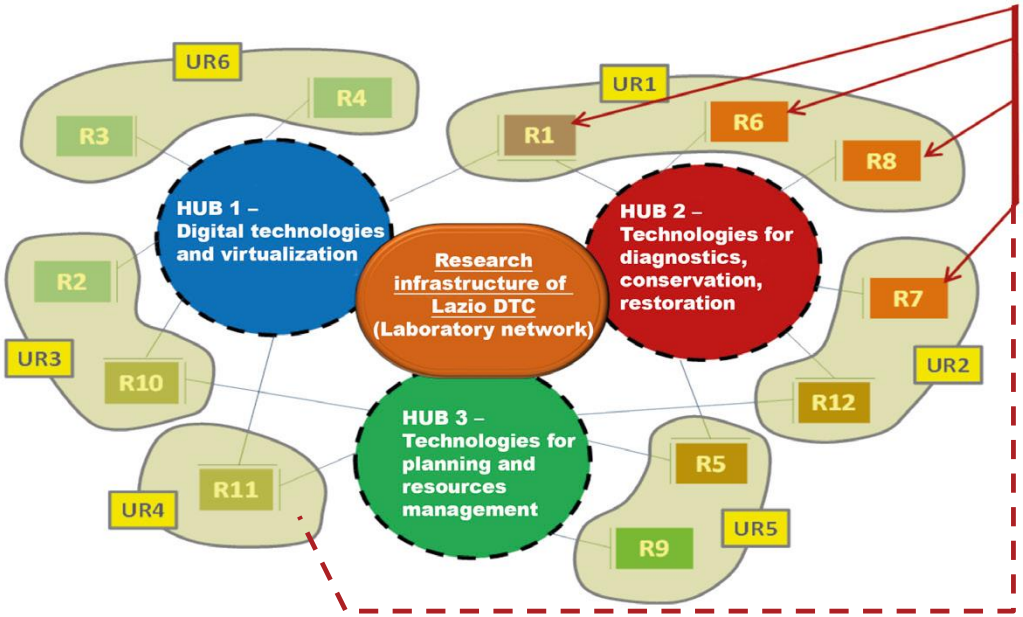
ADAMO-Analysis, Diagnostics and Monitoring for Cultural Heritage project, a technology transfer experience in the Latium Region

ADAMO

TECNOLOGIE DI ANALISI, DIAGNOSTICA E MONITORAGGIO PER LA CONSERVAZIONE E IL RESTAURO DI BENI CULTURALI

Project coordinator: Roberta Fantoni [ENEA]

District of Technologies for Culture



ADAMO

CH Tech portal

UR1) New methodologies, technologies and instrumentation for diagnostics and analysis aiming at improving protective techniques on CH in order to preserve and monitor CH artifacts;

UR2) New materials, technologies, instrumentation and devices for monitoring, conservation, protection and restoration of CH.

R1) Specialized technologies for antiquities, archaeology, history of art;
R6) Chemico-physical sciences and technologies;
R7) Nanotechnologies, materials, sensors and devices;
R8) Applied bio-technologies, archaeo-botanics, environmental biology, molecular anthropology;
R11) Technologies for the development and sustainable management of territorial resources and tourism.

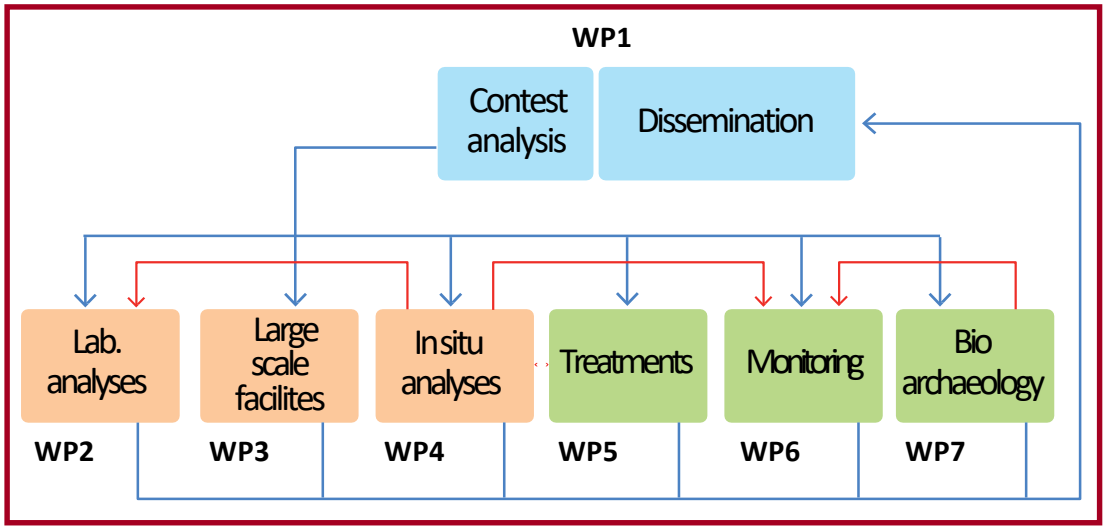
DTC LAZIO

Università di Roma Tor Vergata

ENEA INFN

Partners and role

WP0	Management	Roberta Fantoni ENEA
WP1	Construction, consolidation and sharing	Maria Prezioso RM2
WP2	Analyses and diagnostics by chemico-physical technologies	Maria Antonietta Ricci RM3
WP3	Analysis and diagnostic by large scale facilities	Mariangela Cestelli Guidl INFN
WP4	In-situ and remote analysis and diagnostics	Mauro Missori CNR
WP5	Analysis of materials for conservation and restoration, and treatments evaluation	Claudia Pelosi TUS
WP6	Advanced systems for environmental monitoring	Marialaura Santarelli RM1
WP7	Bio-archaeology, anthropology and environmental biology	Laura Sadori RM1



