# THE IMPACT OF SOLUBLE SALTS ON THE DETERIORATION OF PHARAONIC AND COPTIC WALL PAINTINGS AT AL QURNA, EGYPT: MINERALOGY AND CHEMISTRY\*

## A. M. A. MOUSSA,<sup>1,2</sup> N. KANTIRANIS,<sup>3</sup> K. S. VOUDOURIS,<sup>1</sup> J. A. STRATIS,<sup>4</sup> M. F. ALI<sup>2</sup> and V. CHRISTARAS<sup>1</sup>

 <sup>1</sup>Laboratory of Engineering Geology & Hydrogeology, Department of Geology, School of Geology, Faculty of Sciences, Aristotle University, 54124 Thessaloniki, Greece
 <sup>2</sup>Laboratory of Wall Paintings Conservation, Department of Conservation, Faculty of Archaeology, Cairo University, 12611 Orman, Giza, Egypt
 <sup>3</sup>Department of Mineralogy–Petrology–Economic Geology, School of Geology, Faculty of Sciences, Aristotle University, 54124 Thessaloniki, Greece
 <sup>4</sup>Laboratory of Analytical Chemistry, School of Chemistry, Faculty of Sciences, Aristotle University, 54124 Thessaloniki, Greece

The wall paintings of Al Qurna in Egypt were studied by means of XRD and ICP–AES in order to determine their mineralogical and chemical composition, and to evaluate the impact of soluble salts on their deterioration, including the identification of the building materials and pigments used. Soluble salts analysis showed that NaCl is the most common soluble salt in the bedrock, ground water and surface water samples. The building materials are affected by the ground water, while the wall paintings in the area are affected by the Upper Egypt climatic conditions, which were studied in order to detect their role in the deterioration cycle in the area.

KEYWORDS: ESNA SHALE, MORTARS, PLASTERS, PIGMENTS, XRD ANALYSIS, SOLUBLE SALTS ANALYSIS

#### INTRODUCTION

Al Qurna is located on the Nile's west bank opposite Thebes, at about 25.67°N and 32.70°E, and its height is about 88 m above sea level (Fig. 1). For Copts, it has been an important place, as they inhabited the ancient Egyptian tombs and temples during the age of the Roman Persecution, in which some scenes that were considered as symbols of atheism were destroyed, while others were imitated and covered by new religious imagery in the phenomenon termed as 'overpainting'. Our study will focus on those tombs and temples.

Today, integrated protection of the wall paintings poses not only cultural but also scientific challenges. For this purpose, many studies have been carried out to contribute to a better understanding of the crucial role played by geological and climatic factors in the deterioration of wall paintings (Christensen 1995; Dei *et al.* 1998; Rodriguez-Navarro and Doehne 1999; McFadden *et al.* 2005; Sawdy and Price 2005).

The aim of this study is to verify the effect of soluble salts on the deterioration of the Coptic wall paintings at Al Qurna, using geochemical and geological data, in addition to identification of the building materials in the studied objects used.

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Figure 1 The location of the study area (Source: http://www.lib.utexas.edu/maps/).

## THE CLIMATIC CONDITIONS

Based on the meteorological data of the area for the period 1941–81, it is concluded that the lowest average monthly temperature recorded in the area was 13.9°C, registered in January, while the highest was 32.5°C in July. It can be said that the temperature at Al Qurna is one of the highest in Egypt, due to the location of the area in the desert. Generally, rain is very rare at Al Qurna, rainfall in the area being zero for most months of the year. The three or four rainy months have a maximum of 8 mm per month, while some seasonal rains are usually expected in the summer and can cause flash floods.

## MATERIALS AND METHODS

Gypsum and lime-based mortars, plasters, pigments and natural stones used in the tombs have been sampled for laboratory analyses to determine the materials used in the construction of the

Samples	An	С	Q	Pl	На	М	Do	Cl
Esna shale	_	24	10	_	6	_	22	38
Hard limestone	_	100	_	_	_	_	_	_
Soft limestone	29	27	_	_	-	_	44	_
Cement material	-	96	2	-	2	-	-	-

Table 1 The mineralogical composition (w/w %) of the Al Qurna geological samples

An, anhydrite; C, calcite; Q, quartz; Pl, plagioclase; Ha, halite; M, micas; Do, dolomite; Cl, clay minerals.

tombs. X-ray diffraction (XRD) was performed on powdered samples, using a Philips (PW 1710) diffractometer with Ni-filtered Cu-K<sub> $\alpha$ </sub> radiation. The samples were scanned over the 3–63° 2 $\theta$  interval, at a scanning speed of 1.2° min<sup>-1</sup>. A quantitative estimate of the abundance of the mineral phases was derived from the XRD data, using the intensity of certain reflections and external standard mixtures of minerals. The detection limits of the method were ±1 w/w %.

