

A Light for Science





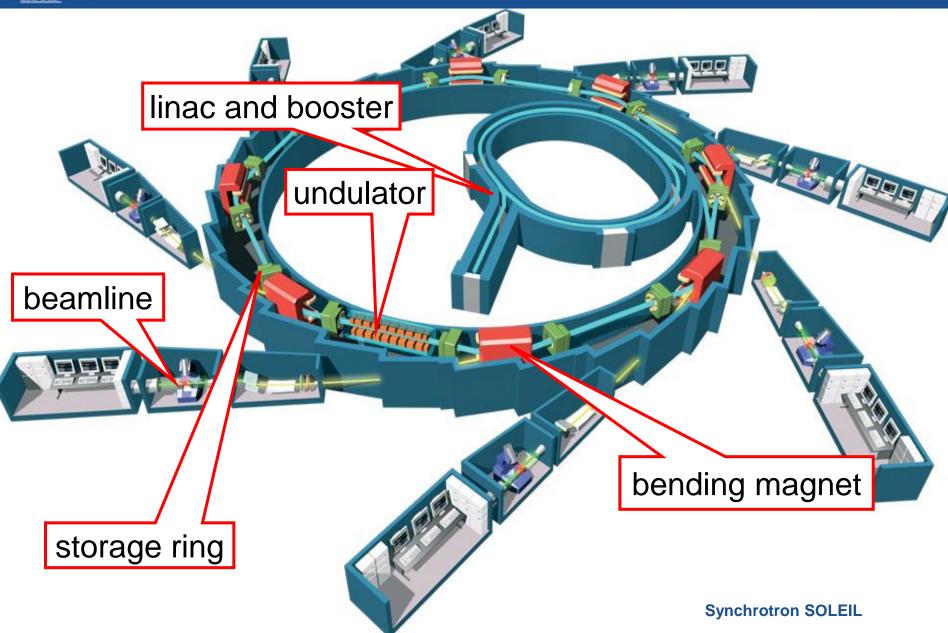
Synchrotron Radiation Imaging: Palaeontology and **Cultural Heritage Studies**

Francesco Sette - ESRF BP 220 - 38043 Grenoble - France

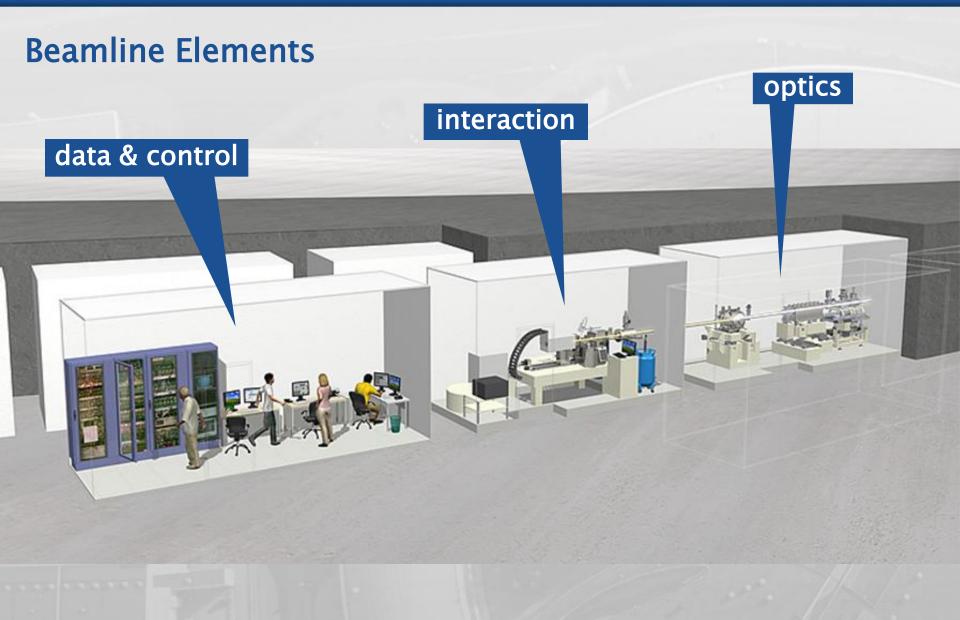
- X-rays and Synchrotron Radiation
- X-ray Synchrotron Imaging: A Revolution for Paleontology
- Life at a Synchrotron Facility: the ESRF
- X-ray Synchrotron Imaging: **ESRF & Cultural Heritage**







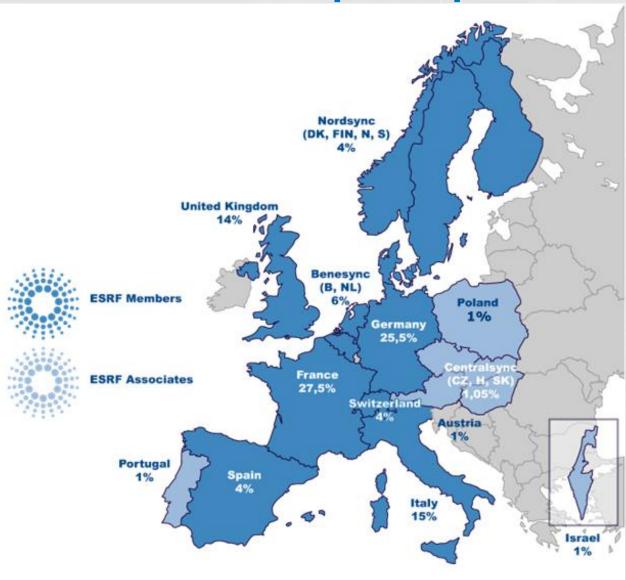






ESRF Members & their financial participation

27.5% France 25.5% Germany 15% Italy 14% **United Kingdom** 4% **Spain Switzerland** 4% 6% Benesync (BE, NL) **Nordsync** 4% (DK, SF, NO, SE) 1% **Portugal** 1% Israel 1.3 % **Austria** 1% **Poland** 1.05% Centralsync (CZ, HU, SV)





ESRF Facts and Figures

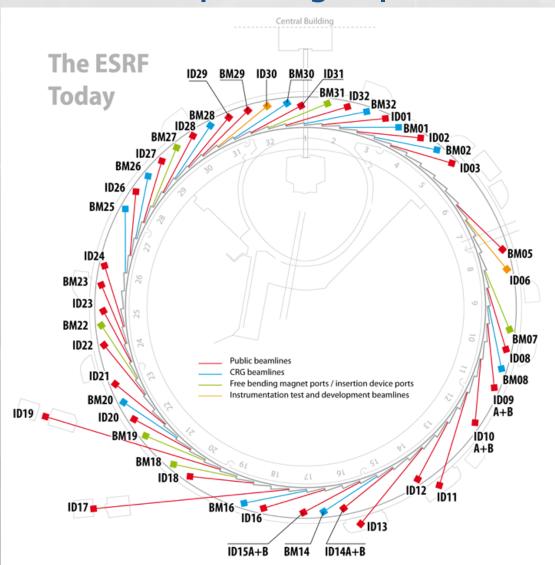
- 600 staff from > 40 countries
- 155 scientists, ~25% on permanent positions
- ~ 400 staff from other institutes are working on site
- 1500 experiments per year
- 1900 publications in peer-reviewed journals (2011)
- 52 publications in the Nature Group journals (2011)
- ~6 000 scientists come to the ESRF per year (2011)
- ~25% of experiments have an industry-involvement
- ~2% of capacity is directly sold to industry



