



ARCHLAB ACCESS REPORT

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Title of the ARCHLAB TNA Project: Yellowish Gypsum Efflorescences on Wall Paintings from the 14th Century in the Cathedral of Schleswig in Northern Germany

Project Acronym: GypsEffSchleswig

User Group:

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Period of the visit: Monday 10th Oct – Friday 14th Oct 2016

Date of the report: 22.11.2016

Background to the project:

The research visit at the “Opificio delle Pietre Dure” (OPD) in Florence was performed within a project funded by the DBU (*Deutsche Bundesstiftung Umwelt*, project number 32169-45) with the title: “The historical wall paintings in the ‘Schwahl’ of the dome St. Peter in Schleswig: Analysis concerning transformation, mobilisation and re-crystallisation of Gypsum on a substrate heavily affected by salt contamination”. Mobilisation of gypsum and damages caused by its crystallisation, both in the presence of hygroscopic salts, as well as dissolution

cycles in porous media are also part of my PhD project at the University of Hamburg in the working group of Prof. Dr. Michael Steiger in the Department of Chemistry.

The Schwahl is the cloister of the St. Peter cathedral in Schleswig which was constructed between 1310 and 1320. As the cathedral is not a monastery, the cloister had more the function of a procession corridor and was used for spiritual events. The uniqueness of the cloister for the area of Northern Germany is given by wall paintings (see also Figure 1) which decorate its walls and vaults. While vaults and courtyard-sided walls show polychrome paintings of apostles, mythical creatures and leaf tendrils, the 22 bays on the remaining walls are decorated with monochrome lime or lime casein paintings. Executed with a red pigment they tell the story of Christ's life. Only little information is available about the artist, but it is attributed to a workshop in Lübeck. The restoration history of the object started quite early with various revisions, reparations, corrections and also whitewashes. As the documentation about the interventions started only in the late 19th century it is quite hard to distinguish between original substance and renovation.

At the beginning of the DBU project it was known that the bays suffered from yellowish crusts whose extend varied from bay to bay, affecting not only the aesthetic appearance. Also damages in form of scaling and partly losses of the painted layer were observed. In depth behind the painted layers most of the bays were affected by salt contamination, especially by nitrates and chlorides. Due to a very humid and consequently advantageous climate the salts remain dissolved most of the time. In the past, from 2010 to 2013, the object was investigated and a high enrichment of gypsum on the surface of the wall paintings was detected, leading to the assumption that the yellowish crusts are a result of gypsum encrustations. After a restoration and consolidation with the barium method the yellowish crusts returned quickly even though salt contents in the first centimetres and the gypsum enrichment were initially reduced directly after the procedure. The DBU project should investigate the situation of the wall paintings to establish a suitable conservation concept for the object which is an important part of the German cultural heritage from the Middle Ages. Parallel to lab experiments with the goal to investigate the influence of hygroscopic salts on the (re-)crystallisation and the damage caused by gypsum as well as its mobility, the influence of the crusts on the moisture content and hygric behaviour of the walls should be investigated, to name only two of the main objectives treated in the project.



Figure 1: Photographs from the *Schwahl* in Schleswig. a) bay no. 5 showing the murder of innocents in Bethlehem b) example for the polychrome decorated vaults c) detail of bay 5 with an extreme presence of yellowish encrustations on its surface.

Questions addressed by Access:

Until now the source for gypsum is not clearly identified and the situation in the cloister is far from being understood. The visit at the OPD was requested to help understand the yellowish crusts and the reason for the fast re-crystallisation of gypsum after its transformation. The applicability of the barium method on this object with high contents of nitrates was another aspect to be discussed. Access to reports and information in combination with the expertise at the OPD were a support to understand the object and its situation and consequently a help in the process to find a concept to cure and preserve it.

Main objectives of the project proposal (max 1 p):

The special situation of the wall paintings in the cloister in Schleswig with a quickly returning yellowish encrustation after gypsum transformation and consolidation in combination with a high salination with nitrates were the two main objectives that should be followed during the visit at the OPD. For that purpose the reports and documents from the OPD concerning performed restorations and investigations of wall paintings were examined with regard to find similar symptoms. The precise problem present in Schleswig was directly discussed with experts from the OPD and there was the possibility to analyse samples of the wall paintings from Schleswig with the methods usually applied at the OPD.

