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Condition Assessment of Ancient Architectural Monuments in the Pergamon Museum – Investigation of Paint and Stone Substitute Material by Micro Analytical Methods

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Abstract

Paint samples from several ancient architectural objects in the Pergomon Museum in Berlin have been subjected to analysis. Additionally the composition of a stone substitute, which has been used for the reconstruction of these monuments was investigated with the intention to use a similar material for necessary restoration measures. The results showed that a modern paint system was used on all objects on the stone substitute material. It consisted mostly of a silicate paint (potassium water glass) with gypsum and lime as fillers as well as lithopone white, umbra and traces of ochre as pigments. Besides modern paints remnants of ancient paints were discovered as well. Those consisted either of lime paint with yellow ochre or Egyptian Blue as pigments or a paint with red ochre and an organic binder. One sample of an ancient paint was discovered containing lead white as pigment. The stone substitute consisted of a mortar with white cement as binder and marble saw dust as aggregate. The material showed a average binder/aggregate ratio of 1:1.7 by mass and a maximum grain size of 1 mm. The results have been obtained by a variety of analytical techniques. To acquire cross chemical data a micro XRF has been untilized. This instrument can be used to get chemical data of very small samples and can be considered as a semi-destructive technique.

1 Introduction

Beginning from 1875 several excavation campaigns of the Berlin Museums were carried out near the Turkish coast, mainly in Pergamon, Priene and Magnesia, which lasted until the beginning of the 20th century. To exhibit the excavated objects in an adequate environment it was planned to build a new museum in Berlin, which was opened as Pergamon Museum in 1930. From the beginning the museum was designed to facilitate the architectural objects in their live size. However, over the recent years many defects of the museum building were recorded and repair seemed inevitable. Since many of the records documenting the objects in the museum were destroyed or missing during World War II, it has been decided to perform an assessment of condition and materials of the objects before any interventions were carried out.

2 Scope and Aim of the Study

In the context of the assessment of the ancient objects an extensive study concerning paints has been carried out. At first the study was focused on the modern paint systems used after the reconstruction of the ancient monuments during the end of the 1920's. During this period the stone substitute, which was used to complement the marble structures, proved to be too white and therefore a paint has been applied in order to render the stone substitute with the same appearance as the original marble. The main objective was therefore to analyze the used paint system concerning its layering and composition (binder and pigments).

Surprisingly during the course of the study remnants of ancient paints have been discovered as well. Originally most of the marble objects have been cleaned before and after reconstruction. Therefore no ancient paint was expected to be left on these parts. According to this new findings the study has been extended from one ancient monument to five more objects, now with the additional objective to find and analyze ancient paint fragments.

Another objective consisted in the analysis of the stone substitute, which was used for the reconstruction as mentioned above. At some of the monuments interventions are planned and it is desired to use a stone substitute as similar as possible to the one utilized for the first reconstruction.

3 Provenance and Type of Samples

For performing the paint analysis six monuments were probed with in total 71 samples. Table 1 lists the sampled monuments with the number of samples and some additional information concerning the buildings.

Most of the paint samples were ranging in amount from a few mg to several 100 mg. Usually the paint layer was still attached to the substrate, either marble or stone substitute. Each of the paint samples recovered from the monuments were documented in corresponding drawings.

The analysis for the stone substitute was carried out on one sample of about 50 g.

Table 1. Provenance and number of samples.

Monument	No. samples	Remarks
Market gate of Milet	31	Roman, built ca. 120 AC, excavated 1903-1907
Relief from the pediment of the Trajaneum/Pergamon	5	Roman, built 2nd Cent. AC
Entrance of the Athena sanctuary/Pergamon	15	Greek, built 1st half 2nd Cent. BC
Artemis temple/Magnesia	5	Greek, built 130 BC
Athena temple/Priene	7	Greek, built 350-330 BC
Attalos Exedra	6	Greek, built under King Attalos II (159-138 BC)

4 Methodology

All the paint samples were subjected to an extensive investigative program. First the samples were observed unprepared under a stereo microscope. After this first examination most of the samples were embedded in a resin and then sectioned by grinding and polishing perpendicular to the paint strata. The preparation of the cross sections was carried out dry in order to preserve material, which is soluble in water or organic solvents.

The cross sections were then analyzed under a polarizing microscope in reflected light mode under circularly polarized or UV light. Using this method the micro texture (number of paint layers and thickness) as well as the color of pigments were determined.

