ARCHAEOMETRIC AND PETRO-MINERALOGICAL REMARKS ON DAMAGED EGYPTIAN WALL PAINTINGS, EL-QURNA NECROPOLIS, UPPER EGYPT

ARCHEOMETRIAI ÉS PETROARCHEOLÓGIAI MEGFIGYELÉSEK A FELSŐ-EGYIPTOMI EL-QURNA NEKROPOLISZ MEGRONGÁLÓDOTT FALFESTMÉNYEIN

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Abstract

The present study aims at characterizing the main deterioration mechanisms affecting some Egyptian wall paintings of Theban tombs (TT277&278), El-Qurna, Upper Egypt. Several weathering products were observed on the painted surfaces representing different degrees of decay. The morphology and microanalysis of the studied samples were performed by scanning electron microscopy equipped with an energy dispersive X-ray analysis system (SEM−EDS). The mineralogical characterization was carried out using X-ray powder diffraction analysis (XRPD), while the petrographic examination on the prepared thin sections was carried out using the polarized light microscope (PLM). The results showed that the limestone types in the area are microsparry calcite embedded in a micrite matrix rich in fossils and grains of quartz. XRPD data showed that the main crystalline phases in the limestone samples are calcite, quartz, anhydrite, halite and clay minerals. The results showed that the damage of the examined wall paintings is mainly attributable to the effect of different salts such as halite (NaCl), gypsum ($CaSO_4{\cdot}2H_2O$), and sylvite (KCl). The blue pigment was identified as Egyptian blue (Cuprorivaite), the red pigment as hematite (red ochre) and the yellow pigment as goethite (yellow ochre). The obtained results will help in drawing a conservation plan for the damaged wall paintings in the area.

Kivonat

Ez a tanulmány a thébai (Egyiptom) sírkamrák falfestményeit leggyakrabban károsító tényezők jellemzésével foglalkozik a TT277&278 jelű objektumok (El-Qurna, Felső Egyiptom) vizsgálata alapján. A festett felületeken többféle mállási terméket lehetett megfigyelni a károsodás különféle stádiumaiban. A vizsgált minták morfológiai és kémiai elemzését energia-diszperzív Röntgen-spektrométerrel felszerelt pásztázó eléektronmikroszkóppal végeztük (SEM−EDS). Az ásványtani vizsgálatokat Röntgen-pordiffrakcióval (XRPD), a kőzettani meghatározást polarizációs kőzettani mikroszkóppal (PLM) végeztük el megfelelően előkészített vékonycsiszolatokon. Eredményeink szerint a területen használt mészkövek mikropátitos kalcitot és kvarc-szemcséket tartalmaznak ősmaradványokban gazdag mikrites alapanyagba ágyazottan. A röntgen pordiffrakciós vizsgálat szerint a fő ásványfázisok a kalcit, kvarc, anhidrit, kősó és a különféle agyagásványok. A falfestmények károsodását leginkább különféle sók okozzák, így a kősó (NaCl), a gipsz ($CaSO_4{\cdot}2H_2O$), és a szilvit (KCl). A kék festékanyagban az ú.n. egyiptomi kék *pigmentet ismertük fel, a vörös festék anyaga hematit (vörös okker), a sárga festékanyag götit(sárga okker). Eredményeink hozzájárulnak a területen előforduló falfestmények védelmére megfelelő konzerválási stratégia kialakításához.*

KEYWORDS: EL-QURNA, WALL PAINTINGS, PETROGRAPHY, XRPD, SEM–EDS, SALTS

KULCSSZAVAK: EL-QURNA, FALFESTMÉNY, KŐZETTAN, RÖNTGEN PORDIFFRAKCIÓ, PÁSZTÁZÓ ELEKTRONMIKROSZKÓPIA, ENERGIA DISZPERZÍV RÖNTGENSPEKTROSZKÓPIA, SÓK

Introduction

The Theban necropolis is located in the west bank of the river Nile at the city of Luxor (about 670 km south of Cairo). The tombs of the Nobles are spread over an area of about two square miles from Dra Abu el Nega in the north to Der el Medina in the south. There are more than three hundred tombs belong to officials of the New Kingdom (c.1570–1070 BC) (Kamil 1976). The main objective of this study was to emphasis some archeaometric, petrographic and mineralogical remarks through the application of different analytical techniques (PLM, XRPD and SEM–EDS) to study samples collected from the wall paintings of two Theban tombs (Tomb No. TT277 of Amenemonet (Jmn-m-jn.t), divine father of the mansion of Amenophis III, the 19th Dynasty (Foucart 1918; Gautier 1920) & Tomb

