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Investigation about ancient mortars and plasters in the Mondovì cathedral (Cuneo, Italy)

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Abstract

St. Donato Cathedral of Mondovi (Cuneo Province, North-West Italy) is the last project of the famous architect Francesco Gallo (1672-1750). The construction started in 1744, but it has been consecrated only in 1763. The building is an impressive brick-made church with a main nave and two lateral aisles, which remarkable length is 56 meters and it is 24 meters wide. Its style is mainly baroque with some neoclassical additions. After the edification, the decoration of the interior walls was very simple; probably it was a white finish of smooth plaster consisting of lime and magnesian lime mortar. There are some evidences of a basic decoration: a uniform bluish or grayish tinge. Around 1850 a plan for a new decorative apparatus was made and some of the most important painters of that period were committed to paint sacred subjects on the vault and apse, and to provide the decorations of the walls. In early 2012 started some important restoration works in the Cathedral. One of the main purpose of the Restoration Team is to get scientific and historical information about the work of ancient painters and decorators. The scientific investigation on mortar layers was conducted on various samples, several of them were resin included polished sections, using Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) supported by Energy Dispersive Microprobe spectroscopy (EDS). The analyses carried out on the samples clearly showed the historical stratifications of different layers. The first stratification is made of mortars and plasters dating around the middle of 18th century, and shows different compositions and very neat layers. While the last stratification is a more recent mortar plaster, which is coarse-grained, used as a background for the new decorations done in the middle of 19th century.

Key words: Mortar; Plaster; EDS Maps; Cultural Heritage; Mondovì Cathedral.

Introduction and historical background

The San Donato Cathedral of Mondovì (Cuneo Province, North-West Italy, Figure 1) is an 18th century building, by the great architect from Mondovì Francesco Gallo (Figure 2). Erected in 1743 on the structures of the ancient Franciscan church (Grassi, 1789; Casalis, 1842), the building works lasted for decades and were followed by important architects such as Bernardo Antonio Vittone and the first architect of the king, Benedetto Alfieri. The façade was built in 1777 by master builder Quadrone with structural stone from Vico, following faithfully the design of architect Gallo. The building is an impressive church, it has a three naves structure, with lateral chapels and a large transept where two lateral chapels are situated on the side of the presbytery and two large chapels at the heads. It is of a considerable length of 56 meters and a width of 24 meters, and a wide dome on corbels is located at the crossing of the ribs (Figure 3).

Figure 1. Location of Mondovì city.

Also the compartment presbytery for which the original design of Gallo was changed by Alfieri, under way of construction, is of particular importance. It is formed by a minor dome over the Sancta Santorum and by an apsidal vault over the choir. After the construction, the interior decoration of the church walls was very simple, probably with a white finish of smooth plaster made of lime and magnesian lime. There are some analytical evidences of a very simple decoration like a uniform bluish or grayish tinge.

The building wasn't appreciated anymore during the post-Napoleonic age. Its walls had never been decorated with colours or frescoes, the interior was too dark and the ratio length/width of the central nave was not considered agreeable. At the end of the thirties of the 19th century, the Bishop Francesco Gaetano Buglioni from Monale wanted to rebuild completely the compartment choir-presbytery, as a first step for the general redecoration of the whole cathedral. In 1838 he entrusted the project, with considerable ambition, to the first designer and art director for the Royal Palaces of king Carlo Alberto, Pelagio Pelagi from Bologna. The works, limited only to the choir-presbytery, were ended in 1842 (Crosetti, 1969).

Only twenty years later, at the time of bishop Ghilardi, the cathedral was the object of some new projects of transformation as a function of a changed political-institutional time, to give the Cathedral the modern dignity of a church-

Figure 2. The Cathedral of Mondovì, dedicated to San Donato. Courtesy of the Mondovì Curia.

