Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile

EMSLIBS 2019

Complementary characterization of ancient Roman frescoes by PIXE and LIBS techniques

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Brno September 11, 2019

REGIONE LAZIO

ADAMO Technologies of Analysis, Diagnostics and Monitoring for the preservation and restoration of Cultural Heritage

ADAMO

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

A Research project in the Center of Excellence of the District of Technologies for Culture of Lazio Region

Participants: ENEA, INFN, CNR, Uni. Rome Sapienza, Uni. Rome Tor Vergata, Uni. Roma Tre, Uni. Tuscia (Viterbo)

Oct. 2, 2018 – Jan 1, 2020

Progettoadamo.enea.it

Project objectives

1. Technology transfer on relevant themes
2. Services to enterprises based on facilities offered by DTC partners
3. Demonstrations in selected cases studies
4. Development of prototypes and test of innovative products

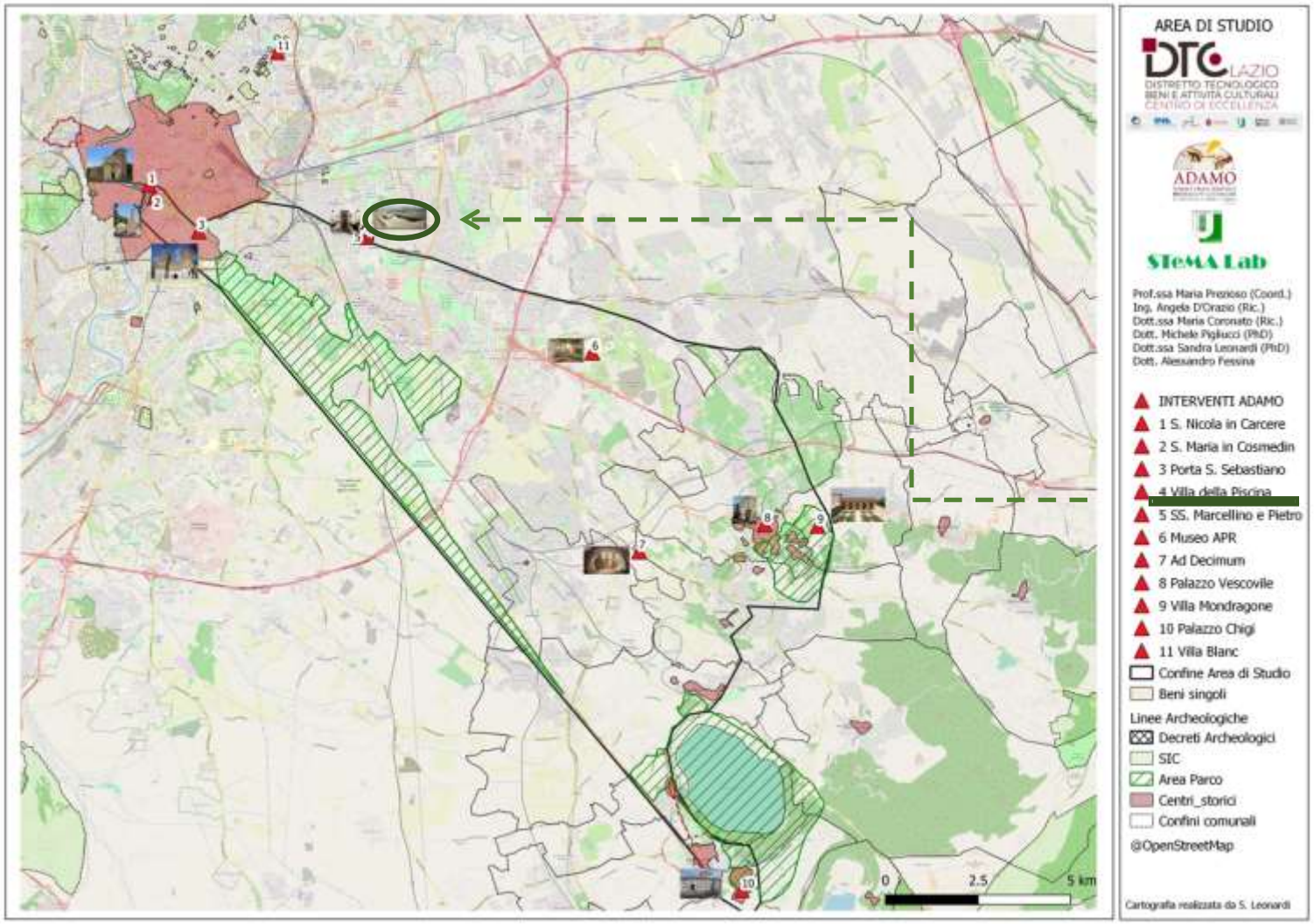
Integrate applications of remote, in-situ and laboratory instruments for spectroscopic diagnostics

DTC LAZIO

CENTRO DI ECCELLENZA

ENEA INFN

Contest analysis and choice of demonstration sites



Characterization of Roman fresco's fragments from «Villa della Piscina» archaeological site in Rome

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

The size of the problem in Archaeology

Hundreds of fragments from the Roman frescoes of Villa Della Piscina were found in two different excavation campaigns. Frescoes were realized in the Villa during different building periods from I cen. BC to IV cen. AD.

Laboratory and in-situ measurements on the fresco fragments

*M. Sbroscia et al. TECHNART2019, Submitted To Microchem. Journal

Aim of the work:

- Pigments characterization by means of non destructive techniques (reflectance FORS, Raman and FT-IR spectroscopy , LIF and XRF on 40 fragments)
- Mortar characterization by micro-sampling
- Geograical origin of materials and dating
- Realization technologies (optical microscopy and SEM, different types of stratigraphy)

Participants: UniRoma3, INFN, ENEA, CNR

Results on pigments*:

Composition: Cinnabar, earths (hematite and magnetite, goethite, celadonite), malachite, Egyptian Blue, calcite e dolomite, carbon black.

Provenance hypotesis: Celadonite (green earth) from Verona area, cinnabar from Almadèn Spanish mines.

Realization technologies: Use of mineral pigments with different granulometry, also in overlapped layers with different composition.

Open questions:

- Elemental analysis of light elements, either not detected by XRF or present in non Raman active compounds – correlation analyses
- Complete stratigraphic investigation on the painted layer

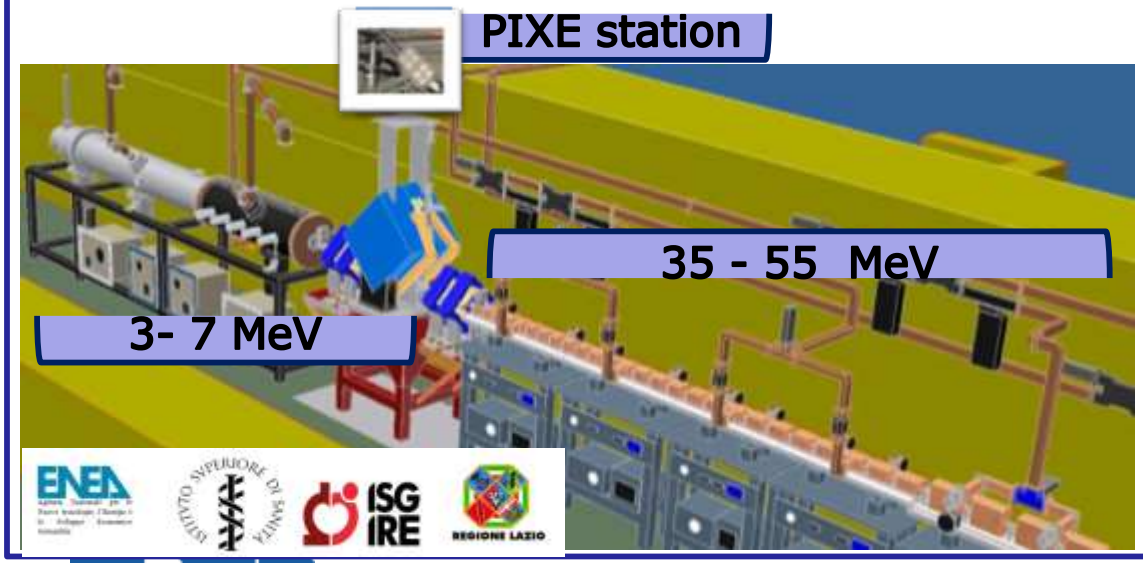
Possible solution:
PIXE and LIBS

ENEA PIXE demonstrator based on a linear accelerator of protons

PIXE: Particle Induced X-ray Emission

It consist of the analysis of X Ray emitted from the sample after proton bombardment. The ***non destructive investigation*** can supplies qualitative and quantitative information on **surface atomic composition** of the target.
By using **different beam energies it is possible** to extract information at **different sample depth.**

TOP-IMPLART Accelerator at APAM lab. ENEA Frascati



The accelerator is a «full LINAC» for oncologic applications (proton-therapy).

