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A MULTI-ANALYTICAL STUDY OF BUILDING MATERIALS AND DETERIORATION PRODUCTS OF THE ROYAL TOMBS TO TANIS (SAN EL- HAGAR)

Ragab Abu EL-HASSAN, Nabil.A. ABD EL-TAWAB*

[1]MUST University, Faculty of Archaeology and Tourism Guidance, Restoration and Conservation Deptment, 1 Alhayi Almutamayiz St, 12568, Giza, Egypt
[2] Zagazig University, Faculty of Archaeology, Conservation Department, 2 City Council Street, 44642, San Elhager, Egypt

Abstract

The city of Tanis is one of the most important cities in ancient Egypt. It was the northern capital of Egypt and the royal headquarters of the kings of the twenty -first and twenty -two dynasty. It is in the east of the Delta, about 150 km northeast of Cairo, on the ancient Tanis branch of the Nile. The Royal tombs of Tanis was discovered by the French archaeological Pierre Monte in 1999. The material building materials are currently suffering due to many aspects and factors of physical, chemical, biological, and human damage, such as the deterioration and loss of many stone blocks, binding mortar, and decorative units, accumulation of dusts and cracks that are varied in shapes and sizes in the painting, crystallization of salts on the surface and between layers, which led to the separation, fragmentation and peeling of the stone surface and the disappearance of many decorative elements, scenery and colored relives. Therefore, the research aims to study the materials for building tombs to find out the most important physical and chemical changes that occurred to them and led to their deterioration in preparation for the development of a scientific plan for the restoration and conservation of these tombs and their decorative elements. The components of the tombs were studied through investigation and using various analysis methods such as X-Ray Diffraction (XRD), Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) analysis of elements, Polarizing Microscope (PM). physical and mechanical properties of the stones used in the construction of graves were carried out. The results The results indicated that, the tombs were constructed using blocks of restricted limestone and were linked with a mortar of Gypsum, sand and stone powder and used some granite pieces in the doorstep over the entrances, and the main reason for the damage of building materials is a group of natural factors, the most important of which is rain water, the ground water and the various salts it contains due to the low location of the tombs within the archaeological hill and the proximity of the archaeological hill to the salty water sources represented in Lake Manzala, agricultural lands, waterways and agricultural banks.

Keywords*: Sanjar Al-Hajar; Royal tombs; Limestone; Groundwater; Deterioration; Analysis*

Introduction

Tanis is located at the entrance to the city of San EL-Hagar, and the center of Al-Husayniyah city, Al-Sharqiyah Governorate, northeast of the city of Cairo, is about 130km away from it, and about 20km south of Lake Manzala (Fig. 1). The dimensions of archaeological hill that contains the royal tombs is about 3km north of the south, 1.5km East-West, and the maximum height is about 30m [1].

* Corresponding author: nabilahmed@zu.edu.eg

Fig. 1. A map showing the location of Tanis in the eastern delta, modified from (https://en.wikipedia.org/wiki/File:Lower_Egypt-en.png)

The origin of the of the hill of San EL-Hagar is partly due to the accumulations of the source of the human being represented in the remains of daily life and the waste of the building materials, in addition to the geological origin of the hill, which consists of sand dunes dating back to the Pleistocene era in the form of a 'sand island' and the sand can easily see where archaeological excavation falls enough to reach its level, and this appears clear in the tombs area [2]. The credit for revealing the royal tombs in Tanis (Fig. 2) is due to the French archaeological mission, which was working in Tanis, headed by the archaeological 'Pierre Montees', where the mission took place in the 1939 season while lifting debris from the side of the southern wall of the great temple.

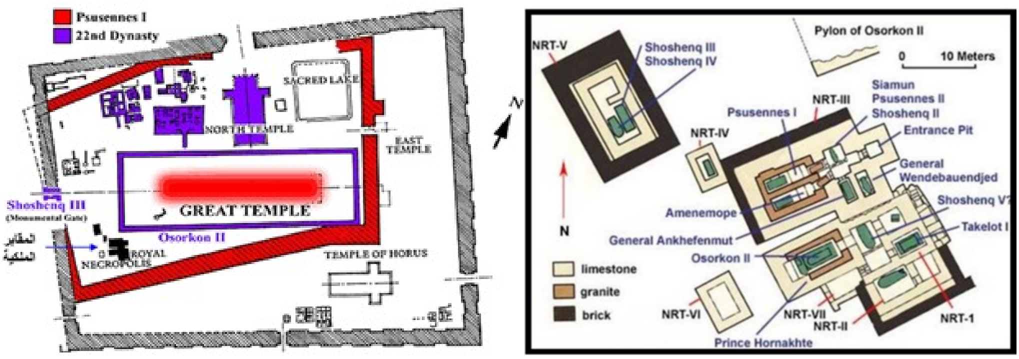


Fig. 2. Royal tombs of Tanis (Jimmy Dunn)[3]: a - the location; b - horizontal plan

The most important royal tombs contained in the archaeological hill in San El-Hajar, including:

➢ The tomb I "Osorkon II" who lived during the 3rd Intermediate Period (Dynasty 22, c. 912-745 BC). It consists of a granite room surrounded by limestone and the east a room opened on rooms 3,2 and it appears that the entrance to the cemetery was initially to the east. It seems that there are many modifications that occurred in the tomb, but it is difficult to identify them. The tomb is still a mystery and confusion in relation to its date, and for what was revealed, due to its subjected to the theft in the past, as well as the large number of changes whether from the family kings themselves or after. The cemetery is rich in religious inscriptions that look at the religious ideas spread in Egypt in those periods of belief in arithmetic, punishment, trial of the dead and the journey of the deceased in the other world [4].

- Tomb III "Psusennes I" consists of a well and a corridor from the eastern side, two granite rooms and two rooms that were added in a later era. The tomb is constructed to the Pharaoh "Psusennes I" and his funerary furniture as well as his wife. The III tomb included something new innovative, as the Pharaoh included a place in his tomb to his wife 'death of star "It is known that the Pharaohs in the modern dynasty did not include their wives with their tombs [5].
- The tomb V "Shoshenq III" (945-712 BC) is characterized by simplicity of the construction and that the level of its base is located along the level of the ceiling of other tombs, it consists of a well about 2 x 3m and a funerary room is about 3 x 5m in connection with each other through a corridor It is about 1.0m and a narrow width. It is constructed of limestone raped from the tomb of individuals as a possibility of the family [6].

