOM) Study

Optical (or light) microscopes are used to magnify small objects and can provide information about the structure and characteristics of a sample. Thin sections of stone can be studied to identify their mineral composition and their source. The investigation pictures showed that the limestone consisted mainly of bioclasts, pellets, intraclasts and quartz embedded in sparite cement. The cement was stained in some parts by iron oxide. The rock showed texture range between clasts and bioclasts. The rock is packstone to grainstone, according to Dunham's classification (Fig. 12A, B, C, D, E, F, G, H and J).

Biological study results

Identification of microorganisms

Identification of fungi was carried out on the basis of the macroscopic features of colonies, their morphological and structural characteristics, according to relevant publications [12, 15]. A light microscope with a magnification of 40X was used for preliminary identification of the moulds to a generic level. A light microscope with a magnification of 400X was used for preliminary identification of the fungi, including Aspergillus niger, Aspergillus fumigates, St. Verruculosum, Alternaria alternate, Fusarium moniliforme.

Identification of Bacteria: During the identification of bacterial isolates from Leptis Magna, we identified Pseudomonas sp., Clostridium sp., Pseudomonas sp., Bacillus cereus, Bacillus pumilus, Staphylococcus sp. as shown in Figure 13.
Discussion

Considering the observations on-site, together with our analysis, it was possible to explain the processes of alveolar weathering at Leptis-Magna. In the present study we observed, studied and explained all the destruction factors dominating in the study area and the main components of the weathering phenomena (their "mechanism and the resulted forms"). There is a consensus in relevant publications that the relative importance of physical and chemical weathering processes for alveoli to develop is related to lithology and the structure of rocks and to topographical and environmental conditions. Therefore, alveolar weathering can only be satisfactorily explained by invoking the synergism of a range of weathering mechanisms.

The results we obtained by optical microscopy and SEM showed that weathering in Leptis Magna took place through the following combined chemical and physical processes, which led to granular disaggregation and ultimately to alveolar weathering: cement dissolution, chemical decomposition and physical action of salt crystallization. Our SEM observations also showed that salts were found deeper in the studied samples. Chemically weathered quartz grains were described and we established that silica dissolution was enhanced under saline conditions (e.g. by sodium chloride) [16]. Considering the above mentioned, we concluded that the etching features observed in some quartz grains could have been caused by the effect of the salt from the sea-water that sprayed the stone. The petrographic characteristics of decayed stones indicated that cement dissolution occurred under the action of sea-water spraying. The ionic strength of the saline solution that wets the stones under direct exposure to the salt spraying effect should increase the dissolution of the cement [17]. The carbonate cement dissolution leads to a well-connected porous network and, as a consequence, favors an increment of the total porosity. This allows a deeper capillary migration of solutions towards the interior of the stone. The concept that honeycomb weathering results from the physical action of salt crystallization was first proposed by W.F. Hume in 1925 [18], who observed masses of fibrous salt crystals associated with honeycomb structures in nodular limestone samples from the Ma'aza plateau, east of the Nile river, in Egypt. Salts may be introduced by the migration in fluids or from salts contained within the original sediment. Salt crystallization, otherwise known as haloclasty, causes the disintegration of stone, when saline solutions seep into cracks and joints in the rocks and evaporate, leaving salt crystals behind. These salt crystals expand as they are heated up, exerting pressure on the confining rock. Salt crystallization may also take place when solutions decompose limestone to form salt solutions of sodium chloride, of which the solvent evaporates and they form their respective salt crystals. These salts can expand up to three times their size, or even more. It is normally associated with arid climates where strong heating causes strong evaporation and therefore salt crystallization. It is also common along coasts. An example of salt weathering can be seen in the honeycombed stones in a sea wall. Our results in regard to the mineralogical composition study, conducted by XRD, completely agree with others obtained by XRF.
Our field observations revealed that honeycomb the weathering at Leptis Magna was caused by the surrounding environment of the buildings. To form a solution, it is necessary to have a water source other than rainwater, which leaches salts from the stone surface. Water vapors proceed from sea-water spray droplets, whose input has been confirmed by the enrichment factors [19]. Condensation may also wet stone surfaces. Then, a brine solution has to be formed and, before drying, has to wet the stone surface long enough to migrate towards the inside of the stone. V.P. de Freitas et al., in 1996 [20] concluded that a high relative humidity, such as that reported in Leptis Magna (e.g. average yearly RH75%), and the variation of the relative humidity through 75% (the equilibrium relative humidity for NaCl at 25°C is 75.03%), may allow the formation of a solution. Thus, for a relative humidity of 75%, water fixation led to the dissolution of salts present in the stones. The solution penetration is determined by the pore network. Moisture must be present to allow for the salt to settle on the rocks, so that, as the salt solution evaporates, due to variations in humidity and temperature, the salt begins to crystallize within the pores of the rock. A porous rock is also a requirement, so that there are pore-spaces for the salt to crystallize in. These salt crystals pry apart the mineral grains, leaving them vulnerable to other forms of weathering. It seems that this local supersaturation and the subsequent buildup of salt crystallization pressure ultimately resulted in the formation of honeycomb features [6]. The hydrostatic pressure generated by salt crystallization disintegrated the stone. Salt-induced decay of porous, granular oolitic limestone is often manifested initially by contour scaling, followed by retreatment of the rapid surface through granular disintegration and/or multiple flaking [21].

