

# INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE



Volume 16, Issue 2, 2025: 855-870

DOI: 10. 36868/IJCS.2025.02.07

# BIODEGRADATION AND WEATHERING OF MERIT-AMUN STATUE INDUCED BY INSECTS AND ENVIRONMENTAL FACTORS

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#### Abstract

The Egyptian queen Merit-Amun is well known for her beautiful limestone statue, which was discovered lying face-down in 1981 within the temple complex dedicated to her father (Rameses II), in Akhmim, Upper Egypt. This statue is regarded as the tallest representation of an ancient Egyptian queen. The primary objective of this study is to evaluate the degradation processes of the statue caused by certain insects including Hymenopter, Oriental hornets and Mud-daubers, which can be related to the environment and its changes over time. Furthermore, effects of other deterioration dominated in the study area, particularly groundwater. Some samples (stone, deteriorated surfaces and nests) were collected from varies locations on the statue to study the forms of deterioration. Light digital microscope (LDM), polarizing microscope (PM), scanning electronic microscopy equipped with EDX unit (SEM-EDX) and X-Ray diffraction (XRD) were applied to analyze the composition of the stone substrate, the composition and microstructure of deteriorated products. Fourier transform infrared spectroscopy (FTIR) was used to evaluate the nests of dominated insects, furthermore, Atomic absorption spectroscopy (AAS) and ion selective electrode (ISE) were used to study the chemical components of groundwater samples and the microbiological study. The results revealed that the statue was carved from very fine-grained limestone (micrite) and it was seriously affected by on one hand, bad environmental factors while buried underground, due to the relatively moist soil conditions. On the other hand, effects of saline water, bio-deterioration, insect damage and abrupt fluctuations in temperature and humidity after excavation. All of these factors led to micro-dissolution processes and subsequent calcite recrystallization, especially in the presence of other salt minerals (mainly sulfates) and iron ions. which increased the dissolution rate. This may eventually compromise the stone's durability, creating voids and hairline cracks and resulting in surfaces that are more susceptible to water absorption.

Keywords: Limestone; Merit-Amun statue; Dorsal pillar; Insects; Biodegradation; Hymenopter; Oriental hornets; Analyses

#### Introduction

A sculpture is characterized by its permanence as a work of art. In order to achieve this objective, statues were preferably constructed using stone or other resilient materials, such as hardwood or metal [1, 2]. Many sculptures are susceptible to erosion when exposed to the weather or when buried. As degradation occurs for different reasons, the factors contributing to the degradation of exposed standing stones are distinct from those affecting buried and excavated stones [3]. The Egyptian Queen Merit-Amun is well known for her beautiful limestone statue, the tallest statue of an ancient queen and one of the most beautiful statues from ancient Egypt [4]. Since its discovery in 1981, it is often referred to as the bride by the people of Akhmim in Sohag

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since her charm and Pharaonic beauty radiate around the city. The statue, approximately 11.5 meters high, was crafted from limestone and underwent restoration (Fig.1).



Fig. 1. Deterioration patterns affected the dorsal pillar and the back of the statue; a., e. & f. cavities and digging of insects, b. crusting and salt efflorescence, c. soiling and biological colonization, d. roughening and erosion of the stone, e. salts efflorescence and dust accumulation on the stone surface, f. swab from inside of the cavities, g. powdering and flaking of the stone surface, h. & i. dissolution of the stone surface and bio-pitting.

The statue is excellently preserved, with the facial features retaining their original paintwork, particularly the red pigments of the lips, the holes for the nostrils and the girdle around the waist. The dorsal pillar bears a double column of inscriptions containing the queen's name, her titles and a tribute to her beauty. Furthermore, an inscription on the base praised Merit-Amun describing her as "fair of face, beautiful in the palace, the beloved of the Lord of Two Lands, much like her mother" [5]. An in-situ visual investigation of the temple of King Ramses II and his daughter Merit-Amun in Akhmim was conducted to assess the overall condition of the statue. The prominent weathering indices were identified, documented through photography and categorized through macroscopic examination. The visible patterns of degradation present on the statue's body are due to disintegration and dissolution of the stone surfaces.