43 experimental stations operating in parallel

User operation:

- >~5200 hrs/year machine operation for users (for a total of ~200 000 hrs/year of users' beam time)
- >24h/24h and 6d/7d availability
- >>98.5% reliability





Major synchrotrons in the world



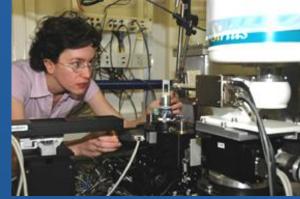
The ESRF is today the world's number one synchrotron:

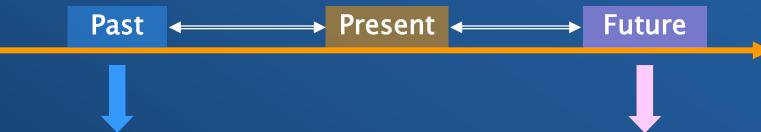
- > Numbers of users
- > Numbers of publications
- > Reliability & quality of service

http://www.esrf.eu/



Why analyzing precious artifacts? Marine Cotte – ESRF





Historical knowledge:

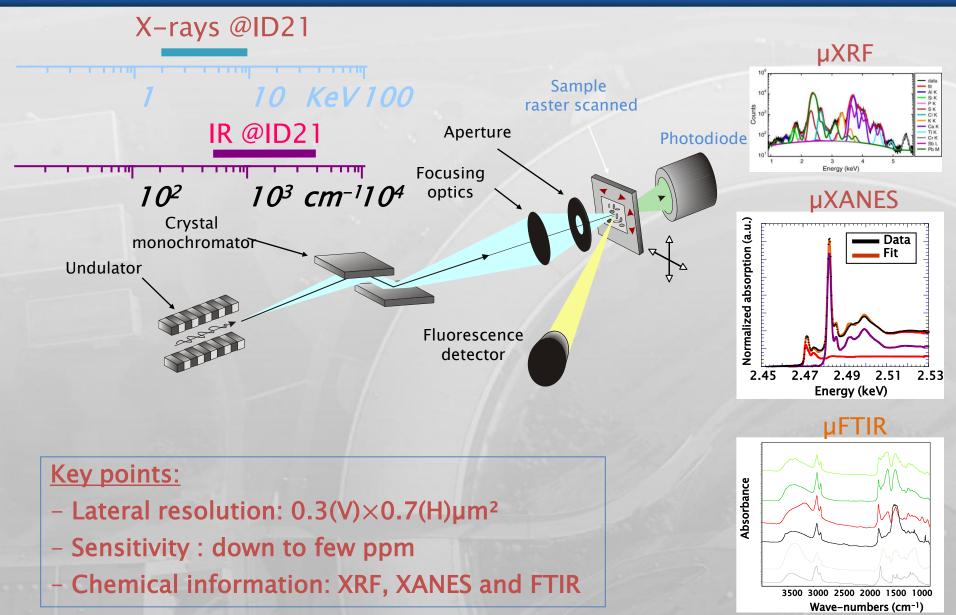
- Manufactirung techniques
- Pigment synthesis
- Trades
- · Dating, authentication...

Restoration and conservation:

- Alteration mechanisms
- Conservation and restoration treatments
- Storage conditions...



Micro-spectroscopies on ID21 at the ESRF











Italian Renaissance pottery

Padovani, *Applied Physics A*, 2004 - GILDA, ESRF





Sicilian decorated pottery, 18th B.C.- 16th A.D.

Barilaro, *Journal of Applied Physics*, 2007 - GILDA, ESRF



Roman ancient glass

Lahlil, *Applied Physics A*, 2010, ID21, ESRF



Italian medieval glass

Quartieri, *Journal of Non-Crystalline Solids*, 2005, GILDA, ESRF



Egyptian ancient glass

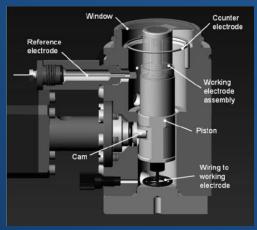
Lahlil, *Applied Physics A*, 2010, ID21, ESRF



Metals



Neff, Corrosion science, 2005 Requer, Corrosion science, 2007



Adrians, Surface Engineering, 2008 Dowsett, Anal. Chem., 2008 Adrians, JAAS, 2008

Wood



Sandstrom, *Nature*, 2002

Sandstrom, *PNAS*, 2005

Wetherall,

J. Archaeological Science, 2008

Inks and papers



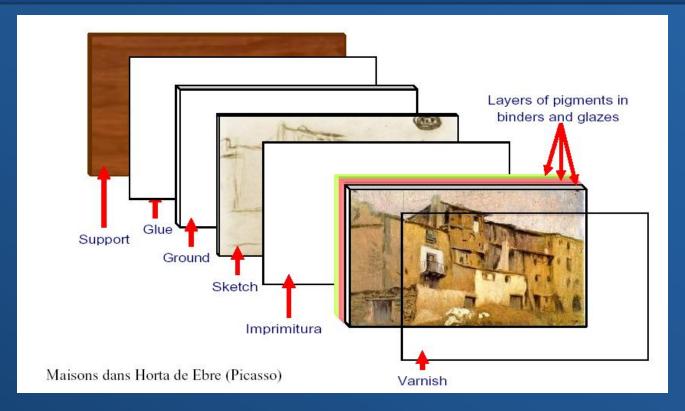
Pigments

Cotte, Anal. Chem, 2006 Cotte, *JAAS*, 2008



Proost, NIMB, 2004 Wilke, *JAAS*, 2009 Kanngeisser, Spectrochimica Acta B, 2004





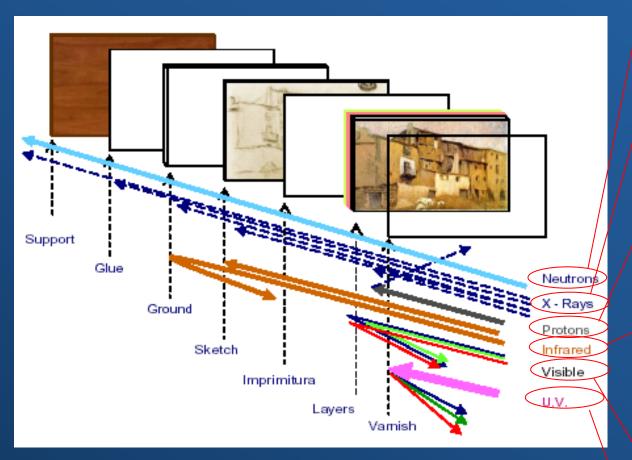
Alteration is usually, but not systematically developing on the surface of the painting.