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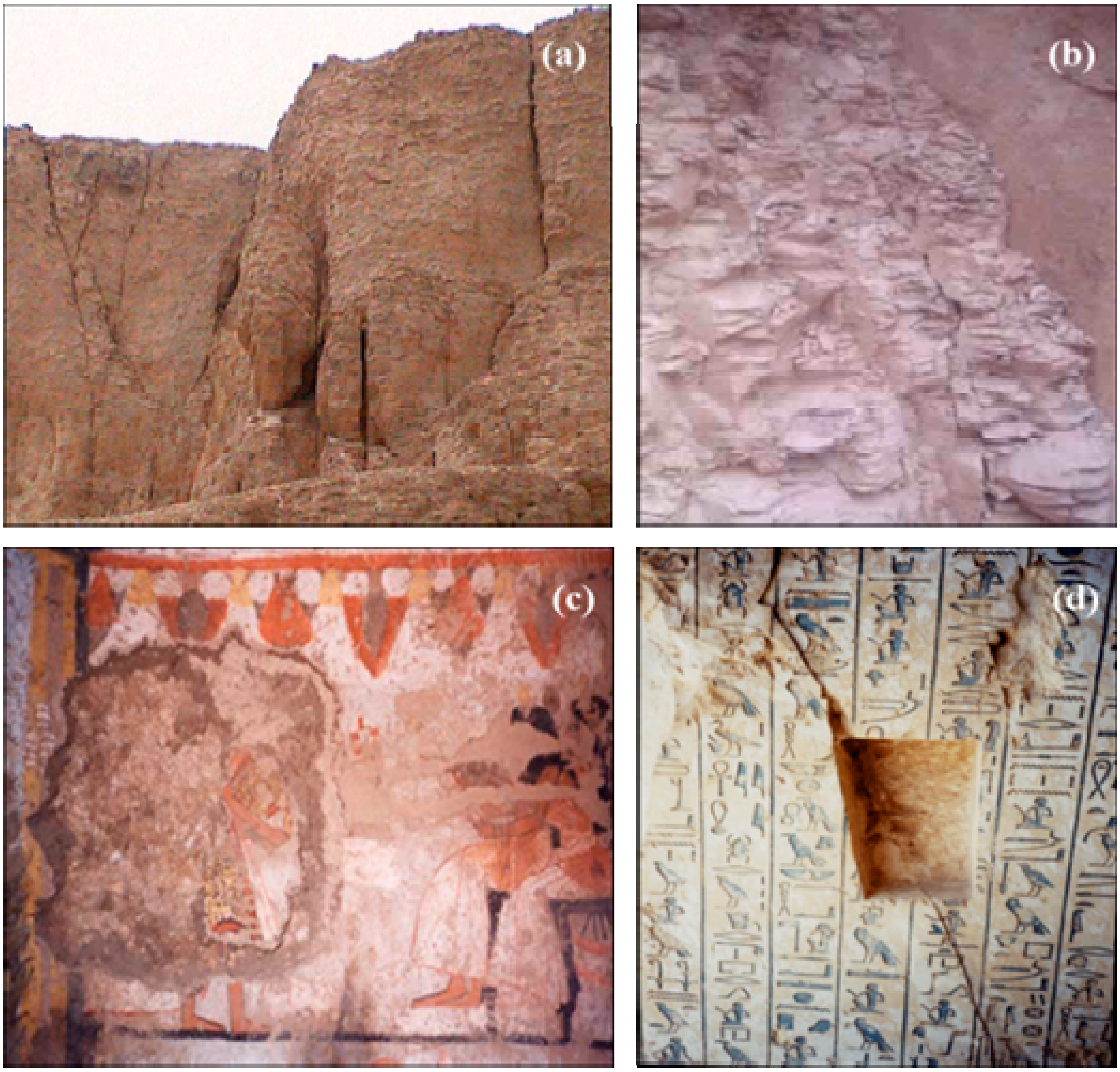

Fig. 1.: a) several rock joints in the Theban Mountain, b) marl and soft limestone at the Theban formation, c) detachments in the wall paintings (Tomb No. TT278), d) micro and macro cracks in a painted limestone relief (Tomb No. TT192).

