

RESTORATION AND PRESERVATION OF ENGRAVED LIMESTONE BLOCKS DISCOVERED IN ABU MOUSA EXCAVATION, SUEZ- EGYPT

Nabil A. Abd El-Tawab [♦], Walid.K Al-GHARIB ^{♦♦}

Corresponding author E. mail: drnabil_bader@yahoo.com

Abstract:

A lot of engraved limestone blocks were discovered at Awlad Abu Musa (east of Suez, Egypt) in 1995/2007 by Supreme Council of Antiquities. The stone blocks were seriously affected by archaeological environments during burial environment in agriculture land. They were covered with thick clay layer with soil particles that disfigured them and hid their inscriptions. Prior to the conservation intervention, the materials were characterized by X-ray diffraction, optical microscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy, Chemical analyses of ground water and microbiological study. After the material characterization, the conservation and restoration of the stone blocks were carried out including cleaning, consolidation, reduction of salts, Re-jointing, restoration and completion of lost parts. After that the blocks were exhibited in Suez museum.

Key words: Excavation, Awlad Mousa, Safety Discover, Analysis, Treatment, Consolidation, Desalination, Suez museum.

1. Introduction:

Almost 10.000 engraved limestone blocks were found out at Awlad Abu Musa excavation during seasons "1995/2007". The land of Awlad Abu Musa is located at Abu Amer village located at 12 km east of Suez, eastward the Ismailia Canal about 350m, west of the Suez Canal about 600 cm. The excavation site centered the site of

^{♦1}Conservation Dept., Faculty of Archaeology, South Valley Univ., Qena , Egypt.

^{♦♦ 2}Ministry of State for the Antiquities Affairs, Egypt

agricultural land. The site was subjected to protection of law by decision No. 387/1999. The area of the site is " one carat and half and eighteen shares". It was believed that this building moved from somewhere temple or tomb and was then re-built. History of the discovery of the site is due to a farmer in 1995 reported the existence of stone blocks in his land. He found it while plowing the ground. Supreme Council of Antiquities did excavation in the same year and detected the form of an architectural unit (takes the form of U in English), consisting of limestone blocks taking regular shape and different sizes. Through writings recorded on these stones, the name of King Nkhtanbo II (Nxt Hr Hb) was found. Supreme Council of Antiquities completed the excavation at 2006 season and discovered a large number of engraved blocks with inscriptions belonging to the King Nkhtanbo II. The Supreme Council of Antiquities did excavation in 2007 to complete what the previous excavation revealed in 1995 to detect any extension for architectural elements, they found some architectural elements of the extension building. The second site revealed number of blocks carrying inscriptions on both sides, the first side had the Royal name of the King Ptolemous II (Wsr kA ra mry imn), (sA ra nb xaw), "the name of his Coronation " and the second side holds a drawing of a person standing in front of him and was written (Granted the foreign country). Also one blocks bearing text, is read "with mottled feathers abroad of the horizon". Some archeologists believe that, these stones may be transferred from the temple of Ptolemous II⁽¹⁾. The aim of this current work is to study the effect of the preservation state of engraved limestone blocks in Abu Musa excavation, study the stone blocks to identify its components and introduce a scientific study for its treatment in order to discover as much as possible the reliefs and reveal the surfaces details that will

(¹) Report from the Suez monuments region - Ministry of State for Archaeology.

be of potential interest to the historian to explore the origin of these blocks.



Figure 1 shows the Abu Musa Excavation during 2001 season.



Figure 2 shows the Abu Musa Excavation during 2006 season.

2. Deterioration factors of the engraved stones

Through field inspection of the site a wide range of alterations and/or degradation phenomena were noticed. The stone blocks were seriously affected by archaeological environments, it was found buried inside clay soil that saturated with underground water and salts. As long as stone was in contact with clay soil, it undergoes chemical, mechanical, physical and biological weathering processes. The stone blocks had a stable form in relation to the environment in which it exists and approached a stable equilibrium. In the burial environment, stone blocks were broken down by physical, chemical and biological processes. Physically, stone can be modified by being broken by saturation with water soluble salts, abrasion and stone will also be adversely affected by acids and other substances in the ground water⁽²⁾. Changes will be resumed as soon as the stone was uncovered in the ground and was suddenly exposed to new environmental condition. After the discovering of these blocks, it was leaved in the same site more over four years exposing to air, the process of deterioration begins again and may be obvious after as little time as a few seconds. The

⁽²⁾ S. Catharine, Conservation Manual for the Field Archaeologist, Archaeological Research,

most damaging feature of excavation is the change in the water content of their environment. Those exposed to damp or wet deposits suffer from loss of water and those from extremely dry conditions or from the presence of water. More often than not, stone blocks lost water to the atmosphere on excavation since air is drier than most deposits; this is compounded by drying wind and sunshine. Loss of water can have several deleterious effects. The most notorious damage is due to soluble salts. When the solution in the pores finally dries out after excavation, the salts crystallize ⁽³⁾. Damage occurs where the salt solution is so concentrated that the crystals fill up the pores exerting, as they grow, enormous pressure on the walls of the pores. Greater and even more damaging pressure occurs if the humidity now rises again, for the salts hydrate, taking water into their crystal structure without dissolving. This volume increase produces pressures of hundreds if not thousands of atmospheres; these pressures are recurrent and very damaging ⁽⁴⁾. The salt crystallization and hydration processes lead to loss of cohesion between grains and causes the spalling, current detachment of individual grains (fig.3,4), pushing surface layer of stone (fig.5), different type of cracks (fig.6), powdering/crumbling with possible appearance of white efflorescence of salts (fig.7), high failure, fragile and flaking, Some reliefs were eroded because of exfoliation, detachment of the superficial layers (fig.8) and granular disintegration into powder (fig.9). Discoloration and removal of reliefs were observed in as a result of the high humidity and the presence of soluble (fig.10). Very dense layers of biological colonization accumulated on the surface of stone blocks observed

⁽³⁾ J. Cronyn, *The Elements of Archaeological Conservation*, New Fetter Lane, London, (1990), p.17

⁽⁴⁾ B. Smith, A. Torok, J. McAlister, Y. Megarry, *Observations on the factors influencing stability of building stones following contour scaling: a case study of oolitic limestones from Budapest, Hungary*. *Building and Environment* 38, (2003), pp.73–83.

the accumulation of black to dark-colored crust tracing the surface and brown, green and white stains of microorganisms caused the discoloration of stone surface (fig.11). Black rust was found in the surface of some limestone blocks (fig.12). All stone blocks surfaces were covered with thick clay layer with soil particles and vascular plants. Roots are growing which disfigured them and hid their reliefs (fig.13). The deterioration caused by plants is both mechanical and chemical. In this case the chemical action is influenced. The chemical action is due to the acidity of the root tips and the acidity and chelating properties of the exudates. Certain plants, for instance ivy, can also cause a change in stone color as a result of the release of organic compounds ⁽⁵⁾. Also the main weathering forms characterizing deposits on the stone blocks were the growth algae. These are in fact extremely simple plants which live in very damp places or in water. They appear as greenish or brownish slimes or suspensions in water; a sudden increase in their numbers gives a dense bright coloration known as a bloom (fig.16).



Fig. (3a,b) crystallization of different salts to light-colored crust tracing the surface and between layers of engraved limestone.

Fig.(4) loss of cohesion between grains caused the current detachment of individual grains.

⁽⁵⁾G. Caneva, A. Altieri, Biochemical mechanisms of stone weathering induced by plant growth, Proceeding of the 6th international congress on deterioration and conservation of stone, Torun, Poland, 1988, pp.32-44.



