The role of Rock Composition in the Deterioration of Wall Paintings, Saqqara Area, Egypt: Information from Petrography and Mineralogy

1Adel I.M. Akarish and 2Ahamed S. A. Shoeib

1Geological Sciences Dept., National Research Centre, Cairo, Egypt. 2Dept. of Conservation, Faculty of Archaeology, Cairo University, Giza, Egypt.

Abstract: Petrographical and mineralogical studies have been combined to decipher the causes of deterioration of the wall paintings inside the burial chambers of the rock tombs in the Saqqara area of Egypt, which are hewn within Upper Eocene (Maadi Formation) sediments. The samples were analyzed by polarizing microscope, X-rays diffraction (XRD) and thermal differential (DTA) techniques; along with acid insoluble residues (AIR) were examined using the binocular microscope. The studies reveal that the quality of the support of the wall paintings (the mother rock, or bedrock) in this area is particularly poor. It comprises two various types of lithotopes, marlstone and limestone (mostly argillaceous limestone), which are particularly susceptible to weathering processes in this region. The combination of rock texture, mineralogical composition and diagenetic processes contribute, to a great extent, to the deterioration recognized in the bedrock and in the preparatory plaster layer. The composition of the bedrock and plaster layer being too weak to resist the interaction between the exogenic (surrounding climate) and endogenic (related to the nature of the rock types) conditions over the thousands of years since their construction. The durability of the bedrock is mainly related to clay content and porosity. Furthermore, the obtained results will enhance the stones’ conservation and development of suitable conservation/ restoration techniques.

Key words: Rock Tombs; Bedrock; Rock texture; plaster layer, Clay minerals

INTRODUCTION

The protection and conservation of archaeological sites presents major challenges for the future and is a major responsibility for our current generation. Many archaeological sites in Egypt in general, and in the Saqqara area in particular, have recently suffered from severe degradation, compared to the conditions in which they were originally discovered and excavated, due to: (1) the absence of durable conservation practice, (2) exposure to semi-arid climatic conditions, (3) increasing pollution, and (4) ever-increasing pressure from tourism. The temples, pyramids and tombs of this region are composed of rocks of different types, most commonly limestones. Most of these remains show various signs of degradation (Nakhla, 2003). However, the degree of degradation depends primarily on the interaction of exogenic factors related to surrounding environmental conditions and to endogenic factors related to the sediment texture and composition.

Saqqara is the oldest Ancient Egyptian cemetery, and lies south-west of Cairo (Fig. 1). It is considered to be one of the richest and most highly varied archaeological sites in Egypt. The Saqqara region is a plateau, formed mainly of well-stratified, yellowish, argillaceous limestone, marl and calcareous claystones, with a relatively high content of gypsum veinlets of late Eocene age (Youssef, et al., 1984). In this area, many rock tombs, mostly dated to the Old Kingdom, have been hewn within these Upper Eocene sediments.

The bedrock in the burial chambers of these tombs is coated with plaster (preparatory plaster layer), onto which the decorations are painted. Most of these paintings show signs of decay, however. The bed rock, plaster layers and pigments at these sites have been subjected to different decaying phenomena, both ancient and recent, that need to be taken into consideration when evaluating the requirements for their conservation.

The most important stage of any stone conservation process is the characterization of the stones’ composition and the investigation into the causes of deterioration. If the chemical, mineralogical and petrographical properties of the rocks are not taken into consideration, the choice of intervention technique may be unsuitable, to the extent that it damages the appearance or integrity of the stone. If the causes of the decay are not evaluated and corrective measures taken to stabilize the deterioration, successful intervention may, in fact, be only a temporary palliative (Expert et al., 1981; Preussen, 1987; Price, 1996). As the authors are aware, no detailed work has been carried out to characterize the stones of the wall paintings support of the rock tombs on Saqqara region.

Corresponding Author: Adel I.M. Akarish, Geological Sciences Dept., National Research Centre, Cairo, Egypt.
The present work focuses mainly on deciphering the causes of deterioration of the wall paintings in one of the tombs in the Saqqara region, the Idut tomb (Old Kingdom, 6th Dynasty). The work comprise of an investigation into the petrographic characteristics and mineralogical composition of the wall painting support (mother rock or bedrock) and the preparatory plaster layer, in order to characterize the used rocks. It is hoped this strategy will enhance the stones’ conservation and development of suitable conservation/ restoration techniques.