1. ábra: a) Töredezett kőzetek a Thébai Hegységben, b) márga és puha mészkő a Thébai Formációban, c) leváló falfestmények (TT278 sz. sírkamra), d) mikro- és makrorepedések egy festett mészkő reliefen (TT192 sz. sírkamra).

No. TT278 of Amenemheb (Jmn-m-hb, Jmn-m-h3b), herdsman of Amen-re, the 20th Dynasty (Vandier d'Abbadie 1954; Porter & Moss 1960; Kampp 1966), Qurnet Murai, El-Qurna, Upper Egypt. The obtained results will be of importance to characterize the composition of these wall paintings and to understand the main weathering mechanisms affecting in order to ensure the best conservation decision. **Figure 1** illustrates several deterioration forms on the wall paintings of the Theban tombs.

Petrographic examinations allow us to determine the exact typology of the stone, its physicochemical properties and its state of preservation. In addition to the identification of specific minerals, thin section petrography also involves the study of mineral and rock textures, coarseness, and the relative or quantitative percentage of various constituents (Reedy 1994). On the other hand, X-ray diffraction is considered the most famous method widely used for characterizing crystalline compounds of cultural heritage materials. X-ray diffraction technique plays an important role in the study of works of art and museum objects; also it helps in answering questions related to degradation processes (Corbeil 2004).

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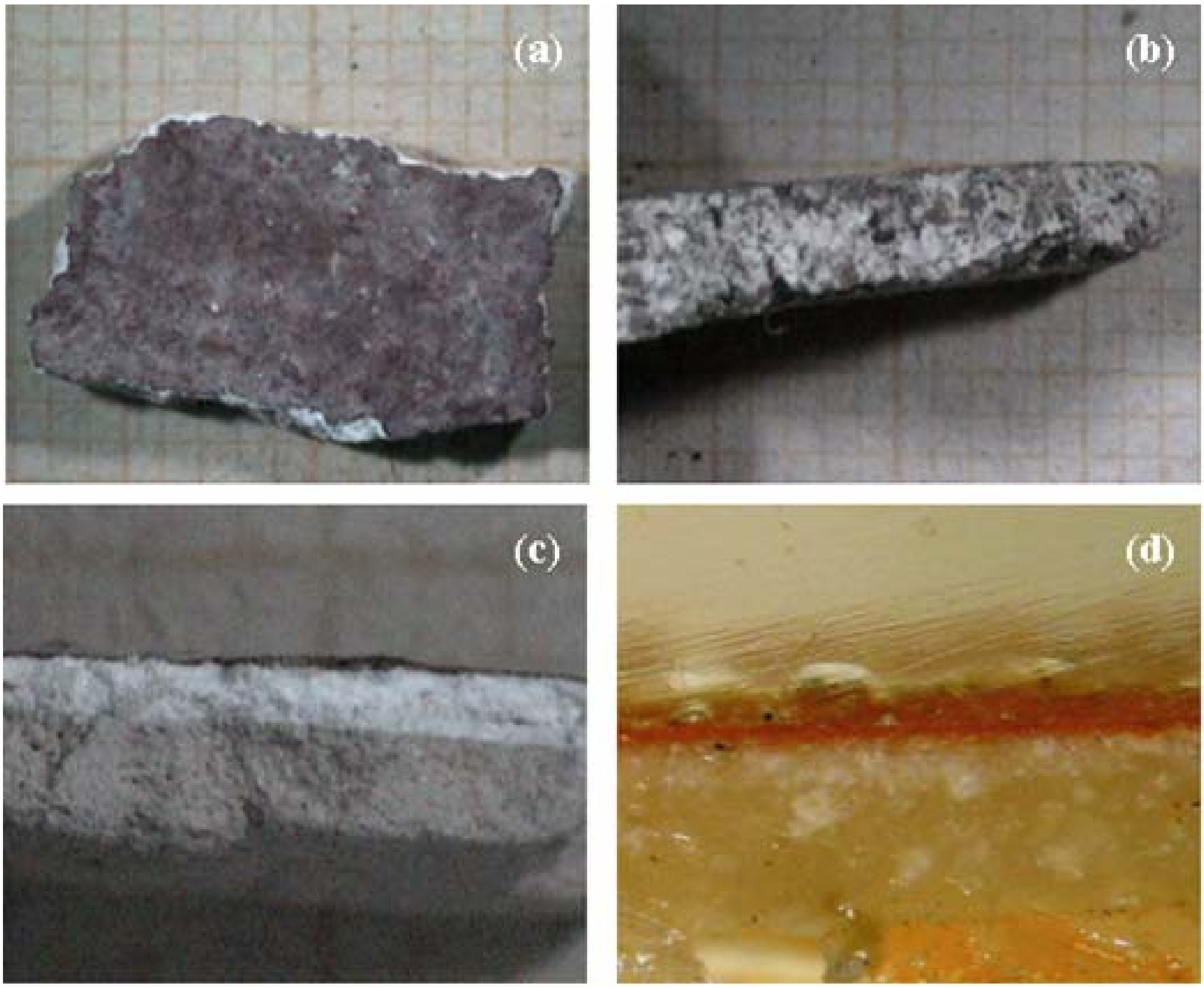