Fig. (5) Crystals of soluble salts pushing off a surface layer of stone.



Fig.(6) shows the cracks and microcracks.



Fig. (7) powdering/crumbling of the engraving stone due to salts efflorescence.



Fig. (8) Exfoliation of the engraving limestone in Abu Musa Excavation.



Fig. 9 shows the disintegration of the engraving limestone.



Fig. (10a,b discoloration of the engraving limestone in Abu Musa Excavation.



Fig. (11) Microbiological colonization to dark-colored crust tracing the surface of reliefs.



Fig. (12) Black rust found in the surface of some limestone blocks.

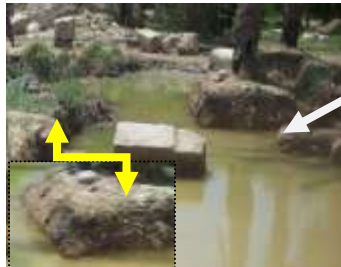


Fig. (13) Stone blocks were covered with thick clay & soil particles and vascular planets.

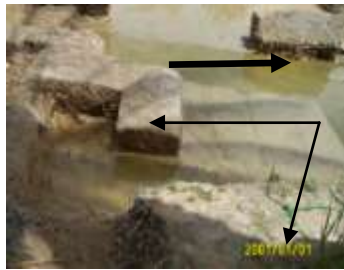


Fig. (14) Growth of algae as greenish, brownish slimes at stone blocks.



Fig. (15) The process of water suction suddenly from the area of Abu Musa



Fig. (16) Wrong storage between grass and areas of high humidity

3. Materials and Methods

Some degraded engraved limestone was sampled. Salt efflorescence was sampled by brush. Collected samples were analyzed and studied to identify the different weathering forms. The analysis is based on non-destructive methods such as:

3.1. Petrographic examination

Thin sections were prepared and optically analyzed using polarized transmitted light microscope model (Olympus BX51 TF japan) attached with digital camera under magnification 20x up to 40x.

3.2. Scanning electron microscope (SEM-EDX)

Scanning electron microscopy (SEM) investigations of the samples were carried out using (SEM JEOL Japan, JSM 5500) with magnification ranges from 500x up to 4000x, coupled with an Oxford energy dispersive X-ray spectrometer (EDS) system with link isis software and model 6587 X-ray detector to reveal details of the diagenetic processes and micro-scale features in the stone samples. Small limestone samples were coated with gold.

3.3. X-ray diffraction (XRD)

Samples was investigated by X-Ray diffraction patterns (XRD), using a Philips PW 1840 diffractometer, the patterns were run with Ni-filtered Cu K α radiation ($\lambda= 1.54056\text{\AA}$) at 40 kv and 10mA. The scanning was limited from $2_{\theta} = 1$ to $2_{\theta} = 80^{\circ}$ range.

3.4. Biodeterioration study of the engraved limestone

A survey of biodeterioration phenomena was performed in several limestone blocks by squashed and crumbed (aggregated). For each sample, 1g was diluted with 9 ml of sterilized saline. Samples were shaken vigorously to form uniform solution of 10-1 concentrations. The decimal serial dilutions (10-1 to 10-5) were prepared using the method of Ejifor & Okafor (1985). For the isolation of fungi, plate count method (Raper & Fennell, 1965) was used as follows: a known volume of the diluted sample, from sample serial dilutions, was used to inoculate the used medium in plates. The plates contained Czapek's agar medium (Smith & Dawson, 1944) that was melted and kept at 45°C. Czapek's medium comprised (g l-1): sodium nitrate, 3.0; potassium dihydrogen phosphate, 1.0; magnesium sulfate, 0.5; potassium chloride, 0.5; ferrous sulfate, 0.01; glucose, 10; agar, 15. Chloramphenicol (0.05 mg/ml) was used as bacteriostatic agent (Al-Doory, 1980). The plates were incubated at 28°C for 5-7 days during which the developing fungi colonies were counted and identified (Domsch et al., 1980). The microbial population in the original sample was then calculated using the following equation: Organisms /g sample = number of colonies/ (amount plated x 1/dilution).

The same method was used for the isolation of bacteria, by using nutrient agar medium (NA) instead of Czapek's. The medium comprised (gl-1): beef extract, 3.0; peptone, 5.0; agar, 15; pH= 7 (Seeley & VanDemark, 1981). The inoculated plates were incubated at 37°C from 24 to 48h. The evaluation of microorganism total concentration in each sample was determined by plate counting of serial dilutions according to the equation: Colony forming units (CFU)/g = Number of colonies X 1/dilution.

3.5. Chemical studies of groundwater

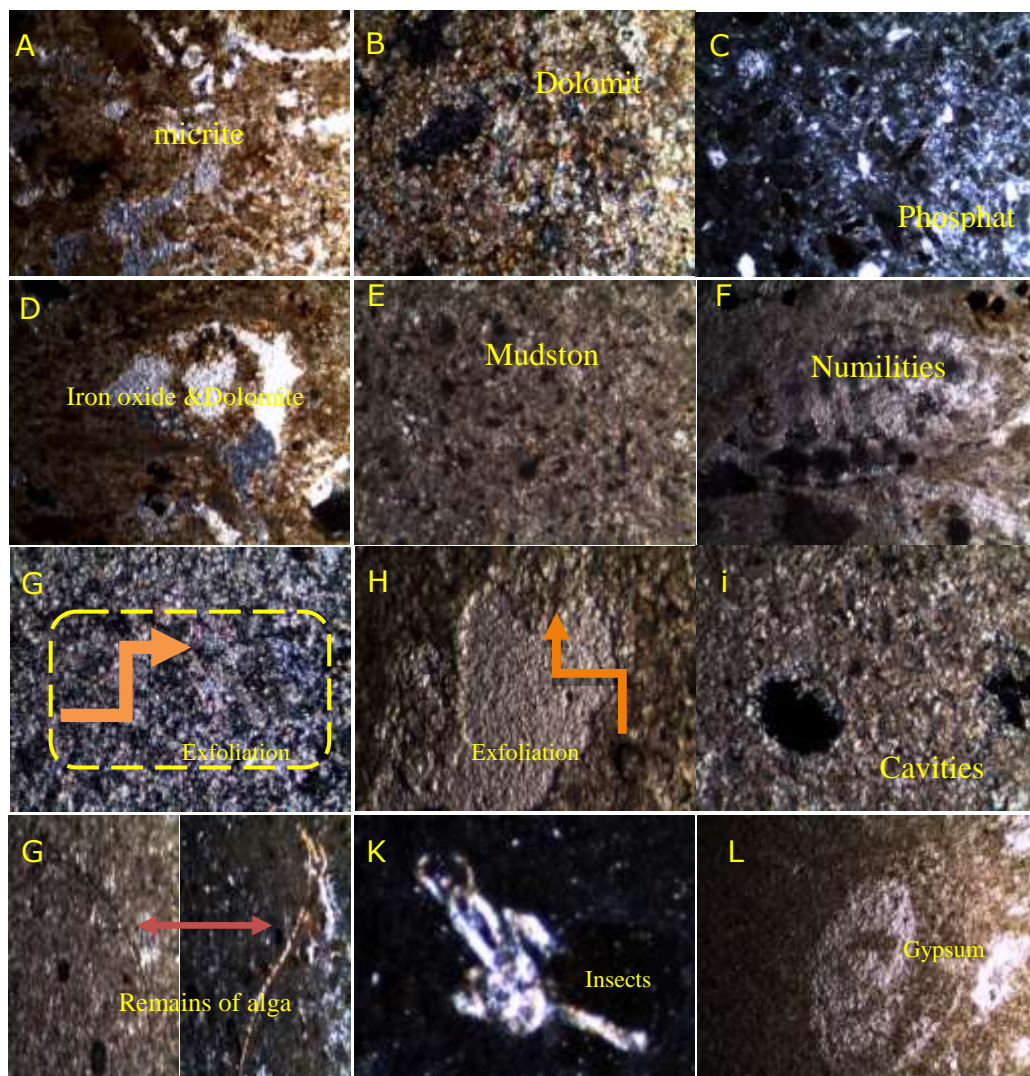
Water sample was taken from Abu Musa excavation in sterile bottle in order to avoid any local contamination or evaporation. The

samples were analyzed for the major cations (K^+ , Na^+ , Mg^{2+} and Ca^{2+}) and the major anions (Cl^- , SO_4^{2-} , CO_3^{2-} and HCO_3^-) using chemical methods and Atomic Absorption spectrometer, model(A Analyst 100, Perkin Elmer), as well as water temperature and pH were measured.

