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Salt Weathering on Buildings and Stone Sculptures

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Salt efflorescence and subflorescence in Baroque frescos and the role of bat droppings in the decay wall paintings

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ABSTRACT

Baroque frescos of Sümeg church (18th century) have been studied in details to understand the processes that lead to rapid and catastrophic surface loss. The decay was triggered by intense water seepage through a damaged roof which was covered by bat droppings. In situ moisture content measurements, UV, UV luminescence, IR and thermograph imaging techniques were used to locate the moist and salt effected zones. Samples were gathered both from the wall paintings and from the substrate and were studied by using optical microscopy, SEM-EDX, XRD and Thermogravimetric analyses. The major salts responsible for the scaling and loss of wall paintings are potassium-nitrate and gypsum. Additionally, organic-rich crystals that are associated to bat guano caused brownish taint and stains of the frescos. The presence of salts was extremely well visualized under UV excitation while in visible light these features were less detectable. The study demonstrates that bat guano provides salts of different types than bird droppings.

Keywords: potassium-nitrate, gypsum, SEM, UV luminescence, bat guano

1 INTRODUCTION

Salt efflorescence very often causes significant damage in wall paintings (Harsányi et al. 2000). The damages are related to the crystallization pressure (Scherer 1999, Steiger 2005a, 2005b) and in many cases to chemical alterations and colour changes (Harsányi et al. 2001). The source of salt is either from ground water, sea spray (Robinson & Moses 2002, Mottershead et al. 2003), atmospheric pollutants (Sabbioni 1995, Torfs et al. 1997, Bonazza et al. 2005), biological activity (Benavente et al. 2011) or it can be mobilised from the construction material itself. In some cases the origin of the salt is ubiquitous. Bird droppings (Gomez-Heras et al. 2004) and even bat droppings (Harsányi et al. 2001, Hosono et al. 2006, Siedel et al. 2010) could provide compounds that form harmful salts to construction materials and wall paintings.

The present paper focuses on a case study when salts derived from bat droppings caused significant damage in a unique wall painting. The studied fresco is one of the nicest Baroque examples, that is located in a church in W-Hungary (Sümeg). The main aim of the research was to perform a complex diagnostic study to understand the deterioration mechanism of the fresco and also to provide information for the future restoration programme. The objectives of the tests were: i) to identify the painted layers and type of mortar/plaster, ii) to delineate the damaged zones of the wall painting, iii) to analyze and to identify the composition of salts and iv) to clarify the origin of salts. In situ photo techniques on site non destructive test methods and laboratory analyses were applied to answer the above listed points. The methodology applied in this study can be used as a guideline for further research on damaged wall paintings.

2 THE WALL PAINTING

The wall painting is found in the entire interior of a Baroque Church. The church is located in the small town of Sümeg (Central W-Hungary) (Fig. 1). The settlement is also known as one of the residence towns of Hungarian archbishop's. The church was elevated in 1756 while the famous wall paintings were prepared between 1757-1759 by Franz Anton Maulbertsch. The artist is known as one of the most famous ecclesial painter of Central Europe (Austria, Hungary). The paintings depict scenes from the life of Jesus covering full interior of the church. The church enclosing the wall painting is also called the "Baroque Sistine Chapel". The damaged part of the wall painting is fortunately limited to a smaller section above the NW Choir of the church (app. 20 m^2).

Figure 1. Location of the church in Hungary (Sümeg) and the main façade with the spire.


Figure 2. The interior of the Church with the frescos.

3 METHODS

The wall painting documentation began with the photo technical analyses. The main techniques applied were: normal light -, raking light -, Ultraviolet (UV) luminescence-, and Infra Red (IR) photography. Thermo-vision camera was also applied.

From the non destructive in situ measurements, moisture content detection (equipment: GANN Hidromette UNI) was aimed to delineate the moist and dry zones of the wall painting. Besides areal recording, vertical profiles were also measured.

Small samples were obtained from the painting and from the plaster for laboratory analyses. Altogether 40 samples were collected by scalpel and by drilling. The two drillings were made at places where no frescos remained on the damaged wall.

The physical properties of plaster samples were tested under laboratory conditions. Bulk density, material density, porosity and water absorption of plasters were measured. Nitrate content of distilled water extract of samples and pH was also recorded. The SiO2, CaO and MgO content of selected samples were analyzed. Thin sections were also prepared from the plasters and described by using polarized light microscopy.

