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MORTAR ANALYSIS OF WALL PAINTING AT AMFISSA CATHEDRAL FOR CONSERVATION – RESTORATION PURPOSES

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ABSTRACT

Contemporary artist Spyros Papaloukas in 1932 undertook a major artistic venture, the painting of the interior murals of the Amfissa Cathedral (Church of the Annunciation) a cross-domed church built in 1868 on the ruins of an early Christian basilica. In this 1000 sq monumental work, Papaloukas, even though he follows the strictly established rules of Byzantine ecclesiastical art, he dares to attempt a new approach to the aesthetic merits of Byzantine iconography by introducing elements of the post- Impressionists, the Fauves and the Nabis. Following our earlier work of spectroscopy of mural paintings in this Cathedral, here we present the analysis of ten mortar wall samples regarding granulometry and mineralogy, by XRD, SEM, as well as, a study of resistance-breaking and the level of mechanical strength was determined by comparing the diagrams of power – displacement, where the compressive strength of mortars ranged between 0.5-0.8MPa.

KEYWORDS: *Amfissa, mortar, conservation, cathedral, Papaloukas, wall painting, granulometry, SEM, XRD, mechanical strength*

1. INTRODUCTION

The scientific projects that concern the characterization of wall paintings range from prehistoric to Classical, Hellenistic to Roman, Medieval and recent times (Kakkouli, 2002; Mills & White, 1993; Lucas & Happis, 1962); Mantler & Schreiner, 2001; Liritzis & Polychroniadou, 2007; Wallert, 1995)

In particular XRF, XRD and mineralogical microscopic examinations of wall paintings were reported (Filippakis et al, 1976, 1979; Cameron et al. 1977; Calamiotou et al, 1983; Leona et al, 2001)

Here we present the first results of pigment and substrate analysis of unique wall paintings of Amfissa Cathedral, made by famous artist Papaloukas, an initial stage towards a conservation project of the church (Fig.1)

Figure 1. View of the Cathedral (Church of the Annunciation) at Amfissa (near Delphi, Central Greece)

2. HISTORICAL AND ARCHITECTURAL CONTEXT

Spyros Papaloukas, is undoubtedly a significant figure among the artists who largely contributed to the development of contemporary Greek art (Spiteris, 198216]. He was born in 1892 at Desfina, a village close to the archaeological site of Delphi. The environmental landscape and the archaeological site of Delphi were the first impressions and later inspirations depicted in a large part of his works including the decorative and figurative painting on the interior walls and ceiling of the Amfissa Cathedral. The artistic movements of the 20^{th} century he became acquainted with during his studies in Paris, had a marked influence on his artistic development. Throughout his career, Papaloukas wondered over the boundaries of painting, in a constant search of new themes and incentive, an elaborated perfectionist whose creative abilities and esoteric quality enabled him to explore the complex trends in modern painting and produce a series of works varied from impressionism to early expressionism. Between 1926-1932 he undertook a major artistic venture, the painting of the interior murals of the Amfissa Cathedral (Church of the Annunciation) a cross-domed church built in 1868 on the ruins of an early Christian basilica. Papaloukas, in this 1000 sq monumental work, even though he follows the strictly established rules of Byzantine ecclesiastical art, he dares to attempt a new approach to the aesthetic merits of Byzantine iconography by introducing elements of the post- Impressionists[1] the Fauves[2] and the Nabis[3] (see also, Dictionary of Art and Artists, Thames and Hudson, London (1966); Binder, 1997) (Fig.2).

Figure 2. Some characteristic painting images a) dormition of theotokos (Jesus' mother)

In Greece, Byzantine art was adhered to rigid rules. It was a Christian art dedicated to the service of the Church controlled at a major part by the Church. In that concept any attempt for evolution and renovation was not acceptable. Papaloukas' revolutionary approach, although appreciated at an early stage by

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[1] Artistic movement in France (1880-1900) an extension of impressionism. The term Post-Impressionism is applied to the work of late 19th-century painters as Paul Cézanne, Georges Seurat, Paul Gaugun, Vincent van Gogh , Henri de Toulouse-Lautrec, and others.