After this first two steps a micro chemical analysis with low resolution was performed in order to get the cross chemical composition of the paint layers and the substrates. In most cases these results together with the microscopic data gave an important indication concerning the type of pigments used. The analysis was realized with a micro x-ray fluorescence spectrometer (MXRF). A MXRF consists of a x-ray tube, EDX detector and a movable stage. The x-ray beam can be focused by a system of micro capillaries in the range of 30 to 200 µm. The movable stage allows to locate the sample for the analysis in a range of 100x100x100 mm. The samples needed not to be coated or prepared. Therefore not only the cross sections of paint were analyzed but also the unprepared surface of the paint layer. For the analysis a rhodium tube was used. The lightest element detected was of sodium.

Since the sample is moved under the x-ray beam the instrument can also be used for acquiring maps of two dimensional elemental distributions and one dimensional elemental profiles (line scans) of a flat sample area up to 70 x 60 mm (Müller, 2004). The method is an ideal complementation to known high resolution micro chemical techniques such as electron microprobe or SEM-EDX. The large sample chamber allows to perform a chemical analysis of a surface of a small object (maximum size 15 x 10 x 7 cm) non-destructively. For large objects such as architectural materials the methods works semi-destructive since the resolution of the x-ray beam allows an analysis with a very small amount of sample material.

In addition, some of the cross sections were investigated by the scanning electron microscope (SEM) and the energy dispersive micro chemical x-ray analysis (EDX). This was carried out, when higher resolutions were required. The measurements were performed under low vacuum conditions, therefore the samples were not coated.

In order to analyze organic components of the binder and to investigate specific questions concerning the pigments other methods were employed as well. Attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) and x-ray diffraction (XRD) was used to characterize the type of organic binder and the phase composition of pigments.

The stone substitute was studied by optical microscopy on thin sections. Due to the nature of the material it was not possible to perform a wet chemical analysis for determining the binder/aggregate ratio and to perform a normal sieve analysis by dissolving the binder with hydrochloric acid. These date were instead estimated from thin section photo micrographs of the material by using digital image analysis.

5 RESULTS

5.1 Paint samples

In essence the following types of samples were characterized during the analysis:

- Ancient paint
- Modern paint (paint from the 20th Century)
- Sinter layers and crusts
- Discoloration of stone (patina)

Based on this classification the results of the paint analysis has been summarized in Table 2.

5.1.1 Ancient paint

Only few samples exhibited ancient paint. On the actual constructions the paint appeared on areas of a few mm^2 only. Ancient paint was discovered on parts of the market gate of Milet and the entrance hall of the Athena sanctuary of Pergamon.

Two types of lime paint were found on the market gate of Milet. A lime paint with yellow ochre appeared on a pillar of the lower order. It exhibited a dense texture with inclusions of the yellow ochre. On the paint surface appeared a crust of iron hydroxide, which gave the paint fragment a more brownish color.

The second type of lime paint was found in the cornice of the lower order. Here Egyptian Blue was used as a pigment. In the ancient world Egyptian Blue was widely manufactured, utilized and traded from Egyptian times until the Roman period (Bayer 1975, Tite et al. 1987, Ullrich 1987, Eggert 1991, Riederer 1997). The blue pigment was commonly melted from a copper ore, usually cuprite or malachite, quartz sand, limes-

Table 2. Results of the paint analysis.

Sample	Type of sample
Ancient paint	Lime paint with yellow ochre Lime paint with Egyptian Blue Paint with red ochre Paint with yellow ochre and lead white
Modern Paint	Silicate paint with lithopone, gypsum, lime, umbra Silicate paint with gypsum, chalk, kaolin, charcoal, ultramarine (synthetic)
Sinter layers and crusts	Consisting of calcite, gypsum Consisting of apatite
Discoloration of stone	Consisting of gypsum with inclusions of Fe-oxide/hydroxid

tone and a flux, usually potash or sodium carbonate, at temperatures of 850° to 900°C. The blue reaction product is identical with the mineral cuprorivaite $CaCuSi_4O_{10}$ (Riederer 1997). Usually crystals of cuprorivaite are embedded in a silicate glass matrix, which both together form the pigment.

Figure 1. Egyptian Blue pigment (arrow) in the lime paint from the Market Gate of Milet (photo micrograph, reflected light, crossed polars).

