SR in Archaeological and Cultural Heritage Science

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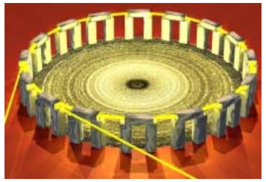
Daresbury Laboratory, UK.

http://srs.dl.ac.uk/arch/



ARCHAEOLOGY is about people

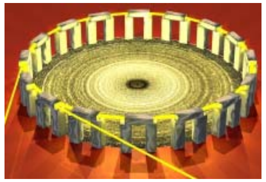
"the full range of past human experience - how people organized themselves into social groups and exploited their surroundings; what they ate, made, and believed; how they communicated and why their societies changed" (Renfrew and Bahn, 1996).

i.e. NOT about things *per se*!

But:

"Because archaeologists study the past, they are unable to observe human behaviour directly. Unlike historians, they also lack access to verbally encoded records of the past. Instead they must attempt to infer human behaviour and beliefs from the surviving remains of what people made and used before they can begin, like other social scientists, to explain phenomena." (Trigger, 1988)

i.e. information from SR must be relatable to social context

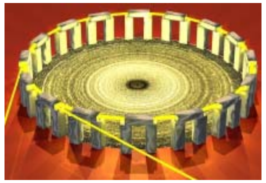


Material Remains in Archaeology

- Human remains (bone, teeth, hair, soft tissue)
- Inorganic remains (stone, pottery, metal, glass)
- Organic remains (animal bone, wood, textile)
- Archaeological sites at various scales
- Associated environmental evidence of human activity

Traditional Questions:

- What? Identification of material e.g. pigments
- How? Manufacturing technology, e.g. alloy or glaze composition
- Where? Chemical fingerprinting of raw material source
- When? Chemical/technological typologies to assist dating/provenance/'authenticity'
- Why? Technological choices - practical/conservative/'ritual'



SR in Archaeological and Cultural Heritage Science

The starting point

SR-based Materials Science methods can be used for Archaeomaterials.

The whole of the SR spectrum (0.01eV to 100KeV) and all SR techniques can be utilised at maximum advantage.

The existing infrastructure covers most current ARCH needs.

SR in ARCH has come of age

It has played a key role in the recent rapid growth of applications.

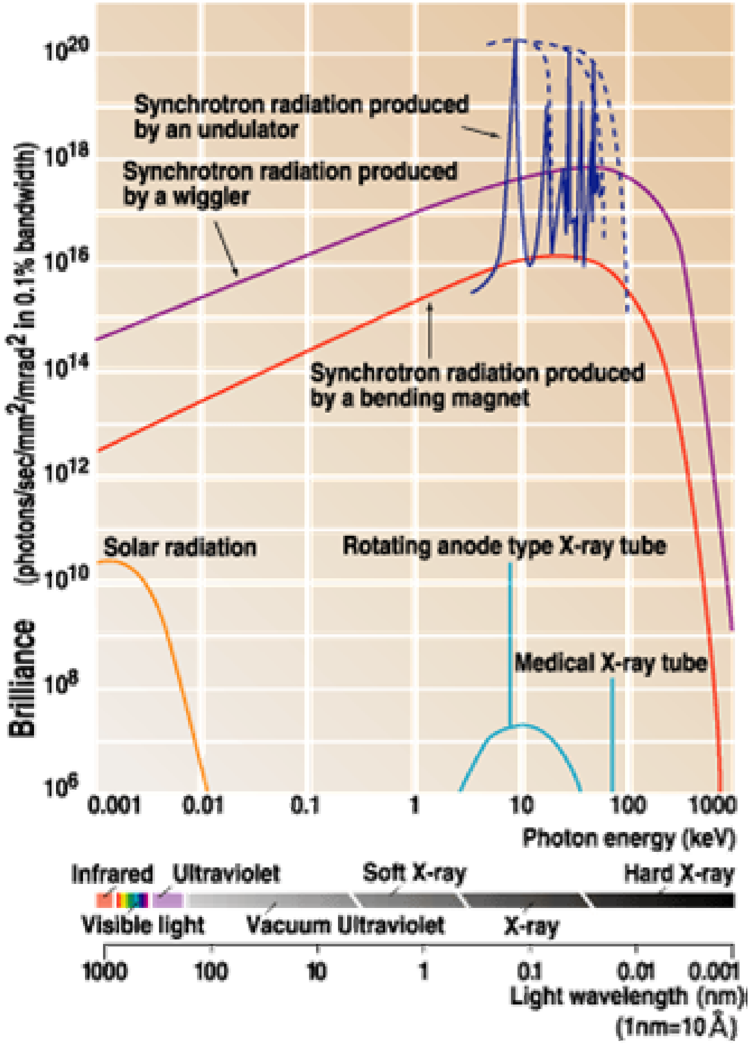
1st Int.Workshop at DL, Nov. 1999, sponsored by SR Round Table.
2nd Int. Workshop SSRL, Oct. 2000.
SR papers in several symposia, workshops and conferences in 2002.

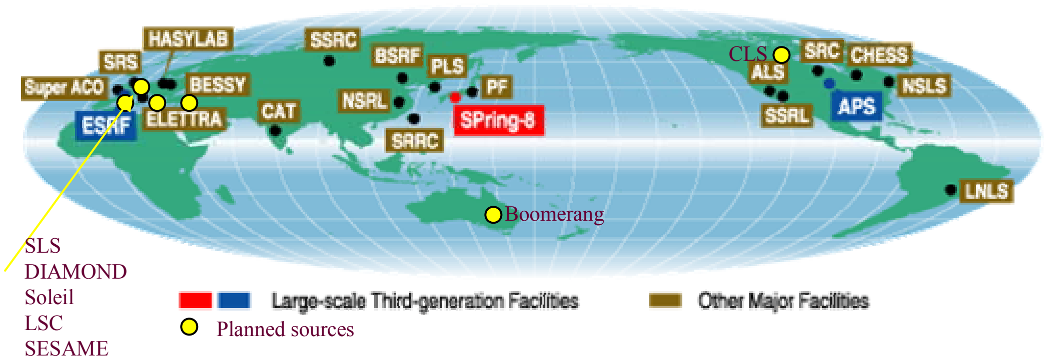
The Three **Key** SR Features

Brilliance: Fast sampling & mapping, Small size or weight of sample

Beam footprint: 2D or 3D studies at mm to sub-micron length scale

Wavelength tunability: Choose the energy to suit the problem

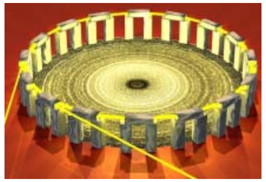




SR sources around the world

http://www.spring8.or.jp/ENGLISH/general_info/overview/sr.html

SR has enabled the development of techniques for advanced Materials Science



SR-ARCH is
Growing Globally

DL, ESRF, LURE, ESRF, LURE, SLS, HASYLAB, BESSY II, APS, ALS, NSLS, PF, SPRING-8, BEJING are all active in attracting new users.

DL has played a key facilitator role in SR-ARCH networking

New SR sources include ARCH in their research portfolio.

High profile of SR in recent ARCH conferences: Enabling technology

Partnerships between SR scientists and archaeologists/museum scientists

Cultural Heritage highly valued in Europe

ARCH is multi-disciplinary and fundamentally of international interest

Lustres

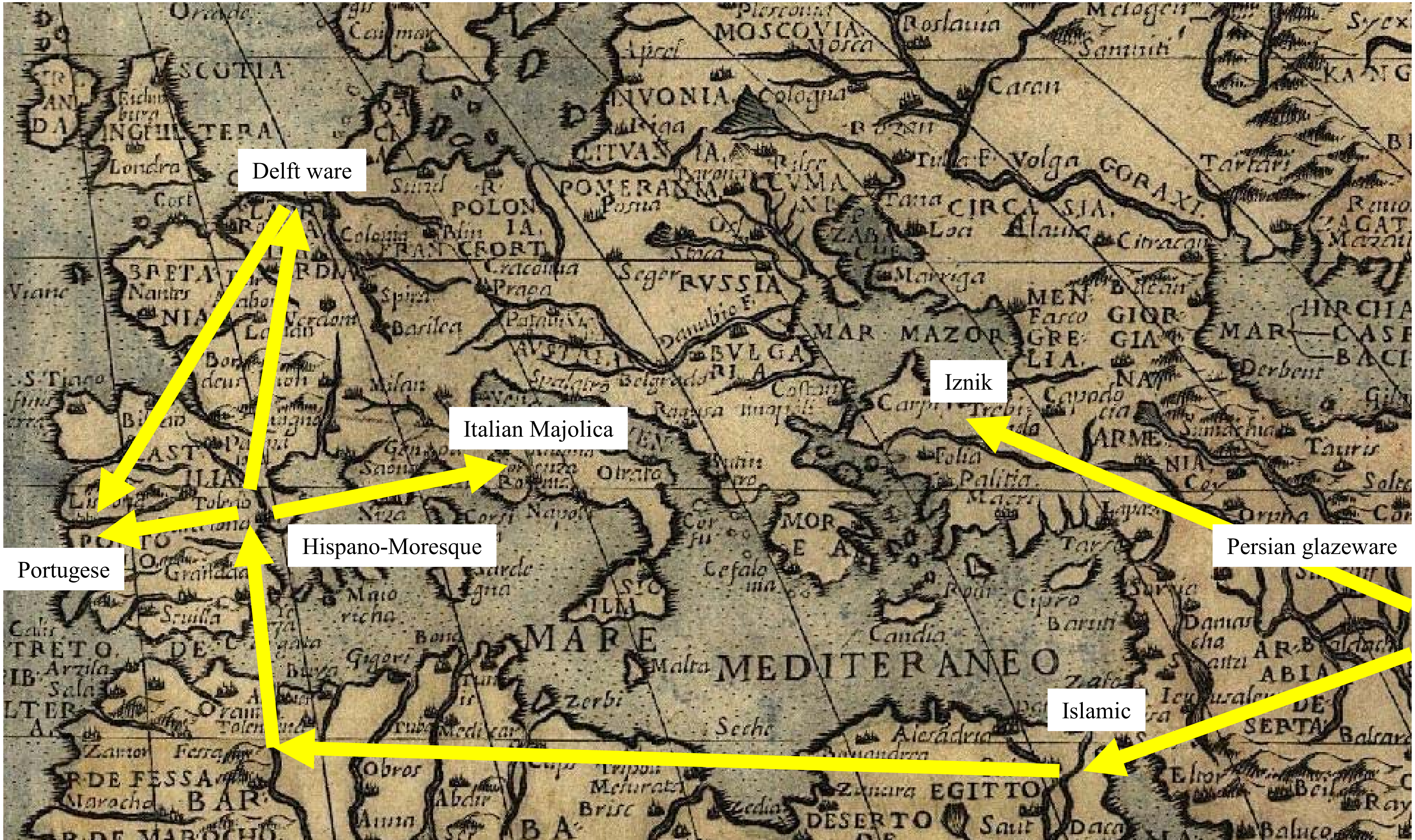
THE ANCIENT LUSTRE CERAMICS

LUSTRE : Is a decorative metal-like film applied on the surface of medieval glazed luxury ceramics pottery giving a gold-like metallic shine.

A typical 15th century lustre decorated dish from de Hispano Moresque workshop of Paterna.

Museum of Ceramics, Palau Real, Barcelona

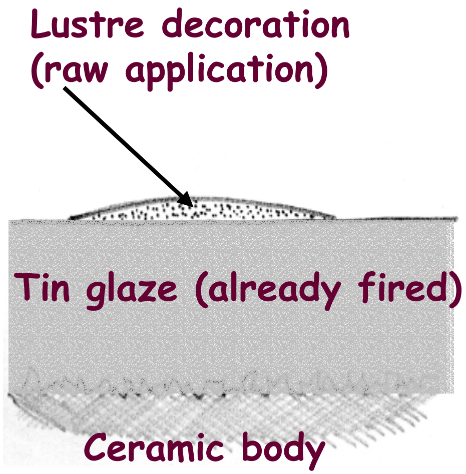
Ceramic Glaze Technology Transfer

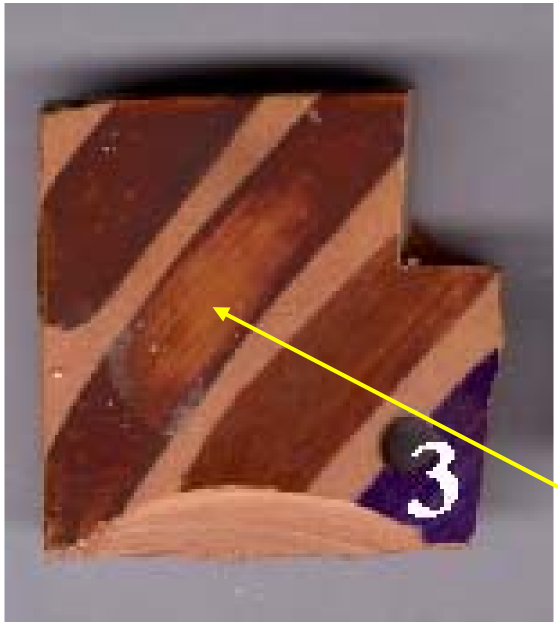


Vniversale descrittione di tvtta la terra conoscivta fin qvi. Forlani, Paolo. Published in Venezia]: F. Berteli, 1565.

METHODOLOGY OF PRODUCTION OF THE LUSTRE LAYER

Lustre is applied by brush on a previously fired tin glazed ceramic and fired in special kilns at near 600°C with a reduction process.

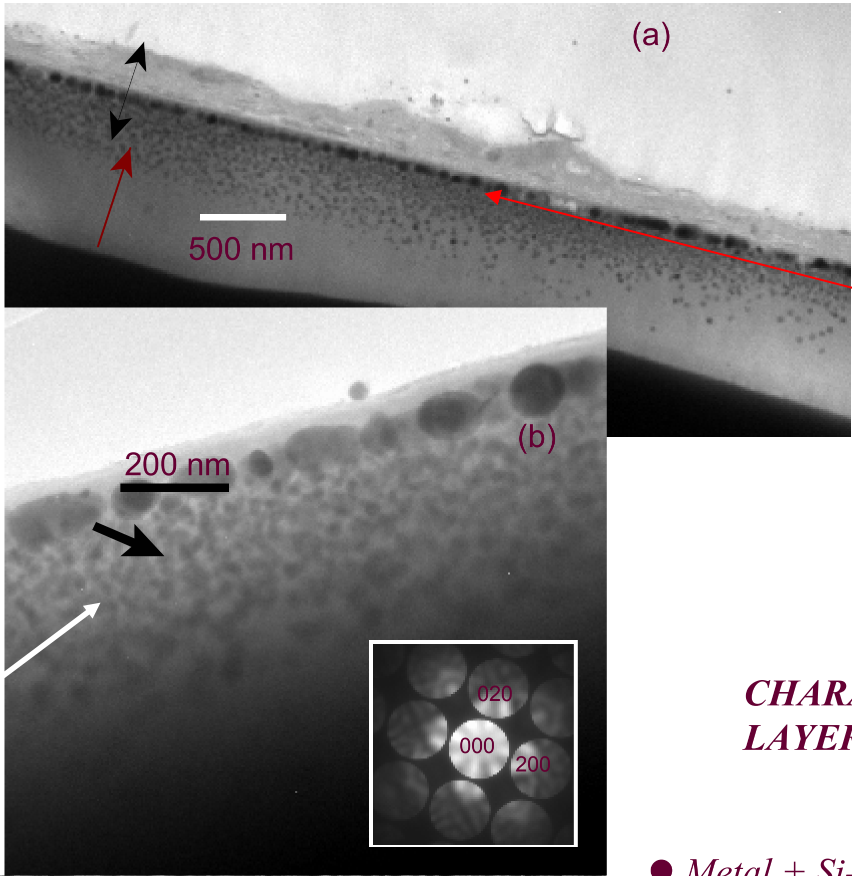




After firing the excess of powder is mechanically removed to show the metallic lustre.

Composite layer 200-500 nm

tin glaze

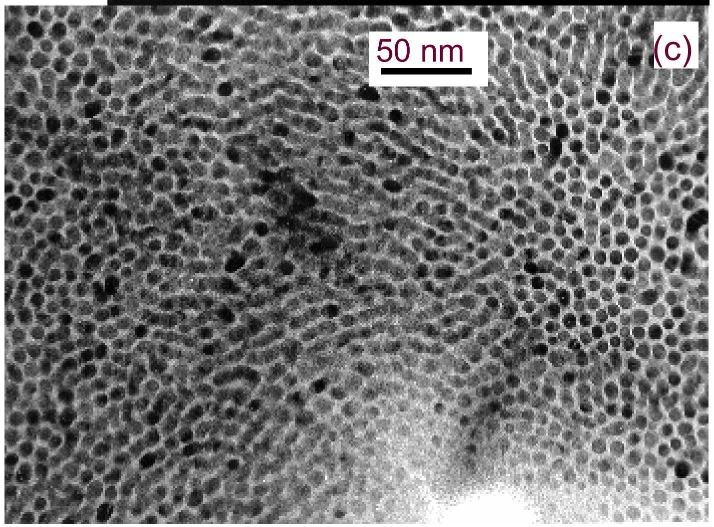


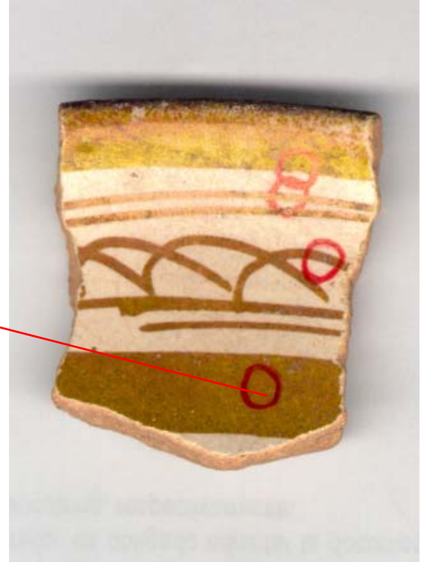
Glassy layer

copper nanocrystals

(10-50 nm size)

Silver nanocrystals (5-10 nm size)





CHARACTERISTICS OF THE LUSTRE LAYER:

- *Metal + Si- glass composite layer (200-500 nm thickness) of typical composition 13%Al_2O_3, 71%SiO_2, 1.7%FeO, 1.5%PbO, 2.5%K_2O, 5%CaO and 4.5%Na_2O.*

- *Copper and silver nanocrystals (5 to 50 nm size).*

- *The lustre layer is stuck on the tin opacified lead glaze, of typical composition 49%SiO_2, 36%PbO, 5%SnO_2, 6% K_2O, 2%Al_2O_3 and 2%CaO.*

The problem of cinnabar

- **Composition of the lustre powder found in the workshop (Paterna s. XIII). (Molera et al., 2001)**

Table I. Lustre raw powder composition deduced from chemical (X-ray Fluorescence) and phase analysis (X-ray Diffraction) and comparing with the chemical composition of the workshop clay.

