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Monitoring Coptic Masonry Affected by Clay Minerals and Microorganisms at the Church of Virgin Mary, Wadi El-Natrun (Egypt)

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Abstract: This paper focuses on the role played by the clay minerals and microorganisms in the deterioration process of Coptic architecture units at the church of Virgin Mary, Wadi El-Natrun region. For this purpose building materials (mainly mortars and plasters) from the studied church were examined using X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscope with energy dispersive spectroscopy (SEM-EDS); in order to identify their composition and were investigated petro-graphically to determine the real response of the masonry structure to the deformation imposed at the endogenous factors. Wall gypsum mortars in the church contain halloysite as a dominant clay mineral while plaster is clay free; concerning microorganisms, the fungal flora *Aspergillus glaucus* represent the most dominant fungi constituting (22.22%), *Aspergillus flavus*, *Aspergillus flavus*, *Aspergillus fumigatus*, *Aspergillus occhraceus*, and *Aspergillus caudidus* were also isolated.

Keywords: coptic; masonry; clay minerals; microorganisms; XRD; XRF; Wadi El-Natrun

Citation: Moussa, A.; Roshdy, M. Monitoring Coptic Masonry Affected by Clay Minerals and Microorganisms at the Church of Virgin Mary, Wadi El-Natrun (Egypt). *Heritage* **2021**, *4*, 4056–4067. https://doi.org/10.3390/heritage4040223

Academic Editors: Christofilis Maggidis, Nikolaos Lazaridis, Omar Abdel-Kareem and Robin Skeates

Received: 23 August 2021
Accepted: 26 October 2021
Published: 29 October 2021

1. Introduction

Wadi El Natrun, is a sandy depression located in the western part of the Nile delta, latitude 30°17′ and 30°38′ N, longitude 30°02′ and 30°30′ E. It is directed NW-SE, about 22 m under sea level. In the region many salty alkaline lakes are found half-way between Cairo and Alexandria. Wadi El-Natrun is one of the oldest centers of monastic settlements in Egypt, Figure 1.

Figure 1. A map showing the location of Wadi El-Natrun area (http://www.lib.utexas.edu/maps/, accessed on 18 October 2021).

Deir "Monastery" Al-Surian, where the studied church is located, was called Al-Surian because it was owned by the Syrians. Its real name is Monastery of Saint Mary. It was constructed in the first half of the (1st AD) century in the place of the Monastery of St. John the Short and was listed in the history of monasteries. It was a secondary monastery that emerged as an independent unit in the second half of the 3rd AD century. In (817 AD), the monastery—as well as others—was destroyed, and the Syrian monks rebuilt it. It did not have a wall until the late 9th AD century. The Monastery of Saint Mary (Al-Surian) in Wadi El-Natrun is rectangular and measures 150 m long and 45 m wide, Figure 2.

Figure 2. A general view of Deir "Monastery" Al-Surian, Wadi El-Natrun area.

It is divided into two parts: the western and the eastern part. The western part up to the west of the gate contains palaces. It was built in (850 AD) before the building of the wall. In contrast, the eastern part is the largest and contains the Church of Virgin Mary adjunct to the northern wall, a mill in front of the church, and a garden of palm trees in the east. The church is a rectangular church, where its horizontal projection is a rectangle of 24 m long and 10 m wide from inside. It has two covered roofs: the northern and the southern that was separated when building the wall of the monastery. The eastern part of the church is divided into three altars bordered from the west by the choir across the church. The church also contains porticos: a middle portico, side porticos, and the entrance of the portico. The southern entrance was separated when building the wall. The current northern entrance dates back to (980–1000 AD) Figure 3.