These include roughening, powdering, erosion of the stone surfaces and bio-pitting which are primarily concentrated on the statue's back and the dorsal pillar. Cavities caused by insect activity, growth of microorganisms, salt efflorescence and dust accumulation on the stone's surface were also observed (Fig. 1). Therefore, this study aims to investigate the major forms of deterioration of the statue, specifically focusing on disintegration, dissolution of the stone surfaces, as well as cavities and holes used by insects (bees or wasps) for nesting, particularly in the dorsal pillar and the back of the statue.

The statue displayed cavities and holes that penetrated the stone, serving as nesting sites for insects, such as bees or wasps. These cavities were primarily located in the posterior section and the dorsal pillar, varying in size from millimeters to centimeters (Fig. 2a and b). According to Vergès-Belmin, these cavities (perforations) could be defined, as a single or multiple surface punctures, holes or gaps created by animals under specific circumstances, like wasps on very soft stones (diameter: c. 5mm). These perforations are deeper than they are wide, extending into the body of the stone (Fig. 2c). The mason bee (Hymenoptera) is known to bore into stone to build its nest and remove clay ground material from them [6]. The primary species that affected the statue are Hymenopters, Oriental hornets and Mud-dauber "Sphecidae".



Fig. 2. Some cavities and holes in the statue's back and the dorsal pillar, which the insects (*wasps and bees*) used as nests, where the nests sample were collected

*Hymenopter* is a very diverse group. Certain species of social Hymenoptera, namely bees, ants and wasps, are widely recognized by the general populace. The aculeata, a sub-division of the Hymenoptera known as the apocrite or "waisted" Hymenoptera, includes bees, wasps, ants and solitary wasps. These species are together referred to as the stinging Hymenoptera. It can be found in a wide range of terrestrial habitats across the globe, spanning from arid deserts to swamps and from subarctic tundra to tropical rainforests. The majority of Hymenopterans are insects of small to medium size, possessing mouth-parts that are adapted for chewing or a combination of chewing and lapping. They often have slender antennae that exhibit a noticeable bend, elongated wings with a simple venation pattern and an ovipositor commonly extended to function as a sting, saw or drill [7].

Most adult Hymenoptera depend on the consumption of carbohydrates for their sustenance, obtaining nourishment from sources, such as honeydew, nectar and various plant secretions. The host habitat location is determined by the parasitoid's response to many environmental conditions, including temperature, shade, humidity and the overall vegetation type [8]. Through field inspection, the researchers identified two Hymenoptera insects that use these holes and cavities as nests (Vespa orientalis - Sphecidae). A brief review of these species is presented in the following sections. *Oriental hornets* are a *Vespinae subfamily* known as hornets. They are a species known for their digging behavior. It is a widespread species distributed across several regions of the globe and belong to insects known for their stinging capabilities. They predominantly construct their nests in subterranean crevices and cavities, forming yearly colonies that consist of a queen and a multitude of workers [9].

Some authors studied the nesting biology of *V. orientalis* in Egypt [10]. The hornet activity is very low in winter, spring and early summer. The abundance gradually increases, peaking in autumn, particularly in October, followed by a decrease in November and a complete absence in

December. The optimal temperature for the nesting environment is typically observed to be 29 °C [11]. In Egypt, nests are usually underground or in a space in a rock or wall 30-270 cm above the ground [12]. *Mud-dauber* or Sphecidae (mud-dauber and thread-waisted wasps) are a large family of solitary (usually) hunting wasps, which may be of different shapes, sizes and colors. The organisms in question are classified within the superfamily Apoidea, which falls under the taxonomic order Hymenoptera [13]. The family has three subfamilies: *Sphecinae*, *Ammophilinae* and *Sceliphrinae* [14]. The *Sphecid* wasps found in Egypt and the Sinai region have garnered significant scholarly interest since the publication of Spinola's 1839 study *N. Gadallah* [15] provided a review and simplified key for the 60 genera of the family *Sphecidae* present in the Egyptian fauna.