Fig. 2.: Optical images of surface and stratigraphic sections of some painted plasters, a) painted fragment, b) cross section in the coarse plaster layer, c) stratigraphic section of the fine plaster and white wash, d) a close up in red paint layer under reflected light.

2. ábra: Festett vakolat felszín és metszet a) festett töredék, b) durva vakolatréteg metszete, c) finom vakolat és meszelési réteg metszete, d) vörös festékréteg nagyított képe visszavert fényben

The application of the scanning electron microscopy (SEM) to study materials of cultural heritage provides information about mineral morphology, crystal features, and chemical composition. In general, many papers have been devoted to study the geologic structure of Thebes Mountains and to characterize stones from tombs and temples at El-Qurna necropolis (Rutherford & Romer 1977; Curtis 1979; Crutis & Rutherford 1981; El-Baz 1987; El-Banna & Pinińska 1996; McLane & Wüst 2000; Wüst & McLane 2000; Wüst & Schlüchter 2000; Marey Mahmoud 2004; Aubry et al. 2009; Moussa et al. 2009).

Geological background

The Thebes Limestone Formation was defined by Said (1960) and the Thebes Mountains are composed of 350 meter thick Eocene marls and limestones overlying the 60 meter thick Esna shale Formation. The lower levels of the Theban Formation are composed of slightly clayey, sub-chalky limestone, which serves to enclose a few bedrock layers of flint nodules and becomes more massive at greater depths (Guillaume & Piau 2003). Moussa et al. (2009) reported that hard limestone from El-Qurna is a pure calcite, while the soft one consists of dolomite, anhydrite and calcite. Planktonic foraminifera occur sporadically in the Thebes Limestone at Gebel Gurnah, and include, i.al., Ac. interposita, Ac. pentacamerata, Ac. triplex, Ac. pseudotopilensis, Igorina broedermanni, M. aragonensis, M. caucasica, Pseudohastigerina wilcoxensis, Subbotina patagonica / rosnaesensis group (Aubry et al. 2009).

