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The environmental factors affecting the archaeological buildings in Egypt, “IV deterioration by synergistic marine effects”

Mohamed A. El-Gohary^{1*}

Abstract

This paper investigates the marine effects that affect Qait Bey Fortress in Alexandria—Egypt. It presents the results of scientific studies and examinations to evaluate the deterioration conditions that affected archaeological buildings in the *marine environment*. In Alexandria, many monumental sites and stone buildings have suffered from many aggressive factors of deterioration (mechanical, chemical, and biological), which have caused great harmful appearances and threatened to eradicate them. These effects include the chemical actions resulting from seawater and marine aerosol and the mechanical actions of water waves. (*Qait Bey Fortress*), as a case study, was periodically investigated by many scientific techniques over five years to check its decay conditions and to define the most suitable conservation approaches and non-destructive methods for preservation. Different techniques and examinations were carried out to evaluate the current deterioration state of the fortress. For example, XRD analysis and PM investigation were used to study the mineralogical compositions, lithotype, and petrographic characteristics of the stone samples. SEM was used to investigate the morphological features of the same samples. AAS was also used for studying the chemical constituents of seawater samples. In addition, microbiological investigations were conducted to evaluate the colored hard crusts that affected the stone surfaces in the fortress. Our results proved that severe deterioration factors influenced the fortress by collaborating with chemical, mechanical, and biological mechanisms. These mechanisms caused several manifestations, such as *abrasion and attrition, crystallizing of salt species, mortar desegregation, pitting and minerals' honeycomb (Alveolar), color changes, in addition to the accumulation of black and colored biogenic hard crusts composed of numerous tightly adjoining pits of several centimeters. Crusts, such as yellow to bluish green, resulted from P. aeruginosa and granular appearance having brownish ting in the center resulted from P. clacis. In addition, other pigmented features resulted from Bacillus firmus and Bacillus atrophaeus. The presence of some black and dark color crusts was attributed to the growth of some fungal species, such as A. niger, A. phoenicis, Cladosporium cladosporioides, and Alternaria alternata.*

Keywords Qait Bey Fortress, Marine environment, Weathering, Seawater, Marine aerosol

Introduction

Alexandria, one of the most famous cities in the Mediterranean basin- contains many monumental sites and stone buildings [1, 2], which have suffered from several aggressive deterioration factors, resulting in different deterioration mechanisms and significant harmful manifestations [3, 4]. These monuments must be investigated from time to time by scientific techniques to check their decay conditions and define the most suitable and non-destructive

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conservation approaches to preserve them [5, 6]. Qait Bey Fortress was built using different stone blocks, especially oolitic limestone and sandy dolostone. Historically, the fortress, Fig. 1a, b was built in 1477–1479 AD (882–884 AH). [7] by Sultan Al-Ashraf Qait Bey [8] on the ruins of the ancient Alexandria Lighthouse (*Fanar*) [9]. Therefore, it was later named the fortress of the minaret or minor minaret [10]. In the same context, historians tell us that this tower was divided into four parts; *a mosque, an oven, a mill, and a hawasel* (warehousing) filled with weapons and makahel [7]. Topographically, the fortress rises on the end of the northern part from Ras-Eltean Island and consists mainly of two parts. The 1st is surrounding walls, and the 2nd is the main tower. There is a similarity between this fortress and Qait Bey Fortress in Rashid [11]. The walls of the fortress are divided into *interior* and *exterior*. The interior walls are a group of chambers used for soldiers, and the exterior walls are similar to the others present in most Islamic towns. They surround the fortress from the main directions, “north, south, east, and west” [12]. Environmentally, the study area is part of the Mediterranean region, an area of transition between the semi-arid climate of the continental area at the lower latitudes and the humid temperature maritime climate at the higher latitudes [13]. It is characterized by an aggressively humid environment, especially in summer, and heavy rain in winter. These environmental conditions mostly create severe losses in archaeological sites [14]. Climatically, the study area is located in the north coast between latitudes of 31° 11' 52.80" N and longitudes of 29° 55' 9.12" E. It is characterized by large changes in recorded climatic elements, as listed in Table 1. These changes enhance some serious effects of seawater and marine aerosol throughout the year and lead to deterioration processes [15–17].

Qait Bey Fortress was made completely of limestone as an essential material in addition to some other secondary

Table 1 Recorded climatic elements study area (Alexandria, monthly in 2021–2022)

| Factor | Climatic elements | | | |
|--------|-------------------|-------------|-------------|--------------------|
| | AT °C | RH % | RF mm | WS _{knot} |
| Max | 30.4 in Aug | 71 in Aug | 52.8 in Jan | 44 in Aug |
| Min | 9.1 in Jan | 65 in April | 0 in July | 7 in Dec |
| Mean | 19.75 | 68 | 26.4 | 25.5 |

(After: https://www.weather-atlas.com/en/egypt/alexandria-climate#google_vignette & <https://www.Time-anddate.com/weather/egypt/alexandria/historic?month=12&year=2021,2021-2022>)

materials (red brick and wood); each of these materials has its deterioration problems and patterns. Moreover, the site around the fortress is subject to natural deterioration effects from seawater and marine aerosol, which can play a significant role through chemical mechanisms created by chemical reactions between these water constituents and the fortress's wall components [18]. The present paper focuses on the degradation of the northern wall of the fortress as one of the most important exterior walls exposed directly to the aggressive effects of seawater, marine aerosol, and water waves. Explaining the physical, chemical, and biological deterioration mechanisms and harmful forms affecting this wall, the paper also presents some laboratory experiments to explore the significant changes affecting the microstructure and mineralogy of the wall caused by the interaction among extremely harmful seawater, marine aerosol, and water waves commonly found in such environments.

