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Non-invasive Materials Analysis Using Portable X-ray Fluorescence (XRF) in the Examination of Two Mural Paintings in the Catacombs of San Giovanni, Syracuse

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Abstract. X-ray Fluorescence Spectroscopy was performed to characterize pigment materials in a preliminary study of two mural paintings in the Catacombs of San Giovanni. XRF was one non-invasive, analytical technique employed as part of a comprehensive examination, which also included multispectral imaging and 3D modeling. XRF analysis contributed towards a better idea of the materials present, but definitive assignments for the pigments were not possible. The murals show some signs of degradation products including a calcium sulfate surface encrustation, and a bluish-black copper based pigment, which we suspect is the degradation of azurite into tenorite.

Keywords: Materials Characterization, X-ray Fluorescence (XRF), Non-invasive, Mural Paintings, Conservation, Pigment Identification.

1 Introduction

A preliminary imaging and analytical diagnostic assessment was made on two mural paintings in the catacombs of San Giovanni in Syracuse. The documentation was made in half a day, and serves as the first scientific documentation of the state of conservation of the mural paintings. Both portable and non-invasive, the complementary techniques of multispectral imaging and x-ray fluorescence spectroscopy were carried out in this first phase of study.

1.1 The Catacombs of San Giovanni

The Catacombs of San Giovanni (St. John the Evangelist) in Syracuse are the most important example of underground architecture originating from the period of Late

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Antiquity in Sicily. They form an impressive post-Constantinian community cemetery, which exists entirely underground, and was used throughout the fourth and fifth centuries, until the first half of the sixth century AD. [1]

A long gallery, the *decumanus maximus*, divides the site into two regions. The southern region is characterized by three large, round structural features, potentially prior cisterns [2]; and the northern region is intersected perpendicularly by a *decumanus minor*, where there is one large round structure, see map figure 1.

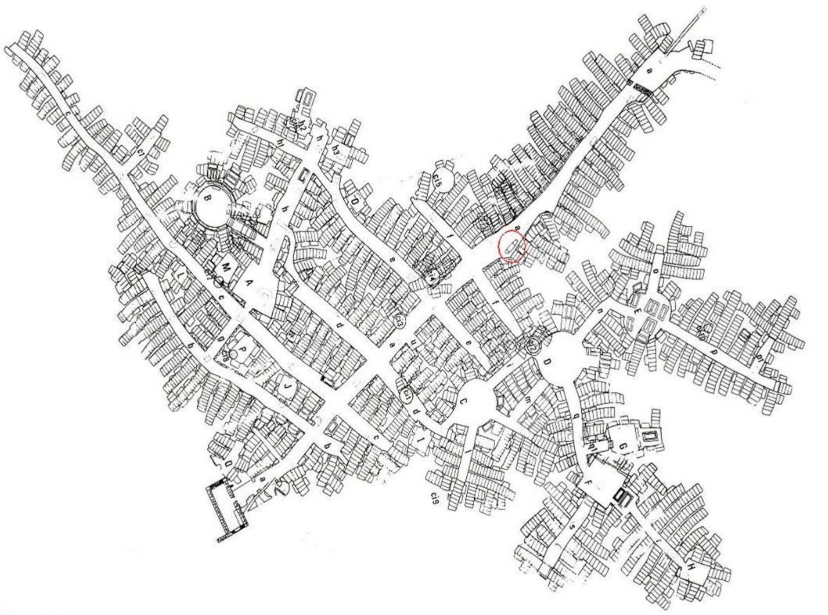


Fig. 1. Map of the catacombs. The circled area shows the location of the Deodata Arcosolio. Facing the arcosolio from the corridor, the Madonna mural is located to the left.

The cemetery exhibits an expansive and monumental architectural layout, which is conceivable only in a socio-cultural climate that had an adequate availability of economic resources and ecclesiastical hierarchy. Thus the construction must have taken place in the era after the Peace of the Church of Constantine (313 AD), when the surrounding community was almost entirely Christianized.

