A multi-analytical approach for the characterisation of the oldest pictorial cycle in the 12th century monastery Santa Maria delle Cerrate

Giuseppe E. De Benedetto,[1] Antonella Savino,[1] Daniela Fico,[1] Daniela Rizzo,[1] Antonio Pennetta,[1] Antonio Cassiano,[2] Brizia Minerva[2]

[1]Laboratory of Analytic and Isotopic Mass Spectrometry, Department of Cultural Heritage, University of Salento, Lecce; [2]S. Castromediano Provincial Museum, Lecce, Italy

Abstract

A multidisciplinary research, currently in progress at the University of Salento in collaboration with the Lecce Provincial Museum, interests different artistic expressions widespread in the Salento peninsula (South Italy). In the present study, the characterisation of organic and inorganic materials used in the oldest pictorial cycle found in the 12th century monastery Santa Maria delle Cerrate was carried out thanks to a multi-analytical approach. Previous investigations have focused on the problem of dating the frescoes mainly on the basis of the stylistic aspects and the material characterisation has been definitely under-investigated. Chromatographic and spectrometric techniques were used: micro-Raman spectroscopy was used for recognising pigments and gas chromatography with mass spectrometric detection for analysing organic binders. These techniques enabled us to characterise pigments and binders. The presence of both true fresco and tempera bound pigments was assessed. Among the different pigments detected, the results relevant to the blue paints were interesting: two different blue pigments were, indeed, identified, lapis lazuli and smalt (cobalt blue glass) both unexpected. As a result, Santa Maria delle Cerrate appears to be the first known example of their use in South Italy. From a conservation point of view, moreover, the knowledge of the palette permitted to highlight the reason of observed decay of some paints: for instance, lead white was used in some panels, explaining their blackening.

Introduction

The monastery of Santa Maria delle Cerrate is an Italo-Greek monastery, whose history is partly shrouded in mystery. Built by the Norman counts of Lecce, although it is unclear who of the three counts Accardo, Bohemond and Tancred built it. What is most fascinating aspect of this church is the apparent contradiction between the typical Western architecture and the openly Byzantine iconography. Archaeometric analysis conducted in this study was aimed to investigate the chemical composition of the frescoes in the church, in order to understand which materials were used and how they were prepared.

The monastery of Santa Maria delle Cerrate is located in the country about 15 km north-east of Lecce, a few kilometers from the Adriatic Sea and the Squinzano and Surbo. It is in the Salento peninsula in the eastern part of Italy, next to so called italian east door, Otranto, facing Greece and Asia minor, once the center of Byzantine empire. Still remain uncertain, the founding year of construction of the church and monastery and the name *Cerrate*, due to the lack of written sources and iconographic and archaeological evidence. There are few documents relating to the historical context: at the end of 11th century the monastery was founded by monk Nicodemo, the monastery is named in a parchment of 1133 and in a manuscript of 1154, the colophon demonstrate the presence of the Scriptorium. Finally Antonio De Ferraris (1444-1517) describes in his *De situ Japigiae* the abbey desert and in ruin (De Ferraris, 2004).

In the last decade, after the discovery of an inscription thank to the French historian Jacobs, art historians seems to agree the church was built in the second half of the 12th century.

Beyond the history, the monastery was large and included the residence of the monks, refectory, library, scriptorium, furnaces, mills, stables (Castromediano, 1877). Only part of the monastery has come to us and much of it has been extensively modified over the centuries. However, the monastery of Santa Maria delle Cerrate is very interesting for several reasons. First, the architectural structure of the church of Santa Maria delle Cerrate presents typical features of the Romanesque style (Romanico), whereas its iconography is typically Byzantine. Outside, the building presents a tuff masonry wall with elegant arches carved on the facade, which mark the side walls and the exterior of the apses. The facade has a finely carved rosette, the central nave higher than the aisles, all with *roofs at straws* and an extensive portal with porch added at the end of 12th century. The internal structure of the church is simple: a basilica divided into three naves by two rows of columns with finely carved capitals that support pointed arches and ending in three apses, according to the classical western canon. The church has undergone several pictorial cycles. The oldest pictorial cycle which was discovered only in 1975, when the 15th century frescoes were detached and exhibited in the next museum, is considered of very high quality and, on the basis, firstly, of the manner in which the iconographic programme is worked out and, secondly, of the stylistic and morphological features it is likely that the oldest cycle could date from the end of 12th century to the 13th century. The surviving frescoes are camped along the aisles, in the apses and arches (Pellegrino and De Luca, 2004).