- chemical degradations
- physical degradations
- biological degradations

"Nuclear physics and painting: sub-topic of the wide and fascinating field of Science and Art" R. Leonardi, *Nuclear Physics A*, 752, 659c–674c (2005)c



Which radiation for which information?



"Nuclear physics and painting: sub-topic of the wide and fascinating field of Science and Art"

R. Leonardi, *Nuclear Physics A*, 752, 659c-674c (2005)c

Neutrons:

- high penetration
- · activation of the nuclei of the elements (autoradiography)

X-rays:

 high penetration, strongly correlated to the Z of elements (radiography)

Particles:

· lower penetration, superficial analysis (elemental)

Infrared (MIR):

· identification of binders and pigments thanks to vibrational excitation of molecular groups

Visible:

 observation of the surface (white light, monochromatic, grazing...)

Ultra-violet:

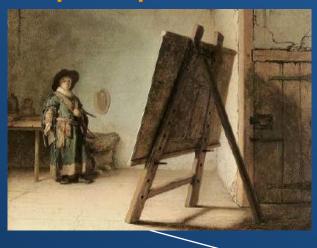
 luminescent processes of varnish and binding media, increasing with age



Two orthogonal approaches

No sampling

- Non-invasive
- Depth of penetration



Micro-sampling

- Micro-probe
 - size of the sample
 - layers thickness

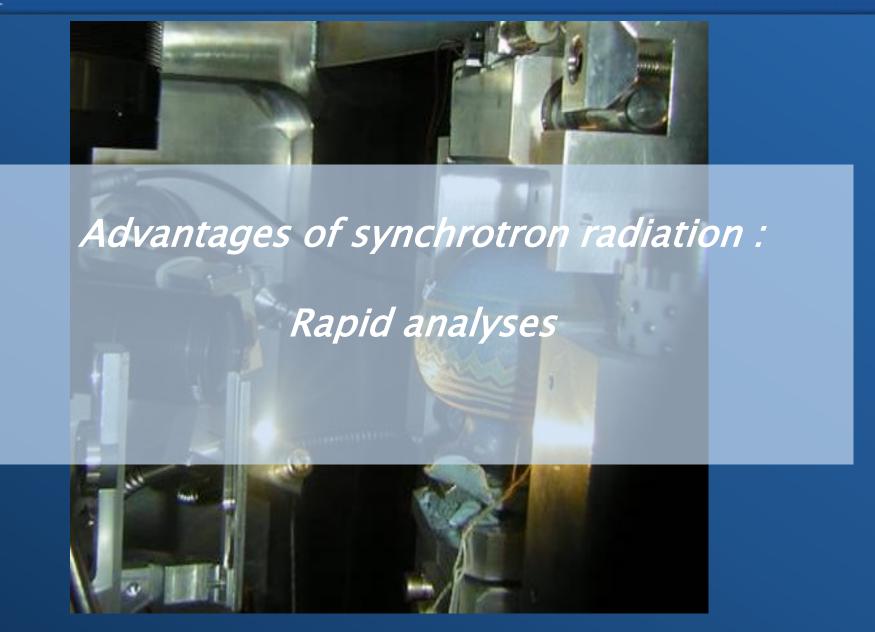


Heterogeneities at the micron scale:

organic/mineral, crystallized/amorphous, major/minor/trace

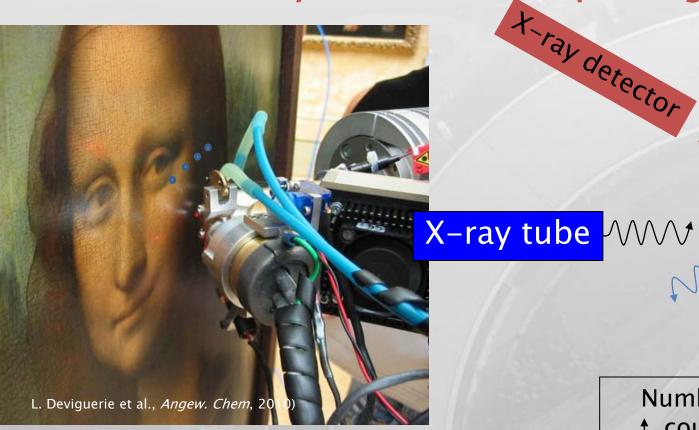
Sensitivities, multi-modal





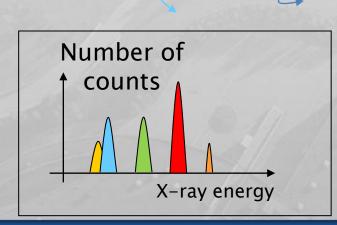
X-Ray fluorescence on paintings

X-ray detector

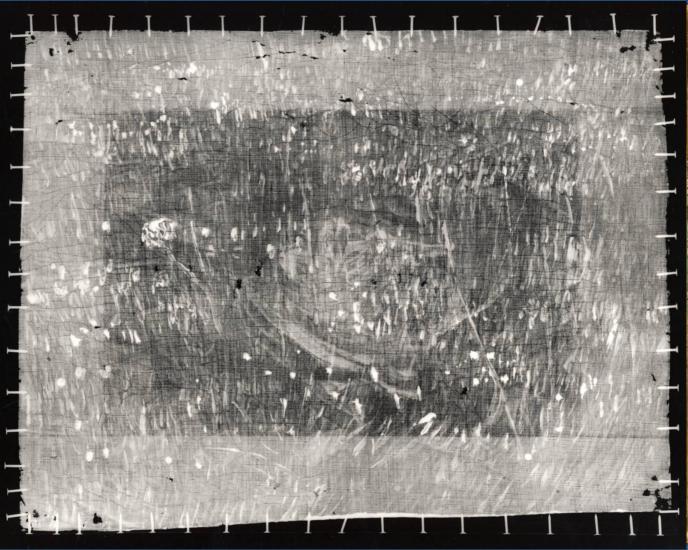


X-ray fluorescence measurements on Mona Lisa (in the Louvre) ~ 12 points/painting

~5 minutes per point







Vincent van Gogh Patch of grass Paris, 1886

Kroeller Mueller Museum Otterlo, Pays-Bas X-Radiography

> Portrait of a woman? Nuenen, 1884/1885?