The finest pictorial evidence preserved in the catacombs can be found in the Eastern part of the *decumanus maximus*. Here we have chosen two murals to be the object of our study: The arcosolio of the Virgin of Syracuse, exhibits the mural which we have called "Madonna" and the monumental *arcosolio monosomo* also part of a preexisting aqueduct, and covered in full by a fresco palimpsest, which we call "Deodata". Both of these mural paintings display more than one layer, and we shall reference upper and lower layers in accordance with the observed strata of plaster. In the top area of the "Deodata" (fig. 3), on the lower painted layer, there is a rich floral decoration in the center, along with an inscription engraved near a crown of laurel, flanked by two birds at the bottom of a geometric decoration of faux marble mirrors. In the upper layer, at the top, the central scene is set in a heavenly habitat anddominated by the defunct Virgin crowned by Christ, between the alpha and omega,with two saints on either side of the composition (probably Peter and Paul, to the left to the right, respectively). In the bottom area of the "Deodata", the panel shows an inscription in six lines, which refers to the protagonist as 'the most chaste virgin *Philadelpheia*, the servant of God, whose memory is remembered by his brother, *Syrakosios*.' The eschatological and otherworldly connotation of the entire pictorial composition is, therefore, explicit.

Next to the "Deodata" is another example of a well-preserved burial decoration, the one we have chosen to study and have called "Madonna". This mural painting presents, in addition to the Virgin, a veiled mother sitting on a chair with a baby in her arms, and flanked by two large circles with the monogram XP. [3]

1.2 Project Aim and Scope

Due to the constraints posed by the location and researchers, only one half-day was allotted for analysis, therefore we designed the study to be a preliminary assessment that could be used to guide further research. First, imaging in multiple bands (UV-VIS-IR) provided a basis on which to select a comprehensive set of spots analyzed with XRF spectroscopy, in order to represent the variety of pigments used in the mural painting palette. The XRF analysis was meant to be qualitative in nature, as to rule out modern pigments, or confirm the presence of certain metal elements. As XRF is a surface sensitive elemental technique, we aim to understand and clarify the limitations of its use in pigment identification when the interpreting the resulting spectra.

2 Experimental

X-ray Fluorescence Spectroscopy (pXRF) was used as a non-invasive portable tool to investigate the elemental composition of the pigments used in the frescoes present in the catacombs. Multispectral imaging was also taken as a complementary and visual technique for documentation of state-of-conservation and pigment analysis. The identification of material composition for pigments could help identify different periods of application or points of later addition or restoration.

2.1 Instrumentation

XRF is frequently used as a non-invasive portable tool to investigate the elemental composition of pigments used in works of art, generally and specifically on mural paintings [4]. The instrument used was a handheld Bruker AXS Tracer III-SD® (Kennewick, WA, USA), equipped with a Rh anode for the production of x-rays, operating at 40keV maximum voltage, and capable of a selecting a tube current between 2-25uA. Spectra were collected by means of a Si-SDD detector with a resolution of 145eV, FWHM at Mn (5.9 keV). Detector and source are oriented in 45° geometry, and the spot size is of elliptical shape approximately three by four millimeters (9.4 mm^2). All measurements were performed in air, with a voltage of 40 kV, a current of 11.2 μA, and an acquisition time of 30s. The scans were taken with comparatively short acquisition times, only 30s versus the typically longer times (up to 300s). These settings allowed the detection of elements of atomic number 13 (Al) or higher, however the detector is most efficient in identifying elements above atomic number 20 (Ca). The settings also provided a sufficient raw count rate (range 50,000-110,000, avg. 90,000) to acquire good spectra without saturating the detector (saturation occurs over 125,000 counts). The instrument was operated in the field using a rechargeable Li-ion battery and a laptop computer for control and data storage. A total of 29 spots were analyzed, and the resulting spectra were subsequently processed and visualized using Bruker S1PXRF and ARTAX software.

Multispectral imaging was also taken as a complementary analytical and visual technique for documentation of state-of-conservation and pigment analysis. The identification of material composition for pigments could help identify different periods of application or points of later addition or restoration. The panoramic technique described in [4] was used, including the description of filter combinations and lighting setup. The camera used was a Nikon D800 DSLR (36 MP, CMOS sensor) modified for full spectrum acquisition (built-in IR filter removed). The results of the multispectral imaging will not be shown in this paper; however, their relation to the interpretation of the XRF data for pigment identification will be discussed.