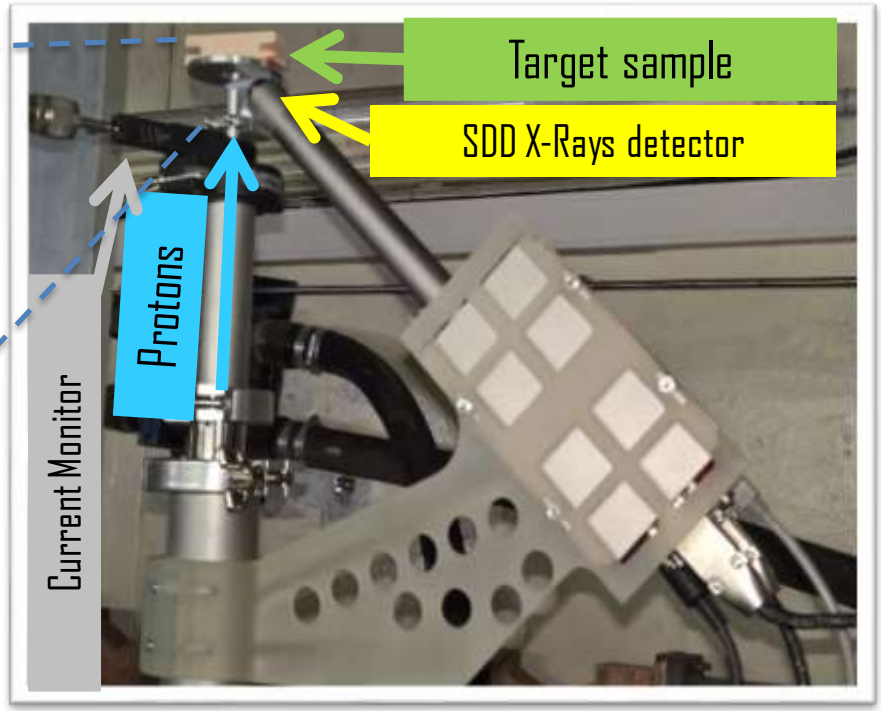
It generates a pulsed proton beam with adjustable energy.

PIXE Set-up

ENEA PIXE set-up in cooperation with INFN-LABEC on the vertical beam line (Emax 7KeV). It consists of:

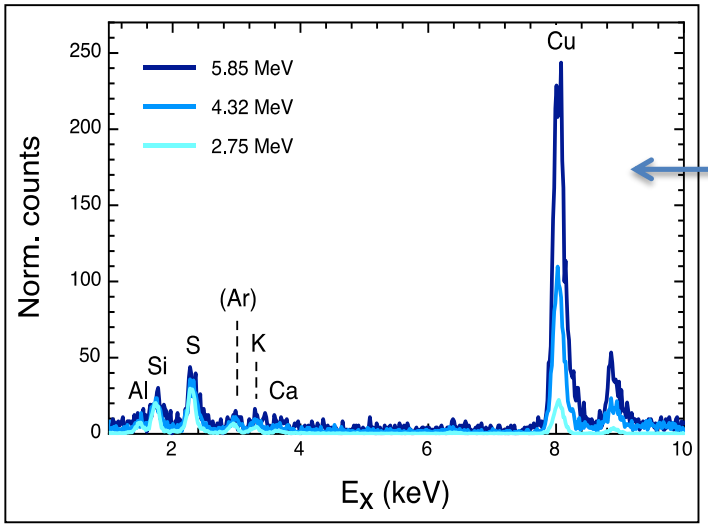
- A graphite-titanium collimator,
- An extraction window (Upilex, 7.5 μm thickness - 300 μm diameter),
- An Amptek detector (XR-100SDD FAST SDD with 50 mm^2 active area (500 μm active thickness/ 12.5 μm Be window), equipped with a filter made of 560 μm thick Mylar foil with a 1.6 mm diameter central hole (4% of the active area).

Details of the sample holder and collimator



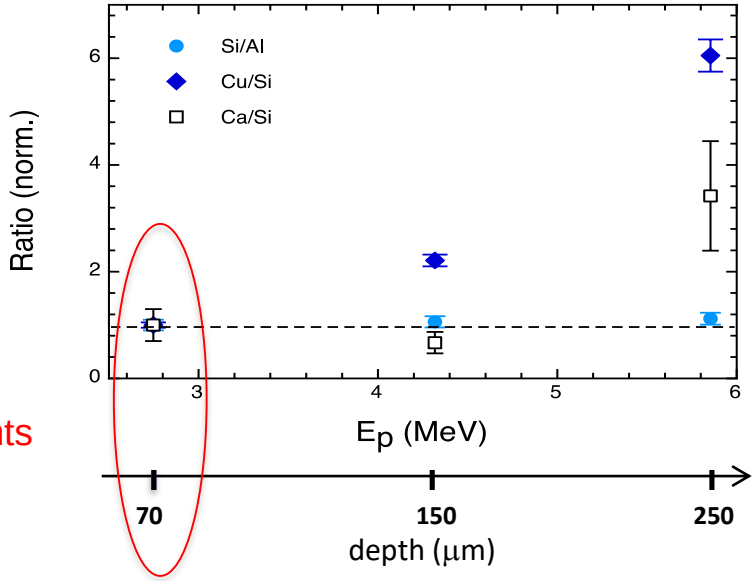
Differential PIXE analyis - Stratigraphy

A reference blue fresco sample, prepared on gypsum by OPD in Florence, has been investigated at different depths, by using different bream energies available.



Proton energy resolved measurements show the presence of a lapis-lazuli (with Si and Al) outer layer on top of the inner azurite (Cu) layer.

Plot of significant element ratio's at different energies (i.e. depth) show azurite prevalence under the surface layer.



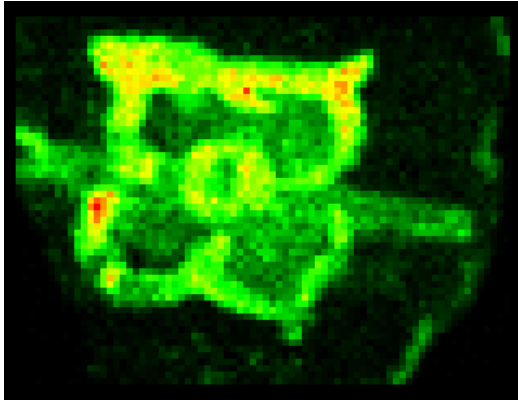
Good correspondence with LIBS measurements in the first 50 shots

PIXE measurements on Roman fresco's fragments from «Villa della Piscina»

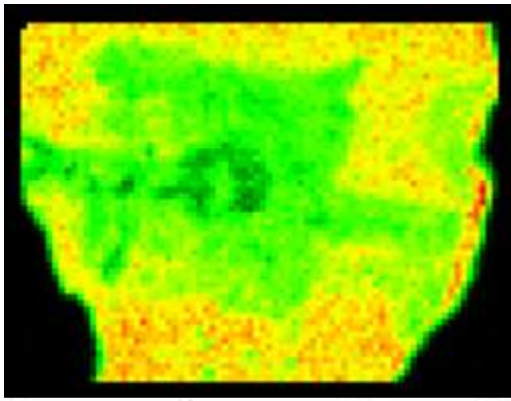
The pigment composition pigments is confirmed:

- The brown and yellow are iron oxides / hydroxides (hematite / goethite), containing different Fe quantities.
- Gray/blue leaves contain copper. The contemporary presence of silicon, supports the assignment to Egyptian blue ($CaCuSi_4O_{10}$).
- Calcium is the main constituent of white background (calcite, $CaCO_3$), shaped as grains with strong absorption.
- No clear evidence of Pb based pigments is obtained.