Project layout

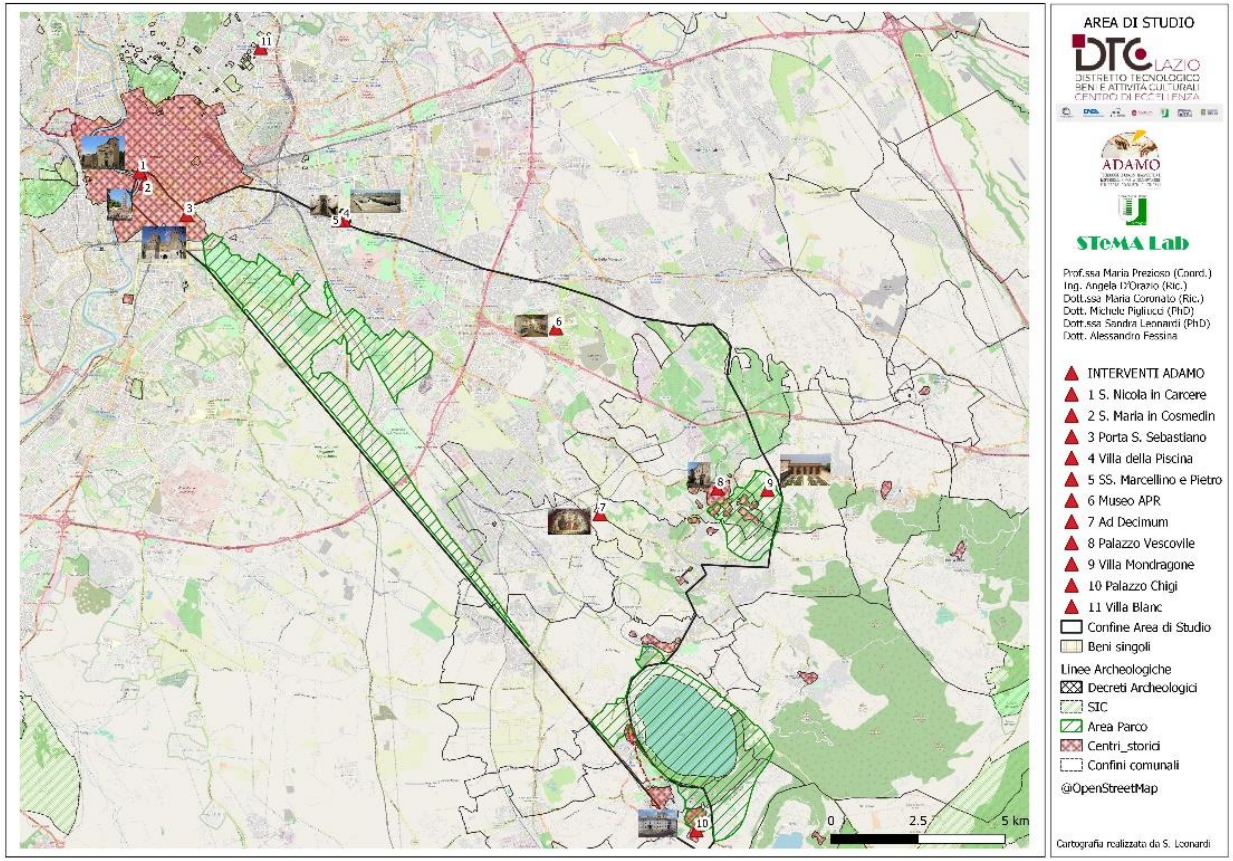
Project web site

Progettoadamo.enea.it

Specific project objectives

1. Technology transfer
2. Offer of HiTEC services to enterprises
3. Demonstration on selected case studies
4. Development of protypes
5. Tests of innovative products

Project sites choice



Considering the variety of conservation problem to be afforded and the potential solution offered within the project, a slice in Rome South-East Area from the center to the Roman Hills was selected, including:

- Basilica of Santa Maria in Cosmedin, Rome
- Basilica of San Nicola in Carcere, Rome
- Aurelian Wall – San Sebastiano Gate
- SS. Peter and Marcellinus Catacombs
- Villa della Piscina, Rome
- APR Museum at Tor Vergata
- Villa Mondragone, Monte Porzio Catone
- Bishop Palace Frascati
- Catacombs Ad decimum, Grottaferrata
- Chigi Palace, Ariccia
- Villa Blanc, Rome

Results on 4 sites are discussed in the following

- Side activities were carried out in additional sites in the Region, whenever specific problems were encountered.
- Additional laboratory activities were performed relevant to technology development.

Basilica of San Nicola in Carcere at Forum Olitorium, Rome

Why was the site selected?

- It was under restoration by the SME **EURES Arte s.r.l**. (Rome) who notified their needs of in situ diagnostics
- It is affected by significant water infiltrations which can be monitored by thermography and other innovative technologies
- It contains fresco's from the «Roman painters of Pius IX pope» in XIX century, which are not well known and have a characteristic palette with the transition from historical mineral pigments and first chemical products (1850).

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Il cantiere di restauro della Basilica di S. Nicola in Carcere: intervento di diagnostica non invasiva sui materiali dell'affresco e sugli agenti biotici responsabili del biodegrado

M. Romani[1], A. Grottoli[2], A. Acconci[3], M. Beccaccioli[2], G. Bonifazi[2], G. Capobianco[2], M. Ciaffi[4], M. Cestelli-Guidi[1], F. Colao[4], R. Fantoni[4], A. C. Felici[2], M. Francucci[4], M. Guarneri[4], M. Mangano[6], M. Marinelli[5], L. Pronti[1], A. Puiu[4], D. Uccelletti[2], M. Reverberi[2], M. L. Santarelli[2], C. Seccaroni[4], S. Serranti[2], A. Tognacci[5], M. Vendittelli[2], G. Verona-Rinati[5]

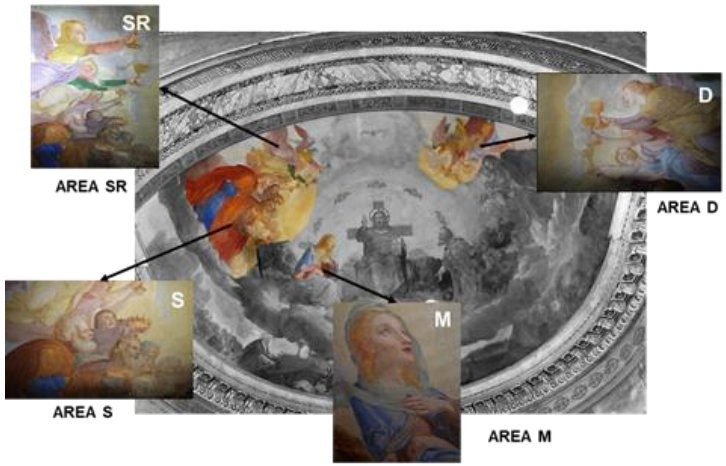
Il lavoro è stato svolto in collaborazione tra i ricercatori di [1]**INFN-LNF,** [2]**Università La Sapienza di Roma,** [4]**ENEA**, [5]**INFN-RM2**, la [3]**Soprintendenza Speciale Archeologia Belle Arti e Paesaggio di Roma** e la ditta di restauro [6]**EURESARTE s.r.l.**, Restauro e conservazione di opere d'arte.

Identification of pictorial materials and High resolution 3D model: Multidisciplinary study on pigments, binders and consolidants on Vincenzo Pasqualoni fresco in the apse (1865-1866)

A joint in situ activity in cooperation by INFN-LNF, Uni. Rome Sapienza, ENEA, INFN-RM2, Soprintendenza Speciale Archeologia Belle Arti e Paesaggio di Roma and the restorer SME EURESARTE s.r.l.

Materials identification was achieved by means of complementary spectroscopic techniques applied in situ and remotely, such as:

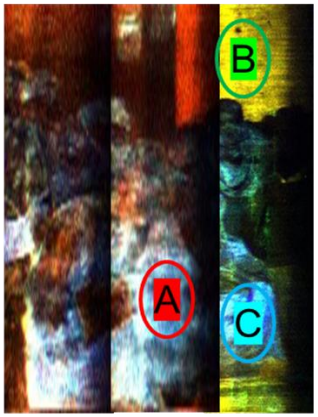
- VIS-SWIR Reflectance ,
- Multispectral Imaging,
- Time resolved Laser induced Fluorescence (TG-LIF),
- X-Ray Fluorescence Spectroscopy (XRF)
- Raman Spectroscopy,
- FT-IR Spectroscopy.



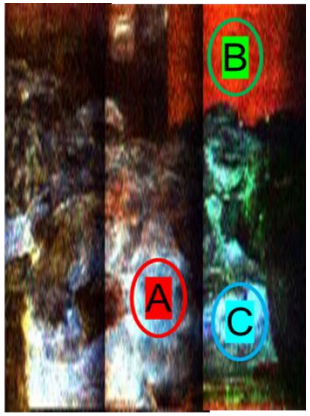
The high resolution 3D model from the RGB-ITIR prototype.

Identification of surface consolidants by means of laser induced fluorescence and FT-IR spectroscopy.