[2] A small group of artists, the wild beast as they were called, who, shortly after the turn of the century, exploded onto the scene with a wild, vibrant style of expressionistic art. Fauvism (1898-1908) grew out of Pointillism and general Post-Impressionism, but is characterized by a more primitive and less naturalistic style. Paul Gauguin's style and his use of colour were especially strong influences. Fauvism was the path to both cubism and modern expressionism

[3] Les Nabis (1891-1899) were a Parisian group of Post-Impressionist artists and illustrators who became very influential in the field of graphic art. Their emphasis on design was shared by the parallel Art Nouveau movement. Both groups also had close ties to the Symbolists. The core of Les Nabis was Pierre Bonnard, Maurice Denis, Ker Xavier Roussel, Felix Vallotton, and Edouard Vuillard.

the local community, it was ended up as a hostile attitude against him, egged by the clergy.

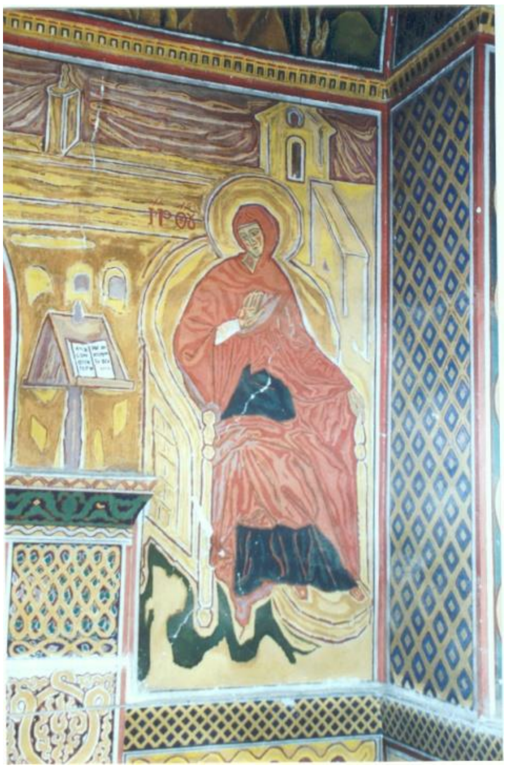


Fig. 2 b) Mother of God from the scene of Annunciation.

3. ORIGINAL TECHNIQUES

As a painter Papaloukas was a colorist from the start. The colour is a subject of major concern for him, a binding essence of his painting. He uses colour not as a merely descriptive adjunct to form, but as the most potent means of expression and the dominant element of his compositions.

Regarding the mural paintings in the Amfissa Cathedral, his main concern was the visual effect of his paint giving less value to the technical process. He experiments with a variety of pigments and bindings not necessarily matched. The paintings were carried out on a single layer of lime plaster applied directly onto the wall, a *secco*. The pigments were applied to the dry ground mixed with lime or casein, egg, animal glue, linseed oil or vegetable gum. The artist renders the contour of the figures by an arbitrary thick line which has a vital quality and applies rich amount of pigments on particular areas of his compositions to achieve distinctive visual effects.

Papaloukas prepared over 320 pre-drawings (anthivolo-a as it is the equivalent in Greek) for his perspective compositions in the Amfissa Cathedral.

He transferred the pre- drawings on the wall by piercing a series of small holes with a pointed instrument, actually the one used at the time by dress makers, so that the drawing would be reproduced by dabbing it on the back side with a gauze sachet filled with charcoal powder.

The *anthivola,* are today exposed to the Amfissa Municipality as the main subject of the Spyros Papaloukas Gallery in Amfissa, near Delphi, central Greece.

4. CURRENT CONDITION AND PREVIOUS INTERVENTIONS

The mural paintings were in poor condition with extensive loss of paint and overall flaking. The serious defects in the initial structure of the building, the low quality of materials provided by local shops, the experimental techniques the artist applied to achieve distinctive visual effects, the ingress of rain water from the roof, and defective conservation treatments and various interventions between 1970-1994 contributed immensely to the loss of a major part of the original painting noticeably worse in areas at the ceiling of the dome, the apses and the ceiling of the gynaeceum (the apartment reserved for women at the upper level of the church) at the right and left nave. The paint layer was in an unstable and deteriorated condition, many areas were insecurely attached, flaking and extremely friable and they tented to shatter even when slightly touched.

Furthermore, the seismic activity of the region was the main cause for the move of structural materials resulted as exhibit of numerous cracks and deterioration of mortar joints

The conservation treatments and several interventions occurred during 1970-1994 were aimed at the stabilization of the structural elements of the building and the mural paintings. There was extensive use of cement for the reinforcement of structural elements, joints of vertical walls and replacement of wooden structures such as the wooden staircase at the left side of the nave leading to the upper floor. Cement was also used as an ingredient of the mortar to fill the losses of the paint. Besides, structural work on the roof of the Cathedral required partial removal of the tiled roof and replacement with new tiles with cement rendering. Loss or weakening of cohesion of the paint layer and flaking were mainly treated with Primal AC-33, Polyvinyl Acetate Emulsions and Casein not yet fully located.