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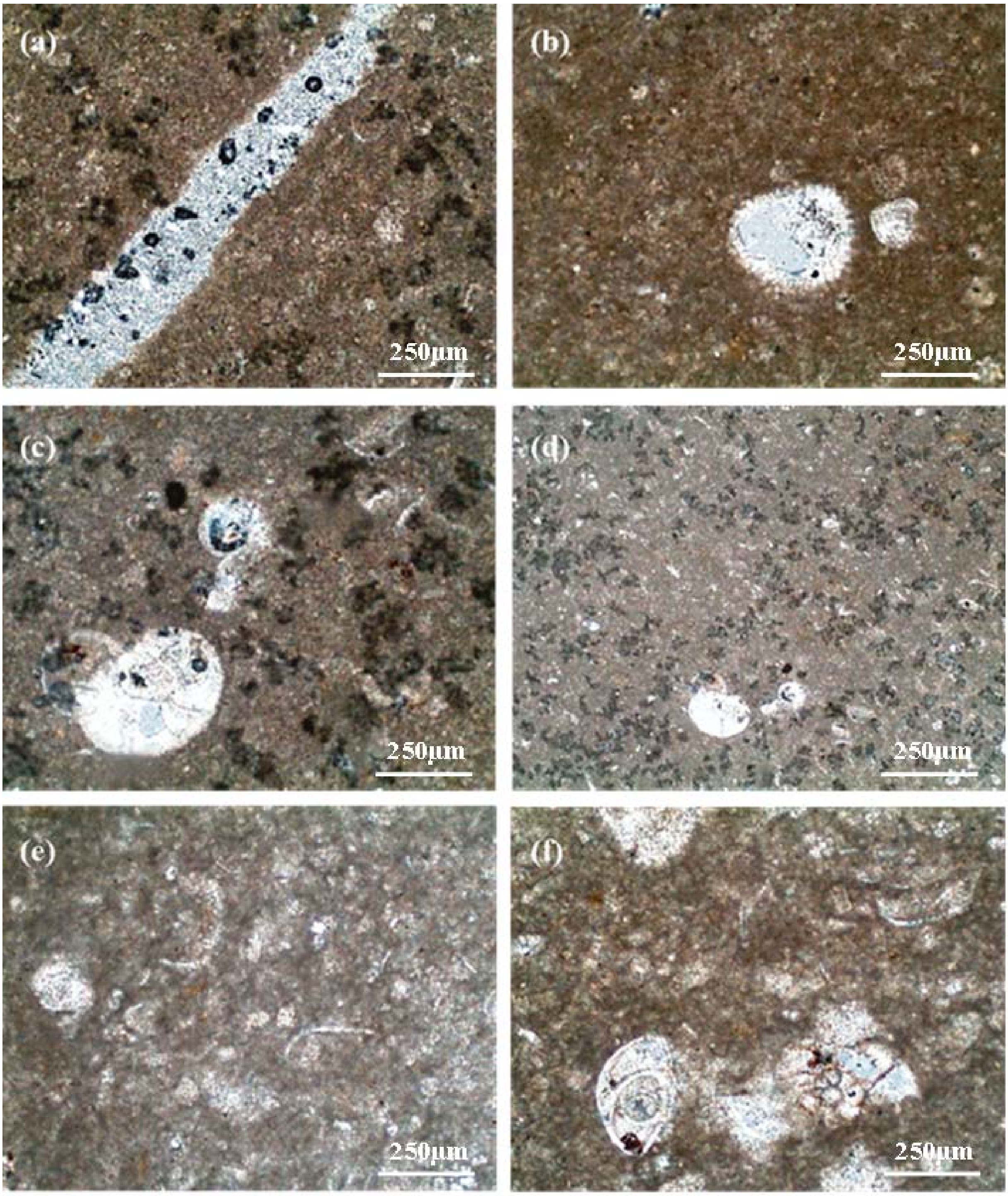

Fig. 3.: Photomicrographs (C.N, 65X) of thin-sections prepared on the limestone samples, a) fossils and amorphous silica grains in a micritic matrix, also we can notice some veins are re-filled with sparry-calcite; b–e) microcrystalline calcite, fossils and quartz grains are embedded in a micritic matrix; f) a typical planktonic foraminiferal embedded in a biomicritic matrix.

3. ábra: Vékonycsiszolati felvételek (X.N, 65x) a mészkő mintákról, a) ősmaradványok és amorf kovaszemcsék mikrites mátrixban, pátitos kalcit erekkel; b–e) mikrokristályos kalcit, ősmaradványok és kvarcszemcsék mikrites mátrixban; f) jellegzetes plankton foraminifera biomikrites mátrixban