Water samples were collected from an ancient well that had been dug inside the temple of Madinet Habu at Al Qurna, which represents the ground water surrounding the temple and the noble tombs in the area. Also rock, stone and mortar samples were analysed by the Perkin Elmer Optima 3100 XL axial viewing inductively coupled plasma atomic emission spectrometer (ICP–AES), in order to identify the soluble salts that they contain. A mass of 100 g of each sample was taken and placed in 200 ml distilled water: the beakers were then put into the ultrasonic stirrer at 60°C for 20 min, and after that the solution was filtered using filter paper to extract the solid residue. The soluble samples that were extracted were then analysed for the major ions  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $HCO_3^-$ . Furthermore, the concentrations of Fe, Pb, Cu and Mn were determined. The overall precision of the water analysis is within  $\pm 5\%$ , as indicated from the ionic balance.

#### RESULTS

The mineralogical composition (w/w %) of the Al Qurna geological and archaeological samples is presented in Tables 1 and 2, respectively.

#### Bedrock and limestone support samples

The region consists of three distinct sedimentary rock formations referred as Dakhla chalk, Esna shale, and Theban limestone, which date to between 35 and 56 million years BP. These different rock formations were extensively affected by geological uplifting in the late Tertiary period, and by erosion caused by the Nile and smaller tributaries during periods of increased rainfall into the early Pleistocene (Reeves and Wilkinson 1996; Reeves 2006). The West Bank at Luxor (ancient Thebes) is primarily made up of the last two layers. The thickness of the limestone formation varies between 60 and 300 m (Masanori *et al.* 2004). The bedrock samples where the tombs have been hewn are mostly of Esna shale. The XRD determination (Fig. 2 (a)) reveals clay minerals (smectite + illite) as its main component (38%), while calcite (24%), dolomite (22%), quartz (10%) and halite (NaCl, 6%) were also detected.

The limestone at Al Qurna can be further divided into a non-jointed soft limestone, which may also be called marly limestone, and a jointed hard limestone. The builders of the tombs

Samples	Site	Location	Place	An	Ca	Q	Pl	На	М	Do	Cl	Си	W	Go	Ja	Orp	Не	О-Н
Clay mortar	Sheikh Abd el-Qurna	Tomb of Daji, TT* 103	Western wall	_	24	50	10	_	_	_	16	_	_	_	_	_	_	_
Gypsum mortar	Sheikh Abd el-Qurna	Tomb of Daji, TT 103	Northern wall of the burial chamber	57	32	9	1	-	-	-	1	-	-	-	-	-	-	-
Gypsum plaster	Sheikh Abd el-Qurna	Tomb of Ra' Mosses, TT 046	Eastern wall	63	24	11	1	_	_	_	1	_	_	_	_	_	_	_
Gypsum plaster	Sheikh Abd el-Qurna	Tomb of Userhat, TT 056	Eastern wall	73	23	3	_	_	_	_	1	_	_	_	_	_	_	_
Blue pigment	Sheikh Abd el-Qurna	Tomb of Userhat, TT 056	Hunting scene	58	28	8	2	_	_	2	_	2	_	_	_	_	_	_
Blue pigment	Sheikh Abd el-Qurna	Tomb of Rekhmire, TT 100	Northern wall	68	22	6	1	_	_	_	1	2	_	_	_	_	_	_
Green pigment	Dra Abu el-Naga	Temple of Madinet Habu	Hypostyle (1), chapel (2)	63	19	14	_	_	_	_	_	_	4	_	_	_	_	_
Red pigment	Dra Abu el-Naga	Temple of Madinet Habu	Hypostyle (1), chapel (4)	59	23	11	2	_	_	_	1	_	_	_	_	_	4	_
Brown pigment	Dra Abu el-Naga	Temple of Madinet Habu	Hypostyle (1), chapel (7)	24	32	15	_	_	5	4	_	_	_	_	_	_	4	16
Yellow pigment	Sheikh Abd el-Qurna	Tomb of Kha' Em Het, TT 057	Down edge of eastern wall	79	18	_	_	_	_	1	_	_	_	2	_	1	_	_
Yellow pigment	Qurnet Marrai	Tomb of Amen Em Hab, TT 278	Tree decoration	45	40	9	2	_	_	_	1	_	_	_	3	_	_	_
White pigment	Sheikh Abd el-Qurna	Tomb of Daji, TT 103	Eastern wall	66	21	11	1	_	_	_	1	_	_	_	_	_	_	_
Black pigment	Sheikh Abd el-Qurna	Tomb of Rekhmire, TT 100	Bread-making scene	13	59	28	_	_	_	_	_	_	_	_	_	_	_	_
Salt sample	Dra Abu el-Naga	Temple of Madinet Habu	Chapel of the god Khonso	96	4	_	_	_	_	_	_	_	_	_	_	_	_	_
Salt sample	Sheikh Abd el-Qurna	Tomb of Daji, TT 103	Northern wall of the burial chamber	-	96	-	-	4	-	-	-	-	-	-	-	-	-	-