These tombs and other monuments in the archaeological hill in the San El-Hager suffer from many serious damage factors, which led to the loss of many of the architectural and decorative elements of these tombs. The main and direct cause of damage and destruction of antiquities in San El-Hager, the high level of the subsurface water under the foundation of the tombs with high levels of various salts. This due to the presence of tombs in very low place of the archaeological hill that are almost buried below the ground level inside the clay soil like large limit the cavernous tombs. The deterioration of building materials in Egypt is primarily due to several types of saline water. When salts are melted in the water absorbed by the archaeological material, they crystallize with the dryness of the material and the evaporation of water from it and the crystallization inside the porous structure leads to expansion forces in the material that can lead to damage, cracking, peeling, then collapse and destruction [7]. This paper aims to study the effect of rising subsurface water and its dissolved salt ions on the royal tombs in San El-Hagar by studying the identification of the most important sources of this water and the reasons for its high salinity and its bad impact on the architectural and artistic elements in the tombs.

There are several diverse and different sources that contribute to increasing the undersurface water and its various salts, which are the main and direct cause of damage and destruction of tombs in San Al -Hagar area:

- It's very low location from the archaeological hill that are almost buried below ground level within the clay soil which is very similar to cave tombs.
- Several drains pass through Saint El Hajar, and the salinity of the water in these drains exceeds 6000 parts per million. The archaeological site is surrounded by a group of these banks [8].
- The archaeological site is surrounded by a network of canals and drains, and these canals are considered their ends, and thus the salts are concentrated in very large proportion, which in turn seeps into the walls of the tombs.
- The archaeological site is sand island that is characterized by its numbers and its high permeability, which makes it a meeting place for many water that leaks from various sources carrying huge amounts of various salts [9].
- Agriculture and irrigation water: It is known that the level of the ground water has started to gradually rise since the beginning of this century after turning the irrigation of menstruation into permanent irrigation and excessive use of water, as the level of the ground water has become very close to the surface in the northern Delta regions [10]. The surplus leaks from irrigation water loaded with salts, after the mixing of irrigation water with water leaked from drains, as well as the leak water from Lake Manzala and the Mediterranean through small channels to the areas near it and ascends to the archaeological buildings in these areas by capillary rising [11].
- Al -Manzala Lake is the northern border of Husayniyah city, where the north of the city is famous for the cultivation of rice, the spread of lakes and fish farms, the city of Tanis is located in the north of the center near Lake Al -Manzala (20km) where the lake water leaks and interferes with irrigation and drainage water, which led to a rise in water level under the surface

in the region and the high salinity. In addition, Lake Manzala is the main future of water drainage and agricultural drainage water for the largest and most important drains in Egypt, which increases the pollution of the lake water and the surrounding areas. This damaged effect is clearly shown in the royal tombs in Tanis and the group of surrounding temples, due to the occurrence of tombs in a relatively low area, which made it an easy goal and a center for crystallization salts on their internal and external surfaces. Among the most important of these salts is the sodium chloride, which proves that a source This salt is a land source connected to sea water [12].

- San Al -Hajar area is located inside the rain belt, due to its proximity to the Mediterranean, where a large amount of rain falls annually, when the rain falls on the archaeological hill, it descends in the direction of the area's most low in the hill (Fig. 3), which is the area where the royal tombs are located where they gather inside with it the salts in the archaeological hill to concentrate inside the tombs, where it takes its way to the walls through the pores, which increases the state worse and deteriorating (Fig. 4).

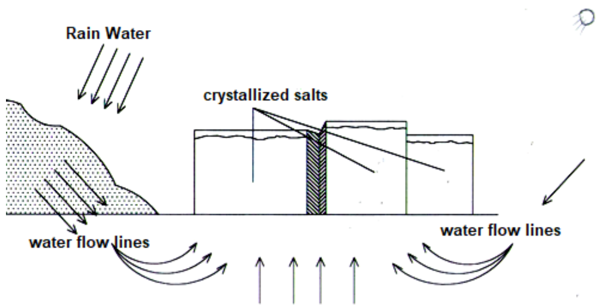


Fig. 3. The effect of rain water on the tombs of San El-Hagar

Fig. 4. The salt crystallizes thickly on the surfaces of the wall inscriptions in the royal tombs in San El-Hagar

Methods and Materials

Some degraded limestone, *Granite* and mortar were sampled from the royal tombs which are directly exposed to the action of subsurface water. Samples of different salts were taken by brush, which were found crystallized on the interior and exterior inscriptions and walls of the royal tombs and two samples of soil was taken under the royal tombs. Collected samples were analyzed and studied to identify the different weathering forms. The analysis is based on non-destructive methods such as:

Petrographic examination

Samples were observed using different types of microscopes. 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.

SEM-EDX

Scanning electron microscopy (SEM) investigations of the samples were carried out using (SEM, JSM 5500, JEOL Japan) 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 digenetic processes and microscale features in the stone samples. Images and elemental analyses were obtained at 15kV and working distance 5.1mm.

X-ray diffraction (XRD)

Several samples taken from different stone blocks and salt samples was made by X-Ray diffraction patterns (XRD), using a Philips PW 1840 Diffractometer, the patterns were run with Ni-filtered Cu Kα radiation (λ = 1.54056Å) at 40kv and 10mA. The scanning was limited from 2θ = 1 to 80º.

Chemical studies of groundwater

A sample of ground water under the royal tombs in San El-Hajar and the concentration of some elements was determined, Water sample was taken in sterile bottle 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.

Study of physical and mechanical properties of granite

Granitic samples were taken from the removal of fragments around the royal tombs in San El Hager under the influence of groundwater and then were cut into cubes samples (2.5cm^3). The samples were cleaned and dried at (105ºC) for at least 24 hours to reach constant weight and left to cool at room temperature to evaluate the physical properties (bulk density, porosity, and water absorption) and mechanical properties (compressive strength) [13, 14].

Results and discussion

Granite samples

General observation from the petrographic study for the samples revealed that, the rock under investigation is coarse grained, rose in color and characterized by hypidiomorphic texture. The rock under investigation composed essentially of *Quartz*, occurs as subrounded and faceless granules (Fig. 5a), *Plagioclase*, occurs as euhedral to subhedral (Fig. 5b and c), *Potash feldspar* (*Microcline*) occurs as *Microcline* crystals showing cross hatching twinning (Fig. 5d). *Mafic minerals* are represented by and *Hornblende*, is represented by euhedral to subhedral; *Hornblende* shows pale brown to mild-green pleochroism (Fig. 5d). *Biotite, Zircon, Brucite, Apatite, Sphene* were clearly noticed (Fig. 5f). This type of granite has been classified as a modern granite and has been named according to the International Union of Geology (IUGS) “Monzo Granite”.