	Workshop clay	Quartz	Haematite	Tenorite (CuO)	Ag_2S	Cinnabar (HgS)
Composition (wt%)	40	7.5	7.5	13	2	30

- *Caiger Smith reports ancient luster recipes containing cinnabar ("active recipes").*
- *Since the final lustre decorations do not show any presence of cinnabar.*

What is the role of cinnabar in the production of Lustre?

… a third part of the blood of a red-headed man

XLVIII. SPANISH GOLD

There is also a gold, called Spanish gold, which is **prepared from red copper, powder of basilisk and human blood and vinegar**. The heathen,who are said to be skilled in this art, produce basilisks for themselves in this way.They have a structure under the ground, made above, below and all round with stones, with two tiny openings, so small that scarcely any light can be seen through them.

In this they place **two old fowls, twelve or fifteen years old**, and they give them plenty to eat. When they have become plump, with the heat of their fatness they copulate and lay eggs. When these have been laid, the fowls are taken away and **toads are introduced to sit on the eggs**, and bread is given them for food. When the eggs are hatched, male chicks emerge like hens' chicks.

After seven days they grow the tails of serpents. If the structure were not paved with stone they would immediately enter the ground. Careful of this,their owners have round bronze vessels of large size, perforated everywhere and with narrow mouths, and they place the chicks in these, block up the mouths with copper lids, and bury them in the ground.

For six months they are nourished with the fine earth entering through the holes. After this, they uncover the vessels and place them on a large fire until the beasts within are completely burned. When this has been done and the vessels have cooled, they take them out and carefully grind them, **adding a third part of the blood of a red-headed man**, which has been dried and ground. These two compounds are mixed with sharp vinegar in a clean vessel.

Then they take very thin sheets of pure red copper, and they smear this preparation over them on each side and put them on the fire. When they are white-hot, they take them off and quench them in the same preparation and wash them, and so they proceed for a long time until this preparation eats through the copper, which,thereupon, takes on the weight and colour of gold. **This gold is suitable for all work**.

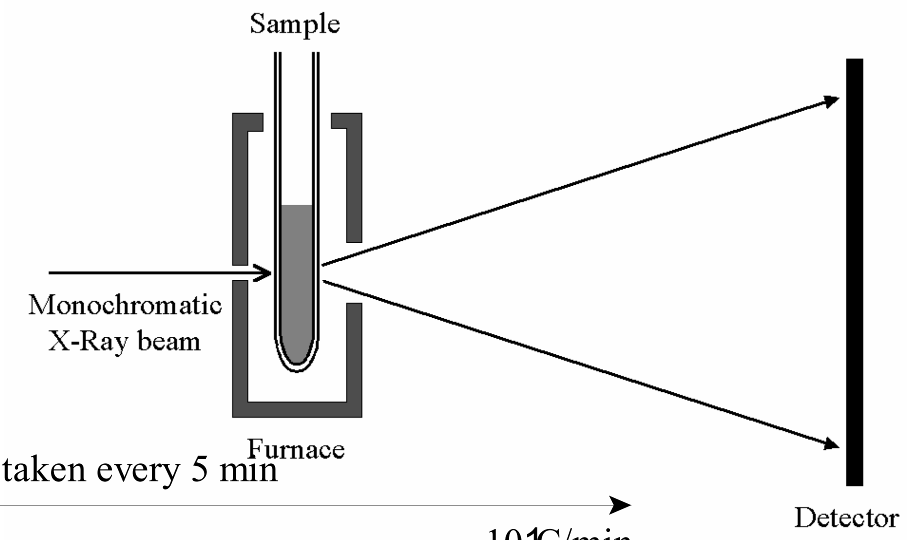
Red-haired males watch out! It works!

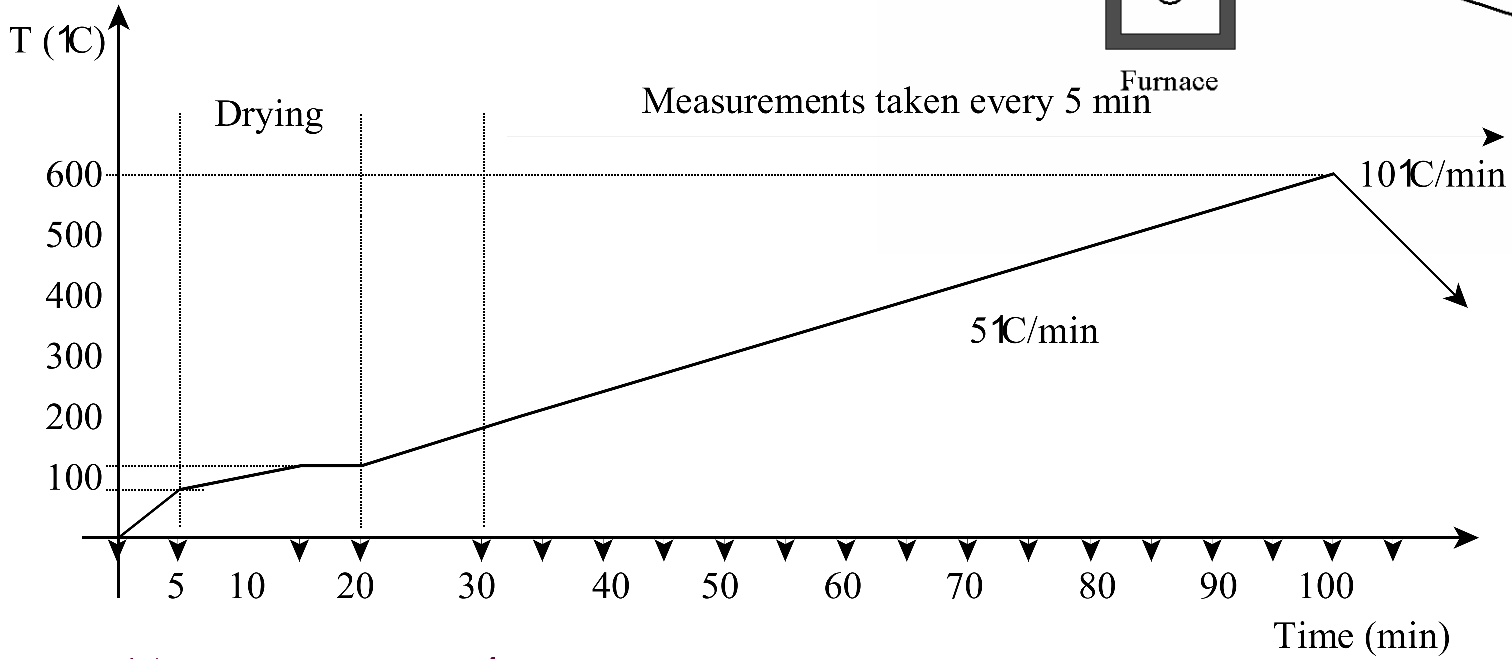
Methods

Theophilus: The Various Arts (De Diversis Artibus) **Published by Clarendon Press, 1986,edited and translated by C.R.Dodwell.**

Setup details at ESRF beamline ID15B.

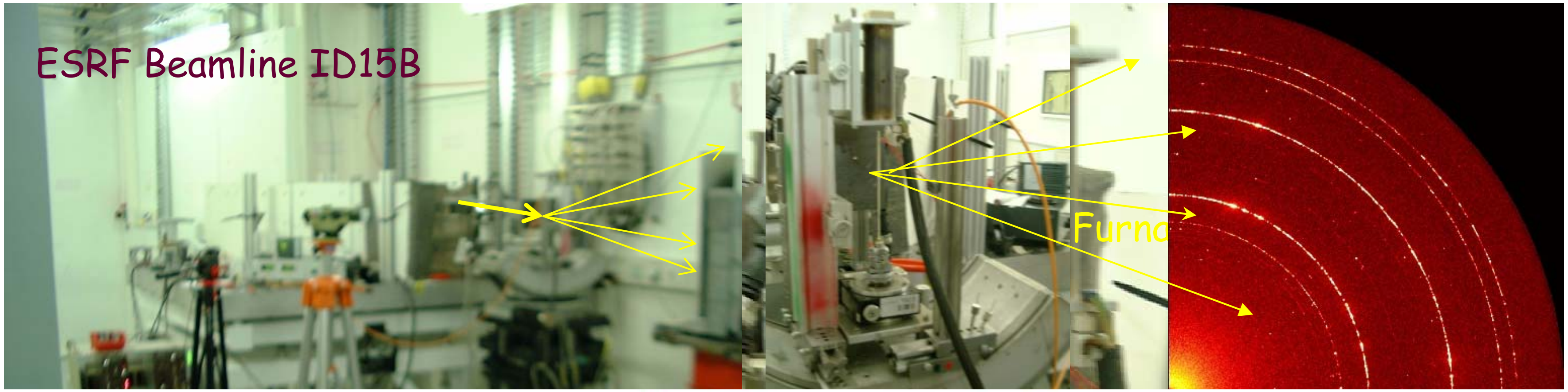
- *high photon flux*
- *high energy X-rays (~90 keV)*
- *MAR345 imaging plate detector.*

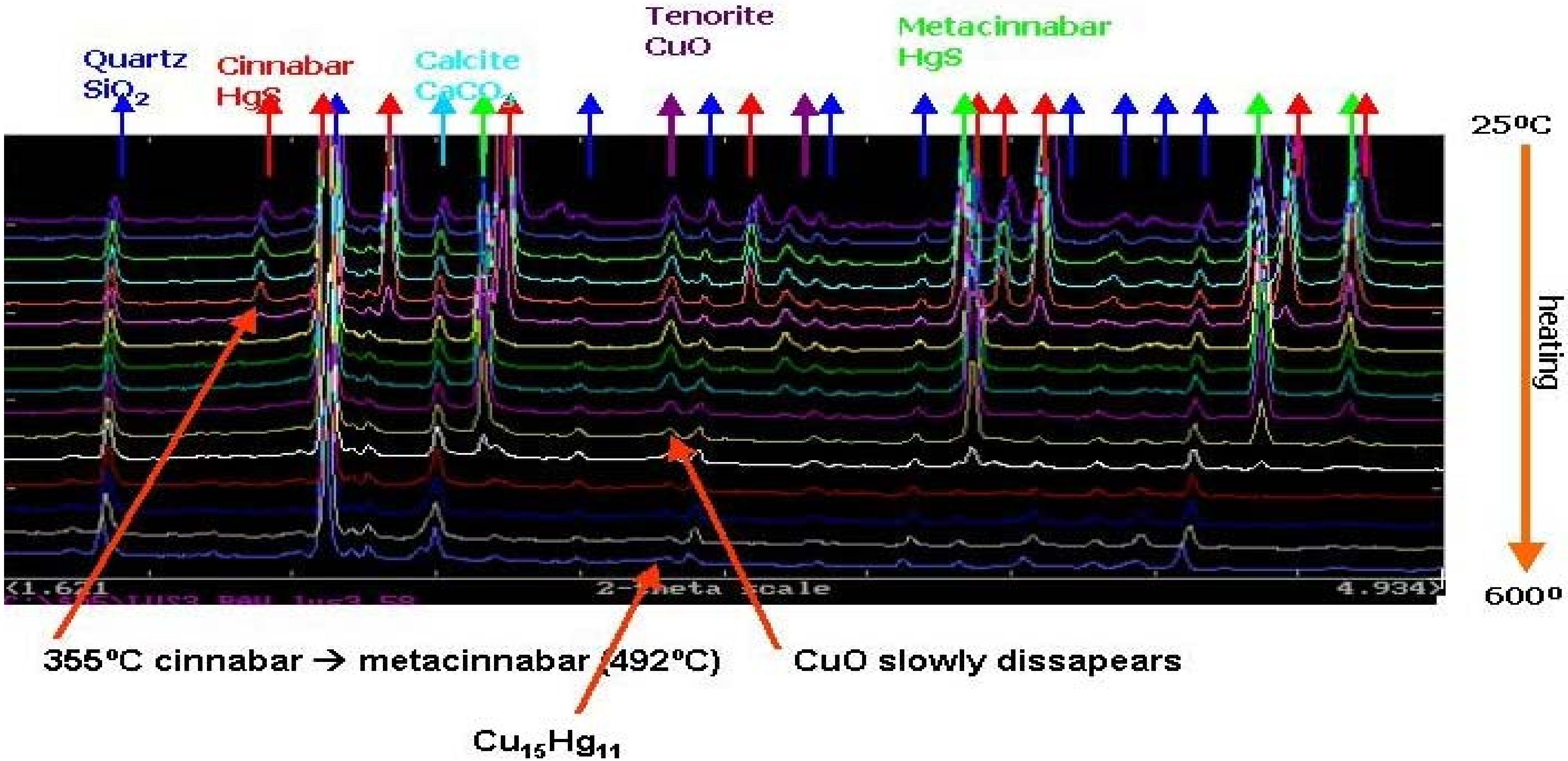




Heating protocol

Time-Resolved Diffraction with hard X-rays





Synthetic mixtures

● ***Mixture S3/N :***

62.5% Illitic clay + 12.5% hematite + 6.25% CuO+ 6.25% $AgNO_3$: without cinnabar

● ***Mixture S3/C :***

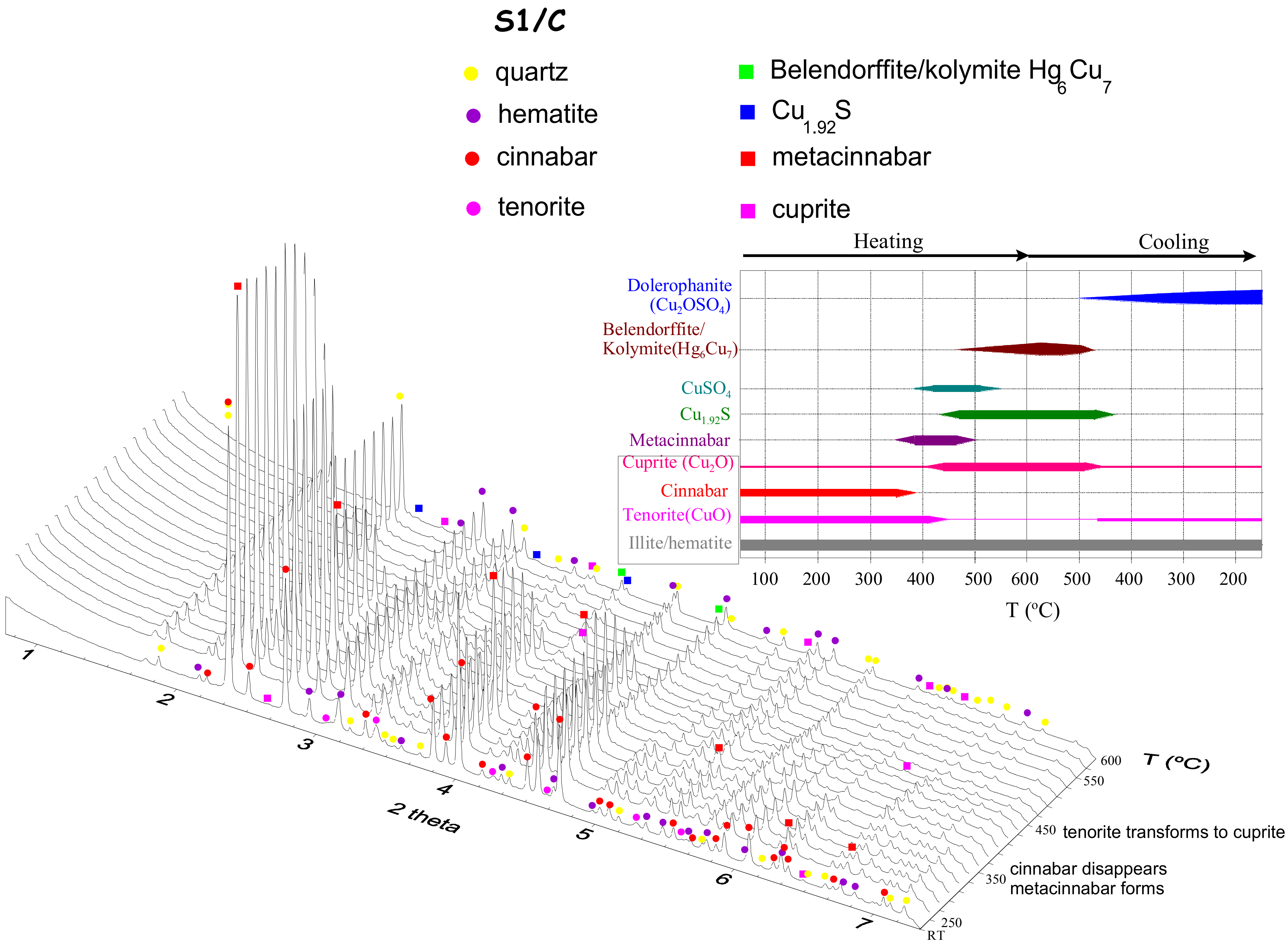
50% Illitic clay + 10% hematite + 5% CuO+ 5% $AgNO_3$ + 30% cinnabar