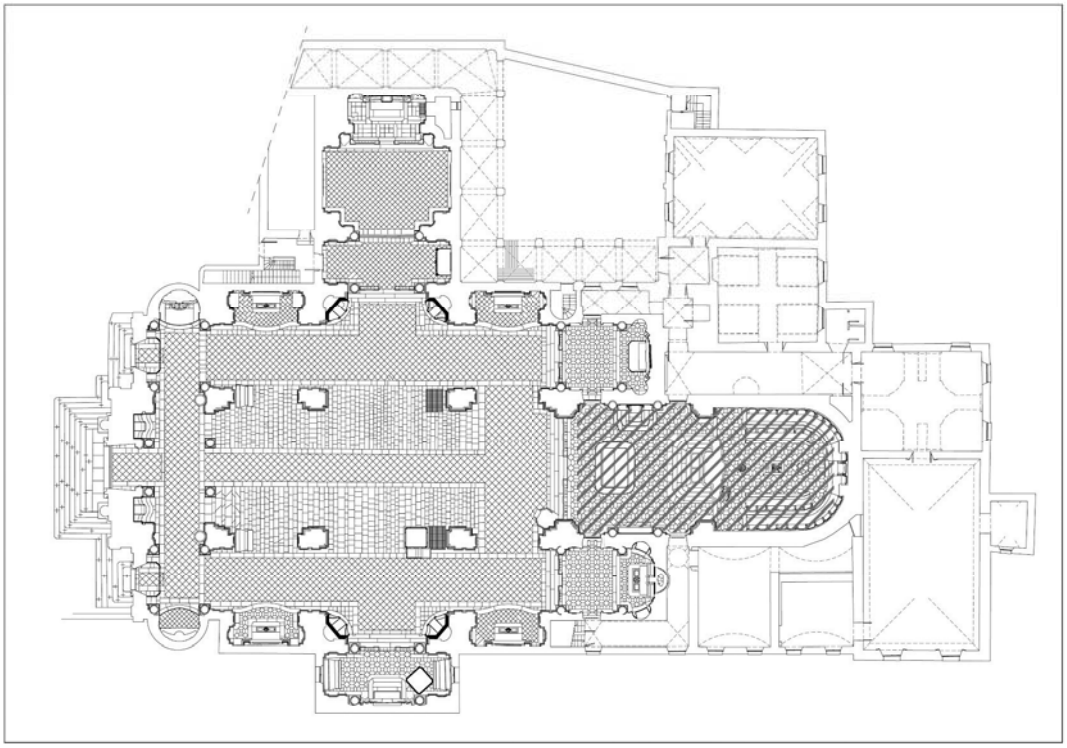

Figure 3. Plan of the Cathedral. The total length of the Church is about 56 m, whereas the width is 24 m. Courtesy of GEOMAR.IT (www.geomar.it).

cathedral including also a wide line of wall paintings. After a number of proposals and the intervention of architect Angelo Marchini, the chapter chose the project of a stucco decorator, Antonio Adami. The architect Giuseppe Leoni from Turin was the responsible for supervising the yard, he had just finished the transformation of the inside of Cuneo Cathedral. Leoni gave opinions to identify the painters suitable to carry out the complex task of painting. The final decisions concerning the choice of the painters were taken at the end of 1856: Paolo Emilio Morgari (who had just finished the great decoration of the church of Saint Massimo in Turin) directed the whole operation and made the painting of the apse, Luigi Hartman realized the great cup of the transept and the Mysteries of Maria under the windows, and Andrea Vinay the dome of the presbytery with the ribs. Some medallions were painted by the painter Isacco Gioacchino Levi, and the representation of the Birth of the Virgin, in the vault, by the painter Francesco Gonin. At the same time the gilder Bartolomeo Ghiglia worked on the stuccos and the architectural parts, entablature and capitals with gildings in silver covered with yellow transparent varnish, to simulate gold plating.

At present time some important restoration works are in progress at the Cathedral, and one of the main purpose of the Restoration Team Cristellotti is to obtain scientific and historical information about the work of builders, painters and decorators, by means of analytical investigations as Optical Microscopy (OM), SEM-

EDS microscopy and other techniques (Artioli, 2010). The analysis carried out on some samples of wall mortars and plasters clearly showed the historical stratification of the different layers.

This paper aims to investigate the materials used during the construction. The purposes of this work are strictly connected to the restoration project. The choosen analytical methods have been selected and planned to provide useful data to help restorers and other conservators to manage the restoration works in the most proper way.

Materials and methods

As reported in the introduction, one of the aims of the analyses in Mondovì Cathedral was to obtain scientific and historical information about the previous works of builders, painters and decorators, focusing on pigments use, and on the identification of the techniques used by different painters. As a consequence of the painting layers sampling, we picked also part of the substrate layers. The stratification includes also the mortars used in the first stage of decoration, dated back to the middle of 18th century, and the ones used in the 1850's second stage of decorations (Figure 4). Determining the composition of binders and aggregates in mortars and plasters is very important. This provides useful information regarding materials employed in mortar preparation and can be also used to verify the "state of health" of the masonry. The knowledge of these factors is essential to choose appropriate restoration

Figure 4. In the picture it is clearly observable the whitish surface of the mid '700 plaster, which was lately in mid '800 scaled with hammer to obtain a rough surface for a better adhesion of the new mortar and pictorial decoration. FOV 40 cm.

techniques and materials. In the sampling stage we collected around fifty samples that have been used for analysis. In this paper we reported the results of a limited selection of samples, chosen to be as representative as possible of the average situation of the Cathedral.

All the samples were picked from the northern part of the church, from the upper portion of the pictorial cycle (Figure 5; Table 1), where the restoration works are now in progress. For the investigation of pigment layers we used different techniques like SEM-EDS, FT-IR, Raman Spectroscopy and ICP-OES (Artioli, 2010), for the investigation of mortar layers -conducted extensively on resin included polished sections- we used Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) supported by Energy Dispersive microprobe Spectroscopy (EDS) (Reed, 2005; Severin, 2004).