Roche pointed out that two Egyptian species of the genus *Chalybion* are metallic blue. This genus exhibits a wide distribution, with its constituent species displaying a nesting behavior characterized by the utilization of pre-existing cavities in walls, holes in wood or abandoned mud nests of *Sceliphron*. Moreover, some members of the *Sphecinae* genus nest in cracks in stone walls and the ground, providing their nests with orthoptera. In the same context, *S. Yuksel and Ö. Eroğlu* [16] reported that the leg structures in most species of this family are highly adapted to excavation. Bees in this group are also called digger bees because most species dig holes in the ground, but some nest in pre-existing cavities, whereas others construct mud nests [17]. However, some species nest between the stones or create tunnels in the mortar of exterior walls, particularly in cases where the mortar is old and friable or very sandy [10, 18]. Active diggers usually prefer friable or sandy soil and some excavate tunnels in old mortars by their front legs [19].

#### Materials and methods

#### Materials

Nine samples were collected as follows: six limestone (LM) fragments from the different parts of the statue (Fig. 1) and three nest samples from cavities and affected areas in the back of the statue by swabs (Fig. 2). Furthermore, a water sample was collected from an ancient well at the temple.

#### Methods

Instrumental analysis is crucial for understanding cultural heritage items and advancing knowledge about their changes and degradation over time [20]. The use of multiple analytical methodologies is essential. This study employed various analytical tools to investigate both intrinsic and external factors influencing the statue, aiming to define its deterioration mechanisms and forms of damage.

#### Light digital microscope (LDM)

A 1000X USB handheld digital electronic microscope (*LDM*) was used to study the stone surface and evaluate notable changes in its original appearance, following the methodology described by *M. El-Gohary* [21].

Polarized transmitted light microscope (PM)

A Leitz polarized transmitted light microscope (*PM*) equipped with a digital camera at 25x magnification was used at the Central Laboratories Sector of the Egyptian Mineral Resources Authority to identify the stone minerals through petrographic analysis of thin sections, prepared according to Lewis and McConchie [22].

Scanning electronic microscopy equipped with an EDX (SEM-EDX)

A Quanta 250 FEG Scanning electronic microscopy equipped with an energy-dispersive X-ray spectroscopy (SEM-EDX) unit was used to explore the morphological characteristics and elemental distribution of the limestone fragments (SF) and wild nests (WN) samples [22].

X-Ray Diffraction (XRD)

A D8 ADVANCE X-Ray diffractometer (*XRD*) with a Cu k $\alpha$  radiation (wavelength: of 1.5406 Å) operating at 40 kV and 40 mA was used to characterize and evaluate the mineralogical composition and the deterioration state of the statue's components, as well as to identify wasp nests [23].

# Fourier transform infrared spectrophotometer (ATR-FTIR)

A Bruker Alpha fourier transform infrared spectrophotometer (*ATR-FTIR*) was used to investigate the components of the nests (WN) and the acid composition of the wasp silk protein [24]. *Atomic Absorption spectroscopy (AAS) and Ion-Selective Electrode (ISE)* 

Chemical analysis of a water sample from an ancient well at the temple was conducted using Perkin Elmer Analyst 400 atomic absorption spectrometer (AAS) at the Faculty of Science, Sohag University, following the methodology described by Abd-Allah and colab. [25]. Furthermore, Ion-Selective Electrode (ISE) was used to determine the dominant cations and anions in the study sample allowing for a correlation between their chemical components with the deterioration features affecting the statue by defining the soluble salts affecting its condition. To assess the biological factors contributing to the statue's degradation, nine swabs were collected from the statue's surface and insect cavities, following the methodology of Baker & Bennett [26]. These samples were further analyzed using LDM, SEM, XRD and FTIR to determine the role of fungi and bacteria in the statue's deterioration.