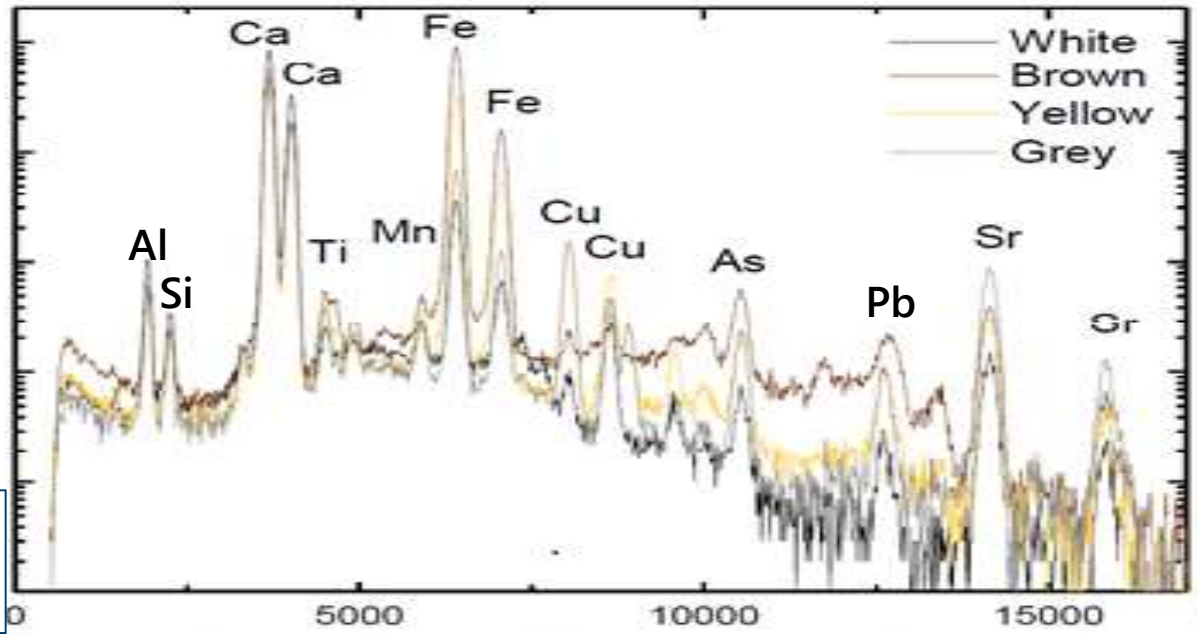
XRF map: Fe (hematite)



XRF Map: Ca (calcite)



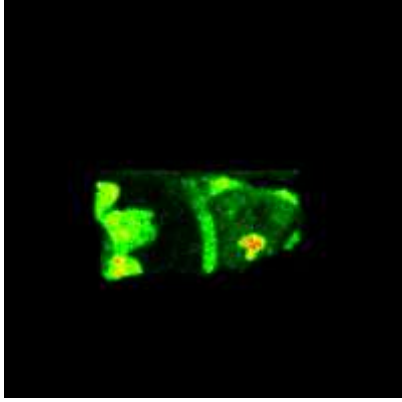
PIXE spectrum @ 3MeV



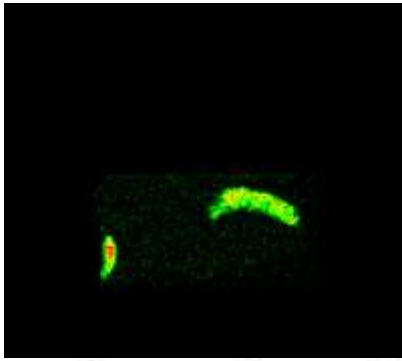
PIXE measurements on Roman fresco's fragments from «Villa della Piscina»

Sample 31

XRF map: Fe (hematite)



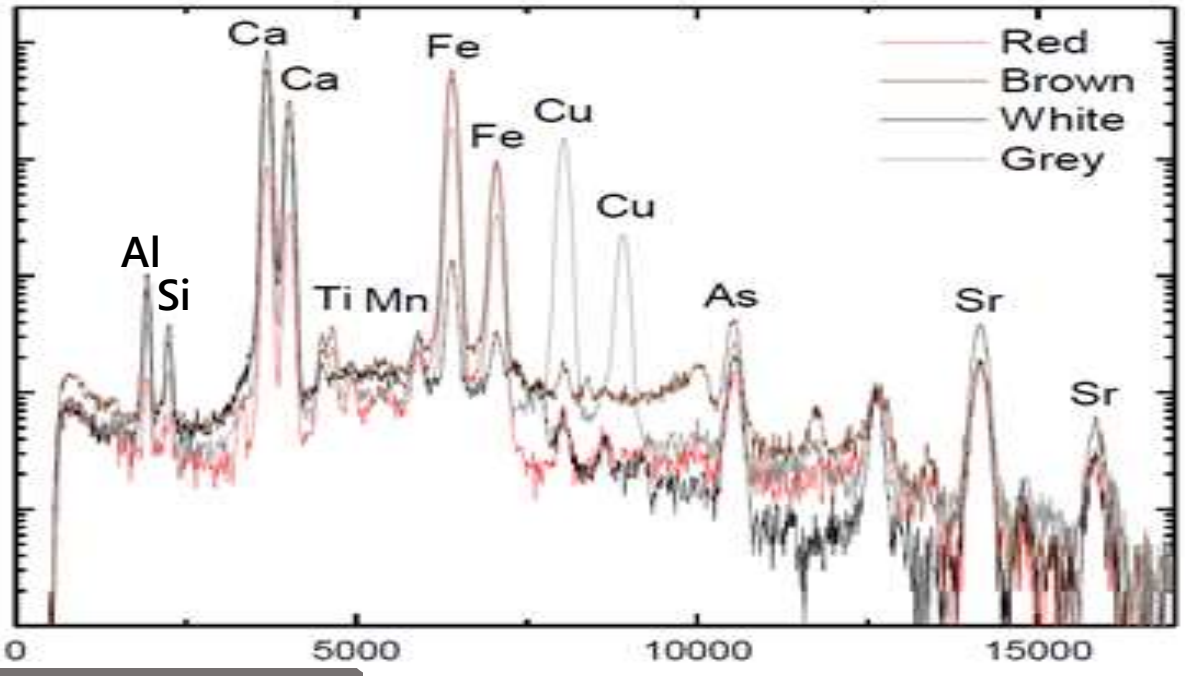
XRF map: Cu (Egyptian blue)



Archaeologists assigned this fragment to the same group as fragment 33 on the basis of style considerations (from I-II century). The detected composition is consistent with this assignment.

- Red and brown (Fe/Ca=0,012) are iron oxides (hematite)
- Egyptian blue is relevant to the gray/blue (Cu/Ca=2,66) part.
- Titanium and arsenic traces are detected. The first mostly on light colors, the second mostly on brown and red color.

PIXE spectrum @ 3MeV



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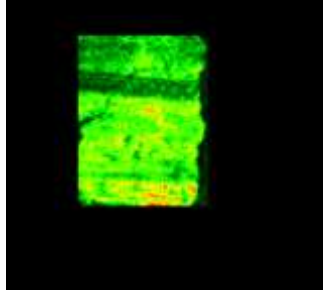
PIXE measurements on Roman fresco's fragments from «Villa della Piscina»

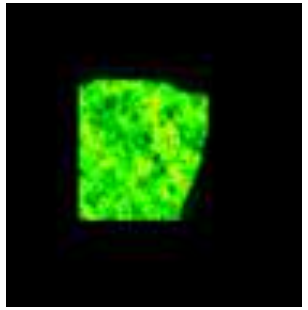
- Red pigment can be associated to the presence of both cinnabar (HgS) and red ochre (F_2O_3, Fe_3O_4). Present data (taken at a single proton energy), do not permit to establish if the red pigment is a mix or a two overlapping layers paint. Overall Fe/Hg=8.5 ratio.
- Arsenic traces are detected in the red pigment, thus either of the two minerals might have origin from Monte Amiata.
- Lead traces, clearly detected in this case, seems not to be associated to any specific pigment, they might come from the calcite substrate.