Main achievements of the ARCHLAB visit (max 2 p):

During the visit at the OPD, funded by the ARCHLAB program, very useful conclusions were obtained which will be demonstrated in the following passages.

The research in literature was mainly focused on the annual journal “*OPD Restauro*” which is published since 1986. The access to reports of restorations and also to case studies in the field of conservation was limited until the visit of the OPD, as such articles are often published in conference transcripts or in media hardly accessible at the University of Hamburg. Hence articles in the “*OPD Restauro*”, dealing with wall paintings with yellowish encrustations or the presence of gypsum, were selected and read carefully. With the first matching articles it was revealed that the yellowish crusts are not a result of superficial gypsum enrichments. Yellowish crusts or patinas also with an irregular distribution on the surface of wall paintings were described in some articles.

Some of these affected objects will be mentioned below. In some cases the used interventions, problems and analysed substances should be pointed out as well because alternative procedures to compresses with ammonium carbonate and barium hydroxide, as it was used in the *Schwahl*, were to be investigated too. Furthermore this should help to find diverse conservative possibilities how the wall paintings in Schleswig could be cured, to understand the situation and to examine reasons for the failure of used interventions. Of course every single object has its own characteristics and it is acknowledged that an equivalent case of degradation does not exist but the information about similar objects and their conservation should be seen as part of a process leading to a suitable treatment of the considered artwork.

The intervention on a *graffito* from the 15th century on the façade of *Palazzo Gerini – Barbolani di Montauto* included similar problems regarding the formation of superficial crusts. The *graffito* suffered from black gypsum crusts and a patina of natural oxalates. After a treatment with compresses with ammonium carbonate solution spots became visible on the surface. Organic substances absorbed by the porous materials in form of impurities in the atmosphere are named as origin for this discolouration. Wet compresses and alkalinity transport them to the surface where they become visible as spots during drying. Absorbing compresses comprising arbocel, sepiolite and a diluted solution of ammonium carbonate were necessary to remove them.^[1]

A yellowish patina was also observed in the “*Cappella della Maddalena*” in the National Museum Bargello in Florence (Figure 2). These wall paintings are dated to the 14th century and were executed by Giotto and his workshop. Also in this case organic materials introduced in past conservation interventions as fixatives (acrylic resins) would have provoked the patina, since it might be dissolved by water and other treatments when they penetrate the *intonaco*. To prevent interactions of agents used for cleaning and pigments or binders as well as dissolution of organic materials responsible for yellowish patinas only a small amount of solvent should penetrate the wall paintings. As an alternative to cellulose an acrylic polymer, “carbogel”^[2], was used in parts whose conditions allowed it. The material shows a high retention of the solvent (here ammonium carbonate solution) and can be

removed completely. Consequently there is a limited penetration of solvents and a faster drying of the wall afterwards. More sensitive parts were treated with varying solutions (ammonium carbonate or ammonium bicarbonate), concentrations, substrates and application. However, also here, yellowish discolorations appeared after the application of the barium method. As a consequence of their difficult removal with absorbing compresses an alternative method for the consolidation was used, which was a dispersion of calcium hydroxide nanoparticles in isopropyl alcohol^[3].^[4]



Figure 2: Yellowish patina on wall paintings in the “*Cappella della Maddalena*”; photo taken from [4].

Another case of affected wall paintings is the “*Annunciazione*” attributed to Michele di Ridolfo del Ghirlandaio. The painting is located in the church of the village Querceto and was painted during the 15th century. Animal glue from former restorations together with oily binders provoked a brownish layer. In this case the presence of organic binders inhibited the use of alkaline substances like ammonium carbonate or barium hydroxide. Caseinates of calcium or ammonium were used for the consolidation of the *intonaco* while the painted layer was treated with ammonium caseinate and synthetic resins. The used methods were chosen depending on the condition and quality of the area. For cleaning agar gel was used as support. This material usually used for paintings on panel or canvas has the characteristic to spread the solvent on the surface while it retains humidity and solvent, preventing their penetration into the inner parts of the wall. A limited penetration of water was necessary due to the executive technique of the painting, the *tempera* technique, which leads to water sensible paintings. Instead of water or ammonium bicarbonate solutions which led to unsatisfactory results ammonium citrate was used as the solvent. This chelating agent enables the removal of materials of atmospheric deposition e.g. with the bivalent calcium cation and with the presence of the base it also affects organic compounds on the surface. As it leads to the swelling of the impurities they could be removed after the removal of the agar compress and rinsing with deionised water with cotton pads.^[5]

Other objects from different restoration campaigns will be summarized briefly.