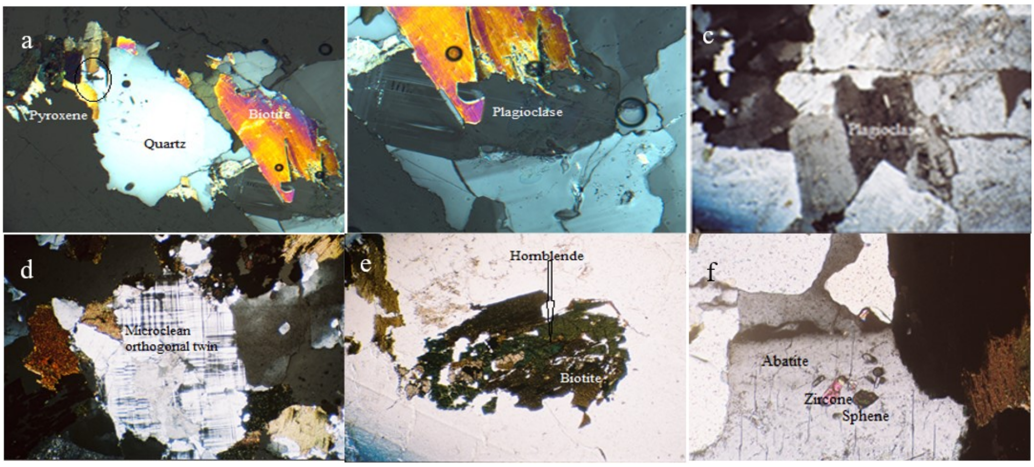


Fig. 5. Petrographic view of the mineral composition of the granite in the tombs of Sun El-Hagar:
a - *Qurtz, Biotite and Pyroxene*; b – *Plagioclase*; c – *Microclean*; d - *Biotite* and *Hornblende*;
e - *Apatite*, *Zircon* and *Sphene*; f - *Quartz* interfere with grains of other minerals

Petrographic study for the samples revealed *Brucite* texture of (*Microcline* - *Brucite*), this texture takes the shape of the veins and vermiform (Fig. 6a), which is the result of the mineral growth of the *Quartz* inside the *Brucite* in the form of the vermiform texture (*Mermyikitic*). It is caused by the growth of *Quartz* inside the plagioclase. Ordinary rang texture in plagioclase mineral and the appearance of twinning in one part and its disappearance in the other (Fig. 6b).

Fig. 6. Petrographic view of the texture of granite in the tombs of Sun El-Hagar:
a - Brucite texture; b - ordinary rang texture; c-gianophilic textyre

The petrographic image also revealed torch texture specific to the presence of the *Brucite* in the form of a flame in the sample. The petrographic examination also confirmed the occurrence of high tectonic movements that resulted in cracks and fractures in *Quartz* (Fig. 7a-c) because it is the hardest mineral in this rock.

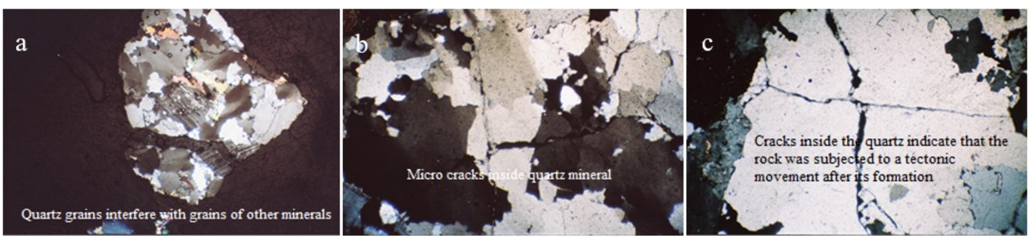


Fig. 7. Petrographic view of granite samples shows the *Quartz* detrital grains contain cracks
with thin layer of iron oxides

SEM micrographs of the deteriorated granite samples showed wide range of deterioration features such as disintegration between crystals, loss in the binding materials between grains by the effect of salts crystallization dusting, small fissures, gaps and cracks, localized cavities, fractures in the minerals, the volume and distribution of the pores (Fig. 8).

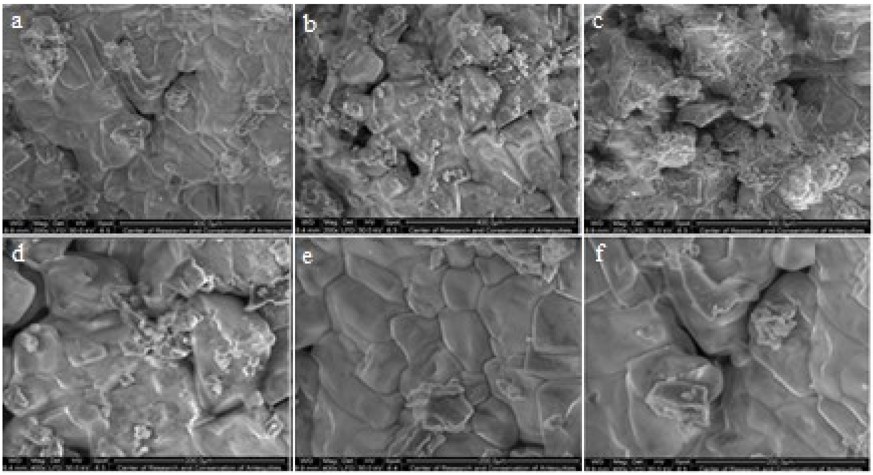
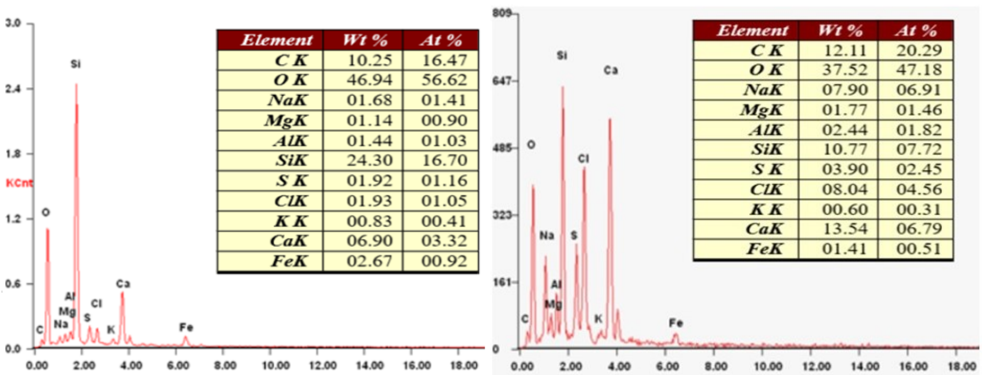


Fig. 8. SEM micrographs of deteriorated granite in royal tombs in San El-HagerCracks, pitting and losses of cohesion between grains, different salt crystals such as *Halite*, destroyed crystals, variety of cracking patterns in grains, collapsed and micro exfoliation of the grains

EDS elemental analysis (Figs. 9a and b) indicate that all granite samples present carbon, oxygen, silicone, sodium, aluminum, chlorine, potassium, calcium, magnesium, iron, and sulfur.



