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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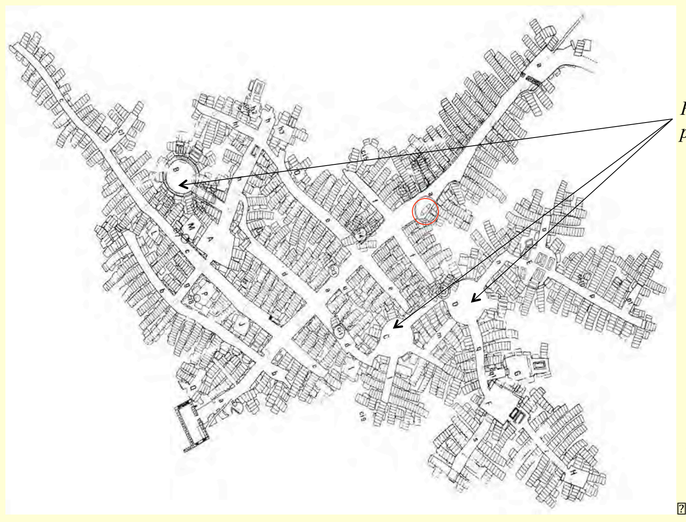
The Catacombs of San Giovanni, Syracuse, Sicily, Italy

The arcosolio of the Virgin of Syracuse, exhibits the mural which we have called "Madonna"



Map of the Catacombs of San Giovanni (St. John the Evangelist). These frescoes are located in the area circled in red.

The arcosolio monosomo, part of a pre-existing aqueduct. The fresco mural palimpsest "Philadelpheia" faces the main corridor of the decimus maximus. The fresco can be seen to exhibit four distinct plaster layers.

- The most important example of underground architecture originating from the period of Late Antiquity in Sicily, forming an impressive post-Constantinian community cemetery, existing entirely underground, and used throughout the 4th and 5th centuries, until the first half of the 6th century AD.

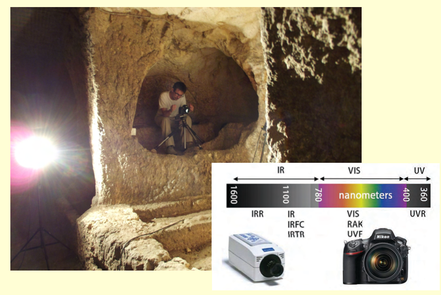
Abstract

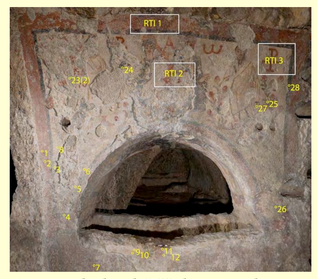
Through complementary non-invasive techniques, a preliminary imaging and analytical diagnostic assessment was made on two mural paintings. The documentation was made in half a day, and serves as the first scientific documentation of the state of conservation of the fresco mural paintings in the Catacombs. Imaging was completed in the IR, VIS, and UV bands; and x-ray fluorescence spectroscopy analysis was carried out using the Tracer III-SD handheld XRF (Bruker).

The purpose of the study was to document and evaluate the frescoes for signs of aging and deterioration, as well as, to characterize the materials present in the pigments that were used. Additionally, the various layers of the frescoes were documented in 3D using Structure from Motion (SfM) and Reflectance Transformation Imaging (RTI).

Methodology

Due to time constraints, we designed the study to be a preliminary assessment that could be used to guide further research.



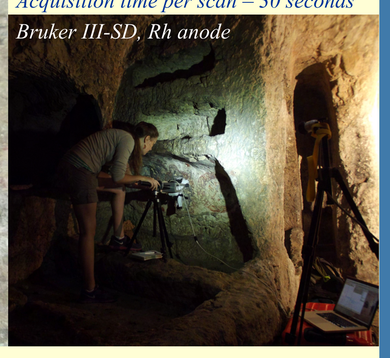


Areas studied with RTI shown in white.

First, imaging in multiple bands (UV-VIS-IR) provided a basis upon 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.

Instrument settings used

Max voltage – 40keV Current – 11.2μA
Raw count rate – 50,000 to 115,000
Acquisition time per scan – 30 seconds

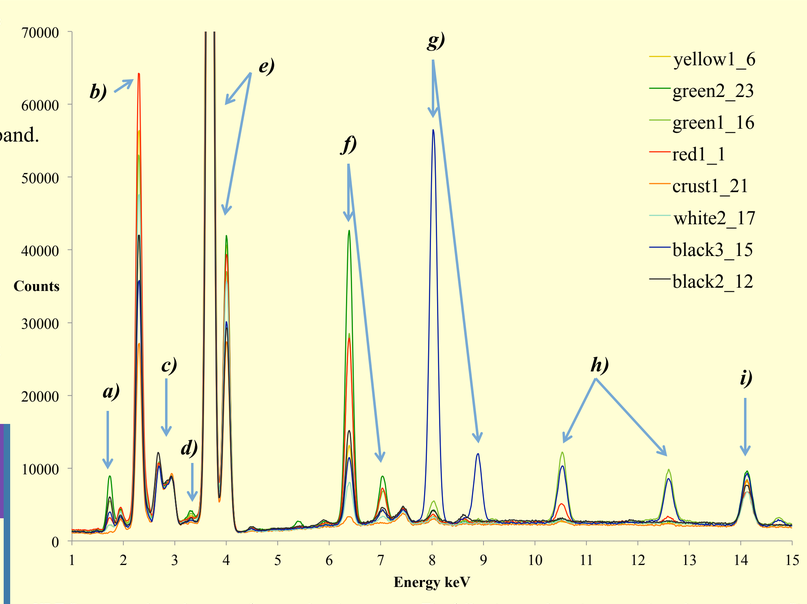


Bruker III-SD, Rh anode

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 interpreting the resulting spectra.

Data Analysis and Interpretation

- Note the sulfur content is generally quite high, indicating the degradation of calcite into calcium sulfate. An increased sulfur peak was expected in the encrustation, spectrum "crust" but instead we do not observe it.
- The red and yellow pigments have elevated levels of Fe, pointing to the use of ochre ($FeO(OH)\cdot nH_2O$ / Fe_2O_3), confirmed by viewing pigment transparency in the infrared band.
- The green pigment is likely green earth (complex almuminosilicate minerals, formula: $K[(Al, Fe^{III}),(Fe^{II}, Mg](AlSi_3,Si_4)O_{10}(OH)_2$).
  (In point 23 probably mixed with yellow ochre, explaining the large Fe peak.)
- Point 15 appeared "black" in the visible but was actually closer to "blue" based on the XRF and the multispectral imaging behavior. The large copper signal, points to azurite as the original source.
- Both black and white points studied did not show any elements outside of those present in the plaster itself. White is likely calcite. The black is likely carbon based, not detectable by XRF, but intense absorption was observed infrared band.



*XRF Spectra: selected spectra 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 and Kβ, **g)** Cu Kα and Kβ, **h)** Pb L, **i)** Sr Kα.*

Conclusions

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).

From the data gathered through MSI and XRF characterization, the pigments present were determined to be original materials, of natural origin, in some cases with existing degradation processes. In particular we observed 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, $Cu(CO_3)_2(OH)_2$ into tenorite, CuO.

The information obtained will be very useful to determine further action, both in terms of subsequent analysis and in the event that a conservation plan should be developed. The dataset will also serve as a record of the state-of-conservation of the fresco mural paintings.

Contact and Acknowledgements

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QR code ->

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