4. Results and discussions

4.1 Petrographic investigation

The examination of thin sections of the limestone samples under plan polarized light microscope (PLM) revealed that, the limestone consists of fine grained calcite (micrite), iron oxides, dolomite, fossil fragments, phosphate, clay minerals and some fine grained quartz. Also micrographs revealed deterioration aspects such as, micro-exfoliation of calcite grains, cavities and cracking in calcite grains, remains of alga, insects, and Gypsum crystals. The micro cracks, halite and gypsum crystals related to weathering processes, all of these features are shown in figure (17 a-l).

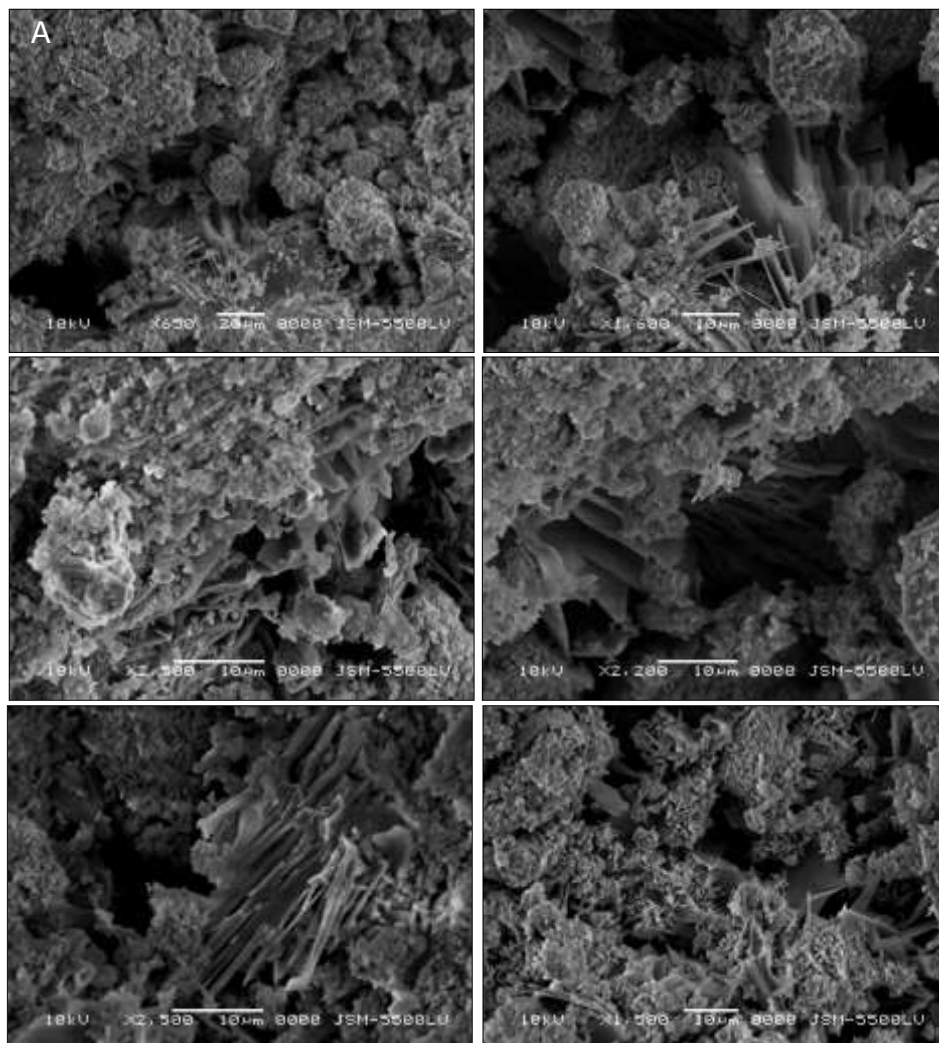


Figure(17) The examination of the limestone samples under polarized microscope shows **a** fine grained calcite (micrite), **b** Dolomite and iron oxides, **c** phosphate, **d** iron oxide and dolomite **e** mudstone **f** Numilities, **g,h** micro-exfoliation of calcite grains, **i** cavities and variety of cracking in calcite grains **g** remains of alga, **k** remains of insects, **l** Gypsum crystals.

4.2. SEM Investigation

The scanning electron microscope results confirm that a major deterioration is the abundance of soluble salts in the rock. SEM photomicrographs show that there is wide range of deterioration features as shown in (Fig.18a-l) such as disintegration

between calcite crystals. Dissolution of some parts of calcite crystals and loss in the binding materials between grains by the effect of salts crystallization, dusting, small fissures and cracks, localized cavities, the clay minerals is also exiting among the calcite grains; also, it showed the content of gypsum in the samples is due to the transformation of calcite into gypsum. Scanning study also indicated growth of hyphae of fungi and remains of alga.