**General Geological Background:**

The geology of the Saqqara region has been investigated by several workers (e.g. Hume, 1911; Blanckenhorn, 1921; Cuvillier; 1930; Youssef et al., 1984; Papa, 2003). According to Youssef et al. 1984 who performed a detailed study, the Saqqara area necropolis is located on a plateau, at 17m elevation from the alluvial plain of the Nile Valley. This plateau is formed mainly of Upper Eocene limestones, marls and claystones. These rocks (Fig.1) constitute a characteristic lithostratigraphic unit, the Saqqara Member, of the Maadi Formation, which was previously referred to as the Saqqara Limestone by Hume. The area around the Saqqara Pyramid, as well as the bulk of the Saqqara plateau, is formed mainly of an alternating succession (22m thick) of hard, light yellow limestone and semi-hard, yellow marls, exposed along the steep eastern face of the Saqqara plateau. This succession belongs to the upper unit of the Saqqara Member, termed the Upper Calcareous Beds. The Upper Calcareous Beds overlie the Basal Shales Unit (the lower unit of the Saqqara Member). The Basal Shales Unit (4m of exposed thickness) consists of marls and shales with gypsum veins, representing the well-exposed older strata, which can be seen only in the north, at the foot of the Abusir plateau, alongside the remnant Abusir Lake. In the area to the northwest of the plateau, and west of Abusir village, the lithologies differ from those around the Saqqara pyramids. Here, the upper member of the Maadi Formation (Gerain El-ful Member) is exposed. It is about 17.5m thick and formed of highly fossiliferous, sandy and marly limestones and shale. Locally, this member unconformably underlies the early Pliocene Kom El Shallul Formation. The plateau has a cover of Quaternary and Recent gravels, sands and conglomerates of varying thicknesses. The gravels lying above the Calcareous Beds along the eastern edge of the Abusir-Saqqara plateau contain frequent white quartz pebbles (about 10%) and are equated to the highest gravelly terrace of the River Nile, and are known as the Idfu Gravels (Lower Pleistocene). They were deposited during the active phase of transportation of sediments in the history of the River Nile, when substantial rainfall was experienced in the region (Youssef et al., 1984; Papa, 2003).

Structurally, the Saqqara plateau has been little affected by faulting. The general location of the faults can be assumed on the basis of adjacent features, rather than that the faults themselves are exposed. The fault along the foot of the Saqqara-Abusir plateau may be considered as one of a system of parallel faults that often define the limits of the Nile. All faults recorded in the Saqqara area are the result of geologically ancient ground movements and not currently active. Therefore, they pose no significant hazard to the monument sites in the area.

In the location of the studied tomb, the lithologic characteristics of the bedrock can be examined in exposures in the surrounding area. The most useful one lies to the north of the Idut tomb, at the entrance to the southern Zoser tomb. This exposure belongs to the Upper Calcareous Unit of the Saqqara Member and comprises three rhythmites, each consisting of well-stratified (Fig.2A) beds showing repeated changes in lithology, each bed varying in thickness. The upper bed of each rhythmite is yellowish to green, calcareous, massive and nodular claystone (shale) with high gypsum content (~ 0.30-0.45m thick). This is underlain by grey, hard limestone that passes down into semi-hard argillaceous limestone (~ 0.80-1.20m), and is then underlain by greenish, soft, thinly laminated, papery marl (~1.0-1.5m). Fractures (Fig.2B), cavities and gypsum veinlets are the main diagnostic features observed.