The results of the XRD analysis showed that the samples from the market gate included in fact cuprorivaite as the crystalline phase of the pigment. Under the microscope the pigments could easily be detected by their blue color (Fig. 1). SEM images acquired in backscatter mode revealed the pigment's texture (Fig. 2). The silicate glass matrix was clearly discernible from the crystals of cuprorivaite. The composition of the glass matrix showed a high content of silicon, an intermediate amount of sodium and potassium and a minor content of calcium, magnesium and aluminum. One of the samples exhibited also quartz grains, which were partially molten and embedded in the silicate glass matrix. These grains represented remnants of the original quartz sand used for the manufacturing process of Egyptian Blue.

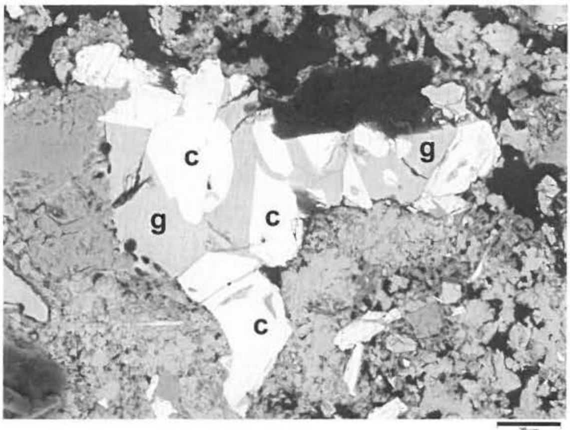

Figure 2. Egyptian Blue under the SEM. Clearly discernible are the crystals of cuprorivaite (c) and the glass matrix (g).

On parts of the entrance hall of the Athena sanctuary from Pergamon fragments of a red paint were found. The paint consisted mostly of red ochre, which was probably associated with an organic binder. However, traces of organic components could not be found and might have been transformed by microorganisms. The photo micrograph in Figure 3 shows a dense texture of the red ochre. The composition detected by SEM and XRD analysis was similar to the one stated by Schweppe (1993). It contained clay

Figure 3. Original paint sample from the Athena sanctuary of Pergamon, containing red ochre as a pigment (photo micrograph, reflected light, crossed polars).

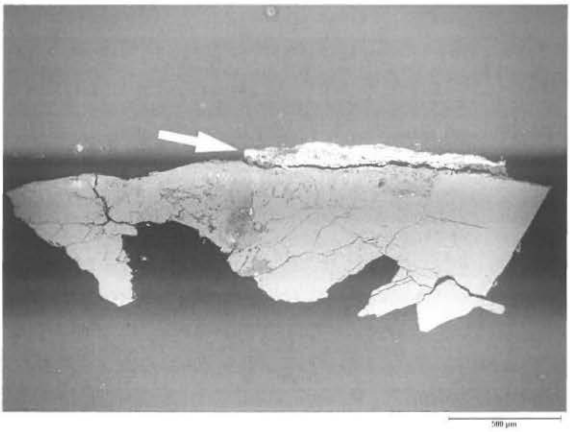

Figure 4. Original paint sample from the Athena sanctuary of Pergamon (arrow), containing lead white as a pigment (SEM image, backscatter mode).

minerals, hematite, calcite and few amounts of feldspars. The paint showed usually an intergrowth with gypsum, which was enriched at the interface to the substrate. This indicates that the original marble was transformed on the surface into gypsum. Part of the gypsum grew into the paint layer and formed little nests and agglomerations.

Another sample from the Athena sanctuary was composed of lead white as a pigment. The binder could not be determined because of an insufficient amount of sample material. The same transformation layer of gypsum as in the red ochre paint appeared in this sample (Fig. 4). The gypsum was formed at the surface but went also deep into the marble filling fissures and narrow cracks. The layer was formed when sulfate bearing solutions penetrated the paint layer and reacted with the marble surface. This happened probably over a long time period when the marble parts were buried in the soil.

5.1.2 Modern paint

In essence two main types of modern paint were characterized from the samples. Both types consisted of silicate paint based on a potassium water glass binder. Silicate paint from the 1920's is without exception a two component system with water glass as component one and the pigments and fillers as component two. One component silicate paint with a polymeric additive, however, appeared not before the 1950's (Oswald & Snetlage 1996).

The most abundant type of the two paint systems – it could be found on most of the reconstructions – was pigmented with lithopone white and umbra and traces of ochre.