Optical microscopy observation (OM) in reflection mode was the first technique we used to observe the samples, in order to examine painting layers, mortars, their deterioration and other features. The images were obtained with the instrumentation of the Dipartimento di Chimica of Turin University, using a stereo microscope Leica MZ16 equipped with CCD camera and imaging acquisition software. The samples were observed without a specific preparation to check the general surface appearance, and as polished section to check the stratigraphy of specimens. All the samples were observed using the instrumentation of the Dipartimento di Scienze della Terra of the University of Turin, a Cambridge 360 Stereoscan SEM equipped with Oxford Inca Energy 200 EDS Microanalysis suite, PentaFET detector (SATW). EDS analyses and maps were performed at 15 kV acceleration voltage, and 1 nA beam current. Although the EDS was equipped with ultra-thin windows, to allow direct analysis of carbon and oxygen, the graphite coating didn't allow us to perform the required quantification. Thus the analytical concentrations are obtained as oxide and recalculated to a 100% sum, without considering elements lighter than nitrogen.

We did not use any grinding or sieving methods due to the limited amount of available material. We impregnated the wall fragments with epoxy resin and made some thick sections polished to optical finishing. We elaborated some visual estimation on the samples; the ratio aggregate/binder in mortars and plasters has been calculated, processing the SEM-BSE pictures

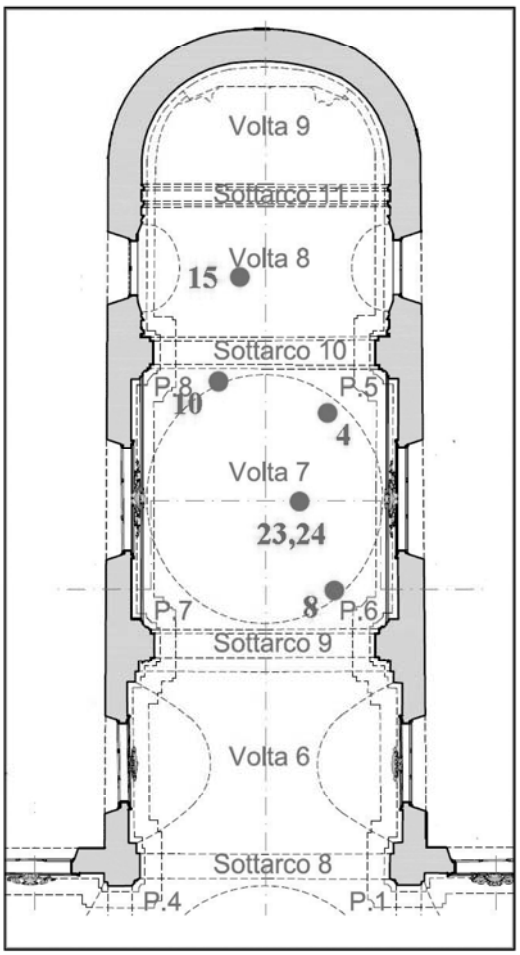

Figure 5. Sampling position in the north portion of the Church. Courtesy of GEOMAR.IT (www.geomar.it).

Table 1. Position and characteristic of the samples used in the present paper.

Sample	Sampling point	Age (century)	Description
Cp 4	Vault 7, Plume 5	Middle XVIII Middle XIX	Fragment of mortar made of different layers, involving the painting.
Cp 8	Vault 8, plume 6	Middle XIX	Fragment of mortar, involving the painting.
Cp 10	Vault 7, Arch 10	Middle XVIII	Fragment of mortar and plaster
Cp 15	Vault 8	Middle XIX	Fragment of mortar, involving the painting.
Cp 23	Vault 7, Dome	Middle XIX	Fragment of mortar with painting layer
Cp 24	Vault 7, Dome	Middle XVIII	Fragment of mortar and plaster

and using image analysis software like ImageJ (Ferreira, 2011). The image analysis needs obviously to consider factors such as resolution, minimal dimension of particles and corner blurring (Carò, 2004).

Results and discussion

The study of the sections is useful to recognize techniques and materials used in both of the different historical moments. Starting from the oldest layers findings, using Optical Microscopy we can observe (Figure 6):

- a mid-'700 mortar, with fine-grained aggregate. It is almost monomineralic and it is composed of subangular quartz grains. The binder is mainly calcic/magnesian lime (the composition was verified by EDS analysis). We will show here images and analysis of samples 10 and 24 (numeration of the samples follows the original order, in which more sample were analyzed for pigments and other characteristics);
- a mid-'700 finishing plaster, very fine grained and almost without aggregate phases, coated in many layers, with a total thickness usually below 1 mm; (sample 4, 10 and 24);
- a mid-'800 plaster, very rough, with some coarse grained aggregate, made by quartz and rare feldspar (verified lately by EDS analysis), almost equidimensional, with rounded grains; (samples 4 and 23);
- a very thin layer of gypsum probably used as a preparative ground colour (sample 3 and 4); this thin layer was observed and identified with the aim of SEM-EDS analysis.

In this paper we use the term "mortars" to indicate a mixture of lime, aggregate and water used as a masonry mortar between the constructive blocks (stones, bricks) or as a rough finishing of the wall. The term "plaster" is intended as a mixture of lime and water, without any aggregate, that could be used for the finishing of the wall surface after the use of mortars (UNI, 2001).