 Table 2
 The mineralogical composition (w/w %) of the Al Qurna archaeological samples

An, anhydrite; C, calcite; Q, quartz; Pl, plagioclase; Ha, halite; M, micas; Do, dolomite; Cl, clay minerals; Cu, cuprorivaite; W, parawollastonite; Go, goethite; Ja, jarosite; Orp, orpiment; He, hematite; O-H, calcium iron sulphate hydroxide hydrate [Ca<sub>6</sub>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH<sub>2</sub>)·26H<sub>2</sub>O].

\*TT, Theban tomb.

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Figure 2 XRD patterns of the studied bedrocks and mortar samples from Al Qurna.

selected the soft limestone as the most suitable rock unit for excavating the underground tombs. However, they found this rock unit through some trial and error (Said 1981, 1990; Masanori *et al.* 2004). The two kinds of limestone strata were analysed by mean of XRD (Figs 2 (b) and (c)); the hard one was a pure calcite (100%), while the soft one consists of dolomite (44%), anhydrite (29%) and calcite (27%). A sample from the cement material between the limestone strata formations in the area was analysed (Fig. 2 (d)), with the following results: calcite (96%), quartz (2%) and halite (2%).

## Mortar samples

Mortar is a material resulting from the intimate mixture of sand grains, a binder (lime, gypsum etc.) and water. It acts as a link between other materials, such as stones, bricks and so on (Blanco-Varéla and Fortés-Revilla 2004), while plaster (the skin of the building) covers the walls, columns and façades of the building, preserving them from external weathering conditions and providing a paintable surface (Moussa 2001). Mortars in ancient Egypt appear to be basically processed gypsum, which is plentiful in Egypt. In mortars, gypsum usually includes small percentages of sand and limestone powder, thus supporting the concept that gypsum was used as processed: 70-90% gypsum, 8-17% crushed limestone and 2-8% sand (Snell and Snell 2000). Clay mortars that were derived from the Nile mud are usually of clay mixed with animal dung, shaped straw or horse hair (British Standards Institution 2000). Clay soils used in building are generally a graded mixture of particles in the clay and silt size ranges, which exhibit cohesion and plasticity (Van Balen and Price 2000). The presence of clay mortars exerts a considerable influence on the properties of other building materials (Millrath et al. 2001). Four mortar samples were collected from the area (gypsum, clay and two gypsum plasters); the gypsum mortar sample (from the tomb of Daji—a Coptic character) consists of anhydrite (57%), calcite (32%), quartz (9%), plagioclase (albite) (1%) and clay minerals (1%) (Fig. 2 (e)). The clay mortar sample (tomb of Daji) consists of quartz (50%), calcite (24%), clay minerals (16%) and plagioclase (albite) (10%) (Fig. 2 (f)). In the first plaster sample, derived from the tomb of Ra' Mosses (a prince from the New Kingdom), the analysis detected anhydrite (73%), calcite (23%), quartz (3%) and clay minerals (1%) (Fig. 2 (g)). In the second sample, from the tomb of Userhat (a royal scribe under the king Amenhotep II), the analysis detected anhydrite (58%), calcite (28%), quartz (8%), plagioclase (albite) (2%) and clay minerals (2%) (Fig. 2 (h)).