It is a high square building that can be accessed through a path with a high pointed arch in the wall and arched doorstep as well. From the inside, the projection is square. On the western side, there is a door with an arched doorstep and double entrance. Moreover, the eastern wall has a similar entrance to the "Presbyterian Church". The dome of the entrance is pointed and based on a square that became an octagon by four corner squinches, then a circle by eight small Turkish triangles. The middle portico is covered by a 9 m high vault. Although it is one block, it is divided by a 1.25 m high section of buildings. Consequently, the eastern section represents an archway used as a choir. It is known as the Laqan Basin, which is shallow and filled with water on the Maundy Thursday that commemorates the Washing of the Feet (Maundy) of Jesus Christ with the Apostles. To the west of the middle portico, there is a portico with an arch holding half dome based on wooden beams on the western wall. This dome was built of small stones. Side porticos are covered by half-cylindrical vaults of 4.5 m high about half of the middle portico. Their projection is 1.50 m wide. In the eastern ending, the porticos are blocked with no doors to the choir. The eastern archway of each portico is separated by a short section, which completes the section separating the portico that adjoins to the external choir, finally the separated section is covered by a vault. Above the southern portico, there are upper windows with a set of bars that form octagons and small triangles with glass pieces. The choir is covered by an 11 m high dome. The only entrance to the middle portico to the choir is an opening with a semi-circular doorstep. The side columns have a door that dates back to the (10th AD) century. The middle part of the choir facing the middle altar is topped by a pointed dome based on two wide pointed arches. The dome is supported by a half dome on the northern and southern endings of the choir. The middle altar is covered by a high dome of 10 m high based on an octagon. Its ground is higher than the choir by three wide steps. There are two squinches on the northern and southern walls of the middle altar. These two walls have entrances leading to the side altars. Moreover, the doors of the altars are fixed on wooden door jams similar to the doors of the choir. In other words, they are opened from the middle and based from the back on bronze hinges. Each door has three shutters, each of which contains seven panels. The doors date back to the (8th AD) century. The altar is a hollow square of buildings and covered by a square-circular tile (i.e., a side is square and the other is semicircular, unlike the churches of the desert). It is made of marble or a black marble-like stone block. Two entrances in the form of a narrow room that is a bit longer than the middle altar with circular doorsteps lead from the choir to the side altars. This pattern was common in the (9th AD) century. Each room has a small altar and an eastern squinch. Concerning side altars, each side altar is covered by a semi-cylindrical vault that is 4.5 m high, Figure 4, [1–6].

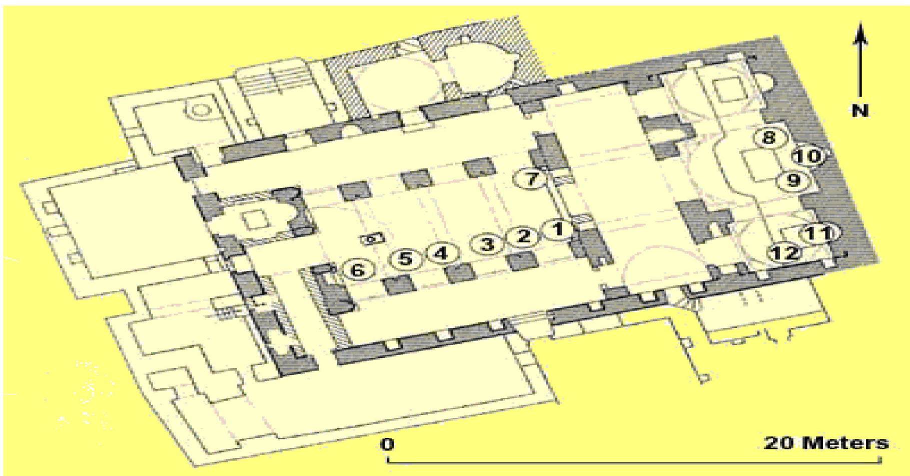


Figure 3. A plan of the Church of the Virgin showing: **1.** Annunciation. **2.** Visitation. **3.** Nativity. **4.** Baptism of Christ. **5.** Tow jars on Table. **6.** Entry to Jerusalem. **7.** Pentecost. **8.** Sacrifice of Isaac. **9.** Meeting of Abraham and Melchizedec. **10.** Christ and the Holly Virgin enthroned. **11.** Saints. **12.** Saints.

Figure 4. (**Left**): The church of the Virgin, Deir al-Surian, Wadi El-Natrun. (**Right**): A 3D model of the church of the Virgin, Deir al-Surian, Wadi El-Natrun.

Atmospheric weathering of quarried aggregates is capable to produce clay minerals; the swelling of clay minerals develops sufficient pressure to break up the building materials [7]. An important role is played by the microscopic fungi in atmosphere-exposed environment. The problem of longevity increase of archaeological buildings can be solved only with deep understanding of the mechanisms of deterioration. As it is known from other inorganic materials (stones, mortars, plasters and pigments) a special attention should be given to interactions of materials with microorganisms and to the processes of their microbial degradation [8]. The current study aims essentially to assess the effect of clay minerals and microorganisms in the deterioration cycle of Coptic architectural units at the Church of Virgin Mary, Wadi El-Natrun, using chemical and physical analyses; this may be very useful in correctly analyzing the development of damage picture. By this way the results of the present study may be extrapolated to be used in similar cases suffering from the same problems.