5. THE CONSERVATION PROJECT

Lengthy discussions and the obvious need for restoration of the Amfissa Cathedral interior mural paintings led to the appointment of a conservation team and conservation scientists to undertake the preliminary study before the actual conservation procedure. The conservation project started on May 2001 (Liritzis & Polychroniadou, 2007). A thorough examination of the structure and its condition, of the ground and of the paint layers, the study of the method of execution, the definition of the aesthetic and historical values were determinant elements for the establishment of appropriate conservation treatment

6. EARLIER WORK

Previous work on the Cathedral included non-destructive techniques were preferred though in cases minute samples (millimeter scale) were permitted to obtain. Any invasive sampling was avoided. The spectroscopy techniques of FTIR (Fourier Transform Infrared), RAMAN , EDXRF (Energy Dispersive X-ray Fluorescence), XRD (X-ray Diffraction), optical microscopy (in the visible and UV regions) and GC-MS (Gas Chromatography by Mass Spectrometry) were combined, as an integral part of the technical examination (Liritzis & Polychroniadou 2007). The analyses carried out to support the conservation project at the Amfissa Cathedral identified a variety of pigments used by the Greek 20th century artist Spyros Papaloukas including, ultramarine, coal, hematite, yellow ochre, Prussian blue, lead white, chrome yellow, ultramarine, red ochre (anhydrous iron oxide), carbon black, and calcium carbonate (calcite) used as white pigment.

A6

A1

A2

A7

A7 close up

Figures 3 Sampling locations (see Table 1)

Spectroscopic analysis was applied to identify tempera (egg binder) and animal glue. Animal glue, casein and egg were identified as binding substances.

Several successive painted layers were recognized through optical microscopy (in some cases five layers), consisting of yellow ochre, calcite for white, red ochre, carbon black, and ultramarine. The painter did not follow the usual *a secco* practice, instead he combined several painting techniques (pigments mixed with lime, tempera and oil) to open up new area of creative possibilities and mastered the natural characteristics of the pigments by the quality of his brushstrokes and the particular medium's degree of gloss.

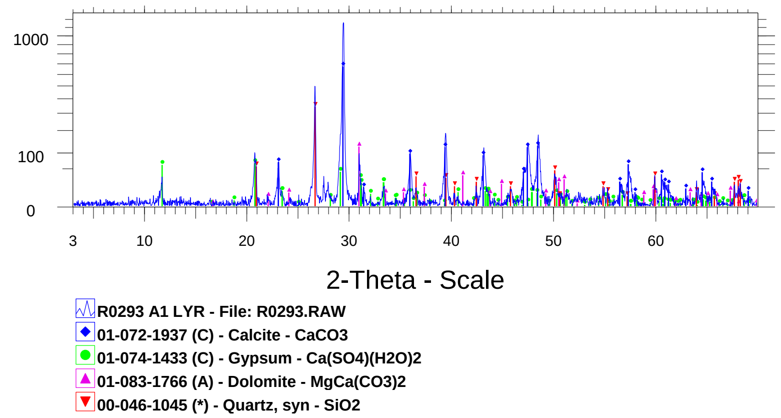
That work and the present one result to a prerequisite step to any further conservation work. Sampling locations ranged from in apparent deteriorated and thus exposed wall parts (Schwan, 1998; Baumann et al., 1998) (Figs 1-3 & Table 1).

7. PHYSICOSCHEMICAL CHARACTERISATION OF MORTARS

7.1 XRD Analysis & Grain Size

X-Ray Diffraction for powder by D500 Siemens Cu radiation was used. The evaluation used Diffrac Plus of Brucker. The quantitative analysis was carried out by Rietveld method. Qualitative and quantitative content of samples is given in Table 1 and Figs.4). Samples are calcareous mortars with significant quartz and lower feldspars, while apparent presence of gypsum is in only two samples (A1, A8) derived mostly from upper coating. Optical microscopy Polished cross-sections of the samples, containing all the microstratigraphy from the surface to the mortar substrate, were prepared and studied by an optical polarizing microscope in reflected light. Micro photos were taken, by a digital camera, which were analyzed by image analysis techniques, using the software Image Pro Plus.