2.2 Characterization

Table 1. XRF points were selected to analyze each of the colors in the palette and include the various plaster layers observed in the two murals

Map #	Mural Painting	Pigment Color (visible)	Relative Layer	Spectrum Name
5	Deodata	yellow	upper	yellow1_5
6	Deodata	yellow	upper	yellow1_6
9	Deodata	yellow	lower	yellow2_9
10	Deodata	yellow	lower	yellow2_10
8	Deodata	white	upper	white1_8
17	Madonna	white	lower	white2_17
23(1)	Madonna	white	lower	white2_23
21	Madonna	encrustation (white)	upper	crust1_21
1	Deodata	red	upper	red1_1
2	Deodata	red	upper	red1_2
7	Deodata	red	lower	red2_7
11	Deodata	red	lower	red3_11
14	Madonna	red	lower	red4_14

Table 1. (*continued*)

22	Madonna	red	lower	red4_22
23(2)	Deodata	green	lower	green2_23
25	Deodata	green	lower	green3_25
26	Deodata	green	lower	green4_26
13	Madonna	green	upper	green1_13
16	Madonna	green	upper	green1_16
20	Madonna	green	upper	green1_20
3	Deodata	black	upper	black1_3
4	Deodata	black	upper	black1_4
12	Deodata	black	lower	black2_12
24	Deodata	black	lower	black3_24
27	Deodata	black	upper	blackI_27
28	Deodata	black	upper	black1_28
15	Madonna	black	lower	black3_15
18	Madonna	black	lower	black3_18
19	Madonna	black	lower	black3_19

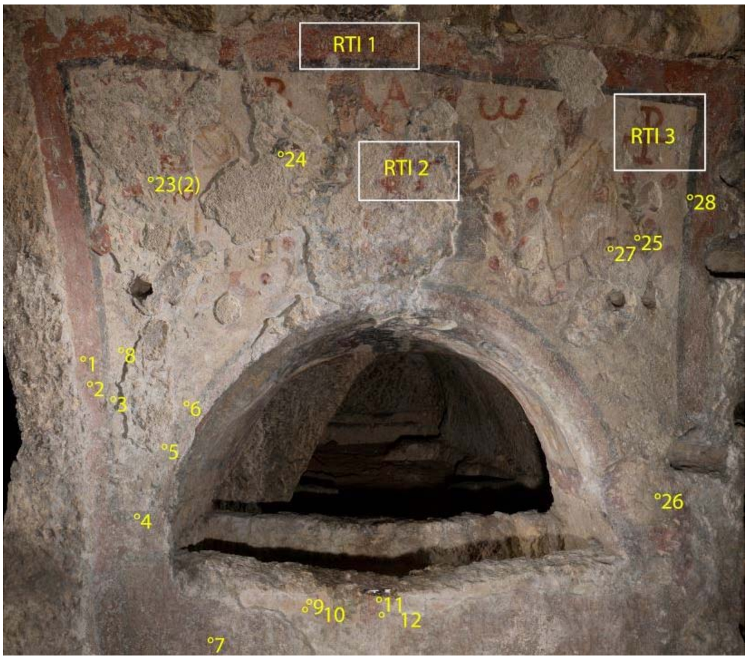
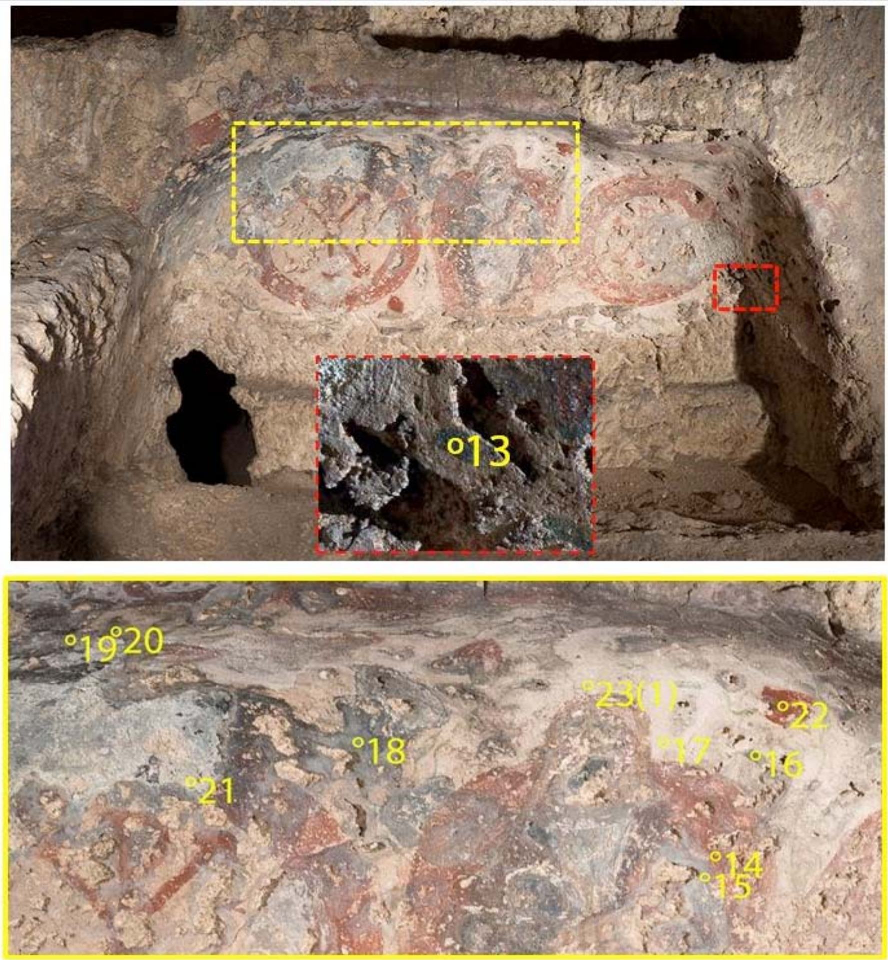


