

ANALYTICAL IDENTIFICATION AND CONSERVATION ISSUES OF PAINTED PLASTER FROM QASER AMRA IN JORDAN

Firas ALAWNEH^{*}, Fadi BALAA'WI, Naif A. HADDAD, Yahya AL-SHAWABKEH

Queen Rania's Institute of Tourism and Heritage, The Hashemite University, Zarqa, Jordan

Abstract

Knowing the composition of painted plaster is of great importance for conservation; an understanding of the ancient materials and technology is necessary when creating new plasters or mortars to be used in restoration. There is little knowledge of the specific techniques used in those plasters and particularly the combination of various materials used to create more sophisticated plaster. This paper presents a complete technological study of the Qusayr Amra painted plaster in Jordan. It also attempts to propose sustainable general preservation strategy, based on a holistic methodology, integrating novel scientific techniques for non-invasive in situ examination with state-of-the art non-destructive analysis of micro samples at their molecular level. 15 samples of plaster pigments were collected from various locations in the palace, which represented all deterioration features and pigments. The methodology used to identify and investigate the painting plasters, involved the use of different techniques, namely, electron microprobe analysis, X-ray diffraction, scanning electron and optical microscopy analysis with SEM-EDX, and in addition, a micro-chemical analysis. The pigments used were mainly pigments from local sources (red and yellow ochres and malachite and blue), similar to those traditionally used in ancient times.

Keywords: Painted plaster; Characterization; conservation; plaster composition; pigment.

Introduction

Knowledge of the technology of the ancients in terms of materials and applications is a necessary step prior to any conservation activity aimed at preserving decorative plasters and stuccoes. In order to preserve these irreplaceable artworks, it is essential to identify the materials used in them and the processes of decay that affected them. The inherently complex, composite nature of materials found in such works requires elaborate and often case-specific analysis and conservation procedures. However, the use of scientific methods for the analysis and conservation of cultural heritage decorative plasters and stuccoes greatly contributes to our knowledge about their materials, their interactions with the environment and eventually their protection.

Through a range of scientific methods and experimental procedures of documentation and conservation, this study attempts to identify the Umayyad method of applying plaster for paint layers in Qusayr Amra and to find out what could be termed as the Umayyad technique. This helps us learn more about the building technology used in Umayyad and, hence, about

^{*} Corresponding author: Firas-alawneh@hu.edu.jo, 0096253903333, Ext. (4674)

their culture and history and it also allows us to compare it with the other cultures of that time and about the influences they had on each other.

Our analysis was carried out with a range of methods aimed to identify in the mural paintings from Quasar, the material structure, composition and additives in the plaster/mortar layers, the pigments used and to determine the deterioration factors that affected them. Additionally, it was important to study the microstructure of the layers, their strata, including the top painted surface layer, as well as to identify the pigments present and their binding media, when possible. We used Electron microprobe analysis, X-ray diffraction, scanning electron and optical microscopy analysis with differential thermal analysis, SEM-EDX, together with Micro-chemical analysis.

Painted Plaster Application Techniques: Historical Background

Plasters and mortars, were already developed in prehistoric times; they consist mostly of very small amounts of burnt lime mixed with anthropogenic debris, soil, and sediment, that can be identified by a series of experiments on plasters using petrographic methods. Lime has a transitional texture of partially carbonized slaked lime, that can be observed in the lime lumps and in the binding matrix. Usually it is found in the form of ill-crystallized portlandite and calcite mixtures or cryptocrystalline calcite. Plaster and mortars used to be made by mixing damp anthropogenic dirt, as aggregate, and fragments of quicklime, a technique known as "hot mixing."[1].

In Jordan, painted plaster remains can be found dating from early historical times. Particularly in the area of Petra, scanty painted plaster remains were found at the Neolithic site of al-Bayda [2]. The paint traces included purple red, ochre red, brown, black lines and red painted on a greyish green surface. In the Bronze Age, the plaster layer onto which the paint layer was applied was often the only layer and it consisted mainly of calcite. A clay plaster formed the backing between the lime plaster coat and the actual wall surface. The pigments identified were: yellow ochre, haematite (red), cuprorivaite (Egyptian blue), indigo and possibly riebeckite for blue, charcoal (black), calcite (white), and a combination of black and red for purple. The technique of *al fresco* painting was employed extensively, a technique already in use since the start of the Late Minoan I phase in Crete [3]. At the Iron Age site of Tell Dayr 'Alla, in Jordan , red and black paint was found on a 7 mm plaster made of chalk and chopped straws were present over the clay plaster which coated mud brick walls[4]. The wall painting consisted of drawings and a text in the alphabet script of the northwestern Semitic language. Soot from burning oil lamp was used for the black ink, while for the red they used an iron oxide mineral.

