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Case study

Diagnosis of weathered Coptic wall paintings in the Wadi El Natrun region, Egypt

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Abstract

This paper deals with the impact of soluble salts on the deterioration of wall paintings in the region of Wadi El Natrun in Egypt, including the identification of the building materials and pigments used. For this purpose we used XRD analysis which proved that the green pigment in the Church of the Virgin, Wadi El Natrun is a mix of malachite and hydrocerussite, and the black pigment is graphite. The results proved that the building materials (stones, mortar, and plaster) in Wadi El Natrun are affected by ground water as they have the same soluble salts at different concentrations. The Wadi El Natrun lakes are the native source of natron salt, which has been used in mummification techniques. Soda lakes represent the major types of naturally occurring highly alkaline environments. The factors leading to the formation of the alkaline saline deposits may be divided into climatic, geological, and topographical. Climatic and topographical factors control the amount of water entering the system as rainfall or surface runoff and the amount leaving by evaporation. Geochemical factors determine which ions enter the system. Solutions of carbon dioxide result in the formation of a weak carbonic acid, which dissolutes the mineral components of the surrounding rocks and archaeological buildings, leading to their ion release.

Keywords: Mortar; Plaster; Pigments; XRD analysis; Soluble salts analysis

1. Introduction

Wadi El Natrun is a sandy depression located in the western part of the Nile delta, latitude 30°17′ and 30°38′ N, longitude 30°02′ and 30°30′ E. It is orientated NW–SE, about 22 m below sea level. Many salty alkaline lakes are found in the region half way between Cairo and Alexandria. Wadi El Natrun is one of the oldest centres of monastic settlements in Egypt. Four monasteries have survived and are still inhabited: Deir (''Monastery'') Abu Maqar, Deir Anba Bishoi, Deir al-Surian and Deir al-Baramus. These monasteries date from the period between the fourth and the sixth century and are known to have been inhabited almost continuously. Their architecture and collections of icons and manuscripts reflect the traditions of fifteen centuries of Christian history in Egypt. Deir al-Surian, or ''The Monastery of the Syrians'', occupies a special position among the Coptic monasteries. Built by monks from the neighbouring Deir Anba Bishoi in the sixth century, it passed into the hands of Syrian monks, probably during the eighth or ninth century. Syrians visit Wadi El Natrun as pilgrims, merchants or as refugees in times of trouble.

The aim of this study was to verify the effect of soluble salts on the deterioration of the Coptic wall paintings in Wadi El Natrun, using geochemical and geological data, in addition to identifying the building materials used in the studied objects.

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2. Climatic conditions

The average temperature in Wadi El Natrun ranges from 13.3 °C in January to 27.6 °C in August. This average range is very high, and has an impact on the archaeological buildings in Wadi El Natrun, as the difference between contracting and expanding is great, leading to the loss of cement material from between stone crystals and of binding mortar from between the stone blocks. The relative humidity in Wadi El Natrun varies between 44.6% in May and 63.0% in November. The relative wind velocity ranges from 8.1 knots in December to 11.4 knots in April. In Wadi El Natrun the highest amount of rainfall occurs in November, reaching up to 9 mm/month as registered in November 1980. In some years no rain is registered in November, and overall, rain in Wadi El Natrun is rare and occurs in the wet season (October to April). The degree of evaporation in the area is very important as it controls the salinity of the lake and the stability of building materials through saturation and desiccation, depending on the temperature; evaporation is very high in summer months, reaching 15.7 mm/month in May 1978 and while in January of 1983 it was lower than 3.8 mm/month.

3. Materials and methods

Building materials from the Church of the Virgin were sampled for laboratory analyses in order to determine their components. Powder X-ray diffraction (PXRD) analysis was performed using a Philips (PW 1710) diffractometer with Ni-filtered Cu−Kα radiation. The samples were scanned over the 3−63° 2θ intervals with a scanning speed of 1.2°/min. A quantitative estimation of the abundance of the mineral phases was derived from the PXRD data, using the intensity of certain reflections and external standard mixtures of minerals. The detection limit of the method was ±2 w/w%.

Water and aqueous extract of mortar, pottery and sand 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 content. The calibration procedure was made according to Zachariadis et al. [1] using combined standard solutions. A mass of 100 g was treated with 200 ml distilled water in an ultrasonic stirrer at 60 °C for 20 min, then the solid residue was removed by filtration using filter paper and in the liquid phase were determined the major ions Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}. The concentrations of heavy metals Fe, Pb, Cu, and Mn were also determined. The overall precision of the water analysis was within ±5%, as indicated by the ionic balance.

4. Results

The mineralogical composition (w/w %) of the samples from Wadi El Natrun is presented in Table 1.

Table 1
Mineralogical composition (w/w %) of the studied Wadi El Natrun samples.

Sample/ components	Sand	Mortar-1	Mortar-2	Plaster	Green pigment	Black pigment
Anhydrite	–	17	5	–	–	–
Gypsum	–	36	32	–	–	–
Calcite	48	14	50	91	88	91
Quartz	41	31	11	7	–	7
Halite	7	2	–	–	–	–
Plagioclase	2	–	2	2	–	–
Natron	2	–	–	–	–	–
Graphite	–	–	–	–	–	2
Malachite	–	–	–	–	2	–
Hydrocerussite	–	–	–	–	10	–

4.1. Lake samples

The Wadi El Natrun Lake is the most effective factor in the deterioration of the archaeological buildings in the area. A sand sample from the bottom of the lake was analysed and found to contain: calcite 48%, quartz 41%, halite 7%, plagioclase 2% and natron salt ($Na_2CO_3 \cdot 10H_2O$) 2% (Fig. 1a).

4.2. Mortar samples

Two mortar samples from the Church of the Virgin were analysed; the first sample (mortar-1) contained gypsum 36%, quartz 31%, anhydrite 17%, calcite 14% and halite 2% (Fig. 1b), while the second sample (mortar-2) contained calcite 51%, gypsum 32%, quartz 11%, anhydrite 5% and plagioclase 2% (Fig. 1c). Halloysite was also detected using clay mineralogy techniques, comprising the major phase in the clay fraction of the studied mortar samples.

4.3. Plaster samples

Plaster in the Church of the Virgin was applied in five layers; the layer from which the sample was taken was the surface layer, which was added in 1781/2 AD in a re-plastering process [2,3]. The sample contained calcite 91%, quartz 7% and plagioclase 2% (Fig. 1d).

4.4. Pigment samples

4.4.1. Green pigment

The green pigment sample, which was obtained from the altar of the Church, contained calcite 88%, hydrocerussite $Pb_3(CO_3)_2(OH)_2$ 10% and malachite 2% (Fig. 1e).

4.4.2. Black pigment

No evidence has existed until now for synthetic black pigments in ancient Egyptian wall paintings. The black pigment sample contained calcite 91%, quartz 7% and graphite 2% (Fig. 1f).

5. Discussion

Anhydrite was detected along with gypsum in mortar samples, which may indicate that:

1. The gypsum has completely changed into anhydrite, and, because of high relative humidity, anhydrite has begun to