● ***Mixture S1/C :***

50% Illitic clay + 10% hematite + 10% CuO + 30% cinnabar

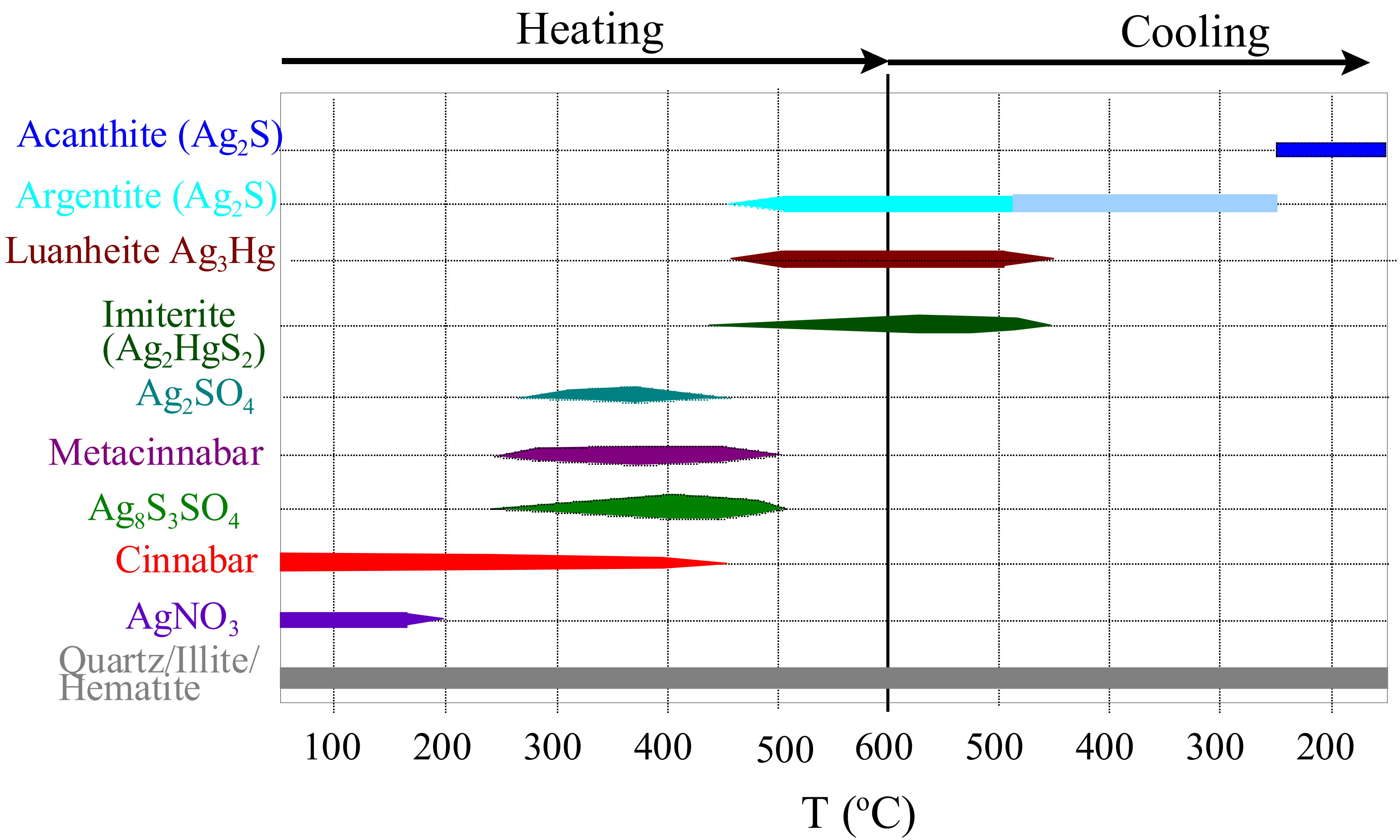
● ***Mixture S2/C :***

50% Illitic clay + 10% hematite +10% $AgNO_3$ + 30% cinnabar



S1/C
quartz
hematite
cinnabar
tenorite
Belendorffite/kolymite Hg_6Cu_7
$Cu_{1.92}S$
metacinnabar
cuprite
Heating
Cooling
Dolerophanite (Cu_2OSO_4)
Belendorffite/ Kolymite(Hg_6Cu_7)
$CuSO_4$
$Cu_{1.92}S$
Metacinnabar
Cuprite (Cu_2O)
Cinnabar
Tenorite(CuO)
Illite/hematite
100 200 300 400 500 600 500 400 300 200
T (ºC)
1 2 3 4 5 6 7
2 theta
T (ºC)
600
550
450 tenorite transforms to cuprite
350 cinnabar disappears
metacinnabar forms
250
RT

S2/C PHASE TRANSFORMATIONS



Review of main results

- Silver is more easily reduced than copper. In the mixture without cinnabar, metallic silver is formed at temperatures of about 350ºC. Copper oxide stays as tenorite (CuO).

- The decomposition of cinnabar produces the reduction of the tenorite (CuO) to cuprite (Cu_2O) and the formation of copper and silver sulfates and sulfides at temperatures below 500ºC.

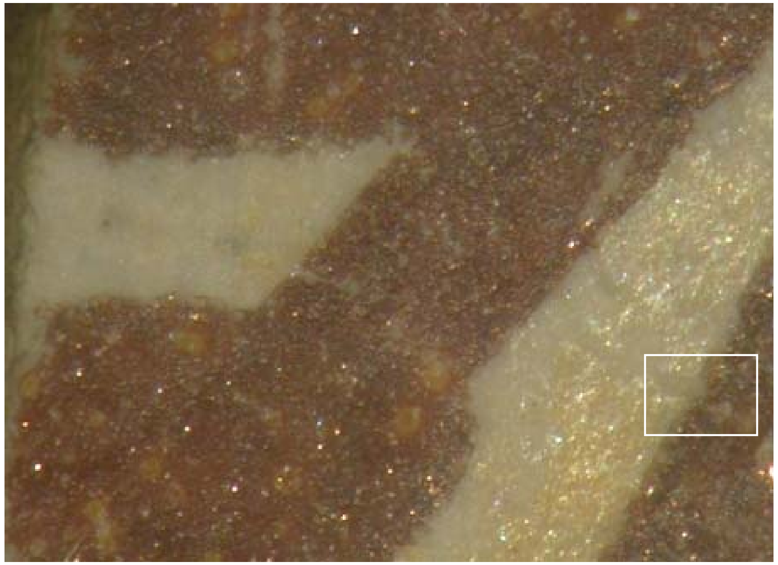
- At temperatures above 500ºC copper and silver amalgams are formed.

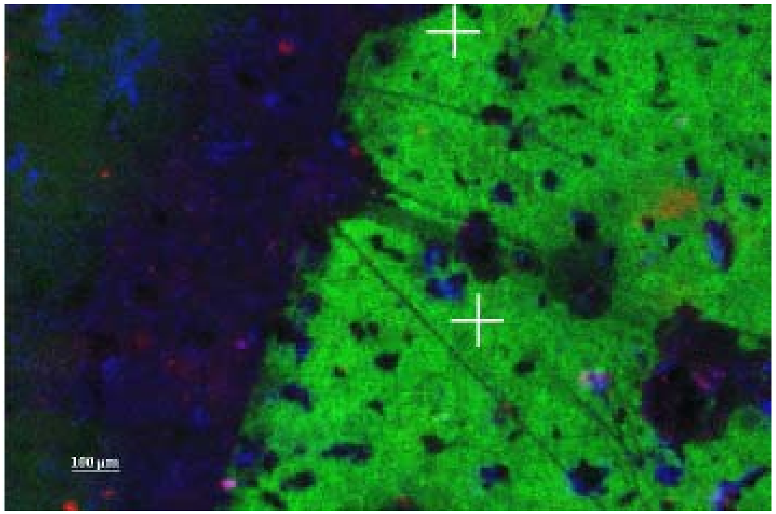
- During the cooling, a cubic silver sulfide (argentite) is formed which changes at low temperatures changes to the monoclinic form (acanthite).

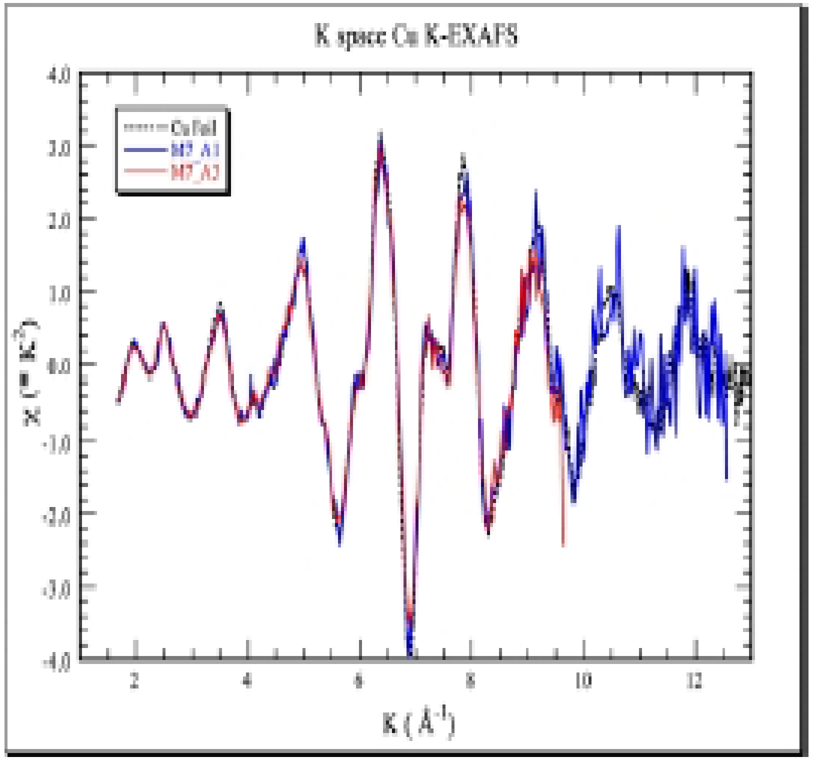
- During the cooling, the copper sulfate, Dolerophanite is the final stable phase.

µXAS

Micro-XRF/XAS of Hispano-Moresque glazes





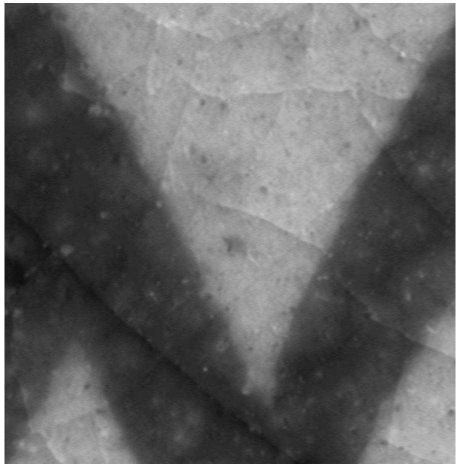


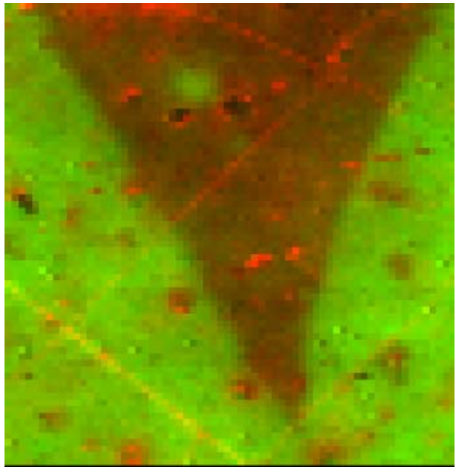
Cu K-edge EXAFS at two positions on glaze and copper foil.

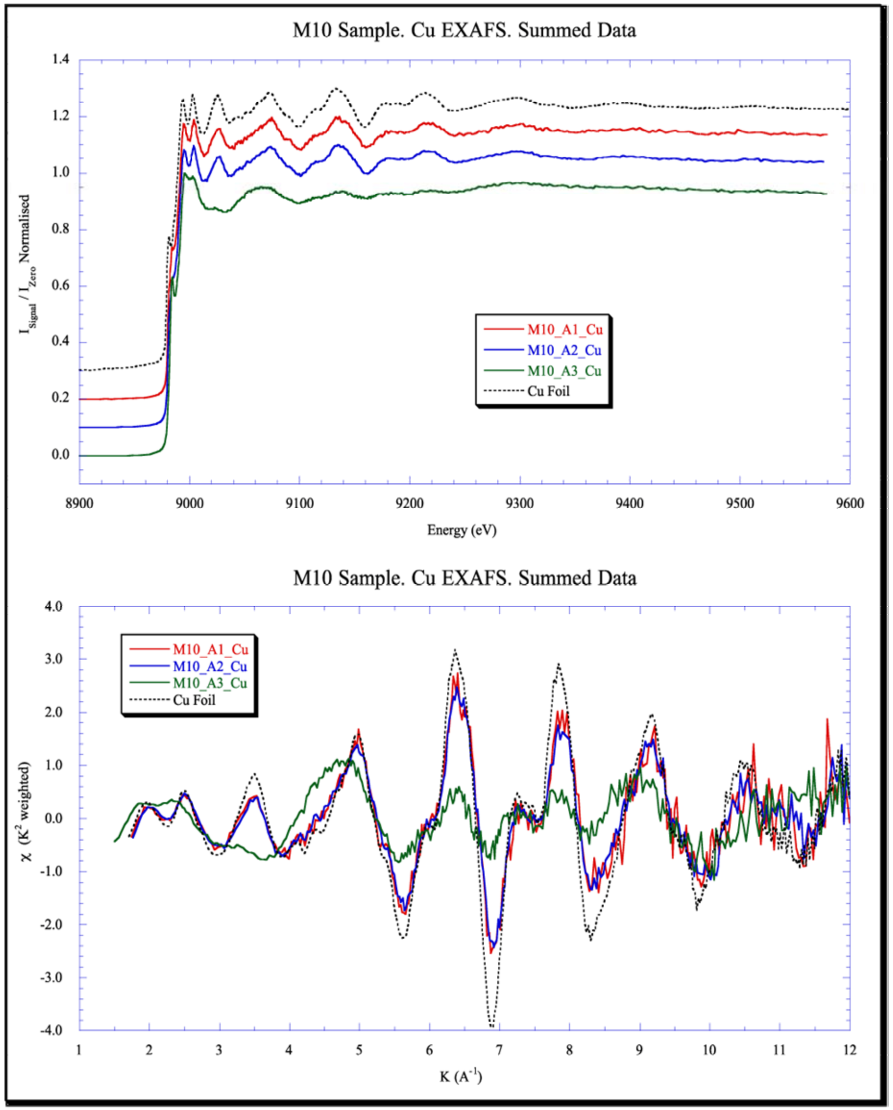
Tricolour elemental map of glazed area.
Blue: Calcium, Green : Copper , Red : Iron

From *MicroXAFS studies into the oxidation states of different coloured Islamic and Hispano-moresque lustre decorations, ALS Compedium, May 2002.*
<u>A.D.Smith</u>, T.Pradell, J. Molera, M.Vendrell, M.Marcus and E.Pantos

Micro-XRF/XAS of Hispano-Moresque glazes





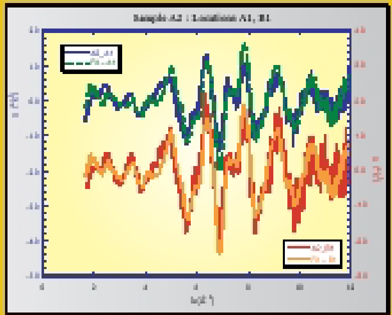


Tricolour elemental map of glazed area:
Blue: Calcium, Green: Copper, Red: Iron.

EXAFS at the Cu K-edge for three copper-rich areas compared to EXAFS of copper foil.

ALS Beamline 10.3.2

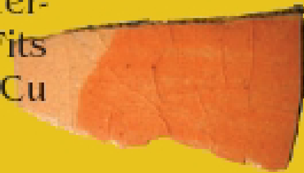
Reproduction of Hispano-Moresque glazes



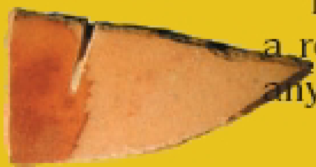
The lustre layer has acquired a red–brown colour.

Some variation in copper phases is observed across the sample, EXAFS can be fitted tolerably well by combining Cu metal with Cu_2O. Fits shown are for 50% Cu (location A1) & 60% Cu (location B1), remainder Cu_2O.

A2

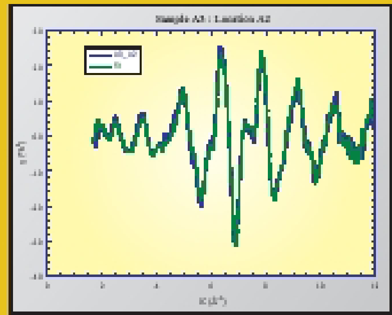


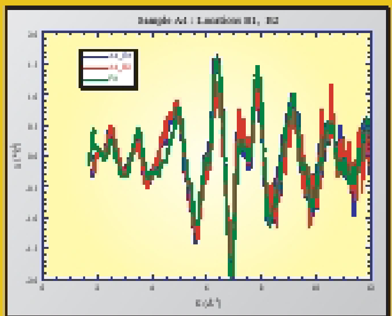
A3



The lustre layer has a metallic finish.

The Cu EXAFS can be fitted to Cu metal with a reduced amplitude of 80%. The presence of any oxide phase can no longer be confirmed.





Fully fired. The lustre layer has a deep metallic shine.

Again the Cu EXAFS can be fitted to pure metal, however for this sample an amplitude reduction of 50% is required, consistent with nanoclustering of the copper.