Physio-weathering due to water waves' action is the main threat affecting our case marine due to the Sea-Level Rise (SLR), storm, and increasing wave energy that lead to greater flooding, marine erosion, marine squeeze, and saline intrusion as described by Pearson and Williams [19]. Furthermore, the erosion of fortress stones through water waves increases when global warming

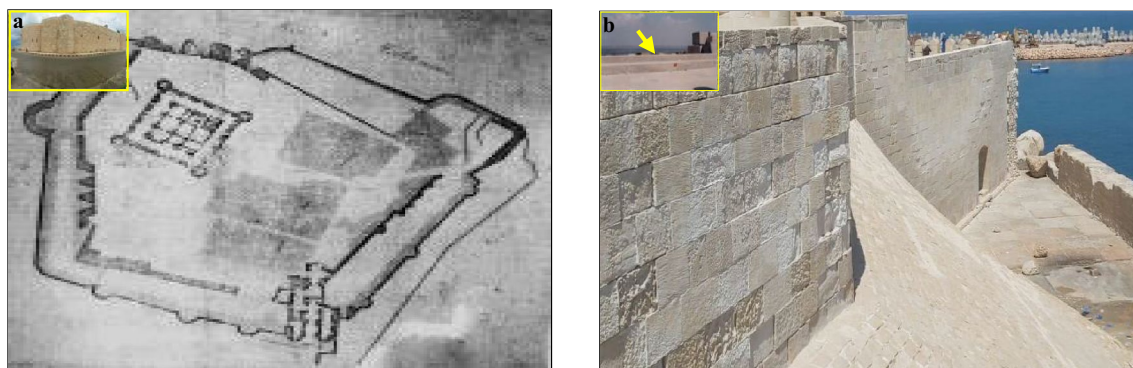


Fig. 1 Shows **a** an ancient drawing of the castle surrounded by the sea with a focus on the northern wall of the fortress exposed directly to seawater, **b** the fortress with surrounding walls, after (Salem, 1982)

causes the SLR [20]. This type of erosion usually results from conditions (e.g., *high tide, large waves, and wind direction and strength*). In addition, storm surges, especially with low atmospheric pressure and humidity variations characterizing the study area, which produce effective wetting and drying cycles [20]. Another deterioration mechanism attributed to the harmful action of seawater waves leads to the corroding of the stone surface, damaging the pore structure, then moving the salts inside the stone core and the decay of the masonry and mortar of the fortress as discussed by Rodriguez-Navarro et al. [21]. *Chemo-weathering* of historical buildings made from natural stones in marine environments is a great problem on which research activities have increasingly concentrated in recent years [22]. In our case, this issue is caused by the effects of seawater and marine aerosol dominating this environment. It is mainly attributed to the effects of marine aerosol and sea vapor. It finally leads to a critical weathering cycle affecting the fortress stones' durability through dissolution and crystallization mechanisms [23]. This durability depends on their physical, chemical, or mechanical properties [24], the properties of the different saline solutions, and their chemical interaction with the host rock [25]. *Bio-weathering* or bio-deterioration is an important deterioration mechanism caused by microorganisms [26] that is clearly related to environmental conditions (materials types, building architectural properties, expositional parameters, and stone-conserving treatments [27–30]. In our case, this mechanism affected the fortress stones, which, in permanent contact with seawater, through the accumulating of microorganisms (fungi, bacteria, etc.) as attested

previously in similar cases [31, 32]. Their effects mostly occurred by anodic and cathodic electrochemical reactions and were promoted by the corrosive metabolites produced by the biofouling fauna [33]. The three mechanisms led to severe alteration appearances, such as (I) abrasion and attrition, (II) crystallization of salt species, (III) mortar desegregation, (IV) pitting, (V) honeycomb (Alveolar), and (VI) color changes due to the accumulation of black and colored biogenic hard crusts, Fig. 2.

Materials

Materials

Some assemblages collected from other locations and heights of the fortress wall were investigated using instrumental techniques to define their main components and weathering products. These assemblages contain *stone samples, mortars, superficial surfaces, components of weathering products, and petrographic characteristics* of the samples, in addition to *water samples* as listed in Table 2.

Table 2 Sampling and techniques

| Analytical techniques | Sample types | | | | Water |
|-----------------------|--------------|----------------------|---------|---------------------|-------|
| | Limestone | Superficial surfaces | Mortars | Weathering products | |
| XRD | 3 | 3 | 2 | 3 | – |
| PM | 3 | 3 | 2 | 3 | – |
| SEM | 3 | 3 | 2 | 3 | – |
| AAS | – | – | – | – | 3 |



Fig. 2 Shows different deterioration forms affecting Qait Bey Fortress in Alexandria

Methods

Laboratory investigation is one of the most delicate aspects of the analytical approach to studying art and archaeological findings. This technique was applied to numerous studies of the deterioration of historical monuments [34–39]. Different experiments were performed according to some laboratory standards to investigate the decaying processes of limestone under the effect of seawater. *XRD-600 Shimadzu X-ray diffractometer with Cu k- α radiation* was used by applying the following conditions: CuK radiation (1.5418 Å) with 30 kV, 30 mA energy, and Graphite Monochromator for investigating the mineralogical composition of the samples mentioned above. Furthermore, *Leica optical microscope-4500 P* attached to DFC500 Camera-Leica Microsystems was used to define the petrographic characteristics of the samples. *JSM 5300 Scanning Electron Microscope coupled with Energy Dispersive X-ray Spectroscopy (SEM–EDX)* was elevated for studying the morphological surfaces of wet stone, mortars, and highly contaminated surface hard crust, in addition to the chemical components of the decayed wall. *Perkin Elmer AAS Analyst 400 Spectrophotometer “Unico-1200”* and *chemical titration* were performed to investigate the chemical components of seawater and saline solution extracted from surface salt crusts taken from five points around the Fortress’s northern wall. Finally, an initial microbiological study was conducted to isolate marine bacteria. A nutrient agar (NA) supplemented with 50 mg l⁻¹ cycloheximide was used, while Malt Extract Agar (MEA) was used to isolate marine fungi with 100 mg l⁻¹ chloramphenicol and streptomycin. The compositions of the different media were as follows: NA medium contained peptone at 10 g/l, beef extract at three g/l, NaCl at 5 g/l, and agar at 15 g/l (pH 7.3); MEA medium contained malt extract at 130 g/l, chloramphenicol at 0.1 g/l, and agar at 15 g/l (pH 6.0) [40]. Under aseptic conditions, the outer surface of the fortress rocks was swabbed with sterile cotton swabs for microorganism isolation. The swabs were then immersed and shaken in one ml of sterile marine water, and the suspensions were then spread on (NA) plates for bacterial isolation and another spread on (MEA) for fungal isolation. After that, all plates were incubated at 30 °C (for three days in a bacterial case and seven days in a fungal case) [41]. Several biochemical tests were performed to identify physiological characteristic bacterial isolates using Bergey’s Manual and ABIS 7 online software. The principal tests used for this purpose were Lactose Fermentation Test (LAC), Indole Test (IND), Methyl Red Test (MR), Voges-Proskauer Test (VP), Citrate Utilization Test (CIT), Urease Test (URE), Nitrate Reduction Test (NIT), Oxidase Test (OXI), Catalase Test (CAT), Hydrogen Sulphide Production (H₂S), and Aerobic and