Element	Wt %	At %
C K	10.25	16.47
O K	46.94	56.62
NaK	01.68	01.41
MgK	01.14	00.90
AlK	01.44	01.03
SiK	24.30	16.70
S K	01.92	01.16
ClK	01.93	01.05
K K	00.83	00.41
CaK	06.90	03.32
FeK	02.67	00.92

Element	Wt %	At %
C K	12.11	20.29
O K	37.52	47.18
NaK	07.90	06.91
MgK	01.77	01.46
AlK	02.44	01.82
SiK	10.77	07.72
S K	03.90	02.45
ClK	08.04	04.56
K K	00.60	00.31
CaK	13.54	06.79
FeK	01.41	00.51

Fig. 9. EDX pattern of granite samples: a - Granit sample samlple from Psusennes I; b - Granite sample from Shoshenq III

Samples from the granite were analyzed by XRD. The results are summarized in table 1. X-ray diffraction analysis indicates that most abundant phase in the granite samples is *Quartz* (SiO_2), *K-Feldspar-Orthoclase* ($KASi_3O_8$), *Microcline* ($KAlSi_3O_8$). XRD analysis showed salts as *Halite* (NaCl) and *Gypsum* ($CaSO_4 \cdot 2H_2O$) as impurities damage to granite.

The physical properties (bulk density, water absorption, porosity) detected that the granite in royal tombs in San El-Hager is characterized by high porosity (1.16%), which gives the stone a high-water absorption rate (2.2%) and its consequent ability to absorb water with salt solution and this is the main cause of deterioration. The bulk density of the samples gives 1.68g/cm^3.

Mechanical properties (Compressive strength) were determined for granite samples (Fig. 10), the results showed that the strength of granite characterized by poor mechanical characteristics by 281kg/cm^2 Dry and 210kg/cm^2 Wet. The changes of physical and mechanical properties of the stone were a result of weathering process.

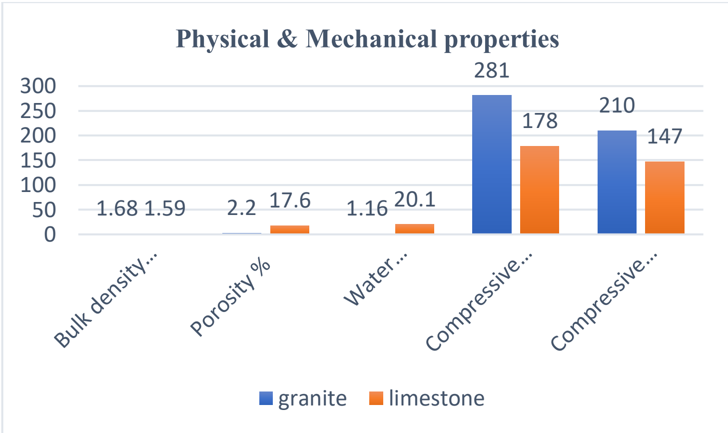


Fig. 10. Physical and mechanical properties of granite and limestone samples from royal tombs in San El-Hager

Limestone samples

General observation from the petrographic study for the limestone samples taken from the tombs of Osorcon and Psusennes 1shwed that, the rock consists mainly of *Calcite*, rich with fossils fragments (5%) and sand grains (1-5%) embedded and coherent with *Calcite* cement. Most of the *Quartz* grains are medium to coarse, sharp to semi sharp, weak sorting. The microscopic examination of sample indicated that limestone of this tomb is exposed to high pressures resulted from movements, earthquakes, and diagenetic processes. These pressures affected on the *Calcite* grains, most of these grains have cracks and eating edges with the effect of the cement materials (*Calcite*). The fossil remains suffer from post-transformation changes, especially (recrystallization, dolomite, solutions (Fig. 11), all these factors lead to the large or small size of the grains that are followed by the appearance of cracks or gaps or both together in the stone, which facilitates the work of the undersurface water especially in archaeological sites.

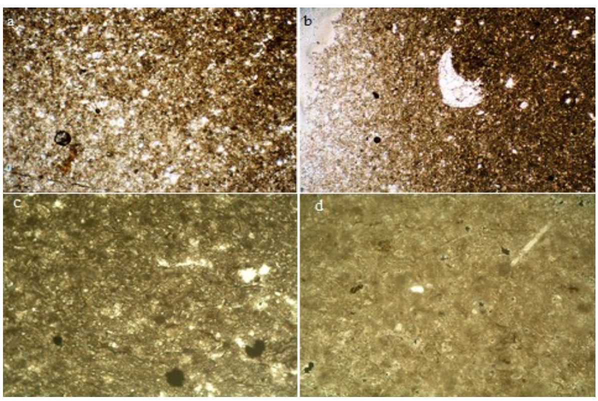


Fig. 11. The examination of the limestone samples under polarized microscope shows: a - Dissolution of silica (*Quartz*) granules with *Calcite*; b - Re-crystallization led to an increase in the size of the grains and the appearance of cracks; c and d - Removal of fossil remains by post-transformation (recrystallization)

The SEM 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. 12) such as disfiguration in *Calcite* crystals, disintegration between *Calcite* crystals, loosing of cohesion between the *Calcite* crystals by the effect of salts crystallization, small fissures and cracks, localized cavities were clearly noticed.