A4

What is the role of cinnabar in the production of Lustre?

- Copper oxides are reduced.
- Metallic silver is not formed at temperatures below 350ºC.
- Copper and silver sulfides and sulfates are formed at temperatures of about 500ºC.

Conclusions

Copper and silver sulfides and sulfates are the forms adequate to react with the tin glaze. A cationic exchange (the copper and silver of the luster raw materials with potassium and sodium belonging to the tin glaze) is needed to introduce copper and silver into the glaze

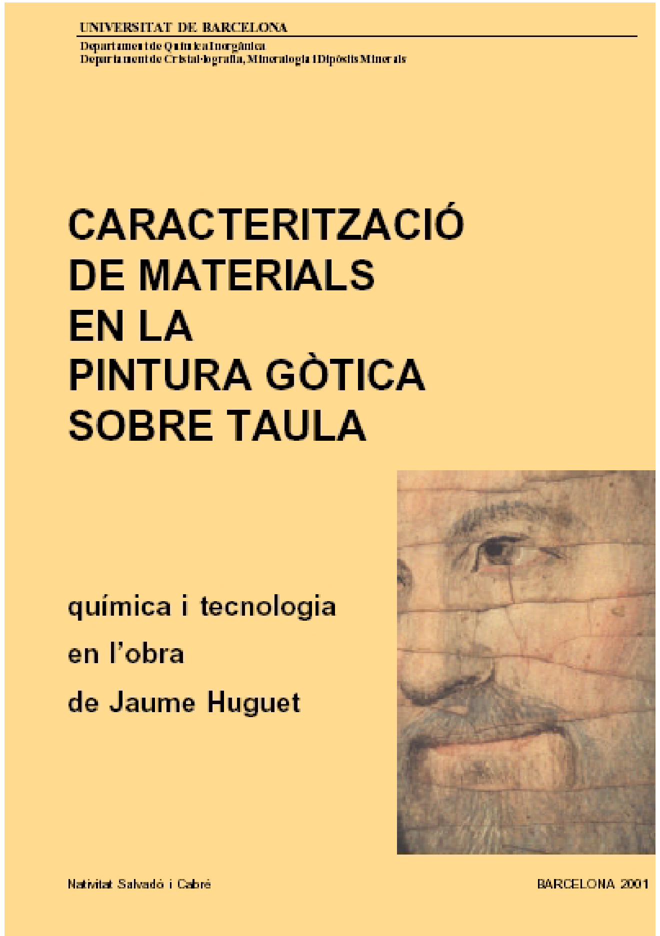
The presence of Sulfur does not allow metallic silver to form at low temperatures and reduces the copper oxides which otherwise are not easily reduced. At 500ºC silver and copper sulfides and sulfates are formed.

Huguet

Gothic Catalan Paintings

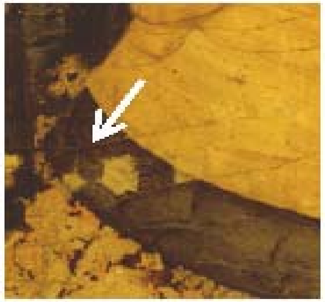
Chapel of St Agatha, Barcelona, Catalunia

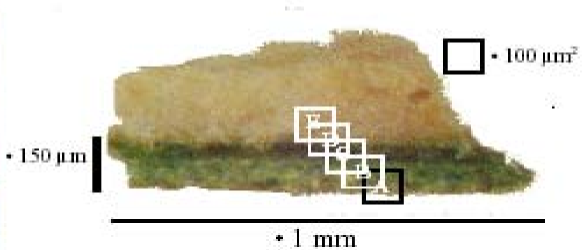
Jaume Huguet
1415-1492
Barcelona

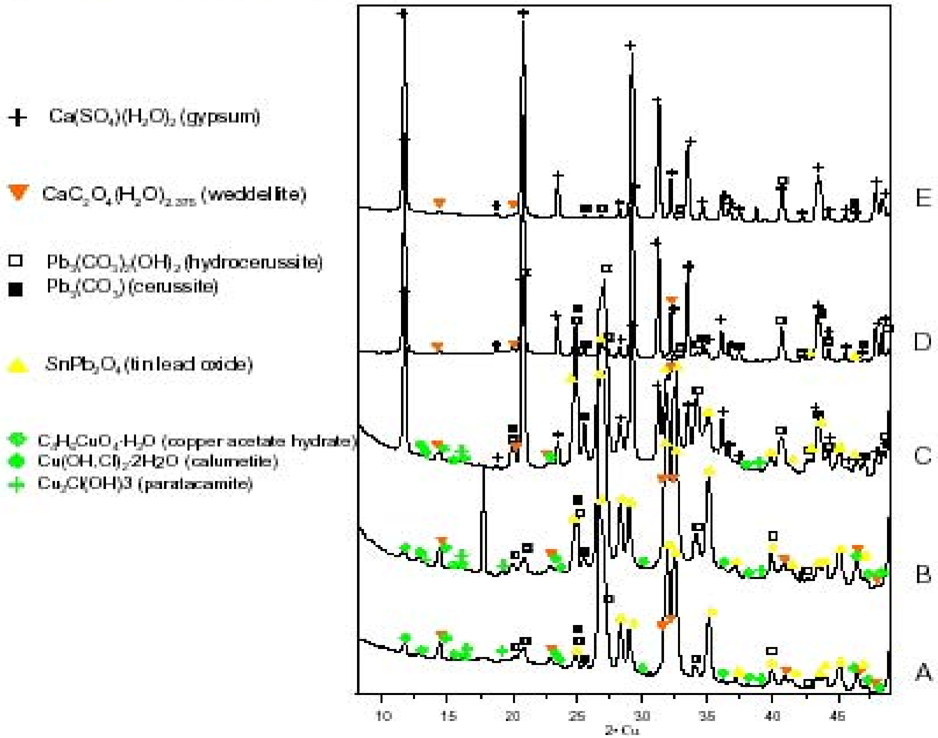


XRD of green pigments from Gothic altarpieces

Jaume Huguet born ca. 1415, Valls died 1492, Barcelona







SRS station 9.5

According to Ancient Sources

Theophilus: The Various Arts (De Diversis Artibus)

XXXV. SALT GREEN (DE VIRIDI SALSO)

If you wish to make a green colour take a piece of oak of whatever length and width you like, and hollow it out in the form of a box. Then take some copper and have it beaten into thin sheets, as wide as you like but long enough to go over the width of the hollow box.

After this, take a dish full of salt and, firmly compressing it, put it in the fire and cover it with coal overnight. The next day, very carefully grind it on a dry stone.

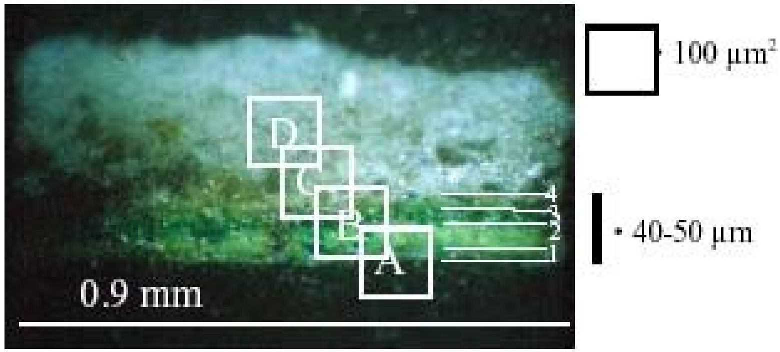
Next, gather some small twigs, place them in the above-mentioned hollow box so that two parts of the cavity are below and a third above, coat the copper sheets on each side with pure honey over which you sprinkle pounded salt, place them together over the twigs and carefully cover them with another piece of wood, prepared for the purpose, so that no vapour can escape.

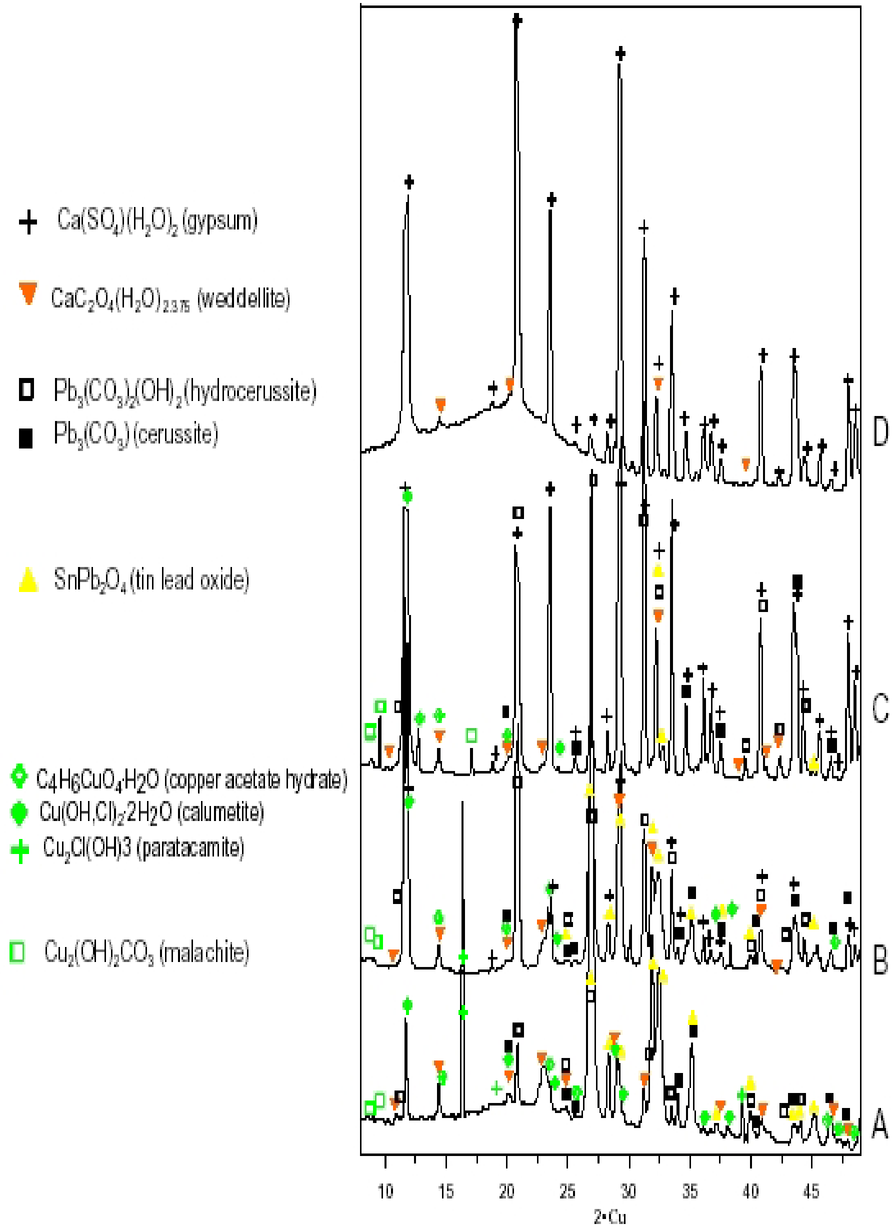
Next, have an opening bored in a corner of this piece of wood through which you can pour warm vinegar or hot urine until at third part of it is filled, and then stop up the opening. You should put this wooden container in a place where you can cover it on every side with dung.

After four weeks take off the cover and whatever you find on the copper scrape off and keep. Replace it again and cover it as above.

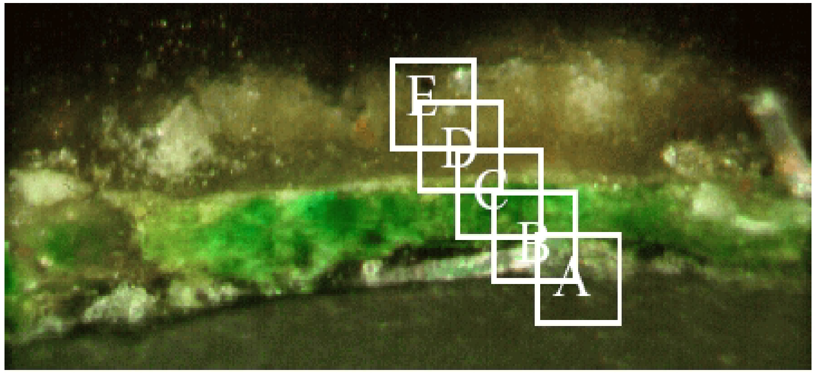
Published by Clarendon Press, 1986,edited and translated by C.R.Dodwell. ISBN 0-19-82206-8

Retaule de Sant *Bernadí* i l'Angel Custodi





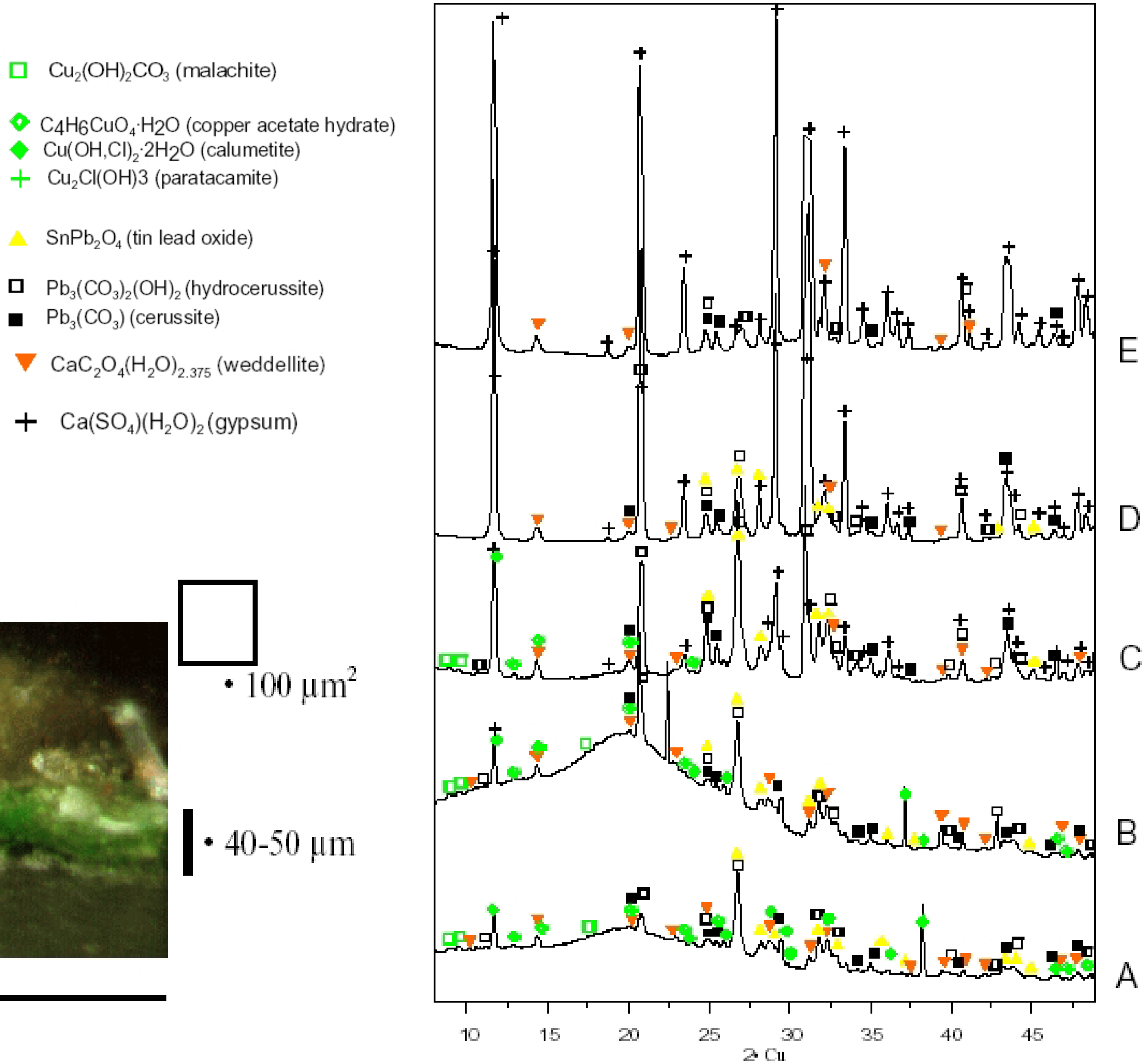
XRD of green pigments from Gothic altarpieces



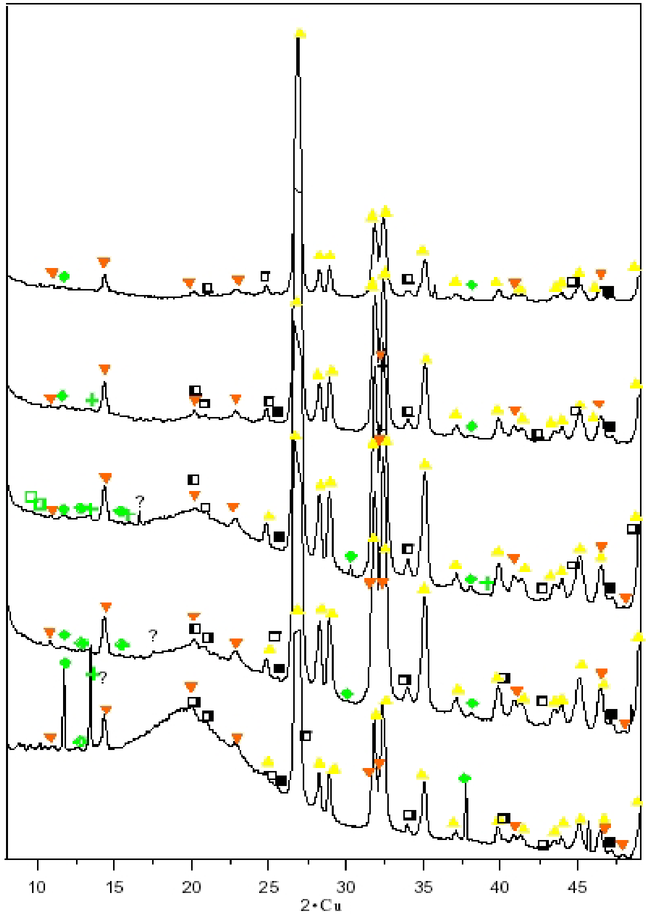
• 100 µm²

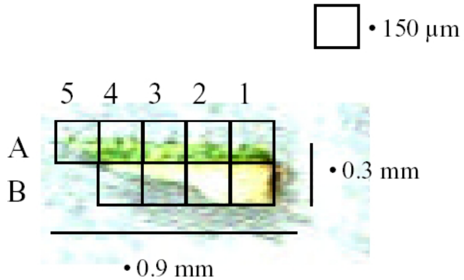
• 40-50 µm

• 1 mm

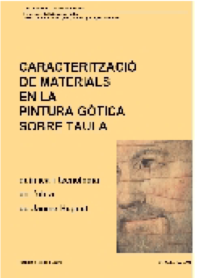


Retaule de Sant Abdó I Sant Semen

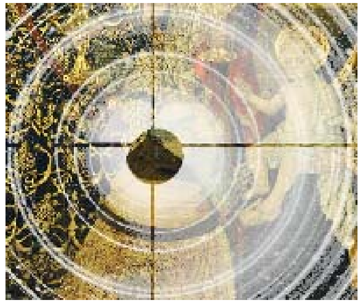




- $SnPb_2O_4$ (tin lead oxide)
- $C_4H_6CuO_4 \cdot H_2O$ (copper acetate hydrate)
- $Cu(OH,Cl)_2 \cdot 2H_2O$ (calumetite)
- $Cu_2Cl(OH)3$ (paratacamite)
- $Cu_2(OH)_2CO_3$ (malachite)
- $Ca(SO_4)(H_2O)_2$ (gypsum)
- $CaC_2O_4(H_2O)_{2.375}$ (weddellite)
- $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite)
- $Pb_3(CO_3)$ (cerussite)



What has been learned about Jaume Huguet's pigments



- *The green pigment is an artificially obtained mixture of phases. Some old recipes (Theophilus*) for obtaining green colours from metallic copper could be responsible for this mixture of compounds identified.*

- *The use of drying oil mixed with the egg tempera may be responsible a partial dissolution of the green pigment.*

- *The green is applied alone or mixed with white or yellow also of artificial origin.*

- ***Substrate***

Pure gypsum -$CaSO_4 \cdot 2H_2O$- was used to prepare the wooden surfaces to be painted.