- The pictorial cycle in the “*Santuario della Verna*”, painted by Baccio Maria Bacci in the 20th century also suffered from a yellowish patina next to opaque areas and black

and green patinas. The presence of an organic material is mentioned (fixative or binder) as nutrient medium for spores.^[6]

- Wall paintings in the cloister of *Sant'Antonino* in the museum of *San Marco* in Florence were treated with the barium method in the seventies. The authors describe the presence of gypsum and yellowish discolourations of varying extends on the lunettes and of organic substances introduced during past restorations.^[7]
- Yellowish spots appeared during drying after a treatment with ammonium carbonate in arbolcel and sepiolite and mash of ammonium bicarbonate in sensitive areas of a tabernacle from the 14th century, today located in the *Via del Sole*. They were removed afterwards with absorbing poultices and also with pads soaked with benzylic alcohol.^[8]
- Wall paintings located in the church *Santa Maria del Carmine* in Florence suffered from a yellowish film attributed to a long lasting whitewash or to a fixative used in the past. A polysaccharide was identified which was removed with cotton pads soaked with a solvent mixture as well as a saturated solution of ammonium bicarbonate on Japan paper followed by swabbing with water in areas which allowed these applications. The latter procedure also eliminated gypsum.^[9]
- After testing the effectiveness of the barium method on wall paintings in the chapel of the ex-monastery di *Santa Verdiana* yellowish discolouration is described.^[10]
- The cleaning of wall paintings from the 14th century in the church of *Santa Croce* showing the Assumption of the Virgin and attributed to Maestro di Figline included a preventive step against possible yellowish spots. After the application of a mash of ammonium carbonate on Japan paper, washing with saturated solution of ammonium carbonate for the removal of organic substances and cleaning with a sponge soaked with water, two sheets of Japan paper impregnated with water were applied until the next day to absorb organic materials, thus inhibiting the occurrence of possible yellowish/brownish patinas. Also after the treatment with the barium method yellow spots became visible which were removed with poultices comprised of arbolcel and sepiolite.^[11]
- Some saloons in *Palazzo Fava* in Bologna are decorated with wall paintings from the 16th century painted by the Carraccis. Before their restoration organic substances were identified including a fixative and varnishes. The latter was removed with acetone while poultices of arbolcel, sepiolite and ammonium carbonate were applied on Japan paper followed by pads with ammonium carbonate to remove the fixative. In some areas of the paintings yellowish extraneous material arose during drying, thus leading to the requirement of several absorbing poultices for their removal.^[12]

This extract of the found articles demonstrate that in all cases in which yellowish patinas or spots are described they are attributed to organic substances or to residues of ageing of these substances which both can have such yellowish or also brownish appearance. Their sources can be found in substances used in old restoration interventions or in impurities of the mortar. In the latter case water or also interventions with wet compresses especially

with alkaline solutions can mobilise them to the surface. Furthermore in talks with the experts from the OPD the aspect of organic residues on the surface instead of gypsum efflorescence responsible for a yellow discolouration was outlined just after a short explanation of the situation found in Schleswig.

A special advantage during the visit of the OPD was the possibility to analyse some samples from the wall paintings in Schleswig with experts, Carlo Galliano Lalli and Federica Innocenti, from the Opificio. Investigated samples were taken from the *intonaco* in unpainted areas in two different bays of the cloister, one of them showing no evident encrustation and two with an extreme discolouring on the outermost layer. With the knowledge and expertise of the experts results of performed stratigraphic analysis (with optical microscopy) and investigations with scanning electron microscopy with energy disperse X-ray spectroscopy could be discussed directly and invaluable results and conclusions could be drawn. It was confirmed that also in the case of yellowish crusts on the wall paintings in the *Schwahl* organic substances are present (see for example Figure 3). Gypsum was not detected in the yellowish areas on the surface. Of course a superficial enrichment of gypsum was detectable but no sulphur or calcium was present in areas of the described crusts. Barium could be identified in parts of these areas but barium sulphate (originate from gypsum transformations performed in the years between 2010 and 2013) is not the only component. This became evident in element mappings. Besides, sections that were identified as the outermost layer and as the described crusts with optical microscopy were only vaguely recognisable in SEM images (Figure 3). A reason for that is the presence of mainly oxygen and carbon in organic materials. These rather light elements lead to darker areas in the images due to a weaker backscatter of electrons.