A) Photo

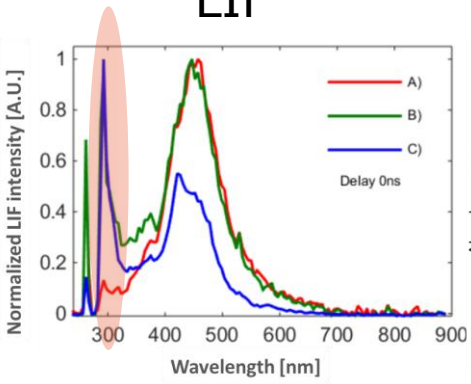


D) Delay 10ns

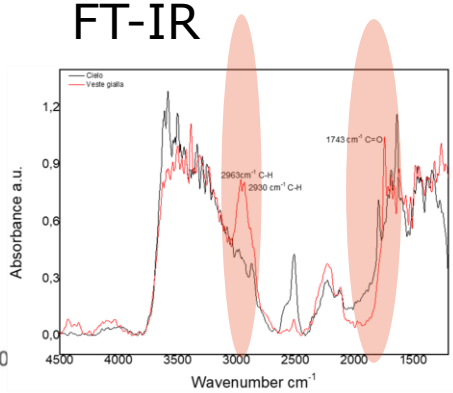


E) Delay 20ns

LIF

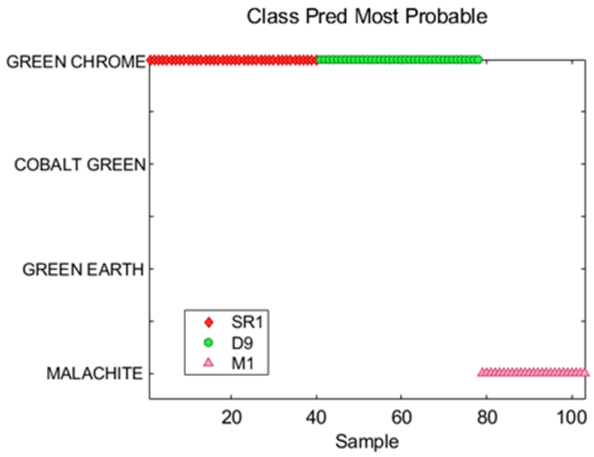


FT-IR



Presence of a synthetic product

Identification of pigments and dyes by means of XRF, Raman, VIS-SWIR reflectance



Integration of results from different in situ diagnostics on the XIX century fresco's in the apse

By means of different spectroscopic and imaging techniques it was possible to:

1. Assign used pigments as:

   Main traditional pigments: earths (yellow and red ochres, green earth), orpiment, cobalt blue, calcite, gypsum.

   Main modern pigments: ultramarine blue, phoenicochroite, green chrome, zinc white.

   Use of metal for gilded features: copper and gold addition.

2. Detect consolidant from former restorations, obtaining as well their space distribution:

   Presence of different consolidants: Paraloid and acrylic compounds

3. Reveal retouches from former restorations, with their space distribution:

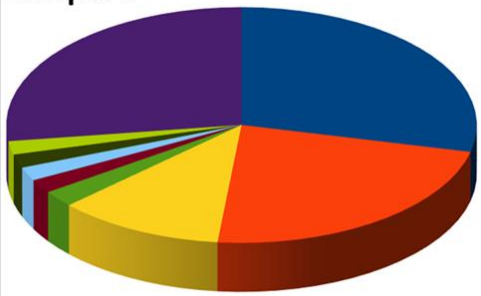
   Use of ZnO for localized white retouches (wings, eyes)

Identification of biotic agents giving rise biodegradation: Identification of bacteria found after sequencing fragments of PCR by means of Oxford Nanopore Technology.

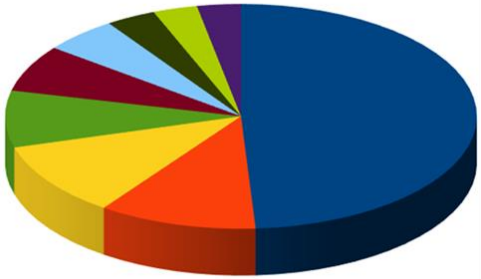
A laboratory study carried out a Uni. Rome Sapienza after in situ micro-sampling

A bio-informatic pipeline, capable to perform a taxonomic analysis by means of BLAST, was developed in order to identify, for each single reading, the corresponding species and so to characterize micro-bioma present in the analyzed sample.

Sample 1



Sample 2



Sample 1		Sample 2	
uncultured bacterium	1171	uncultured bacterium	2302
Nesterenkonia sp.	937	Nocardiopsis nanhaiensis	510
Nesterenkonia xinjiangensis	468	Nesterenkonia sp.	500
Pseudonocardia sp.	92	Aliihoeflea aestuarii	384
Nesterenkonia suensis	77	Luteimonas huabeiensis HB2	316
Amycolatopsis albispora	76	Pseudonocardia sp.	240
Kibdelosporangium kanagawaense	76	uncultured Actinomycetales bacterium	161
Prauserella sp.	75	Lysobacter sp.	143
Other Species	1111	Pseudomonas putida	141

In the cake plot, the percentages of the seven most abundant species found are reported.

Detection of water infiltrations in the apse during restoration works

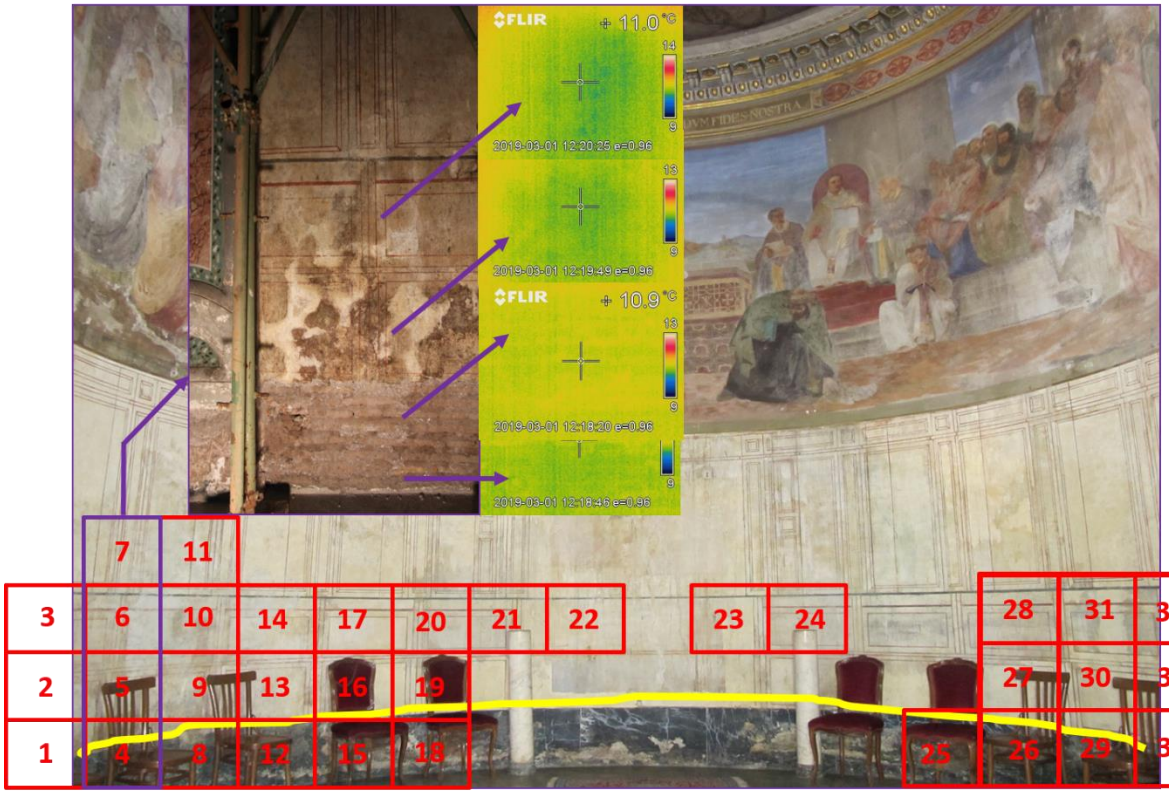
A joint in situ activity in cooperation by CNR-ICVBC (N. Prestileo, L. Luvidi), CNR-ISB (N. Proietti, V. Di Tullio, D.Capitani), CNR-INM (P.Calicchia, S. De Simone), ENEA (F. Colao, A. Tatì), INFN-LNF (M. Romani), Soprintendenza Speciale Archeologia Belle Arti e Paesaggio di Roma and the restorer SME EURESARTE s.r.l

IR thermography (IRT) was used for mapping surface humidity distribution on the apse.
Areas with anomalous water content were identified, since this presence may trigger the occurrence of degrading phenomena.

