Multi-probe analysis for the definition of chemical and physical properties of the medieval frescoes of *Santa Maria di Cerrate*

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Abstract
The complementary use of several diagnostic techniques allows a wide-ranging characterisation of a material and its chemical and physical properties, crossing information of its composition through qualitative and semi-quantitative analyses with the investigation of the crystalline components and the vibrational modes of its molecules. Moreover, studies of macro and micro-imaging can give a morphological description of the evaluated material, viewed both on surface and in cross section. A multi-analytical research carried out at the laboratories of the Center of Applied Physics, Dating and Diagnostics (CEDAD) of the University of Salento using Scanning Electron Microscopy (SEM-EDX), X-ray Diffraction (XRD), Raman Spectroscopy and Radiocarbon Dating by Accelerator Mass Spectrometry (AMS) permitted a deep and complete study on some samples of mortars, pigments, vegetal remains and degradation products from the frescos in the church of Santa Maria di Cerrate (Lecce), during the restoration work promoted by the FAI foundation (FondoAmbienteItaliano), giving a relevant contribution. In fact, in the field of conservation of Cultural Heritage, the physical-chemical characterization of the materials allows to gain fundamental information about both their degradation and the manufacturing techniques used by the artists, helping conservators in the actions of cleaning, consolidation and integration.

1. INTRODUCTION

The church of Santa Maria di Cerrate combines a typical Apulian Romanesque architectural style with a rare example of monumental Byzantine painting, considered as a witness of a complex eastern culture survived in Salento after the dissolution of the Byzantine Empire [1, 2, 3, 4, 5, 6].

2. MATERIALS AND METHODS

2.1 Image analysis

A granulometric study of the mortars was realized through the acquisition and the digital elaboration of images [7], thus being able to estimate the amount of aggregates and to identify their ratio with the binder. Macro and micro-images were taken with the camera Nikon D80 and the Scanning Electron Microscope JEOL JSM-5410LV.
The digital processing of the images was carried out with I*mageJ* software. From the images in 8-bit grayscale, the components were highlighted and segmented by assigning a defined threshold

value of brightness to the pixels. Then, the components were converted into elliptical shapes whose areas were calculated thanks to the association of the number of pixels to a dimensional reference value and the diameter of Feret, defined as the mean value of a series of measures of the distance between two parallel tangents to the perimeter of the projected area from the particle (Fig. 2.1).

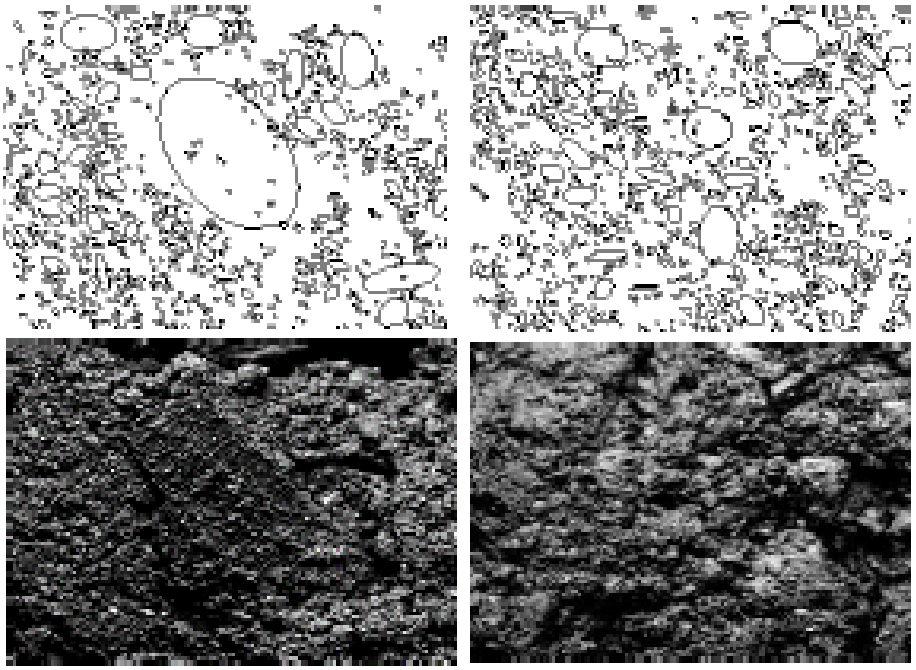

Fig. 2.1 Digital elaboration of the aggregates (a) from some micro-images (b) of the mortars

Pigments and alteration products were analysed by using Scanning Electron Microscope and the Energy Dispersive X-ray microanalysis together with maps of elemental distribution, as well as for one polished cross section used for the artistic technique.

2.2 Structural and molecular analysis

The X-ray diffraction (XRD) with the Rietveld method was performed in order to calculate the crystalline component in the mortars by using a Rigaku diffractometer (model Miniflex) with an X-ray tube operating at 30 kV and 100 mA in step-scan mode from 10° to 80° (speed $0.25°\cdot min^{-1}$) [8].