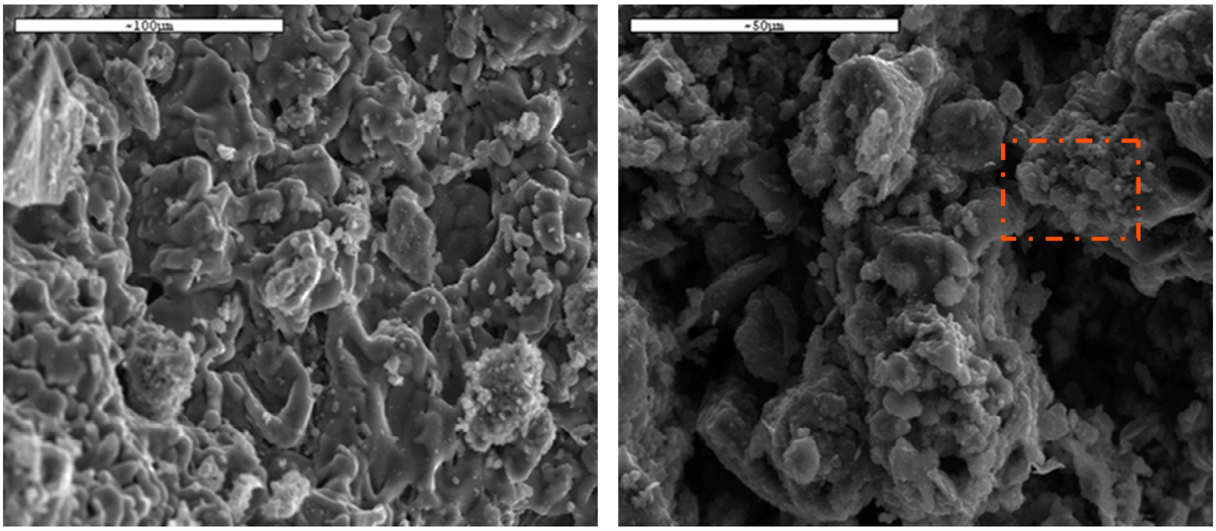

Fig. 4.: Representative SEM micrographs of limestone samples, left): heavy waxy salt coatings of sodium chloride salts; right): crystallization of different salt phases between the grains of the stone surface.

4. ábra: Jellemző pásztázó elektronmikroszkópos kép a mészkövekről, balra): vaskos viaszos kősóréteg a felületen; jobbra): különféle kristályos só fázuisok a szemcsehatárokon.

Materials and methods

Sampling and analytical methods

Representative stone samples were selected and appropriate thin sections were prepared for the petrographic examinations. The powder of the samples was analyzed for the determination of chemical and mineralogical composition. Furthermore, tiny pigment samples were collected under the stereo microscope using a metallic scalpel. The stratigraphic structure of the plaster layers was examined using a Zeiss (stemi DV4) stereomicroscope with a Sony camera (DSC-S85). The prepared thin sections of stone samples were observed using a Leitz Orthoplan polarizing microscope. In this study a JEOL JSM-840A scanning electron microscope equipped with an energy dispersive X-ray (EDS) Oxford ISIS 300 micro analytical system was used to investigate the weathered layers. Operating conditions were: accelerating voltage 20kV, probe current 45nA and counting time 60 seconds, with ZAF correction being provided on-line. The collected damaged layers have been grounded into a powder in an agate mortar and studied by powder X-ray diffraction method (XRPD) in order to determine their mineralogical composition. XRPD analysis was performed using a Phillips PW 1840 diffractometer with Ni-filtered Cu-k_α radiation. The samples were scanned over the 3–63° 2θ intervals at a scanning speed of 1.2°/min.

Results and discussion

Optical examination of the plaster layers

Figure 2 shows optical images obtained on the surface and some stratigraphic sections of the painted plasters. From the optical examination, we can distinguish three plaster layers used to overcome faults in the wall and to produce flat and smoothed surface for painting. The first layer is the smoothed preparation layer (white wash) with a thickness ranges from 100 to 150 µm. The second layer is the thin fine plaster which shows a thickness ranges from 200 to 350 µm. The third one is a slightly thick coarse plaster which shows a thickness ranges from 10 to 30 mm.

Petrographic examination

The results of the petrographic examination of the studied limestone samples are given in **Figure 3.** The microscopic observations show a microcrystalline calcite matrix with fossils and quartz grains are embedded in a micritic matrix. A large number of fossils and grains of quartz can be observed in the bedrock samples (**Fig. 3a**). Foraminifera, grains of quartz in addition to microcrystalline calcite are embedded in a micritic matrix (**Fig. 3b–e**). **Figure 3f** shows typical planktonic foraminifera embedded in a biomicritic matrix. Foraminifera can be major rock forming elements in open -or restricted- shelf as well as deeper marine deposits (Scholle & Dulmer-Scholle 2003).