Sample 40
Ceiling of room
(III century)

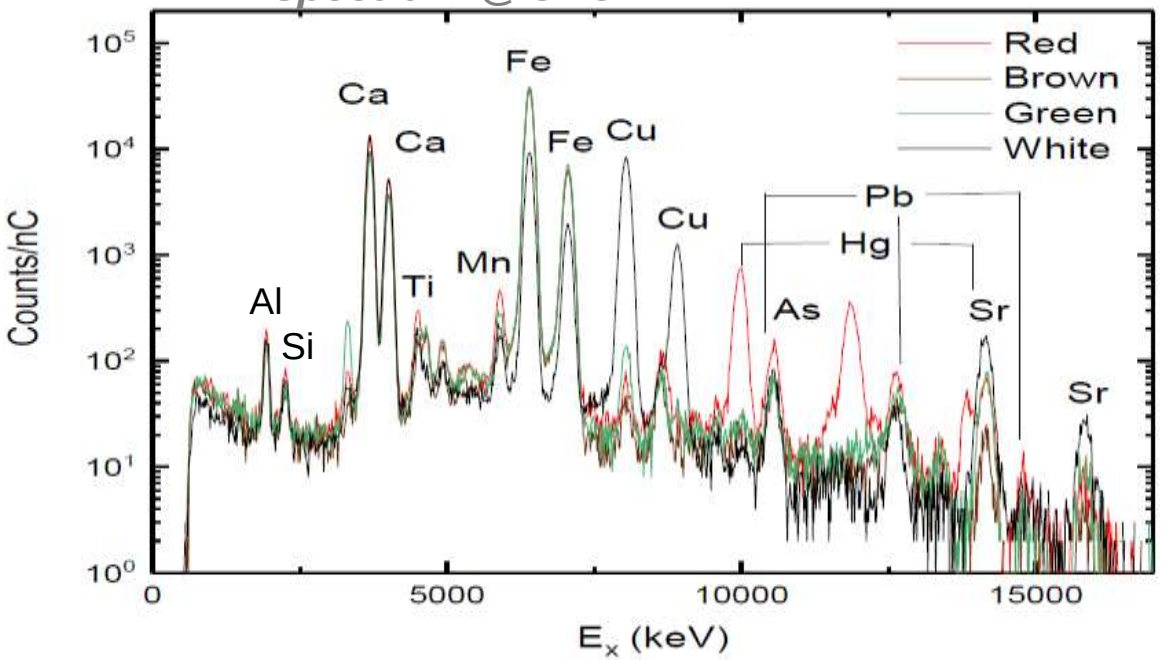
XRF map: Fe (red and green earths)



XRF map: Hg (cinnabar)



PIXE spectrum @ 3MeV



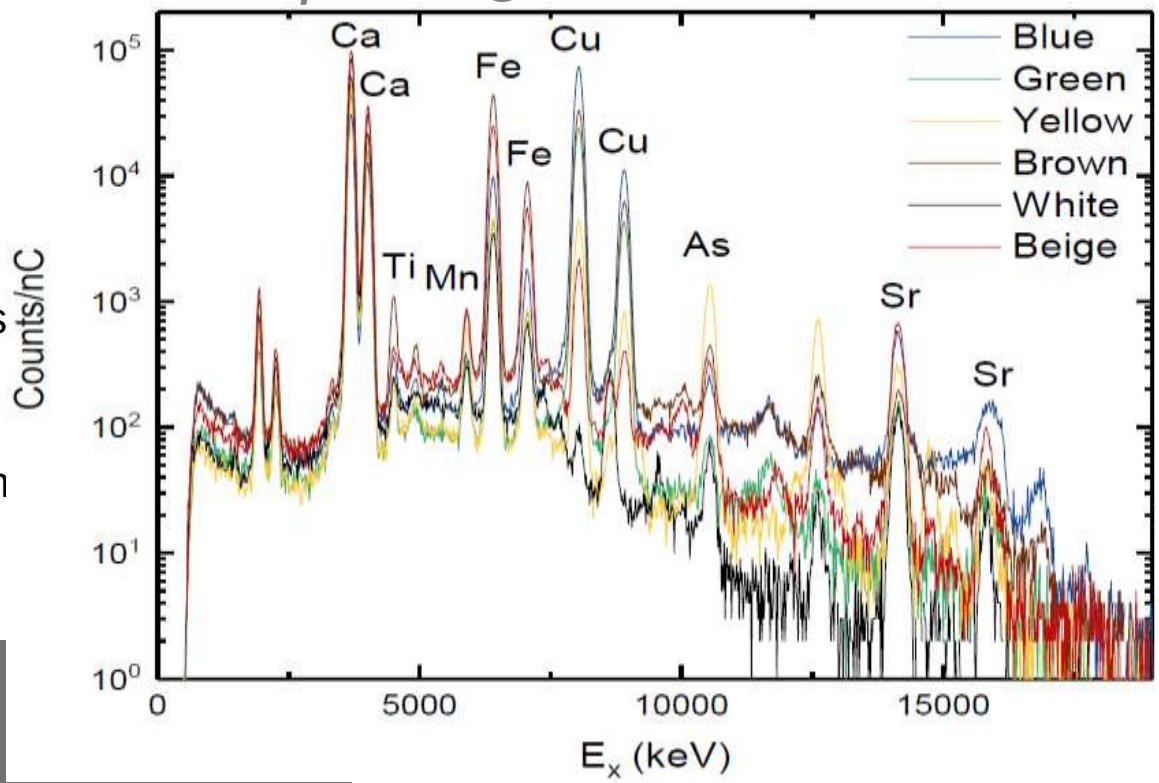
PIXE measurements on Roman fresco's fragments from «Villa della Piscina»

Sample 21
Ceiling of room
(I-II century)

The contemporary presence of a blue layer under the partially collapsed green layer is evident by visual inspection.

- The two layers cannot be resolved at the utilized proton energy.
- The presence of iron (Fe/Ca=0.004) in the green layer suggests the use of celadonite, while the presence of copper from the blue layer (Cu/Ca=0.1) cannot exclude addition of copper based green pigments.
- Titanium traces are on all pigments
- Arsenic traces are on yellow pigments (iron based goethite α-FeO·OH), thus suggesting its origin from Monte Amiata.

PIXE spectrum @ 3MeV

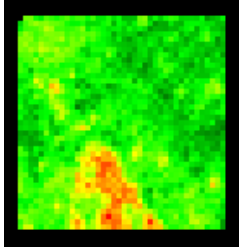


PIXE measurements on Roman fresco's fragments from «Villa della Piscina»

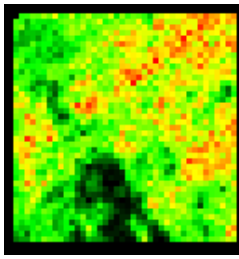
- To green pigments the contributions both from copper (malachite) and iron (celadonite) are detected.
- The low Si/Cu ratio does not support additional use of either Egyptian blue or Egyptian green to modulate the green color.
- Present data (taken at a single proton energy), do not permit to establish if the green pigment is a mix or a two overlapping layers paint.

Sample 39
Ceiling of room
(III century)

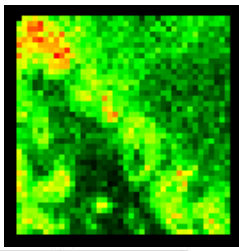
XRF map: Ca (calcite)