IR spectroscopy has shown that it was mixed with an animal glue.

The presence of calcium oxalates like weddellite -$CaC_2O_4 \cdot (H_2O)_{x>2}$- are an alteration characteristic of the organic matter.

- ***Chromatic layers.***

Several layers of green mixed with

white:

$Pb_3(CO_3)_2(OH)_2$, hydrocerussite

$PbCO_3$, cerussite

yellow:

$SnPb_2O_4$, tin lead oxide

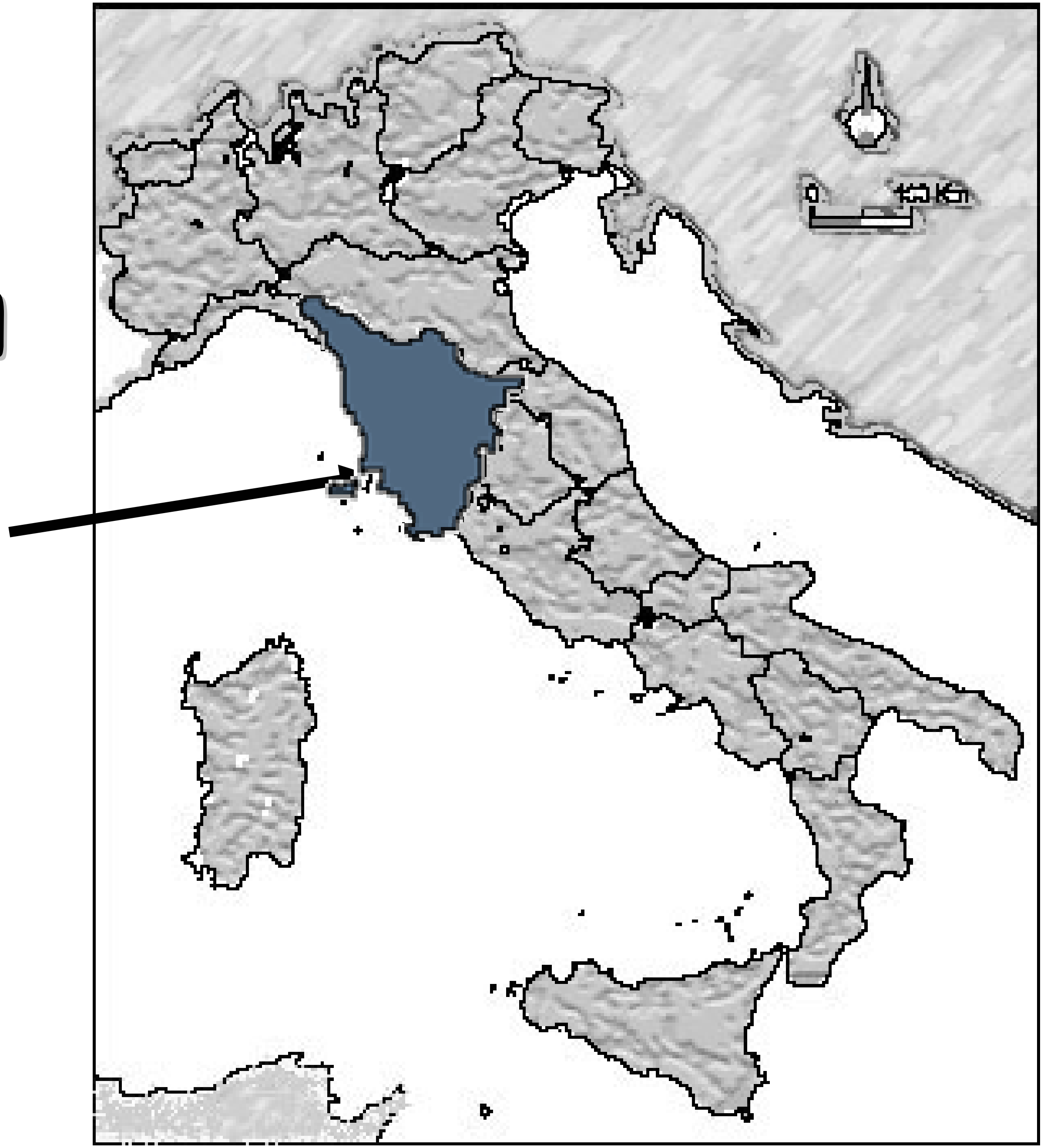
BG

In *Identification of copper based green pigments in Jaume Huguet's Gothic altarpieces by Fourier transform infrared micro-spectroscopy and synchrotron radiation X-ray diffraction*, N. Salvadó, T. Pradell , E. Pantos, M.Z.Papiz, J. Molera, M. Seco and M. Vendrell-Saz, J.Synch.Rad., July 2002.

Black Gloss pottery

NORTHERN AND CENTRAL ETRURIA

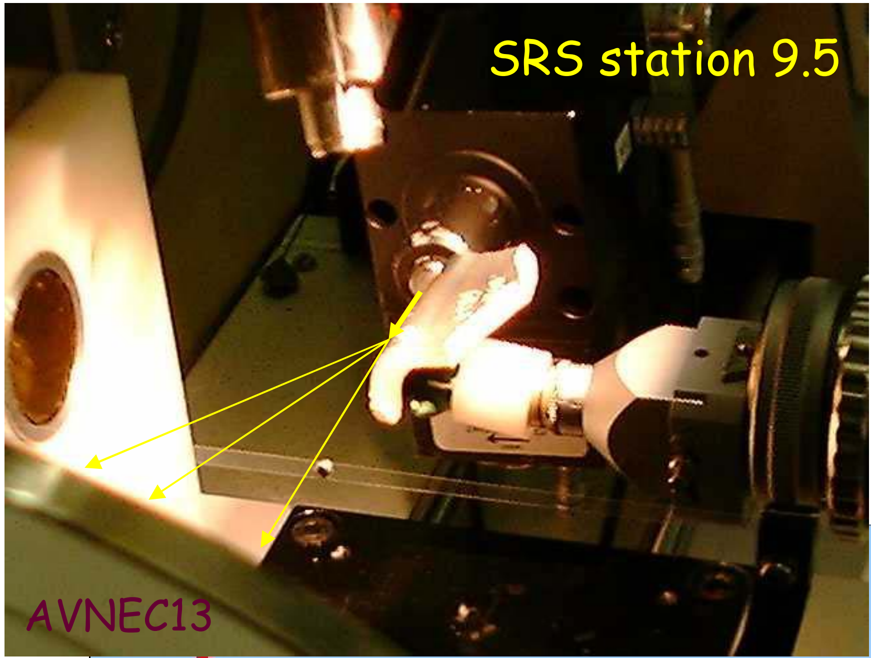
(MODERN TUSCANY)