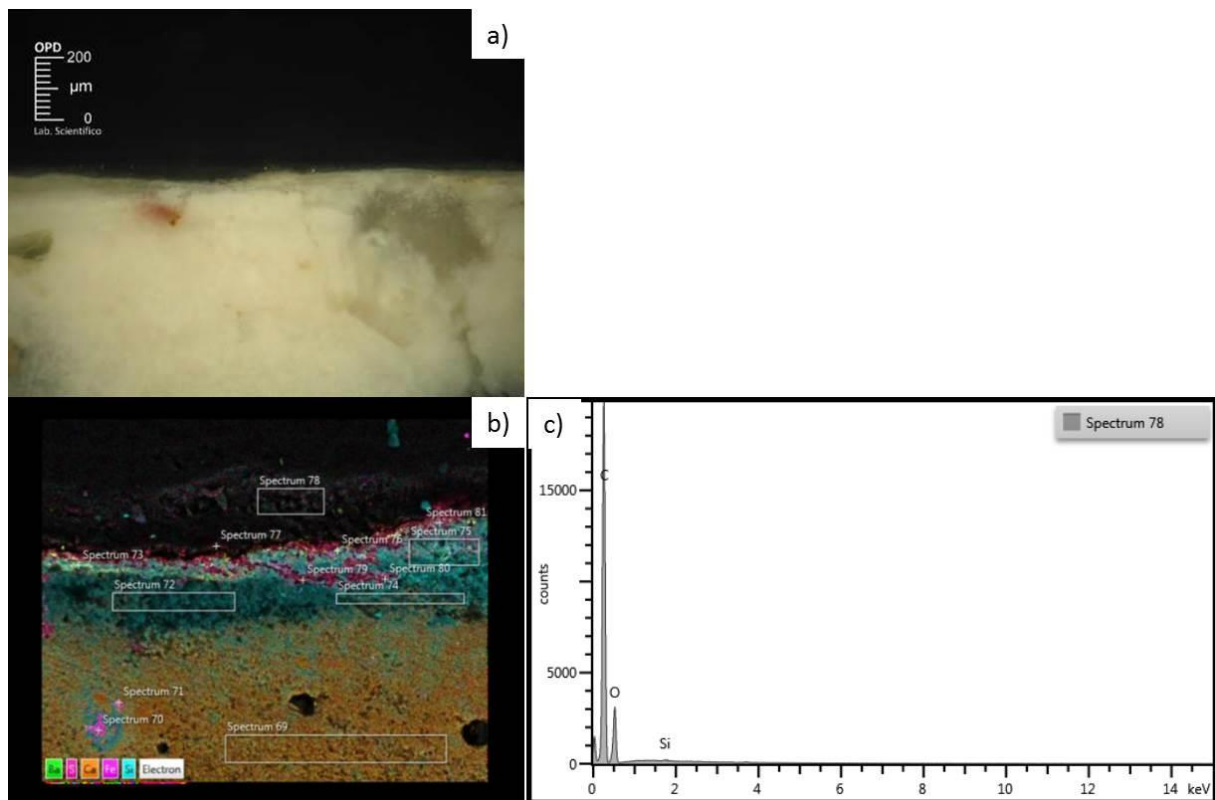


Figure 3: Sample from the *Schwahl* in Schleswig analysed at the OPD a) image from the stratigraphic analysis; b) image of the investigations with SEM with an outermost layer which is only vaguely recognisable; c) X-ray spectrum from this outermost layer showing the presence of an organic material. Figures taken from [13].

Even though the initial suspicion formulated in the application form has been disproved and gypsum is not the origin of the problem, an explanation was found during the visit at the OPD, thereby opening the way of finding solutions to cure the object and to preserve this piece of cultural heritage. Now these findings must be discussed with the participating restorers in Germany to make decisions concerning further procedures.

The ARCHLAB program enabled a very interesting stay at the OPD which helped me to expand my horizon to the field of conservation practise and conservation techniques. Next to results which are important for the wall paintings in Schleswig and also for my PhD thesis I was able to get a lot of interesting facts by reading literature including the fields of art history, painting techniques, restoration and conservation.

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Dissemination:

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| I plan to prepare a publication in an Int Journal in consortium with the ARCHLAB providers | no plans yet |
| I plan to include the results in my thesis | yes |
| I have no plans yet | |

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