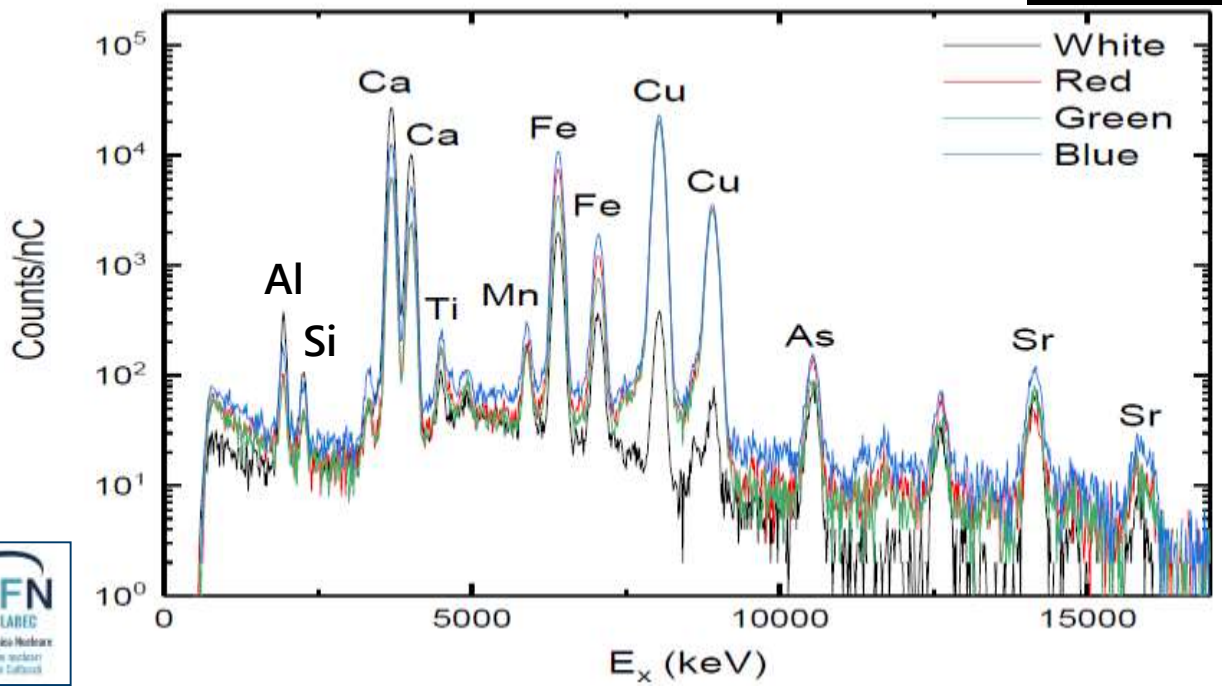
XRF map: Cu (malachite, Egyptian blue)



XRF map: Fe (hematite)



PIXE spectrum @ 3MeV



LIBS measurements on Roman fresco's fragments from «Villa della Piscina»

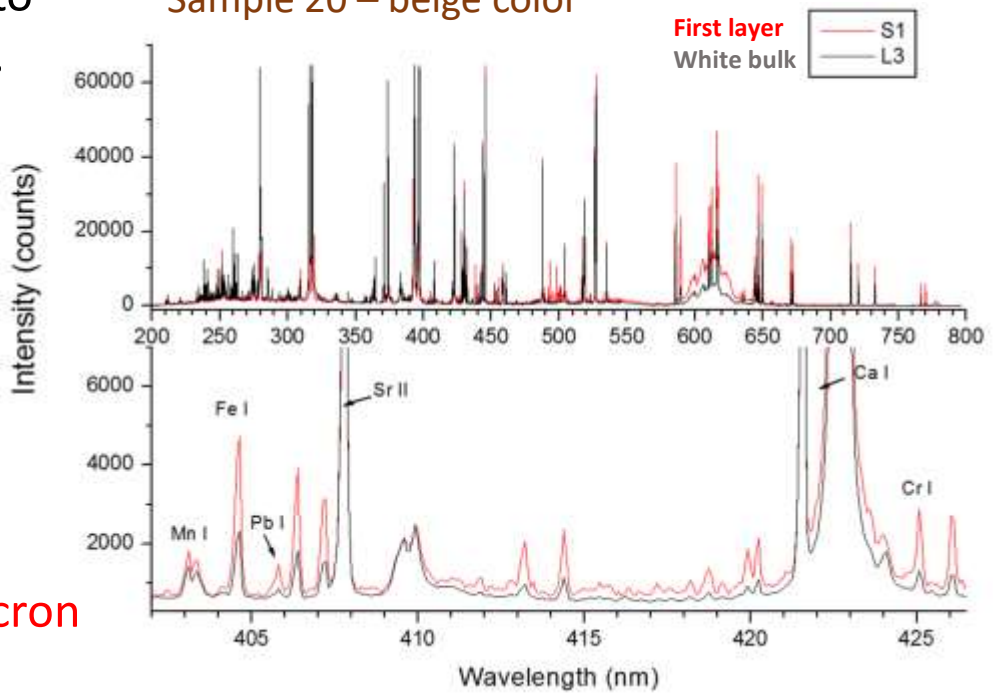
Set-up characteristics:

- 2 lasers: 6 ns, 10 Hz, 2x300 mJ @1064 nm, 2x200 mJ@532 nm
- 4 spettrometers: 200-790 nm range
- X-Y motorized table
- Color photo-camera and laser pointer to precisely select the measurement point.

Sampling conditions:

- Single pulse acquisition
- Energy per pulse at the sample 30 mJ
- Repetition rate 2 Hz
- Spot diameter at the focus: 0.23 mm
- Number of laser pulses at each selecte point 100

Sample 20 – beige color

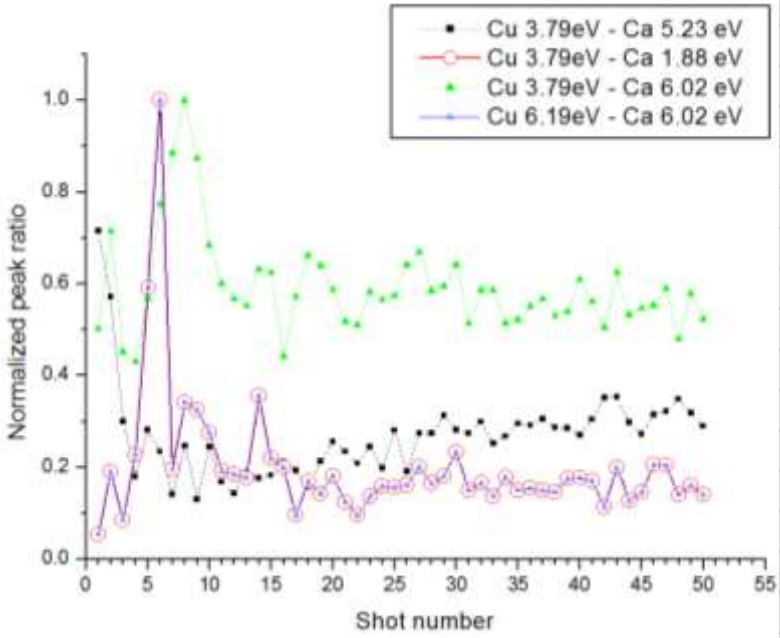


Average thickness ablated per shot 1.2 micron

LIBS measurements on Roman fresco's fragments from «Villa della Piscina»

Normalization on Ca I line – Intensity comparison in stratigraphy

Due to change of the plasma temperature during the crater development, in order to obtain a reliable element distribution in depth it is important to choose the normalizing line with Ek similar or lower than the Ek of the analytical line



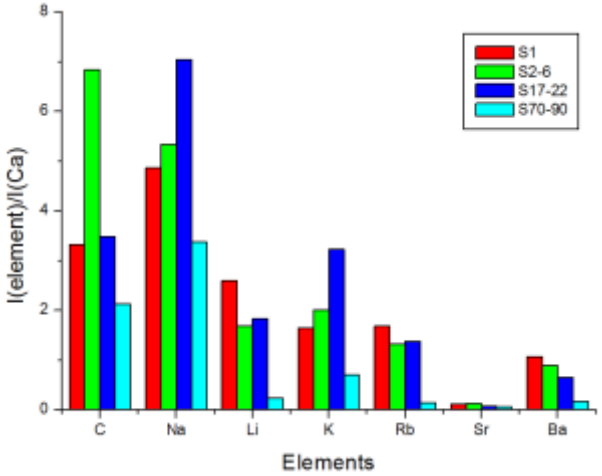
Element	Element line (nm)	Ek element (eV)	Norm.: Ca I line (nm)	Ek Ca I line (eV)
C I	247.86	7.685	300.09	6.016
Mg I	285.21	4.346	429.90	4.769
Si I	288.15	5.082	429.90	4.769
Al I	309.28	4.021	429.90	4.769
Sn I	326.23	4.867	429.90	4.769
Cu I	327.39	3.786	647.17	4.441
Mn I	475.40	4.889	429.90	4.769
Pb I	405.78	4.375	647.17	4.441
Sr II	407.77	3.040	657.28	1.885
Cr I	425.44	2.913	657.28	1.885
V I	437.92	3.130	657.28	1.885
Fe I	438.35	4.312	647.17	4.441
Ba II	455.40	2.722	657.28	1.885
Zn I	472.22	6.654	300.09	6.016
Ti I	489.99	4.409	647.17	4.441
Na I	589.59	2.102	657.28	1.885
Li I	670.78	1.848	657.28	1.885
K I	769.90	1.610	657.28	1.885
Rb I	780.03	1.589	657.28	1.885