Additionally fillers of lime and gypsum were used. Lithopone white is a mixture of barium sulfate and zinc sulfide. Both phases are usually precipitated together in order to form a white pigment. To give the paint a more brownish appearance umbra, a mixture of manganese and iron oxides, was added. Sometimes nodules of amorphous SiO_2 could be observed. The actual paint was applied as a thin layer of 50 µm in average mostly on the stone substitute (Fig. 5). Only in few cases it could be observed on marble adjacent to the stone substitute.

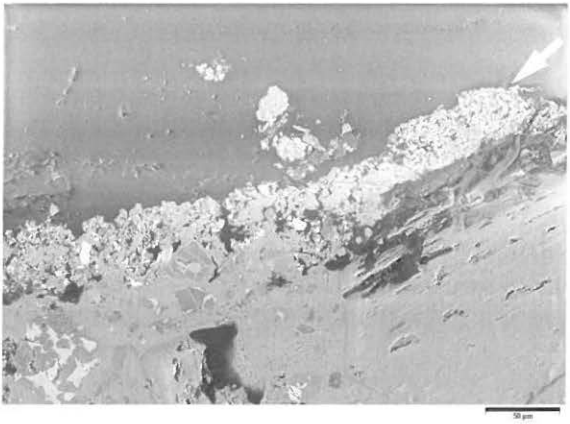

Figure 5. Modern paint (arrow) with a silicate binder and lithopone white and umbra as pigments (SEM image, backscatter mode).

The second type of modern silicate paint was present on the Artemis temple of Magnesia and the Athena temple of Priene only. Instead of lithopone white and umbra as pigments charcoal and synthetic ultramarine with kaolin, gypsum and chalk as fillers were used. The paint was applied in up to three layers (Fig. 6). The interface between substrate and paint showed often a thin layer of pure SiO_2 (Fig. 7). This layer represented presumably an immiscibility between the binder and the pigments of the paint.

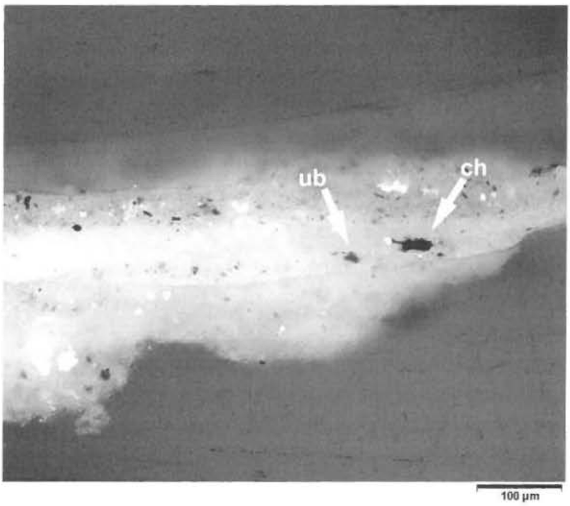

Figure 6. Multi layer modern silicate paint with the pigments charcoal (ch) and synthetic ultramarine blue (ub) (photo micrograph, reflected light, crossed polars).

5.1.3 Sinter crusts and discoloration

A considerable number of the samples consisted of crusts and discolorations on the original marble, which were similar in appearance as paint layers. The crusts consisted mostly of calcite, sometimes in form of multiple layers of several hundred micrometers thickness. In a few cases instead of calcite apatite was found.

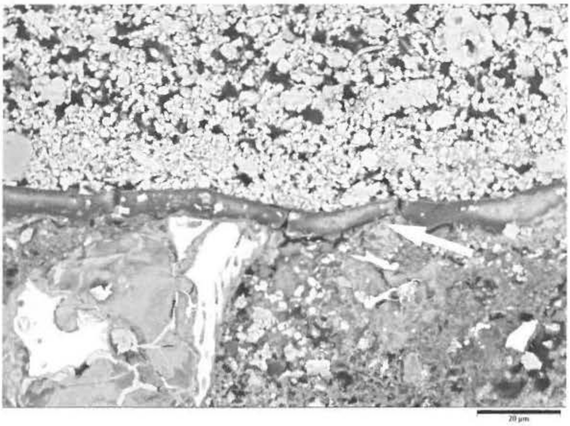

Figure 7. Modern paint showing a layer of amorphous SiO_2 (arrow) between the paint and the substrate (SEM image, backscatter mode).