2D X-ray Fluorescence in the central zone?

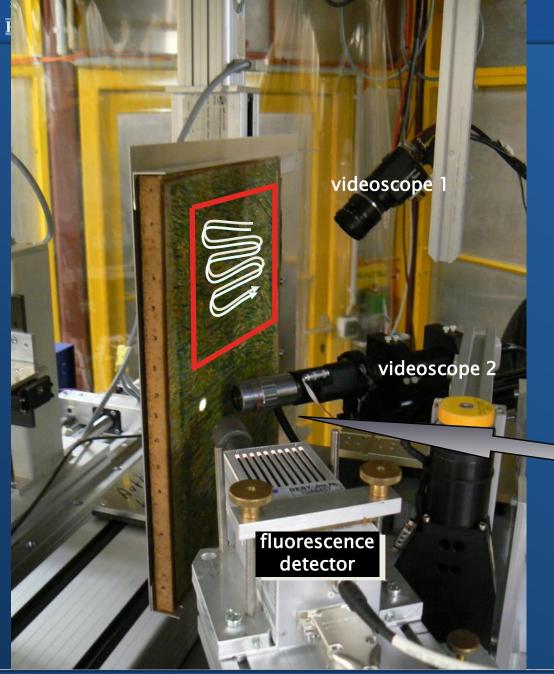
"Visualization of a lost painting by Vincent van Gogh using synchrotron radiation based X-ray fluorescence elemental mapping"

Dik J., Janssens K., Van Der Snickt G., Van Der Loeff L., Rickers K. and Cotte M., Anal. Chem. (2008) 80(16): 6436-6442.

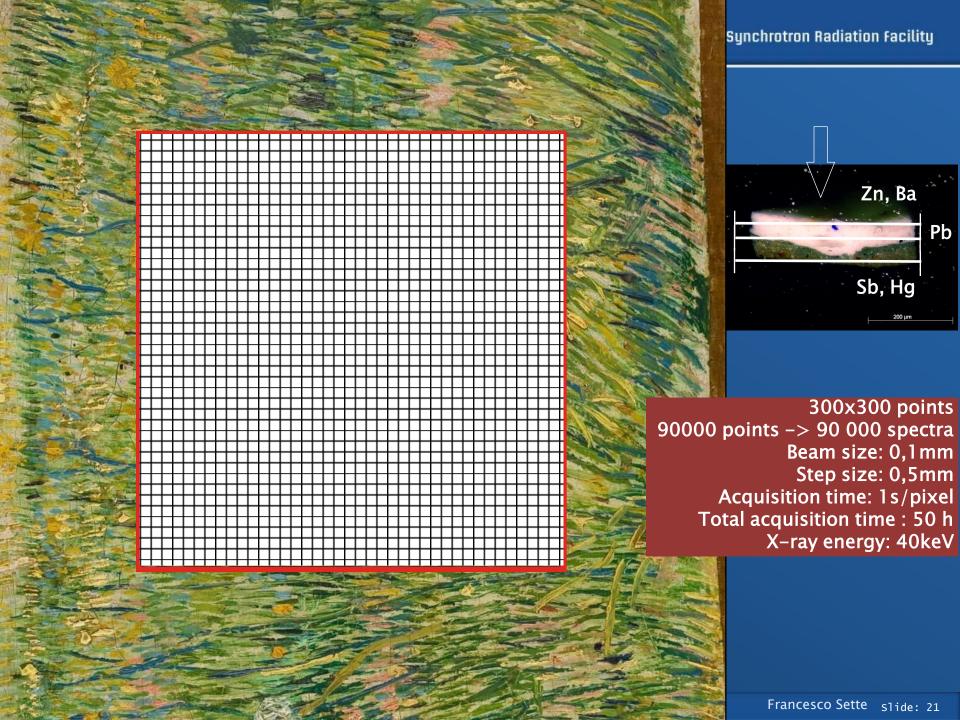








Synchrotron beam







X-Radiography

Reconstruction using elemental cartographies

Existing painting

http://www.esrf.eu/news/general-old/general-2008/vangogh/



Letter of Vincent to Theo:

'I would like to know if the portraits that I sent to you have arrived'





Peasants eating potatoes



Patch of grass

Winter 84/85

Nuenen, Hollande

March 1885

April 1885

Nov. 1885

Anvers

March 1886

Summer 1887

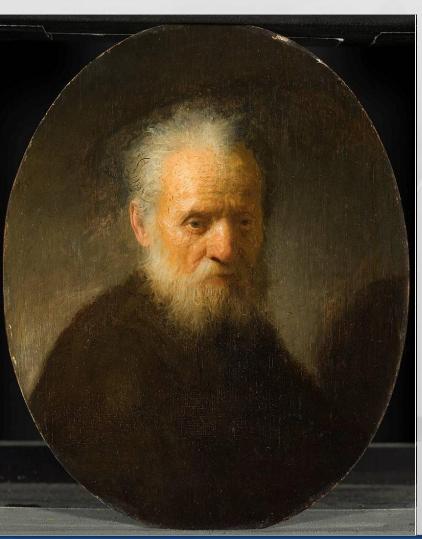
Nuenen, Hollande

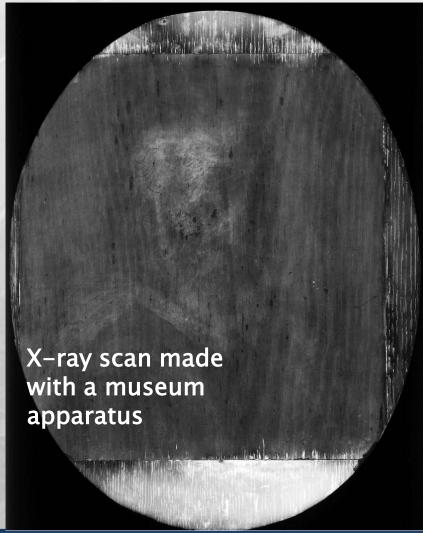
Paris

Paris



Old Man with a Beard - a Rembrandt or not?