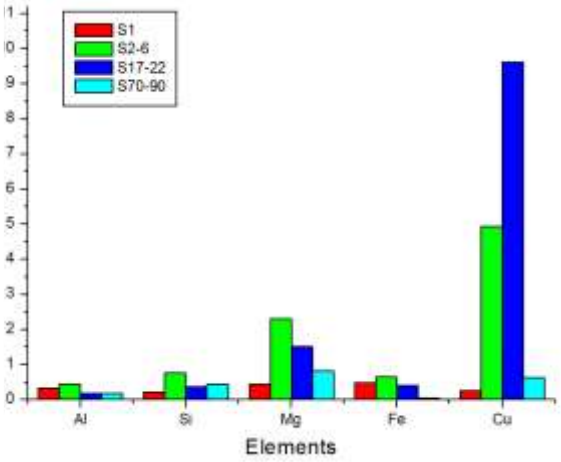
LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»

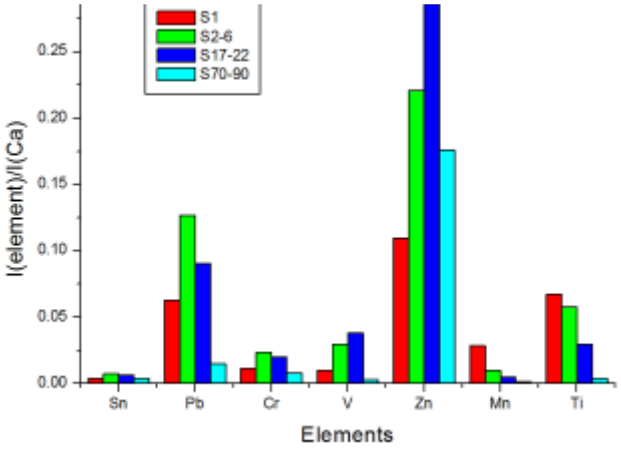
Details of composition and realization

Qualitative analysis and stratigraphy at different colors: T

The green color and the blue underneath







Surface: ↑ Mn, Li, Rb, Ti, Ba

Green: ↑ **Fe, Si, Al, Sn, Mg, Cr, C, Pb,** Cu, Ti

Blue: ↑**Cu, Na, K, V, Zn**

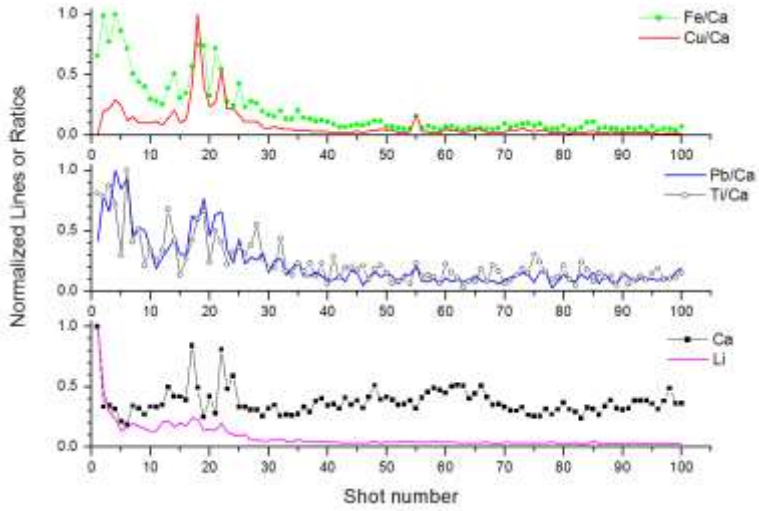
Bulk: ↑Ca, Zn, Mg

Traces of Ti and Pb were puzzling archaeologists

Celadonite (Fe>Cu)

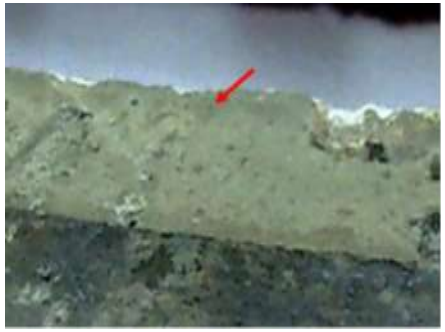
Egyptian blue(Cu>Fe)

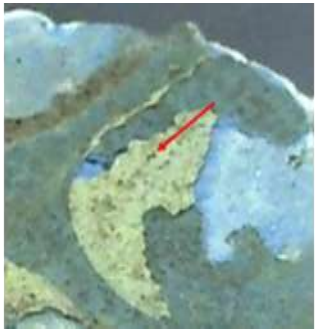
2 overlapped painted layers, 1° layer collapsed at the20th laser shot

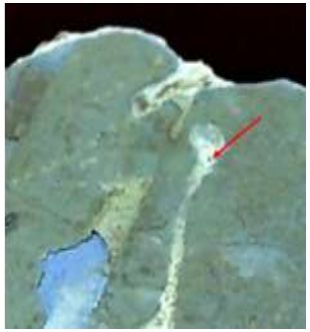


LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»

Multilayered structure: covering mistakes in realization.

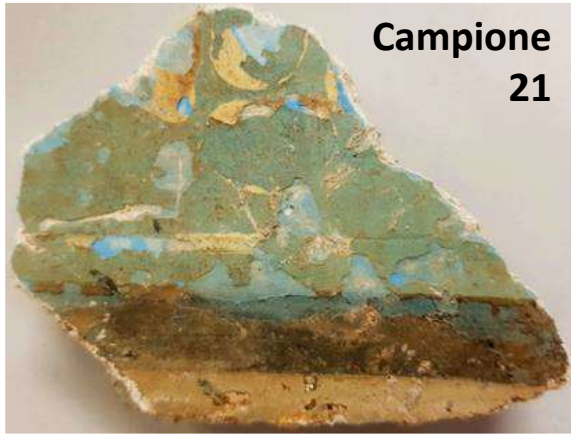






Archeologists' hypothesis after LIBS data: the room top ceiling was made with alternated squares of a different color, a thin blue layer was covered by green pigments once a mistake in alternation occurred during the realization, thus the inner blue layer was much thinner (≈ 2 μm) than the green one (≈ 6-10 μm).

LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»



Open questions on pigments:

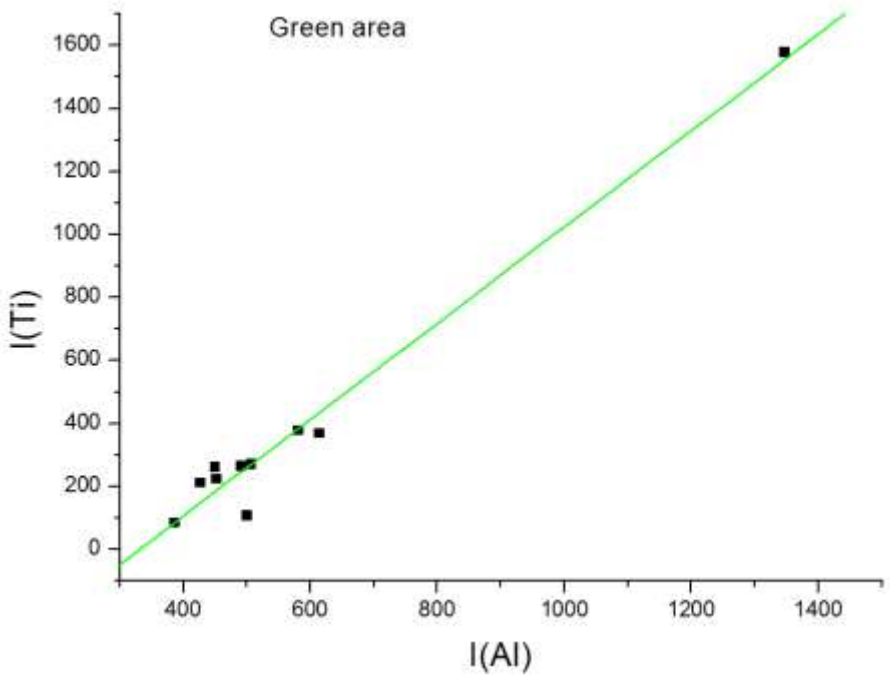
- Hypothesis on the use of kaolinite as whitener after detection of TiO_2 (anatase phase) at correspondence with light colors.