**Archaeological Background:**

The Idut tomb, its shaft and burial chamber, the particular subject of this work, was hewn in a local hillside situated on the southern part of the enclosure wall of the Zoser complex. According to Firth (1927), who first discovered the tomb, the tomb is considered to be Mastaba, dating from the early 6th Dynasty (2420-2280 B.C.). It was originally built for Ikhy, but, was later used as a tomb for Idut, a royal daughter or princess. The tomb has suffered extensive deterioration of its murals, especially the paintings inside the burial chamber (Fig.3), where only fragments are preserved. These are deformed, cracked and largely detached from the supporting wall. In some places, the mortar has completely detached from the wall, together with fragments of bed-rock. The majority of the plaster has already fallen off the walls. In comparing the recently observed deterioration (Figs. 3 C&D) with that recorded by Macramallah (1935) (Figs.3A&B), it is clear that the
deterioration has rapidly accelerated. Examination of these photos (Figs 3C, D) shows that large areas of the plaster, together with the painted layer, have detached from the supporting wall. There is also some deterioration caused by salt crystallisation, as well as mechanical deterioration caused by people.

Fig. 1: Location map and geologic map of Saqqara area (after Youssef et al., 1984).

Fig. 2: A&B: A- Well stratified Upper Eocene rocks. B – Vertical fracture cutting through well stratified beds.

Fig. 3A-D: A&B- photographs showing deterioration exhibited by the studied tomb during its discovery. C&D- show, recently, more advanced deterioration, as large areas of plaster together with paintings have been fallen down.
MATERIALS AND METHODS

For the present study eighteen thin sections, representing the bedrock and plaster supporting the wall paintings, were petrographically examined using a polarizing microscope. The carbonate samples were stained with Alizarin red-S (Friedman, 1971) to reveal the presence of calcite and dolomite. The samples were subjected to X-ray diffraction analysis to determine their mineralogical composition. Both the bulk samples and the clay fractions that were separated from the marlstones and argillaceous limestones were X-rayed. The powder diffraction patterns of the samples were obtained using Cu $\alpha$ radiation and a Ni filter. The scanning speed is 20 °/min at constant voltage 40kV, and 30mA using PW 1390 X-ray diffractometer. Oriented aggregates of the clay particles (<2 µm) were mounted on glass slides (Tucker, 1988). Three Oriented slides of each sample were subjected to X-ray analysis, one unadulterated, the second treated with ethylene glycol, and the third heated at 550°C for two hours. Identification of the minerals was carried out using data given in the ASTM cards by measuring the d-values of the diffraction planes and their relative intensities. Semi-quantitative estimation of the recorded clay minerals was achieved, through the X-ray diffraction of the glycolated oriented-clay-fraction mounts, following the procedure given by Shultz (1964) and Pierce and Siegel (1969). Differential thermal (DTA) and thermal gravimetric (TGA) analyses of the investigated plaster layer were also carried out by using SETARAM LabsysTM TGDS16. The rate of heating was adjusted at 10 °C/min. Acid-insoluble residue (AIR) was determined by treating the samples with 10%HCl. The residue was thoroughly washed by distilled water, dried, weighed and its percentage was calculated. These were then examined using a binocular microscope (Ireland, 1971).

RESULTS AND DISCUSSION

Petrography of the Bedrock:

The bedrock comprises two different lithotopes, limestone/argillaceous limestone and marlstone. The AIR of the argillaceous limestones ranges from 14-19%, whereas in the marlstones it is 43-53%. Binocular microscope examination of the AIR revealed that clay with subordinate sand plus a small amount of gypsum are the dominant components. The AIR of the argillaceous limestone is composed of 86-91% clay, 5-9% sand and 3-5% gypsum, whilst that of the marlstones is 78-84% clay, 9-13% sand and 6 –9% gypsum.

Thin-sections of the limestones revealed a main microfacies association, biopelsparite (Folk, 1959) or bioclastic pelloidal grainstone (Dunham, 1962). The peloids and bioclasts are present in varying proportions (Figs. 4A, B). The bioclastic constituent is 15-25% of the rock volume and is formed of mollusc fragments, echinoid debris, benthic and planktonic foraminifera, together with algae. Some of the fossil chambers are recrystallised and/or infilled with sparite, but have mostly been leached out. Peloids (20-35%), composed of structureless micrite, range in size from 20-110 µm, and are rounded, ovoid, well-sorted and organic rich (Fig.4B). They are formed due to fecal pelleting by certain organisms, such as molluscs and worms. The allochems are embedded in sparitic matrix that is generally sub-translucent with a faint brownish cast in thin section. Pore spaces (both inter- and intraskeletal) are abundant (average 13%), having various size and shape (Figs.4C, D). They may have developed as a result of post-depositional diagentic (dissolution) processes. The non-carbonates are represented by fine nodules of clay and fine detrital quartz grains (~8%).