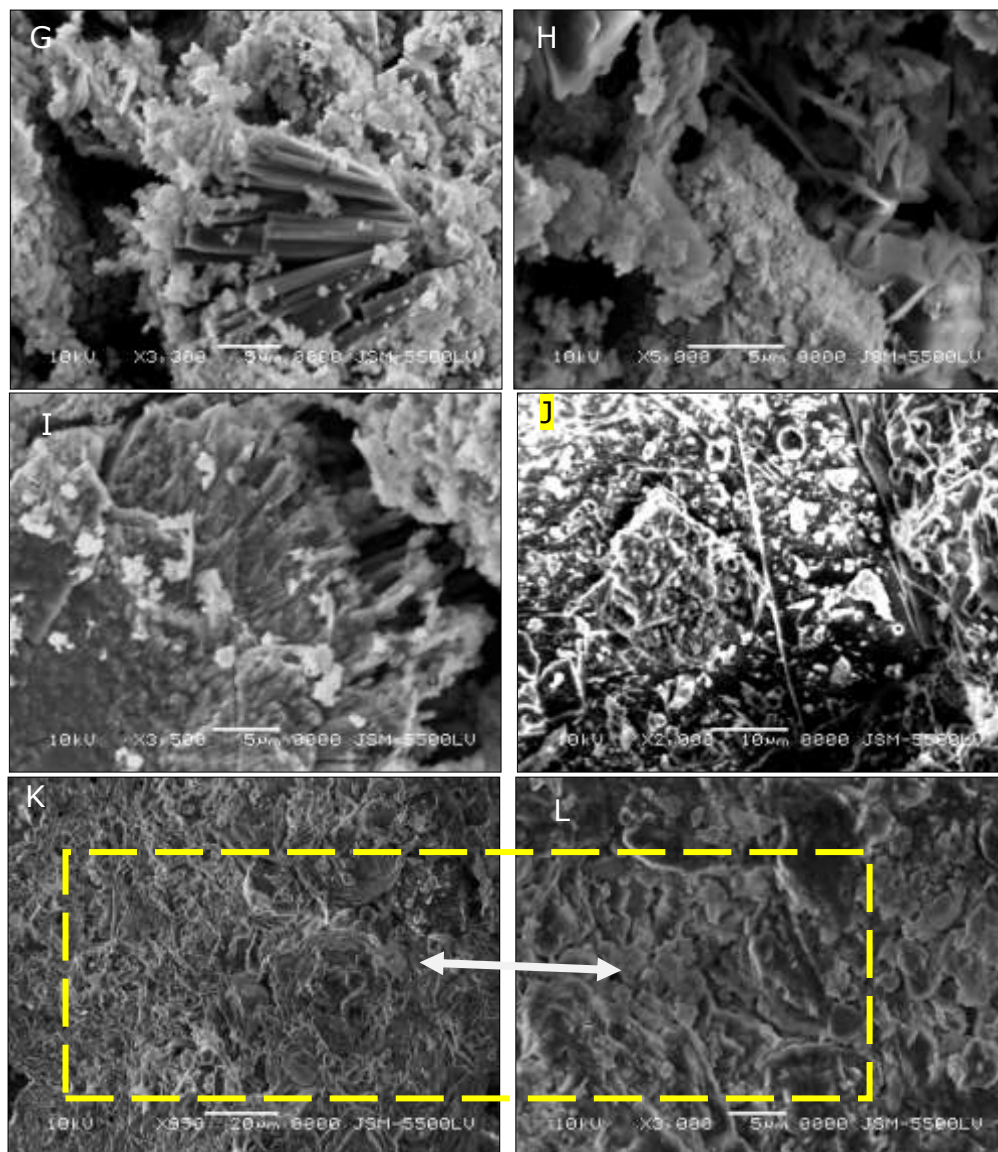


Figure (18) SEM micrographs of deteriorated stone reliefs in Abu Musa excavation, **a** Cracks, pitting and losses of cohesion between grains **b** Different salt crystals such as halite and Gypsum; **c** Destroyed and dissolution of calcite crystals **d** gypsum crystals **e** Halite crystals occur as blocky shaped and rectangular crystals **f** A variety of cracking patterns in calcite grains. **g** Gypsum and halite salts grow on calcite cleavage plane and dissected it into several flakes **h,I** Many cracks and separation of scales from the rock as a result of gypsum and sodium sulphate salts. **J** growth of hyphae of fungi, **k,l** collapsed of grains and micro exfoliation of the calcite grains.

4.3. Energy dispersive X-Ray analysis

EDX microanalysis of various samples listed in (figure 19 and table1) showed that, the samples essentially consist of calcium (Ca), silicon (Si), sulfur (S), chlorine (Cl), sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), iron (Fe), strontium (Sr), phosphates (P), manganese (Mn) and silver (Ag) potassium (K) and phosphorus (P). Ca as a main source of limestone samples is decreasing in all weathered samples compared (92.60, 90.90, 83.77, and 53.78). These variations may have been due to the ions exchange between the main components of stone samples and different salty ions present in groundwater. High concentration of phosphate (P_2O_5 5.84%), it attributed to phosphates salts, which was produced from fertilizers (ammonium phosphates) used in agriculture land of Abu Musa.

Table 2. Quantitative EDS microanalysis (%) of the damaged layer.

Elements %	Samples					
	M1	M2	M3	M4	M5	M6
MgO	1.52	-----	-----	8.07	-----	4.88
Al ₂ O ₃	0.61	-----	-----	0.67	-----	-----
SiO ₂	5.80	3.43	2.5018	3.67	6.82	2.15
K ₂ O	0.34	0.36	0.42	-----	-----	0.35
CaO	90.90	92.60	83.77	91.82	53.78	87.82
Fe ₂ O ₃	0.53	0.44	2.97	2.97	1.68	3.79
SrO	0.25	0.44	0.26	-----	-----	-----
Na ₂ O	-----	0.47	-----	0.42	1.92	-----
SO ₃	-----	0.26	0.25	0.23	29.59	-----
Cl	-----	1.95	0.22	0.32	-----	-----
MnO	-----	-----	0.77	-----	0.19	0.98
SrO	-----	-----	-----	-----	-----	-----
P ₂ O ₅	-----	-----	-----	-----	5.84	-----
Ag ₂ O	-----	-----	0.72	-----	-----	-----

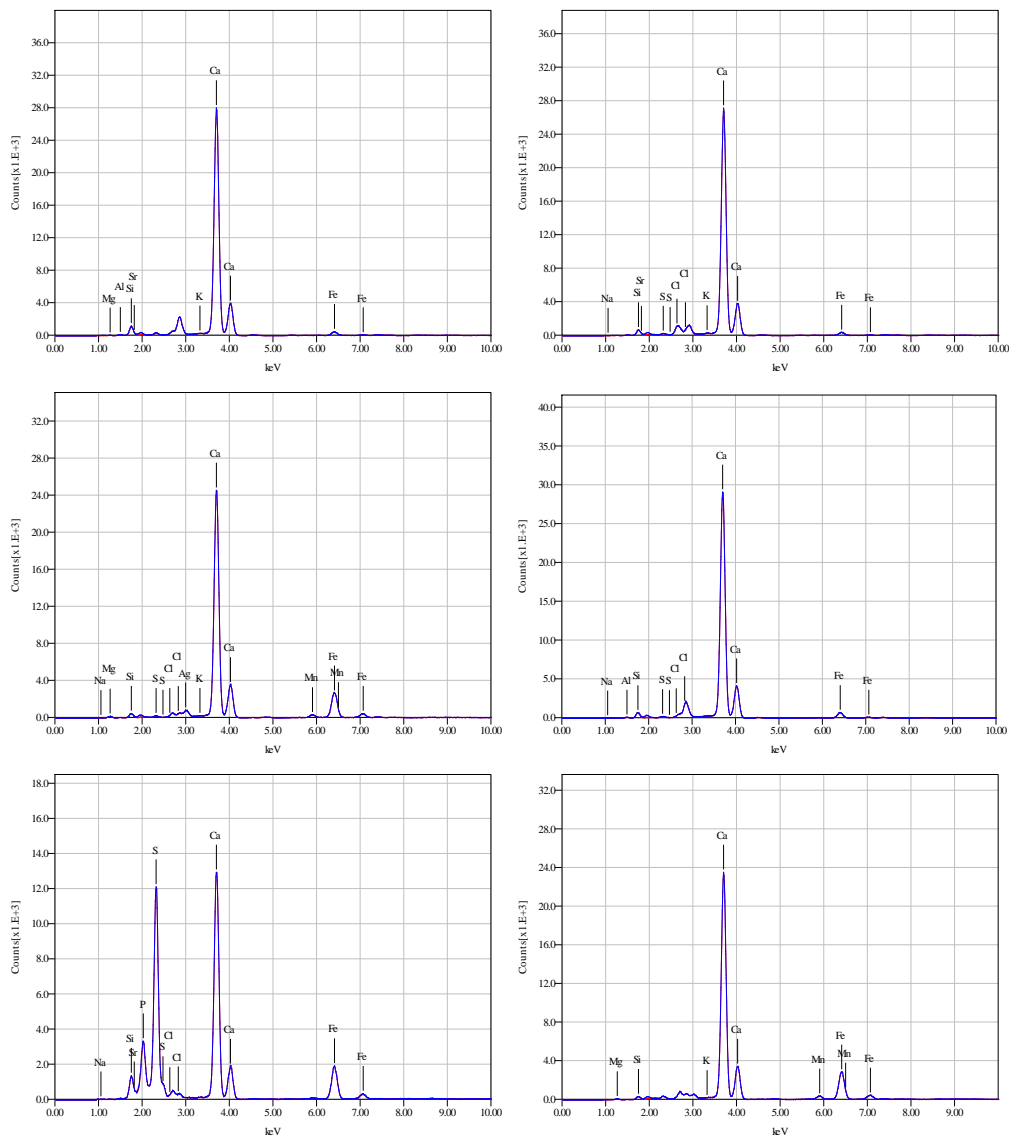


Figure 19 shows EDX patterns of the engraved limestone samples from Abu Musa excavation.