Anerobic Test (Ae/An) [42]. Furthermore, the colony features (color, form, scale, and hyphae) were observed macroscopically. The fungal morphology was examined microscopically using a compound microscope with a digital camera and a lactophenol cotton blue-stained slide fitted with a small portion of the mycelium [43].

Results

The deterioration influences of seawater and marine aerosol that affected Qait Bey Fortress in Alexandria, Egypt, were experimentally analyzed. The following findings were concluded.

X-ray diffraction (XRD) analysis results

The investigated samples proved that they have different deterioration features that could be divided into two categories of deteriorated stone:

- The 1st Category, Fig. 3a: a sample from the bedrock of the fortress consists of *calcite* as a major mineral and *halite* and *sylvite* as salty minerals, in addition to *k-feldspars*, *quartz*, *periclase*, *margarite*, and *anhydrite*.
- The 2nd Category, Fig. 3b: a sample from the fortress’s foundation consists of *quartz* and *calcite* as major minerals, *gypsum* and *halite* as minor minerals, in addition to *sylvite* as a trace.
- The 3rd Category, Fig. 3c: a mortar sample contains calcite, aragonite, and halite.

Lithotype and petrographic characteristics

Investigating the petrographic features of stone samples asserted that they are characterized by heterogeneity indexes due to different occurrences. They could be divided into two sources.

- The 1st type is the bedrock of the Fortress composed of biosparite limestone (*Oolitic limestone*), Fig. 4a.
- The 2nd one (*Sandy dolostone*) is fine grains of quartz cemented by dolomitic cement, Fig. 4b.

SEM investigation results

SEM investigation results proved high disintegration and complete corrosion in the main components of limestone that led to many deterioration forms as follows:

- Salt efflorescence due to seawater waves, sea spray, and marine aerosol, Fig. 5a.
- The presence of Ca platy crystals in addition to some other salt crystals (halite, gypsum, and sylvite), Fig. 5b

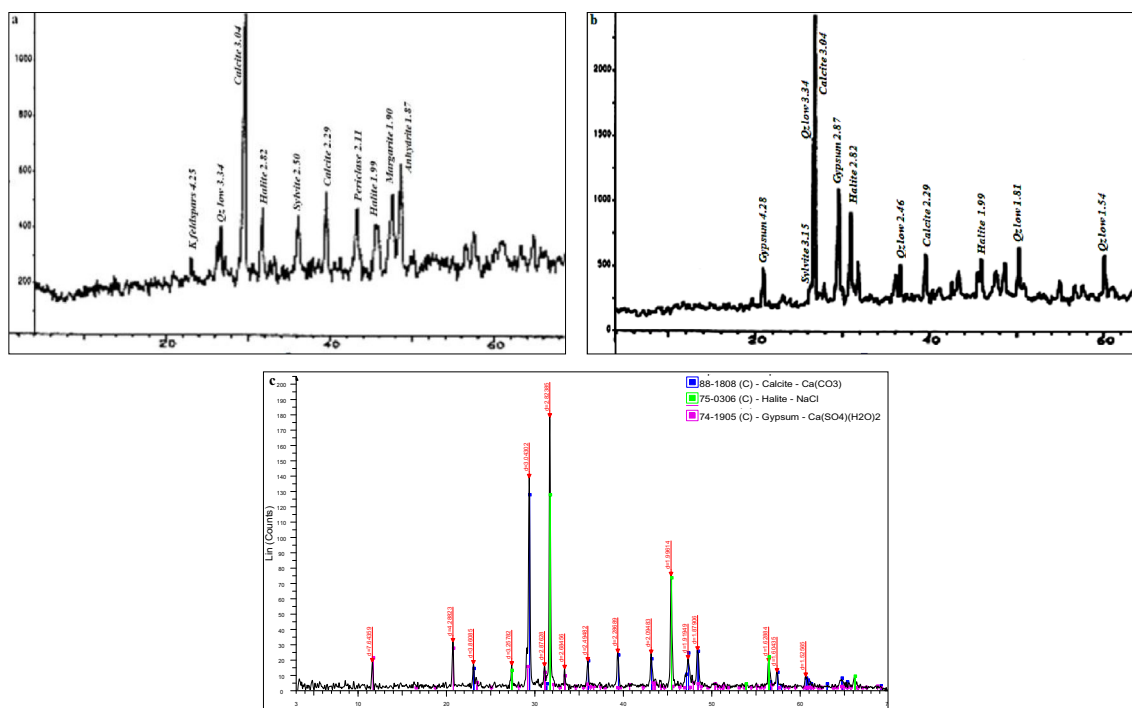


Fig. 3 XRD patterns of the investigated samples collected from the northern wall of the fortress, **a** bedrock, **b** sandy dolostone used in the foundation, and **c** mortar sample (*Kosromil*)