### Pigment samples

The pigment samples from Al Qurna that were analysed are ancient Egyptian pigments, because all the Coptic trials for painting on the walls of the tombs were in a red colour, which was usually hematite (Moussa *et al.* 2006). All of the tombs studied in this paper were inhabited by Copts (Moussa *et al.* 2006) during their persecution by the Romans in AD 201–311 (Groiss 2004). We note that because of the high value of the ancient Egyptian pigments and their application in a thin layer, it has been necessary to collect the samples in their bulk form for easy analysis.

## Blue pigment

The principal blue pigment in ancient Egypt was Egyptian blue (cuprorivaite,  $CaCuSi_4O_{10}$ ), which is a synthetic pigment made by heating together silica, copper alloy filings or a copper

ore such as malachite, lime (calcium oxide) and an alkali such as potash or natron Na<sub>2</sub>CO<sub>3</sub>.NaHCO<sub>3</sub>.2H<sub>2</sub>O (Lee and Quirke 1999). According to Canti and Heathcote (2002), the pigment can be manufactured nowadays by grinding 18 g of black copper oxide (CuO), 14 g of calcium carbonate, 60 g of silica (diatomite) and 8 g of sodium carbonate together, firing the resultant grey powder at 850°C for 4 h to form a weakly sintered dark grey mass, which should be reground and fired again at 850°C for 4 h, followed by re-firing to 950°C for 2 h and then for 5 h at 850°C, to give a deep blue mass of crystals. These should be soaked in strong HCl to clean off any dark residues. There is general agreement that the working temperature must be kept between 850°C and 950°C (Mazzocchin et al. 2003), but Pagès-Camagna and Colinart (2003) noted that to produce an ideal Egyptian blue the mixture must be heated at between 870°C and 1080°C. Even though Spurrell (1895) detected the blue pigment azurite in three examples, there has been no more recent corroboration of his findings (Lucas 1962), perhaps because of the poor quality and impermanence of azurite as a pigment (Blom-Böer 1994). Uda et al. (2002) referred to Amarna blue as a blue pigment, which is believed to have been used only in the 18th and 19th Dynasties (c. 1500 BC to c. 1200 BC), but the scarcity of findings cannot allow it to be classified as a source of blue in ancient Egypt. Two blue pigmented plaster samples were analysed (tomb of Userhat and tomb of Rekhmire), both of which contain Egyptian blue pigment. Egyptian blue appeared in Egypt during the Fourth Dynasty (which began in 2575 BC) (Reeves 1990; Reeves and Wilkinson 1996). The first sample consists of anhydrite (58%), calcite (28%), quartz (8%), plagioclase (2%), dolomite (2%) and cuprorivate (2%) (Fig. 3 (a)). The second one consists of anhydrite (68%), calcite (22%), quartz (6%), plagioclase (1%), clay minerals (1%) and cuprorivate (2%) (Fig. 3 (b)).

## Green pigment

The green pigment in the temple of Madinet Habu is Egyptian green [parawollastonite,  $(CaCu)_3(Si_3O_9)$ ], a mineral detected in the manufacturing process of Egyptian blue at 850°C (Bianchetti *et al.* 2000), and sometimes termed 'green frit' (Scheigl *et al.* 1992). Pagès-Camagna and Colinart (2003) noted that to obtain a perfect Egyptian green, the mixture must contain less copper than calcium, and more flux than for a blue recipe, and must be heated at between 950°C and 1150°C. They also attributed the presence of tin in the Egyptian green pigment to the use of bronze scrap for its production, as has been previously noted by Jaksch (1985), Schiegl (1991, 1994), Schiegl *et al.* (1992), El Goresy *et al.* (1996) and Schiegl and El Goresy (2006). Basic copper paratacamite or atacamite is found in analyses of green pigment samples from surfaces as late as the end of the 12th Dynasty, but recent investigations have led to the conclusion that atacamite may be a degradation product of artificial copper pigments, and that only a few examples of green earlier than the New Kingdom were applied as green (Lee and Quirke 1999). The green-pigmented plaster sample consists of anhydrite (63%), calcite (19%), quartz (14%) and parawollastonite (4%) (Fig. 3 (c)).