4.4. X-Ray diffraction (XRD) analysis

The XRD analysis of studied samples (the results are summarized in table 2 and figure 19) have shown that the, the sample consisted essentially of calcite CaCO_3 , Dolomite $(\text{Ca,Mg})\text{CO}_3$ and small amount of halite NaCl , Quartz SiO_2 , Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Anhydrite CaSO_4 and traces of iron oxide and Orthoclase KAlSi_3O_8 .

Table (2) XRD analytical analysis of limestone samples of Abu Musa Excavation.

Samples	Composition
M1	Calcite(CaCO_3), Quartz(SiO_2), Halite (Nacl)
M2	Calcite(CaCO_3), Halite (Nacl)
M3	Dolomite($\text{Ca,Mg})\text{CO}_3$, Calcite(CaCO_3)
M4	Calcite(CaCO_3), Anhydrite (CaSO_4), Halite(NaCl), Dolomite($\text{Ca,Mg})\text{CO}_3$, Gypsum($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
M5	Anhydrite(CaSO_4), Calcite (CaCO_3) , Quartz(SiO_2), Anhydrite(CaSO_4) Orthoclase(KAlSi_3O_8), Gypsum($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
M6	Calcite(CaCO_3), Dolomite ($\text{Ca,Mg})\text{CO}_3$, Quartz(SiO_2), Halite(NaCl), Magnetite(Fe_3O_4)

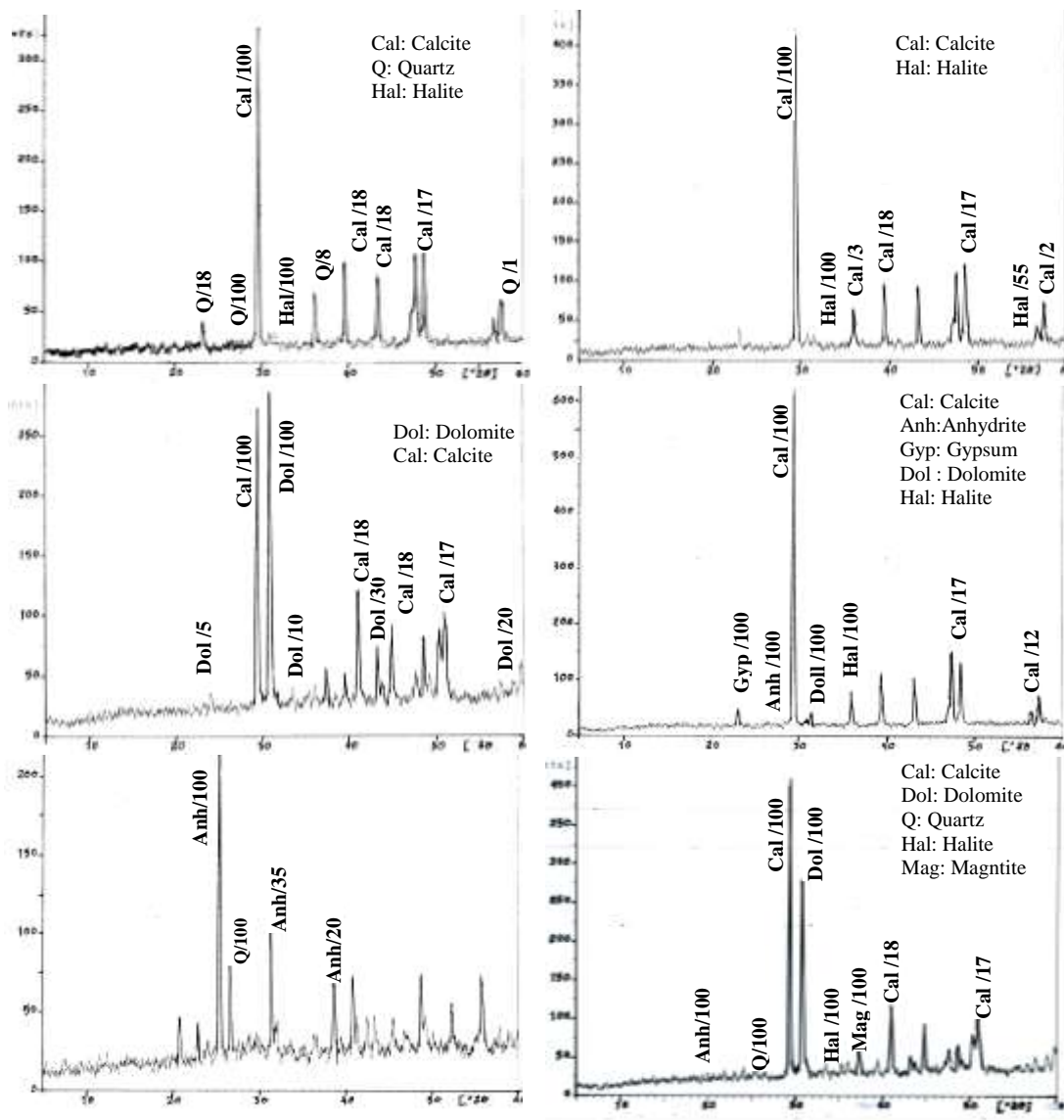


Fig. (20a- g) show the XRD patterns of investigated limestone samples.

4.5. Biodeterioration study

Depending on the conditions at the excavation, various kinds of fungi were identified as shown in (table3 and figure21). and the study revealed growth of Bacillus Bacteria (negative gram), fig.22.

Table 3. Various types of microbiological growths found over limestone samples.

No of sample	Bacteria CFU/g	Fungi CFU/g	Microorganisms
1	1500	7	<i>Asprigillus nigar- Penicillium-Sterile mycelia- Bacillus sp.</i>
2	2500	5	<i>Sterile mycelia- Asperigillus candidus- Stachbotrys state of Melanopsamma pomiformis- Alternaria alternata- Bacillus sp.</i>
3	3000	25	<i>Stachbotrys state of Melanopsamma pomiformis-Sterile mycelia- Bacillus cereus.</i>
4	1900	1	<i>Stachbotrys state of Melanopsamma pomiformis- Bacillus sp.</i>
5	-ve	-ve	-----
6	1200	18	<i>Stachbotrys state of Melanopsamma pomiformis- Sterile mycelia- Penicillium- Bacillus sp.</i>