The importance of Santa Maria delle Cerrate is also linked to the fact that it is the sole survived monastery in the Italo-Greek Salento, on considering that only ruins of San Nicola di Casole, the most important monastery in that period, also known for its poet school, have survived.

The chemical analyses of selected samples allowed us to provide new data and to issue different open questions: as usual the technological, the present seems the very first scientific investigation on the oldest pictorial cycle (painted layer), so there is no knowledge of materials and techniques used. As to the art historical questions, nothing is known about the artist or artists which frescoed the church (there is a letter dated between 1220-1235 attesting the presence of a greek painter in

Correspondence: Giuseppe De Benedetto, Laboratory of Analytic and Isotopic Mass Spectrometry, Department of Cultural Heritage, University of Salento, Lecce, Italy.
Tel./Fax: +39.083.2297104.
E-mail: giuseppe.debenedetto@unisalento.it

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Casole), also materials and techniques could help in confirming both iconography and painter were Byzantine. Moreover, on considering that the church has been built in the second half of the 12th century, are the frescoes coeval? In this respect Pace, the art historian first described these frescoes in the late seventies, name two churches (S. Maria di Anglona and S. Demetrio Corona) that were frescoed only later their construction and Santa Maria delle Cerrate could be the third (Pace, 2008).

Materials and Methods

Samples

A total of 11 samples, listed in Table 1, were taken from the decorative apparatus located in the central apse and the side walls, nine of which were few grains of powders. Only samples 1 and 4 were millimeter-sized fragments permitting the preparation of the relevant cross sections.

All samples were analysed by micro-raman spectroscopy and 4 of them with gas chromatography-mass spectroscopy (GC-MS). The first is an analytical technique widely used for the characterisation of pigments used in works of art or of the decay products, since it is non-destructive and not invasive as it allows the analysis in situ without any sampling. Coupled with a optical microscope also permits the analysis of very small areas (5-10 μm^2). The GC-MS is an analytical technique that can uniquely identify any organic matter present in the sample and was used to identify binders.

Optical microscope

A Nikon microscope ECLIPSE 80i (Nikon, Tokyo, Japan) equipped with a fluorescence source X-Cite 120, a high sensitivity digital camera, and Nikon B-2A and UV-2A (Nikon) filter blocks has been used to carry out optical observations under visible, blue and UV light of cross-sections in order to identify the stratigraphic sequence and the presence of fluorescent materials.

Micro-Raman spectroscopy

The Micro-Raman measurements were carried out with a Renishaw inVia instrument, equipped with two laser sources, a diode and a He-Cd laser with excitation wavelengths of 785 nm and 442 nm, respectively, holographic notch (for the 785 line) and edge (for the 442 line) filter, motorised xy stage and a Leica