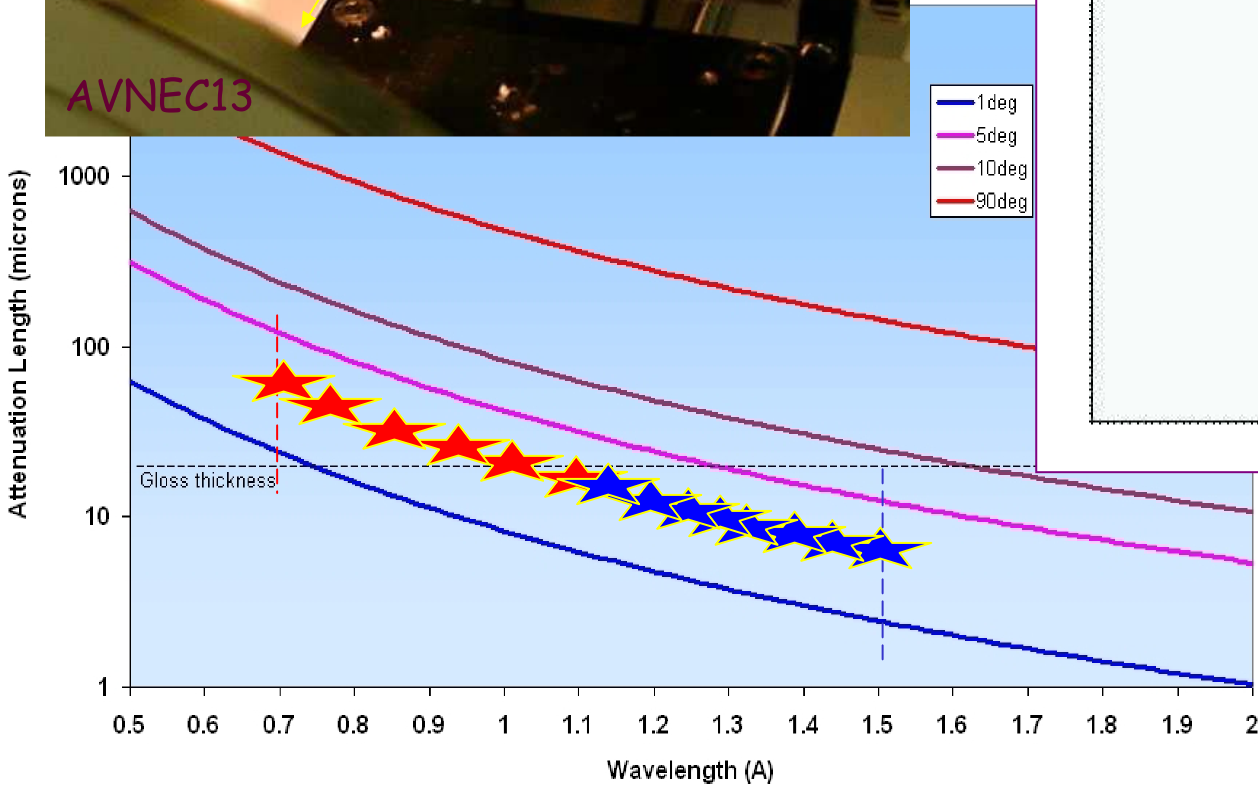


MATERIALS UNDER EXAMINATION

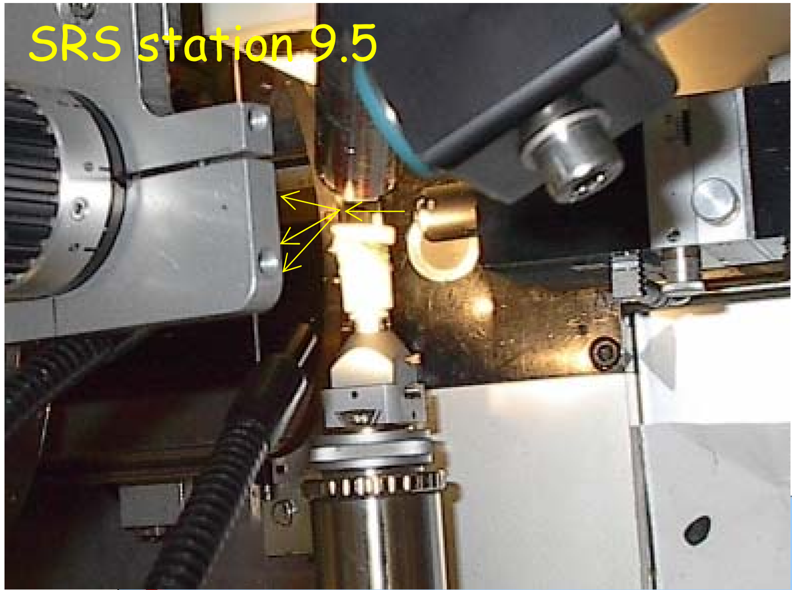
VISUAL APPEARANCE

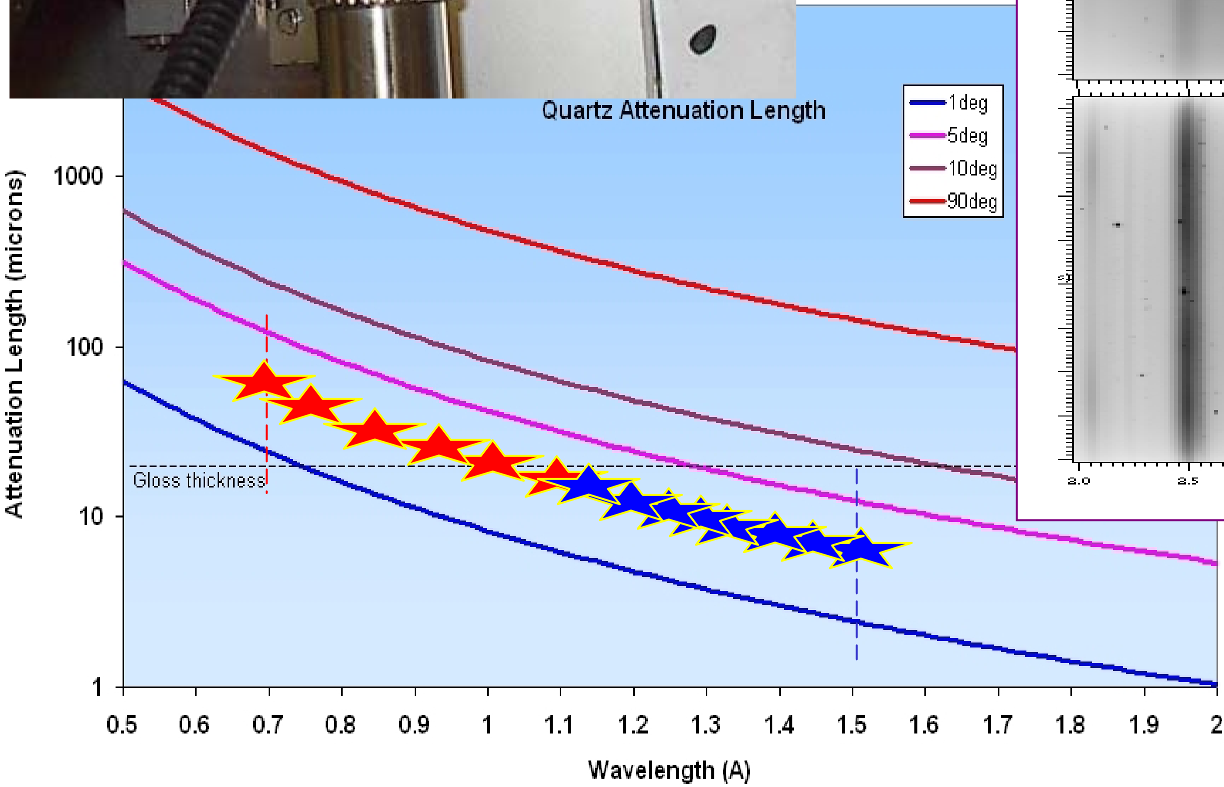
Depth profiling by tuning Wavelength

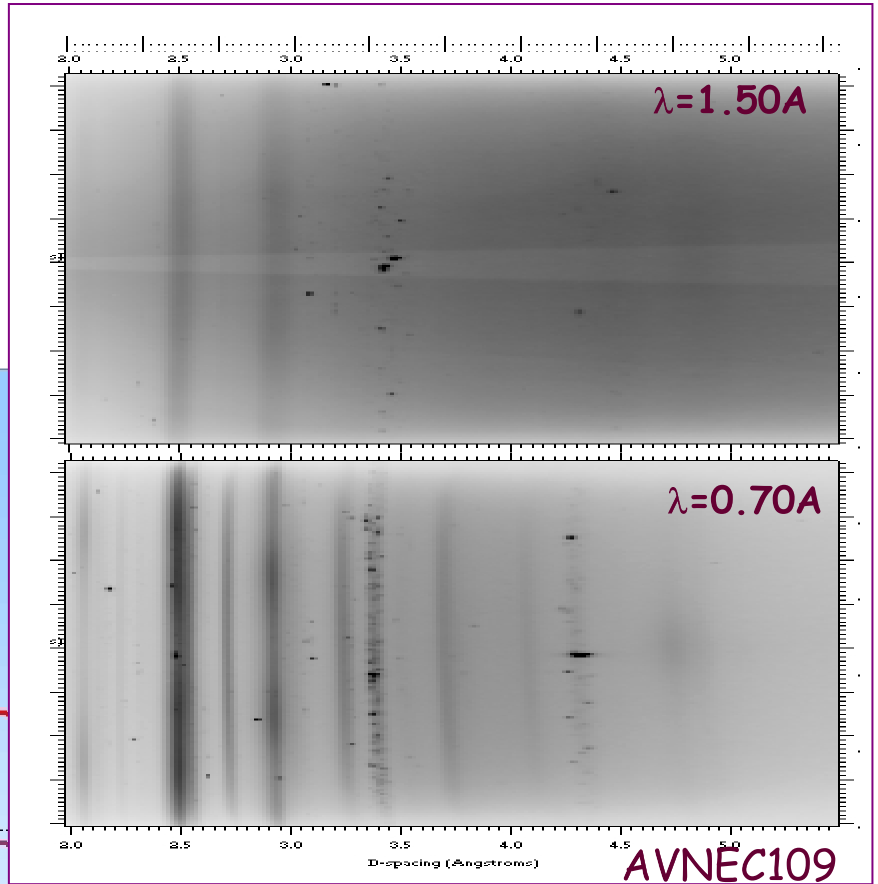




Depth profiling by tuning Wavelength

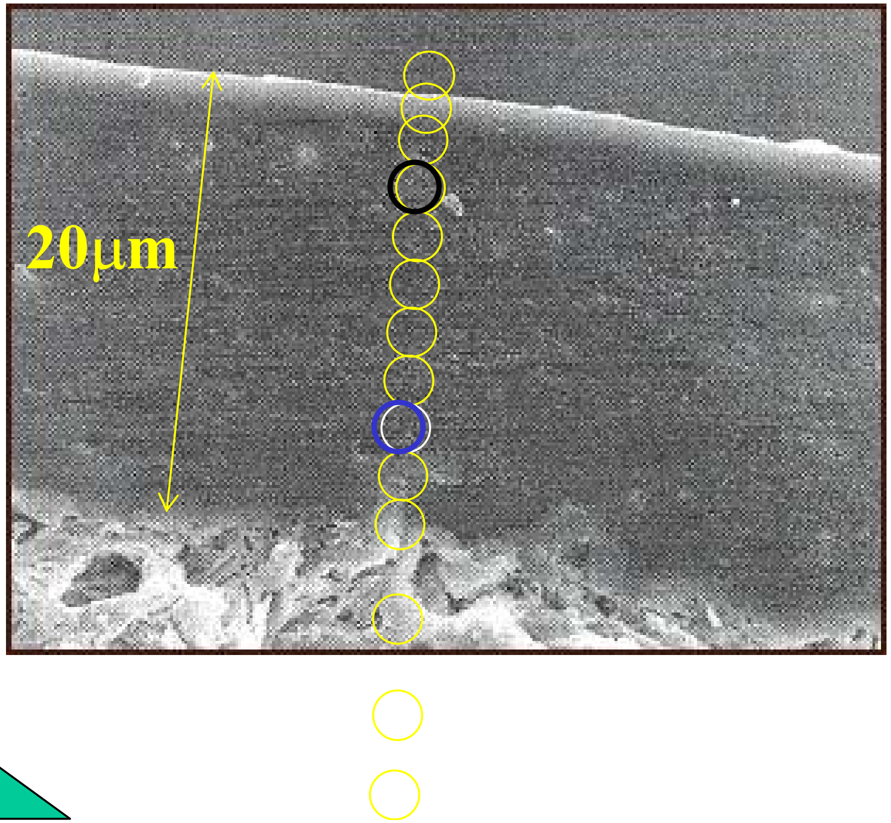


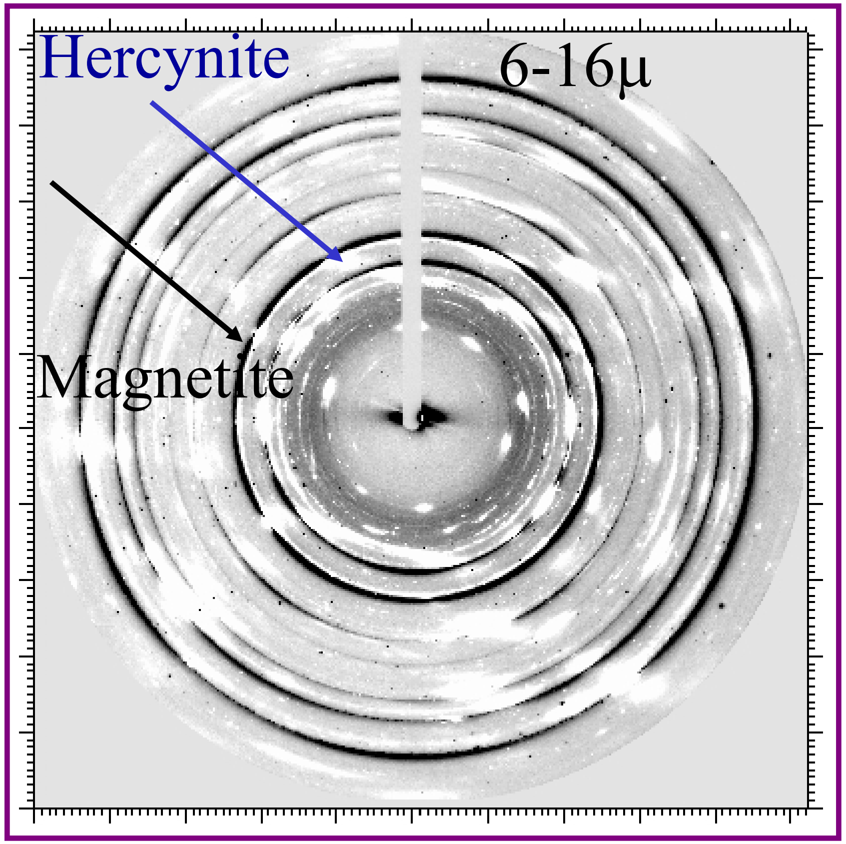




Depth profiling by micro-stepping across thin sections

Thetis Authentics, Athens

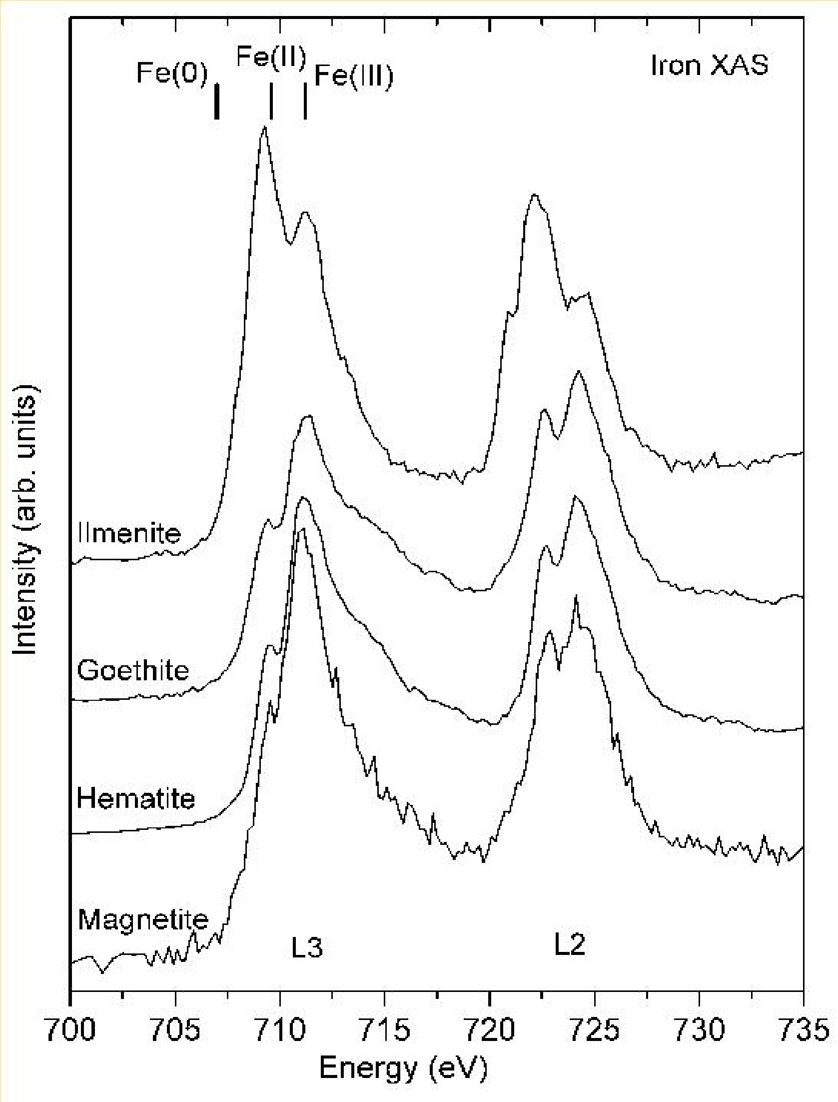


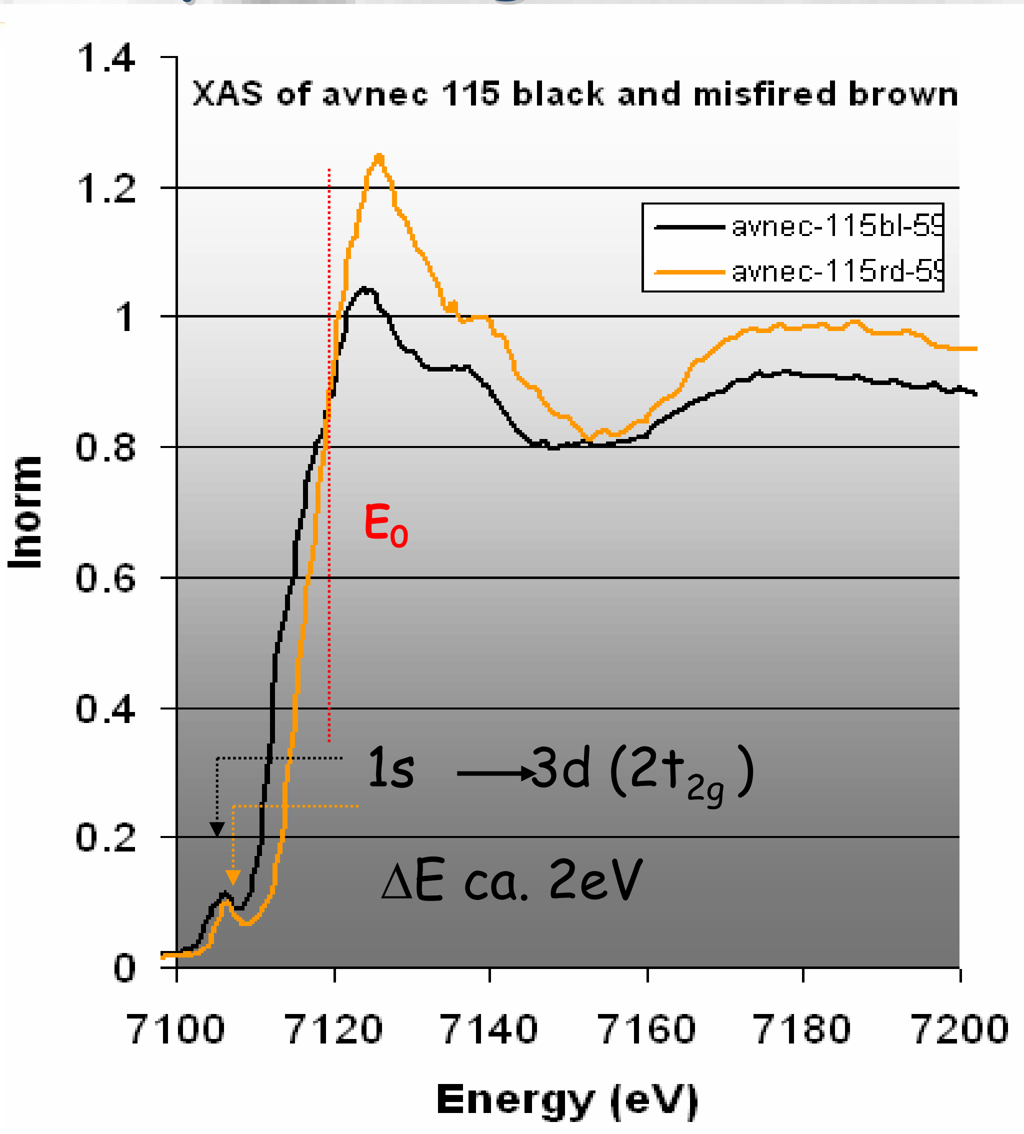


Manfred Burghammer
Microfocus Beamline ID13
European Synchrotron Radiation Source

XAS

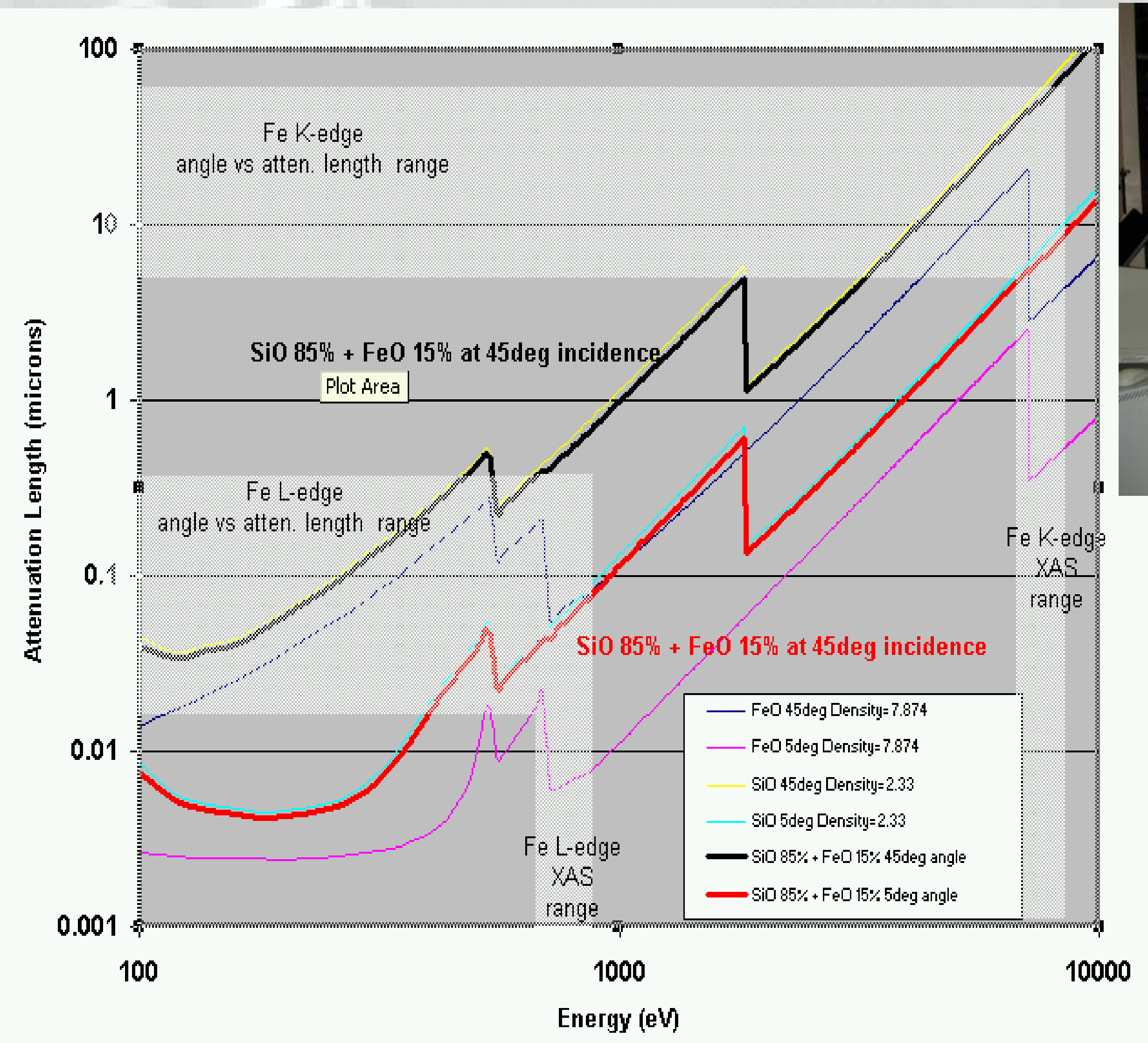
X-Ray Absorption in the energy region of the Fe L or K absorption edges