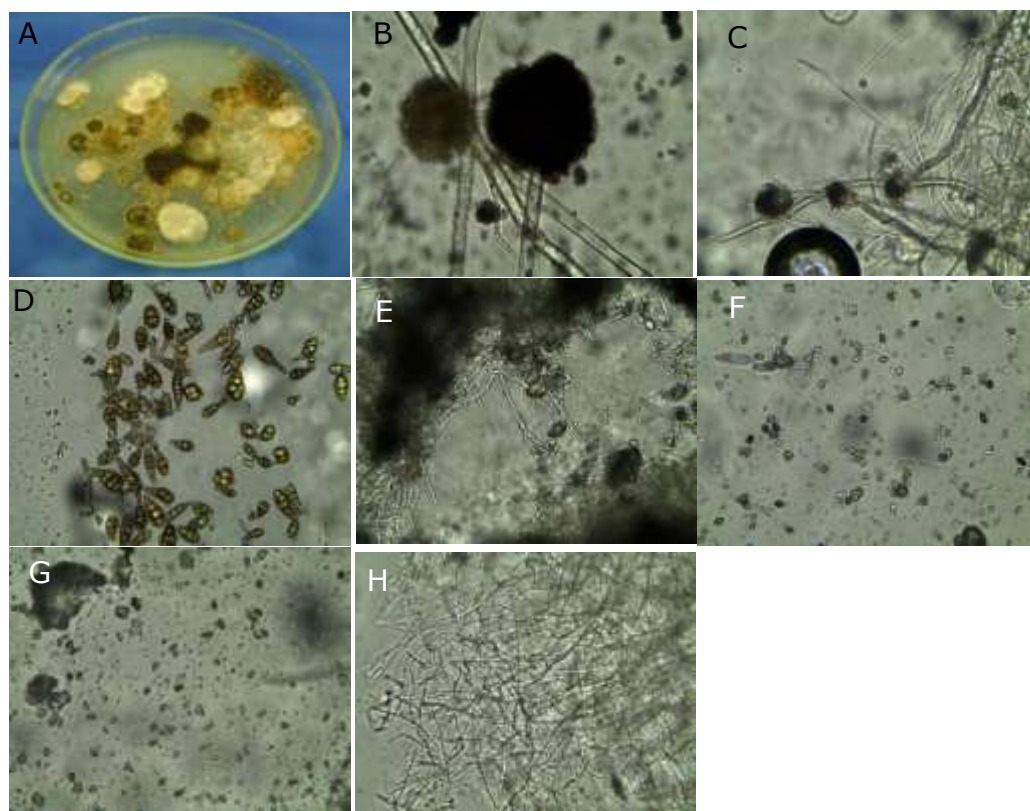


Fig. (21) Light microscope photos of isolated fungi from engraved stone **a** different colonies of isolated fungi. **b** *Aspergillus niger* **c** *candidus*, **d** *Alternaria alternate*, **e** *Penicillium* **f** *Stach state*, **g** *Stachbotrys state*, **h** *Sterile mycelia*.

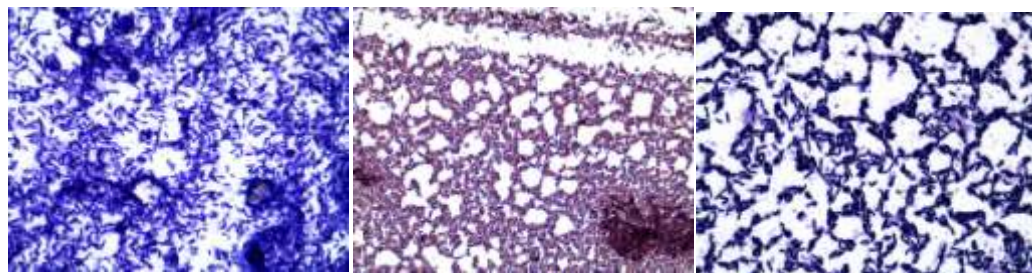


Fig. (22) Light microscope photos of isolated Bacteria from stone infection Bacillus Sp.

4.6. Chemical studies of groundwater

The chemical analysis of the water samples (the results are summarized in figure 23) showed that it is rich in sodium (Na⁺), chloride (Cl⁻), potassium (K⁺), magnesium (Mg²⁺), nitrate NO₃⁻ and calcium (Ca²⁺) ions. The water also has a high content of bicarbonates (HCO₃⁻) and (Cl⁻), sulphates (SO₄⁻). PH was 8.2 and the temperature was 26°C, (fig.23).

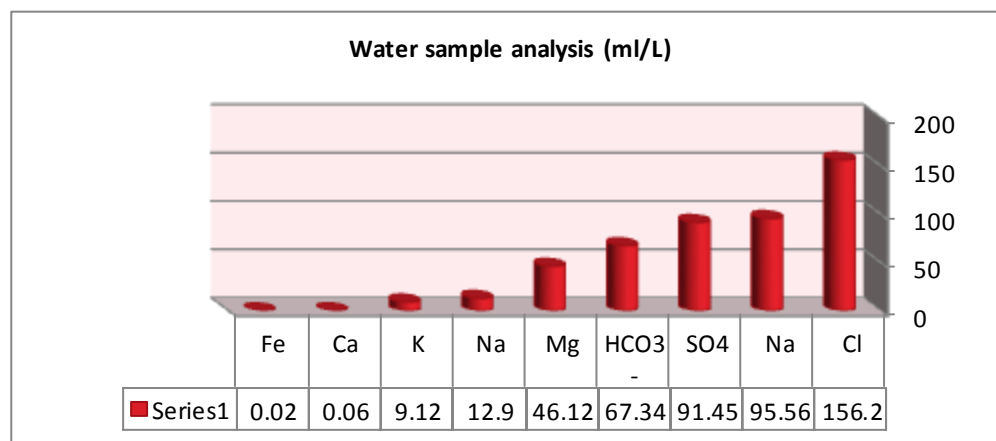


Fig. (23) The chemical analysis and ASS results of groundwater analysis from Abu Musa.

5. Preservation and conservation processes

The main aim of the conservation and preservation works is to preserve the monuments and to adapt it for use. Several engraved limestone blocks were selected and have carried out conservation

and preservation operations until they were processed to be exhibited at Suez museum.

5.1. Cleaning

Stone cleaning can be to the advantage of a surface by displaying the true color of previously obscured and by revealing the quality of carved detail ⁽⁶⁾. The important features of cleaning stone are first to avoid forcing dirt further into the core and second to avoid introducing yet more soluble salts into it. An initial visual inspection of the surfaces of the stone was made, supplemented by information that had been gathered on the deterioration production, subsequently, those foreign substances needing removal; we use two kinds of cleaning.

Mechanical cleaning:

The friable dirties were firstly cleaned mechanically from the surface by using soft brushes and rough brushes with different size advanced to metallic spatulas and scalpels carefully without any damage occurred. Where dirt is particularly ingrained, distilled water with ethyl alcohol was employed by absorbent packs. During mechanical cleaning it was found that some deteriorated scene surfaces were so weak that application of any cleaning process would result in the loss of large amount of scene. Primary consolidant of separated weak surface by using 2% Paraloid B.72 "by spray methods" to consolidate this weak parts and then cleaned.

Chemical cleaning

Chemical cleaning (wet cleaning) was carried out to remove what mechanical cleaning failed to remove. Ingrained dirt, unsightly patchiness and blackened crusts of calcium sulphate were cleaned using two poultices, the first one was absorbent poultices loaded with mixture of 10% sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

⁽⁶⁾E. Maureen, Young, D. Urquhart, R. Laing., Maintenance and repair issues for stone cleaned sandstone and granite building facades, Building and Environment , N.38, (2003), pp.1125 – 1131.

+ 5% Ammonium Carbonate with distilled water. After that, we use distilled water with ethyl Alcohol to rinse treatment places to remove ammonium sulphate with severe susceptibility to water solubility. The second one employs the sodium salt of the ethylenediaminetetra-acetic acid, abbreviated as (EDTA) as active ingredient. They are particularly appropriate for gypsum crusts because EDTA forms a stable complex with Ca^{2+} ions. Thus gypsum is transformed into soluble sodium sulfate (Na_2SO_4) that is mobilized into the poultice as well as into the stone. The pigments produced by the fungi and alga which were brown and black pigments were cleaned by using poultice of Methyl Cellulose + Triethanolamine + Ethylenediaminetetra-acetic acid (EDTA) with Preventol R.80 as biocide.