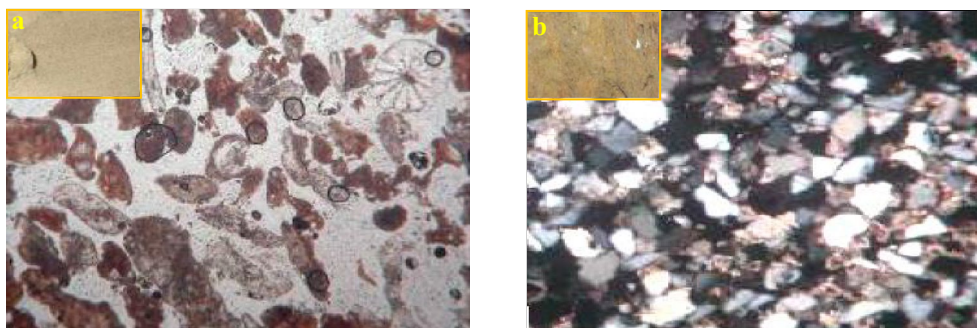


Fig. 4 Shows a megascopic and microscopic overview of **a** biosparite limestone (bedrock under the fortress) and **b** sandy dolostone used in the fortress foundation

- Many deterioration features, especially fully eroded Qz grains, due to *physio-weathering* and *chemo-weathering* (Fig. 5c)
- The presence of *Alveolar* as a unique-deteriorated symptom characterizing the marine environment, Fig. 5d

Atomic absorption spectroscopy (AAS) results

The analytical results of seawater samples and dissolved salty crusts made by AAS pointed to the presence of the

main chemical components of both limestone and seawater. These data are listed in Tables 3, 4, 5.

Microbiological investigation results

The resulting data of affected microorganisms proved that a total of 11 bacterial isolates and 12 fungal isolates were reported in the present study. All these different strains were isolated on the basis of distinct physiological and morphological characteristics. Morphological features, such as size, shape, color, and margins, were checked and recorded. The final identification results are summarized in Table 6 and Fig. 6a, b.

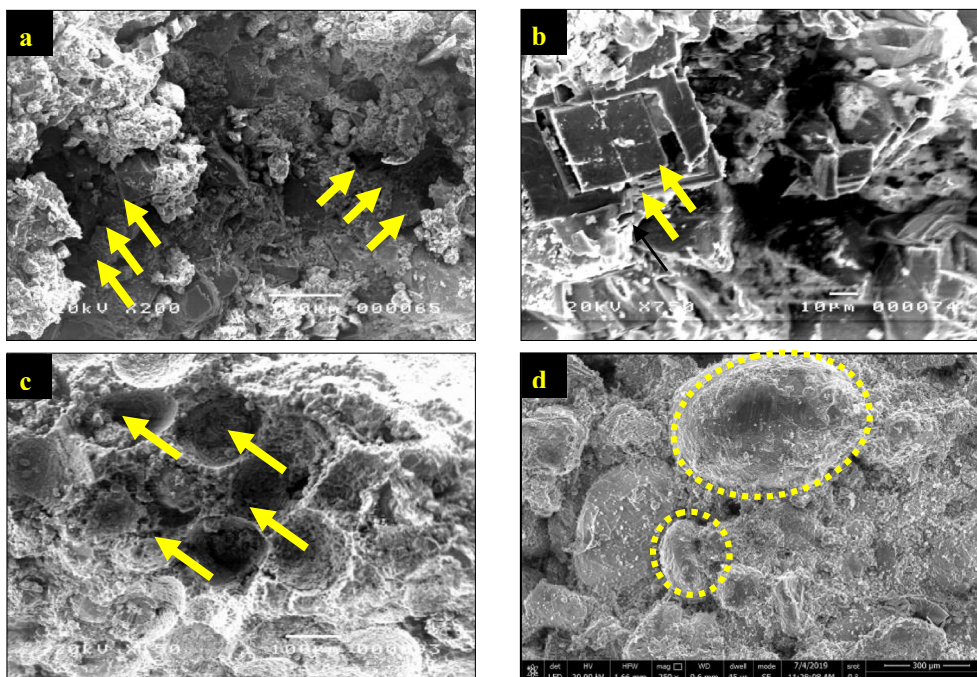


Fig. 5 Shows SEM photomicrographs of morphological features from the fortress’s northern wall **a** calcium crystals mixed with other salts (halite, gypsum, and sylvite); **b** platy halite crystals participated after the evaporation of seawater and spray; **c** honeycomb or splash as privet-deterioration symptoms characterizing the marine environment; **d** deterioration of calcite crystals in the disintegration of mortars due to the effects of saline water

Table 3 AAS average (Mg/L) of the analytical results of seawater around Qait Bey Fortress and in other sites

| Analytical Ref | Analytical results Mg/L | | | | | | |
|----------------|-------------------------|------------------|-----------------|----------------|-------------------------------|-----------------|-------------------------------|
| | Cations | | | | Anions | | |
| | Ca ⁺⁺ | Mg ⁺⁺ | Na ⁺ | K ⁺ | HCO ₃ ⁻ | Cl ⁻ | So ₄ ⁻⁻ |
| EC Lab., 2003 | 500 | 1304 | 9898 | 391 | 167 | 21,313 | 2715 |
| Hopkins, 2001 | 412 | 1290 | 10,770 | 399 | 140 | 19,354 | 2649 |
| Brewer, 1975 | 412 | 1290 | 10,770 | 380 | 142 | 18,800 | 2712 |
| Riley, 1971 | 413 | 1296 | 10,800 | 407 | 137 | 19,010 | 2717 |
| Turekian, 1968 | 411 | 1290 | 10,800 | 392 | 142 | 19,400 | 2709 |
| Mason, 1966 | 400 | 1272 | 10,556 | 380 | 140 | 19,980 | 2649 |

Discussion

It is well known that without specifying the environmental and deterioration factors affecting archaeological buildings, most of them will evanesce and perish, causing the loss of important historical data. According to Crisci et al. [44], coastal zones and marine environments significantly impact the deterioration of stone and archaeological buildings, as marine waters and aerosols contribute to deterioration cycles through three main mechanisms dependent on different climatic variables, such as AT, RH, RW, and WE. [45]. In addition, the

effects of underground water, sea levels rise, air pollution, and tides [46] lead to physical, chemical, and biological deterioration mechanisms [47]. From a specialized point of view, it could be claimed that the archaeological buildings in the study area are the most vulnerable to the dominating climate changes [48, 49].