A significant difference in behavior was observed between the «wetter» left side and the «drier» right side.

Areas investigated by thermography imaging (CNR-ICVBC)

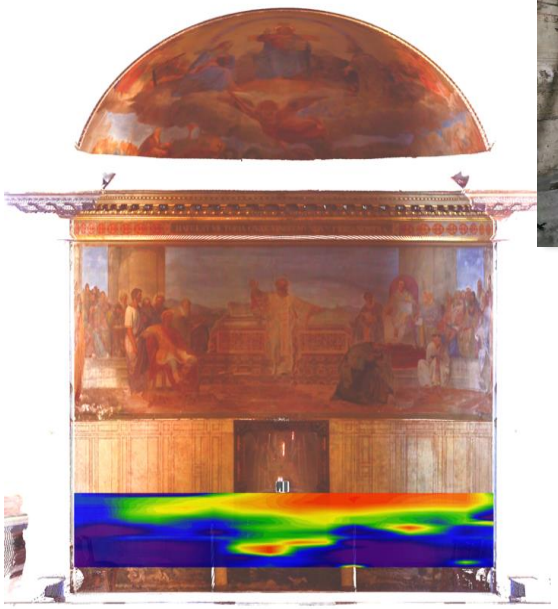
a detail of the colunm 4-7 characterized by high humidity is shown in the inset

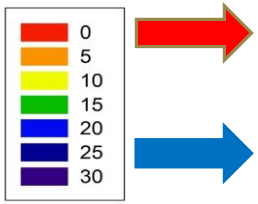


Abside di San Nicola in carcere, particolare dei rilievi termografici delle aree 4-7 interessate da elevata presenza di umidità

Analises by means of portable NMR spectrometer

CNR-ISB





Dry

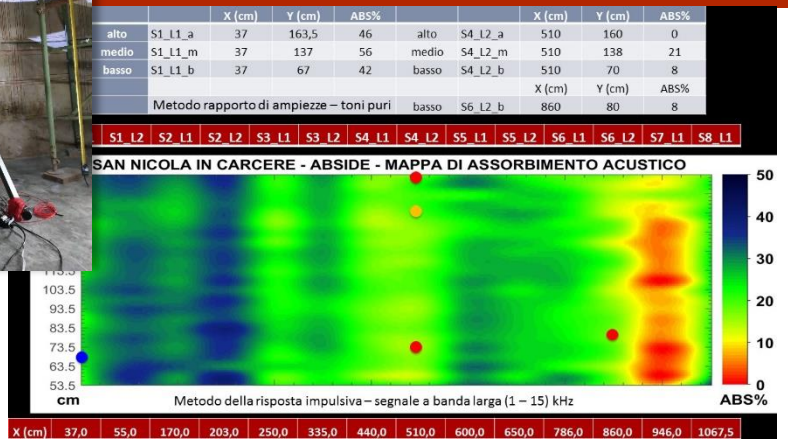
Wet

<u>Information achieved</u>:

1) Humidity distribution
2) Quantitative data on water content

Contactless measurements of acustic absorbance in reflection mode

CNR-INM

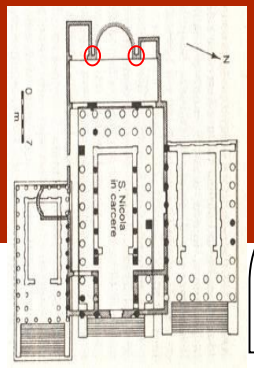


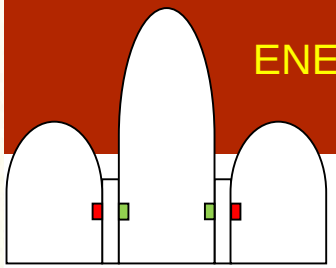
Il sistema di controllo e acquisizione rileva il segnale dell'onda sonora diretta e dell'onda riflessa dalla superficie e lo elabora per estrarre l'informazione sull'assorbimento acustico

-muratura umida valori di assorbimento acustico ABS% elevato;
-zone asciutte valori di assorbimento acustico ABS% bassi;

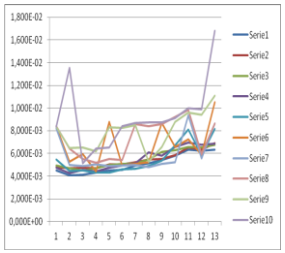
Sonic Tomography

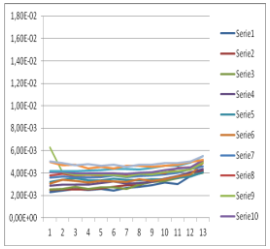
ENEA

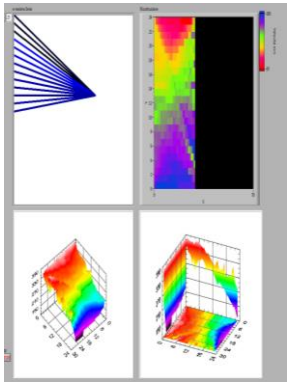


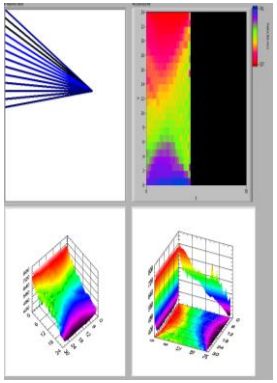


Red – accelerometer
Green – instrumented hammer





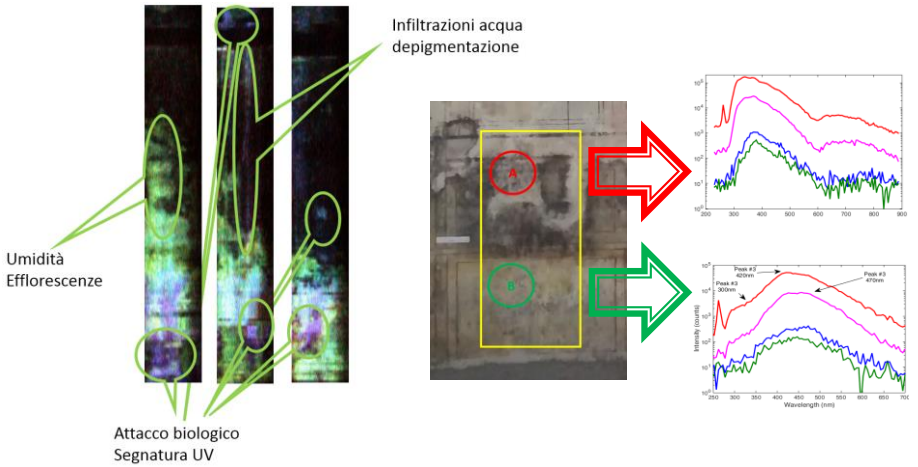




Transit times (sec) of sonic waves at different height on the pillars.
Left pillars shows higher times which correspond to larger degradation.

TG-LIF measurements: identification of bio-attacks, water infiltrations and salt efflorescence

ENEA, INFN-LNF



Band center (nm)	Band width (nm)	Decay time (ns)	Consistent with reference	Notes
320	30	3.8	YES	Proteic substances (No reference data for TR measurements)
420	30	6.5	N/A	Not assigned
460	80	5.8	YES	Substrate (calcite)

The used technology is based on the spectral and temporal characteristics of laser induced fluorescence which allows for both the determination of original materials and the early recognition of degradation either due to biotic and a-biotic factors.

Catacombs of SS. Peter and Marcellinus at Tor Pignattara

Uni.Roma Tor Vergata, ENEA

Why was the site selected?