A1 LYR



A2 LYR

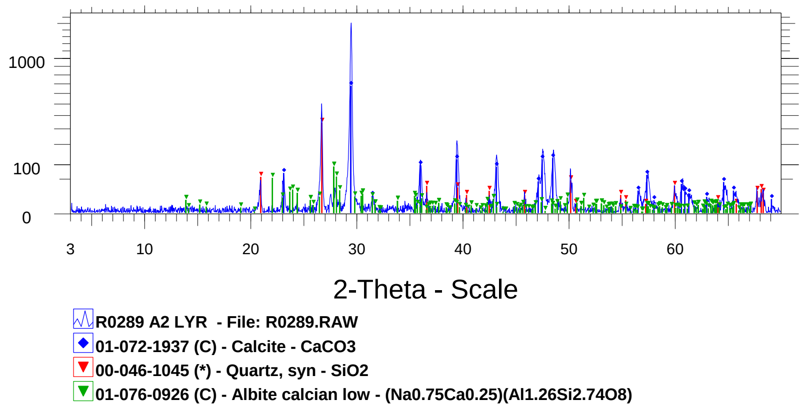


Figure 4. XRD spectra of A1, A2

TABLE 1. Mineralogical content and sampling location of mortars (relative numbers).

SAMPLE	Calcitic $CaCO_3$	Dolomite $CaMg(CO_3)_2$	Quartz SiO_2	Feldspar $(Ca,Na)AlSi_3O_8$	Gypsum $CaSO_4\ 2H_2O$
A1 coating from stairs to gynaeceum (womens' zenana)	67	-	18	5	10
A2 gynaeceum (womens' zenana), coating	74	-	18	6	2
A2.2	75	-	20	5	0
A3 Upper ladder, coating	67	-	28	4	1
A4 between masonry in A1	84	-	12	3	1
A5 mortar from zenana in A2	74	-	19	6	1
A6 mortar from arch of ladder in A3	82	-	14	4	-
A7 mortar from gynaeceum plus stone from A2	90	-	7	2	1
A8 mortar from gynaeceum in A2	56	-	22	11	11
EVA-1 mortar	90	-	6	3	1
EVA-2 plaster	91	-	6	3	-
EVA-3 mortar	89		7	4	-