The mid-'700 mortar

We can describe sample 10, one of the mid '700 mortar. It is characterized by a rough layer of mortar with quartz sand, made of subangular grains, not well sorted and sized normally below 1 mm (Wentworth, 1922). The binder is a whitish-greyish magnesian lime (as showed by

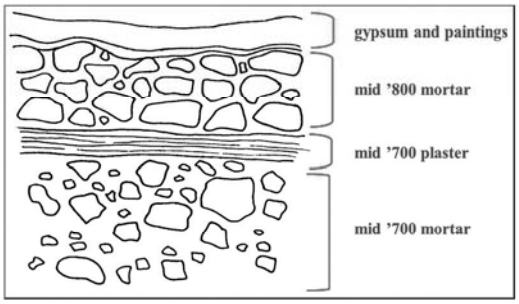

Figure 6. Schematic stratigraphy of the mortars and plaster.

EDS analysis), with no or very little amount of sulphates (Figure 7A). Observing the section in electron microscopy, using backscattered electron mode (BSE), position, size and shape of quartz grains (Figure 7B, confirmed as quartz in EDS spectra) became immediately visible. We also found rare grains of mineral others than quartz, such as feldspar, clearly visible in the elaborated image (obtained ascribing false colours to different gray levels) (Figure 7C). The different gray levels of SEM-BSE image are also very useful for image analysis, carried out with software Image-J. Gray levels are used to identify the pixels with a determinate tonal value, e.g. the quartz is light gray and the binder mass is dark gray (Carò, 2008; Miriello, 2006). Thereafter the software made some calculation regarding the amount of pixels and their total area, the number of grains, the shape and roundness of the aggregate particle (Figure 7D and 7E). The program was used to determine the ratio between binder and aggregate. The results showed that the aggregate is roughly 20% of the volume, a very scarce value. This probably represents a low original content of aggregate in the mortar.

An interesting observation regarding the magnesian lime, used as binder, is the absence of any silica content (detection limits of the EDS are 1000 ppm equivalent to 0.1%). A little amount of sulphur can be observed in EDS spectra and it could be originated by sulphation of the mortar during years. In other sections of the church the degradation by sulphates is due to water percolating through the ceiling and led to severe damage of mortars and wall paintings. Sulphates can also derive from the practice of mixing lime with a small amount of gypsum, to increase its hardening speed and its adherence (Turco, 1990).

The mid-'700 finishing plaster

A thin finishing material made of lime and magnesian lime lies on the surface of the mid '700 mortar (Figure 8A and 8B). The total thickness of this layer in usually less than 1 mm, but in this very subtle coating we can recognize up to seven different strata of variable composition (Figure 9). The layer is fine grained and, in optical microscopy observation, shows a very brilliant-white finishing. Only in one sample we noticed a blackish-gray horizon containing a little amount of charcoal. In one of the strata we also found lime lumps. This sequence was probably obtained by multiple brush application of a diluted lime suspension (whitewash).

In the picture (Figure 10) the stacking of the layers is clearly visible. False colour EDS map shows compositional differences, confirmed by EDS analysis (Table 2). All the analyses were obtained on small area to mediate the imperfection and to have a better fitting with higher count ratio. Sum of oxides is recalculated to approximate 100% total weight, despite of the presence of water and other substances not analyzed (Franzini, 1999). Strong variations in the Mg/Ca can be observed. Analysis n. 11 was performed in a quartz grain. The different distribution of magnesium in the layer rises a question: why are there so many strata in this layer? The sampled surface is around 15 m high from the church floor, a white coat periodically painted for cleaning purpose every few years is quite unconvincing. The entire layer was probably made during the same period while the wooden scaffolding was still in place. But if the work was done in the same time frame, why are