Kaolinite is a hydrated silicate of alumina $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

TiO_2 as kaolinite impurity

Ti-Al correlation

Color	Shots	R (Al/Ti)	remarks
Beige	1-5	**0.94**	White layer from S6
Brown	1-7	**NO**	
Yellow	1-12	**0.98**	
White	1-5	0.69	Start new layer
Blue	1-5	**0.98**	Thin pigment
Green	1-12	**0.98**	



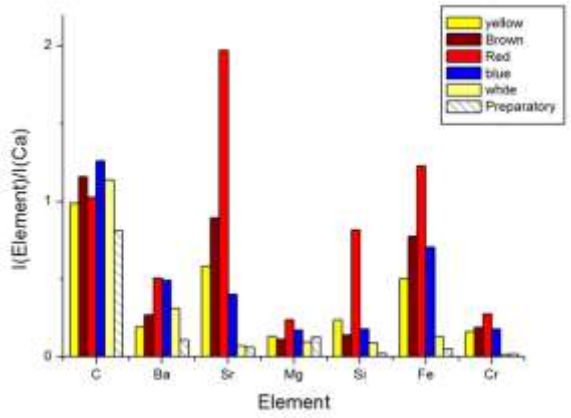
High Ti-Al correlation in all pigments, but the brown

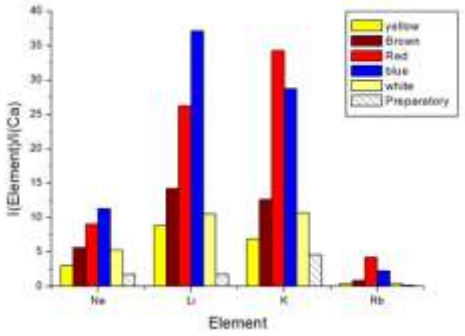
LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»

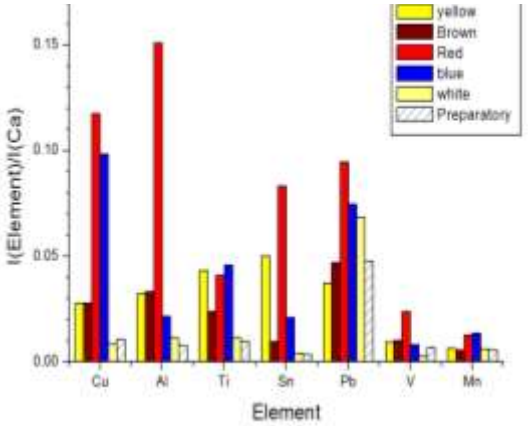
Sample 31

Open questions on pigments:

- There is a problem with lead not associated to any pigment in the Raman spectra. Is it related to surface contamination or is it an impurity in the plaster matrix (calcite)?

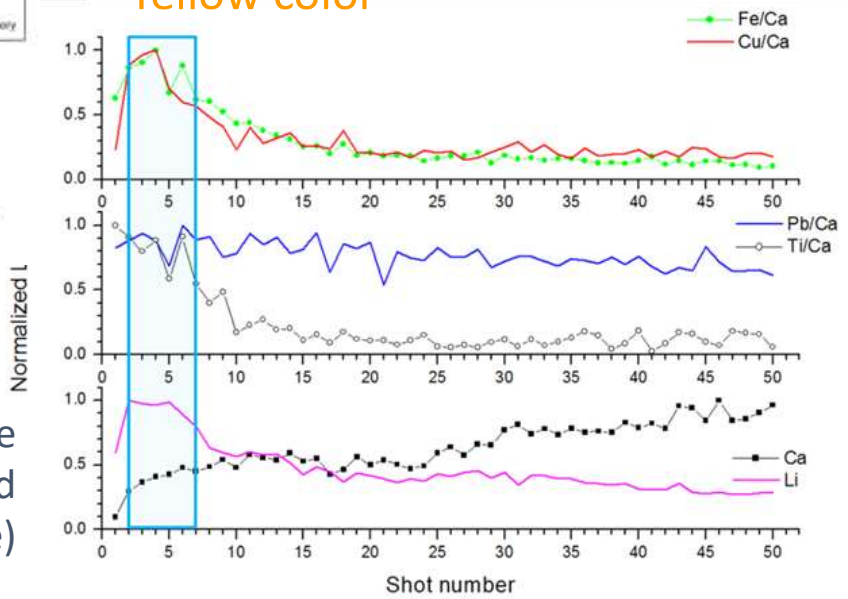






The same results were obtained on the red pigment (hematite)

Yellow color

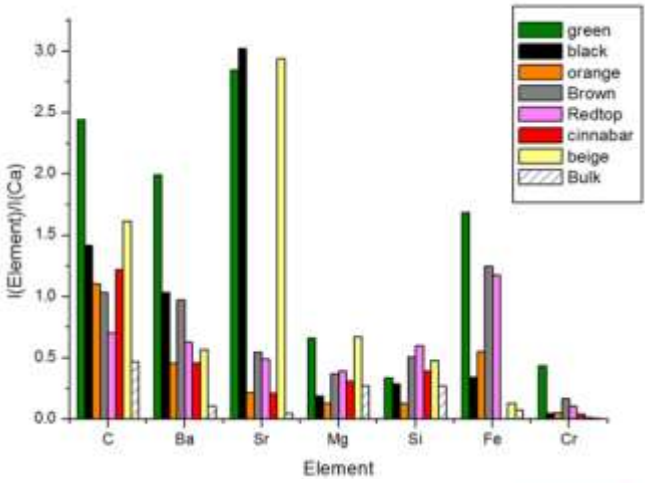


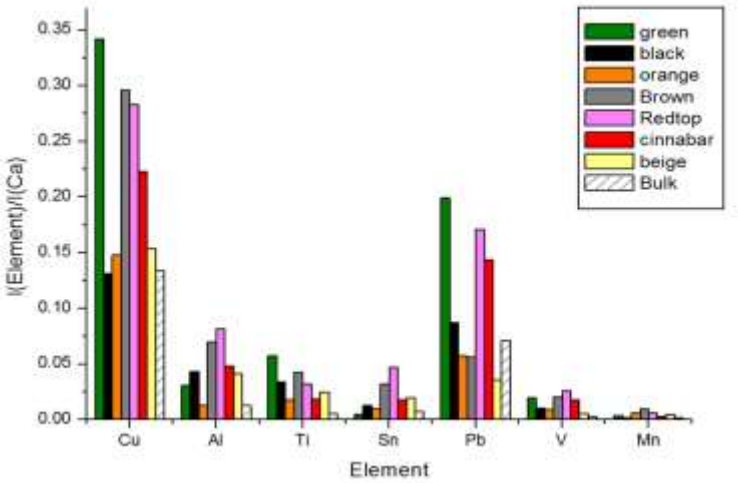
1. The yellow pigment contains Fe (goethite) and Cu traces.
2. Pb concentration on the yellow color is the same as in the bulk.
3. Ti is localized in the surface decoration layer (whitener).

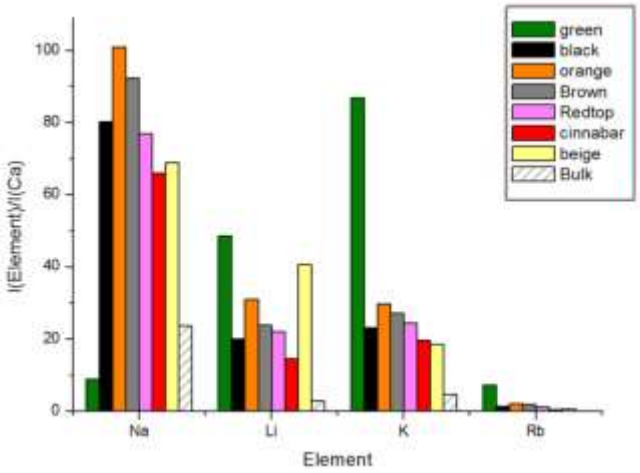
LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»

Sample 35

Open questions on pigments: the green composition

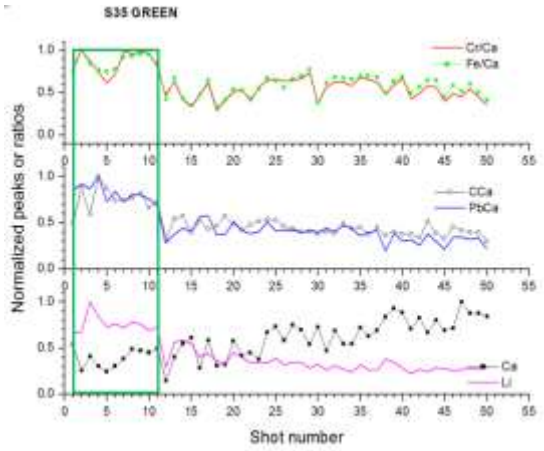






- Green earth **Celadonite** is the main pigment $K(Mg,Fe^{2+})(Fe^{3+},Al)(OH)_2$
- The presence of copper/carbon, suggests <u>a mixture</u> with **Malachite** $Cu_2(CO_3)OH_2$ in the same painted layer.