From the painted layers cross-sections were prepared and studied by using optical and fluorescence microscopy. Polarized light microscopy technique helped in the identification of pigments. Mineralogical composition of pigments and plasters was also determined SEM-EDX. Micro-fabric and crystal morphology was also documented by SEM and BSEM. The mineral composition of bat droppings and salts were cross checked with XRD (Philips PW 105). Thermogravimetric analyses were used to determine the mineral composition of plasters (MOM Q-1500 D).

4 RESULTS

The photo technical analyses, especially IR and UV luminescence techniques have shown that the frescos were previously repaired. For the former interventions different materials were used.

The UV luminescent images revealed that salts were precipitated on the surface of the wall painting. The salts showed strong predominantly bluish luminescence, clearly depicting the damaged areas (Fig. 3). This technique was also very useful in recording the organic discoloration related to migrating salts. Organic decomposition resulted in the formation of brownish stain. Raking light and macro photos clearly show that white salt efflorescence and brown stains on the surface (Fig. 4).

Figure 3. Normal light (left) and UV luminescence (right) image depicting the badly damaged zone (bright zones on the UV image) of the fresco, in the the NW Choir of the church.

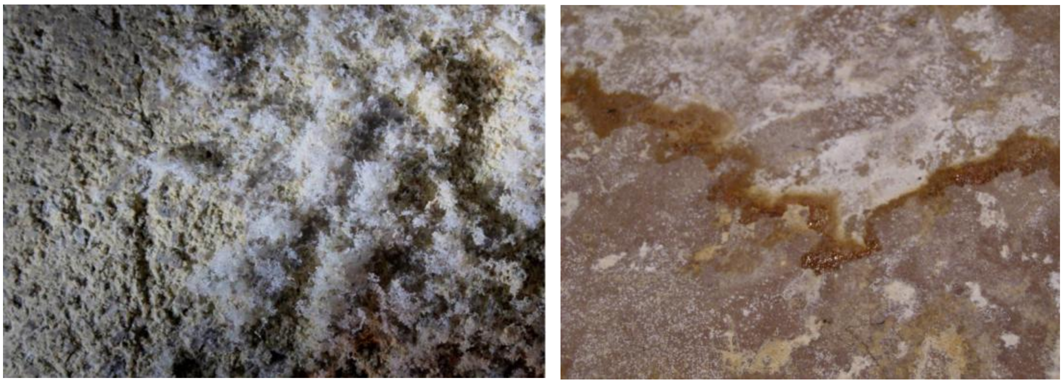

Figure 4. Macro photos of the white salt efflorescence (left) and brownish stain (right).

In situ moisture content measurements clearly demonstrated that areas where salts were accumulated had elevated moisture content. Along vertical profiles the highest moisture content was recorded close to the ceiling (Fig. 5.). The difference in moisture content between the driest point and most wet one was at least more than double.

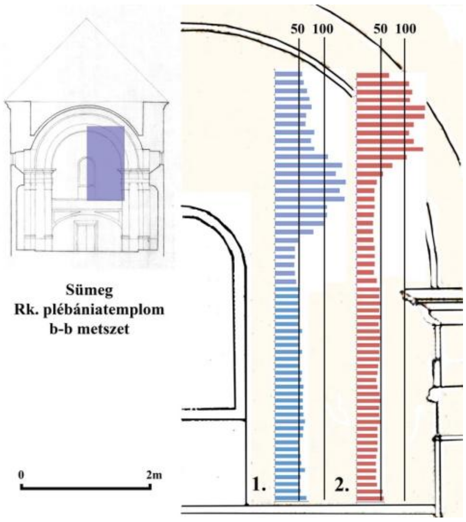

Figure 5. Cross section of the church (left) with two moisture content measurements (right) showing increasing moisture content along vertical profiles of the choir showing the downward migration of moisture from the ceiling (length of horizontal bars are proportional with the moisture content).

The bulk density of the plaster samples were in between 1636-1849 kg/m3. Water absorption of these samples were in the range of 15.7 to 25.8 V%, while the apparent porosity values were 28.0 and 40.0 V%. These wide ranges of values reflect compositional differences of plaster layers. Polarized light microscopic analyses of the micro-fabric of plasters revealed that the lower layers of the plaster are composed of larger grains (up to 2-3 mm) of quartz- and quartzite pebbles. The upper layers consist of finer grains (0.5 mm and less) of quartz and limestone sand. The binder is predominantly calcitic (Fig. 6).