Fig. 3. Map of the spots analyzed with XRF spectroscopy on the “Deodata” mural painting. Reflectance Transformation Imaging (RTI) was also carried out, white box areas, in a subsequent study (in preparation).



3 Results

An attempt was made to survey the color palette and identify the pigments present in the mural paintings, and to explore the potential difference between the layers of the painting (upper, and exposed lower).

3.1 Data

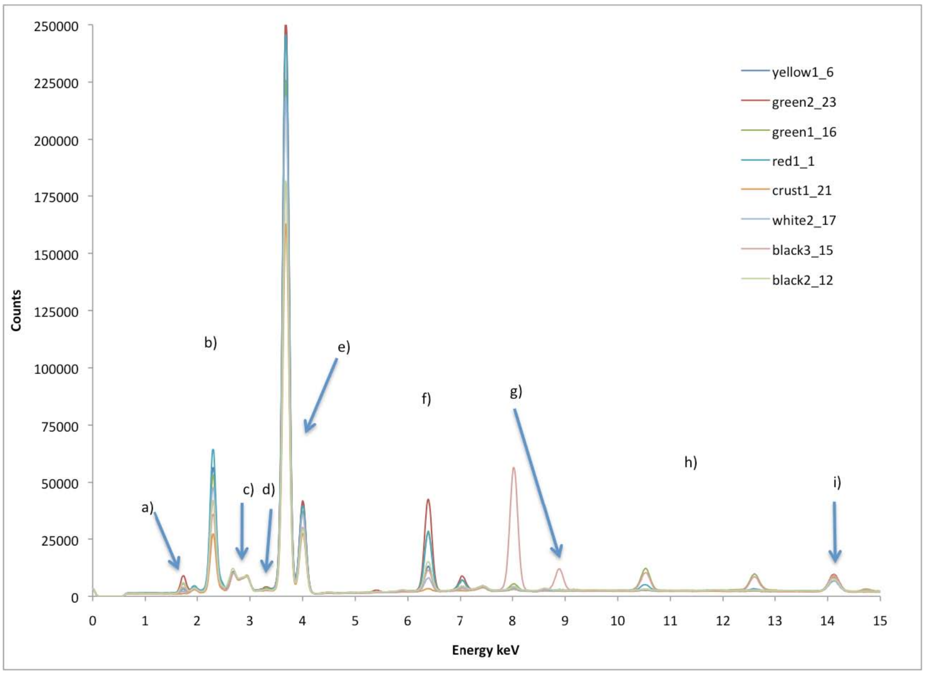


Fig. 4. XRF Spectra showing a selected spectrum from each color present. The following peak assignments have been made **a)** Si Kα, **b)** S Kα, **c)** Rh L (beam), **d)** K Kα, **e)** Ca Kα and Kβ, **f)** Fe Kα, **g)** Cu Kα and Kβ, **h)** Pb L, **i)** Sr Kα.

3.2 Interpretation

The white areas or plaster were studied at points 17, 21, and 23(1). All share the same elemental composition, though intensity of the peaks does vary between the points due to the granularity and inhomogeneity of the sample matrix. There is quite a high presence of sulfur throughout both of the murals. Higher sulfur content was expected in the encrustation, but instead we do not observe it, although a bit more Sr is present along with a decrease of Si and Fe.