## Results

#### LDM optical examinations

The USB LDM results revealed changes in the stone surface appearance and nest features due to various deterioration factors prevalent in the study area (Fig. 3).



Fig. 3. Various deterioration features under LDM optical

#### PM examinations results

Thin sections analysis of the limestone samples confirmed that they were composed of very fine-grained limestone. A significant number of microfossils of different sizes and shapes were scattered in the matrix of the sample. In addition, some pore spaces were detected scattered in the sample (Fig. 4).



Fig. 4. limestone sample under a polarizing microscope, the sample are characterized by very fine-grained (left), occurring of significant number of microfossils scattered in the matrix of the sample (right)

# SEM-EDX data

The data indicated that the samples exhibited deterioration features attributed to dominant factors and their related mechanisms, particularly the effects of insect nests (Table 1 and Fig. 6) The morphological characterization of (SF & WN) was investigated using SEM to deduce the surface topology and fiber distribution.

Investigated LM Samples			Elemental Ratios %										
		Ca	С	0	Si	Na	Cl	S	Fe	Mg	K	Al	Ti
	1	48.3	7.5	38.3	2.0	-	-	4.0	-	-	-	-	-
Semi-deteriorated	2	32.9	8.5	40.4	5.3	-	0.8	6.3	2.3	-	0.7	2.7	-
	3	32.5	10.5	38.4	6.3	-	0.6	4.5	2.8	1.0	1.1	2.5	-
	4	26.9	6.60	41.4	6.7	1.7	1.2	7.3	3.1	1.0	1.4	2.9	-
Highly-deteriorated	5	19.8	6.1	43.8	7.5	2.0	1.6	12	2.3	1	1.6	2.5	-
	6	8.8	23.9	36.1	7.2	0.6	-	0.5	2.3	0.8	1.1	3.6	15.8





**Fig. 5.** SEM photomicrographs of the investigated (SF); a. dissolution and breaking of calcite crystals in, presence of small fissures and cracks, b. detached calcite crystals because of loss in the binding materials between grains by the effect of salts crystallization, c. clay minerals and salts crystals in the stone texture, d. topology and fiber of (WN)

# XRD data

The XRD data of the deterioration state of the statue and the mineralogical compositions of the stones (LF) and wasp nests (WN) samples confirmed that the samples were affected by dominant deterioration effects (Fig. 6).



Fig. 6. XRD patterns of a. LM sample, b. WN

# FTIR data

Detailed FTIR analysis of the samples revealed characteristic bands of the animal silk protein chain, recorded in transmittance mode between 3500 and 500cm<sup>-1</sup>. All recorded data are shown in (Fig. 7).



Fig. 7. FT-IR spectra of silk film of the wasp (WN), two samples

#### AAS & ISE analytical data

Chemical analytical results of the water sample from the ancient well located in the temple, including ion concentrations and suggested main salts, are listed in (Table 2-a). The mass balance of the cations and anion was estimated and it was found that the error percentage (difference between them in equivalent percentage) is 4.49%, which is in the acceptable range. The stoichiometry is re-estimated to determine the most predominant salts in the water samples in the study area. Based on this estimation, the hypothetical salts are estimated as listed in (Table 2-b).

Cation	Eq weight	ррт	Epm	Epm %	Anions	Eq weight	ррт	Epm	Epm%
Ca <sup>2+</sup>	20.04	104.7	5.22	39.57	HCO <sub>3</sub> -	61	325.4	5.3	44.3
Mg <sup>2+</sup>	12.15	42.1	3.46	26.24	SO4 <sup>2-</sup>	48	198.5	4.1	34.3
Na <sup>+</sup>	20.10	101.6	4.42	44.47	Cŀ	35.5	84.3	2.4	19.7
<b>K</b> <sup>+</sup>	39.10	3.7	0.10	0.72	NO <sub>3</sub> -	62	12.2	0.2	1.6
Total	91.39	252.1	13.20	100	Total	212.5	620.4	12.04	100
Error	4.6%								
pН	9.4								
TDS	881ppm								