2. Materials and Methods

X-ray diffraction (XRD) analysis was performed using a Philips (PW1840) diffractometer with Ni-filtered Cu-Kα radiation. The samples were scanned over the 5–70° 2Θ intervals at a scanning speed of 1.2° min^{-1} A° quantitative estimation of the abundance of the mineral phases was derived from the XRD data using the intensity of certain reflections and external standard mixtures of minerals compared to the JCPDS standards of 1967 [9]. The µ-XRF analyses used a diffractometer type: SPECTRO, Model: COPRA "Compact Portable Roentgen Analyzer", potential acceleration: 35 kV, lamp stream: 0.9 mA, analysis time: 300 s. for the SEM-EDS analyses; samples were coated by the JEOL JEE-4X High vacuum evacuator with carbon coating (carbon rods). The SEM is the JEOL JSM-840A, with an EDS analytical attached of OXFORD instruments ISIS, working distance (WD) 20 mm, and current 1 mA, accelerate voltage 20 kV. For the clay mineralogy study, grain size determination of the material and textural classification was performed on each sample following the Folk method [10]. A 20 g split of each sample was subjected to the following chemical treatments [11]: 1 N sodium acetate-acetic acid buffer solution with pH = 5.0 for carbonate removal; 30% H_2O_2, for organic matter and Mn-oxides removal; 0.3 M sodium citrate and 1 M sodium bicarbonate buffer solution with pH = 7.3 to which 1 g increments (up to 3 g) of sodium dithionite were periodically added to remove free Fe-oxides and Fe-Al-hydroxides. Fractions having dimension less than 2 microns were separated into other three different fractions (2–1, 1–0.25 and <0.25 µm) by an international equipment company (IEC) centrifuge. The sample fractions were dried in room temperature. Subsequently, random and oriented mounts were prepared for XRD analysis. All the oriented mounts were reanalyzed after treatment with an ethylene-glycol solution to distinguish the expandable mineral phases. Some were heated for 2 h at 550 °C for chlorite detection [12]. Semi-quantitative estimates of the mineral abundance based on the peak area of the oriented mounts, were made from the XRD data, using the method described in [13]; the study was carried out in the School of Geology, Aristotle University of Thessaloniki, Greece. Concerning the biological study Czapeck's medium [14,15], was used for isolating and growing microorganisms. Three replicate plates were prepared for each sample. After 1 week incubation period at 28 °C, fungal colonies were purified using Martin medium, purified fungal isolates were identified using PDA medium, which was used as a slant stock cultures for fungi according to [15–17]. The study was achieved in the School of Veterinary, Aristotle University of Thessaloniki, Greece.

3. Results

A mortar sample from the western wall inside the church was analyzed using the XRD method. The sample is composed of 51% calcite ($CaCO_3$), 32% gypsum ($CaSO_42H_2O$), 5% anhydrite ($CaSO_4$) and 1% plagioclase (mainly albite), as seen in Figure 5 (left). The same results were emphasized by the SEM-EDS analysis, calcium, sulfur, oxygen and carbon are the main sample components, as shown in Figure 6a. The presence of high amount of gypsum in the sample was also assured by the use of μ-XRF, as seen in Figure 7a.

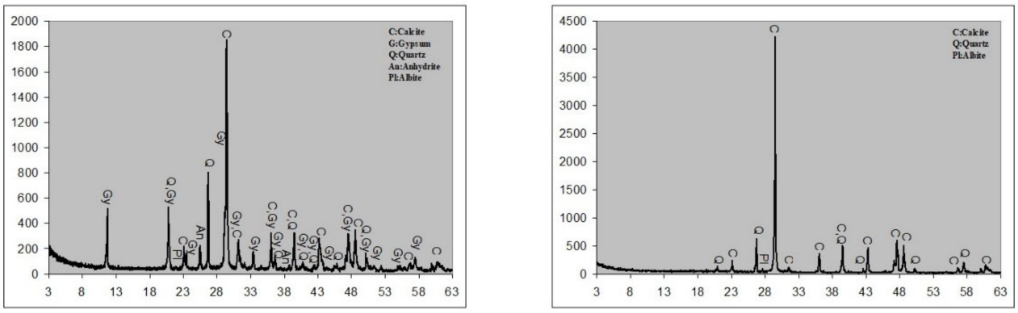


Figure 5. Powder X-ray diffraction patterns from the church of the Virgin showing: (**Left**) The mortar sample which composes mainly of calcite and gypsum. (**Right**) The plaster sample which composes mainly of calcite (*X*-axis = 2Θ, *Y*-axis = Counts).