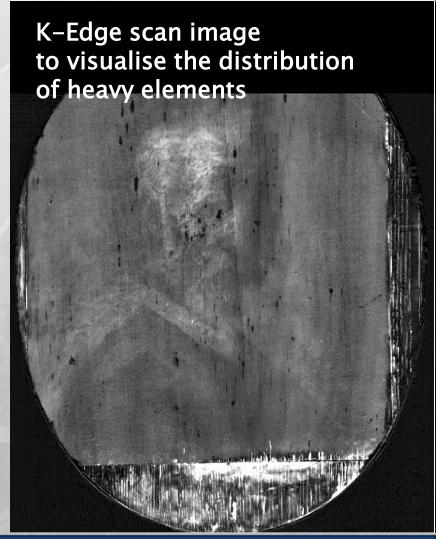




The painting is brought, with several dozen other paintings, to ESRF beamline ID17

Result: no complete 2nd painting



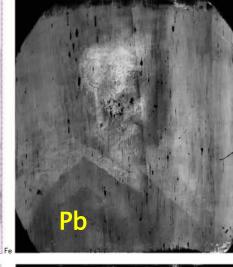


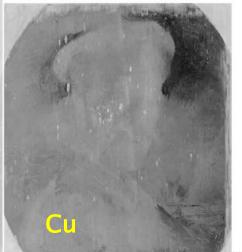


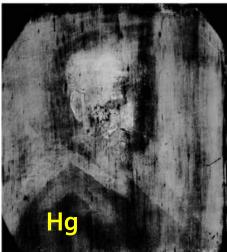
A detailed scan, element per element, is performed at the NSLS in Brookhaven (U.S.)













Copper distribution with contours superimposed in red, compared with two Rembrandt self portraits from around 1630.

Pb - Hg - Fe: surface pigments in whitish/pink fleshtones and brown Cu: a different shape (beret and clothes) in blue

http://www.esrf.eu/news/general/hidden-rembrandt/index_html/







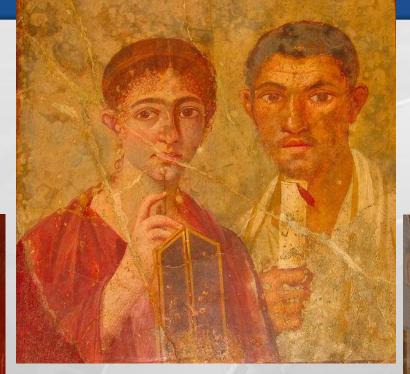














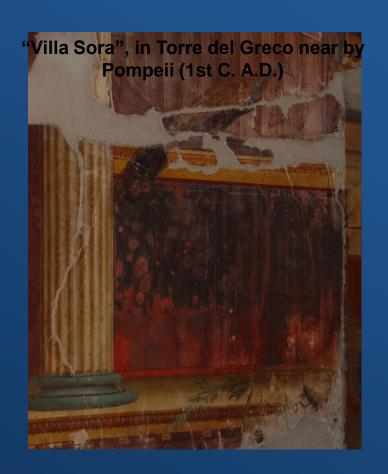


The European Light Source Int. School on Scientific Journ. & Comm. - ERICE 1-4 August 2012



Blackening of Pompeian Cinnabar paintings

J. Susini¹, N. Metrich², A. Moscato³, C. Gratziu³, A. Bertagnini⁴, M. Pagano⁵ ¹ ESRF, ² LPS, ³ Univ. di Pisa, ⁴ Istituto Nazionale di Geofisica e Vulcanologia, ⁵ Beni Archeologici del Molise





SAFE

ALTERED

ALTERED

Blackening of Pompeian painting

Safe **Altered Altered** sample sample sample

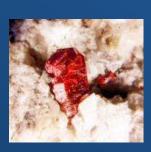


The classical explanation

HgS (hexagonal) Red cinnabar

Light

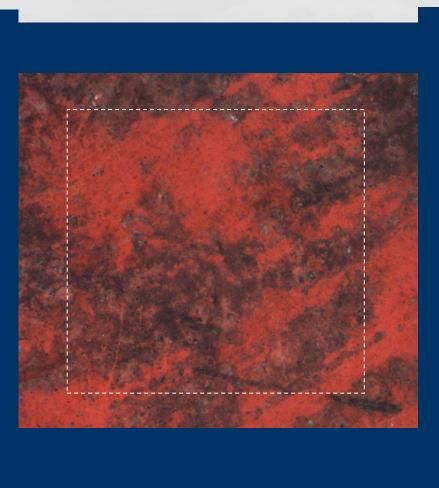
HgS (cubic) Black metacinnabar

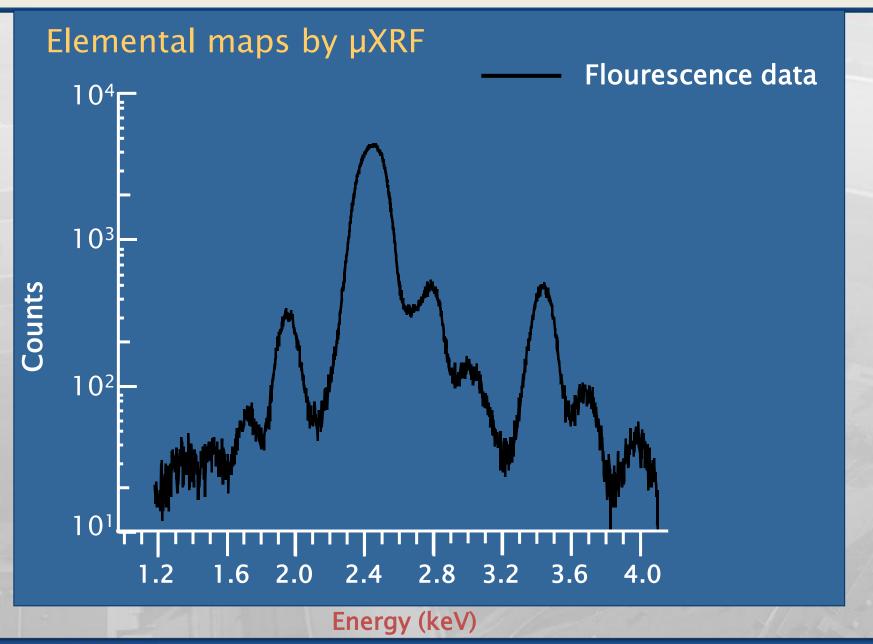


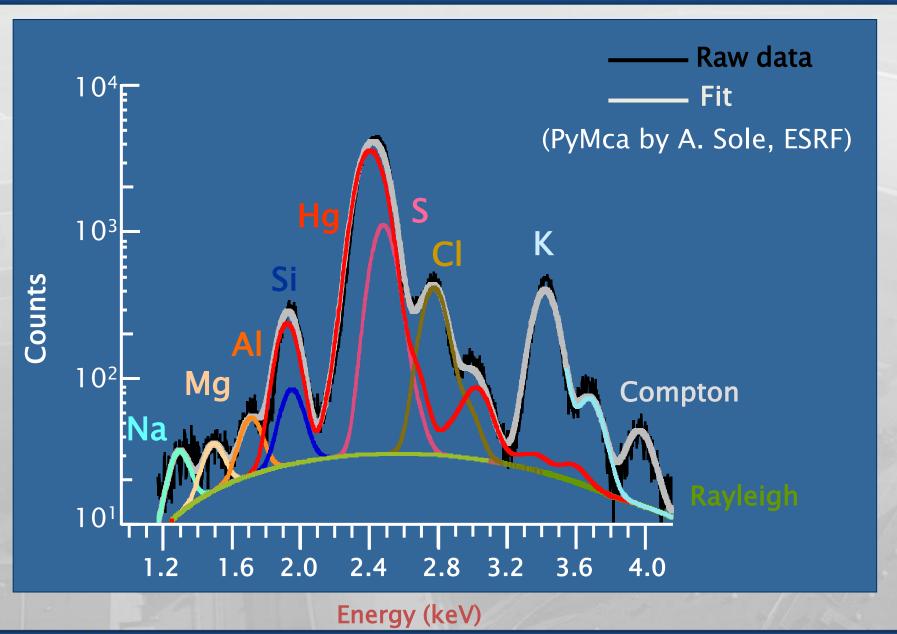
Not so "simple"!