#### Red and brown pigments

Since hematite is almost red, it has been used since prehistoric times in cave paintings for red and brown pigments. In ancient Egypt, the pigment was used in a thick layer upon the gypsum whitewash, to provide a good covering power, because it is very difficult to grind the mineral well or to mix it well with a paint medium (Dang *et al.* 1998; Rozenberg *et al.* 2002; Cornell and Schwertmann 2003). A red-pigmented plaster sample from the temple of Madinet Habu



Figure 3 XRD patterns of the studied pigments and salt samples from Al Qurna.

was analysed, with the following results: anhydrite (59%), calcite (23%), quartz (11%), hematite (4%), plagioclase (2%) and clay minerals (1%) (Fig. 3 (d)). The brown-pigmented plaster in the same temple consists of anhydrite (24%), calcite (32%), calcium iron sulphate hydroxide hydrate [(Ca<sub>6</sub>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>.26H<sub>2</sub>O)] (16%), quartz (15%), micas (5%), hematite (4%) and dolomite (4%) (Fig. 3 (e)).

## Yellow pigment

The yellow-pigmented plaster in the tomb of Kha' Em Het consists of anhydrite (78%), calcite (18%), goethite (2%), orpiment (1%) and quartz (1%) (Fig. 3 (f)), while in the tomb of Amen Em Habit it consists of anhydrite (45%), calcite (40%), quartz (9%), jarosite (3%), plagioclase (2%) and clay minerals (1%) (Fig. 3 (g)). Goethite [FeO(OH)] was the main source of yellow and it can be naturally found in clays as a result of their weathering processes (Smitt *et al.* 2003). Orpiment (As<sub>2</sub>S<sub>3</sub>) has been mixed with goethite to give a bright yellow colour (Noll 1978). Jarosite [KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] has been used for yellow on pottery jars from the 11th Dynasty (Noll 1978; Jaksch 1985).

### Black and white pigments

The black pigment in the tomb of Rekhmire is organic amorphous carbon; no evidence for a crystallized pigment was detected in the black-pigmented plaster sample, and it consists of anhydrite (13%), calcite (59%) and plagioclase (28%) (Fig. 3 (h)). Graphite (inorganic carbon), amorphous carbon (organic), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and pyrolusite (MnO<sub>2</sub>) were used for black pigment throughout the ancient Egyptian civilization (Winter 1983; Kohler *et al.* 1997; Pearce *et al.* 2006). The white-pigmented plaster in the tomb of Daji consists of anhydrite (66%), calcite (21%), quartz (11%), plagioclase (1%) and clay minerals (1%) (Fig. 3 (i)). Gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), limestone powder (calcite, CaCO<sub>3</sub>) and huntite [CaCO<sub>3</sub>.3MgCO<sub>3</sub> or CaMg<sub>3</sub>(CO<sub>3</sub>)<sub>4</sub>] were almost all the most famous sources of white pigment in ancient Egypt (Graf and Bradley 1962; Kinsman 1967; Barbieri and Calderoni 1974; Riederer 1974; Noll 1978; El Goresy *et al.* 1986).

## Salt samples

Two samples were collected from the efflorescent salts. The first one, from the temple of Madinet Habu, consists of anhydrite (94%) and calcite (4%) (Fig. 3 (j)). The second sample, from the tomb of Daji, consists of calcium carbonates (96%) and halite (4%) (Fig. 3 (k)).

#### DISCUSSION

XRD analysis of the Al Qurna samples (soft limestone and all archaeological samples) revealed anhydrite as the dominant compound. According to Wüst and Schlüchter (2000), soluble salts are endogenous to the marine sediments of the Esna shale and the Thebes Formation in central Egypt, and the most effective of them are halite (NaCl), anhydrite (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O). The sulphates in the rocks of the Thebes Mountains exist in different hydration states. Each state has its characteristic specific volume. As sulphate transforms into a higher hydrous state, the volume increases due to adsorption of water. During the transformation of anhydrite to gypsum, a volume expansion of up to 61% is possible (Wüst and