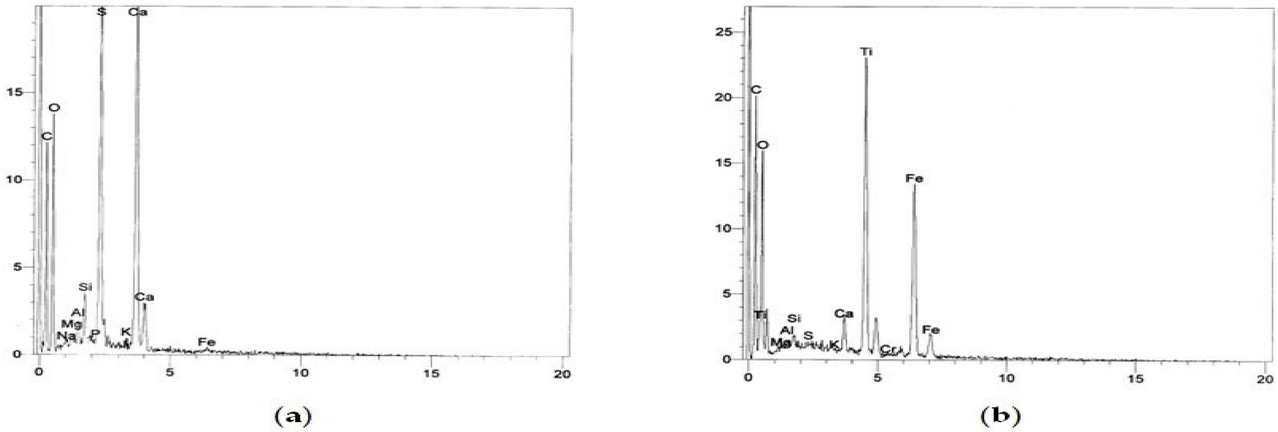
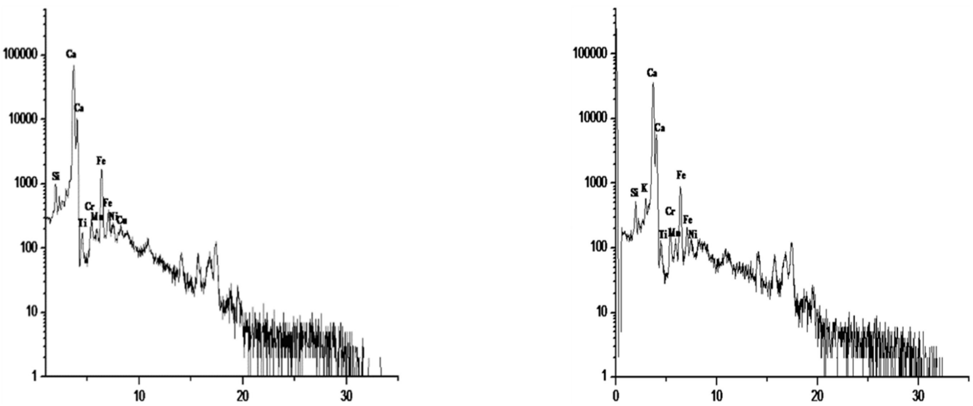


Figure 6. Energy dispersive spectrum from the church of the Virgin showing: (**a**) A mortar sample from the west wall inside the church of the Virgin; (**b**) The plaster sample from the west wall inside the church of the Virgin, (*X*-axis = E/keV, *Y*-axis = Cps.).



(**a**) (**b**)

Figure 7. μ-XRF analysis patterns from the church of the Virgin showing: (**a**) A mortar sample from the west wall inside the church of the Virgin; (**b**) The plaster sample from the west wall inside the church of the Virgin, (*X*-axis = E/keV, *Y*-axis = Imp.).