In the Roman period, frescoes were painted by artists on the still damp plaster of the wall, so that the painting became part of the wall, actually colored plaster. In 27 BC Vitruvius, the Roman architect and engineer, in his Book 7, discussed the appropriate techniques of preparing and applying plaster and stucco, and also mentions the technique of wall painting and the types of pigments used. Vitruvius (VII, ii. 1-2) [5] described the method of crushing, burning and slaking lime and recommended the polishing of the plaster with specialized tools, "liaculorum". For in stucco vaulting, Vitruvius (VII, iii,1-3) [5] recommends fastening wooden strips in a curve and tying flattened reeds to them, over which lime and sand mortar is poured and a final coat is applied to the lower surface. Vitruvius (VII, iii, 4-7) [5], recommends the application of three layers of rough sand mortar, followed by three other successive layers of finer mortar, made with marble powder, upon which the final layer of paint should be applied on wet plaster. Many ancient wall paintings dating from the Roman period were found decorating the interiors of several tombs at Quwaylibe (Abila), in Jordan. Those paintings consist of a variety of themes, including human, mythological, animal and geometric representations. Even though not all Roman plaster was executed in the manner recommended

by Vitruvius, there are examples of the application of 6 layers, such as in the Farnesina villa in Rome [6, 7].

In Nabataean times plastering was considered a profession in itself among craftsmen. The raw materials used in the preparation of plasters, support and paint preparation layers, in addition to the paint layers themselves, can be found in abundance Petra/Jordan and its immediate surroundings. Gypsum/anhydrite, lime, dolomitic limestone, and quartz were extensively used in the mixing of plasters [7]. The techniques and materials used in Nabataean Petra were quite common in other areas during the Hellenistic and Roman period. However, there are some distinguishable peculiarities for Petra. Among them is the fat lime coating, often applied as a first layer, which implied that the Nabataean knew of the sandstone properties and its fragility and porosity. It seems that for the preparation of lime plaster, aggregates were collected from the nearest river beds and often mixed with pure lime and, in some cases, with dolomitic lime.

During the transitional period between Greco-Roman and Byzantine times, the art of wall painting introduced a wide spectrum of painting materials that reflected the social structure and organization of the period, the provincial and trans-regional interactions and the technological *savoir faire*. Those materials include natural minerals — locally available or imported — organic fibers, gums, oils, artificially produced, high-fired vitreous composites and other chemically synthesized products. For the substrate of the wall paintings plaster, analyses show the presence of calcite with additional traces of alumino-silicate materials (sand) and large quantities of thin whitish fibers. In many examined samples the presence of egg yolk as a binding medium was suggested, indicating that a mixed technique involving both fresco and secco was employed [8]. However, the best known wall paintings in Jordan are those covering the significant interior walls and ceilings of Qusayr 'Amra, dating from to the Umayyad period and registered as a UNESCO World Heritage Site since 1985.

Description and Significance of Qusayr 'Amra

Qusayr 'Amra (705–715), an Umayyad bath complex Located east of 'Amman, was part of the Umayyad settlement policy in the region between the cities of Amman and Azraq. The bathhouse in Qusayr 'Amra was the centre of a larger complex of buildings. It is composed of three long halls with vaulted ceilings resting on transverse arches: the audience hall, the baths and the hydraulic system [9-12]. The audience hall is rectangular in shape with a throne alcove in the middle of the south side. The bath complex comprises 3 rooms, corresponding to the *frigidarium, tepidarium* and *calidarium* (Fig 1).

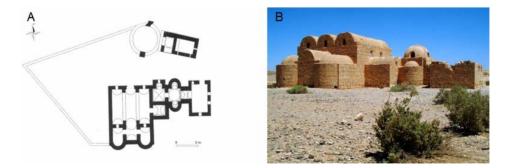


Fig. 1. The Qusayr Amra: A – the plan [10] and B - general view

In terms of preservation status, Amra is the best preserved among the Umayyad desert palaces. It was added to the UNESCO's World Heritage list in 1985, which has proven vital to some of the conservation and preservation efforts of this building complex [13]. Qusayr 'Amra,

is the most outstanding Umayyad palace and it is famous for its wall and ceiling frescoes. Those exquisite paintings are characterized by a rich iconographic repertoire that consist a major component of the Umayyad cultural heritage and an invaluable source of historical, artistic and technical information.

The most notable feature of Qusayr 'Amra, one that has fascinated scholars and travelers since the end of the nineteenth century, is the frescoed interior of the bath complex. Indeed, these four hundred-and-fifty square meters of painted walls are among the most extensive and complete decorative programs to survive from the ancient world in Jordan.

The extensive Fresco paintings of Qusayr Amra depict a seemingly disparate collection of subjects, hunting and bathing scenes, athletic activity, mythological images, dancing girls, acrobats and wrestlers, musicians, royal portraits, astronomical representations, as well as craftsmen at work (see figure 2). It has been suggested that such scenes depict the pastimes of members of the ruling elite as a way of indicating their royal status. According to the Arabian and Greek captions, one famous fresco in the Bath / palace depicts the enthroned caliph being paid homage by six contemporary rulers, among which *Basileus* (the king) of Byzantium. That scene, in particular, emphasizes the self-esteem felt by Umayyad rulers, after their decade-long conquest of lands from Spain to the Hindu Kush. They were a kind of secular self-celebration of success and wealth [14]. As a whole the frescoes in Qusayr 'Amra generate the impression that the new rulers adopted the lifestyle and tastes, as well as the desire for power, from their Byzantine predecessors [10-12].