Schlüchter 2000; Yilmaz 2001). This develops a hydration pressure, which depends on the temperature and humidity of the air. According to Yilmaz (2001), anhydrite is stable above 58°C at a pressure of about 100 kPa, while gypsum is stable below 38°C. Increasing humidity results in increasing pressure release of sulphate minerals according to the expansion of anhydrite during its transformation to gypsum. The solubility of gypsum (2.4 g  $\Gamma^1$  at 20°C and pH 7) is more than 200 times greater than that of calcite (Nord 1992), but the solubility of sulphates is much less than that of chlorides. A number of factors influence salt crystallization damage in porous materials, including: (1) pore size and porosity; (2) the nature of the salt, the ease with which it achieves high saturations by evaporation and/or variations in environmental temperature, and the energy difference between the crystal and the pore wall; (3) the transport of the solution, in terms of the supply rate of the solution and the evaporation of water; and (4) strength, which is the material's resistance to crystallization pressure (Benavente *et al.* 2007).

Calcium sulphate can appear as three distinct minerals: gypsum (dihydrate), bassanite (hemihydrate) and anhydrite (anhydrous). It is possible that the dehydration–hydration reaction plays a critical role in the deterioration mechanism (Charola and Centeno 2002).

The bedrock type (mainly its mineralogical composition) and the climatic conditions to which it is exposed will determine the predominant weathering phenomena and deterioration patterns. The presence of swelling clay minerals adversely influences the stability of the construction through expansion and shrinkage of their structure during saturation and desiccation cycles, respectively, while any possible pathways for moisture within the stonework caused by architectural factors or structural damage will enhance the distribution of salts and air pollutants and their concentration (Pitzurra et al. 2000; Warscheid and Braams 2000). In the Al Qurna region, both the high content of swelling clay minerals contained in the Esna shale bedrock and the high content of anhydrite contained in the soft limestone, where the tombs were hewn, control the stability of the inside-hewn tombs. For halite, the salt solutions from the subsurface intrude by capillary rise into the walls of the monuments, and salts-especially halite—are precipitated on the stone surface or in the pore space of the rock close to the surface (Fitzner et al. 2002). In the marls of the Thebes Formation, rainwater dissolves halite first, then gypsum, anhydrite and alabaster (Wüst and Schlüchter 2000). Ties between stone crystals that are composed of anhydrite, calcite and halite (all are soluble salts) could be lost through weathering, and stone bleeding (friability) is widely visible in the area (Moussa et al. 2006).

There is a high possibility of plaster detachment due to the chemical and climatic effect, especially if salts crystallize between the plaster layers, or between the support (rock-stone) and the plaster. Falling mortar and plaster and friability are visible phenomena in the tombs (Moussa *et al.* 2006). In addition, if salt crystals are precipitated at the surface, they will retain moisture at the wall surface and reduce the moisture gradient further (Obika *et al.* 1992). The dehydration of gypsum is extremely slow below 42°C and is affected by the nature of other materials present in the system, as would be the case in monuments: thus the nature and porosity of the substrate plays a critical role in determining the amount of damage suffered (Charola 2003). They also determine the amount of moisture absorbed by hygroscopic salts (Charola and Weber 1992; Charola and Puhringer 2005). Minimal changes in relative humidity, if repeated for long enough—that is, cycling between 43 and 55% RH over 6 months—will induce damage. Rapid changes in humidity (2–4 days) induce more damage than gradual changes (3 weeks) (Von Konow 2001).

Photochemical degradation, heat and moisture contributed as oxidizing factors in the discolouring phenomenon of the brown pigment in the temple of Madinet Habu. The presence of calcium iron sulphate hydroxide hydrate  $[Ca_6Fe_2(SO_4)_3(OH)_2 \cdot 26H_2O]$  (16% of the sample) is a result of the reaction of gypsum with red hematite due to the climatic conditions. Spalling, paleness and blistering of painted layers in the area due to salts efflorescence can also be detected. This process needs water-soluble salts present in the masonry units, mortar or plasters, a sufficient moisture level in the masonry structure to put the salts into solution, and a path for the solution to migrate through (Brunetti 2003). All of these conditions are met in the Al Qurna wall paintings.

#### Soluble salts analysis

This study shows that sodium chloride (NaCl) is the predominant salt species (Table 3). Sulphates  $(SO_4)$ , anhydrite (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) also occur in the limestone deposits of the Thebes Formation and the underlying shale deposits of the Esna Formation. The member of the Thebes Formation into which most of the ancient tombs were hewn shows the highest amount of soluble salts. In addition, the porosity and permeability of the marls in that member are high, enhancing water and brine migration. Wetting and drying of the tomb surfaces in the past have affected solution, transportation and recrystallization of water-soluble minerals, and has led to major destruction of wall paintings and ornamentation (Appelo and Postma 1996).