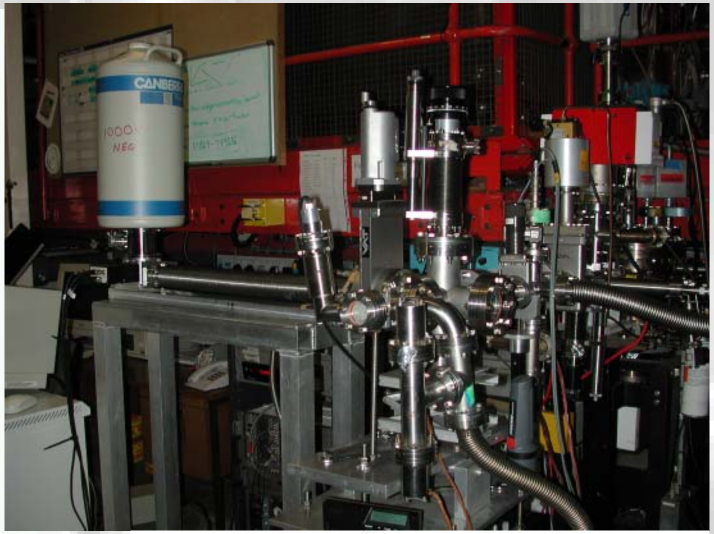


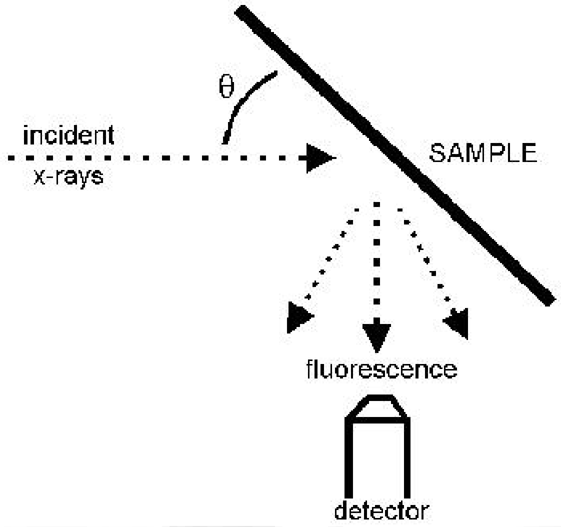


IRON K-EDGE: X-rays probe the whole volume of the gloss

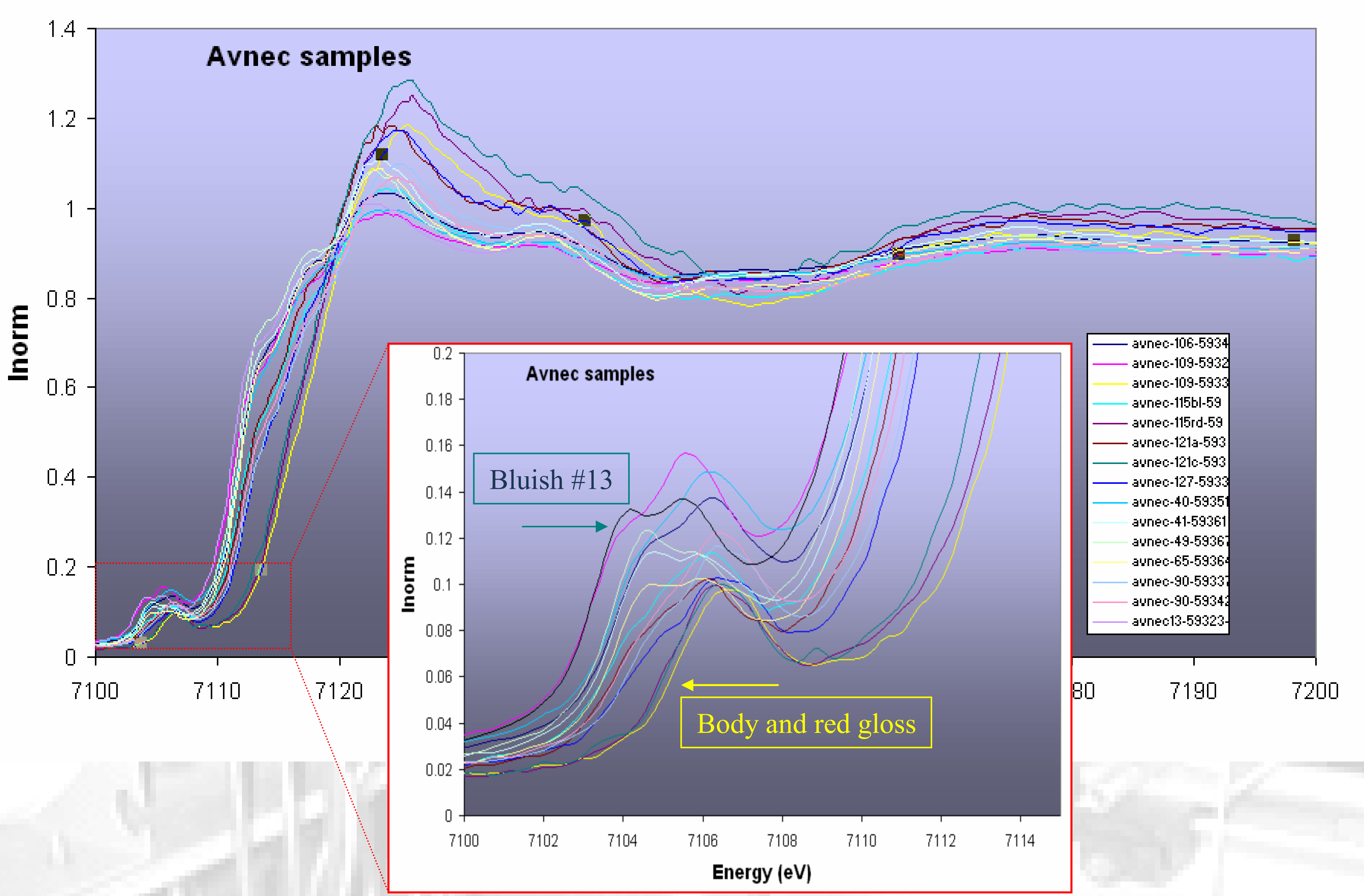
IRON L-EDGE: X-rays probe only the top 1 micron



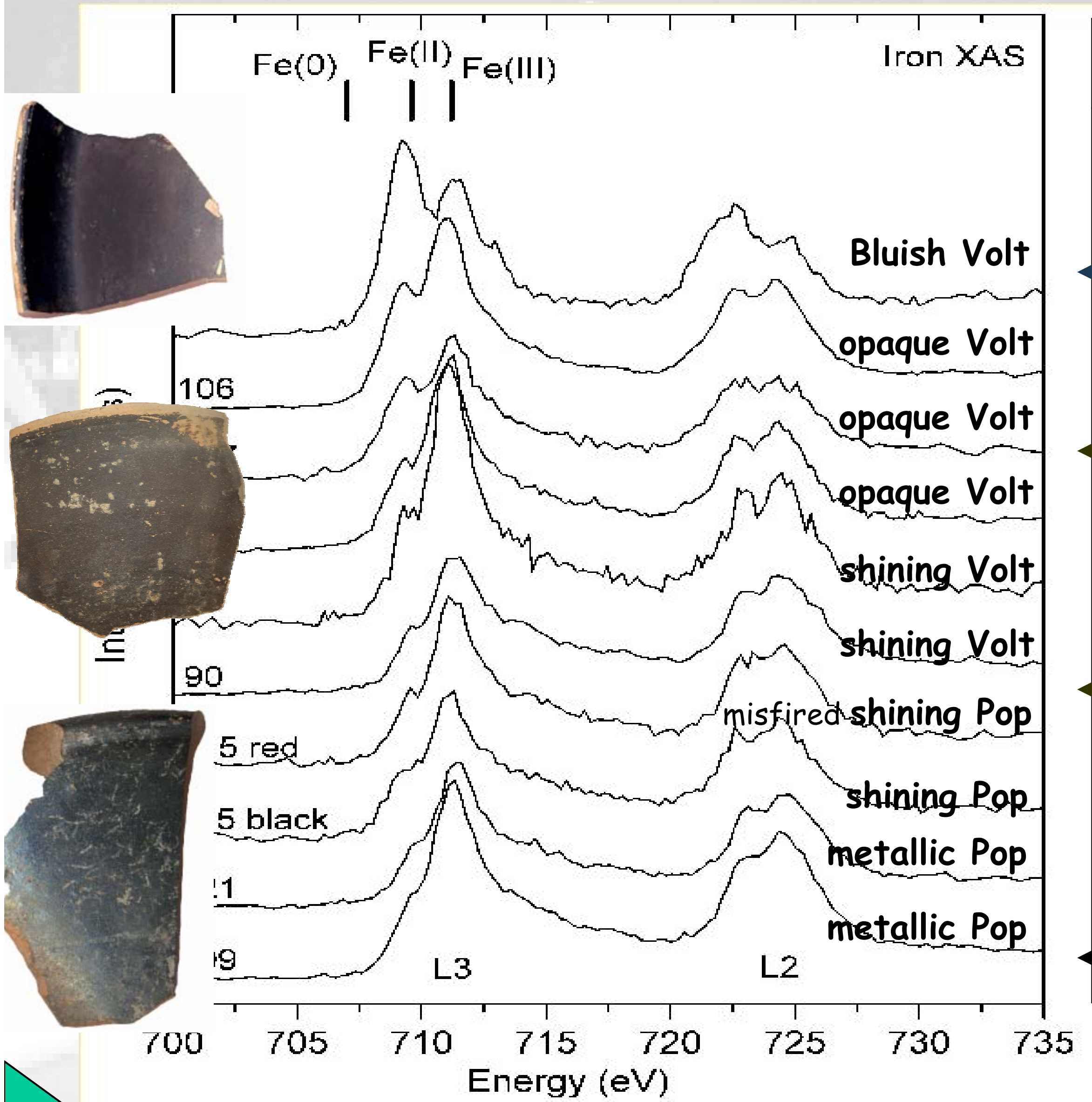




IRON K-EDGE XAS



IRON L-EDGE XAS

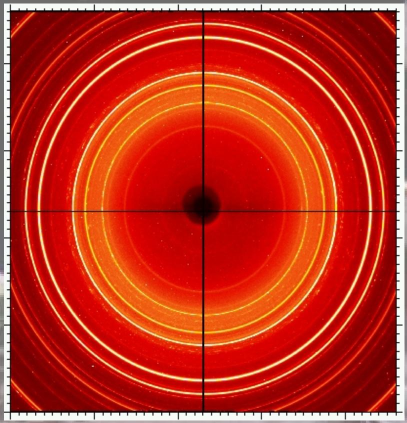


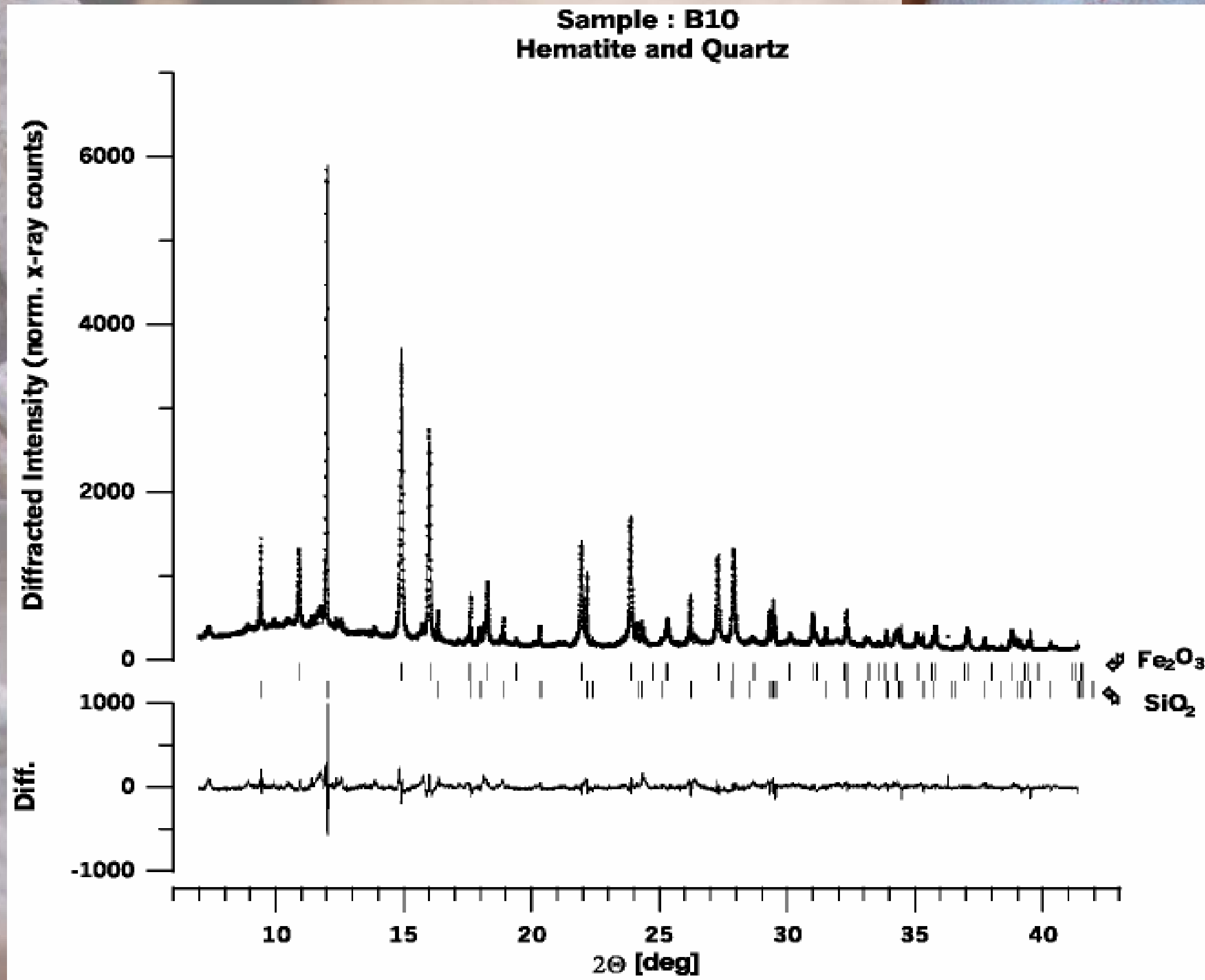
SEM/EDX	TEM
FeO 14.99 wt% Fe^{+2} rich	Hercynite+
FeO 13.27 wt%	
Fe^{+3} rich FeO 13.06 wt%	Hematite+
FeO 14.88 wt% Fe^{+2} + Fe^{+3} rich	Magnetite+