5.2. Reduction of Salts:

Mechanical methods were used for reducing the crystallized salts by scalpel to remove thicker layers of salts. Cleaning by brush was used to remove the fine grains of salts. A mixture of Bentonite and paper fiber poultice mixed with distilled water was applied to the stone surface, to draw out the halite salts; this poultice is often favored by conservators of stone used for desalination, to draw out soluble salts or as a cleaning method on substrates such as limestone that respond to water cleaning⁽⁷⁾. The poultices completely covered the stone surface to a uniform thickness of about 1cm. They were allowed to dry over a period of about 48 hours. During this time, white salt crystals formed on the peaks of the clay poultice. When these salts were removed and tested, they matched those that had been found in the water droplets. The poultice treatment was repeated ten times. It is noncable; the first

⁽⁷⁾ M. Angeli, C. David, J. Bigas, Influence of temperature and salt concentration on the salt weathering of a sedimentary stone with sodium sulphate, In book: Natural Stone Resources for Historical Monuments, Edited by; R. Prikryl and A. Torok, Published by: The Geological Society, London. (2010).

two poultices were easily removed and did not require an intervention layer of clay and paper.

5.3. Consolidation

As a consequence of the combined effects of chemical and mechanical weathering, stone lost its cohesion as shown by SEM, and treatment become necessary to restore its integrity. Consolidation is an in-depth treatment that re-establishes the cohesion between particles of deteriorated stone ⁽⁸⁾. The water repellent product Ethyl silicate, tetraethox silane" TEOS" was applied on the limestone surface after the fundamental restoration works (cleaning, reduction of salts) were carried out. The tetraethoxysilane-based impregnates are superior to other synthetic polymers (applied in conservation) because they preserve water wet ability of such treated stones ⁽⁹⁾ and according to (Kumar and Price 1994)¹⁰, the ethyl silicate also can be used to reduction of salts. In some very weak limestone parts, after using Ethyl silicate it was used Paraloid B.72 to improve their physio-mechanical properties. The hydrophobic product was applied by brushes on the dry stone surface.

5.4. Re-jointing/Reconstruction processes

After the fundamental restoration works (cleaning, salt extraction and consolidation), ten stone blocks have sunken reliefs representing the King Nkhtenbo II carries Lotus flower plant and behind him rows of hieroglyphic writing, were chosen. These

⁽⁸⁾ J. Marie, Alkoxysilanes consolidation of stone and earthen building materials, A thesis, submitted to science Dept, University of Pennsylvania, (1992), pp.1-18, 1-20.

⁽⁹⁾ W. Łukaszewicz, Reinforcement of historical limestone objects by means of tetraethoxysilane-based treatments, Recent progress in the consolidation of calcareous materials, stone core, 21. / 22. April 2010, Litomyšl, Czech Republic.

⁽¹⁰⁾ R. Kumar, C. Price, The influence of salts on the hydrolysis and condensation of methyltrimethoxysilane. In La conservazione dei monumenti nel bacino del Mediterraneo, ed. V. Fassina, H. Ott, and F. Zezza, 861-65. Venice: Soprintendenza ai Beni Artistici e Storici di Venezia. 1994.

blocks were collected and grouped to obtain an accurate profile of a relief or design, so as to be displayed and to keep contiguous blocks together to avoid further abrasion during storage. Re-jointing and linking of these blocks were carried out by using lime mortar only, consisting of 1 lime + 2 fine sand mixed with 20% primal Ac33 and then complete the missing gaps and spaces with the same lime mortar components. The mortar was applied by a spatula to flatten the putty and smooth it out until it comes well to the edges of the stone surface. The last mortar had very fine-grains and its level was less than the level of the existed archaeological surface according to the known restoration rules. Wood stand was designed for the exposition after completing restoration processes in Suez Canal Museum.



Figure. 23 restorations steps of stone blocks (a) mechanical cleaning (b) absorbent poultices (c) the stone block after poultice. (D,E) Completion of missing parts (E,G) Re-jointing the stone blocks, (H) the blocks after restoration in Excavation field (I)the exhibition of stone blocks at Suez museum.

5. Discussion

The analytical data obtained by the previous analysis and diagnosis methods might be sufficient identify the harmful factors that have affected engraved limestone and the resulted deterioration forms. This is shown as follows:

Plan polarized light microscope (PLM) displayed that; the micrite is the main component of limestone cemented by sparry calcite. Amount fossil fragment, Numulities and insects embedded in a micrite matrix. Remains of remainder of micritized red alga are also observed. Opaque minerals and shapeless aggregates that coated by ferruginous martial are also observed. Impregnating ferrous substances are probably responsible for the reddish color of some limestone blocks. Dolomite crystals are also noticed in the sample (M3). Numerous grains of Quartz are found, occurring as sub-rounded to angular grains. Slide showed the intrusions of Gypsum. Phosphate crystals are noticed in the sample (M5). The photographs showed an increase in porosity, more micro-cracks and micro-exfoliation within the thin section, this increase the rate of stone decay, (fig15,16).

SEM photomicrographs showed disintegration between calcite crystals. Lose in the binding materials between grains by the effect of salts crystallization. Decayed samples show etching features in some calcite grains indicating micro-dissolution processes (chemical weathering). Carbonate cement dissolution and subsequent calcite recrystallization are also observed. Halite crystals are found in glassy shape. Observation by SEM also showed destroys of calcite grains, droplets of halite mixed with clay minerals crystals. Gypsum in white crusts accumulates below the surface of the crust was detected. This suggests that reprecipitation takes place on moisture exposed surfaces where white crusts are forming after gypsum dissolution. SEM observation indicated the hyphae of micro-organisms.

The mineralogical analysis using XRD of the limestone samples have shown that, the salt layers consists mainly of halite and phases of sulphates (gypsum and anhydrate). The halite salts related to groundwater salinity from Sues Canal and cultivated land. Gypsum was produced by the reaction between the SO_4^{2-} ions present in the acid deposition and the calcium carbonate (CaCO_3) present in limestone or perhaps it is a natural mineral in the stone, it is generally found in Abu Musa limestone in the form of dehydrated sulphate($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) Gypsum and Anhydrate (CaSO_4). The most important source of sulphate is atmospheric pollution, Agriculture land as Abu Musa region, sea sprat from Suez Canal and micro-organisms. Transformation of Gypsum to anhydrate by heating in summer causes a great change in the volume of the crystal of gypsum which decreases when transformed to anhydrite resulting in many cracks and microcracks in blocks, gypsum loses water after reaching 42°C transforming into Anhydrite. So, the most common damaging salts consist of sulfate and chloride anions. The problem is more complicated by the existence of aluminum and Quartz may be attributed to the clay minerals. The SEM photograph documented these results. Also iron oxide is found in the samples as traces minerals; it could be argued that the fracturing form affected the samples exposed to salty bath contains due to the presence of the Fe ion, which leads to the creation of sever deterioration forms. These forms are due to the effect of alternative cycles between hydration and crystallization pressures created by the effects of contact with the oxygen and moisture in the open environment. This cycle leads Fe ions to change into hydrous iron oxide (the density is 7.8) which occupies a much larger volume than the parent Iron (the density is 3). This difference leads to the pressure generated in the confined spaces by this volumetric increase is large enough to fracture the stone⁽¹¹⁾.