Fig. 4A-D: A-Biopelsparite, limestone lithotope, P.P.L. B- Rounded peloids embedded in sparite matrix, P.P.L. C&D- Pore spaces (both inter- and intraskeletal) having various size and shape, biopelsparite association, C.N.
The marlstones are very heterogeneous, but with different grain-sizes that range from 10 to 250 µm. They have a higher percentage of terrigenous material represented by clays that admixed with the micritic matrix. The latter is composed of very fine microcrystalline carbonate that is commonly recrystallized into microsparite. These rocks contain <10% fossil fragments, randomly scattered throughout the recrystallized micrite matrix, and so can be tentatively classified as fossiliferous micrite (Folk, 1959) (Fig.5A) or lime-mudstone (Dunham, 1962). Some of these fragments are leached or replaced by recrystallized sparry calcite. They contain many micro-cracks, some of which have been filled with sparite.

Petrography of the Plaster Layer:

Plaster preparatory layer was applied directly onto the bedrock with varying thickness. Plaster over the limestone is fine enough to allow relief carving or other manipulation. The rock surface was smoothed and covered by a reinforcing rough mortar layer, formed of coarse gypsum, in which thin limestone flakes or powder, together with fine sand, was added as filler material. Over this coarse layer, a fine layer composed mainly of gypsum was applied. Therefore, the plaster layer was used to treat irregularities and smooth the surface of the bedrock (Lee and Quirke, 2003).

Microscopically, the plaster layer is texturally heterogeneous. The groundmass consists mainly of fine-grained gypsum in which coarse gypsum crystals are widely distributed (Fig.5B). These crystals are occasionally dehydrated into anhydrite; characterized by higher relief and stronger birefringence (Fig.5C). Voids (Fig.5D) of various size and shape with sharp outlines, occasionally delineated by fine gypsum grains, are additionally present. Some fine- to medium-sized quartz grains were also observed. Patches of iron oxide (hematite) occur as staining, with a red to blood-red colour.

Mineralogy of the Bedrock:

X-ray analysis of the bedrock indicated that calcite and little quartz are the main non-clay minerals recorded in all samples (Fig.6A,B), whereas halite and/or gypsum are revealed in some marlstone samples. The clay mineral assemblages identified within the clay fractions (Figs.7, as an example) include montmorillonite, kaolinite and illite, in order of decreasing abundance. Both types of montmorillonite were encountered in the studied Upper Eocene sediments. Montmorillonite is identified by reflections occurring around 14 Å (for Ca-,montmorillonite) and around 12.5 Å (for Na- montmorillonite) of the untreated clay fraction, which shifts to ~18 Å (with increase in intensity) and ~10 Å upon glycolation and heating, respectively. Kaolinite is characterized by its basal reflections at d-spacing 7.13 Å and 3.58 Å. These reflections are not affected by glycolation, while disappeared upon heating treatment. Illite is identified by a peak at 10.04 Å, which was neither affected by heating nor glycolation. The semi-quantitative estimation of the recorded clays implies that the montmorillonite (the expandable clay mineral) is the predominant clay, ranging from 61%–70% with an average 66%. Kaolinite is the second in abundance, ranging from 23%–31% and averaging 26%, whereas illite averages 7%.
Mineralogy of the Plaster Layer:

X-ray diffraction pattern of the plaster (Fig.8A, B) indicates that gypsum with subordinate anhydrite, in addition to bassanite and a little quartz are the main components. Gypsum was investigated by its main peaks, occurring at d-values 7.63 Å, 4.28 Å and 3.06 Å. On the other hand, the peaks at 3.49 Å, 2.84 Å, 2.32 Å and 2.20 Å identify anhydrite. Bassanite (hemihydrate) was identified by the peaks at 3.02 Å, 3.48 Å, 2.82 Å and 5.97 Å.
The differential thermal analysis (DTA) of the plaster is shown in Fig. 9. The DTA curves show the presence of two large endothermic peaks and one small endothermic peak. The first large endothermic peak occurs in the range of 145ºC – 155ºC, implying the formation of a hemihydrate phase (Flek et al., 1960). The weight loss corresponding to this peak, as revealed from the TGA curve (Fig. 9), is about 9-12%; this represents about 75% of the total weight loss (~16%) of the sample; i.e. about 1.5 moles of the combined H2O. The second large endothermic effect occurs in the vicinity of 185ºC - 188ºC, indicating a dehydration of hemihydrate to soluble anhydrite and loss of the remaining 0.5 mole of H2O. Such total loss (~16%) implies that the present plaster layer is not formed of pure gypsum (theoretical total weight loss ~ 21%) but contains an amount of anhydrite and/or bassanite; corroborating the results obtained from the petrographic studies, as well as the X-ray analysis. The very small endothermic effect may be attributed to the loss of the last traces of water held in the hemihydrate structure (Kuntze, 1962).

Discussion:

The process of decay of the wall paintings likely had already started in ancient times. It progressed, bit by bit, over thousands of years, until the time of the archaeological discovery in the year 1927. Ancient burial chambers, because of their isolation from external factors, ensured a somewhat stable environment for the paintings. After the tomb was opened, this environment had been totally distorted. Susceptible materials started to react to new temperature and humidity conditions. The petrography and mineralogy of the bedrock contribute to the deterioration of the paintings and, in turn, caused the mortar and the painted layer to detach from the bedrock. These rocks are too weak to resist the interaction between exogenic (climate, including rain water, humidity, and temperature variation) and endogenic (related to the nature of the rock types) conditions, since their construction, thousands of years ago. These agents of deterioration often act in conjunction and also potentiate one another (Mora et al., 1984).

Our results indicate that the limestone bedrock is composed of grainstones with relatively low mud content, compared to the marlstones. According to Sperber, et al. (1984) and Dawans and Swart, 1988, Grainstones (sparites) are sufficiently permeable and porous facies, facilitating fluids to interact within the rock and influence their components. Moreover, the studied bedrock had originally suffered from diagenetic dissolution processes. It is believed that dissolution was mainly achieved by the action of circulating meteoric water in an active zone (Longman, 1980). Dissolution resulted in the development of inter-and intraskeletal pores through the removal of peloids, shell fragments and/or leaching of their cores (Figs. 4C, D). This process also produced irregular voids and vugs (Figs. 4D), with various sizes and shapes, or caverns (observed in the field). Such features might have led to a drastic increase in the bedrock porosity (Abu-Zeid, 1989; Tucker et al., 1989).
2001). Such sediments with high porosity and high pore connectivity favor the diffusion of rain water and humidity and help in water sorption, increasing the capillary pressure inside the rock, and finally giving rise to its disintegration, as indicated by Espert, et al. (1981). It is also evident that the higher the rock porosity, the higher the tendency to disaggregate (Espert, et al. 1981).

It is worth mentioning that, in the Saqqara area, the relative humidity ranges from 26-88% in the summer and from about 34-90% in the winter. On the other hand, the determined moisture content of the argillaceous limestone samples ranges from 0.9 to 1.6% and in the marlstones from 1.7 to 2.1%, statistics in accordance with the results given by Soliman (1998) and indicating a relatively higher percentage.