Wind action was invoked to have caused the formation of alveoli in the Leptis Magna stone. Buildings were exposed to overall winds "The dominant wind directions are NW and SW (from the Mediterranean)". Honeycomb weathering is a type of salt weathering common on coastal and semi-arid limestone structures. It was experimentally proven to be the result of a dynamic balance between the corrosive action of salt crystallization and wind exposure by G.E. Mustoe in 1982 [6]. Wind action was reported in relevant studies to be a key factor for the formation of alveolar weathering. A heterogeneous wind which flows over a stone surface is important in the development of this weathering pattern. Wind promotes evaporative salt growth between grains on a stone surface, resulting in the development of small, randomly distributed cavities. A reduction in air pressure within the cavities results in increased wind speed and rapid evaporation. The high evaporation rate leads to the evaporative cooling of the saline solution in the cavity, which leads to a faster and a greater granular disintegration than in the surrounding areas. It seems that this local supersaturation and the subsequent buildup of salt crystallization pressure ultimately resulted in the formation of honeycomb features. For the first time, these experimental results demonstrate the close relationship between salts, wind and honeycomb weathering. They also offer new ways to understand the genesis of this striking and sometimes harmful weathering pattern [22]. Wind action is essential for removing the debris from the interior of the cavities (which in the current area could be done by marine breezes) such that alveolar weathering is known to be a self-propagating process [23]. Short-term fluctuations in temperature in the Leptis Magna stone surfaces could have occurred in the current area in response to variations in wind-speed and cloud cover, which may ultimately have contributed to the stone breakdown through ‘fatigue’ effects.

The optical and electronic microscopy revealed the presence of fungi hyphate and algae and the microbiological study identified several kinds of fungi, including *Aspergillus niger*, *Aspergillus fumigates*, *St. Verruculosum*, *Alternaria alternate*, *Fusarium moniliforma* and several kinds of bacteria, including *Pseudomonas sp.*, *Clostridium sp.*, *Bacillus cereus*, *Bacillus pumilus*, *Staphylococcus sp.*.

Honeycomb weathering results from a dynamic balance between the corrosive action of salt and the protective effects of endolithic microbes. Cavity patterns produced by complex interactions between inorganic processes and biologic activities provide a geological model of
'self-organization' [6]. A biodeteriogen is an organism that is capable of causing biodeterioration. A wide variety of biodeteriogens have been identified on stone monuments in tropical environments, due to the particularly favorable environmental conditions (high relative humidity, high temperatures, and heavy rainfall) in those regions. These organisms can cause direct or indirect damage to many kinds of stone. In some cases, the ability to cause serious damage has been well established; in others, it remains conjectural. The biophysical deterioration of stone may occur due to the pressure exerted on the surrounding surface material during the growth or movement of an organism or its parts, such as the hyphae and extensive root systems, which penetrate deeply into the stone through preexisting cracks or crevices, causing stresses that lead to the physical damage of the surrounding stone material [24]. Biochemical deterioration resulting from assimilatory processes, where the organism uses the stone surface as a source of nutrition, is probably more easily understood than deterioration resulting from dissimilatory processes, where the organism produces a variety of metabolites that react chemically with the stone surface [25]. Most autotrophic microorganisms produce acids that can attack and dissolve some types of stone, such as the Pseudomonas sp. (autotrophic nitrifying bacteria), which can play an important role in degradation, by oxidizing ammonia to nitrite and nitrate ions, which may result in the formation of nitric acid. Stone dissolution, powdering and the formation of soluble nitrate salts that appear as efflorescences on the stone surface are processes that have all been demonstrated experimentally [26]. Heterotrophic organisms, such as the Clostridium sp., also produce organic acids that are capable of dissolving minerals of stone, with the leaching of cations. Inorganic and organic acids decompose stone minerals by producing salts and chelates. An increased volume of soluble salts or chelates may also cause stresses in the pores, resulting in the formation of cracks.

The limestone at Leptis Magna, exposed to the weathering effects of the ocean, were dissolved and eroded to make a fascinating landscape east of Tripoli, Libya. The weathering of limestone involves carbon dioxide and water. Carbon dioxide dissolved in water provides ions that produce free hydrogen. The carbon dioxide in the atmosphere combines with water, to form carbonic acid (H$_2$CO$_3$): $ \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3 $. Nevertheless, it is weak, when carbonic acid is combined with a mineral like calcite (CaCO$_3$), an important part of limestone, but the calcium and bicarbonate ions are removed, causing the rock to erode away. The uneven effects of this process create pockets, caves, and crevices, as seen in Fig.3. Granular disintegration was attributed to chemical alteration along the grain surface, causing swelling and shrinking of interstitial clay [27]. The solution in limestone formed as a result of carbon dioxide that dissolved in the rainwater, producing weak carbonic acid in unpolluted environments, which reacted with calcium carbonate (the limestone) and formed calcium bicarbonate. This process speeds up as temperature decreases. That plays a very important role in the transformation of carbonaceous building stone components, which turn into bicarbonate, which dissolves slowly [22].

Conclusion

From the research we concluded that:

- The stone blocks of Leptis Magna/Labia, limestone from the Lower Cretaceous age, display extensive honeycomb weathering features. Spatial variations in the degree of weathering, together with geochemical evidence, suggest that marine water spraying played a key role in the development of the honeycombs.

- The main weathering mechanisms involved were granular disintegration and micro delamination, induced by chemical alteration, along with inter-grain boundaries and the differential swelling and the contraction of clays within the rock.
Salt crystallization and hydration pressures within the rock pores appear to have played a minor role in this case.

Honeycomb weathering results from a dynamic balance between the corrosive action of salt and the protective effects of endolithic microbes. Cavity patterns were produced by complex interactions between inorganic processes and biologic activities.

References


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