Concerning plaster, only one sample was available. This sample was taken from the surficial layer in an unpainted part of the western wall inside the church. The plaster layer from which the sample was derived has been added in 1781/2 during a re-plastering process [1–6]. According to the XRD analyses, Figure 5 (right), the plaster is lime plaster, and is composed of 92% calcite ($CaCO_3$), 7% quartz (SiO_2) and 1% plagioclase (mainly albite). By the analyses of both µ-XRF (Figure 6b) and SEM (Figure 7b), the sample is lime, composed basically of calcite and quartz. Tables 1 and 2 highlight the major and minor elements detected in the studied mortar and plaster samples.

Table 1. The chemistry of the studied mortar sample from the church of the Virgin, Wadi El Natrun.

Element %		Atomic %	Compound %	
Na	3.58	3.54	Na_2O	4.83
Mg	5.75	5.37	MgO	9.54
Al	4.17	3.51	Al_2O_3	7.89
Si	21.57	17.44	SiO_2	46.14
S	0.24	0.17	SO_3	0.60
Cl	12.32	7.89		0.00
K	1.07	0.62	K_2O	1.29
Ca	9.40	5.33	CaO	13.15
Fe	3.30	1.34	FeO	4.24
O	38.59	54.78	-	-
Total	100%	100%	-	87.68%

Table 2. The chemistry of the studied plaster sample from the church of the Virgin, Wadi El Natrun.

Element %		Atomic %	Compound %	
Na	39.09	43.51	Na_2O	52.69
Mg	0.06	0.07	MgO	0.10
Al	0.11	0.11	Al_2O_3	0.21
Si	0.26	0.24	SiO_2	0.56
S	−0.06	−0.05	SO_3	−0.14
Cl	45.28	32.68		0.00
K	0.12	0.08	K_2O	0.14
Ca	0.66	0.42	CaO	0.92
Fe	0.18	0.08	FeO	0.23
O	14.29	22.86	-	-
Total	100%	100%	-	54.72%

3.1. Clay Mineralogy

The mortar sample that was taken from the western wall of the church of the Virgin in Wadi El Natrun was treated according to the same methodology mentioned before (materials and methods), the sample, in the oriented phase, was found to contain only a layer of halloysite clay mineral at 11.6 A°, while the peak appears at 21 A° stands for Quartz (SiO_2), Figure 8a. In the glycolated phase the same layer "halloysite" was detected at 11.3 A°, while the peak appears at 21 A° stands for quartz (SiO_2) (Figure 8b). After heating, the halloysite layer disappeared and no other clay minerals were detected in the sample in that phase, while the studied plaster sample did not show any residues of any kind of clay minerals at the three phases (oriented, glycolated, heated).

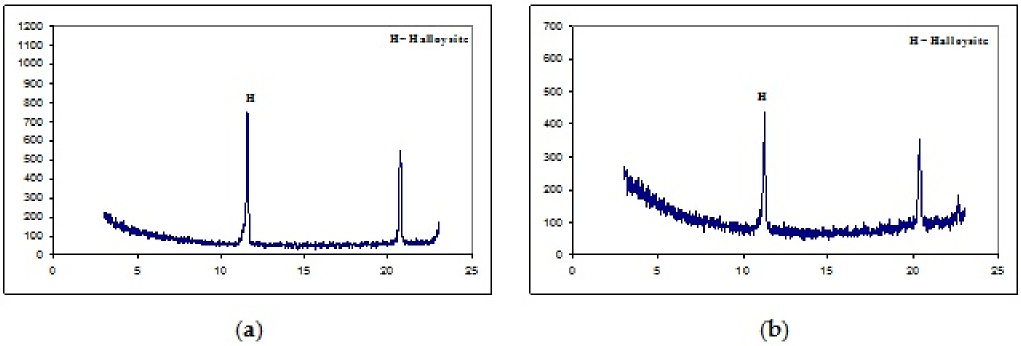


Figure 8. XRD patterns of the studied mortar sample from the church of the Virgin showing: (**a**) Oriented phase; (**b**) Glycolated phase (*X*-axis = 2Θ, *Y*-axis = Counts).