Based on chemical analysis of a groundwater sample collected from the well, it is concluded that the water belongs to a Na<sup>+</sup>–Cl<sup>-</sup> hydrochemical water type (Fig. 4). The Na<sup>+</sup> concentration is 22 800 mg l<sup>-1</sup> and the Cl<sup>-</sup> concentration is 42 000 mg l<sup>-1</sup>. Other important ions are  $SO_4^{2-}$  and  $Mg^{2+}$ , with concentrations of 4300 mg l<sup>-1</sup> and 303 mg l<sup>-1</sup>, respectively.

The soluble salts detected in both geological and building materials samples from Al Qurna show similar behaviour (Figs 5 (a) and (b)). The order of abundance of major cations is  $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ , while that of anions is  $Cl^- > SO_4^{2-} > HCO_3^-$ . The general order of dominance for the heavy metals in soluble salts in both the geological and the building materials samples is as follows: Fe > Pb > Mn > Cu > Zn.

The main propelling factor is water, derived either from ground water (soil), flash floods or transpiration and respiration of human beings. Every year, several hundred thousand tourists visit the tombs of the Valleys of the Kings and the Queens and Al Qurna. The visitors have a major effect on the humidity and temperature conditions of the tombs. Each tourist entering a tomb or a pyramid perspires about 20 g of water vapour, which might potentially dissolve a considerable amount of salt (Torraca 1983; Oliver *et al.* 1997).



Figure 4 Radial and stiff diagrams for the ground water collected from the well at Al Qurna.

Salt ions (mg $l^{-1}$ )	Ground water	Esna shale	Limestone	Cement material	Honeycoml	b weathering		
Ca	7.29	877	182	372	7	34		
Mg	303	763	75.9	150	1	.47		
Na	22 800	20 200	8 090	11 500	15 000			
Κ	185	143 100		190	340			
Cl	42 000	10 230	7 890	6 540	7	240		
HCO <sub>3</sub>	140	132	154	160	1	62		
$SO_4$	4 300	2 300 3 100		4 720	3 740			
Fe	35.3	17.8	1.07	37.3	1	3.3		
Cu	0.21	1.36	0.25	0.96	0	.14		
Mn	3.7	1.93	0.209	3.97	1	.47		
Pb	5.92	4.82	2.35	4.43	4.13			
Zn	0.755	0.744	0.763	0.276	0.885			
Salt ions (mg l <sup>-1</sup> )	Gypsum plaster	Mud p	laster (1)	Mud plaster (2)	Hiba (1)	Hiba (2)		
Ca	5.34	9	5.6	1 870	140	288		
Mg	Saturated	9	8.7	895	61.3 15			
Na	14 700	21	100	14 700	7 380	10 600		
К	482	2	250	100	230	530		
Cl	7 930	2	300	1 900	2 740	2 930		
HCO <sub>3</sub>	92		43	52	62	69		
$SO_4$	183	58		49	103	82		
Fe	Saturated	3	.38	83.90	0.70	7.69		
Cu	0.29	0	.57	1.02	0.42 0.40			
Mn	0.58	0	.46	8.70	0.17 0.89			
Pb	3.99	5	.64	4.54	2.57 2.48			
Zn	0.94		1.2	0.23	0.47	0.54		

Table 3 Soluble salts detected in the geological and building materials samples from Al Qurna

## Salts forecasting

According to previous results, some salts are expected to be found after the evaporation of water from the brine. Among these salts are sodium chloride, potassium chloride, magnesium chloride, calcium chloride, magnesium sulphates, calcium sulphates and calcium carbonates. The formation of these salts depends on two factors (Moussa 2001; Moussa *et al.* 2006):

(1) The solubility factor of the salt and its ability to be transferred from the ground water into the building materials.

(2) The porosity of the building materials.

Sodium chloride is the salt most likely to be formed in the building materials of the Al Qurna tombs, due to its high solubility factor, while calcium chloride is the least expected salt to be formed in the building materials.