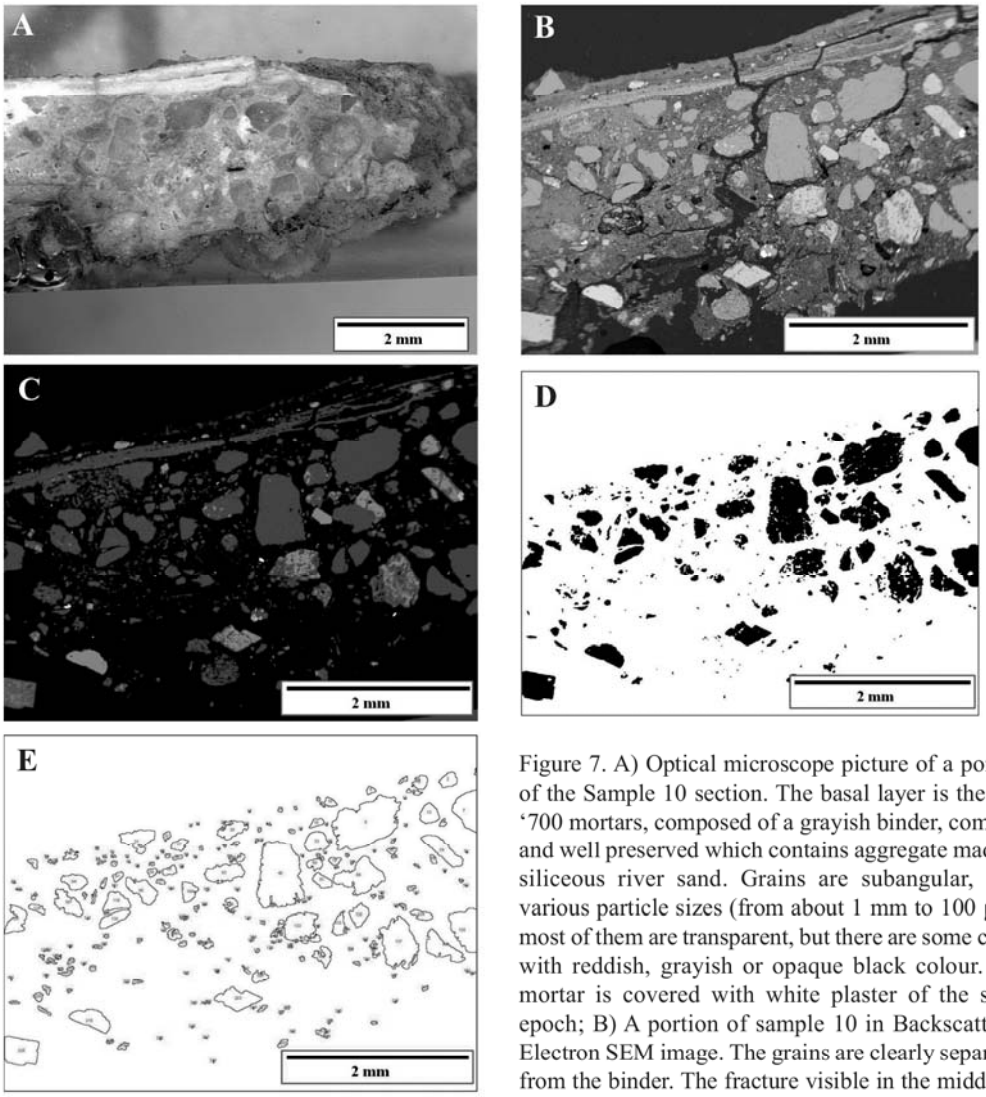

Figure 7. A) Optical microscope picture of a portion of the Sample 10 section. The basal layer is the mid '700 mortars, composed of a grayish binder, compact and well preserved which contains aggregate made of siliceous river sand. Grains are subangular, with various particle sizes (from about 1 mm to 100 μm); most of them are transparent, but there are some clasts with reddish, grayish or opaque black colour. The mortar is covered with white plaster of the same epoch; B) A portion of sample 10 in Backscattered Electron SEM image. The grains are clearly separated from the binder. The fracture visible in the middle of the section is a consequence of the preparation and was not in the original mortar sample; C) The false colour BSE image could enhance the subtle difference between similar gray levels. It is possible, in this way, to distinguish between quartz (deep blue) and feldspar (light blue). The biggest portion of the mineral phase is represented by quartz; D) An opportune treatment and thresholding of the gray levels with the ImageJ software permit to isolate the grain contour in the mortar; E) The ImageJ software made the automatic count of the particles and sum their total area.

there so big differences in composition between layers? We hypothesize the presence of Mg-containing silicatic minerals, but no silicon is showed by EDS spectra.

In the picture (Figure 11) it is clearly visible a small portion of the '700 plaster containing some charcoal fragments, shaped as blackish dots and lumps. EDS analysis reported a small quantity of

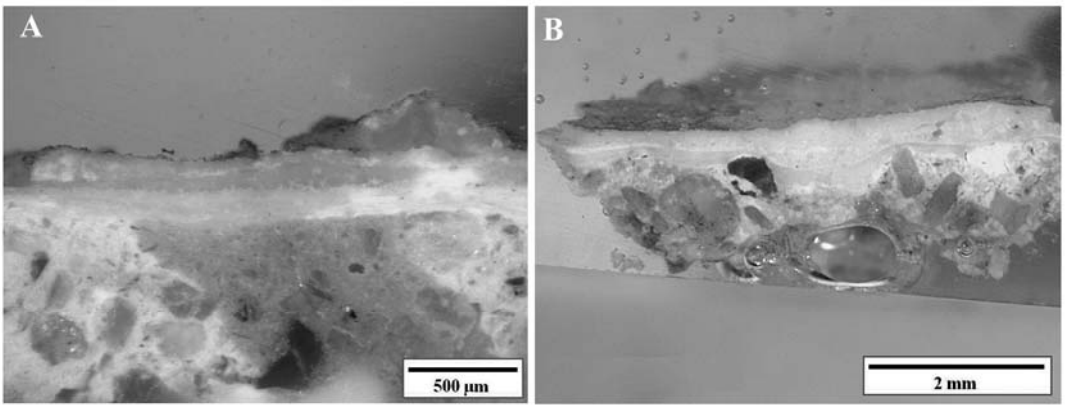

Figure 8. A) The finishing layer is composed of a very compact and homogeneous plaster, milky white, fine textured and almost without aggregate, coated in many layers (as shown in Figure 8). Sample 10 taken in OM picture; B) Another portion of the white brilliant plaster in an area of sample 24. The layer is very thin, but it follows the rough surface and in some place has a higher thickness.

potassium inside the otherwise very pure coal; this suggests the nature of the coal as charcoal, obtained by the combustion of vegetal matter. We found it only in one sample, and we suspect a contamination of coal from lime furnace, rather than a charcoal pencil sign (Rinaldi, 1986; Bevilacqua, 2010).