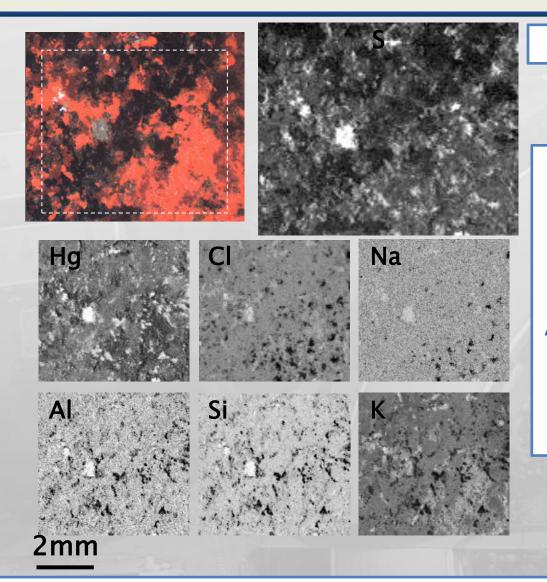
What about the other elements? Can we explain the phenomena?

=> X-ray micro fluorescence









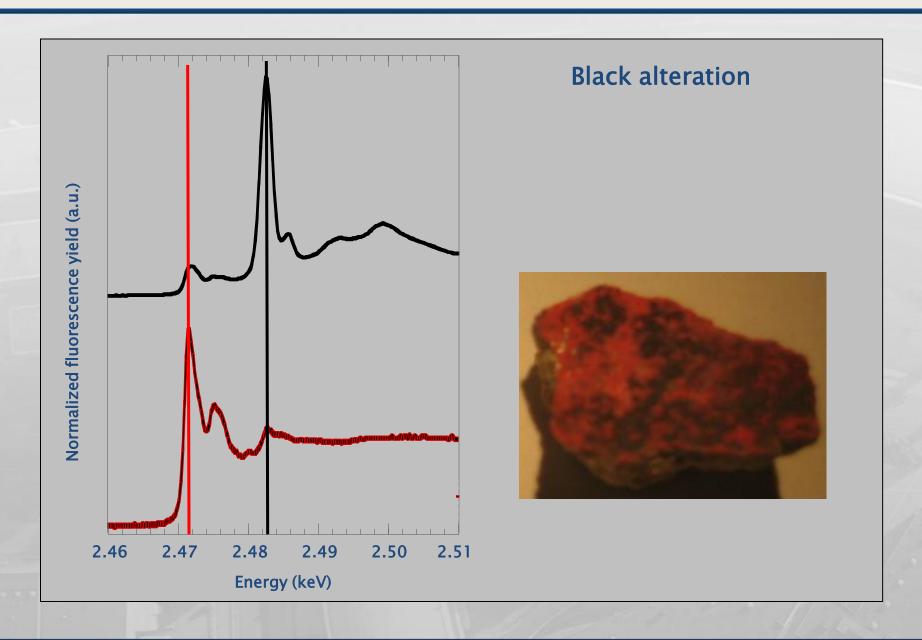
Black alteration

Correlation [sulphur] - black aspect

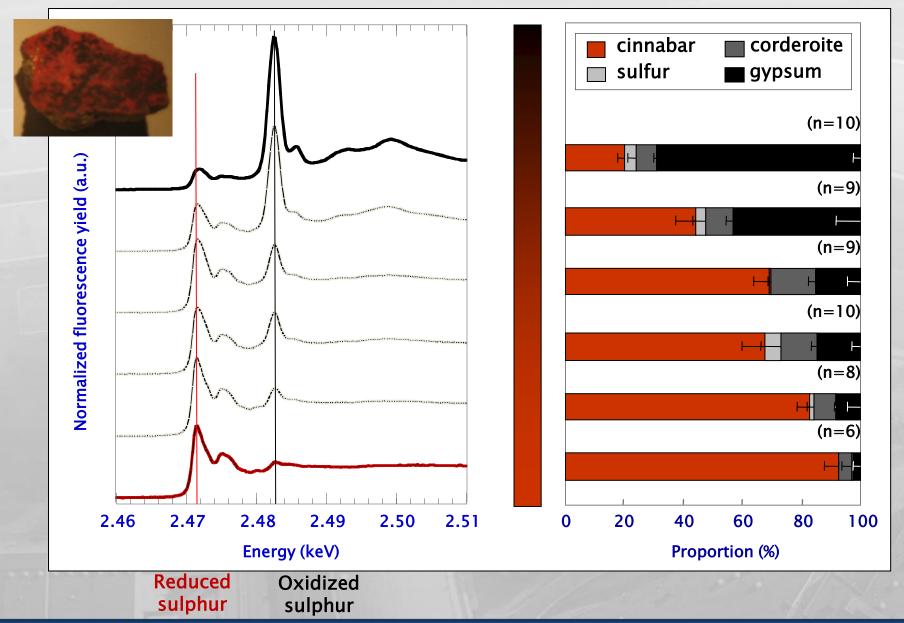
Are the sulphur compounds the same in the two regions?