- An important catacomb with painted rooms, nearby Centocelle Park.
- Interest to preventive conservation of recently restored frescoes.
- On going parallel physiologic characterization of bio-deteriogen micro-organisms formerly isolated in «Catacombe di San Callisto».
- Tests of essential oils vs commercial products as biocide.

Samples from the hypogeal site

Fresco fragments were examined in order to identify agents responsible for biodegradation and to test biocide effectiveness.

Major achievements in laboratory tests from a fresco fragment

- **characterization of microbe communities** present inside the catacombs, in order to compare with those ones detected in different hypogea around Roma area;
- definition and test of new strategy to reduce the phototrophic growth on frescoes inside the considered Catacombs by means of **essential oils,** which demonstrated biocide capacity;
- evaluation by means of **laser induced fluorescence** (LIF) and **reflectance** of both chemical composition and color changes onto the painted surface due to the treatment

Test of Essential Oils (EOs) presence on the substrate

EOs application

Two EOs were applied either singly or in combination.

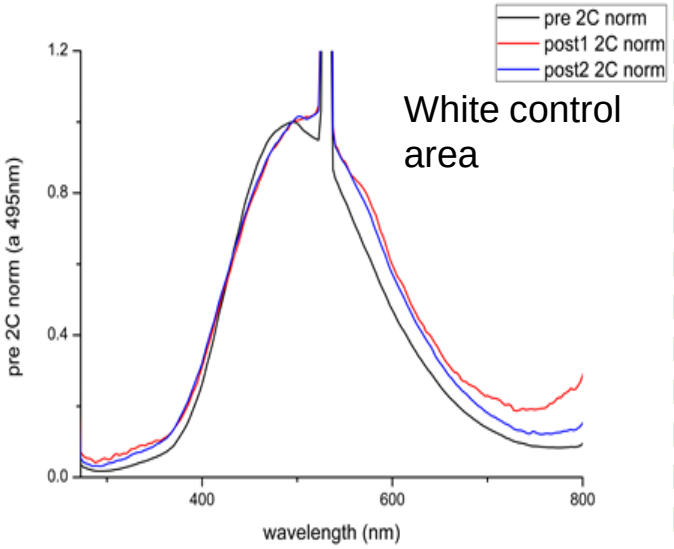
1 Chemical modifications of the surface

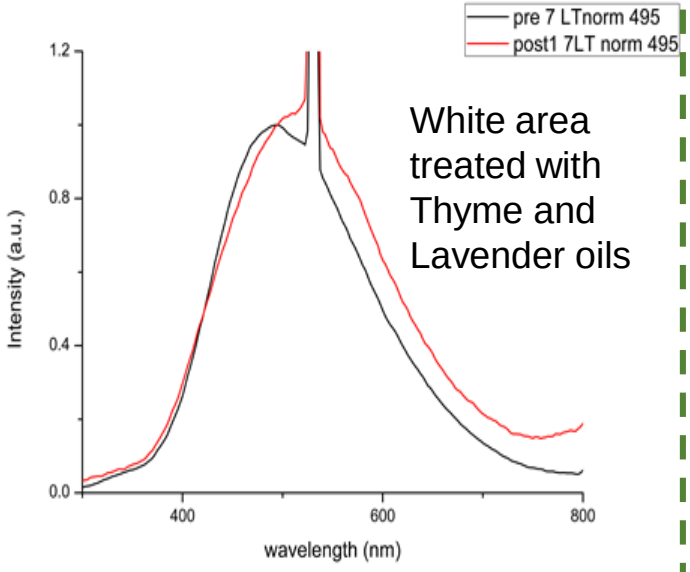
2 Color modifications of the surface

No detectable chemical change
No color variation

1 Laser Induced Fluorescence

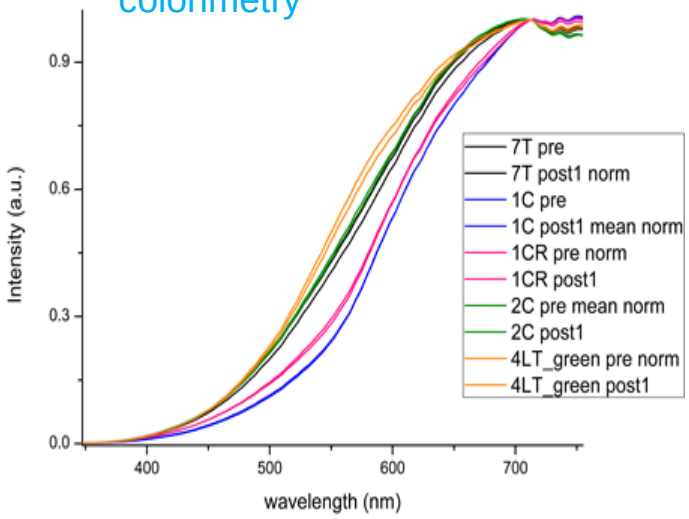
Remote Imaging





2 Reflectance and colorimetry

Standard contact colorimetry



L. Bruno, L. Rugnini, A. Canini, V. Spizzichino, L. Caneve, N. Ellwood «Biodeterioration of Roman hypogea: the case studies of the Catacombs of SS Marcellino and Pietro (Rome, Italy)» Annals of Microbiology 2019 https://doi.org/10.1007/s13213-019-01460-z on-line.

Villa della Piscina at Centocelle (RM)

UniRoma3, INFN, ENEA, CNR-ISC

Why was the site selected?

- Relevant to Park fruition. The ruins are now **buried** but frescoes' fragments are kept in a repository, virtual fruition of reconstructed painted wall would be possible.
- Fragments come from different walls as suggested by stylistic considerations, the problem is to support with data on composition their assignment to each wall.

Activities carried out and major achievements

- Pigment palette of a wall from the 2nd half of Ist century a.D., by means of Raman spectroscopy, LIF, LIBS, XRF, FT-IR and PIXE on 34 samples.
- Laboratory measurements on mortars XRD, analyses with micro-sampling.
- Geographical origin and possible dating of materials.
- Realization technologies (optical microscopy and SEM, stratigraphy).
- Assignment of 11 fragments to a wall on the basis of in-situ UV-vis reflectance measurements.

DTC LAZIO

Non destructive multi-analytical investigation of pictorial apparatus of Villa della Piscina at Centocelle

Marco Sbroscia, Armida Sodo, Maria Antonietta Ricci – Univ. Roma Tre
Lucilla Pronti, Martina Romani, Mariangela Cestelli Guidi– INFN-LNF
Claudia Marconi*, Mauro Missori – Isc-CNR, (*) and Univ. Sapienza
Francesco Colao, Violeta Laziz, Monia Vadrucci, Roberta Fantoni – ENEA Frascati
Daniele Mirabile Gattia, Franca Persia – ENEA Casaccia
Marco Marinelli, Gianluca Verona Rinati – INFN – Tor Vergata
Claudia Gioia, Stella Falzone – Undependent researchers
Patrizia Gioia, Ersilia Maria Loreti – Sovrintendenza Capitolina Beni Culturali

- Classification of framments upon stilistic basis
  - 5 different groups including walls and roof ceilings
- Characterization of painted framments dated back to the I-II cen. a.D.
- Individuation of common characteristics among the fragments to support the successive reconstruction of pictorial systems and to the site valorization.