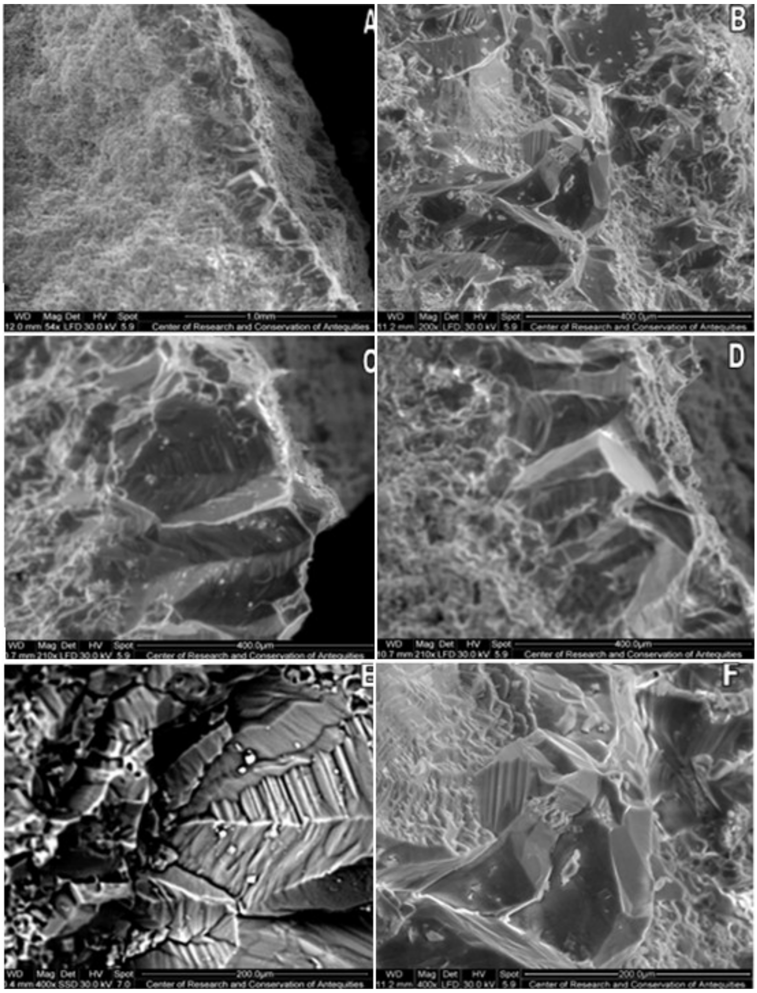
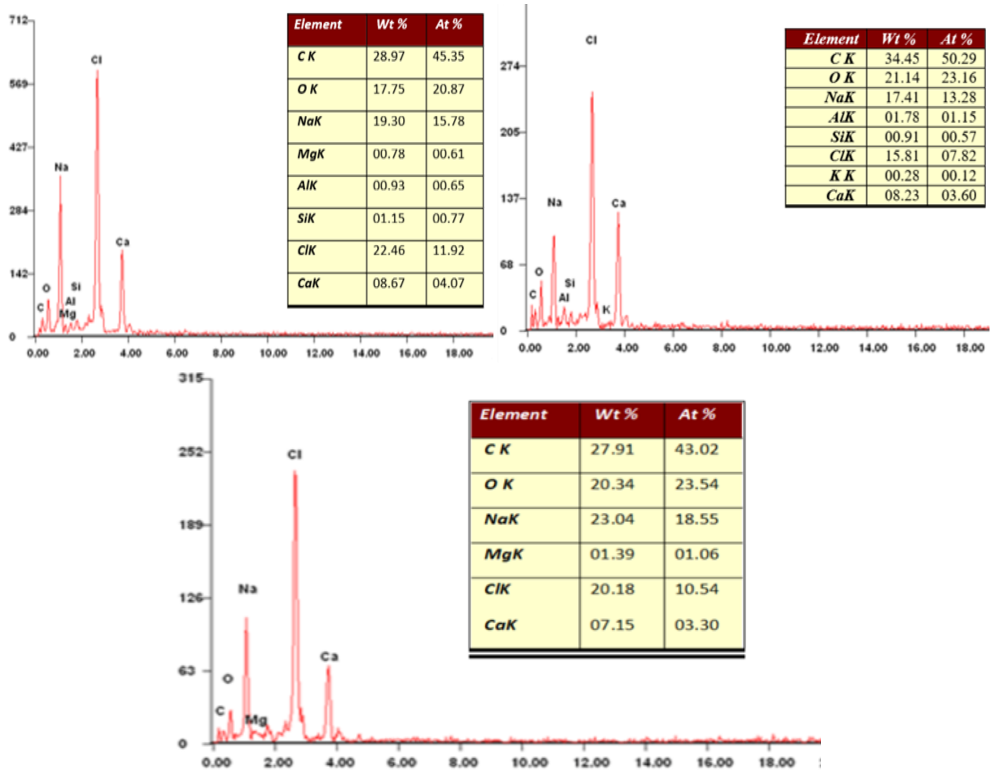


Fig. 12. SEM micrographs of a limestone sample with different magnifications shows a thick layer *of Halite* salt deposited on its surface. It shows the interference of *Halite* crystals in the surface of the stone and the destruction and concealment of the surface of the stone

The EDX analysis of the limestone indicated the presence of calcium, silicon, aluminum, potassium, and high percentage of sodium and chlorine (Fig. 13a-c).

According to the XRD analysis, the limestone mineral composition consists essentially of *Clcite* ($CaCO_3$) and *Dolomite* ($Ca,Mg(CO_3)_2$) and small amount of *Halite* (NaCl). XRD analysis indicated that, the stone in the royal tombs consisted of *Calcite* as a major minerals and high ratio of dolomite (Dolomitic limestone). The presence of *Halite* is related to salts.



Element	Wt %	At %
C K	28.97	45.35
O K	17.75	20.87
NaK	19.30	15.78
MgK	00.78	00.61
AlK	00.93	00.65
SiK	01.15	00.77
ClK	22.46	11.92
CaK	08.67	04.07

Element	Wt %	At %
C K	34.45	50.29
O K	21.14	23.16
NaK	17.41	13.28
AlK	01.78	01.15
SiK	00.91	00.57
ClK	15.81	07.82
K K	00.28	00.12
CaK	08.23	03.60

Element	Wt %	At %
C K	27.91	43.02
O K	20.34	23.54
NaK	23.04	18.55
MgK	01.39	01.06
ClK	20.18	10.54
CaK	07.15	03.30

Fig. 13. EDX pattern of limestone samples:
a - from Osorkon II, b - sample from Psusennes I, c - sample from Shoshenq III

Mortar samples

According to the XRD analysis (tab.1), the mortar mineral composition consists mainly of *Gypsum* ($CaSO_4 \cdot 2H_2O$), *Calcite* ($CaCO_3$), *Dolomite* ($Ca,Mg(CO_3)_2$), *Quartz* (SiO_2) and *Halite* (NaCl). The *Gypsum* is the binder materials of mortar, the *Calcite* and dolomite can originate from limestone powder, *Quartz* from aggregates and *Halite* from salts.