Analysis of the red and yellow pigments pointed to the use of ochre ($FeO(OH)\cdot nH_2O$ / Fe_2O_3), which is confirmed by viewing pigment transparency in the infrared image. Point 22 can be observed in the visible image that the pigment is very bright and appears without any sign of degradation, meaning that it is likely a retouching. Indeed, we observe a diminished quantity of sulfur, and a very strong iron peak. This attests to the absence of the $CaSO_4$ degradation product on the surface, and to the increased pigment concentration of the red.

Two types of black pigments were observed. Certain points that appeared “black” in the visible were actually closer to “blue” based on the XRF and the multispectral imaging behavior. The copper content observed in the XRF spectra for these areas, points to the potential degradation of azurite to tenorite, documented as occurring in alkaline environments according to [5]. The other black areas analyzed contained the same elements present in plaster; therefore, in accordance with their infrared absorption we might assume that they have been realized in carbon black (carbon not detectable with XRF).

Points 13, 16, 20, on "Madonna", and 23(2), 25, and 26 on "Deodata" appeared visibly green. The presence of a small amount of lead content is observed in the spectra from the Madonna. The spectra do not indicate elevated levels of a particular metal element that we know to be associated to a green pigment (Cr, Cu, or Fe). In spectra 23(2) and 25 there is a small amount of Cr, but it could come from mineral sources. This could mean that the green pigment is a mixture of a yellow ochre and a blue dye, or it could also be earth based, (complex almuminosilicate minerals, formula: $K[(Al, Fe^{III}),(Fe^{II}, Mg](AlSi_3,Si_4)O_{10}(OH)_2)$. Sampling would probably be required to confirm the identity of the green pigment.

4 Conclusions and Further Research

The XRF analysis was an ideal first step in performing a non-invasive analytical survey that complemented the multispectral imaging documentation. The materials were characterized and judged to be original materials, in some cases with existing degradation processes. Certainly the information obtained from this study will be very useful to determine further action, both for analysis and should a conservation plan be developed.

Additional studies have been already performed, including reflectance transformation imaging (RTI) on some areas of graffiti on the mural paintings. A 3D documentation using structure from motion (SfM) has been made, and this can serve as a digital scaffold for other datasets.

In particular, analytical techniques providing molecular or crystallographic (Raman spectroscopy or X-ray Diffraction) information would be of great use to gain more specific information about the pigments present and their state of degradation. In certain cases, these can be performed in-situ but the instrumentation is less commonly available, for the best results samples would need to be taken.

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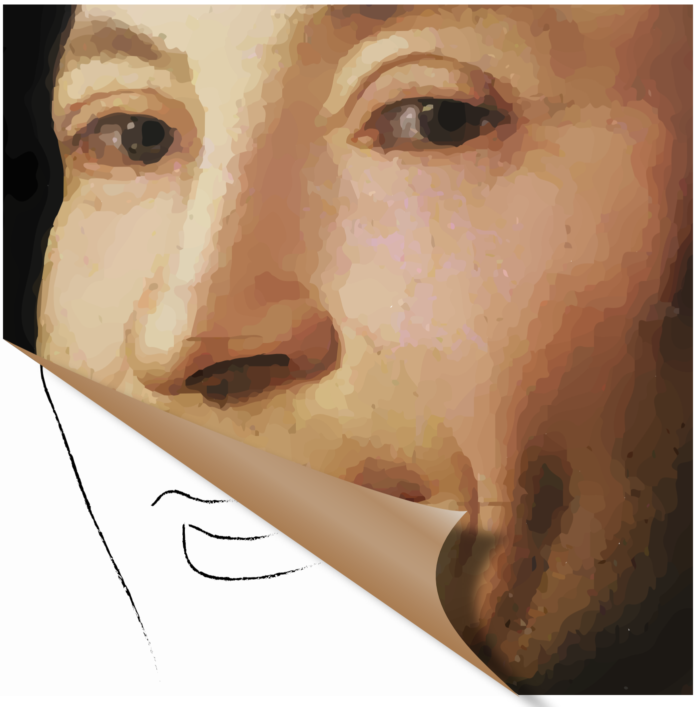

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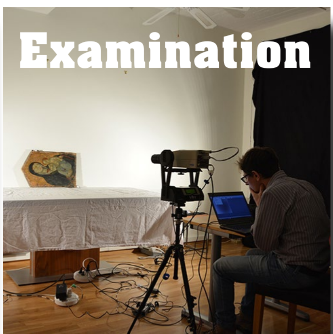

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