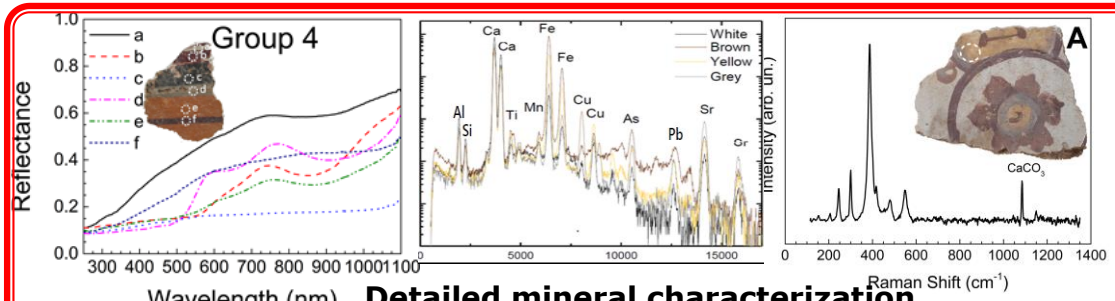
Non destructive multi-analytical investigation of pictorial apparatus of Villa della Piscina at Centocelle

- In situ application of portable instrumentation, either commercial or developed within ADAMO project
- Fast material screening by optical techniques (FORS), which is of paramount importance when working with thousands fragments

➢ <u>Multi-analytical approach</u>:

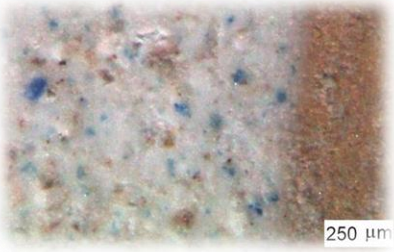
- Elemental analysis of materials by XRF, EDS, LIBS
- Molecular analysis of minerals by Raman and IR spectroscopies
- Study of crystallographic phases by XRD
- Optical and electronic Microscopy

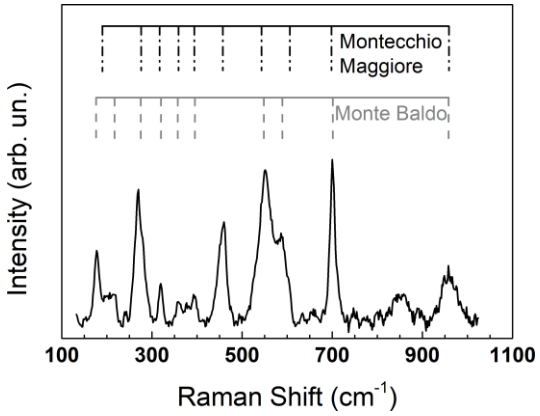
Non destructive multi-analytical investigation of pictorial apparatus of Villa della Piscina at Centocelle



Detailed mineral characterization

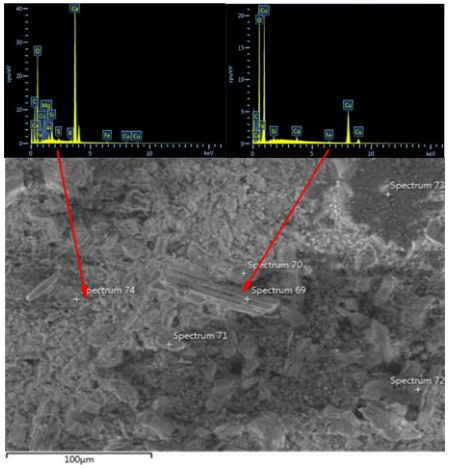
Study of pigments mixtures

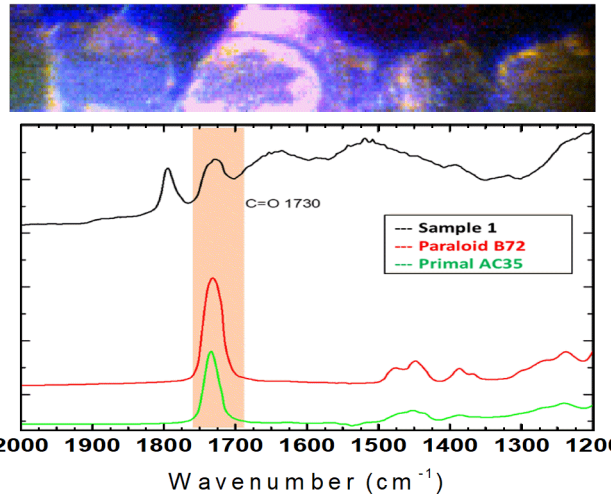




Provenance study on minerals through pecific signatures (trace elements)

Morphology, realization techniques and material quality





Characterization and space distribiton of surface treatments due to former conservative interventions

Determination of pigments palette

Results of micro-Raman Spectroscopy

Red = cinnabar HgS;

Brown = red ochres (hematite Fe_2O_3 e magnetite Fe_3O_4);

Yellow = yellow ochres (goethite FeOOH);

Verdi = green earths (celadonite $(K(Mg,Fe^{2+})(Fe^{3+}Al)Si_4O10(OH)_2)$, mix of celadonite with malachite ($CuCO_3$) or with Egyptian blue ($CaCuSi_4O_{10}$);

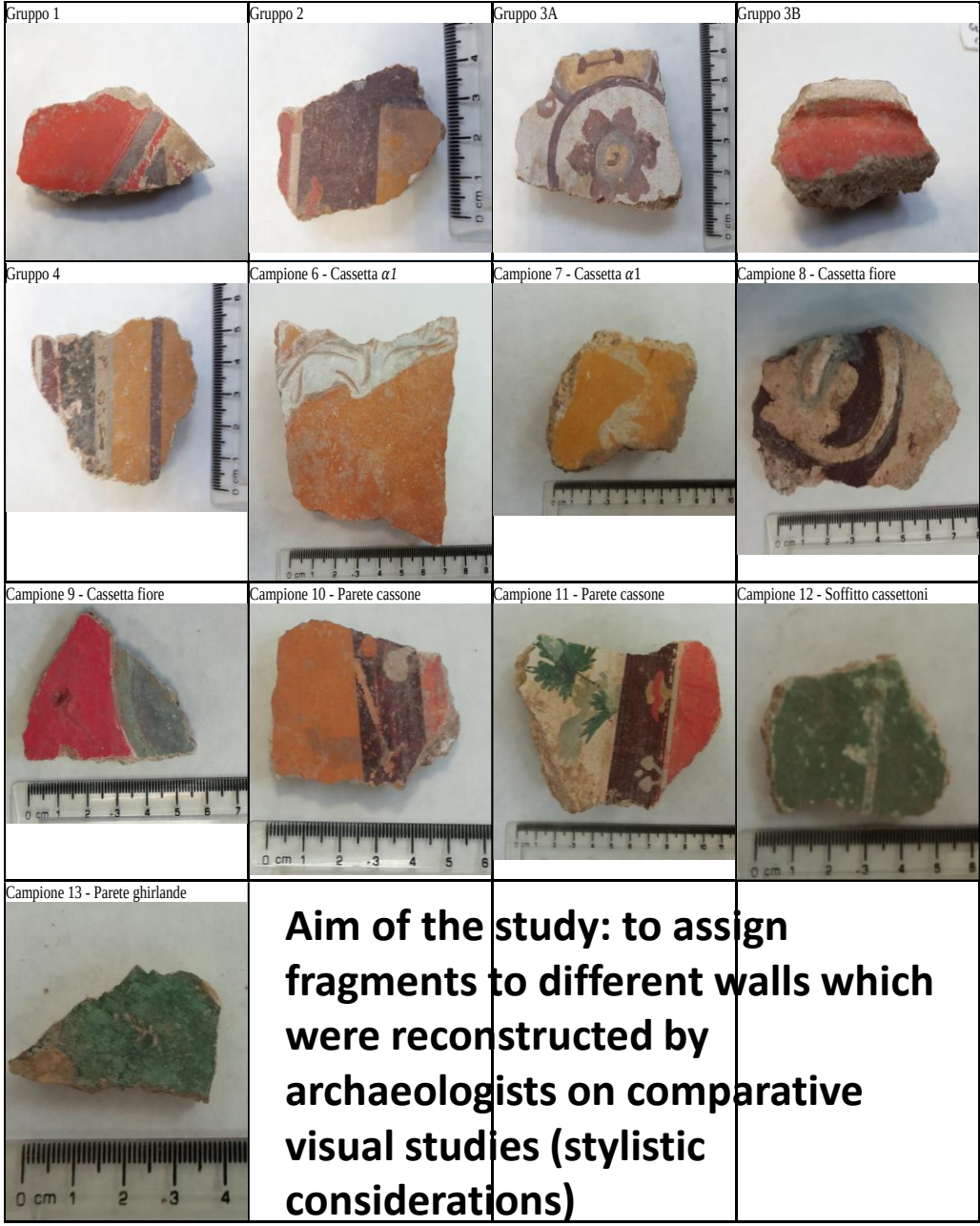
Blu = ($CaCuSi_4O_{10}$);

Gray = mix of red and yellow ochres with Egyptian blue and ash black.