SEM investigation of the wet mortar samples showed the collapse of internal structure, voids, loose of binding material and *Halite* salts crystallization between mineral grains. It also showed how the *Halite* salt exits from inside the mortar in the form of gaps like the crater of the volcano, as it shows the *Gypsum* mineral and its severe impact on moisture (Fig. 14).

Considering the EDX results (Fig. 15a and b), it can be concluded that, the mortar between limestone blocks in royal tombs, were prepared with lime and *Gypsum*. The presence of chloride and sodium reflects the *Halite* salts which play an active role in the deterioration of the building materials in royal tombs in San El Hager.

Samples of soil were taken under the royal tombs in Tanis. According to the XRD analysis indicated that it consists essentially of *Quartz*, *Halite*, *Calcite*, *Gothite* and *Orthoclase* were also found (Table 1).

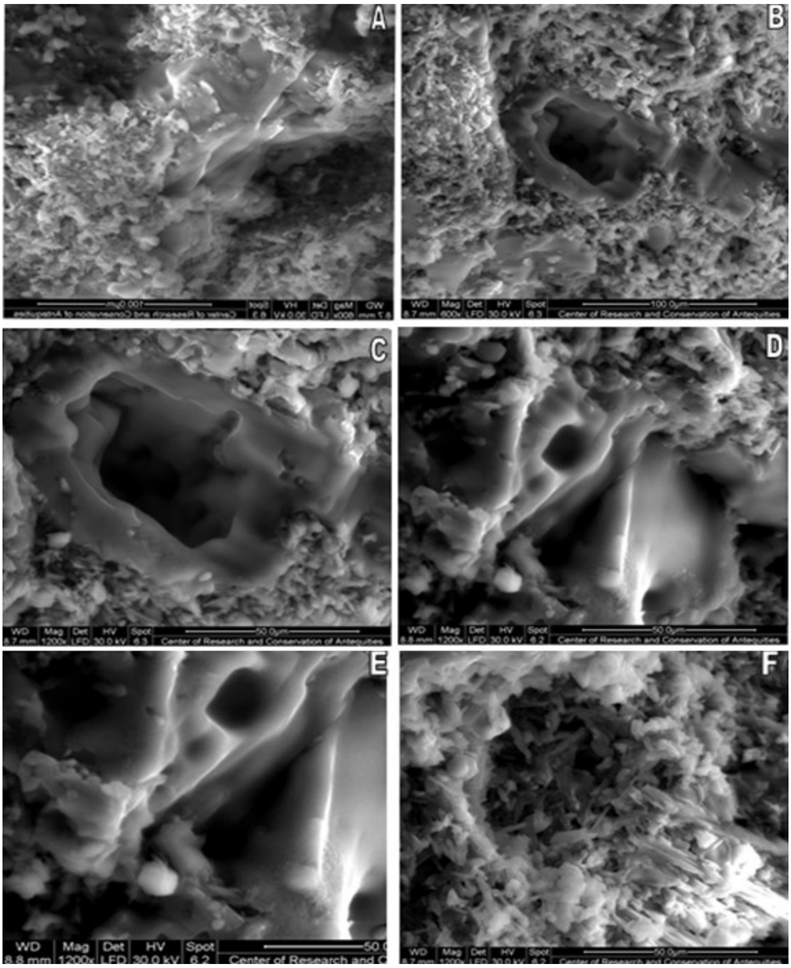
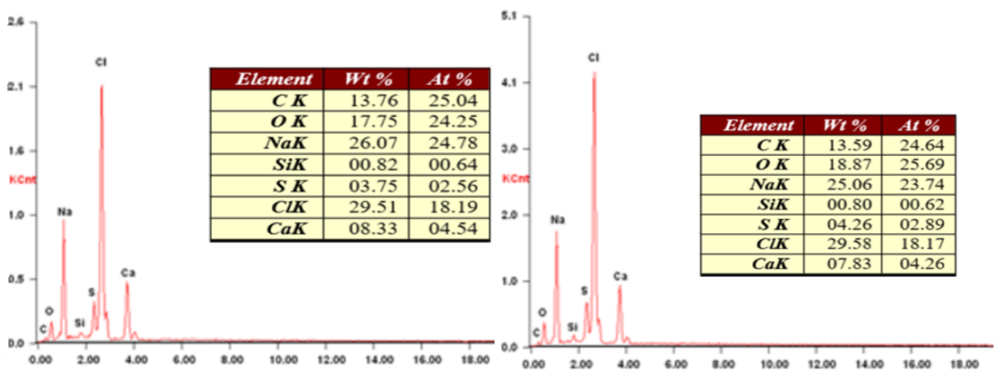


Fig. 14. SEM micrographs of a wet mortar sample with a high percentage of salts at different magnifications shows the salt encapsulation of the mortar grains. It also shows how the *Halite* salt exits from inside the mortar in the form of gaps similar to the crater of the volcano, as it shows the Gypsum mineral and its severe impact on moisture



Element	Wt %	At %
C K	13.76	25.04
O K	17.75	24.25
NaK	26.07	24.78
SiK	00.82	00.64
S K	03.75	02.56
ClK	29.51	18.19
CaK	08.33	04.54

Element	Wt %	At %
C K	13.59	24.64
O K	18.87	25.69
NaK	25.06	23.74
SiK	00.80	00.62
S K	04.26	02.89
ClK	29.58	18.17
CaK	07.83	04.26

Fig. 15. EDX pattern of mortar samples, a- from Osorkon II, b-sample from Psusennes I