Fig. 2. Views of the interior of Amra palace showing different decoration features.

Deterioration Causes for the Umayyad Wall Painting of Qusayr 'Amra

The interior of the Bath/palace indicates an intensive and very rapid rate of deterioration. The wall paintings are currently in a bad condition. The frescoes appear darkened and severely damaged due to the deterioration of their surface treatments and to the widespread effects of different salts. They caused significant exfoliation of the painting layers [14]. The main deterioration factors are as follows:

- Salt from several sources; one of the most frequent and aggressive factors of weathering decay is the water-soluble salt, which is known since antiquity and is still an unsolved conservation problem. It affects not only building materials, but also causes serious deterioration both to the rendering and to the painted layers. In the case of building materials, the main sources are: stone and mortar, soil, materials used for conservation and repairs,

polluted atmosphere and organisms. The weather, rain water and underground water, affected especially the paintings on the top walls and made the plaster and mortar moist, affecting the binder of the mixture as well, making it powdery in some areas. Rain water adds another problem; by threaten to cause the collapse of the walls painting. Rain water enters the main rooms through the ventilation opening in the ceiling, running on the plaster and paint and producing soluble salts. The salts dissolve in rainwater or condensed moisture and migrate through the porous matrix of the plaster. Thus, salt will concentrate in the plaster, causing the complete destruction thereof and, eventually, completely erasing the paintings (see figure 3).

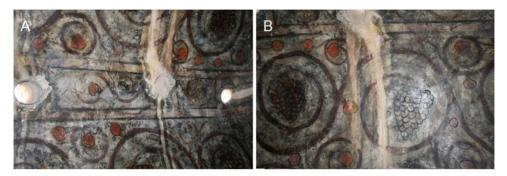


Fig. 3. Photos with the effect of rainwater flowing through ventilation openings

- *Micro-organisms and organisms;* they play an important role in the decay mechanisms of organic and inorganic materials. The important acids and salts produced by micro-organisms are chlorides and nitrates and excreted sodium chloride. Micro-organisms produce nitrates from excrement and waste [15]. Atmospheric factors, such as chemical components and climate (temperature, water and light) influence their capacity for biological growth, which is enhanced in warm and humid areas. Figure 4 shows a sample of organism growth.



Fig. 4. Organism growth

- *Human Factors*; although visitors are important for the tourism industry, they are a risk to the preservation of the monument. In fact, the continuous inflow and outflow of air caused by visitors, allows the formation of incrustation, due to evaporation or condensation of humidity on the surface of the murals [16]. Moreover, some damages were noticed on the painting, due to

the use of cement and adhesive materials from previous restorations, as in the case of the wall of the second entrance (Fig. 5). Another serious damaging factor to this monument is vandalism Fig. 6).



Fig. 5. The effects of salt crystals on both painting and mortars



Fig .6. Vandalism actions

Experimental

Methodology Characterization for Mortar, Plaster and Pigments Identification

In order to conduct the different analytical techniques, we collected 15 samples of plasters pigments, from various locations representing all deterioration features and pigments, to study their structures and basic characteristics. Broken parts and cross-sections indicated the approximate thicknesses of the layers of plasters and mortars. The plasters that support the paint layers were characterized by using the analytical methodology that enabled us to evaluate their mineralogical and chemical properties. The size of each sample was the minimum that could guarantee the success of the analysis and the confirmation for future studies. Micro-fragments of paint layers from one of the paintings, corresponding to different colors, were sampled with a small chisel by a specialist.

Analytically, the methodology integrates the use of the following techniques:

1. Op: Optical microscopy was used as the initial examination and on polished crosssections, to identify the structure of the plasters and mortars as well as the painted layers. Cross-sections of the micro fragments of paint layers were prepared and analyzed using optical microscopy.

- Micro-chemical analysis; of water-soluble salt, to identify sulphate, chloride, carbonate, nitrite and nitrate as well as the identification of calcium alumina silicate. Scanning electron microscopy and energy dispersive spectroscopy (SEM & EDS) was used for the elements present.
- 3. Standard methods were used to identify the quantitative and qualitative nature of the mortar composition (SM).
- 4. X-ray diffraction was used to identify the mineralogical composition of the pigments used.
- 5. X-ray powder diffraction was used to identify the elementary compounds of the plasters and mortars.