⁽¹¹⁾ N. Agnew, S. Maekawa, Investigation of environmentally driven deterioration of the Great Sphinx and concepts for protection, A. Roy and P. Smith (ed.), Archaeological

Chemical analysis showed that the water sample is very rich in Sodium (Na^+), chloride (Cl^-), potassium (K), magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions. The water also has a high content of bicarbonates (HCO_3^-) and sulphates (SO_4^{2-}). Sample from groundwater was analyzed for comparison with the samples from the stone blocks to see how much the water had affected them, The analysis of several stone blocks and salt samples showed similar results and the presence of the same salts in addition to percentage of sodium and chloride, which are contained in halite, sulphate, potassium, magnesium and calcium related to the presence of gypsum and anhydrate. The results in the present study proved that the engraved stone is affected by the water of the nearby canals (Ismailia and the Suez Canal represent the main source of water in the Abu Musa area).

Biodeterioration study revealed seven fungi isolated from weathered samples (*A.niger*, *candidus*, *Alternaria alternate*, *Penicillium*, *Stach state*, *Stachbotrys*). These micro-organisms play an important and substantial role in all alteration processes that occur in the stone. It was estimated that, biological weathering is 100-1000 times greater than inorganic weathering ⁽¹²⁾. Biodeterioration of stone blocks in the Abu Musa excavation classified broadly into three categories: biophysical, biochemical, and aesthetic deterioration ^{(13),(14)}. The aesthetic or visual effects of biodeterioration resulting in the engraved stone from the growth of

Conservation and its Consequences, Preprint of the contributions of the Copenhagen Congress, 1996, International Institute for Conservation of Historic and Artistic Works, London, 1997, pp. 116-120

⁽¹²⁾ R. Aghamiri, D. Schwartzman, weathering rates of bedrock by lichens; A mini watershed study, *Chemical Geology*, 188(304), 2002, pp.249-259

⁽¹³⁾ G.Caneva, P. Nugari, O. Salvadori, *Biology in the Conservation of Works of Art*. Rome, ICCROM. 1991

⁽¹⁴⁾ K.. Jain, K. Mishra, T. Singh, Biodeterioration of stone, A review of mechanism involved. In *Recent Advances in Biodeterioration and Biodegradation*, 1993 vol. 1, ed. K. L. Garg, Neelima Garg, and K. G. Mukerji, 323-54. Calcutta: Naya Prokash.

microbiological colonization to dark-colored crust tracing the stone surfaces alter their appearance due to chromatic alterations and development of biological patinas ⁽¹⁵⁾. Biophysical deterioration of stone may occur due to pressure exerted on the surrounding surface material during the growth or movement of an organism or its parts. The biochemical action of fungi on stone appears to be a more important process than mechanical degradation. The deterioration of limestone by filamentous fungi through the action of excreted oxalic and citric acids, the acids produced by various species of fungi function as chelating agents that can leach metallic cations, such as calcium, iron, or magnesium, from the stone surface ⁽¹⁶⁾. Oxalic acid can cause extensive corrosion of primary minerals. Fungal species such as *Aspergillus niger* were able to solubilize powdered stone and chelate various minerals in a rich glucose medium because they produce organic acids such as gluconic, citric and oxalic acids ⁽¹⁷⁾. Many detromycetes belonging to the families of hyphomycetes and coelomycetes (such as *Alternaria*, *Penicillium*), there are common in the soil and in the air and that can be producers of melanin, can also develop in stone, but only in more favorable condition, they tend to be involved more frequently in the degradation of restored stone artifacts as stone in Abu Musa region, their capacity for producing organic acids and dissolving carbonates ⁽¹⁸⁾. The biodeterioration study detected the presence of

⁽¹⁵⁾P. Martinez, J. Castro, A. Sanchez, The biodeterioration of cultural property of Cuba. In Recent Advances in Biodeterioration and Biodégradation, vol. 1, ed. K. L. Garg, Neelima Garg, and K. G. Mukerji, Calcutta: Naya Prokash. 1993.

⁽¹⁶⁾G. Caneva, O. Salvadori, Biodeterioration of stone, In deterioration and conservation of stone, studies and documents on the cultural heritage, No. 16. Paris, 1989, pp 182-234.

⁽¹⁷⁾F. Eckhardt, Mechanisms of the microbial degradation of minerals in sandstone monuments, medieval frescoes and plaster, Proceedings of 5th International Congress; on Deterioration and Conservation of Stone, Lausanne, 25-27 September 1985, vol. 2, 1985.

⁽¹⁸⁾ C. McNamara, T. Perry, D. Zinn, Microbial processes in the deterioration of Maya archaeological buildings in southern Mexico. In (Eds.), Art, biology and conservation; Biodeterioration of work of art, the Metropolitan museum of art, New York, 1991, pp.248-256

Thiobacillus. Caniva and Nugari ⁽¹⁹⁾ stated that, the sulphate, frequently found on stone, may be caused by the sulphur-oxidizing bacteria.

The restoration and preservation work of the stone blocks in Abu Musa includes, cleaning (mechanical and chemical cleaning), desalination, consolidation, completion and re-jointing. In the re-jointing/reconstruction processes, we decided not to use any steel bars or strong adhesive like epoxy to link these blocks as it is the practice in such cases, because all stone blocks which were discovered in Abu Musa excavation which is about 10,000 pieces of stone, mostly have reliefs, are now subject to processes of the study, classification and translation of the hieroglyphic texts for the arrival to the form and the correct architecture structure for this blocks. So if these study result about of the correct of architectural structure of the temple and see where those blocks place, they can take theme and reused in their original position without further damage.

6. Conclusion:

According to the study, results concluded as follow:

- Site Abu Musa was discovered in the agricultural land located near the Suez and Ismailia Canal, which had a profound impact on the damage of those engraved blocks. These blocks were in very bad condition as a result of water irrigation, salts, biodeterioration and sudden changes in temperature and moisture degrees (environmental shock).
- The experiments in the present study clearly indicate that saline water is one of the most aggressive factors of deterioration of limestone blocks. The investigation showed that the composition of the limestone is calcite, dolomite and Quartz. The presence of

⁽¹⁹⁾G. Caniva, M. Nugari, O. Salvadori, Planet biology for cultural heritage, Biodeterioration and conservation, the Getty Conservation Institute, Los Angeles, 2008, pp.131-135

such minerals in such noticeable ratios is mostly ascribed to direct effect salts crystallization transported, by rising damp, ground water, irrigation water or relative humidity leads to several deterioration forms related to drying conditions.

- SEM examination showed that there is a weakness in the limestone due to deterioration factors as interference of sodium chloride and gypsum between grains, and indicated the fungi hyphate between the grains which is ascribed to direct effect of the biodeterioration.
- The analysis of several stone blocks and salt samples showed similar results and the presence of the same salts in the groundwater samples.
- According to the results, seven fungi have been isolated from weathered stone blocks at Abu Musa excavation. These micro-organisms play an important and substantial role in all alteration processes that occur in the stone
- The restoration and conservation work of the stone blocks includes, cleaning (mechanical and chemical cleaning), desalination, consolidation, restoration process, completion and exposure several stone blocks at Suez museum.

Recommendation:

The role of conservators must be activated during excavation and during finding out the artifacts from burial ground to follow the correct rule in safety exposure of the monuments to new environment. This preservation is part of the field conservator's job. In the absence of conservators, the archaeologist can't take certain positive preventive steps to ensure that an object will remain intact long enough to be taken to trained conservators for proper treatment. It is essential for any one undertaking this responsibility to have good grasp of some basic concept of conservation so that no irreparable damage is inadvertently done to the object.

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