"Blackening of Pompeian Cinnabar paintings studied by X-ray micro-spectroscopic imaging" M. Cotte¹, J. Susini¹, N. Metrich², A. Moscato³, C. Gratziu³, A. Bertagnini⁴, M. Pagano⁵, Anal. Chem., 78, 7484-7492 (2006)

XANES at the Sulfur K-edge on Pompeian paintings

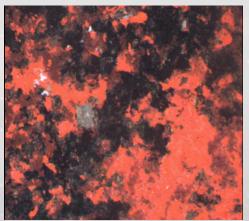


XANES at the S K-edge: towards semi-quantification



Chemical mapping of sulfur, black sample

Light microscopy In-plane analysis



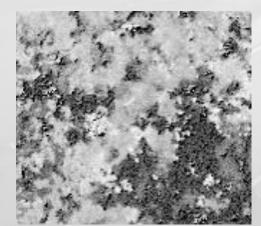
map size, 2×2mm² beam size 100µmØ

In-depth analysis

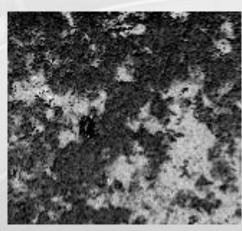


map size, $60 \times 95 \, \mu \text{m}^2$ beam size $0.3 \times 0.7 \mu m^2$

Sulphides



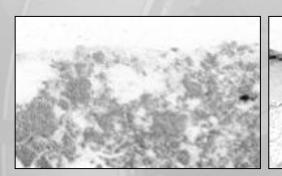
Sulphates



max

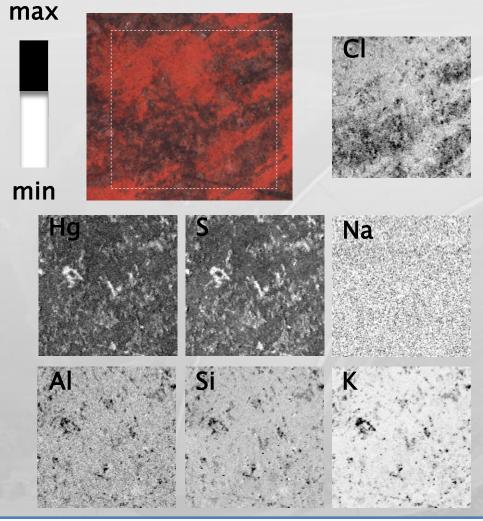


min



Very superficial alteration (~5µm)

Elemental mapping, grey sample



Correlation between degradation and presence of chlorine. Several mechanisms can occur.

Blackening of Pompeian painting

Possible chlorine sources

Sea proximity



A remedy already known to the Romans

"Cera punica"

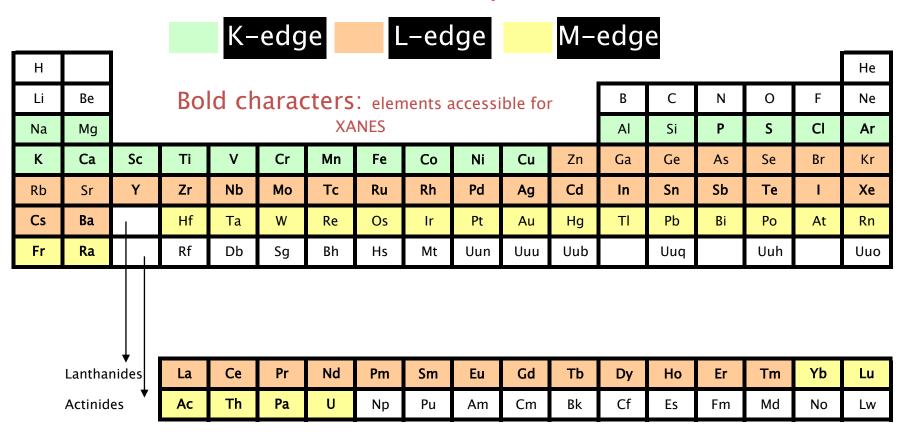
Punica fit hoc modo: ventilatur sub diu saepius cera fulva, dein fervet in aqua marina ex alto petita addito nitro. inde lingulis hauriunt florem, id est candidissima quaeque, transfunduntque in vas, quod exiquum frigidae habeat, et rursus marina decocunt separatim, de "in vas ipsum aut aquam refrigerant."

PLINIUS. Naturalis Historia - XXI

http://www.esrf.eu/UsersAndScience/Publications/Highlights/2006/XIM/IMA08



Elements accessible for X-ray fluorescence at ID21





Bamiyan Buddhist mural paintings (Afghanistan)



Samples taken in a framework of a UNESCO Conservation Project of the Bamiyan Site

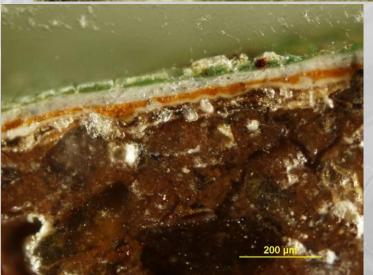


The blast altered the samples on their surface



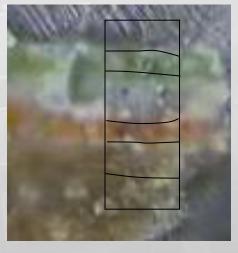


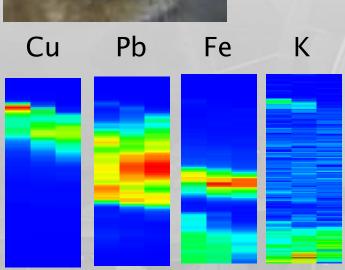




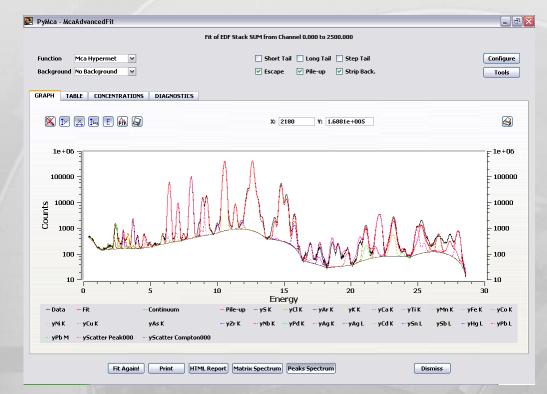


Identify key elements with µXRF/µXRD (ID18F)





Fluorescence spectrum of one point



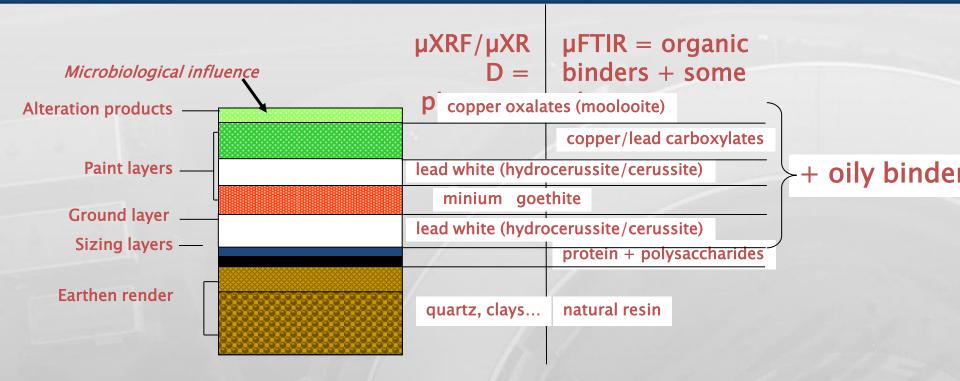
Map: $150 \times 60 \mu m^2$ $1 \times 15 \mu m^2$

Step: $1 \times 30 \mu m^2$

Beam:



A very complex stack of components



http://www.esrf.eu/UsersAndScience/Publications/Highlights/2008/imaging/ imaging8

naturenews

Published online 22 April 2008 | Nature | doi:10.1038/news.2008.770

Ancient Buddhas painted in oils

Were painters on the Silk Road way ahead of the Europeans?