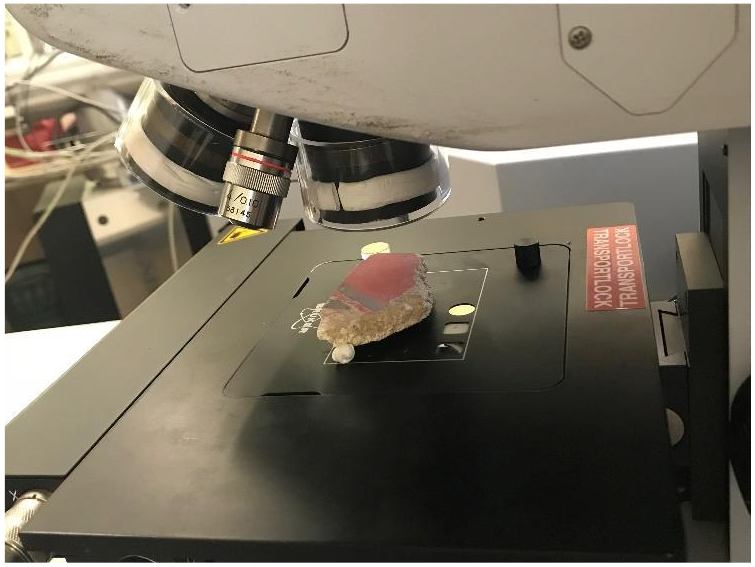
White = calcite ($CaCO_3(OH)_2$), dolomite ($MgCaCO_3$), anatase (TiO_2) from kaolinite

Violet = mix of cinnabar, Egyptian blue, celadonite;

Black = amorphous carbon (ash black).

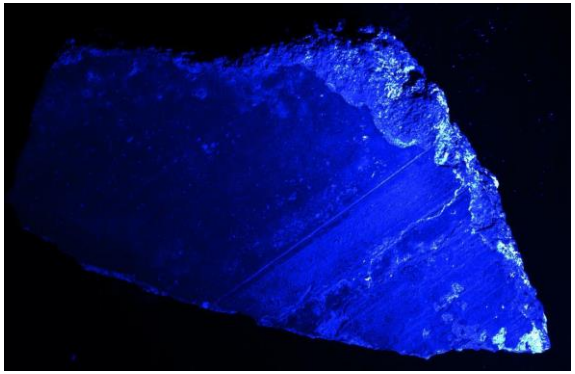


Aim of the study: to assign fragments to different walls which were reconstructed by archaeologists on comparative visual studies (stylistic considerations)



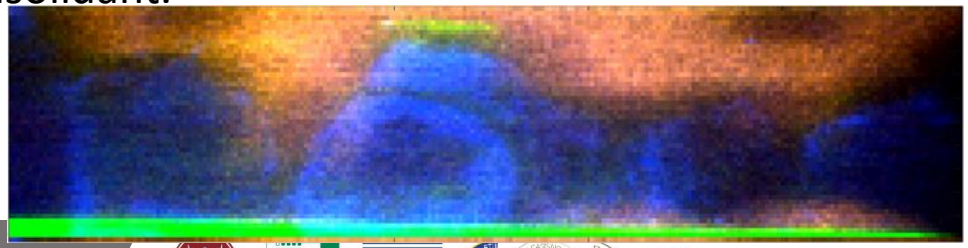
- **Determination of surface components by means of FT-IR spectroscopy**

Rough confirmation of pigments palette:
Red = cinnabar
Brown= red ochres
Yellow= yellow ochre
Green = green earth
Blue = Egyptian blue
White = calcite



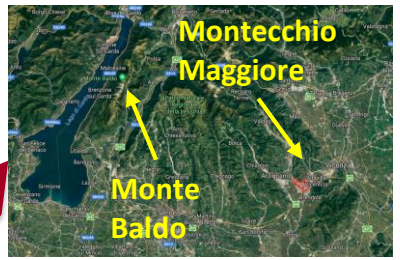
- **Detection and distribution of a surface patina from UV reflectography and LIF imaging**

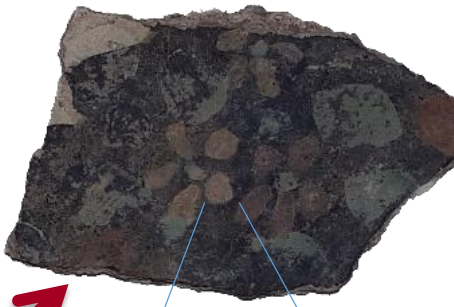
The patina was assigned by **FT-IR spectroscopy** to a modern synthesis compound, an acrylic consolidant.



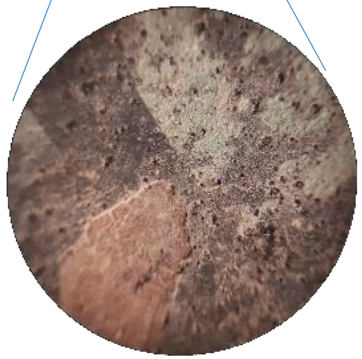
Further results from Raman analyses

- Much care was dedicated to the realization of pigments mixture; noticeable the use **kaolin** (white clay) as **whitener on ochres**.
- **No mix** among iron based **yellow ochres and lead oxides** was used for yellow colors.
- A detailed literature analysis support the **provenance of green earths in Veneto Region (near Verona)**





- **The realization technique of a single sample labelled as «sample 15», which was considered stylistically meaningful is peculiar for :**
  - **Significant multilayered structure**
  - **Care to the color hue (Grain of Egyptian blue were found within ochres)**
  - **Majority of large malachite grains mixed with earths in green**
  - **Cinnabar mixed to ochres to on bright red decorations**
  - **Ash black background to enhance contrast with decorations**



This fragments is probably relevant to another group of artifacts from a later period (III century a.D.)

Non destructive multi-analytical investigation of pictorial apparatus of Villa della Piscina at Centocelle

CONCLUSIONS

- Identification of the color palette and demonstration of homogeneity in different pictorial apparatus ascribed to the same historical period
- Archaeometric investigation to support former comparative and stylistic studies
- Information on the execution techniques
- Provenance study of pigment in order to confirm ancient commercial routes
- Recognition of modern conservation interventions

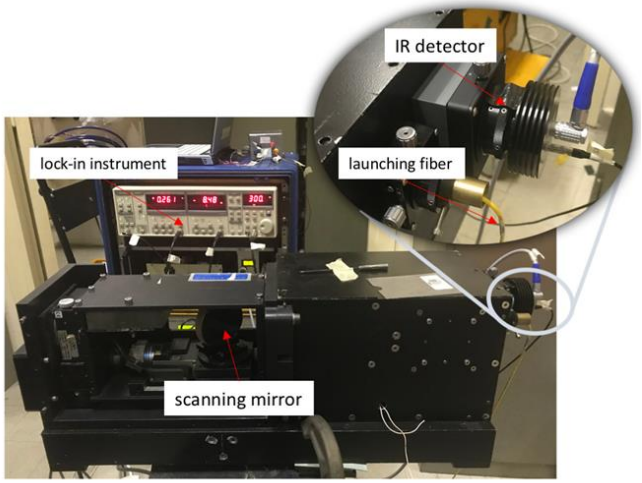
The Bishop's Palace in Frascati

Why was the site selected?