The Physical methods provided useful information on the mineralogical composition and the surface structures of samples, not only by determining the different causes of deterioration and decay, but also by showing the crystallization form of salts. Morphological changes were observed by optical microscopy (OM) and field emission scanning electron microscopy (FESEM), and were coupled with weight loss measurements. X-ray powder diffraction patterns were obtained for pigments and plasters, with a Rigaku D/MAX-IIB X-ray diffractometer with $CuK\alpha$ radiation. Scans of different 20 ranges between 1° to 100° were made, with steps of 0.01°/s. Scanning electron microscopy (SEM) observations for deterioration reaction products and for samples were made using a Hitachi S-4700 (equipped with an EDAX EDS system) field emission scanning electron microscope. Elemental analysis of individual reaction product particles was accomplished by energy dispersive X-ray spectroscopy (EDS), using a EDAX Phoenix system coupled with the Hitachi 4700. Acceleration voltages of 1-25 kV were used for the samples.

Results and discussions

Examination of the samples showed that the mixture of the plasters mainly contained lime, as a binder, mixed with brick powder, fine grain size, ironstone, quartzite, various shell fragments and charcoal (Fig. 7). In addition, organic material (straws) was found in the mixture of some samples. Samples were covered with an adhesive material used in previous restorations, allowing us to investigate it in section, as shown in figure 8. Some plasters were very hard and dry and some other samples were not; micro cracks were visible on the top surface with a rough structure. The examination revealed that the plaster mostly contained two different layers with *intonaco*. The thickness of plasters ranged between 7 and 15mm, with some up to 25mm. It seems that the mixture of the plasters used was more or less the same, but the thickness of *intonaco* applied for the paintings differed, as shown in figure 7.

The thickness of first layers was about 0.3-10mm and the subsequent layers were about 5-10mm thick . Not all the fragments were of the same thickness, because they came from different locations on the walls; on some samples, the plaster was very thin, mainly about 0.1-3mm. The *intonaco* layers were painted in different colors with a paint thickness of about 0.1-0.1.5mm. The colors used were; pink, blue, black, green, red, grey, yellow, cream and brown. The plasters were covered with a very thin layer of calcite film and on some areas they formed a yellowish crust. It is worth mentioning that the plaster of the first layer was very hard and dry;

the use of crushed marble crystals with the mixture made it hard, compared to the second one, which was softer.

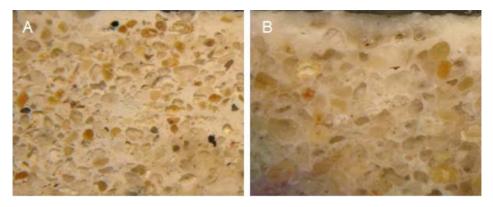


Fig. 7. Photomicrographs showing the similarities among plaster contents (40X magnification).



Fig. 8. Photomicrograph of adhesive material from previous restorations

Actually, broken parts and cross-sections allowed us to see the material structure and determine the characteristics of the materials used, such as the shape of the gravel, sand crystals, etc. before using chemical analysis. Polished cross-sections gave us an approximate measurement of the applied layer thickness (Table 1).

Table 1. Examination of Cross-Sections: Measurements of Plaster

Sample No	Painted layer	<i>Intonaco</i> layer	Plaster layer (1)	Plaster layer (2)
	mm	mm	mm	mm
F. 1	-	-	5-5.5	0.2-0.4.5

Cracks were visible on some samples, not only inside the plaster, due to mechanical stress, but also on the surface, as shown in figures 9, 10 and 11. Microanalysis showed variations in the microstructure of the surface deterioration, in all samples. Aragonite crystals were found in some cracks, which were probably the result of the dissolution and crystallization of carbonates in the mortar.

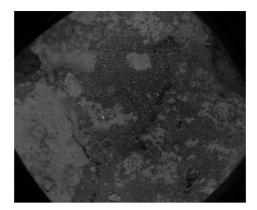


Fig. 9. The surface structure of plaster sample F. 4/2 and the elements present on the surface. The photograph shows the general surface and you can clearly see the cracks present on the surface.

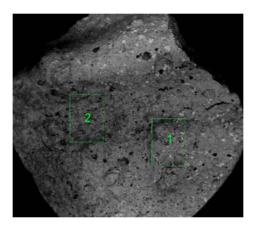


Fig. 10. Photograph using SEM of the surface structure

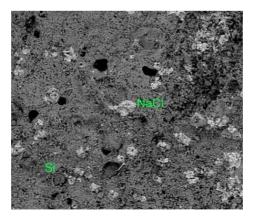


Fig. 11. Two different analysis areas with similar elements, but in different amounts. The most important elements observed were: Ca, Si, Al, S, Mg, Na and Cl. In B you can clearly see the white spots on the surface (Figure 10, area 1 and 2). Higher magnification indicated that they were NaCl and Si, on the surface.

On polished section samples, SEM results show the damage of the surface caused by the layer of sodium chloride (NaCl) accumulated on the left side of the sample (as shown in figure 12 a). However, the salt found underneath the *intonaco* layer surrounded and dissolved the binder mixture, as shown in figures 12 b and 12 c. The *intonaco* layer was very pure calcium (Ca), with quartz grains. You can clearly see the grains on the top, indicating the dissolving of lime, which uncovered the grains.