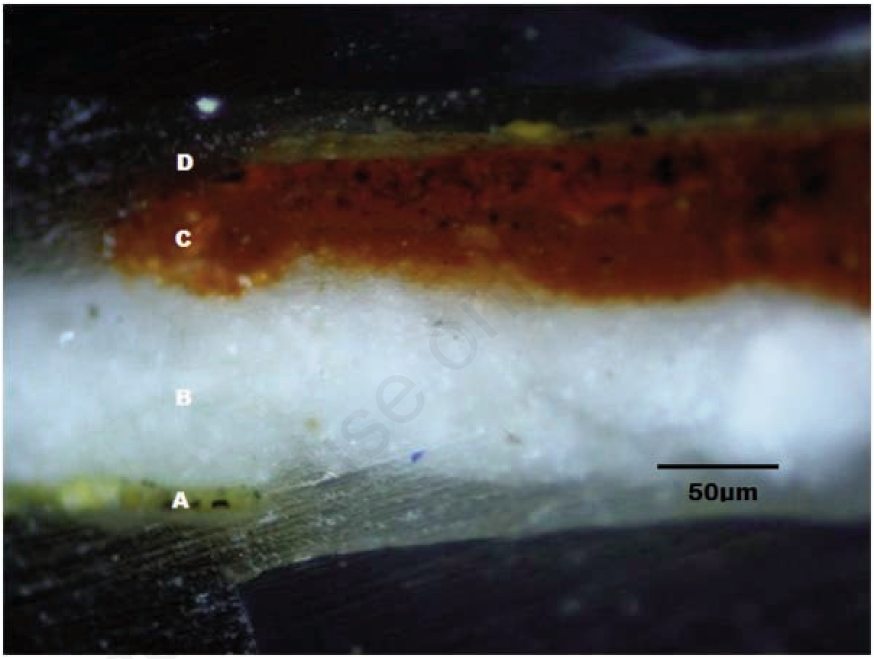

Figure 1. Cross section of sample 1. The first layer (A) measures 23 μm and contains carbon; the second layer (B) measures 137 μm and is a mixture of white lead and calcite with rare lapis lazuli crystals; the third layer (C) is thick about 96 μm and contains red and yellow ochre, white lead and coal; the external yellow layer (D) measures 21 μm and is composed exclusively of massicot.

Table 1. List of the analysed samples with the relevant Raman results.

Label	Collocation	Description	Identified pigments
1	Central apse	The compact fragment shows an orange layer and a white uniform side	Red ochre, yellow ochre, massicot, white lead, calcite, black coal, lapis lazuli
2	Left wall	The fragment shows a white side (preparation) with blue crystals and a black layer	Black coal, calcite, smalt
2a	Left wall	The powder shows a dark side and a white side	Black coal, calcite, smalt
3	Left wall	It is a white powder	Red ochre, calcite
4	Lateral apse	The compact fragment shows a light yellow side with dark blue crystals in a corner, on the other side, the sample is pinkish with red and blacks crystals	Red ochre, yellow ochre, massicot, white lead, calcite, black coal, lapis lazuli
5a	Right wall	The fragment shows a white side (preparation) with red crystals; in a corner there is a dark layer	Black coal, calcite, lapis lazuli
6	Right wall	White fragment	Yellow ochre, white lead, calcite
6a	Right wall	The powder shows a white layer (preparation) and a light yellow paint layer	Red ochre, yellow ochre, white lead, calcite, black coal
6b	Right wall	The fragment shows a homogeneous white layer with blue, red and black crystals. The painted layer is red-orange	Red ochre, massicot, white lead, calcite, black coal, lapis lazuli
7	Left wall	The fragment shows a white layer (preparation) and a dark painted layer	Red ochre, black coal, calcite
7a	Left wall	It is a dark powder with red, black and blue crystals	Red ochre, massicot, calcite, black coal, lapis lazuli

DMLM microscope (Leica, Solms, Germany) with objectives up to 50x with a spatial resolution of about 2 μm. The light at 785 nm from a diode laser (maximum power 300 mW) was generally used for excitation. Neutral density filters were employed to keep the laser power at a low level (0.1-2 mW) on the samples, to avoid undesired heating effects such as laser induced transformations, which are well known to occur, for example, on iron oxide or hydroxides. The spectra were collected with repeated acquisitions (3-5, according to the signal/noise ratio) each of 10-20 s. The calibration of the spectrometer was checked using the most intense pure silicon Raman peak at 520.5 cm^{-1}. The spectral resolution is about 2 cm^{-1}.