3.2. Biological Study

The identification process which was achieved according to [18] proved that; the fungal flora *Aspergillus glaucus* represent the most dominant fungi constituting (22.22%) of the total fungal isolates from the fresco paintings in Wadi El Natrun and it was found to attack green, red pigments, plasters and it was also isolated from the air of the church of the Virgin. Other Aspergillus species identified were: *Aspergillus flavus* (11.11%) which was found to attack black and white pigments. *Aspergillus flavus* + *Aspergillus niger* which were found to attack white, green and orange pigments in the fresco paintings of the church. *Aspergillus fumigatus* (16.66%) which has been identified in the isolates taken from the plasters applied on walls and columns in the church. The *Aspergillus occhraceus* group was found only on the yellow pigment in the church. *Aspergillus caudidus* was identified in Wadi El Natrun fresco paintings and was found to grow on yellow and black pigments. Other genera were: *Mucor* spp. which was found only in the internal air of the church of the Virgin. The fungus *Geotrichum* spp. has been found to grow only on the red pigment in the church. *Geotrichum* spp. and *Aspergillus fumigatus* were identified only in the isolates taken from the un-plastered walls of the church (Figures 9a,b, 10a,b and 11a,b and Table 3).

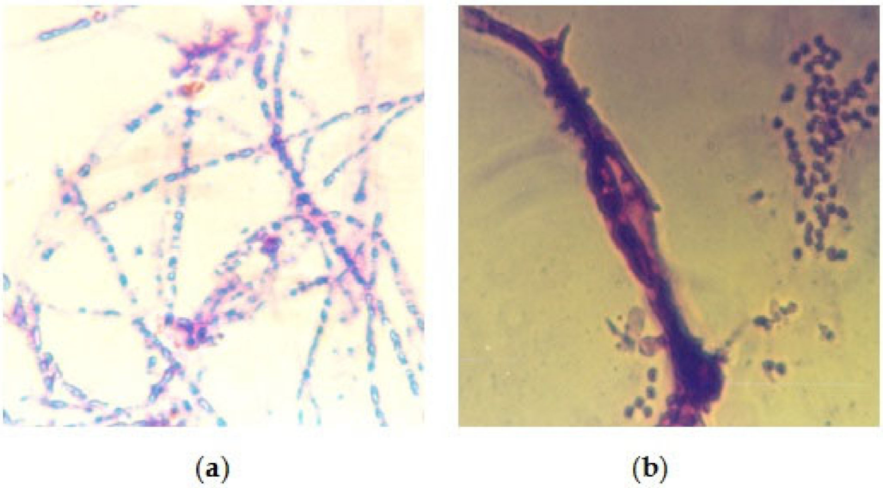
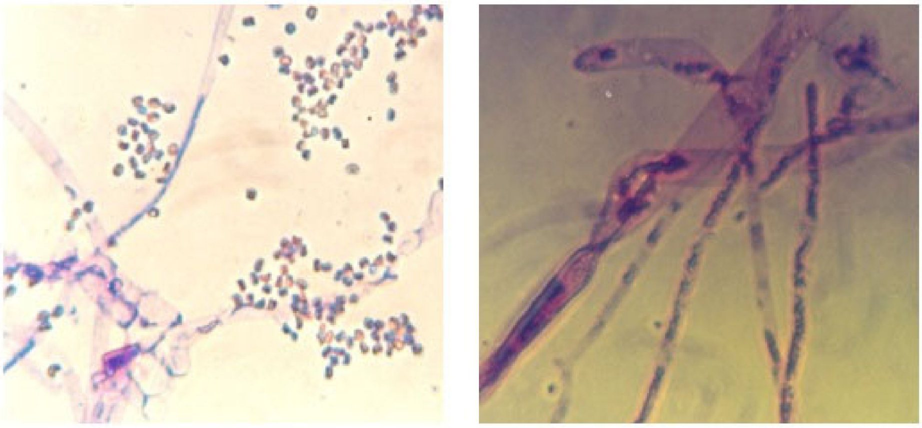
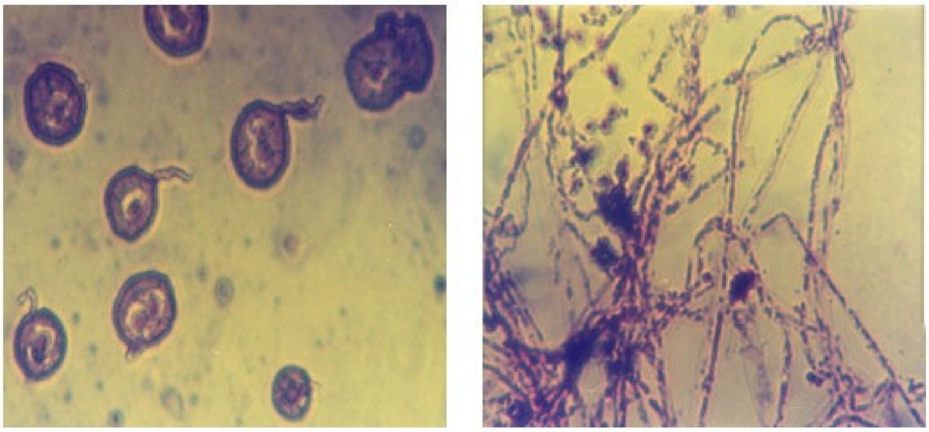


Figure 9. The fungal flora *Aspergillus caudidus* (**a**) under microscope (**b**) (un-plastered walls of the church—1500×).