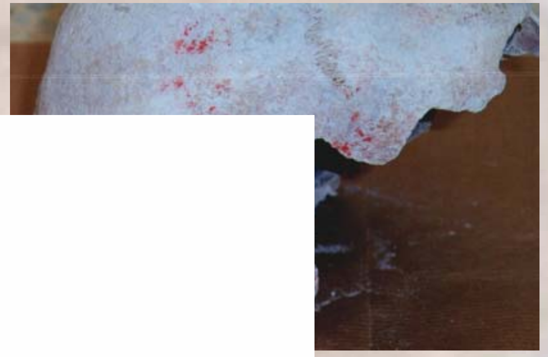
Cosmetics

ELEMENTAL AND MINERALOGICAL ANALYSIS OF PUNIC MAKE-UP

Naceur Ayed, Housam Binous, Univ. Tunisia
Ashfia Huq, P.W. Stephens, NSLS

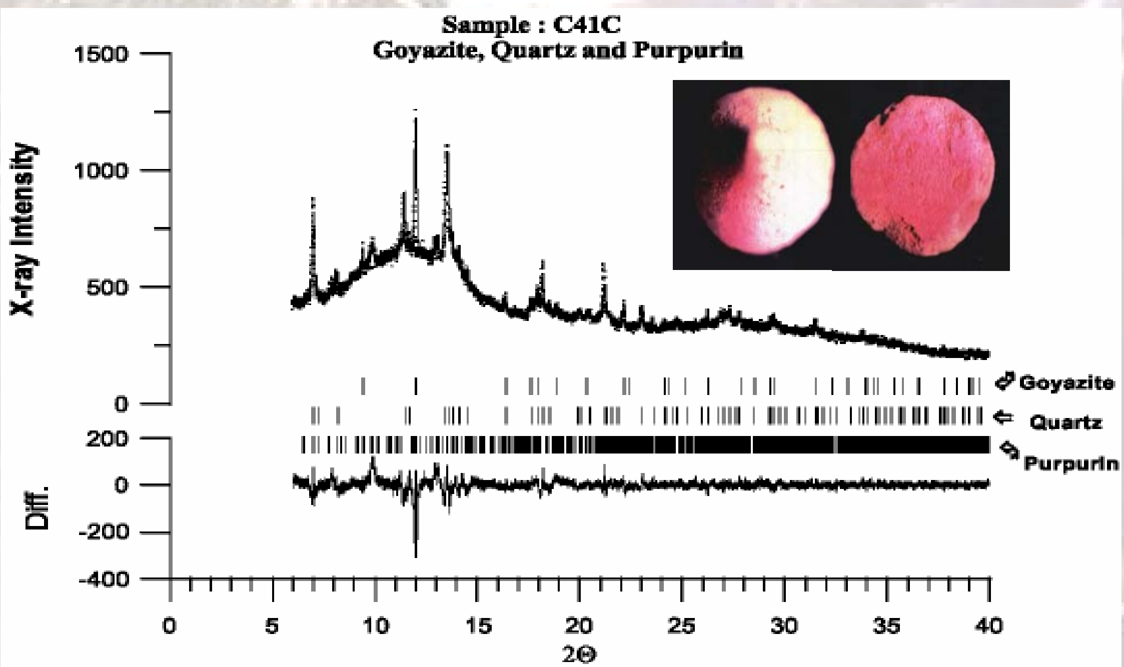


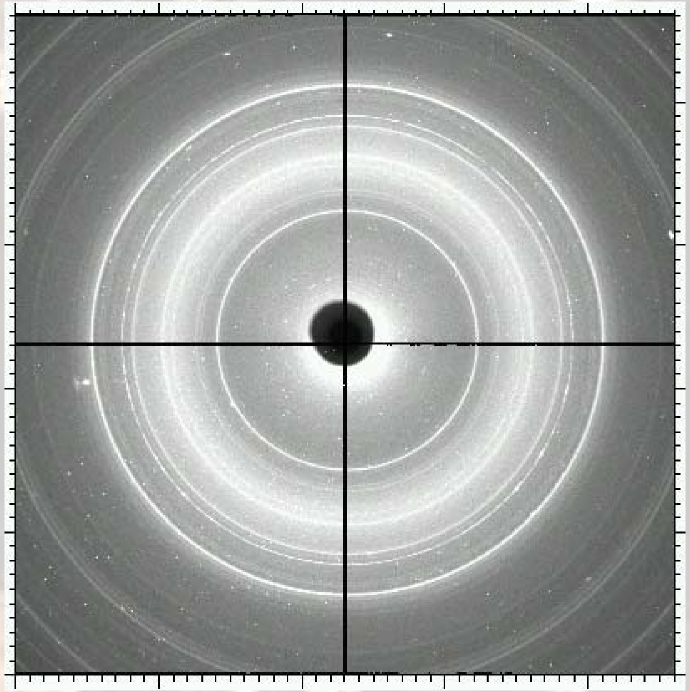


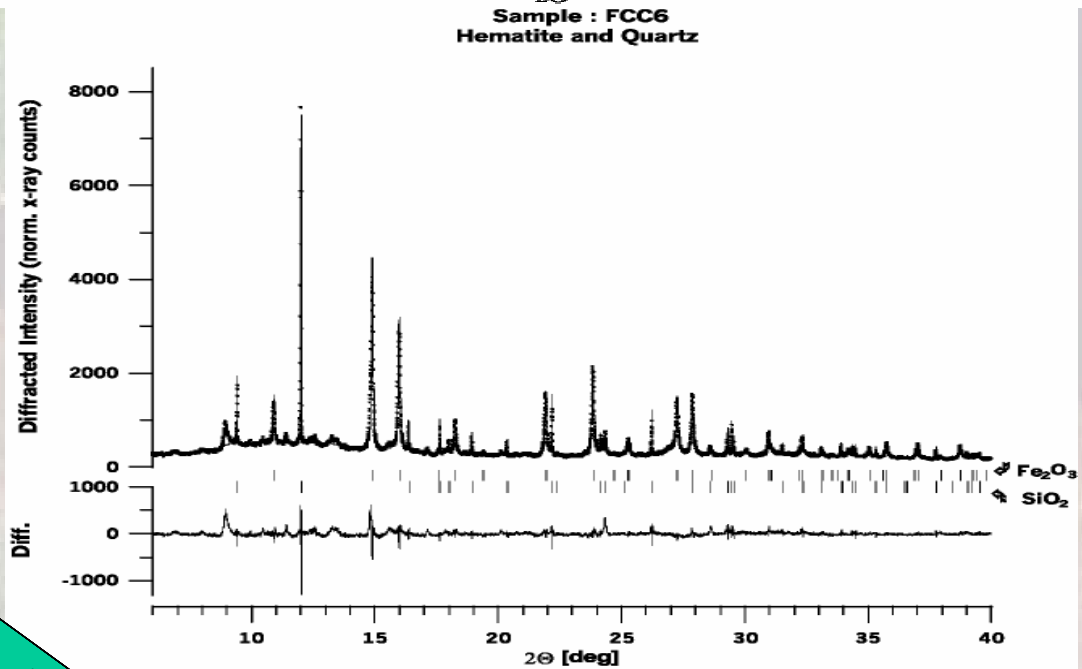


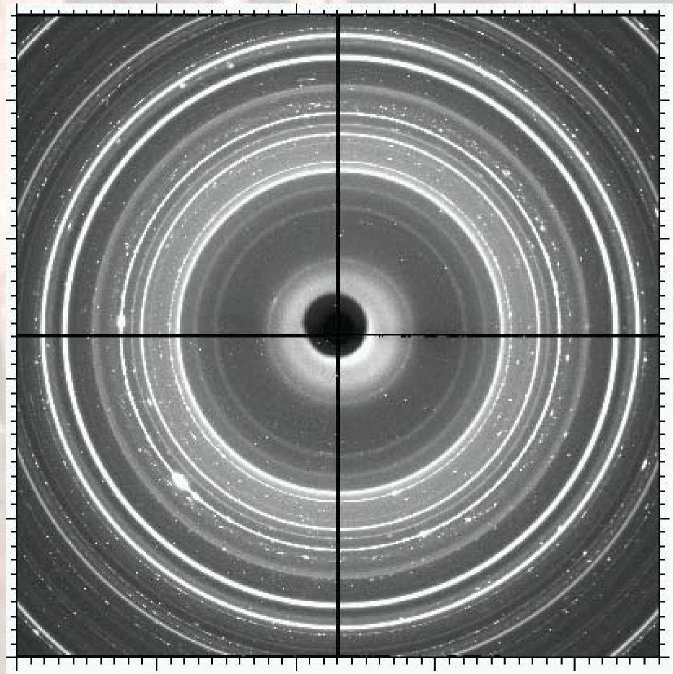
SR CCD-XRD (SRS) for mineralogical characterization

High Resolution Powder diffraction (NSLS) and Rietveld analysis for quantitative analysis.


Sample : C41C
Goyazite, Quartz and Purpurin
X-ray Intensity
1500
1000
500
0
200
0
-200
-400
Diff.
Goyazite
Quartz
Purpurin
0
5
10
15
20
25
30
35
40
2Θ




Sample : FCC6
Hematite and Quartz
Diffracted Intensity (norm. x-ray counts)
8000
6000
4000
2000
0
1000
0
-1000
Diff.
Fe_2O_3
SiO_2
10
15
20
25
30
35
40
2Θ [deg]



W&N

A dead painter's palette?

Winsor and Newton watercolour palette
Victoria & Albert Museum.

The painter who used this unique paint palette, now at the V&A, is not known, yet.

It is suspected to have belonged to an important English watercolour artist of the 19th century.

The paint cakes were initially examined, non-destructively, by XRF and Raman (Dr Lucia Burgio).

Unambiguous identification of painting pigments is an important issue for art historians and conservation scientists, world-wide.

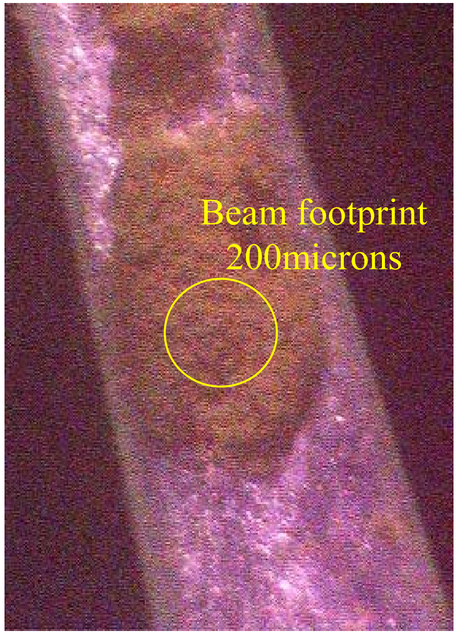
X-ray diffraction can provide unambiguous identification of crystalline pigments.

The amount of material that can be taken from museum objects has to be extremely small.

SR-XRD is ideally suited for such studies.

Watercolour. Stonehenge ca. 1836.

W&N Pigments



Small quantities of paint were carefully scraped from the paint cakes and inserted into thin glass capillaries.

Diffraction patterns from some 100 samples were recorded by a CCD detector at the crystallography station 9.6 of the SRS, Daresbury Laboratory.

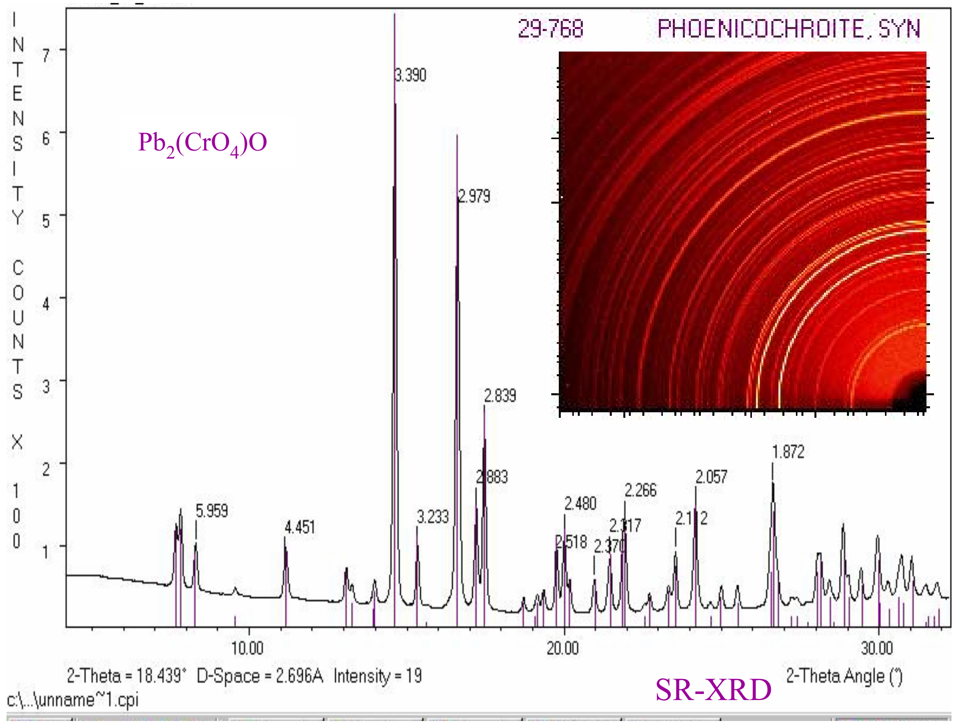
Some of the paints may be "trade marks", the painter's favourites. Pigment "fingerprints" can be used for authentication of paintings.

Cake A3: Const.White: Barite, $BaSO_4$

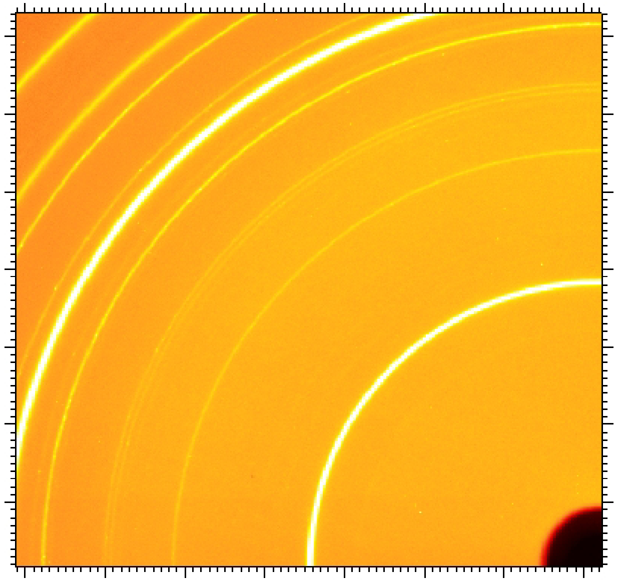
Several of the paints are composed of mixed mineral pigments and non-crystalline organic dyes, often diluted with extenders (e.g, gypsum).

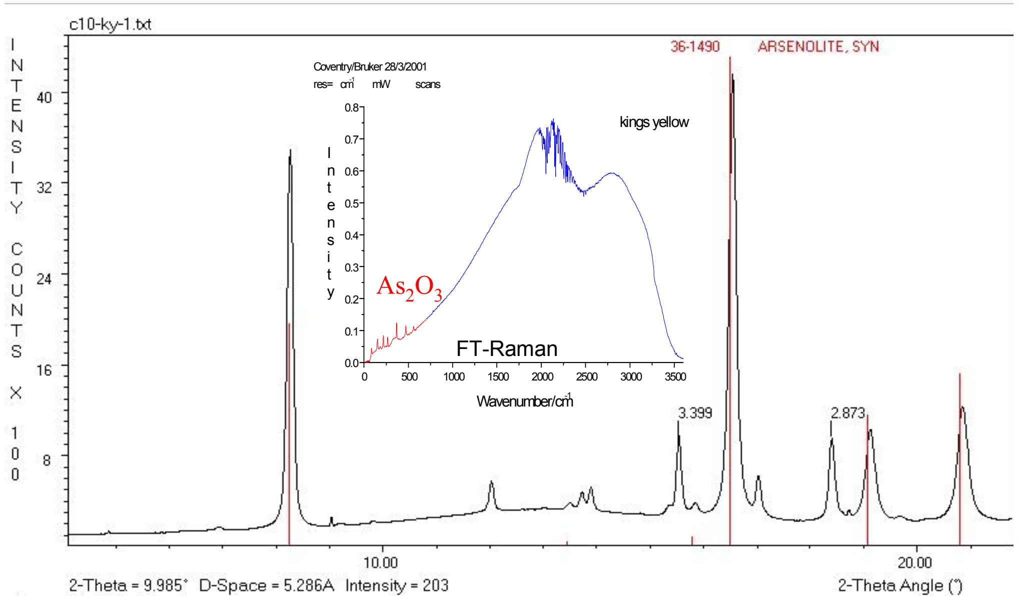
This often makes it difficult to identify them by Raman or XRD alone.

Combination of analytical techniques is necessary.

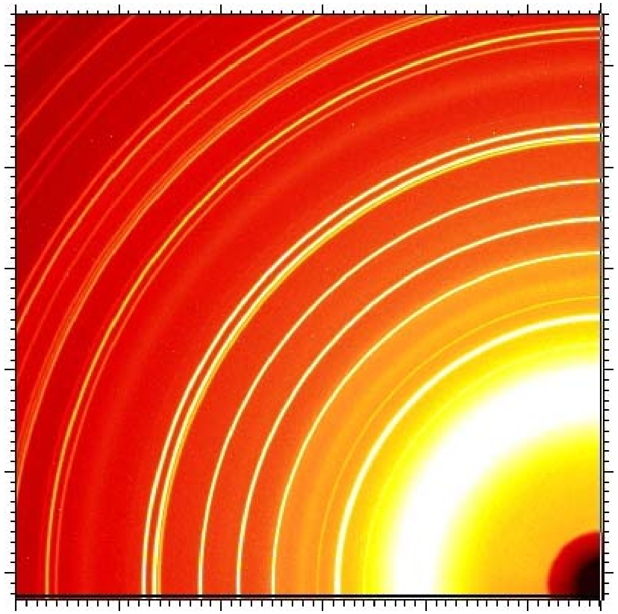


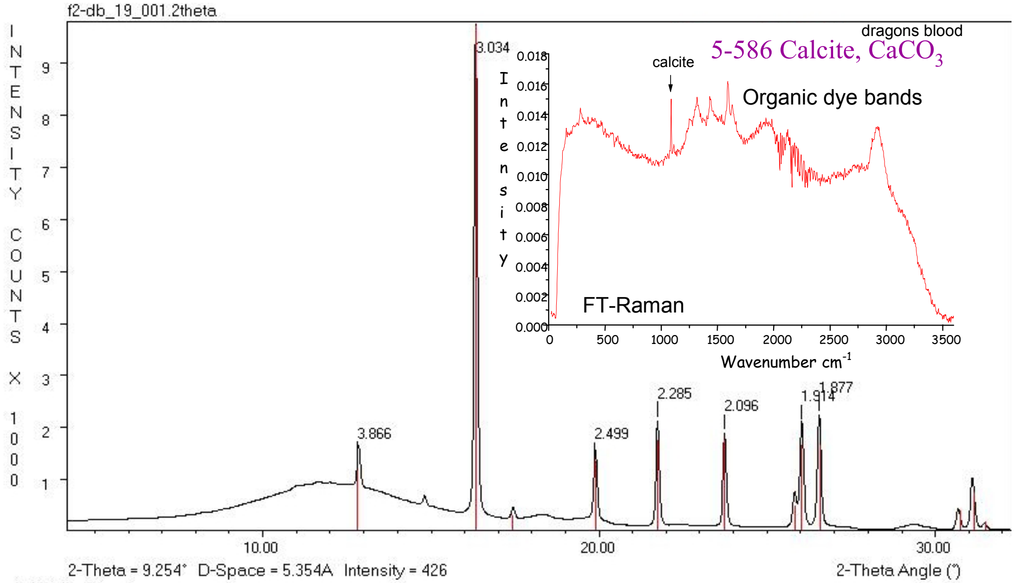
V&A-DL collaboration under NERC SR grant 38064. PI Prof. G. Martin, V&A.





Cake C10: Kings Yellow. Two phase identified by XRD and Raman are Arsenolite, As_2O_3, and S.





Cake F2: Dragon's Blood. Single crystalline phase, Calcite. XRF shows the presence of traces of Fe, As and Sr. The red colour is caused by a non-crystalline dye, detectable by Raman, giving rise to the diffuse scattering.

Territories to be Explored

Micro-beam techniques: FTIR/XRF/XRD/XAS/SAXS

Combined techniques: Same area, same time

Time-resolved EXPERIMENTS: Technology reproduction

X-ray Tomography and Tomoscopy: Degradation & Ageing

VUV to Soft X-ray energy region: Luminescence properties

Magnetic, polarisation and time-structure: ???

Archaeocrystallography?

New breed of young archaeologists and museum scientists not inhibited by new technology

Collaborators

Polytechnic University of Catalunia: Trinitat Pradell, Nati Salvadó

University of Barcelona: Marius Vendrell, Judit Molera

University of Zaragosa: Josefina Perez-Arantegui

Siena University: Elisabetta Gliozzo, Isabella Memmi

The Manchester Museum: John Prag
Victoria & Albert Museum: Lucia Borgio, Graham Martin
Thetis Authentics: Eleni Aloupi
Tunisia University: Housam Binous, Naceur Ayed

<u>Daresbury Laboratory</u>

Fariba Bahrami
Graham Clark
Ian Kirkman
Miroslav Papiz
Sunil Patel
Mark Roberts
Andy Smith

<u>ESRF</u>

Manfred Burghammer
Marco Di Michie

<u>NSLS/SUNY</u>

Ashfia Huq, Peter Stephens

<u>Advanced Light Source</u>

Marcus Matthew