The second layer showed mainly quartz grains with lime (pure) and sometime with quartz, as shown in figure 12 d. The salt dissolved the binding material in the second layer as well. This may indicate that this layer, which is close to the wall, transferred salt from the wall structure to the mortar and affected the material. It is worth mentioning that NaCl was mainly found in areas near the surface. This factor should be taken into consideration in any conservation treatment of the salt problem.

It is remarkable that the initial analysis of the elements present in the first and second layers was confirmed by the micro-chemical test.

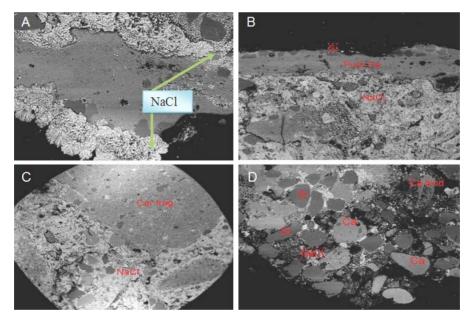


Fig. 12 SEM images of the polished samples a, b, c, d, shows the damaged surface caused by the accumulated layer of sodium chloride (NaCl).

From our observations during the examination, we found that soil deposits were present on the top surface and it formed a layer of accumulated dust and/or dirt. That layer was in yellowish and soft and could easily be removed by scalpel during the examination. A general analysis of the first layer revealed that the main element present was calcium (Ca) and we also found magnesium (Mg) and silicon (Si), indicating that the first layer of the plaster was mainly of calcium (see Table 2). However, the magnesium present in the lime mix may cause expansion if hydrated [17].

Sample		Elements											
No.	Area	Na ₂ O	MgO	Al_2O_3	SiO_2	Y_2O_3	P_2O_5	SO_3	Cl_2O	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
First layer	Overall analysis	0.31	2.40	0.57	1.34	1.64	0.16	0.71	0.28	0.33	91.81	0.19	0.26
Second layer	General bulk	1.61	2.24	10.26	34.00	1.22	0.25	0.72	0.35	1.88	43.37	0.56	3.55

 Table 2. Chemical Composition from the EDS analysis (Wt %).

X-ray powder diffraction patterns were obtained for pigments and plaster with a Rigaku D/MAX-IIB X-ray diffractometer, with $CuK\alpha$ radiation. Scans were taken of different 20 ranges between 1° to 100°, with steps of 0.01°/s. The x-ray results showed that the main compounds of the first layer was calcite, dolomite and a negligible amount of quartz. The second layer indicated the presence of calcite and quartz and, as the sample was sufficient, it was difficult to confirm the presence of other compounds. The results are typical for hydrologic lime mortars prepared with calcitic lime and siliceous sand. The application of adhesives (probably PVA- poly vinyl acetate) was used as a lacquer for restoration and for a small amount of pigments. Therefore, it was difficult to obtain an accurate result using X-RD. However, in figure 13 some samples of green and red pigments indicated the presence of halite and of a potassium and sodium chloride, a mixed sodium and potassium sulfate and calcite, which indicated to the use the *fresco*[3, 13].The colors present were mainly the earth colors: red ochre, yellow ochre, green earth, black soot or charcoal, white-lime or chalk, pink was found as lime with red ochre, as identified by chemical analysis. Green earth was found on carbon black (possibly soot or charcoal).

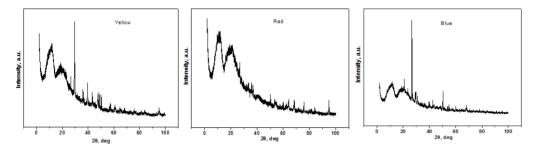


Fig.13. X-ray diffraction for A - yellow sample, B - red sample and C - blue sample.

Micro-chemical test were carried out where necessary, to identify the type of the plaster and the mixture used. A solution of the samples (the first and second layers) was made, before washing the residue in separate test-tubes, to identify any calcium aluminum silicate, by using caustic soda (10%). The results revealed that both layers indicated the presence of aluminum silicate in high concentration, possibly from the lime/sand/aggregate. A 10% solution of hydrochloric acid (HCl) was used to dissolve the lime/carbonate material, after the separation of the two layers, in order to identify the residue of each layer. The first layer (grey) dissolved in HCl acid with a residue of charcoal, quartz sand (very fine), quartzite and brick fragments (a few pieces). The second layer reacted with the acid and we could clearly identify the residue of the layer, which contained: quartz sand, quartzite, brick fragments and charcoal. The plaster was calcareous, containing lime as a binder. However, the sample was too small to estimate the ratio of lime to aggregate used.

Micro-chemical tests was also carried out for the identification of iron, as we observed that the solution was yellowish. A part of the solution was taken and tested by using ferrocyanide (2%). In the presence of iron the solution turns blue. The result indicated that the solution of the first layer had traces of iron, as it turned light blue, whereas, the solution of the second layer turned very dark blue after adding ferrocyanide, possibly because of the brick fragments used inside the mixture.