Painted layer analyses revealed that historical Baroque pigments were used. Mainly earth pigments such as iron-oxide (ochre) with red and yellow colours, and green earth (celadonite) were found in the painted layers (Fig 7). The blue color was smalt (cobalt containing glass). The wall painting generally consists of two or three layers. The salts did not change the original colors of these historic pigments, but caused physical damage by crystallization pressure and the new brownish stain appeared on the surface.

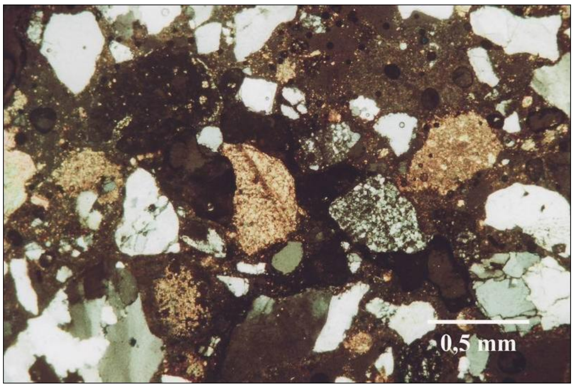

Figure 6. Fine angular grains of various mineral composition (quartz, calcite) in the upper plaster layer embedded in calcareous matrix (transmitted light microscopic image, crossed polars).

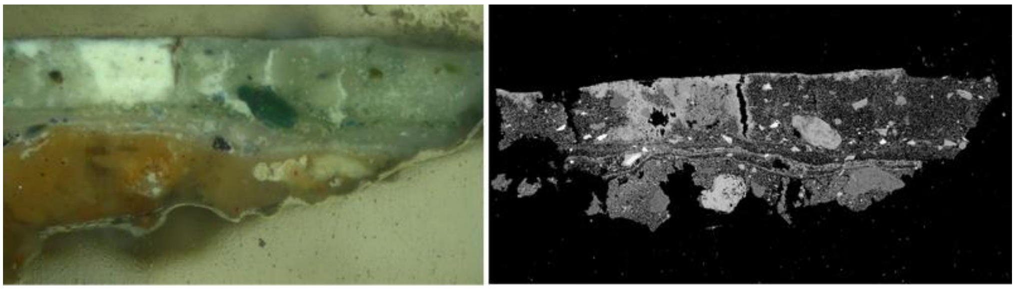

Figure 7. Cross section of the original painted layers, showing a light blue underpaint with smalt, and a greenish layer with green earth and lime. (left: reflected light, right: SEM –BSE).

Wet chemistry analyses of salts indicated high sulphate and nitrate content both in the painted layers and in the plaster below. The nitrate content was in between 0.1 and 2.5 %, while the sulphate content varied between 0.04 and 2.26%. The nitrate content decreased from the painted surface to the plaster. Meanwhile higher concentration of sulphate was detected within the plaster than in the painted layers. The sulphate is in the form of gypsum (DTA-DTG and XRD analyses), while the nitrate forms K-nitrate crystals (XRD). By analyzing the crystal morphology with SEM, it is evident that gypsum forms rosette-like crystals (Fig. 8) while potassium-nitrate is in the form of curved crystals.

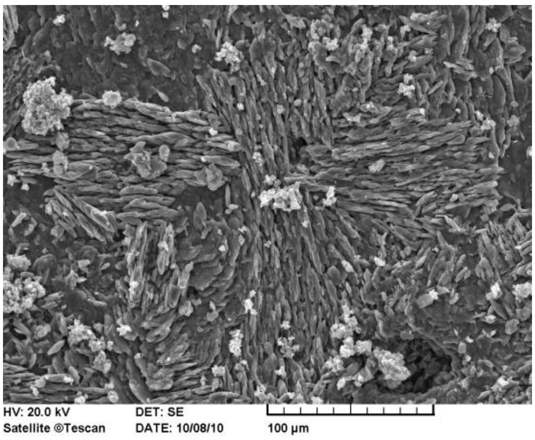

Figure 8. Rosette- like gypsum crystals cover the surface of the sample (SEM image).

XRD analyses of evaporated dissolved bat droppings indicated that the samples are enriched in potassium-sulphate (arcanite), Ca-oxalate (weddellite) and in ammonium-phosphates. Based on these analyses and the brownish stain on the surface of the wall paint it is very probable that the source of salt is the bat dropping itself. The bat droppings were also boiled in water and after the evaporation of water the crystallized salts were visualized by microscopic techniques. The crystals were idiomorphic and had a brownish organic stain (Fig. 9). Due to the presence of brownish organic matter micro-organisms start to grow immediately after the evaporation of the water on these crystals.