The micro-Raman tool InVia Renishaw equipped with an Argon ions laser with a wavelength of 514.5 nm was used for the molecular analysis and the acquisition of information regarding the presence of crystalline forms for the pigments and the alteration products.

2.3 Radiocarbon dating with AMS

The vegetal remains were treated by following the standard acid-alkali-acid (AAA) procedure [9]. The CO_2 obtained after the combustion in quartz tubes flame-sealed under vacuum was cryogenically purified and converted at 600°C to graphite by using hydrogen as the reducing agent and iron powder as the catalyst. The radiocarbon content was measured by the ^{14}C-AMS beamline at CEDAD using a 3MV HVEE Tandetron accelerator (Mod. 4130HC), correcting the processing background and the isotopic fractionation and using certified standard samples of sucrose C6 and

oxalic acid. Conventional radiocarbon ages were calibrated to calendar ages through the Oxcal 4.3 software and the INTCAL13 curve based on atmospheric data.

3. RESULTS

All the mortar samples had a low content of impurities and a consistent siliceous component with a high presence of quartz, denoting a strong accuracy in the selection of the sand. However, the ratios between the amount of calcium carbonate, silicon and aluminium oxides and between the compounds related to the aggregates (silicon, aluminium and magnesium oxides) highlighted great differences in their composition, due to different raw materials. A differentiation is evident also for their morphological characteristics and the ratio between aggregates and binder.

In Raman Spectroscopy, the diffused presence of lazurite showed an extensive use of the lapis lazuli blue, a pigment of great value which was rarely used on frescoes (Fig. 3.1).

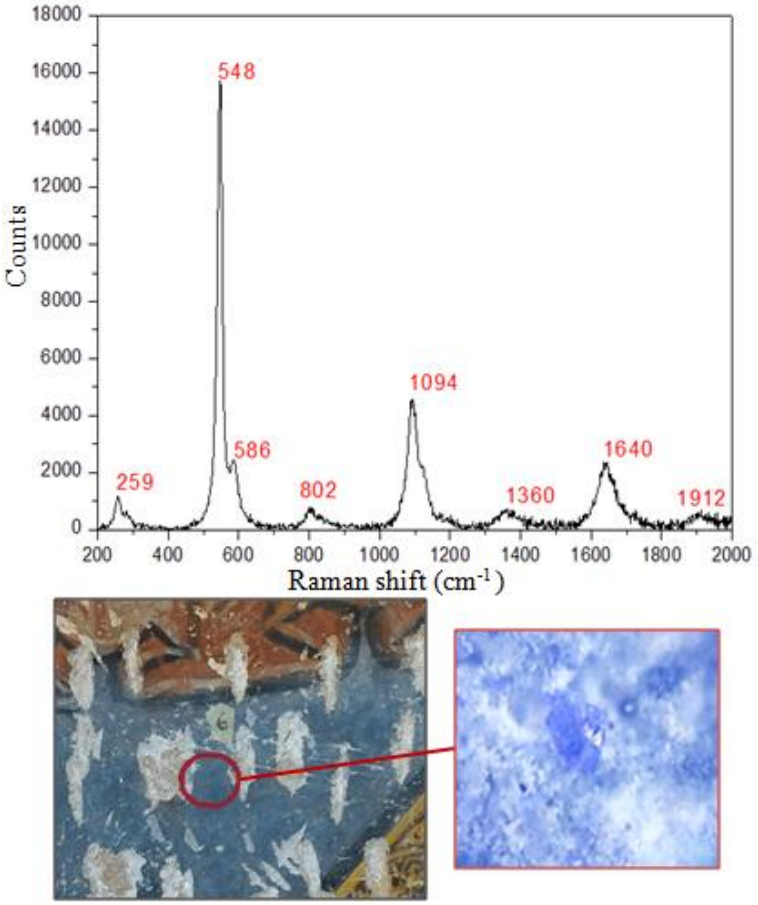

Fig. 3.1 Raman spectrum of the mineral lazurite from a blue sample

A black pigment was detected in the background of the frescoes thanks to the characteristic vibrational modes of the bond C=C. Hematite, goethite and iron oxides belonging to red and yellow ochre, commonly used for their great stability in the fresco technique, were found in Raman Spectroscopy and SEM-EDX. The presence of chromium, cobalt and titanium respectively for the green pigment and some blue samples from a restored area indicates modern conservation actions (Fig. 3.2).