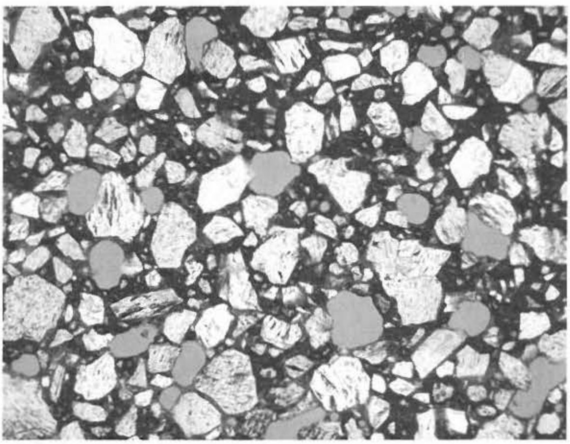

Figure 8. The texture of the stone substitute with cement binder, angular calcite crystals and rounded air voids (photo micrograph, transmitted light).

Discolorations (or the patina) usually were yellow to red brown and consisted of a thin gypsum layer with iron oxides/hydroxides, quartz and feldspars as components. These discolorations were only superficial but give the surface of the marble parts its typical yellowish to light brownish appearance.

5.2 Stone substitute

The XRD analysis and the microscopic examination revealed that the stone substitute was composed of a white cement as binder and marble dust as aggregate (Fig. 8). Because of the nature of the aggregate it was not possible to perform a wet chemical analysis in order to determine the binder aggregate ratio. Instead the ratio was evaluated from photo micrographs of two thin sections by digital image analysis (Fig. 9). The fractions of binder and aggregate were determined by the method suggested by Larbi & van Hees (2000) and RILEM (2001).

The estimation of the binder aggregate ratios by digital image analysis of two thin sections yielded values (mass fractions) of 1:1,4 and 1:1,9, respectively. From the equivalent diameter of the aggregate the grain size distribution was determined. It showed a maximum grain size of 1 mm, a minimum of 0,03 mm with an average at 0,2 mm.

From the texture of the substitute it could be concluded, that the material was mixed by hand with a fairly low water cement ratio. The pore structure suggested a densification of the fresh mortar with a tamper, after the material was cast into the molds.

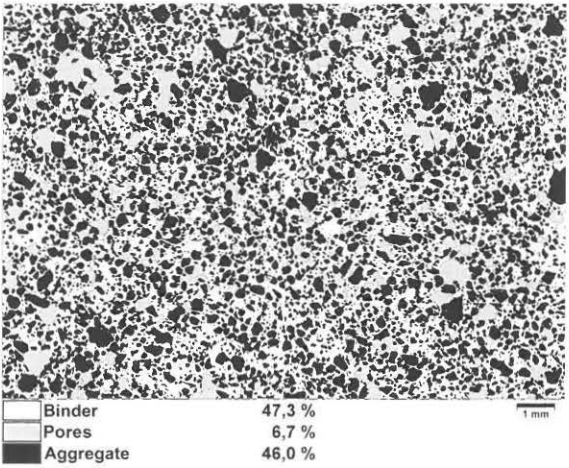

Figure 9. Results of the volume estimation of binder, air voids and aggregate by digital image analysis. Represented is only a fraction of the entire evaluated areas.

6 Conclusions

The results concerning the modern paint revealed the use of a silicate paint system with potassium water glass as binder and lithopone white, umbra, gypsum and lime as pigments and fillers. This paint was used for coating the stone substitute in order to adjust its appearance towards the original marble of the ancient monuments. Only on small areas at two reconstructions another silicate paint with charcoal and synthetic ultramarine was found. It is most likely that the latter paint was used at an earlier time or that it consisted of a trial version.

Surprisingly ancient paint could be discovered as well. This was not expected since extensive cleaning measures of the past did not suggest the possibility of still finding original paint. The findings now raise the interesting question how the reconstructed monuments should be treated in the future. Further cleaning cycles would undoubtedly remove remaining fragments of original paint and therefore entail a loss of important information concerning their original color scheme. The discussion concerning the treatment of original marble surfaces is still ongoing since structural instabilities of some of the ancient monuments makes interventions unavoidable. However, now different alternatives in how to deal with original surfaces were considered in order to preserve existing original paint.

7 Acknowledgements

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