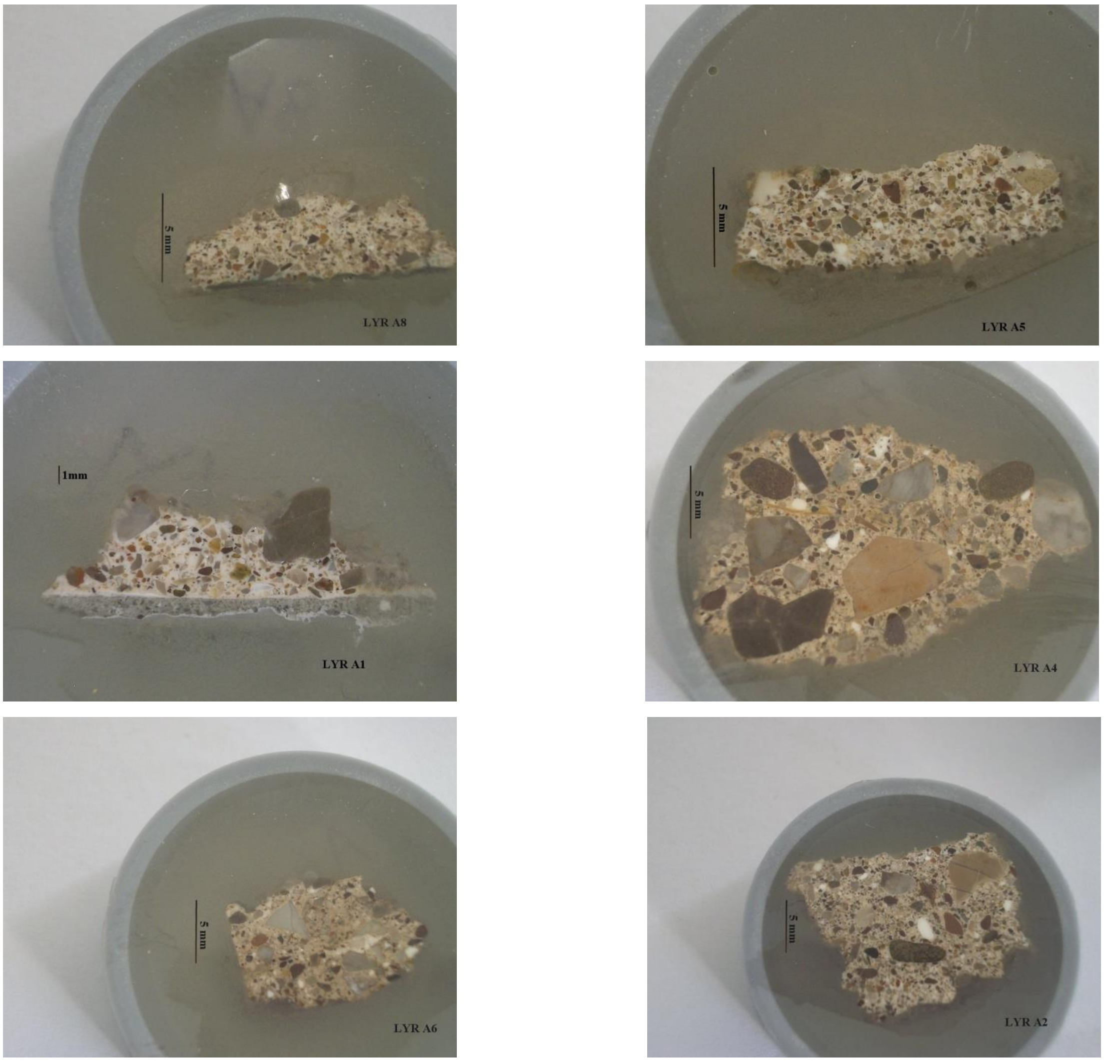


Figure 5. Macrophotographs of mortar samples prepared for optical study.