The marlstones and argillaceous limestones of the bedrock contain a considerable quantity of clays, with high percentage of expanding clay minerals; montmorillonite (average 66%) is the main clay mineral. Montmorillonite is one of the clay minerals, belonging to the smectite group, all of which possess the property of being able to expand and contract their structures while keeping crystallographic integrity (Moore and Reynolds, 1997). This property is the main control on the physical characteristics of natural materials in which smectites are present. The swelling capacity of clays is a desirable feature (Bell and Maud, 1995; Wilson et al., 2006). In the presence of water swelling clays is one of the most significant factors of deterioration (Houben and Guillaud, 1994; Nelson and Miller, 1997; Meisina, 2004). Montmorillonite contains differing amounts of water due to a negative charge and the concomitant presence of exchangeable cations. These cations tend to form hydrates through attracting water molecules, whenever some water is present. Ca and Mg ions retain H2O more strongly (VanRanst, 1993). According to VanRanst (op. cit.), at every temperature, equilibrium exists between the amount of water found in the interlayer space and atmospheric water (relative humidity). As the relative humidity increases, the mineral will absorb more water out of the air until a new equilibrium is reached. Two types of clay swelling can be distinguished: a) osmotic or interparticle swelling, which takes place in any clay when saturated with water, and b) intracrystalline swelling, which only occurs in expandable clays (e.g., smectites); it may finally lead to structural failure (Rodriguez-Navarro et al., 1998), which is the case in the present study. The smectites can swell to a volume that can be several times the volume of the dry clay, depending on the amount of water available. In dry conditions, most of the adsorbed water is lost through evaporation, causing a strong shrinking. It can therefore be presumed that periodic swelling and shrinkage during alternating wet and dry seasons, favored by humidity and temperature fluctuations, may have led to disintegration or severe damage to the bedrock. In turn this critically effects the stability of the wall paintings, especially with an increase in water content. Moreover, during the swelling process, the cohesion of the clay particles may have decreased, resulting in very low shear strength of the rock; the clay particles slide easily over each other and cause a lot of damage. Consequently, the bedrock has been damaged and in turn the plaster layer has collapsed and fallen down.

It is well known that evaporites (gypsum, halite and other water-soluble salts) are originally present in the Upper Eocene limestone used for monument construction. They are mainly primary or secondary, due to the drainage (Soliman, 1998). The studied rocks have a considerable amount of gypsum and halite, as indicated from X-ray. Presence of soluble salts (especially halite) in our samples represent one of the most important causes of stone decay and a serious damaging effect, as reported by many authors (e.g. Lewin, 1982, Bongrani and Fanfoni, 1995; Goudie and Viles, 1997). The salt-bearing solutions migrate through the rock, and under suitable conditions water evaporates and salts are deposited. The growth of salt crystals within the pores of a rock can generate stresses that are sufficient to overcome the rock’s tensile strength and cause damage and disruptions, sometimes turning the stone to a powder (Jewaka, 1981; Zehnder and Arnold; 1989; Steiger, 2005). Moreover, crypto-efflorescence of these salts between the bedrock and plaster may have caused the detachment of the plaster and painting layers.

The plaster contains anhydrite and bassanite minerals. These minerals may be developed during dehydra
tion of gypsum. The dehydration process leads to net reduction in the bulk density and the resulting anhydrite is going to be more porous than its compact original gypsum (Goldman, 1952). Furthermore, rupture deformation may originate due to volume decrease during transformation. Such process may also contribute to the detachment of the plaster layer. However, the main cause of the destruction of the paintings appears to be due to changes in the volume of the bedrock, due to the changes in humidity.

Conclusions:

Petrographical and mineralogical studies have been used to shed light on the causes of deterioration of the wall paintings inside the burial chambers of the rock tombs in the Saqqara area. The quality of the bedrock (support of the wall paintings) is particularly poor. It consists mainly of two various lithotopes, marlstone and limestone (mostly argillaceous limestone), that are susceptible to weathering processes in this region. The
petrography and mineralogy of the bedrock and the plaster contribute to the deterioration of the paintings and, in turn, caused the mortar and the painted layer to detach from the bedrock. Their composition are too weak to resist the interaction between exogenic (climate, including rain water, humidity, and temperature variation) and endogenic (related to the nature of the rock types) factors of alteration that often worked together and also potentiate one another, causing a lot of decay. The durability of the mother rocks is mainly governed by clay content and porosity.

We recommend that traditional methods of conservation cannot be applied to the studied tomb because of the critical conditions of the bedrock and the plaster that have suffered from severe conditions of deterioration that affected the wall paintings. Therefore, the best way of saving the wall paintings in the Idout tomb, and in other tombs in the Saqqara area suffering from similar conditions would be to detach them from the harmful bedrock, using the Stacco technique. Then, place them on new supports formed of synthetic materials and mount them back in their original locations. This is the only way to isolate the paintings from the influence of their original destructive support.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Jackie A. Lees, Department of Earth Sciences, University College London for reviewing the manuscript and for valuable comments.

REFERENCES