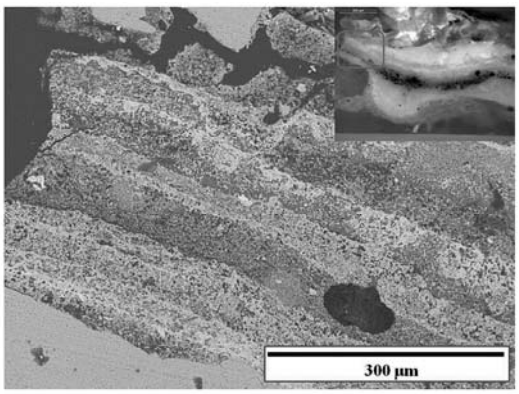

Figure 9. The white mid '700 plaster observed in BSE image shows its nature composed by multiple layer (the small insert is the same area in OM picture). Light gray levels are calcium rich, whereas darker levels are magnesium-rich. Up to seven different layers could be identified in this high resolution image.

In Figure 12 we can observe white particles surrounded by whitish plaster. Analysis on fragments showed that these are pure calcium carbonate, with magnesium content below the

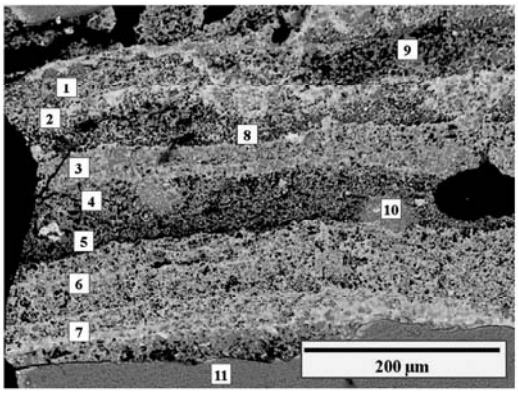

Figure 10. A false colour EDS map of the same area of Figure 9, with the analysis localizations (results are shown in Table 2). In this image Ca concentration is coded in green, Mg concentration is coded in red and silicium content is rendered in blue. We can clearly observe a silica grain at the base of the strata, but there is no silica in the magnesian lime of the plaster. Different layers have different compositions, alternating magnesium-rich lime to magnesium-poor lime.

Table 2. The EDS analysis from different areas of the EDS Map of Figure 10. Values are in weight %

Area	MgO	SiO_2	SO_2	CaO	MnO	FeO
1	44.8	1.2	5.5	49.2	< 0.1	< 0.1
2	33.2	1.1	7.5	57.2	0.7	0.3
3	27.3	0.8	3.4	68.1	< 0.1	0.6
4	36.2	1.0	3.7	59.3	< 0.1	0.2
5	49.0	0.3	4.7	46.3	< 0.1	< 0.1
6	29.1	0.8	3.3	67.8	< 0.1	< 0.1
7	24.6	0.4	4.2	69.6	0.3	0.9
8	54.2	1.9	4.2	38.9	0.1	0.7
9	21.6	1.2	8.2	69.9	< 0.1	< 0.1
10	60.4	< 0.1	3.6	36.0	0.4	< 0.1
11	0.0	99.6	0.3	< 0.1	< 0.1	0.1

EDS detection limit (0.1%). This particle can be a grain of calcite or pure limestone deposited in the layer. The unusual size of this particle could be due to an incorrect grinding of the raw material (Kirk Othmer, 2001).

The mid-'800 mortar

The mid '800 mortar is more coarse than the previous century's one (Figure 13); quartz grains are the main aggregate phase, by comparison with the '700 mortar, the mean dimension of the grains is bigger and the ratio aggregate/binder is highest. The binder is magnesian lime, with variable content of magnesium, from 5 to 30% expressed as MgO. In Figure 14A and 14B, we can observe the structure of the mortar, sampled from different sites of the church dome. Although there are some differences in the samples, the prevalence of quartz and the low content of binder are immediately noticeable.

The plaster from '800 period is a very rough finishing, and on some letters above mentioned, the painters asked the customer to prepare a thin layer of gypsum before painting the decorative pictures (we do not know if this request was due to the mortar peculiarities, or it was a normal procedure for those painters). An interesting consequence, from the point of view of conservation and restoration, of the relatively big dimension of the quartz grains in the mortar is that during years this led to a localized drop of the painting layers, originating a tiny and dense net of small white dots, mainly on dark areas.

Macrophotography of the surface and SEM imaging proved that the distribution of the white dots on the pigment layers matches with the protrusion of quartz particles from the mortar: the adhesion between quartz and the pictorial layer was not strong enough to ensure the grasping of the paint for about 150 years (Figure 15A and 15B).