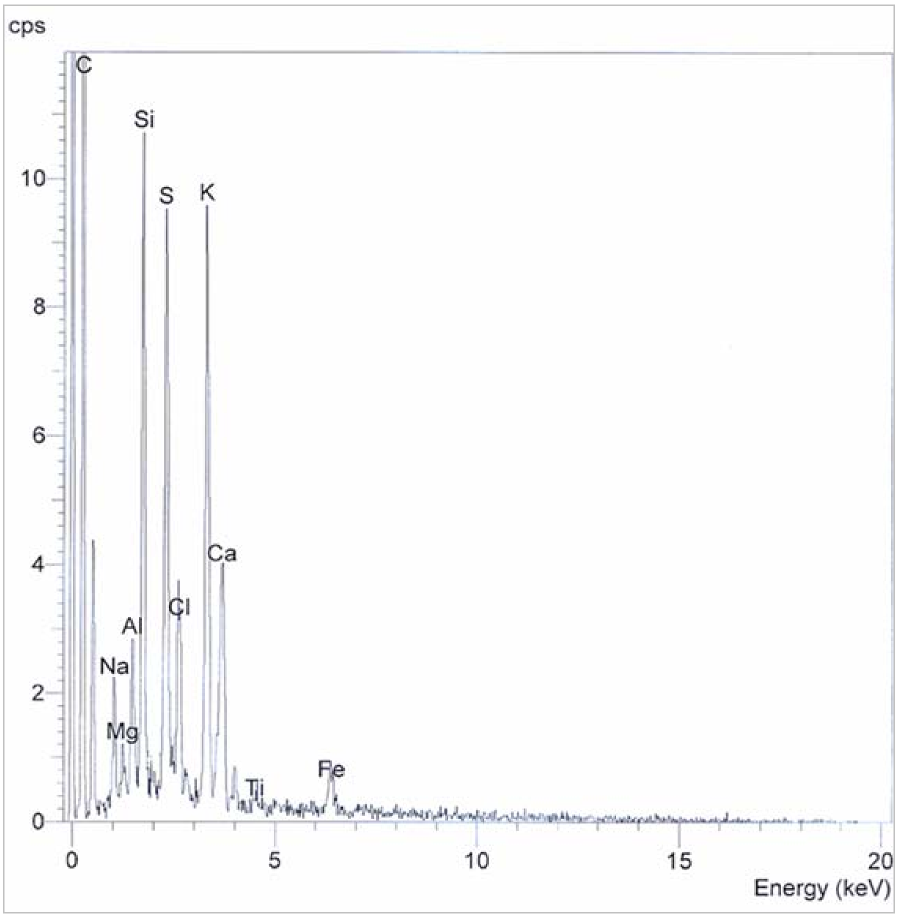

Fig. 5.: An EDS spectrum of a weathered limestone sample.

5. ábra: A mállott mészkő felület EDS spektruma

Mineralogical and morphological characterization

XRPD data showed that limestone samples consist mainly of calcite ($CaCO_3$) with minor amounts are quartz (SiO_2) and anhydrite ($CaSO_4$), while traces of halite (NaCl) and clay minerals (illite-montmorillonite) were also determined. XRD analysis of the plaster layers showed that the preparation layer consists of anhydrite with traces of calcite and quartz. The fine plaster consists mainly of calcite and clay minerals while the coarse plaster consists mainly of quartz, calcite and plagioclase (albite, $NaAlSi_3O_8$). Representative SEM micrographs of the outer surface of the damaged stone samples are shown in **Figure 4**. Salt crystallization is clearly observed in form of waxy coatings of halite and crystals of different salts. The EDS spectrum obtained on a weathered limestone sample, it is highlighted with a red square in figure 4, (**Fig. 5**) showed that the main ions contained in the sample are Si, S and K, with minor ions of Ca, Cl, Al, Na and Mg, while traces of Fe and Ti were also detected. From the XRD data, it was found that the sample is consisting of gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite, dolomite [CaMg $(CO_3)_2$], halite and sylvite (KCl). EDS microanalysis of the blue pigment showed that Ca, Cu and Si are the major ions contained giving the chemical formula of cuprorivaite ($CaCuSi_4O_{10}$), with minor elements of Ca and S while traces of Fe and Ti were also measured. EDS microanalysis of the red pigment showed that the peak of Fe is present which is indicating the existence of iron oxide (probably of hematite, Fe_2O_3) as possible colouring material. Minor ions of Ca and S were also detected, while the low concentration of Si and Al indicates possible existence of aluminosilicate material (clay) naturally found in ochre pigment. EDS microanalysis of the yellow pigment showed the peak of Fe is present which is indicating the existence of iron oxide (probably of goethite, FeOOH).