Chemically, salts in reaction with pigment components play the role of a catalyst in the discolouring phenomenon. Weathering of the Egyptian blue alkali-rich glass can result in the formation of chlorides and/or malachite, a deterioration symptom known as 'copper chloride cancer'. This is a result of the migration of Cu and Cl ions in the NaCl solution—which is found in the stone, mortars and plasters—precipitating atacamite, which changes, after loss of



Figure 5 Pie diagrams for major ions of the soluble salts in (a) the geological samples and (b) the building materials samples from Al Qurna.

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water, to a powder composed of paratacamite (Schiegl 1991; Schiegl et al. 1992; Lee and Quirke 1999).

Mechanically, the clay mineral halloysite  $[Al_2Si_2O_5(OH)_4 \cdot 2H_2O]$  absorbs the soluble salts, resulting—through swelling—in endogenous pressure on the stone blocks and the plaster layer and leading to wall bulking and the falling and cracking of plaster. Rijniers *et al.* (2003) studied the solubility of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> in pores and the bulk using nuclear magnetic resonance (NMR), with the suggestion that sodium carbonate shows super-saturation in pores of 5 nm.

#### CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the XRD analysis, the bedrock at Al Qurna is Esna shale, which contains halite in its composition. The building materials in the tombs studied are the salt provider in the deterioration process: hard limestone is pure calcite, while soft limestone has anhydrite, the cement material contains halite, whereas all mortar, plaster and pigment samples contain anhydrite in their composition. The blue pigment in both the tomb of Userhat and the tomb of Rekhmire-Al Qurna is Egyptian blue (cuprorivaite, CaCuSi<sub>4</sub>O<sub>10</sub>), and the red pigment in the temple of Madinet Habu is hematite, while the brown pigment is a mix of hematite and calcium iron sulphate hydroxide hydrate (altered hematite). The yellow pigment in the tomb of Kha' Em Het is a mix of goethite and orpiment, and in the tomb of Amen Em Hab it is jarosite. The green pigment in the temple of Madinet Habu is Cu-wollastonite, and the black pigment in the tomb of Rekhmire is organic amorphous carbon.

The results are divided into two sections: the first section is geological, while the second section is concerned with the building materials that are used in the preparation of the mural paintings attempting to show the effect of the geochemistry and geological structure on the deterioration of the rock-cut tombs of the area. It is clear that sodium ions are very high in both of the geological and building materials samples: the Esna shale is rich with  $Mg^{2+}$  ions, as well as the mud plaster samples. The salts that are expected to be found in the building materials after crystallization are the same as are expected in the bedrock, but the effect here will be stronger due to the swelling ability of the shale.

The results of the soluble salts analysis have shown that there is a high amount of sodium ions (Na<sup>+</sup>) in the ground water of Al Qurna and a parallel high concentration of chlorides (Cl<sup>-</sup>); this favours the formation of sodium chloride brine inside the mural paintings of the area, or the formation of halite crystals as a result of the crystallization process that takes place as a result of the high temperatures in the area.

The high salt concentration plays many roles in the deterioration phenomenon in the area. Sulphates  $(SO_4^{2-})$  are also among the salts expected to be formed after the crystallization process. The transformation of hydrated calcium sulphate (gypsum) into non-hydrous calcium sulphate (anhydrite) and vice versa is a common phenomenon in the wall paintings of the area—a change that is usually followed by a decrease/increase in the volume of gypsum/anhydrite (Rosvall 1986; Domenico and Schwartz 1990; Charola *et al.* 2007; Zehnder 2007). Due to the high amount of anhydrite in the soft limestone into which the tombs were hewn, the mural paintings are influenced by the pressure that develops due to the expansion of anhydrite during its transformation to gypsum, in addition to endogenous potential pressure as a result of the presence of clay minerals and anhydrite in the natural composition of the building materials (Masanori *et al.* 2004). Building materials are badly affected by the geological structure of the area: bulking and separation of painted layers from the walls are commonly seen symptoms in Al Qurna.

Some recommendations are proposed in order to protect the fresco paintings in the aforementioned areas:

• Due to the critical state of the wall paintings in the area, no salt extraction should be done before the consolidation processes.

• Consolidants should be applied first on models injected with soluble salts, in order to investigate their salt extraction permeability.

• Salt extraction should be achieved using well-trained operatives, usually with attempts made to avoid the pigmented areas of the walls.

Future investigations of the deterioration of frescoes and wall painting in the study areas would benefit from improvements in geochemical data monitoring.

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