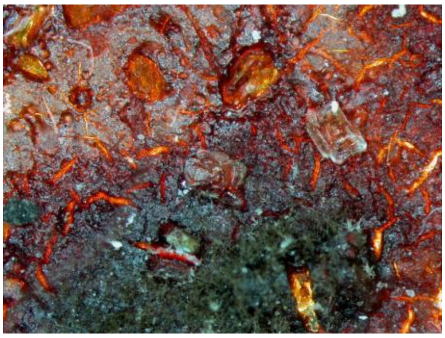

Figure 9. The boiled, evaporated bat droppings contain idiomorphic salt crystals and brownish organic-rich stain (microscopic image, the crystal size approx 0,2 mm)

5 DISCUSSIONS

The salt damage of the wall painting is a complex and multi-stage process. The compounds needed for the mixture of salts found within the wall is derived partly from the porous plaster and partly from external sources. The Ca- source of the main salt gypsum is the calcite of the plaster, while sulphate is most probably came from the bat droppings. The nitrate for the other most common salt, the potassium-nitrate was also mobilized from the bat droppings. The leaking roof allowed significant amount of water inflow into the attic of the church. It dissolved the bat droppings and washed in to the walls via the ceiling.

It has been demonstrated that the distribution of the salts are uneven within the wall. More soluble salts such potassium-nitrate preferentially accumulate on the wall surface as efflorescence in summer period, meanwhile the less soluble gypsum and sulphates are preferentially found in higher concentrations in sub-florescence. These findings are in accordance with the previous studies (Siedel et al. 2010, Benavente et al. 2011, Lee et al. 2011).

Pigeon droppings can have a high salt content of various composition with detected halite, sylvite, potassium calcium sulphate, aphthitalite, apatite, weddellite and gypsum (Gomez-Heras et al. 2004). This mixture of salts causes significant deterioration in construction materials due to acid attack. The formation of acid leachate is very probable in case of bat droppings, too. The composition of bat droppings is different from the pigeon one. According to previous studies (Hosono et al. 2006, Siedel et al. 2010) of Angkor monuments (Cambodia) the bat guano related salt efflorescence contains detectable amount of soluble salts, like nitrate, phosphate and chloride.

In our studies the dissolved bat dropping contains potassium-sulphate, Ca-oxalate and ammonium-phosphates. The composition of bat droppings derived salts from the Egyptian tomb from the Valley of the Kings in Thebes (Harsányi et al. 2001) contained white and brown crystals. According to XRD analyses the previous ones were formed from carbamide and potassium-ammonium-phosphate, while the latter dark colored one was made of guanine. These salts derived from bat droppings also caused brownish stain on the surface of the tomb in the form of dark spots (Harsányi et al. 2001). These brown crystals were made of ammonium-potassium-hydrogen-phosphate. The presence of micro-organisms on the surface of the precipitated crystals of the boiled bat guano suggests that it is very rich in nutrients. Accordingly the colonization of wall paintings by organisms was accelerated by the bat droppings solution that reached the paintings. The bat guano derived salts are commonly fostering microbiological activity (Hosono et al. 2006, Siedel et al. 2010). It has been documented previously that besides salts, the biological and microbiological activity also has a negative effect on the preservation of mural paintings (Mona-I-Fahd 1994, Pedersen 1996, Weiss et al. 1996).

6 CONCLUSIONS

The primary cause of the damage is related to the leaking roof. The second is bat droppings, which contain a mixture of compounds from which water can dissolve salts and organic matter. These solutions have a multiple negative effect on wall paintings. The salts themselves damage the painted surface, mainly by crystallization pressure, but they also stain the fresco. Additionally, organic compounds derived from bat droppings provide nutrient for microorganisms. This microbiological activity also has harmful physical and chemical influence on the wall painting since it causes flaking and generates new types of salts. The complexity of these decay processes are related to the multiple sources of the salts (bat droppings, activity of microorganisms) and to the composition of the construction material (Ca rich plaster). Since bats are strictly protected animals, their activities can not be restricted; therefore the elimination of the contact of bat droppings with water, and with the wall is the main preventive method.

Restoration is difficult since a mixture of salts were found on the wall painting and within the plaster. The simple extraction of salts is not possible since soluble (nitrate) and less soluble (gypsum) salts are found within and on the surface of the wall. A multi phase salt extraction is needed beginning with the removal of efflorescence by means of mechanical methods to prevent the re-penetration of salts into the paint layer. It is necessary to monitor the salt content of poultice and also of the wall itself.

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