Table 1. XRD pattern of building materials at the royal tombs in San El-Hager

Samples	Location	Minerals	Percentage %
Granite	The burial chamber of Osorkon II	*Microcline* ($KAlSi_3O_8$) *Orthoclase* ($KASi_3O_8$) *Quartz* (SiO_2) *Anhydrite* ($CaSO_4$) *Gypsum* ($CaSO_4 \cdot 2H_2O$) *Halite* (NaCl)	49% 21% 21% 4% 3% 2%
Granite	The tomb`s gate of Osorkon II	*Quartz* (SiO_2) *Orthoclase* ($KAlSi_3O_8$) *Microcline* ($KAlSi_3O_8$) *Gypsum* ($CaSO_4 \cdot 2H_2O$) *Halite* (NaCl) *Calcite* ($CaCO_3$)	55 % 18 % 14 % 8 % 3 % 2 %
Limestone	The tomb of Shoshenq III	*Calcite* ($CaCO_3$) *Halite* (NaCl) *Dolomite* ($Ca,Mg(CO_3)_2$)	93 % 4.5 % 2 %
Limestone	Outdoor of Osorkon II tomb	*Calcite* ($CaCO_3$) *Halite* (NaCl)	93% 7%
Salts	The burial chamber of Osorkon II, the burial chamber of Psusennes I, the burial chamber of Shoshenq III, the hall of Psusennes I tomb	*Halite* (NaCl)	100%
Salts	The outer wall of Shoshenq III tomb	*Halite* (NaCl) *Calcite* ($CaCO_3$)	98% 2%
Salts	The outer wall of Psusennes I tomb	*Halite* (NaCl) *Calcite* ($CaCO_3$) *Gypsum* ($CaSO4 \cdot 2H_2O$)	91% 6% 2.5%
Wet mortar sample	The well of Osorkon II tomb	*Halite* (NaCl) *Calcite* ($CaCO_3$) *Gypsum* ($CaSO_4 \cdot 2H_2O$) *Dolomite* ($Ca,Mg(CO_3)_2$) *Hematite* (Fe_2O_3) *Quartz* (SiO_2)	27.5 % 15.5 % 29.3 % 8.9 % 6.9 % 1.9 %
Dry mortar sample	The wall of the hall of Osorkon II tomb	*Quartz* (SiO_2) *Calcite* ($CaCO_3$) *Gypsum* (CaSO4·2H2O)	87 % 7 % 6 %
Wet mortar sample containing salt	The hall of Psusennes I tomb	*Halite* (NaCl) *Gypsum* ($CaSO_4 \cdot 2H_2O$) *Calcite* ($CaCO_3$) *Dolomite* ($Ca,Mg(CO_3)_2$) *Hematite* (Fe_2O_3)	22.9 % 35.1 % 19.6 % 11.8 % 10.4 %
Soil	Soil under Psusennes I tomb	*Quartz* (SiO2) *Calcite* ($CaCO_3$) *Halite* (NaCl) *Diopside* ($CaMgSi_2O_6$) *Tridymite* (SiO_2) *Orthoclase* ($KaAlSi_3O_8$)	% 65 % 18 % 6 % 6 % 3 % 2
Soil	Soil under Osorkon II tomb	*Quartz* (SiO_2) *Halite* (NaCl) *Gothite* (FeO·OH) *Orthoclase* ($KAlSi_3O_8$)	52 % 20 % 13 % 4 %

Chemical studies of groundwater

The chemical analysis of the water samples taken from under the foundation of the royal tombs in San El -Hager showed that the water sample is rich in sodium (Na^+), chloride (Cl^-), potassium (K^+), magnesium (Mg^{2+}) ions. The water also has a high content of bicarbonates (HCO_3^-) sulphates (SO_4^{2-}) and nitrate (NO_3^-). pH was 9 and the temperature was 24°C, the electrical connection (CND) 44.7mL/L and TDS (28.608mL/L). the investigations results are shown in (Fig. 16).

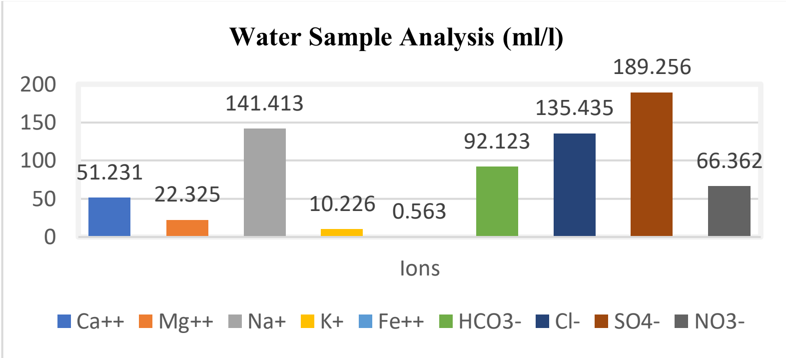


Fig. 16. Show the chemical analysis and ASS results of groundwater analysis from under foundation of tombs at San El-Hager

Physical and mechanical properties of granite and limestone

The physical properties (water absorption, porosity) detected that the limestone in royal tombs in San El-Hager is characterized by high porosity (20.1%), which gives the stone a high-water absorption rate (17.6%) and its consequent ability to absorb water with salt solution and this is the main cause of deterioration.

Mechanical properties (Compressive strength) were determined for untreated limestone samples, the results showed that the strength of limestone in the royal tombs characterized by poor mechanical characteristics by 178kg/cm^2 Dry and 147kg/cm^2 Wet (Fig. 10). The changes of physical and mechanical properties of the stone were a result of weathering process.

Discussion

Through the results of examining samples of granite rock using in the royal tombs in San El-Hager the, it was found that it consists of *Quartz* (SiO_2), *Microcline* ($KAlSi_3O_8$), *Plagioclase* ($NaAlSi_3O_8$), *Biotite* ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)2$, *Brucite* ($Mg(OH)_2$), *Apatite* ($Ca_5(PO_4)_3(F,Cl,OH)$, *Sphene* ($CaTiSiO_5$) and *Hornblende* ($(Ca,Na)_{2–3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$). Also, the microscopic examination indicated large grains of *Quartz* and *Orthoclase* with the presence of erosion. Traces of sodium chloride (*Halite*) salts were found between grains which are considered most strongly influencing the level of stone degradation, the salt pressure crystallization of Sodium chloride between the grains cause main stone exfoliation [15-17]. displacement and separation of some grains and the spread of cracks and gaps with *Halite* salt crystals between the grains. These results confirmed with analysis by EDS.

The physical and mechanical properties tests of granite indicated that, the stone can be classified as weak to medium strength according to the standard tables. This is the result of the effect of various damage factors, especially the effect of subsurface water and its dissolved salt ions.

Through the results of Petrographic examination samples of limestone in royal tombs at San El Hager, it was found that it consists mainly of the *Calcite* in addition to fossils fragments and grains of sand, these grains embedded and coherent with *Calcite* cement. The microscopic examination also showed, most of the fossil fragments suffer from metaphorical changes such as (re-crystallization, dolomitization, solutions). XRD results indicated that, the limestone in the tombs is dolomitic limestone, which consists mainly of *Calcite* and a large proportion of *Dolomite*.