(**a**) (**b**)

Figure 10. The fungal flora *Mocur spp.* (**a**) under microscope (**b**) (the internal air of the church—1500×).



(**a**) (**b**)

Figure 11. *Aspergillus flavus* (**a**) and *Aspergillus niger* (**b**) under microscope (1500×).

Table 3. The fungal flora isolated from the church of the Virgin—Wadi El Natrun.

Isolated Fungal Species	No. of Isolates	Percentage %
Aspergillus flavus group	2	11.11
Aspergillus flavus + *Aspergillus niger*	3	16.66
Aspergillus fumigatus	3	16.66
Aspergillus glaucus	4	22.22
Aspergillus occhraceus group	1	5.55
Mucor spp.	1	5.55
Aspergillus caudidus	2	11.11
Geotrichum spp.	1	5.55
Geotrichum spp. + *Aspergillus fumigatus*	1	5.55
Total isolates	18	100%

4. Discussion

Gypsum and anhydrite were found together in the mortar sample; both gypsum and anhydrite are rock-forming minerals, the formation is sometimes referred to as gyprock. Some of these deposits can be hundreds of meters thick. In dry climates, anhydrite deposits have remained the same for over millennia. However, in the presence of groundwater they can turn into gypsum to some 15 to 40 m depth, this depth increasing two-fold in humid climates. The hydration of anhydrite (generally called gypsification) and the volume expansion associated with this reaction has been considered the cause for the observed powdering of the surface of anhydrite rock into gypsum [19]. Mortars and plasters containing gypsum have a tendency to deterioration because of their solubility and their conversion to anhydrite [20,21]. Plaster in the church was applied in five layers [22,23], the analysis results evidenced the complete change into lime in Egypt after millennia of gypsum and gypsum–lime mixtures. Mortars and plasters consisting primarily of lime and sand has been used as an integral part of masonry structures for thousands of years, this basic formulation remained unchanged until the advent of Portland cement, the latter is sensitive to the attack of sulphates and sea water since calcium aluminates react with (SO_4), forming ettringite (a gypsum salt). Moreover, cement mortars interact with atmospheric (SO_2) forming gypsum and ettringite [24,25].

Most clay silicates occur as thin plates, but halloysite often occurs as tubular or spherical particles [26]. Halloysite is usually found in soils formed from volcanic deposits, particularly volcanic ash and glass [27]. Halloysite is a polytype (hydrated phase) of kaolinite ($Al_2(OH)_4[Si_2O_5]$) and differs mainly in the morphology of the crystals, which are curved or rolled, this leads to structural disorder, particularly in layer stacking [28]. As halloysite is a layer-structured mineral, most of its surfaces are internal (referred to as inner surface). When low molecular weight organic compounds react with these inner surfaces, an expansion occurs along the c-axis [29]. Halloysite is an indicator for arid climate conditions; it is frequently formed under wet conditions in the rock soil interface zone, in hydrothermal springs and subtropical weathering of volcanic rocks, in cracks and around weathering of granite boulders. The presence of halloysite in soils and building materials is associated with movement of surface water to ground water [30,31]. Mechanically, the clay mineral halloysite ($Al_2Si_2O_5(OH)_4.2H_2O$) absorbs the soluble salts resulting—through swelling—in endogenous pressure on the stone blocks and the plaster layer leading to wall bulking, plaster falling and cracking [23].