Gas chromatography-mass spectroscopy

A GC-MS system made up of a 6890N gas chromatograph (Agilent, Santa Clara, CA, USA) equipped with a split / splitless injector and with a quadrupole mass spectrometer detector (model 5973inert) was used to separate and identify the organic compounds. Chromatographic separation was performed on a chemically bonded fused silica capillary column HP-5MSUI (i.d. 0.25 mm, film thickness 0.25 m, length 30 m) with a 5 m deactivated silica pre-column. GC conditions for amino acids were: initial temperature 100°C, 2 min isothermal; 6°C/min up to 280°C, 15 min isothermal; carrier gas He; constant flow rate of 1.2 mL/min. GC conditions for fatty acids: initial temperature 80°C, 2 min isothermal; 10°C/min up to to 200°C; 6°C/min up to 280°C, 8 min isothermal; carrier gas He; constant flow rate of 1.3 mL/min. Samples were treated according to the procedure outlined in Colombini *et al.* (2006).

Results and Discussion

Figure 1 shows the cross section of sample 1 taken from the central apse. It is possible to see the layered structure, the superposition of paint layers which is an important characteristic of Byzantine wall painting. Unfortunately section lacks the plaster layer; however macroscopic investigation of the wall painting surface at the point of greater damage and detachment permitted to detect at least two different layers of plaster. The inner layer, the so called *arriccio*, contains straw. Raman analyses produced interesting results as far as the used palette is considered. Table 1 collects the identified minerals in the different samples (Bell *et al*., 1997; Burgio and Clark, 2001). Overall the pigments used in the frescoes of Santa Maria delle Cerrate were common and easily available, except for blue. As to the red and black

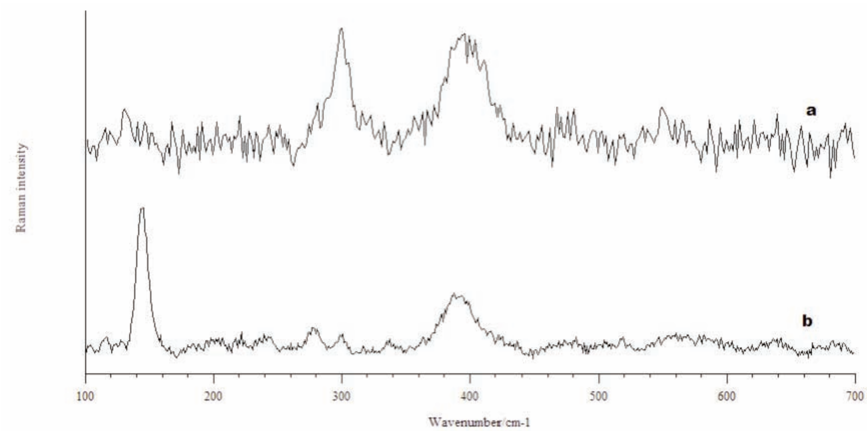

Figure 2. Micro-Raman spectra of yellow pigments identified in the samples: goethite (line a) and massicot (line b). Operating conditions: diode laser operating at 785 nm, 1 mW at the sample, 50 x objective, integration time 10 s, 5 scans. The spectra are baseline-corrected.

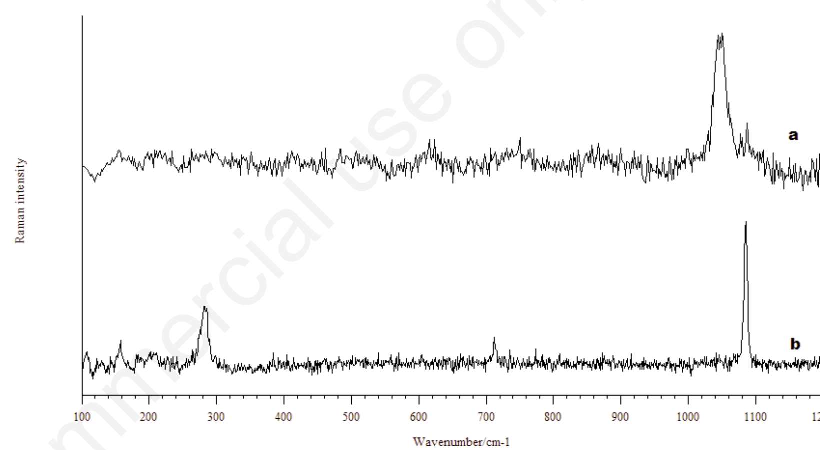

Figure 3. Micro-Raman spectra of white pigments identified in the samples: white lead (line a) and calcite (line b). Operating conditions: He-Cd laser operating at 442 nm, 2 mW at the sample, 50 x objective, integration time 20 s, 10 scans. The spectra are baseline-corrected.