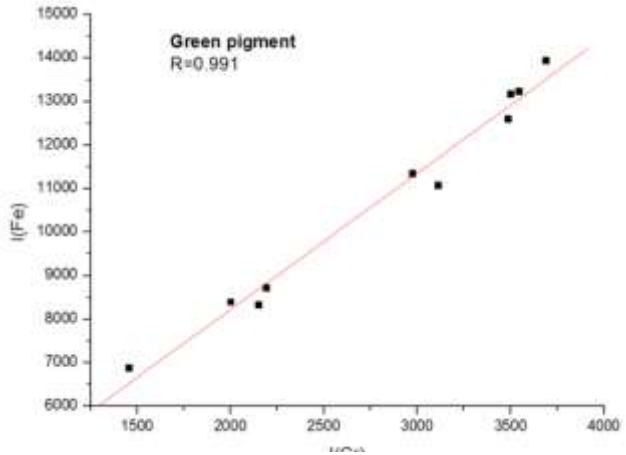
A thick uniform green layer is detected for about 11 shots (13 micron)



LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»

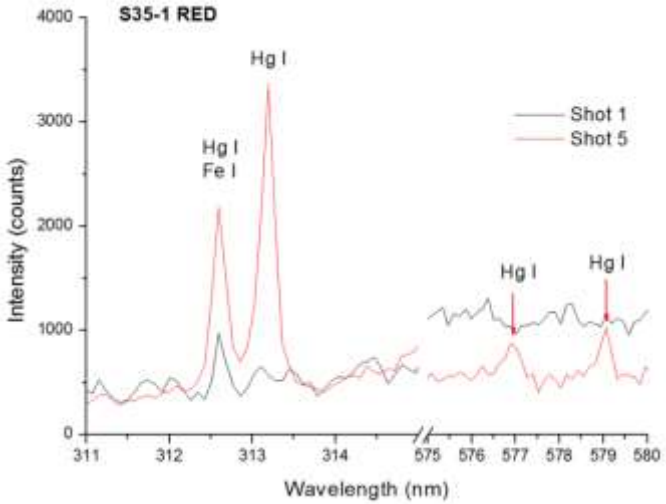
Sample 35

Open questions on pigments: provenance studies



The green earth provenance Ancient celadonite deposits are known in Tuscany and near Verona (Monte Baldo).

Only Verona greens earths presents peculiar traces of Cr oxides, the good correlation found between Fe and Cr in all the investigated green layers allows to establish its origin and to confirm the layer homogeneity.



The cinnabar provenance

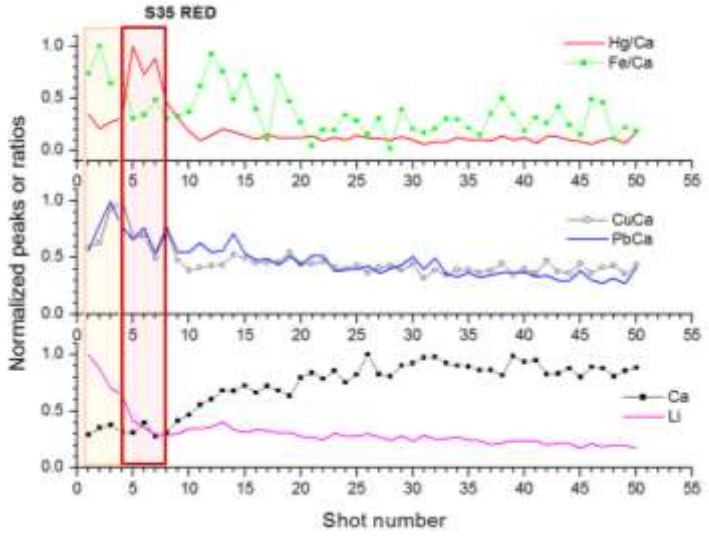
No As traces have been detected together with Hg thus ruling out the provenance of cinnabar from Monte Amiata.

Quartz impurities are characteristic of the historical mine in Almadèn (Spain), a Silicon trace concentration larger than in the bulk has been observed at correspondence with Hg detection, thus supporting the suggested cinnabar provenance from Almadèn mine.

LIBS stratigraphy on Roman fresco's fragments from «Villa della Piscina»

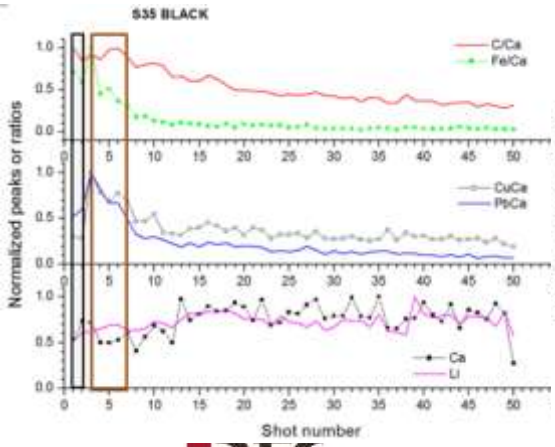
Sample 35

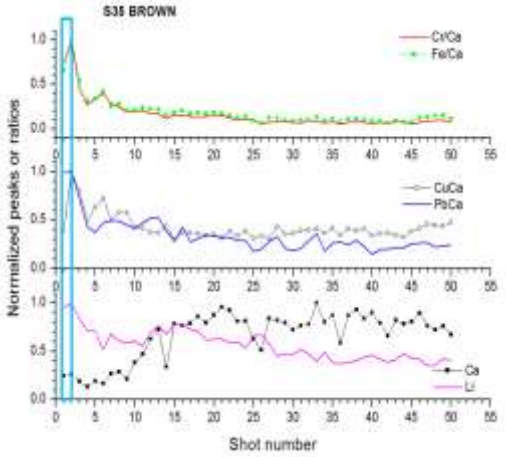
Questioni aperte sui pigmenti: fresco's realization



Overlapping red layers

The final red color is obtained overlapping a back layer of cinnabar with an equally thin layer of red ochre, this is shown by the alternation of Fe and Hg intensity in the stratigraphy at 5 - 9 micron.





Black decorations

Thin carbon layers have been added «*a seco*» on the fresco surface on top of dark pigments (e.g. brown). The carbon black layers result to be 1 – 2.5 micron thick (1-2 laser shots).

Similar thickness are detected for kaolinite whitening addition to light colors in Ti/Al stratigraphy (see sample 21).

Conclusions
LIBS vs PIXE in the considered characterization

Elemental atomic analysis techniques

- Fully multi-elemental
- High sensitive (suitable to trace detection at ppm level)

LIBS

- Laboratory and *in-situ* measurements (portable system and possible remote acquisition)
- Micro-destructive laboratory analyses by microLIBS (crater diameter ~ 10 μ or even lower)
- Possibility of quantitative analysis by use of calibration curve / difficult for frescoes (semi-quantitative data with standardization on Ca from the $CaCO_2$ matrix).
- **Stratigraphy at space resolution** for first two hundred subsurface layers, (on fresco 100 shot ≈ 120 micron as measured by optical microscopy in the current measurements).
- Suitable to correlation analysis at each single layer.
- High sensitivity to light metals (Li, Al, …)

PIXE

- Only laboratory limited sample size
- **Fully Non destructive** at optimized conditions
- Quantitative after proper calibration of the set-up
- Stratigraphy in large steps, possible only in variable proton energy machines. Larger penetration depth (on fresco 250 μm at 6 MeV).
- Directly comparable to XRF mapping
- Sensitive to all heavy non metallic elements (S, P, …)