The analysis of water-soluble salts is one of the essential aspects in the examination of works of art, particularly of wall paintings, as it is known that wall paintings usually contain salts from different sources [19]. It is possible to obtain primary information about the presence of salts, by performing micro-chemical tests, which can be confirmed by physical methods. The identification of salts was carried out, in order to identify sulphates, chlorides nitrites and

nitrates, as those salts were the most important. For our measurements we used a standard of 1g of sulphate and chloride dissolved in one liter of deionised water. Samples of 1-2g were set in 20 ml of deionised water, shaken, and left to precipitate.

According to Teutonico, 1988 [19], after analyses of water-soluble salt, with the exception of carbonate, the samples are dried at 85 °C and weighed, before and after analysis for carbonates, to calculate the percentage of the residue, as well as the dissolved amount. The results of our analysis of the water-soluble salts are listed in Tables 3 and 4.

Samples No	Type of Sample	Sulphates (SO ₄)	Chlorides (Cl)		
1	Lime mortar to fix	+	++ wp		
2	the tesserae	-	++ wp		
3		-	+		
4		-	++ wp		
5		-	+ wp		
6		+-	++ wp		
7	Lime Plasters	+-	++ wp		
8		-	+ wp		
9		+-	+ wp		
10		-	+		
11		-	++		
WP = White precipitates $+-=$ Traces					
++ = Notably present + = Present					

Table 3. Results for Sulphates and Chlorides

- = Absent

Table 4. Results for Nitrates and Nitrites

Samples No	Type of Sample	Nitrates (NO ₃) mg	Nitrites (NO ₂) mg
1	Lime mortar to fix	50	0.5
2	the tesserae	15	0.5
3		25	0.5
4		100	1
5		25	-
6	Lime Plasters	50	-
7		20	0.5
8		25	1
9		25	0.2.5
10		50	5
11		250	1

The results of our analyses indicated that the most significant salts found were chlorides and nitrates (as illustrated in Tables 3 and 4). It is very interesting to notice that the percentages of dissolving samples varied from 0.90 to 7%, the most significant is sample 1, which got to 30%, however, samples 8 and 9 got to 3%, whereas samples 5, 6 and 7 2%. However, the results of the analysis of nitrates and nitrites, as stated in Table 2, show that the highest amount of nitrates, found in sample 11, was 250mg, whereas in samples 1, 6, 10 and 12 it was 50mg and 25mg in samples 3, 5, 8 and 9. The lowest amount of nitrates noticed in samples 2 and 7 was 15-20mg.

Our analysis revealed a full picture of the elements present on the surface. However, most of the elements present were not in large quantities, with the exception of calcium (Ca), found in all samples. The most important elements were: calcium (Ca), silicon (Si) and sulphur (S), aluminium (Al), magnesium (Mg), and some iron (Fe). Chloride (Cl) and sodium (Na) were found in most of the samples. Calcium showed the highest level, then silicon and the other. From the results, we noticed that calcium (Ca) and sulphur (S) were present in some samples.

We may assume that the presence of calcium and sulphate was due to the transformation of calcium carbonate (plaster/mortar or limestone) as a compound of the mixture, into a calcium sulphate, resulting in the process of deterioration and decay that affected the complex. However, a key point to be considered is that the surfaces were not plain. The layers covering the surfaces, which were found in some instances, meant that certain elements in one area may not be present in another of the same sample.

The presence of salts in all samples, may have resulted from the actual materials, or as a result of the decomposition of calcium carbonate.

Deterioration and Conservation Challenges

The long-term *in situ* preservation of this unique painting is extremely challenging. Exposure to the environment and difficult site-management issues impose severe constraints on what can be realistically achieved. Certain fragments of wall paintings showed effects of preferential weathering. Those fragments had extensive soiling and heavily weathered edges. The wall paintings surviving *in situ* displayed erosion and color alteration. The salts and the relative humidity generated by water threaten the physical fabric of the wall paintings. That includes discoloration due to changes in the microclimate. Moreover micro-flaking and different types of paint alteration were observed.

The paintings are also affected by unintentional vandalism (graffiti) and by extensive visiting that led to different degrees of physical damage to the wall paintings. In fact, Qaser Amra admits quite a high number of visitors. The recent conservation and cleaning of the paintings resulted in an increase in the number of tourists coming to visit others desert palaces around Oaser Amra. Although conservation programs continues to advocate far wider sitemanagement aims - improved presentation, interpretation and access for visitors, with the ultimate goal of increasing tourism activities in Qaser Amra area and expanding associated benefits to the local community — they cannot all be achieved immediately. This is welcomed by the local community, even if the Qaser remains are fragile. As the site is severely dusty, eroded, and completely open from the four sides, another visitor-safety issue may arise. The Qaser cannot comfortably accommodate more than 10-15 individuals, so any excess visitor numbers raise further site-protection and visitor-safety issues: tour groups consists of 50 visitors. Overall, the wall paintings pose a number of conservation challenges and imminent threats that affect their preservation. However, the most severe issues to be addressed are the uncontrolled modern human activity and the adverse environmental conditions, including hammering rains. Meanwhile, the most imminent dangers are human activity and uncontrolled microclimate, due to the large number of tourists entering the enclosed space of the Qaser at the same time.