XRD analysis and lithotype and petrographic characteristics

Based on the XRD data, Fig. 3a, b, and petrographic investigation, it could be noted that the essential building

Table 4 AAS average (%) of the analytical results of seawater around Qait Bey Fortress

| Elements | | Analytical results | | |
|----------|--------------------------------|--------------------|------------------|----------------------------|
| | | % | Other properties | |
| Cations | Ca ⁺⁺ | 4.135 | TDS | 35,840 mg/l |
| | Mg ⁺⁺ | 10.78 | PH | 7.87 |
| | Na ⁺ | 81.85 | Alkalinity | 135 mg/l |
| | K ⁺ | 3.233 | Hardness | 6618 mg/l |
| Anions | HCO ₃ ⁻⁻ | 0.690 | EC | 2.8 × 10 ⁻² mho |
| | Cl ⁻ | 88.09 | | |
| | SO ₄ ⁻⁻ | 11.22 | | |

Table 5 AAS average of the analytical results of surfaces salt crusts from Qait Bey Fortress's wall

| Analytical results | | | | | |
|--------------------|--------|-------|--------------------------------|--------|-------|
| Cations | mg/kg | % | Anions | mg/kg | % |
| Ca ⁺⁺ | 9821 | 20.34 | HCO ₃ ⁻⁻ | 2516 | 02.02 |
| Mg ⁺⁺ | 226 | 0.468 | Cl ⁻ | 45,429 | 36.49 |
| Na ⁺ | 37,616 | 77.90 | SO ₄ ⁻⁻ | 76,557 | 61.49 |
| K ⁺ | 625 | 1.294 | | | |

materials are divided into two types. The 1st type used in the fortress bedrock (*Oolitic limestone*) is composed of biosparite limestone. It is a type of **calcite** (CaCO₃) characterized by light beige-grey sandy friable textural characterized and loose features (*very low degree of*

coherence). It contains biosparite and foraminiferal grainstone that consists mainly of sub-angular to sub-rounded calcareous grains, with about 0.3 mm with no cement materials except some points with *meniscus cement* [50], created through the precipitation of aragonite or calcite cement as meniscus-shaped discs at grain. The 2nd type of stone (*Sandy dolostone*) used in the fortress foundation is fine grains of **quartz** (SiO₂) cemented by dolomitic cement. According to [52], it is characterized by yellowish to brownish colors and the presence of (30–70% Ca content) and (60–70 to 20–30% Qz content measured at 60–120 μm). Furthermore, XRD data of the investigated samples, Fig. 3a, b, showed some minor minerals, such as halite, sylvite, and gypsum. They are essential minerals resulting from salt crystallization mechanisms affecting the main building materials. According to some authors [51, 52], **halite** (NaCl) is quite common in coastal environments and abundant in Egyptian soil. It belongs to chlorides and is a main component in the investigated samples. It is considered an important destructive agent of fortress walls due to its high solubility index and good ability to penetrate the porous network of the wall components, Fig. 5a. It produces disruptive pressure forces that lead to micro-cracks after a crystallizing process [53, 54]. On the other hand, it could be claimed that halite, as a prevalent component of the white stain with minor amounts of other salts in semi-deteriorated samples collected from some affected areas, is due to the chemical reaction between seawater and marine aerosol with the fortress main building material [55]. These stains sometimes disappear and reappear after heavy and prolonged

Table 6 Microbiological species affecting Qait Bey Fortress's wal

| Genera and species | | | | | | |
|--------------------|----------------------------|--------|------------------|------------------------------|---------------|----|
| Fungal genera | Fungal species | Counts | Bacterial genera | Bacterial species | Counts | |
| Aspergillus | <i>flavus</i> | 90 | Bacillus | <i>cereus</i> | 100 | |
| | <i>fumigatus</i> | 50 | | <i>brevis</i> | 100 | |
| | <i>niger</i> | 100 | | <i>macerans</i> | 30 | |
| | <i>phoenicis</i> | 60 | | <i>licheniformis</i> | 25 | |
| | <i>heteromorphous</i> | 50 | | Micrococcus | <i>luteus</i> | 60 |
| | <i>awamori</i> | 20 | | | <i>roseus</i> | 50 |
| Penicillium | <i>chrysogenum</i> | 20 | Pseudomonas | <i>aeurginosa</i> | 15 | |
| | <i>corylophyllium</i> | 5 | Thiobacillus | <i>thiooxidans</i> | 5 | |
| | <i>citrinum</i> | 15 | | <i>thioparus</i> | 8 | |
| Others | <i>Trichoderma viride</i> | 10 | Others | <i>Staphylococcus aureus</i> | 50 | |
| | <i>Rhizopus stolonifer</i> | 35 | | <i>Streptomyces</i> | 10 | |
| | <i>Cladosporium</i> | 5 | | <i>E. coli</i> | 30 | |
| | <i>C. cladosporioides</i> | 5 | | | | |
| | <i>Ulocladium</i> | 20 | | | | |
| | <i>A. Alternata</i> | 5 | | | | |