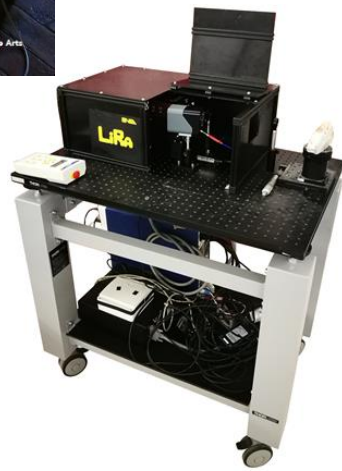
- An historical building from the end of the XV century.
- It contains wall paintings with former problems from water infiltration.
- It contain a large room with wall tissues painted by water colors.

ENEA – FSN – TECFIS- DIM: M.Guarneri, M.Francucci, L.Caneve, V.Spizzichino

ENEA laser scanner prototypes in situ utilized for remote imaging



IR-ITR Laser scanner at 1.55 μm



LIBS – Raman combined systems

DTC LAZIO

Investigation addressed to preservation of inside rooms

The Bishop's Palace in Frascati – The «Landscape» room

Digitalization by the RGB-ITR high resolution scanner

Wall tissue painted with water colors, covers the room.

Questions:

1. Are still present traces from former water infiltrations?
2. Are detectable damages on the painted wall tissue?

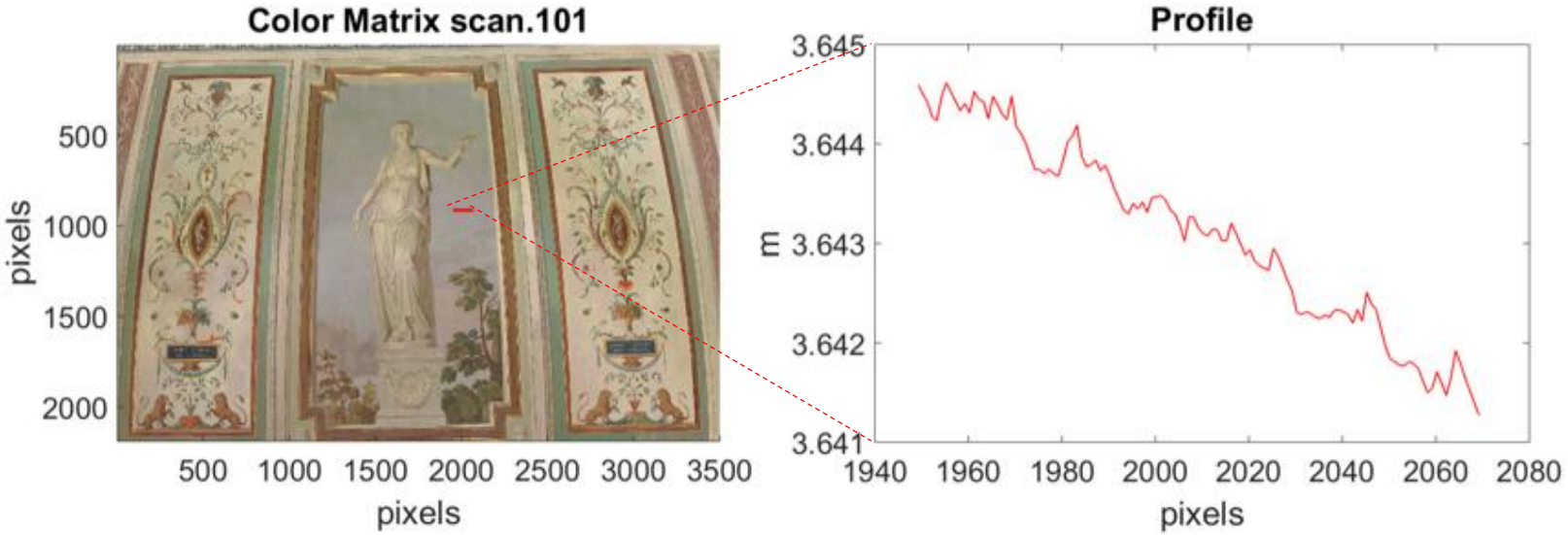
Details of the roof ceiling showing area repainted in the former restauration to compensate for discoloration

Answer 1: YES

Detection of damages from surface morphology and composition

Morphologic anlysis on RGB-ITR data

Detection of irregularities in the tissue fibers



LIF investigation on the painted wood cover of the fireplace

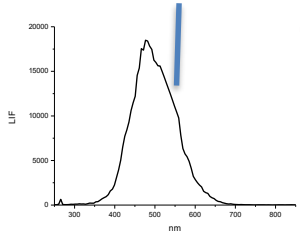
The fluorescence image obtained for the ratio of 380/450 emission channels shows a crack, which was carefully restored by a consolindant and afterwards repainted

Answer 2 – The use of both laser systems allows for revealing both morphologic alteration and difference in composition, the former related to degradation, the latter to restoration.

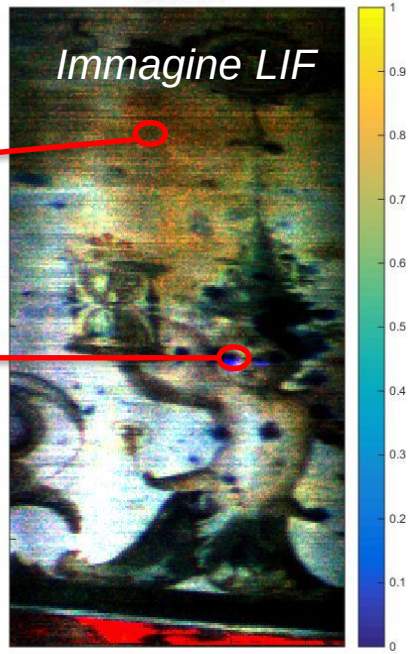
Additional evidence of former restorations and early warning of on-going damages by LIF imaging – The «Stufette» room

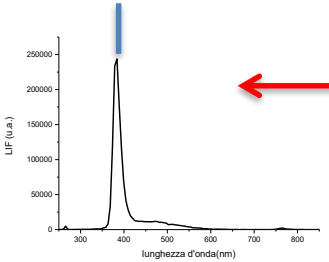
Question:
Isi it possible to have an early detection of alteration in pigmentation?

Answer: YES by LIF, both in the spectral and time domain.

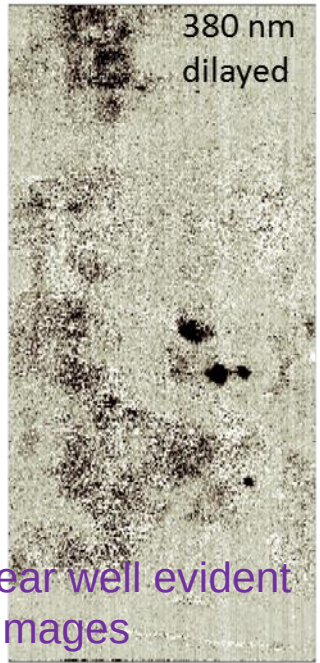


Color degradation @550 nm





ZnO retouches @380 nm



Anomalies appear well evident in delayed LIF images

Investigation by optical and spectroscopic laser scanners of the painted rooms in the Bishop's Palace in Frascati

CONCLUSIONS

- Discoloration associated to former water infiltration were detected on the ceiling

- Morphologic irregularities due to the tissue fiber degradation were observed at high resolution

- The occurrence of former restoration on painted wood and frescoes surface was obtained, with consolidants assignment and distribution.

- Early damage from residual water infiltration was detected on the frescoes by TG LIF imaging.