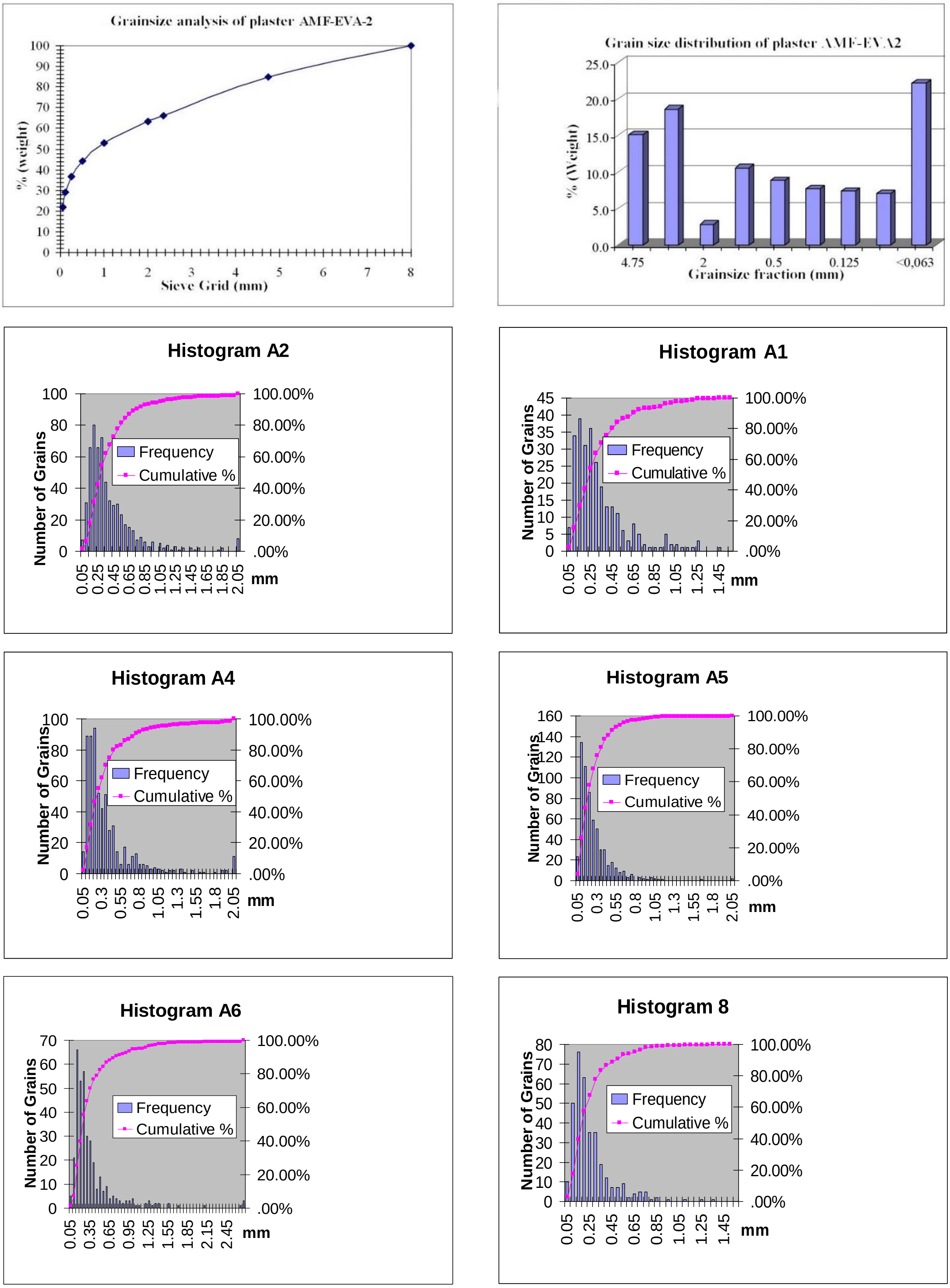


Figure 6 Grain size distribution of samples A1-A8 and EVA-2 in histogram and cumulative curves.

Fig.5 gives the macrophotographs of prepared samples. The binding "cemented-like" material is pure secondary calcite by the carbonation of calcium hydroxide ($Ca(OH)_2$).

The granulometric distribution are given in respective histograms of Figs.6. Around 60% of grain sizes are less than 0.30 mm, and 50%/w of EVA-2 plaster is <1mm.. The morphology of inert matter with rounded grains is characteristic for rivers or sea sand.

The proportion of the adhesive cement (secondary calcite) is of the order of 22 to 25%.

7.2 Scanning Electron Microscope (SEM)

The same samples, which were optically studied, were analyzed by a JEOL JSM 5400 Electron Scanning Microscope, equipped with an Energy Dispersive X-ray Spectrometer, Oxford instruments INCA energy 300 EDS. Microanalysis of single grains down to 1 μm, as well as of the matrix and the total average of the paint layer were performed. X-ray mapping was used to study the element distribution in the sample. The above technique permitted a full microstratigraphic analysis and interpretation of all components of the samples. Figs.7 show respective SEM images and mineral sizes.

7.3 Discussion on XRD, SEM, Microscopy

XRD, Microscopic examination and SEM analysis showed that the mortars are calcitic. The mortar consists of calcite grains with small amounts of quartz or albite. In all cases two generations of calcite were distinguished; primary calcite grains up to 2mm and very fine calcite material with grain size less than 2 μm. That means that the plaster material was primary a mixture of calcite grains and slaked lime ($Ca(OH)_2$), which was then transformed to secondary calcite during drying by carbonization. This secondary calcite acts as a cement binder to the primary calcite grains. The final surface layer consists mainly of secondary calcite. Characteristic in the microanalysis was that in the primary calcite grains only Ca was detected, as expected, while in the secondary calcite matrix Si and Al were found, which are impurities in the slaked ($Ca(OH)_2$).

The morphology of inert matter with rounded grains is characteristic for rivers or sea calcitic sand. The proportion of the adhesive cement (secondary calcite) is of the order of 22 to 25%.

A1

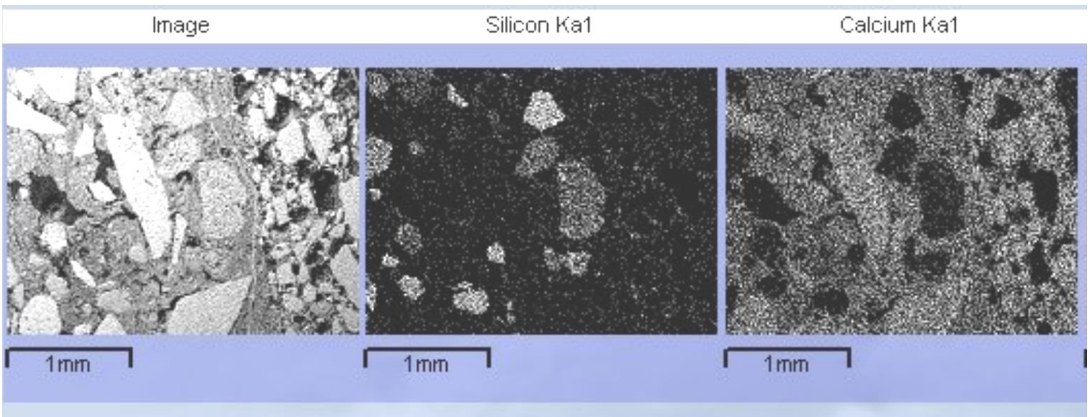


Figure 7 a Distribution of Ca and Si corresponding to calcite and quartz. In secondary electron image (left) the primary calcite is apparent with secondary calcite in between.