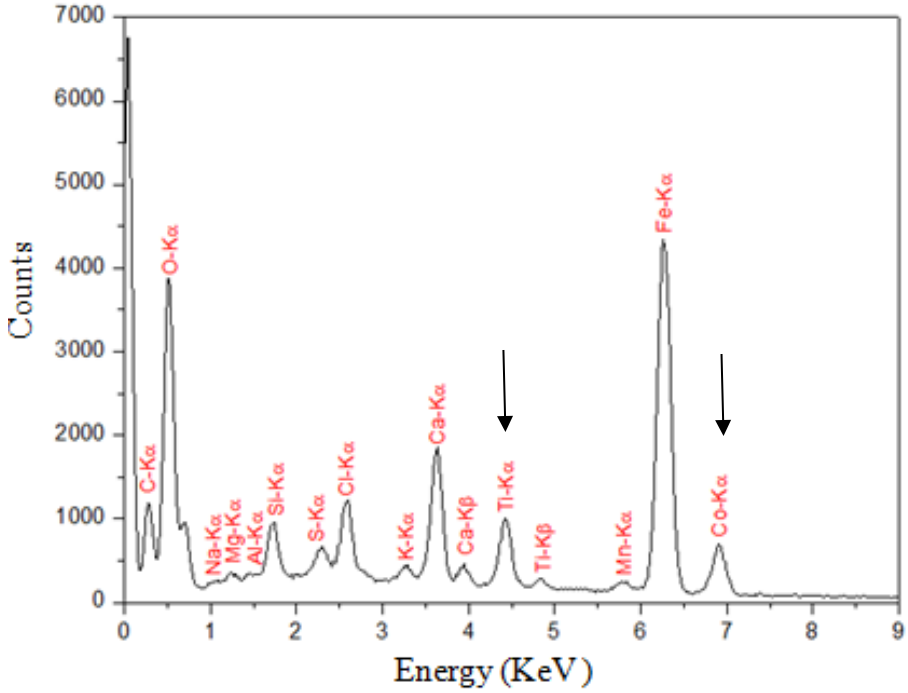

Fig. 3.2 EDX-spectrum with the presence of cobalt and titanium from a restored area

The cross section showed a thin pictorial layer (20-50 μm) and a low diffusion of the pigmented particles, indicating the *mezzo-fresco* technique.

For the alteration products, a widespread existence of titanium crystalline grains in the form of anatase were found. Anatase has a low thermodynamic stability and it can induce photodegradation because of its photocatalytic properties in the UV range, promoting a reiterative process of deterioration with a continuous developing of hydroxyl and hydroperoxyl radicals [10].

This phenomenon, enlarged by high humidity and seepages of water, results in a bleaching appearance of the surface with white powder.

Oxcal 4.3 software and the INTCAL 13 curve based on atmospheric data were used to calibrate the conventional radiocarbon ages (831±45 and 842±45 years BP) obtained from two samples of vegetal remains, used to establish a terminus post quem for the frescoes. The calibrated radiocarbon ages fall in a temporal range between the 12th and the 13th century.

4. CONCLUSIONS

A complete characterisation of the chemical and physical properties of some samples taken from the church of Santa Maria di Cerrate was possible thanks to a complementary use of several diagnostic techniques, gaining morphological, molecular and compositional information.

This analytical research strongly supported the conservation and the historical-artistic studies, suggesting the chronology of the frescoes and highlighting the manufacturing techniques used by the artists and the careful use of materials of great values.

References

[1] C. De Giorgi, *La Chiesa di Santa Maria di Cerrate in territorio di Lecce: note storiche ed archeologiche del cav. prof. Cosimo De Giorgi*, Lazzaretti, Lecce, 1889;

[2] R. Barletta, *Santa Maria di Cerrate: la storia nascosta*, Edizioni del Grifo, Lecce, 2003, 21;

[3] S. Castromediano, *La chiesa di S. Maria di Cerrate nel contado di Lecce, ricerche del duca Sigismondo Castromediano*, Garibaldi, Lecce, 1877;
[4] T. Pellegrino, De Luca V., *Santa Maria a Cerrate: antica abbadia*, Capone, Cavallino, 2004;
[5] M. Falla Castelfranchi, La pittura bizantina in Salento (secoli X-XIV), Ad Ovest di Bisanzio, il Salento medioevale: atti del seminario di studio, Martano 29-30 aprile 1988, Congedo, Galatina, 1990, 129-212;
[6] M. Falla Castelfranchi, *Pittura monumentale bizantina in Puglia*, Electa, Milano, 1991;
[7] D. W. Leuerkens, *Theory and Application of Morphological Analysis: Fine Particles and Surfaces*, CLC Press, 1991, 6-12;
[8]H. M. Rietveld,*The Rietveld method*, PhysicaScripta, Volume 89, Number 9, 2014;
[9] M. D'Elia, L. Calcagnile, G. Quarta, A. Rizzo, C. Sanapo, M. Laudisa, U. Toma, A. Rizzo, *Sample preparation and blank values at the AMS radiocarbon facility of the University of Lecce, Nuclear Instruments and Methods in Physics Research*, 223-224C, Elsevier, 2004, 278-283;
[10] A. Fujishima, T. N. Rao, D. A. Tryk, *Titanium dioxide photocatalysis D. A., Journal of Photochemistry and Photobiology*, Photochemistry Reviews 1, 2000, 1–21.