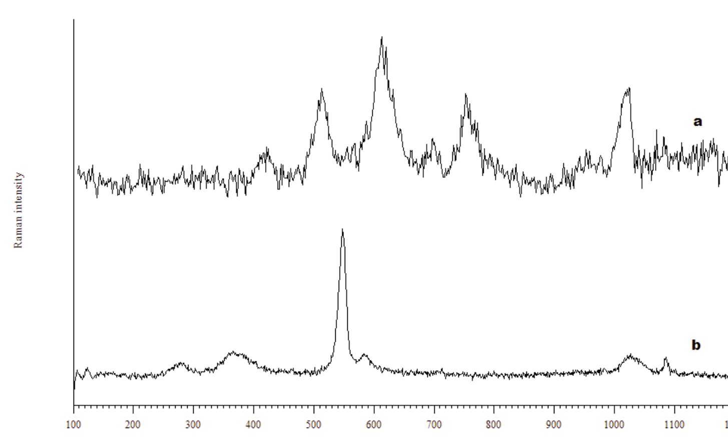

Figure 4. Micro-Raman spectra of the blue pigments identified in the samples: smalt (line a) and lapis lazuli (line b). Operating conditions: He-Cd laser operating at 442 nm, 2 mW at the sample, 50 x objective, integration time 20 s, 10 scans. The spectra are baseline-corrected.

colours hematite and carbon were the only minerals identified. Yellow ochre and massicot, a lead monoxide, were the yellow pigments used in the frescoes (Figure 2). The presence of the former was possible thanks to the identification of goethite, α-FeOOH, a thermodynamically stable iron oxide having an orthorhombic bipiramidal structure. The latter is often confused with litharge, a lead monoxide as well, but mineralogically different. In particular massicot is the product of the heating of white lead at about 300°C. The heat causes the release by the white lead of carbon and water, forming a yellow powder which is precisely the massicot. The production of this pigment is known from ancient times and it was found in Egypt, Italy, Germany, and in general all over Europe and America. Yellow ochre and massicot have been found both mixed (in sample 4) and in different layers (in sample 1, the top layer is of massicot, the intermediate layer contains also yellow ochre). The presence of white lead in different parts of the pictorial cycle (often mixed with lapis lazuli) is also peculiar. As far as we know, it was never used in Byzantine frescoes. On the contrary it is present in the palette of fresco painters working in the second half of 13th century in central Italy. The white pigments comprise obviously calcite but also white lead in different points of the apses and lateral walls (Figure 3).

The occurrence of blue pigments is more complex and interesting (Figure 4). In the frescoes of the left aisle, closer to the apse the smalt was used (Colomban *et al.*, 2006; Daniilia *et al.*, 2007, 2008; Daniilia and Minopoulou, 2009). The analyses of the blue pigmented layers of the apse, the right aisle and sample 7 of the left aisle revealed the use of lapis lazuli. This was a very expensive pigment, used in either tempera, generally an emulsion of egg yolk, water, and vinegar, or fresco technique. It is, indeed, extremely stable under alkaline conditions, but unstable in acidic environment in which it loses color and becomes white-gray. The discovery of smalt and lapis lazuli is peculiar. The smalt is not common in earlier works of art from the 14th century, and the lapis lazuli in general has often been replaced by other blue pigments because of its high price. In the monastery of Santa Maria delle Cerrate lapis lazuli has been used not only on the clothes, even in the background: this result confirms the richness of its clients. Four samples (2, 4, 6b, 7) coming from four different scenes and areas of the church have been subjected to GC-MS analyses. The recognition of the nature of the binding medium was achieved by the quantitative determination of aminoacids and lipids (Colombini *et al.*, 1998, 2006). The results of the analyses on the four samples are collected in Table 2, which shows the mean values of the relative percentage content of stable aminoacids. These values have been compared to the results obtained on reference substances and in particular egg yolk, animal glue, collagen and casein. Pigments on sample 2 have been applied by means of the fresco technique: the absence of organic binders is, in fact, suggested by the protein content less than 0.1% and the lack of some aminoacids. The other samples possibly contain both egg and animal glue. Actually, we think that egg yolk is the binding medium used and animal glue could be the result of the consolidation after the *strappo* technique of the 15th century cycle in the middle seventies.