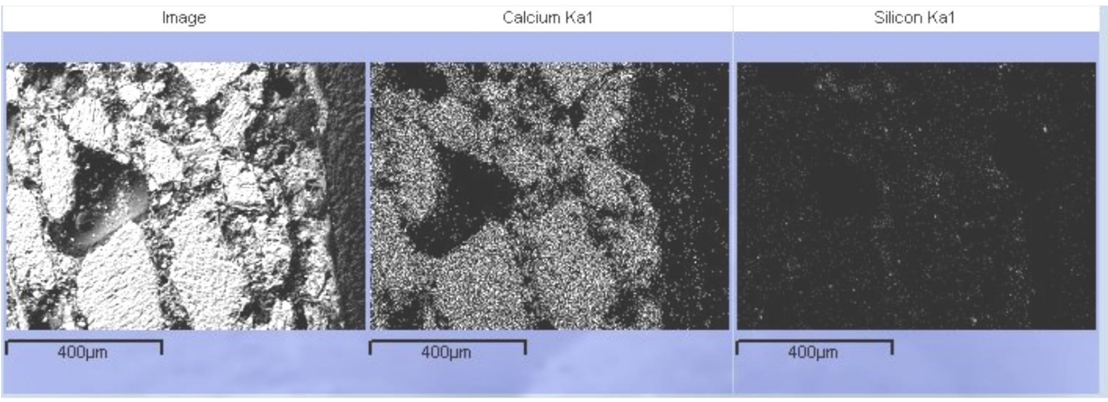


Figure 7 b. Similar to (a) without quartz presence

A2

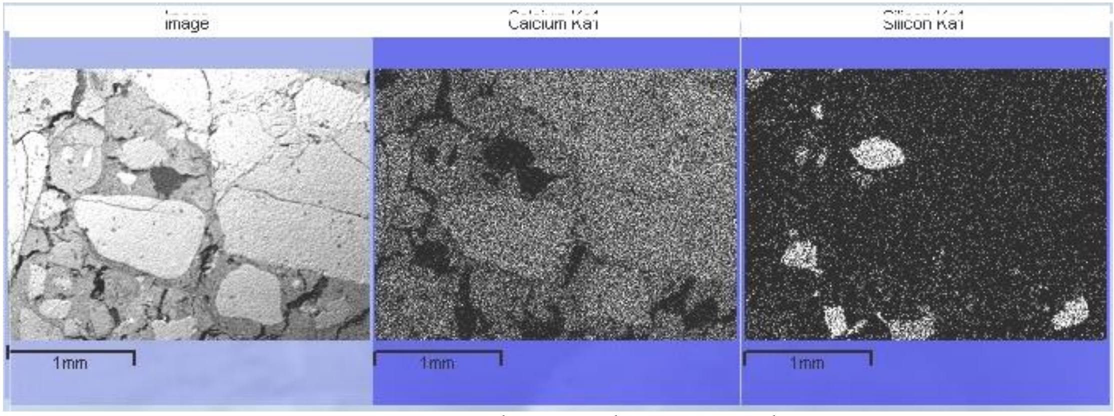


Figure 7 c. Sample A2, similar to A1 sample.

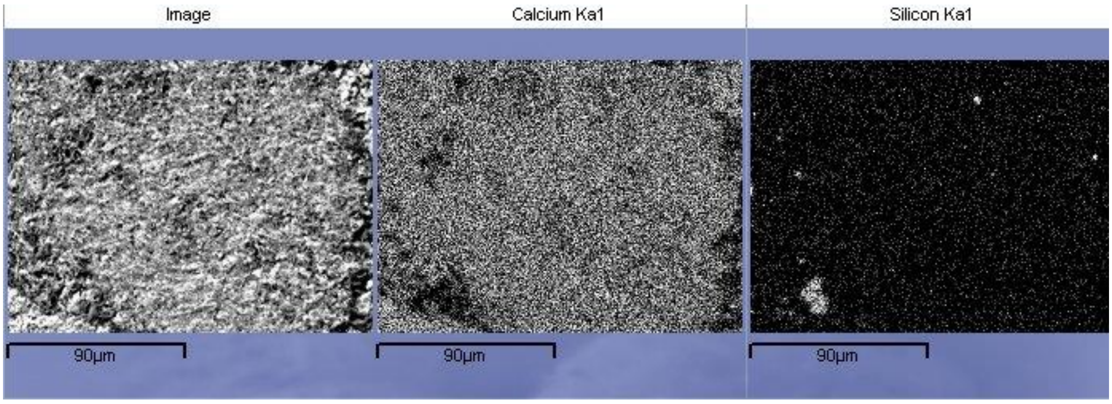


Figure 7 d. Sample A2. Area with secondary calcite. Small size quartz grains are seen within the calcitic mass. The very small granulometry of secondary calcite does not permit imaging of isolated grains. No cemented phases are observed.