Deterioration aspects

The biggest hazard to the area is the flood water that penetrates into the structures. Furthermore, the deterioration becomes more effective due to the presence of swelling clay minerals and soluble salts in the geological structure. Moreover, the water seepage from the nearby houses and the cultivated lands represent another source of saline ions which react with stone material and re-crystallize in form of different salt phases. Salts can damage stone and other building materials through a range of other mechanisms as well, such as differential thermal expansion, osmotic swelling of clays, hydration

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pressure, and enhanced wet/dry cycling caused by deliquescent salts (Smith 1994). NaCl was identified in all samples. Halite is one of the most abundant and ubiquitous (Lubelli et al. 2006), and it is a natural impurity in the Egyptian soil; and a common mineral in marine sediments. Hence, the source of the salts in the Thebes area is mainly the bedrock (Wüst and Schülchter 2000). The deterioration caused by gypsum is the result of its crystallization within the porous material matrix. The damage mechanism can be in form of stresses generated during the growth of gypsum crystals, generally called crystallization pressure. Because of its low mobility, gypsum tends to accumulate in large pores, and in an enhanced moisture retention thus facilitating gypsum re-crystallization and development of larger crystals (Steiger 2003). According to Moussa et al. (2009), Esna shale at the Thebes Mountains is consisting mainly of clay minerals (smectite + illite) with other components of calcite, dolomite, quartz and halite. In her study of A1-Muzawaka cut-rock tombs situated at Dakhla Oases, Western desert in Egypt, Helmi (2000) has reported that the crystalline swelling of clay is well known in expandable clay minerals such as montmorillonite, smectite and vermiculite. Damage of the wall paintings produced by swelling clays and particularly in the presence of salts is mainly resulting in form of detachments, disintegration of the inner structure and micro/macro cracks on the painted surfaces.

Concluding remarks

The archaeometric petro-mineralogical characterization of damaged wall paintings of two Theban tombs (TT277&TT278, EL-Qurna) allowed the identification of the main petrographic parameters and components of these murals. The petrographic analysis revealed the stone type in the area as microcrystalline calcite embedded in a micritic matrix rich in fossils and grains of quartz. Moreover, the mineralogical characterization showed that limestone samples consist of calcite as major component with minor amounts of quartz and anhydrite while traces of halite and clay minerals were also determined. The main deterioration feature affecting the site is mainly the crystallization of different salt phases inside pores of stone or in form of hard crusts. The dominant salts species affecting in the site are halite, gypsum, and sylvite. The stratigraphic structure of the murals showed that three plaster layers are easily distinguishable. The first layer is based mainly on anhydrite and traces of calcite and quartz. The second layer consists of calcite and clay minerals. The third layer is the coarse plaster which consists of quartz, calcite and plagioclase (albite). A common chromatic palette widely used in ancient Egypt was used, the blue pigment was identified as Egyptian blue (Cuprorivaite), the red pigment as hematite (red ochre) and the yellow pigment as goethite (yellow ochre). Several restoration-conservation interventions of the wall paintings were performed; the partially detached painted fragments were faced with polyamide tissue adhered with a 10% solution of Paraloid B-72 (in toluene) and re-adhered to the wall. The missing parts in the plaster layers were filled with a mortar consists of slaked lime, sand, crushed limestone, clays and an acrylic emulsion (Primal E330S) with ratios: 2:3: 0.5:0.25:1, consequently. Moreover, injection grouts based on a mixture of Primal E330S, powder of limestone and local clayey formations- called Hiba- were used to re-adhere the detached plasters. The removal of the hard salt efflorescences on the painted surfaces is typically first removed by mechanical means. In order to desalinate the soluble salts in the porous matrix, wet poultices (saturated with distilled water) of Japanese tissue and cellulose pulps were used. Taking into consideration that a preliminarily consolidation using Wacker OH stone strengthener (ready to use) was thus applied to protect the pictorial layers. The application of an intervention layer was also used to provide additional protection of the painted surfaces. The application time of the poultices was for 3 days with 4−6 repetitions.

On the other hand, the stabilization process of clay minerals depends mainly on the structure and composition of these materials. The properties of swelling clays could be drastically changed by addition of $Mg(OH)_2$ (Wüst & McLane 2000). For long-term protection, a mixture of acrylic/silane products can be used. The consolidation tests performed on weathered limestone specimens from the Theban tombs showed that a mixture of Wacker OH stone strengthener (Tetraethoxysilane) ready to use and 3% Paraloid B-67 (acrylic co-polymer) solution in toluene succeeded to achieve a significant increase in the durability of the treated samples (Marey Mahmoud 2004). Moreover, water-repellent materials such as Wacker Silres BS SMK1311 (a silicone microemulsion based on silanes and siloxanes) can be applied for further protection in case of water penetration.

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