Table 2a. AAS analytical results of a predominant salts in water sample

Salts	%	Name(s)					
Ca(HCO <sub>3</sub> ) <sub>2</sub>	41.53	Calcum bicarbonate or hydrogencarbonate, Cleansing lime, Bicarbonate of lime or Rain salt					
Mg(HCO <sub>3</sub> ) <sub>2</sub>	4.70	Magnesium bicarbonate or Magnesium hydrogencarbonate					
MgCl <sub>2</sub>	5.77	Magnesium chloride or Magnesium dichloride					
NaCl	26.22	Sodium chloride, Halite, Rock salt or Sea salt					
KCI	7.70	Potassium chloride, Sylvite or Muriate of potash					
Na <sub>2</sub> SO <sub>4</sub>	13.58	Sodium sulfate, Thénardite (anhydrous mineral) or Glauber's salt (decahydrate)					
NaNO <sub>3</sub>	0.50	Sodium nitrate, Peru saltpeter, Soda niter or cubic niter					

Table 2b. Hypothetical salts in water sample

#### Microbiological examination

Microbiological examination identified two fungal species (*Aspergillus niger* and *Rhizopus nigircans*), in addition to one gram-positive bacteria (*Bacillus cereus*). These species played an important and substantial role in all alteration processes affecting the statue through biochemical processes. Moreover, the nests' components collected from inside the cavities were mainly composed of two parts, including silk, soil, straw and plant and insect remains. The beige and white parts included silk. The brown parts included soil. There were insect remains, otherwise inorganic materials, especially soil and plant fibers, which were short and thick woody scrapings. XRD analysis of nests presented calcite (CaCO<sub>3</sub>) and quartz (SiO<sub>2</sub>) as the major minerals, with minor amounts of phosphorus (P). In addition, iron oxide (II & III), halite (NaCl), Fe, K and AL were present in the sample as traces.

#### Discussion

The analytical data provide adequate information to identify the detrimental variables affecting the statute and the consequent types of deterioration. The findings revealed a wide range of degradation features, including disintegration and dissolution of stone surfaces [28], loss of cohesion along grain boundaries [29], salt efflorescence and the development of small fissures and cracks due to the spalling off small surface scales [30]. Furthermore, localized cavities, one of the most significant alteration phenomena caused by lichens [31] and fungi, led to the formation of point-like millimetric or sub-millimetric shallow cavities called biopits [32]. Some areas of the statues were stained with iron oxide deposits, likely due to the deposition of air pollutant particles from combustion reactions [33]. As previously mentioned, the statue exhibited numerous cavities and holes that had been used by insects, such as bees or wasps, as nesting sites. These cavities are mostly concentrated on the back of the statue and the dorsal pillar, with sizes ranging from millimeters to a centimeter's scale (Fig. 5b). According to *V. Vergès-Belmin* [34] these cavities (or perforations) are defined as individual or series of surface punctures, holes or gaps, created by animals under specific circumstances, such as wasps on very soft stones (diameter: more than 10mm).



Fig. 8. different cavities features affected the statue body

These cavities that affect the body of the statue (Fig. 8), are also found at several archaeological sites in Egypt, such as the temples in Edfu, Dandara and Ramses II. In many cases, they were largely concealed by the clay nests of the bees, especially when there was no more available space under the cornices. The bees built their nests in the deep lines of the reliefs and in spaces between the stones as well as in the cracks which happened to exist in these stones [35] Iskander, 1964]. These nests are primarily composed of Calcite, Quartz, Halite, Iron oxide (II, III), Potassium, Phosphorus, Iron and Aluminum, (Fig. 7). A similar phenomenon was observed in some Bronze Age buildings at Akrotiri on the island of Santorini (Thera), where insect colonies invaded and built nests, causing significant damage to the walls, as reported by *P. Mourikis et al.* [36] and *A. Sahab et al.* [37]. Within the same context, *J.-Y. Rasplus et al.* [38] points out that most insects that are present in and around ancient buildings create nests and tunnels in the mortar of outside walls, especially those in which the mortar is old and friable or very sandy.