8. EVALUATION OF MECHANICAL PROPERTIES OF MORTARS

For the study of the mechanical strengths of mortars an approximation method is applied that relates the assessment of the hardness of the mortar to macroscale (macro-hardness). During measurement the distortion caused on the sample surface by a metal ball (diameter 8.5mm) is recorded, by applying onto it an increasing load. Of the samples collected and submitted to the above test, only four yielded usable deformation curves, the rest was loose (Table 2).

The level / extent of mechanical strength was determined by comparing the power vs. displacement diagrams of the test samples with the reference chart, which has emerged from the study of a plaster with natural aggregates (river sand). The value of the compressive strength has been determined in cubic samples, with unconfined compression.

The compressive strength of mortars is described in the first step of the curve, wherein the outer layers are compressed, by a relatively small surface (Fig.8) The value of the maximum load is proportional to their maximum strength. The maximum displacement is inversely proportional to the hardness and consistency of samples and is proportional to the thickness of the sample.

A comparison of the diagrams obtained from the samples studied to that of the reference sample it is estimated that the mechanical strength (*tensile strength)* of mortars ranges between 0.5-0.8MPa (modern concrete reaches at least 50 *MPa).* This is considered a low mechanical strength mortar that resembles Portland cement- hydrated lime mortars used for straw bale construction (MacDougal & Vardy 2014).

Table 2 Mechanical results of samples.

Sample	Height (mm)	Area (mm^2)	Displacement/Shift (mm)	Max Load (N)
A1	12	253	8,6	455
A2	20	198	4,2	363
A2-2	20	217	5,4	477
A8	10	275	2,7	256

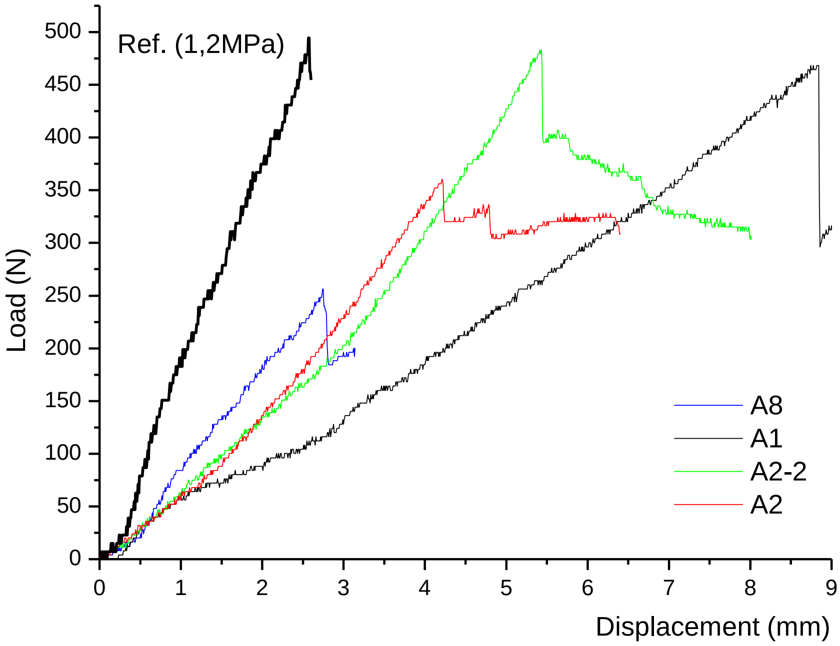


Figure 8. Load versus displacement of analysed mortars.

9. CONCLUSION

Following our earlier work of spectroscopy of mural paintings in this Cathedral, the present mechanical analysis of ten mortar wall samples from four locations in the Church regarding granulometry and mineralogy, by XRD, SEM, as well as, a study of resistance-breaking load and the level of mechanical strength was determined by comparing the diagrams of load – displacement, while the compressive strength of mortars ranged between 0.5-0.8MPa. The work provides a useful information for the subsequent conservation and restoration work.

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