Proposed Sustainable Preservation General Strategy

Promoting high standards of conservation in Eastern Mediterranean countries, such as Jordan, is a priority, especially since there is a demand, by some archaeologists, for professional conservators to treat their finds. At the same time archaeologists, need to allocate an adequate proportion of their budgets to remedy and preventive conservation measures, so as to ensure sound, long-term care of monuments. However, the conservation and cleaning of paintings has raised awareness of its significance, to the extent that broader preservation needs can no longer be ignored. We hope that the conservation program will set in motion the long-term protection and management measures that the site and its unique painting so clearly deserve.

The proposed sustainable strategic plan, to address the deteriorations and threats to the Qaser, should involve interested local groups in the government and in tourism and their support for the development of a holistic management plan. Therefore, access control is a solution not only to protect the painting, but also the site and its visitors. In practice, however,

this presents various difficulties, among which the most important one is securing the government's commitment to a viable management plan.

Barriers to control visitor access would inevitably be physically intrusive, while also creating problems of restricted viewing and congestion. However, there is no guarantee that barriers would provide adequate security for the painting. For the time being, introducing a serial ticket system in which no more than 10 visitors can enter at the same time would provide both security and obviate the need for barriers. It would make access entirely dependent on a designated key-holder. At present, identifying (and paying for) a permanent, responsible and qualified guardian to control visitor numbers and their activities is the only straightforward solution. Another, more radical option — to keep the site permanently closed to visitors — would avoid problems associated with access, but the adverse impact on tourism would inevitably create local resentment, placing the painting under threat.

Due to the complexity and variability of the Qaser and the issues affecting its preservation, any proposed plan should comprise three distinct phases:

- 1. The development of a pilot project to rank the Qaser according to a preservation urgency order, based on historic and artistic values and attributes, as well as on preservation needs. Analytical work should commence, taking into consideration the building stonework, since the occurrence of salt is related to specific deterioration phenomena and to particular microclimates, as well as to hydrological conditions.
- 2. The development of a detailed risk assessment and risk mitigation for the Qaser, based on an in-depth geophysical survey, aimed to assess the state of the site and the stability of the fabric. The assessment will also be based on thorough environmental monitoring and quantification of the damage from occasional rains, as well as on *in situ* scientific investigations of the surviving wall paintings and an assessment of their state of preservation. The results of this survey will lead to the best solutions to address some of the threats facing the site, while providing a list of immediate and long-term maintenance needs.
- 3. The design and implementation of emergency first-aid conservation actions and of preventive measures, taking into consideration, at the same time, the result of this current technical investigation on the identification of painted plaster.

Conclusions

Our present study has shown that, before any intervention, special care must be taken in order to obtain the actual composition of the materials in the painting plaster, for diagnostic purposes, so as to understand the properties and the deterioration processes involved. The scientific analyses of all the painted plasters described above were primarily conducted using non-invasive and minimally invasive non-destructive techniques. The chemical methods revealed the type of the plaster and the mixture, which was confirmed by the physical methods and provided more information about the elements and their composition and gave a clear view about the surface structure as well. Micro chemical tests seemed to be very necessary to distinguish the materials. They indicated the reactions between certain substances, which caused the changes in colour, shape, the precipitation of particles, as observed by the naked eye or with the help of the microscope

The examination and analysis of the plasters/mortars revealed the preparation techniques used for the walls. The analysis of different samples of mortars and plasters from different areas indicated the manufacture of the mixtures used. Quantitative and qualitative analysis has shown variation in composition. A detailed macroscopic study of the painted surface revealed several features indicating that the technique of *al fresco* painting was employed extensively.

The analysis of the plaster revealed two different layers with different compositions. The first layer was mainly calcium with a very small amount of quartz and brick fragments. From

our observation and analysis we found a few particles of brick and the sand was very fine as well, suggesting that those grains were from the lime or that they got in the mixture by accident. The application method of the first plaster was on a polished surface, which allowed all the fine grains and particles to emerge to the surface. The second layer had brick and quartz fragments in the main compound, together with lime. The grey plaster produced from crushed charcoal, which was found inside the mixture and identified, depending on the amount, as well as the particle size used, gave different shades of grayish-blue. The presence of aluminum silicate, identified by chemical analysis, indicated that the lime used was hydrologic lime, especially in the first layer and also in the second layer. Depending on the sand/aggregate used inside the mixture might also contain silicate.