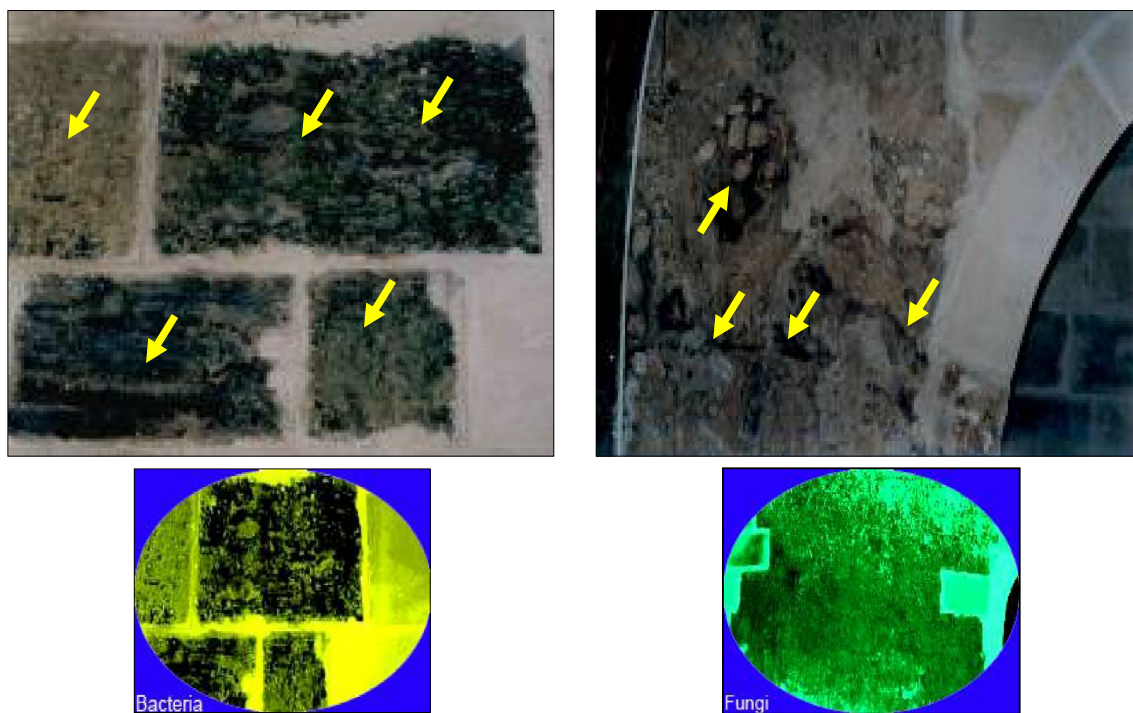


Fig. 6 Shows the effects of some species of *bacteria* and *fungi* on the northern wall of the fortress

rain due to the high index of water solubility of the salts present in the efflorescence [56], in addition to a typical sub-fluorescence with other serious damaging effects, which causes the cracking and detachment of mortar layers due to the alternative crystallization and hydration cycles and their generated pressures [57]. In the same context, **gypsum** [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] salty crusts were created by the high level of sulfur agents dominated in the study area as a pollutant, especially with changes in dry/wet cycles [58]. Its formation may be attributed to the combined action of particulate matter deposition and sulfation process or the significant influence of fungal growth in converting metal sulfide particulate matter to sulfate [59]. This effect can be attributed to sulfur-oxidizing bacteria that convert limestone into gypsum, especially in sulfur-polluted environments [60, 61]. Moreover, detecting gypsum in highly-deteriorated samples is mostly related to complex deterioration mechanisms resulting from the combination between the dominating sources of salts (sulfate-contaminated materials) and some microorganism enzymes dominating the study area [62]. This mechanism is exhausted after some wetting–drying cycles of rainy and sunny days. Finally, these salts and their related mechanisms, especially those resulting from repeated wetting and drying phases, can be greatly amplified or reduced and lead to severe dramatic effects [63], such as volume expansion [64], stone crumbling [65], and

stone bursting [66] depending on several variables, especially hydration action, absorption the dominating rates of ATm RH [51], and other ranges of environmental fluctuations. These fluctuations can activate damage related to several factors (amount of salt undergoing transitions and frequency of environmental fluctuations). **Sylvite** (KCl) is one of the most common components of marine K-Mg salts [67, 68]. It belongs to the halides group, with halite as an essential mineral ingredient of evaporated sediments (salt deposits) [69]. In our case, it is mostly observed when humidity is over 50% RH and leads to conversion reaction accompanied by volume loss to the stone mineral due to dissolution and recrystallization processes [70]. On the other hand, the observed trace minerals contain anhydrite, margarite, periclase, and k-feldspar attributed to the mortar sand [71]. **Anhydrite** (CaSO_4) forms mostly in the presence of acid sulfide, water, and calcium ions [72]. It is an anhydrous calcium sulfate-often component of saline evaporite deposits, which mostly results from dehydrated gypsum and vice versa depending on the temperature and humidity of the air [73]. This reaction is accelerated by other salts, such as halite and sylvite [74]. In our case, it is considered a common feature affecting carbonated rocks due to water evaporation, particularly with continuous alternative wetting and drying cycles [75]. It mostly occurs because of mixing acid-sulfate water with neutral