Philip Ball

Artists in Afghanist practice in Europe,

Yoko Taniguchi of t of Buddhist painting say that the paint la

But Jaap Boon, a sp Amsterdam, the Ne been done.

Los Angeles Times | Business

You are here: LAT Home > Business > Technology



Oil painting appeared centur Home ASIA EUROPE U.S. WORLD WORLD BUSINESS TECHNOLOGY ENTERTAINMENT WORLD SI earlier -- in Asia

tte. ind

c to

and

BBC

The oil is present in a form very similar to

soap

found in

M ABCNews

Earliest oil paintin Afghanistan

Posted Wed Apr 23, 2008 8:23am AEST Updated 5 hours 54 minutes ago

Scientists say they have proved the world's first ever oil paintings were in caves near two destroyed giant statues of Buddha in Afghanistan.

Samples from paintings, dating from the 7th century AD, were taken from caves in Bamiyan.

The European Synchrotron Radiation Facility (ESRF) in



The Taliban destroyed two 6th century giant Buddhas in 2001 (file photo), (Reuters: Goran Tomasevic)

stan (CNN) -- Scientists have found what they described this week as the earliest oil covered.



v oil painting was going on for centuries

Murals found on cave walls in Afghanistan prove that painting with oil had been going on in Asia for centuries before artists used the technique in Europe, scientists said this week

Until now, art historians believed that oil painting started in Europe in the 15th century.

Scientists found the murals in a network of caves where monks lived and prayed in the Afghan region of Bamiyan, according to a statement on the Web site of the European Synchrotron Radiation Facility, where the ancient paintings were analyzed.

Until 2001, two colossal 6th-century statues of Buddhas stood at the mouth of the caves. Then the Taliban, which then ruled Afghanistan, blew up

medium of drying oil, such as linseed oil.

In many European history and art books, oil painting is said to have started in the 15th



RICE 1-4 August 2012

Mi

Sci



European Synchrotron Radiation Facility



16th C.

1st C.

5th C.

12th-13th C. 15th C.

16th C. 19th C

Mesopotamia and Ancient Egypt

Roman Empire

Middle-Ages

Renaissance

Modern times



Alabasters 6th–4th C. B.C. Mesopotamia



Roman mosaic Villa Casale Piazza Armerina 3rdC A.D. Sicily



Merovingian tumbler 6th C. A.D. France



Binding plaque 12th C. A.D. France



Glass bottle 18th C. A.D. Germany

"Synthesis of calcium antimonate nano-crystals by the 18th dynasty Egyptian glassmakers",

S. Lahlil, I. Biron, M. Cotte, J. Susini, N. Mengui, Applied Physics A, 98 (1), 1-8 (2010).

"New insight on the in situ crystallization of calcium antimonite opacified glass during the Roman period",

S. Lahlil, I. Biron, M. Cotte, J. Susini, Applied Physics A, 100, 683-692 (2010)

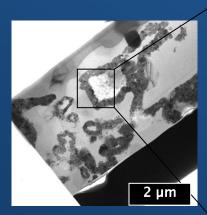


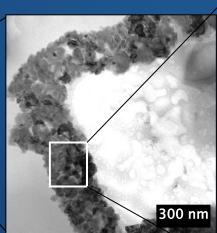
Calcium antimoniate nano -crystals in the Egiptian opaque glasses

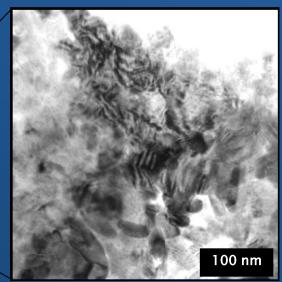


Manufacturing of calcium antimonate nano-crystals: *In-situ* (using stibine, Sb_2S_3)? Or *ex-situ* treatment??

18th Dynasty, (1570–1292 BC)





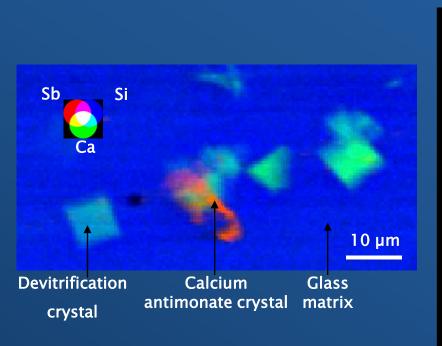


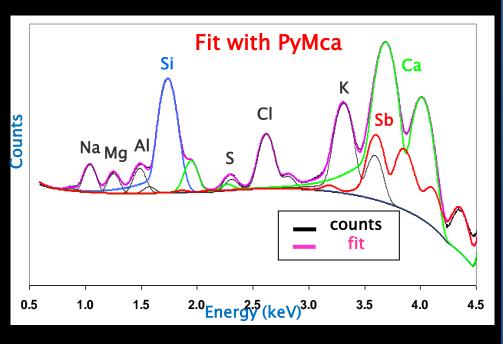
"Synthesis of calcium antimonate nano-crystals by the 18th dynasty Egyptian glassmakers",

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Acquisition of XRF and XANES spectra in the glass matrix





- The $(0.3\times0.7\mu\text{m}^2)$ nano-beam is indispensable
- cartography to identify the crystals in the glass matrix

"A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra", Sole, V. A., Papillon, E., Cotte, M., Walter, P. and Susini, J. Spectrochim. Acta B (2007) 62(1): 63-



Identification of in-situ or ex-situ crystallisation by XANES at the SB L₁ edge

Synthesis *in-situ*:

Sb is present in the glass matrix as Sb^{III} and Sb^V (theratio Sb^{III}/Sb^V is correlated with oxidation state of Sb in the nano-crystal powder)

> Synthesis *ex-situ*: Sb is present in the glass matrix only as SbV



The Romans fabricated their opaque glasses by in-situ crystallisation of Sb₂O₄

The Egyptians fabricated their opaque glasses using synthetic nano-crystals of Ca₂Sb₂O₇

http://www.esrf.eu/UsersAndScience/Public ations/Highlights/2010/imaging/img07





Summary

- 3-D imaging at sub-micrometre spatial resolution
- Diffraction for crystalline/amorphous structure
- Spectroscopy for element/oxidation state mapping
- non-destructive
- micro-samples are often sufficient
- complementary to museum-based techniques
- unveal hidden aspects of the history of an object
- understand how to improve conservation
- inspire the public's interest in science