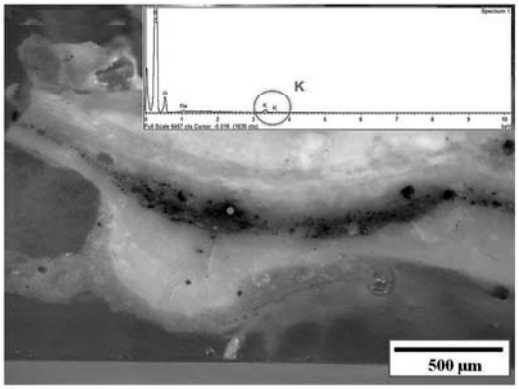

Figure 11. In the OM image the black level of charcoal lumps is visible in a portion of sample 4, mid '700 plaster. The red dot shows the position of the analyses which spectrum is reported in the insert. The red circle evidence the small peak of potassium, typical of carbon from vegetal material.

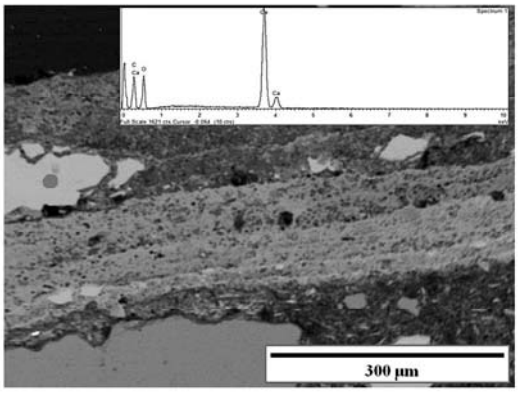

Figure 12. BSE image of some lime fragments in sample 10, mid '700 plaster horizon. The analysis made in the position of the red dot shows a composition made of pure Ca carbonate, almost without magnesium (the EDS spectra in the insert).

The gypsum and pigment layer

This layer has been found in almost all samples. The gypsum (which nature was confirmed by EDS analysis) (Figure 16) is in a dense polycristalline form, represented by an aggregate of minute bacillar cristallites, few micrometers long and very thin; the total thickness of the layer is usually below 100 micrometers, following the roughness and the cavities of the mortar surface below. The reason for that could be that this layer has been painted "a secco", or with organic ligands. For these painting techniques it's necessary to prepare the wall with a layer called "imprimitura", a uniform background for paintings. Usually this is made of very fine lime, but sometimes it may be made of gypsum mixed with water, glue or milk (Forti, 1937).

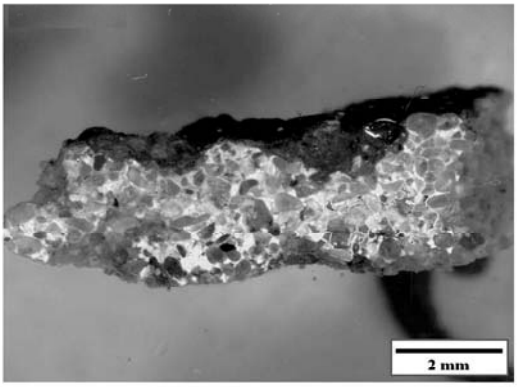

Figure 13. An OM picture of sample 23 showing the very rough mid '800 mortar, quartz rich.

Conclusions

The study of the layering of mortars and plasters in an historical building in which the last construction phase dates no more than 160 years ago is unusual. In spite of this, these investigations could be very useful to deepen the knowledge of the materials used in the construction, and to obtain a match between existing and new products used for restoration. This is to achieve the maximum compatibility, the minimum damage and the best duration of the restoration itself.

During the investigation, we noticed that a recent building can suggest tricky questions, despite the support of historical documentation.

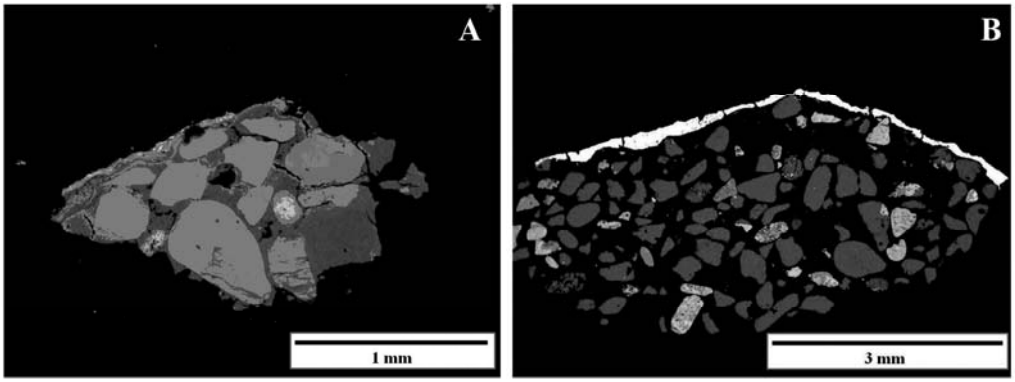

Figure 14. A) A false colour BSE image of sample 8 mid '800 mortar. Silica (quartz) granules are light blue whereas feldspars range from green to orange; B) A false colour BSE image of sample 15 mid '800 mortar. Silica (quartz) granules are light blue whereas feldspars range from green to orange.