chlorides, especially in areas rich in calcium, similar to the area under the study [76]. **Margarite** ($\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$) occurs commonly as an alteration product of some aluminous minerals that exist with feldspars in archaeological mortars containing brick fragments [77] or the combined effects between air pollution and dominating humid agents [78]. In our case, it is largely formed by means of local ion-exchange reactions between the Al-rich precursor and Ca-rich fluids (seawater), as Al-silicates and chloritoid have high Al/Si ratios similar to those of margarite that may facilitate the margaritization of these minerals, as attested by [79]. **Periclase** is a cubic form of magnesium oxide (MgO). In our case, it is attributed, on the one hand, to its usage as a constituent of building materials, particularly those composed of dolomitic limes [80], or using the portland cement in recent conservation works [81], especially with the effect of speed hydration process of the cement paste [82] characterizing the study area. On the other hand, it may be due to ion exchange by the source of magnesium in seawater with calcium hydroxide [83]. **K-feldspar**, or orthoclase (KAlSi_3O_8), a monoclinic type of potassium feldspar, is a common constituent of some felsic igneous rocks. In our case, it may be attributed to the equilibrium reaction between silicate fragments in mortar and seawater at low temperatures with the presence of marine micro-organisms [84]. Regarding the XRD data of **mortar samples**, Fig. 3c, it could be asserted that it is essentially composed of calcite, halite, gypsum, and aragonite (*the main components of Islamic mortars*) known by **Kosromil**, which is composed of lime with pozzolanic additives [85, 86]. In our case, the main reason for mortar desegregation is the effect of efflorescence processes [87] and alternative crystallization/hydration processes of salts, especially chlorides and sulfates [57]. Furthermore, our results showed that this mortar is desegregated due to lime leaching between the stone courses. This mechanism is attributed to the effect of seawater, marine aerosol, or dominated seepage and leakage water that contains some corrosive agents [88–90], in addition to the direct effects of dominated AT and RH [91]. It was proven that it is difficult to separate specific mechanisms of salt deterioration on the effects of AT and RH [92], in addition to the evaporation cycle [93]. Some aggressive deterioration features result from using new materials during various preservation interventions (2000–2002), and bio-colonization and their enzymes, especially in rough surfaces in the presence of cavities [94]. All of these factors are critical for moisture retention in outdoors or open environments [95], especially between stone courses due to the pulverization of mortars to create hollow areas and loss of adhesion among the building elements that finally lead the mortar to be detached [96].

SEM investigation results

SEM photomicrographs, Fig. 5a, b asserted that the studied samples were exposed to aggressive deterioration factors due to many severe mechanisms that created **eroded ages** of calcite platy crystals and the above-mentioned salt crystals. Some **aggressive complex layers** consist of a mixture of proton and organic materials resulting essentially from the combination between evaporated salts and organic materials, characterizing the Mediterranean basin exposed to salt water and salt spray, especially in its more arid parts [97]. These layers reacted with stone surfaces through interferences between the minerals in seawater [98], saline aerosols [99], or crusts of the stone surface itself. This process caused new deteriorated layers, consisting mainly of some new salt species [52, 100]. Furthermore, **abrasion and attrition** from affected stone surfaces, Fig. 5c, were attributed to the direct effects of *hydraulic or water wave action* due to the rush of sea waves (*powerful waves*) into the cracks of the rock, causing mechanical weathering. The air layer traps at the bottom of the crack, compressing it and weakening the rock when the wave retreats. This trapped air is suddenly released with explosive force, cracking away the fragments at the rock face, growing the micro-cracks, and deepening the crack [101]. Also, it could be asserted that this mechanical action led to loose internal stone cohesion and corroded stone grains [102, 103], leaching processes [104, 105], and decreasing the mechanical strength of the stone, particularly with increasing exposure [106]. Figure 5d shows the presence of honeycomb as one of the most severe, common, and cavernous weathering forms [107]. This form is a serious symptom affecting calcareous materials in foggy and humid environments [108, 109]. In our case, this symptom was attributed to the combined effects between relative humidity and salt crystallization as the main reasons [110]. In addition, the effects of wind erosion [111], temperature variations [112], and freeze/thaw actions [113] are the role of intrinsic factors, especially petrographic features and petrophysical characteristics [111, 114]. Finally, seawater mechanical actions cause an indirect effect as physical damage in the deterioration processes that generally undergo a cycle of the soil aggradation (beaches) under the building. This mechanism occurs through erosion actions (*sedimentation cycles*) by sea waves under stable structure (*northern wall of the fortress*) [115]. The differences of these cycles up and down lead to net sediment loss, eroding *the wall* therein/thereon [116], then, creating rough surfaces.

Atomic absorption spectroscopy (AAS) results

AAS analytical data presented in Table 3 clarified that there is a good balance in the qualitative and quantitative

ratios of chemical components of seawater samples both in the study area [117] and other samples studied by many authors [118–121] in similar cases. These data showed that different salty crusts were composed according to the occurrence of the main ions dominating the analyzed water. These salty crusts contained 73.86% (NaCl), 10.78% (MgCl₂), and 7.19% (Na₂SO₄). In addition, some minor salts were rated 7.37% and composed of (Ca₂HCO₃), (Ca Cl₂), and (K₂SO₄). It could be asserted that the grains of calcite samples, Fig. 5c,d, were affected through a dissolution process enhanced under saline conditions, as could be noticed in Tables 4, 5 and Fig. 7. These features suggested that the salty etching components observed in some calcite grains could be due to salt loading from seawater and marine aerosol [54]. Furthermore, it could be concluded that the chemical, mechanical, and biological effects of seawater and marine aerosol cause complicated chemical reactions between their different sources of salts and the constituents of monumental buildings. These reactions may lead to the disintegration of the building material constructions, which can further lead to the weakness of the mechanical properties of these materials.