*LDM* and *PLM* examinations (Figs. 4 & 5), revealed that the rock was composed primarily of calcite, with small amounts of iron oxides and opaque minerals. Calcite occurs as very finegrained (micrite), which is typical of shallow-marine microcrystalline limestone [39], with anhedral crystals representing the sample matrix. Numerous microfossils and fossil fragments were observed within the micritic matrix. *SEM investigation* validated these findings (Fig. 6), revealing various deterioration features, including disintegration of calcite crystals and reduced binding materials between grains, attributed to salt crystallization from saline water and drying cycles caused by rising temperatures [40]. In addition, the decayed samples showed etching features in some calcite grains, indicating micro-dissolution processes (chemical weathering) [41]. Evidence of carbonate cement dissolution and subsequent calcite recrystallization were also observed, due to  $CO_2$  exposure [42].

SEM investigation also revealed significant damage to the calcite grains, including localized cavities, small fissures, cracks and growth of microbial hyphae. *EDX microanalysis* of various samples (Table 1) showed that the main elements present were Ca, O and C, with trace amounts of Si, S, Cl, Na, Mg, Al, K, Fe, Mn, P and Ti. Furthermore, the primary constituent of limestone (Ca), was decreased in all the deteriorated samples, due to the dominated factors of deterioration, where, it recorded (8.8% as a minimum value and 26.9% as a maximum value). Vice versa, the elements that atributed to deterioration products were increased, where, (Si) recorded 2.0% as minimum value a 7.5% as a maximum value, (Na) recorded 0% as minimum value, (S) recorded 0.5% as minimum value a 7.3% as a maximum value, finally, (Fe) recorded 0% as minimum value a 3.1% as a maximum value.

These variations could be due to ion exchange between the main components of stone samples and the salty ions that characterize the groundwater (Na, S and Cl) in the study area [43]. The presence of Fe ions increase the rate of dissolution and might eventually contribute to the degradation of the stone's durability, as voids and hairline cracks develop and create surfaces more susceptible to water absorption [44]. As well as, the problem was more complicated because of the existence of Al, K and Si, which are associated with the high proportions of clay minerals formed during the deposition process. This ultimately led to severe erosion of the material [45].

*Mineralogically*, the mineralogical data by XRD (Fig. 7) indicated the presence of calcite as a major mineral in the samples. Halite, sylvite, nitratite, niter and bischofite, as trace minerals, resulted from a chemical reaction between calcite and different contamination ions that characterize groundwater (e.g.,  $SO_4^{2^2}$ ,  $NO_x^{-}$  and Cl<sup>-</sup>) [46], particularly with alternative cycles between air temperature and different sources of moisture [47]. Moreover, the problem is more complicated due to the existence of pyrite and iron in the samples because the oxidation of pyrite,

in the presence of water and oxygen, producing sulphuric acid and hydrates iron (II) sulphate, which act as an adsorbent for further water from the atmosphere, thereby promoting further oxidation and deterioration [48]. This process increases the rate of the dissolution process, which could lead to the durability of stone materials being degraded and voids and hairline cracks developing, creating more susceptible surfaces to water absorption [41].

*FT-IR measurements* (Fig. 8), it could be noted that the peak at  $1628\text{cm}^{-1}$  could be attributed to Amide I (C — O stretching bonds) region corresponding to  $\beta$ -sheet conformation [49] and the peak at  $1518\text{cm}^{-1}$  could be attributed to Amide II (NH deformation) region corresponding to  $\beta$ -sheet conformation. In the same context, the peaks at  $1232\text{cm}^{-1}$  could be attributed to Amide III (CN stretch, NH bends) region corresponding to  $\beta$ -sheet conformation and  $1234\text{cm}^{-1}$  could be attributed to Amide III (CN stretch, NH bends) region corresponding to  $\beta$ -sheet conformation. Finally, the peak at  $2852\text{cm}^{-1}$  could be attributed to the symmetric C - H stretch of -CH<sub>2</sub> of fatty acids. From this point of view, it could be claimed that the characterization of silk from the Hymenoptera indicated that its amino acid composition differs from that produced by silkworms [50], where the silk produced by larvae of Hymenopteran insects is known to possess a distinct conformation, which sets it apart from the fibrous constructions created by adult spiders and insects, as well as other insect larvae.