The degradation of natural materials depends on the climatic conditions and human activity. In a monument, all building materials are not subjected to the same weathering processes because of their intrinsic properties (mineralogical and chemical composition, petrophysical and mechanical properties) and their position in a monument [32]. Building materials kept in high controlled environments such as museums are also susceptible to the effect of bio-deterioration—especially the effects of fungal and bacterial species. Biocorrosion of building materials can occur through the action of microorganisms leading to stone dissolution and formation of different salts; these salts can be precipitated within the pores of the stone, and upon recrystallization, exert considerable stress in the pore walls [33]. Fungal and bacterial species uses the copper based-pigments as a nutrient, a main source for carbon and energy leading to the chromatic alteration of these pigments [34], the organisms associated with biodeterioration processes on buildings grow, as biofilms, containing a complex community of: microorganisms, particulates and a high percentage of water forming under suitable moisture conditions, a gelatinous film [35]. Gettens and coworkers were among the first to point out, in 1941, that paintings could be defaced or destroyed by the growth of those small, parasitical plants commonly called "mold" or "mildew" [36]. All building materials are porous and the porosity of building material along with ingress of moisture and other harmful chemicals such as acids, chlorides and sulfates affect the material and seriously reduce their strength and service life [37], bio-corrosion can occur through the excretion of organic acids by chemoorganotrophic microorganisms. These acids can also chelate metal cations (e.g., Al, Ca, Fe, Mg, Mn and Si) from minerals to form stable complexes [33]. The presence of significant amounts of carbonate compounds (e.g., >3% *w/w* $CaCO_3$) in calcareous stones or lime mortars, results in the buffering of biogenic metabolic products producing a constant suitable pH-milieu for the growth of microorganisms [38]. Moreover, these microbes are also capable to precipitate $CaCO_3$ via hydrolysis of urea [39]. These species are responsible for the biologically induced corrosion of stone and other building materials in the archaeological sites. Sometimes, death and lyses of these species provide the organic substrates necessary for the growth of heterotrophic species, which are responsible for the colored stains present on the building surface as well as the mechanical damage observed, such as the detachment of portions of the painted layers. Microorganisms which grow on the surface of wall paintings might discolor the painting not only through their own pigments but also by excreting metabolic products which cause discoloration of the paint or change its consistency. In addition, mycelia of fungi can penetrate into the painting and its grounding, resulting in the mechanical destruction of the cultural heritage [40]; generally, two common types of aesthetic damage can be observed: white efflorescence and green-to-black stains. The same deterioration symptoms are observed in our case study. Concerning biological control, recent studies demonstrated that heating the infected area of the building surface to 70 °C for a few minutes by a microwave system represents an effective and sustainable method to devitalize biofilms that grow on the surface of ancient buildings, yielding the same successful devitalization obtained by an abundant biocide application, but avoiding any dispersal of toxic residues in the environment [41].

5. Conclusions

A certain role is played by the clay minerals and microorganisms in the deterioration process of Coptic architecture units at the church of Virgin Mary, Wadi El-Natrun region. Wall gypsum mortars in the church contain halloysite as a dominant clay mineral while plaster is clay free. Concerning microorganisms, the fungal flora *Aspergillus glaucus* represent the most dominant fungi constituting (22.22%), *Aspergillus flavus, Aspergillus flavus, Aspergillus fumigatus, Aspergillus occhraceus,* and *Aspergillus caudidus* were also isolated, the findings of this study are important in correctly analyzing the development of damage cycle and is a rational definition of the restoration work necessary. By this way, the results of the present study may be extrapolated to be used in similar cases suffering from the same problems the mortars proposed for restoration should ensure compatibility with the historic structure and also feature some improved characteristics, for a greater stability and mostly sustainability. These concern, basically, a higher, but not excessive, compressive strength, an adequate tensile strength, elasticity and an enhanced hydraulic character. Concerning biodeterioration, our laboratory experimental work in similar cases assured that the optimum biocide for both fungi and bacteria is marjoram oil (*Origanum vulgare* L. "Lamiaceae"), this oil possesses strong antibacterial and antifungal activities, it can be used as a solution composes of (2 cm^3 marjoram oil, 2 cm^3 acetone and 100 cm^3 distilled water). The biocide can be applied using the spray technique and has no side effects related to the aesthetic or chemical composition of the building materials.

Author Contributions: Conceptualization, A.M. and M.R.; Data curation, A.M. and M.R.; Investigation, A.M.; Methodology, A.M.; Writing–original draft, M.R.; Writing–review & editing, A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available upon request from the authors.

Acknowledgments: We would like to thank Karel Innemie from Leiden University (Netherlands, head of the Dutch archaeological mission at Wadi El-Natrun, who provided us data and some of the figures inserted in this study.

Conflicts of Interest: The authors declare no conflict of interest.

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