The pigments were those traditionally used in classical times. They were identified by chemical analysis, because of the difficulties encountered in using X-RD for the small quantities of samples. The analysis using SEM had some difficulties to achieve accurate data on the elements that were on the surface, because the painted layers were covered with an adhesive used in previous restorations. However, as a result of the research, we obtained a more general picture of the different structures of plasters throughout the complex and we acquired more information on the manufacture technology of the plasters/mortars used and on the relationships between their composition and their place of use.

Analytical work should commence by taking into consideration the building stonework, since the occurrence of salt is related to specific weathering phenomena and to particular microclimates, as well as to hydrological conditions. The most frequent form of weathering decay is caused by water-soluble salts. It affected not only the building materials, but also caused serious deterioration both to the rendering and to the painted layers. Salt could appear from different sources e.g., ground water and rising vapors, the original materials used, the materials used for conservation and repair, biological metabolism etc. Thus, there is a need to implement some environmental interventions - such as blocking certain openings, to reduce the effects of temperature and humidity fluctuations – taking into consideration both the uncertain outcomes of such measures and their potentially adverse impact on the archaeological fabric. In order to control the environmental and physical conditions, regular monitoring procedures have to be implemented, using modern technology.

Acknowledgements

The authors would like to thank the director of the Department of Antiquities of Jordan, Prof. Dr Fawwaz al-Khrayshah, for his support and help during field work.

References

- P. Karkanas, Identification of lime plaster in prehistory using petrographic methods: A review and reconsideration of the data on the basis of experimental and case studies. Geoarchaeology, 22, 7, 2007, pp.775–796.
- [2] D. Kirkbride, *Five Seasons at the Pre-Pottery Neolithic Village of Beidha in Jordan.* Palestine Exploration Quarterly, 98, 1966, pp. 8-72.
- [3] A. Brysbaert, *Painted plaster from Bronze Age Thebes, Boeotia (Greece)*: a technological study, **Journal of Archaeological Science, 35,** 10, 2008, pp. 2761-2769.
- [4] G. Van der Kooij, M. Ibrahim, Picking up the Threads. A Continuing Review of Excavations at Deir Alla, Jordan, University of Leiden Archaeological Center, Leiden, 1989.
- [5] Vitruvius, **On Architecture**, vol. 1 and 2. (editor G.P. Goold). Trans. F. Granger. Loeb Classical Library. Harvard University Press, Cambridge MA, 1931.
- [6] R. Ling, Roman Painting, Cambridge University, Cambridge, 1991.

- [7] M. Shaer, *The Decorative Architectural Surfaces of Petra*, **PhD Thesis**, Technische Universität München, 2004.
- [8] Sister Daniilia, A. Tsakalof, K. Bairachtari, Y. Chryssoulakis, *The Byzantine wall paintings from the Protaton Church on Mount Athos, Greece: tradition and science*, Journal of Archaeological Science, 34, 2007, pp.1971–1984.
- [9] M. Al-Asad, Gh. Bisheh, The Umayyads the Rise of Islamic Art. Amman and Vienna: Ministry of Tourism, Department of Antiquities, Amman, Jordan and Museum With No Frontiers, Vienna, 2000, pp. 50–51.
- [10] K.A.C. Creswell, A Short Account of Early Muslim Architecture, (Revised and supplemented by James W. Allan), The American University Press, 1989, pp.105-117.
- [11] R. Ettinghausen, O. Grabar., The Umayyads and their Art. The Art and Architecture of Islam 650–1250, Yale University Press, New Haven, 1987 pp. 26-74.
- [12] R. Hillenbrand, **The Palace in Islamic Architecture: Form, Function and Meaning**, Edinburgh University Press, Edinburgh, 2000, pp. 443-446.
- [13] S. Bianchin, U. Casellato, M. Favaro, P. Vigato, Painting technique and state of conservation of wall paintings at Qusayr Amra, Amman – Jordan, Journal of Cultural Heritage, 8, 3, 2007, pp. 289-293.
- [14] R. Raed al-Shar'a, *The Craft and Building Scenes in the Fresco Paintings of Qusayr Amra*, Jordan, Jordanian Journal for History and Archaeology, 1, 3, 2009, pp 1-14.
- [15] R.J. Arnold, J.A. Karty, A.D. Ellington, J.P. Reilly, *Monitoring the growth of a bacteria culture by MALDIMS of whole cells*, Analytical Chemistry, 71, 1999, pp.1990-1996.
- [16] G. Torraca, Deterioration Processes of Mural Paintings, in Application of Science in Examination of Works of Art, (editor William J. Young), Museum of Fine Arts, Boston, MA, 1973, pp.170-175.
- [17] J.A.H. Oates, Lime and Limestone: Chemistry and Technology, Production and Uses, Wiley-VCH, 1998.
- [18] J.M. Teutonico, A Laboratory Manual for Architectural Conservators, International Centre for the Study of the Preservation and Restoration of Cultural Property, Rome, 1988.

Received: August, 01, 2011 Accepted: October, 22, 2011