Most noteworthy, the secondary structures of silk sample proteins consisted of  $\beta$ -sheet conformations, where the  $\beta$ -sheet abundance in silk is largely responsible for the silk thermal properties [51]. The laboratory analysis resulted in information for each sample. For instance, FT-IR measurements revealed that the band at 1234 and 1232cm<sup>-1</sup> could be attributed to Aspartic and Glutamic acids C-O side chain stretching vibrations (Fig. 6). In this context, *D. Tobler et al.* [52] assertedd that calcite crystals generated in the presence of aspartic acid had rounded edges and rough surfaces, which explains the damaging effect of this acid on calcium carbonate. Finally, very small and low-intensity bands at 2852cm<sup>-1</sup> (sample 1) could be noted due to the effect of the hydrocarbon remnants in the silk protein [51].

The AAS chemical analysis of water sample revealed significant variations in its chemical constituents, primarily due to the multi-synergetic effects of the dominant salts in the study area [43]. As indicated in (Table 2), the water analysis demonstrates adequate accuracy, with a charge balance error percentage of 4.49%. Hypothetical salt combinations were derived based on the interactions between anions and cations, considering their respective ionic strengths. In this context, it should be noted that the analyses are conducted for a single water sample, as no additional points are available. Consequently, a detailed stoichiometric evaluation would not be beneficial; it is included in the article to illustrate the analyzed samples include (Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>) as the major cations and (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) as the major anions.

Thus, it could be argued that rock formations have been altered by synergetic reactions with saline water, leading to the formation of more soluble salts [53]. These reactions ultimately led to the formation of cavities and perforations due to the dissolution and collapse of soluble rock components [54] as well as the degradation of rock surfaces beneath superficial deposits [55]. From a specialized point of view, the primary geochemical processes likely occurred before the statue was excavated, during its burial underground and increased after its discovery due to the effects of alternating wetting and drying cycles [56]. It could be valuable to estimate the mass balance of the geochemical process in the area. However, this will be addressed in future research, as the necessary data for modeling—such as detailed mineralogical and sedimentological analysis, as well as the anthropogenic sources of cations and anions in the groundwater—are currently unavailable.

*Biodeterioration* refers to the process of degradation that occurs after the initial deterioration caused by inorganic agents. The discernible impacts of biodeterioration can be observed at the initial stages of stone exposure [57]. This process includes different effects of animals, higher plants, insects and microorganisms. From a specialized point of view, it could be asserted that the major effects dominating this study are insects and some species of microorganisms. However, it could not be asserted if insects, whether wasps or bees are the main reason for digging these cavities or if their role is limited to using them as nests. Through field observation it was possible to identify the negative effects of holes and cavities [58] in the statue's back and the dorsal pillar occupied by *Vespa orientalis - Sphecidae*. These effects could be summarized in the following points:

- a) Mechanical damage caused by abrasion and scraping through the movement of the wasps inside the nest, as well as their fanning and digging activities.
- **b)** raising the level of salts and moisture in the stone due to the wasps' daily activities where the relative humidity is more than 90% in the wasps' nests, causing the increasing rate of chemical and physical deterioration [46].
- c) creating a suitable environment for microbiological growth through the presence of excrement and insect remains, the various secretions of wasps and the high moisture content [59], in addition to the darkness that encourages the growth of microorganisms.
- d) Infected wasp nests with various molds and fungus once the adult population disappeared as reported by *Z. Joseph and J. Ishay* [25].