SEM examination showed that the limestone in the tombs consisted of *Calcite* grains with eroded edges, SEM photograph showed that, there a wide range of deterioration features as shown in (Fig. 12), such as micro exfoliation, micro pitting, macro and micro-cracks, etching features in some *Calcite* grains, indicating micro dissolution processes (chemical weathering). The examination also revealed the displacement of the *Calcite* cement, and the presence of *Halite* grains instead of. In addition, complete penetration of salt crystals into the stone were noticed clearly, which causes severe and destructive pressure to the stone resulting in cracks and separation of the layers of the stone. This explains the presence of a thick layer of *Halite* salt covering the wall reliefs in the tombs (Fig. 4).

Considering the EDX and XRD results, it can be concluded that, the mortar between limestone blocks in royal tombs, were prepared with *Gypsum* and limestone powder, in addition to iron oxide. The percentage of mortar components varied from one place to another, even if the percentage of *Gypsum* increased, but the percentage of *Quartz* was not fixed in most of the samples, as it was found in very few percentages in some samples and others were not completely present, while some samples (especially from bonding mortar) showed the presence of large percentage of *Quartz* sometimes reached 87%, however.

The examination also proved that the mortar contained a high percentage of iron oxide (*Hematite* - Fe_2O_3), which reached 11% in most samples, which indicates that ocher was intentionally added to the mortar and plater to reduce the sharpness of the whiteness of the mortar, also the color of the mortar converges to the color of the building stone, and this is customary in the Pharaonic civilization.

XRD, EDS and microscopic examination proved that the mortar is completely saturated with *Halite* salt, as salt was monitored in all mortar samples in very large proportions (reached in some samples 40%), which demonstrates the intensity of the salt weathering of the mortar, which led to the mortar losing its main function of linking the stone blocks with each other to the tombs of San Al-Hagar

It was evident through the study of XRD for the salt samples, sodium chloride is the abundant salt in the building materials in the tomb of San El-Hager, whose percentage reached 100% in most samples, which proved that it is the only salt that causes salt weathering in the royal tombs. This is very dangerous because of the hygroscopic properties and the danger of the process of solubility and re-crystallizing which play an active role in the deterioration of the relives, colored inscriptions and plaster layers in Tanis. These salts are directly visible as efflorescence, which periodically appears and disappears depending on the presence or absence of moisture sources [18]. Moisture must be present to allow for the salt to settle on the rocks, so that as the salt solution evaporates as variation on humidity and temperature [19]. The salt begins to crystallize either on stone surfaces “efflorescence", beneath the surfaces "sub- efflorescence" or within the pore of the stone itself "crypto efflorescence" particularly with repeated wetting and drying cycles which eventually cause stone deformation [20]. Porous rock is also needed so that there are pore-spaces for the salt to crystallize within. These salt crystals pry apart the mineral grains leaving them vulnerable to other forms of weathering. The building material becomes weakened by pressures brought on by salt crystallization in pores until its mechanical strength is surpassed and damage results [21]. The hydrostatic pressure generated by salt crystallization disintegrates the stone. Salt-induced decay of porous, granular limestone is often manifested initially by contour scaling followed by retreatment of the rapid surface through granular disintegration and/or multiple flaking [22]. This action is an aggressive deterioration form that affects all stone surfaces, mortars, and renderings because of saline solutions penetrating the pores of the stone.

Sodium chloride salt was also detected in limestone samples by a rate of 7%, which is a very large percentage, as it was also found in granite samples at a rate of 3% and mortar samples with a rate of 40% and soil samples below the tombs with a rate of 30%. This indicates the extent of the deterioration of the state of the tombs, especially in the event of a permanent source of moisture and salts, and the presence of sodium chloride in the tombs in this amount is strong evidence of the movement of water inside the tombs for long time.

Gypsum was also monitored in some granite samples by a rate of 8 %, which indicates the transmission of *Gypsum* from the mortar to granite through the subsurface water. The source of *Gypsum* in granite samples can also be from air pollution, *M.S. Jones et al.* [23] pointed out the role of sulfur oxides in the damage of granite in the presence of high humidity and its transformation into sulfuric acid, which attacks the surfaces of the granite, where the hydrogen ion H^+ produced from the acid and the calcium ion Ca^{2+} produced from the weathering of plagioclase and some other additional minerals combine to turn into *Gypsum*, which It crystallizes inside the granite, causing micro cracks that lead to an increase in the number of cavities and widening, serving as channels for salt solutions.

It was also clear through the atomic Absorption that the subsurface water in the area around the tombs very salty (24g/L), which gives the impression that it is the main source of salts affecting the deterioration of the condition of the tombs. The concentration of some elements was determined such as sodium (141.5mg/L), calcium (51.55mg/L), magnesium and potassium. The percentage of soluble solids in this water reached (28.6g/L), which led to the high electrical connection coefficient of that water, reaching (44.7mg/L). It was also clear through chemical analysis of soil and groundwater samples that the percentage of chlorine and bicarbonate was high, as sulfate and silica were determined in the soil and groundwater and the pH was 9. The most significant chemical process employing salinity ground water to degrade stone is the production of salt crusts on calcareous stone. On a porous stone, these crusts cause it to crumble into a powder, while on limestone, they cause thick crusts to form [24].

The presence of potassium and magnesium in a high percentage in the groundwater explains that it is likely to be the result of the seepage of agricultural drainage water from drains and agricultural lands surrounding the archaeological site, where potassium is used as fertilizer for agricultural lands. The high percentage of these elements can also be attributed to the intrusion of saline water from Lake Manzala. As for sulfates, their presence is largely due to their leakage from the surrounding agricultural lands, where farmers use them to treat saline soil and it is called agricultural *Gypsum*.

Conclusion

Through the results of the study of components and products of deterioration to the royal tombs in San El-Hager, it showed that it suffers from many deterioration factors, whose effects appear in high moisture in the walls of the tombs, especially the "Psusennes I" and “Osorkon II” tombs, in addition to extensive salts, which contributes to more deterioration with the migration of more salts for the walls, especially as they are rapidly soluble salts in the water, which weakens the structure of the inner stone. Because of the proximity of the tombs to Manzala Lake and Bahr al-Baqar Canal, and the presence of some agricultural drains and highly saline agricultural lands around the archaeological site, they suffer greatly from saltwater intrusion into them, and given the location of the royal tombs in a relatively low area of the archaeological hill, which made it a site for collecting this highly saline water.

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