Conclusions

The chemical analyses conducted on samples from the frescoes of Santa Maria delle Cerrate show a complex situation of construction. The results show the common characteristics of the typical Byzantine painting techniques such as the use of different pigments (Kock and De Waal, 2008), the use of both fresco and secco techniques and the overlap of several layers of paint (Frothingham, 1894; Weitzmann, 1996; Winfield, 1968; Belting, 1974). It is documented the use of tempera on Byzantine frescoes (Daniilia *et al.*, 2000; Anastasiou *et al.*, 2006). It was necessary because of the superposition of paint layers: the painting begins on wet, damp plaster and is later completed by means of the secco technique employing an organic binders, egg yolk very often (Gettens and Stout, 1958; Winfield, 1963). So it seems that both iconography and technique were greek, Byzantine. However, there are some peculiarities such as the use of white lead, smalt and lapis lazuli which are not usual in the frescoes of 12th century (Kitzinger, 1966). The white lead, not particularly suitable for the mural because it alters and becomes brown in color, does not belong to the Byzantine tradition. From a visual inspection of the frescoes the white lead seems to have been widely used in Cerrate possibly in order to increase the brightness. The use of smalt is attested in the frescoes in Europe only since the 15th century and in Italy in 1485 with certainty, because it is used on the frescoes in Santa Maria Novella (Florence) painted by Ghirlandaio. The lapis lazuli, as a pigment, is not mentioned in the sources except in manuscripts from the 14th century when the first *recipes* for its preparation begin to appear, although it seems to have been used in S. Angelo in Formis (Capua) near Caserta. Its presence suggests that, contrary to what emerges from the written sources (Civici *et al.*, 2008), the lapis lazuli was widely used in wall paintings prior to the 14th century, and confirm the high clients of the entire series of paintings of the church, since it was the most expensive pigments. These findings put forward the time the frescoes were painted to the second half of the 12th century, thus confirming the hypothesis of Pace that the church was frescoed well after its edification.

Finally, two different traditions suggest that

Table 2. Gas chromatography-mass spectroscopy results of the analysis of samples 2, 4, 7a and 6b: mean values of the relative percentage content of stable aminoacids are reported.

AA	Sample label			
	2	4	7a	6b
ALA	n.d.	7.9	8.6	10.3
GLY	22.0	13.0	12.1	14.8
VAL	n.d.	5.3	4.3	5.1
LEU	n.d.	11.0	7.0	8.6
ILE	4.0	6.4	4.2	4.2
PRO	8.1	5.6	4.7	10.3
MET	n.d.	3.7	1.5	1.2
SER	14.5	11.8	12.2	11.4
THR	9.0	5.7	7.8	4.2
PHE	n.d.	3.5	3.7	3.6
ASP	n.d.	9.1	6.4	6.8
OHP	n.d.	n.d.	4.0	0.2
GLU	26.9	12.6	10.9	10.7
Wt. (mg)	0.4	0.8	0.1	0.4
AA (%w/w)	0.02	0.18	1.14	0.31

AA, stable aminoacids; ALA, alanine; n.d., not detected; GLY, glycine; VAL, valine; LEU, leucine; ILE, isoleucine; PRO, proline; MET, methionine; SER, serine; THR, threonine; PHE, phenylalanine; ASP, aspartic acid; OHP, hydroxyproline; GLU, glutamic acid.

what is considered a single cycle could be the result of two different phases of the frescoes, or workers of different schools working together. The former possibility is supported by the fact that picketing revealed the presence of a pigmented layer under the 12th century cycle. So in the second phase something was retouched and some covered by a new layer of plaster and repainted.

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