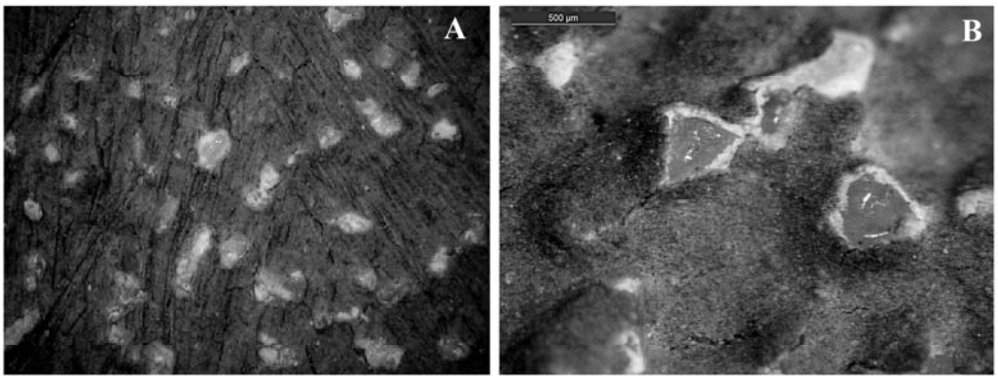

Figure 15. A) A micro-camera image of a pictorial surface with the whitish tiny dots due to detach of the paint layer in correspondence of the quartz grain; B) Magnification of the previous area. The quartz grain protrudes from the surface causing a loss of pictorial layer. The white thin gypsum layer is also visible between the quartz and the paint film.

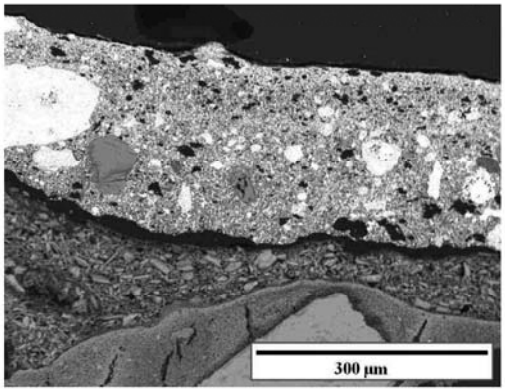

Figure 16. The gypsum layer below the pictorial layer (above) and the mortar (at the base). The texture made of tiny elongated microcrystals of gypsum is clearly pictured in the BSE-SEM image. This layer was requested by the painters as a preparative surface for the painting cycle.

Concerning the mortars, we noticed that in both kinds the dominant aggregate phase is quartz with subordinate feldspar. The old mortar has a less uniform texture, smaller grains, less rounded and sorted. The recent one has a rough and uniform texture, with bigger and more rounded particles. This could suggest a different source of the aggregate used for the wall preparation. Indeed, we have a hint from historical documentation (letters between customer, painters and workers). The sands used for the late works were extracted from two different sites nearby the city of Mondovì, one is the Beinette Lake (actually a small resurgive pond) and the other is the Ellero river banks. We have still not made a comparison of these sands. The content of the samples analyzed by now will be studied to have a better statistical comparison, waiting for a greater number of specimens to pick up during the restoration.

The binder of these mortars is always a magnesian lime with various content of magnesium. Some extraction sites of magnesian limestones and dolostones exist and existed in the past near Mondovì, e.g. in Roccaforte di Mondovì (12 km SW of Mondovì city), where a dolomitic limestone of Triassic age is still quarried, or in Villanova Mondovì (8 km SW) were a gray Triassic dolostone was mined. The natural variation in magnesium content in different depositional levels of these stones could explain the Ca/Mg ratio variability in the binder.

The roughness of the last mortar layer is a bit surprising. We should think to a desired effect, for a better grasping surface of the pigment layer or to hypothesize that the workers during the '700 paid more attention to the precision of the surface than the workers in the '800. E.g. in historical literature some authors state that in wall paintings of IV and V century A.D. the surface was usually more shiny and compact; in the following centuries the aesthetic taste changed and the artists preferred rough surface that avoid reflections and, from a distance, have higher brightness (Perusini, 2004). By the way, documental evidences of financial problems in 1850 do exist, and these difficulties could have, as a consequence, a more approximate work.

Regarding the plasters, the main question is: could this layer be a real preparation stratum that later, at the end of '700, should have been covered with paintings (this painting cycle was never done) or could it be a decorative whitish surface to obtain light and luminous walls as in the nearby "Chiesa della Missione"?

What is the reason for the elaborate structure of the plaster, with up to seven strata of different composition? The complexity of this plaster seems too high for a finishing layer placed at a height of 15 meters above the church floor, in a position where very few people could have noticed the perfection of this kind of work. Nevertheless this plaster could have had a conservative role, a final protective coating of the masonry (Perusini, 2004).

The investigations are still in progress, because we have samples only from the first half portion of the building, and we hope that new samples, coming from other positions, would help us to answer these questions. At the moment we have a good agreement between analytical data and historical documentation, and this supports us in the quality of our verifications. These analyses proved to be a very useful tool to investigate the structure and nature of the materials used during the different construction phases, in order to permit to the restoration Team the best choice between the variety of restoration techniques and substances.

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