Our investigation also revealed two fungi and one bacterium isolated from affected samples (i.e., *Aspergillus niger, Rhizopus nigircans & Bacillus sp*), in addition to one grampositive bacteria (*Bacillus cereus*). These genres are commonly found on stone monuments around the world [60], where they have a significant and integral role in all the processes of modification that take place in the stones. All of these three species affected the body of the statue by feeding on the organic and inorganic residues on the statue's surface or within the nests of bees or wasps, particularly with the presence of sufficient sources of light and water together, as discussed previously by Ortega-Moralesa and colab. [61]. Furthermore, the effects of wetting the statue's surface after the excavation through rainfall encouraged these types to grow in the fissures and cracks, especially in shady or dimly lit parts.

This growth led to the excreting of some acids, especially oxalic and citric, that serve as chelating agents capable of extracting metallic cations, e.g., calcium, iron and magnesium, from the stone's surface. The biophysical degradation of stone can arise from the application of pressure on the adjacent surface material because of the growth or movement of an organism or its components. Moreover, *A. Pinheiro et al.* [62] indicated that *A. niger*, like many rock-dwelling dark-pigmented fungi, can actively penetrate limestone and marble and produce pits of up to 2 cm in diameter on rock surfaces. Within the same context, it could be asserted that the involvement of *Bacillus sp.* in carbonate dissolution played a role in increasing stone porosity and weathering.

Bio-chemically, the statue has been significantly affected by critical bio-chemical processes, due to the presence of enzymes and excrements from insects, which was the main biological factor in the destruction of its structural cohesion. This deterioration process was further enhanced by water penetration more quickly and deeply. Furthermore, it can be argued that the biochemical deterioration' is linked to the presence of moisture and mineral nutrients, in addition to the effects of sunlight in the photo-synthetic process that led to the deposition and enrichment of cellular materials on statue's surface. Within the same context, the statue was affected by another bio-deteriorative mechanism; acidolysis, caused by organic acid excreted by

dominated fungi, algae and lichens as mentioned by several previous studies [63]. This process highlights the role of biochemical reactions, particularly biomineralization, which leads to biocalcification or carbonatogenesis.

This process involves biochemical reactions between dominated ions and compounds in the study area. under optimal conditions, that promote the precipitation of calcium carbonate induced by microorganisms that grow on the insects remains (*food, excretion* and *resulted enzymes*). On the other hand, the statue was affected by specific biochemical reactions resulting from the presence of certain microorganisms prevalent in the area such as *Aspergillums niger*, *Rhizopus nigircans* and *Bacillus cereus*). *Aspergillus*, for example, is one of the most economically important filamentous fungi genera. It is widely distributed and can produce many different kinds of enzymes that affect material substrates [64]. It is considered the easiest and fasten proliferation ability [65]. It has a great ability to solubilize stone and chelate various minerals due to the production of organic acids such as *gluconic*, *citric* and *oxalic* acid. This mechanism was enhanced through physical effects by salty water ingression, solutes and the spread of plants in the study area.

#### Conclusion

In conclusion, it is evident that the statue was significantly impacted by a complex sequence of physical, chemical and biological deterioration processes, both during its burial and after excavation, a phenomenon known as "environmental shock." Current research in archaeological conservation related to such artifacts is primarily concentrated in certain European countries, such as Germany, Italy and Poland, with more recent studies in Egypt. These studies highlight the importance of collaboration between archaeologists and entomologists. Analysis of insect specimens from the statue provided valuable insights into the past environmental conditions of the study area. Three insect species—Hymenoptera, Oriental hornets and Mud-daubers—had significant effects on the statue's deterioration. These species contributed to the statue's biodeterioration through cavity formation, digging, biological colonization and powdering. These changes were primarily driven by biochemical processes influenced by local climatic conditions. Additionally, the statue was affected by organic acids and saline water, with further damage from cavities and holes created by bees and wasps. These factors resulted in etching of calcite grains, micro-dissolution processes and ion exchange within the statue's main components, particularly in the dorsal pillar.

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Received: December 09, 2024 Accepted: May 10, 2025