Microbiological investigation results

The extreme environment of rocks has long been thought to have limited microbial diversity, as the isolation and characterization of bacteria and fungi give an insight into Qait Bey's rocks. Microorganisms play an important role in mineral transformation in the natural environment, especially in the formation of soils from rocks and element cycling [122]. Many studies investigated the variety and distribution of microbial communities found on ancient stone monuments with no conclusive results [123, 124]. Based on Fig. 2f and SEM, Fig. 5a, microbial symptoms affected most of the northern wall of the fortress in numerous tightly adjoining pits of several centimeters [125–127] in similar cases. Table 2 shows that the microbes isolated from deteriorated and moistened

walls of the fortress contain some dominant fungal and bacterial species. On the one hand, bacterial species created some colors on the walls of the fortress, attributed essentially to differentiating degrees in *Pseudomonas* species, mainly *P. aeruginosa* (yellow to bluish green) and *P. clacis* (granular appearance having brownish ting in the center). It is also possible that this coloration resulted from the secretion of the metabolic product called pyocyanin of the *Pseudomonas* species. Pyocyanin is a blue-green phenazine pigment produced in large quantities by active cultures of *Pseudomonas* species [128]. Moreover, *Pseudomonas aeruginosa* is considered one of the most beneficial organisms responsible for producing soluble pigments, such as pyocyanin (blue), pyoverdine (yellow-green), pyorubin (red), and pyomelanin (brown) [129]. Those colors on the stone surface might result from the secretion of some isolated genus related to *Bacillus* species. The natural pigmentation of the *Bacillus* genus sporulating colonies is, therefore, brown. Still, other colors have been documented in spores, e.g., a red-pigmented *Bacillus megaterium*, a pink pigment in some isolates of *Bacillus firmus*, and red- and grey-pigmented *Bacillus atrophaeus* [130]. Some fungal species belonging to the most common fungi genus growing on limestone surfaces [131] were obtained: *Aspergillus* sp. and *Penicillium* sp. They led to different fissures, holes, and cavities through both pore structure and grain bodies. The pores offer a suitable advantage for fungal hyphae penetration, while providing a more hospitable microhabitat depending on the substrate's configuration, chemical composition, and state of conservation [132]. In the same context, the development of metabolites, which react with stone to form secondary minerals, is a part of biogeochemical processes through producing organic acids, such as e.i. oxalic, citric, acetic, formic, gluconic, and fumaric) by fungi [133]. In addition, their products from volatile organic compounds and pigments affected the stone surfaces of the fortress, which is considered a good indicator of biological growth in monumental buildings [134]. Based on our previous studies achieved in 2004 [30], it could be asserted that colored crusts affected the surface walls attributed to fungi species are (black) resulting from the effect of dematiaceous (black) fungi, combined for their capability of forming dark pigments and resulting from the growth of fungi, such as *A. niger*, *A. phoenicis*, *Cladosporium cladosporioides*, and *Alternaria alternata*. This finding agrees with the results of the authors [135–138]. Green and yellow pigments may be referred to as the growth of green-colored fungi, including *A. chevalieri*, *A. flavor-furcatis*, and *Trichoderma viride*, rather than algal and lichens growth, which agrees with [139]. Other pigments may be due to the growth of pigmented fungi or acid-producing fungi,

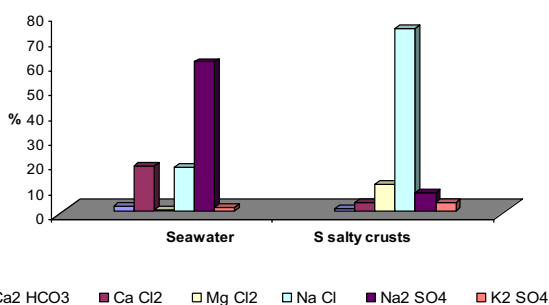


Fig. 7 Shows the qualitative and quantitative ratios of seawater and surface salt crusts that affected the fortress wall

including *Penicillium* species and *Trichothecium roseum*; they can cause a biodeterioration process [140], especially through their high ability for acid production [141].

Conclusion

The ancient maritime archaeological buildings mostly face severe deterioration mechanisms and their resulting forms. The present paper evaluates *physio-weathering*, *chemo-weathering*, and *bio-weathering* mechanisms, working simultaneously to deteriorate the Qait Bey fortress in Alexandria through synergistic marine effects. The fortress has been highly affected by severe alteration manifestations due to previous deterioration mechanisms, and their intensity rates have been enhanced by some helping variables, including salt types, evaporation rate, dominated AT and RH, pH, and some aggressive anions types. The mineralogical analytical results proved the presence of different deterioration products, such as salty crusts (*gypsum and halite as efflorescence layers*), accumulate on the fortress stone surfaces. The morphological features of the investigated samples show some deterioration features, such as calcium crystals mixed with the present salts, honeycomb or splash as privet-deterioration symptoms, and deterioration of calcite crystals in the disintegration of mortars. In addition, AAS results proved that there are notable agreements between the components of seawater and salty crusts affecting the fortress building materials. Furthermore, microbiological investigation proved that a total of 11 bacterial isolates and 12 fungal isolates were reported. Based on the above results, some scientific suggestions are summarized through *interventive conservation procedures* that include three steps. The 1st procedure is fundamental for the mechanical and chemical removal of salt species using desalination processes. These processes could be achieved through poultices by applying wet natural absorbing substances, such as sepiolite, attapulgit, and Japanese paper sheets. On the other hand, desalination by electro-osmosis is based on applying an electric current to porous building materials containing salt species. Finally, the surface is washed using direct water. The 2nd one implies strengthening the void stone blocks by applying pressurized grouting depending on natural grout materials called “masonry-friendly grouts” to avoid the central dilemma related to the influence of chemical substances in cement and similar chemical materials. Then, the missing zones are replaced by stone blocks after curving and cutting or through natural patching mortars or stony pasts. The 3rd procedure relates to final maintenance by applying some water repellants based on colorless treatment materials that mostly apply directly after the cleaning steps. In addition, *preventive conservation procedures* utilize environmental control, which

may be achieved through partial control. Total environmental control is still a relatively difficult task for outdoor immovable cultural heritage and monumental sites.

Acknowledgements

The author is indebted to Prof. Dr. Adel Akarish (National Research Center, Egypt) for supplying the petrographic data of the investigated stones samples.

Author contributions

All data, construction, design and analyses are presented in this study had been achieved by the author, analysed the results, and wrote the paper. All authors read and approved the final manuscript.

Funding

Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB). The author confirms that no funding was presented to this manuscript.

Availability of data and materials

The datasets used and/or analyzed during the present study may be made available from the authors on reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

Received: 16 April 2023 Accepted: 26 May 2023

Published online: 08 June 2023

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