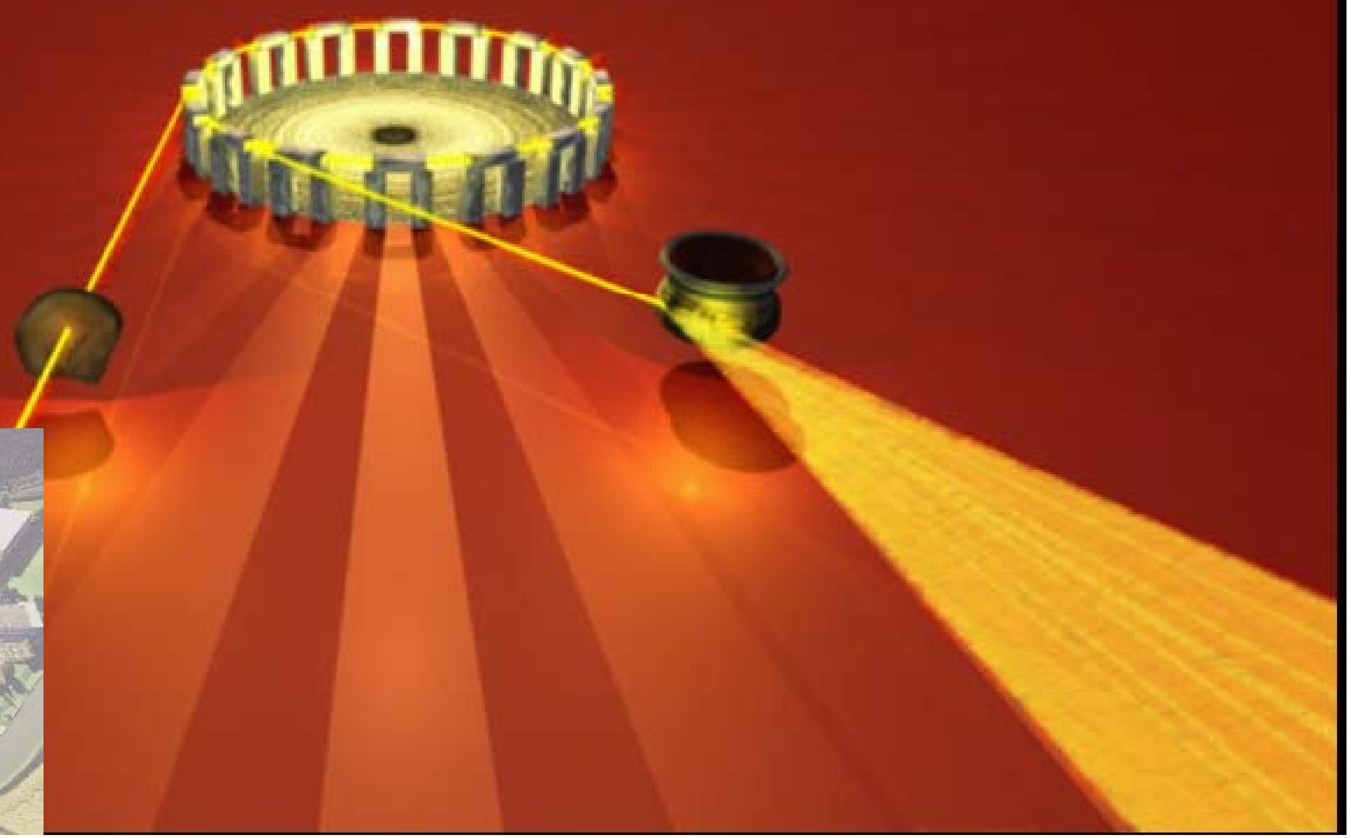
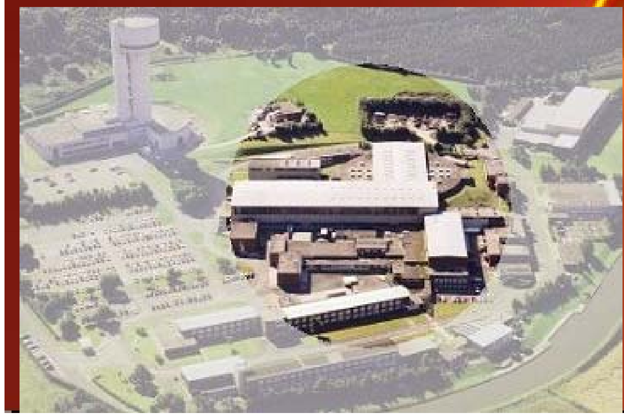
Trends in the Application of Synchrotron Technology to Art and Archaeology

Manolis Pantos
Daresbury Laboratory



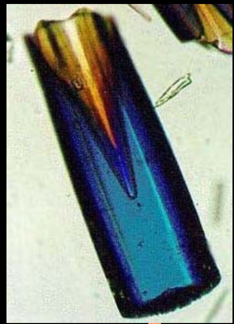
http://srs.dl.ac.uk/arch/

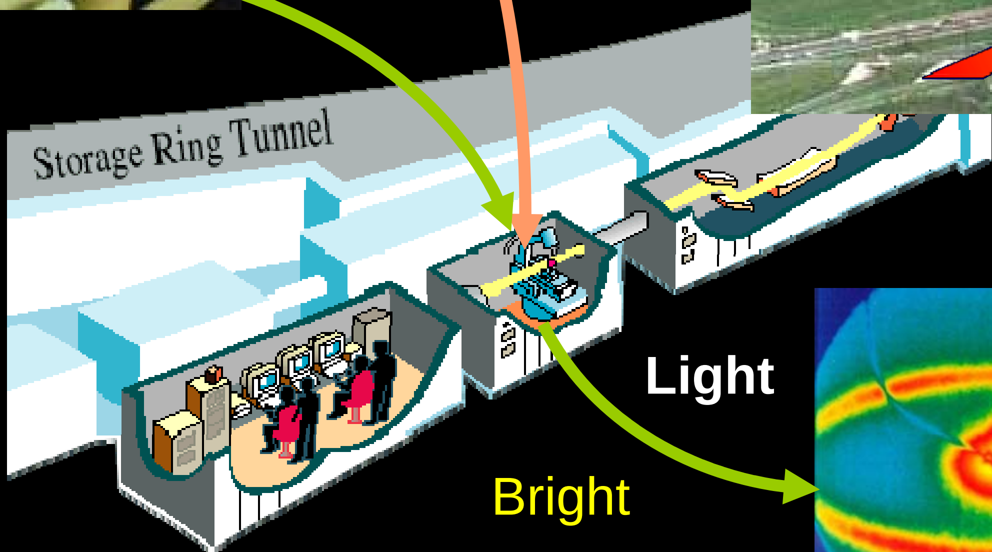


What is a Synchrotron?

Diverse type of samples

Small – Many - Difficult

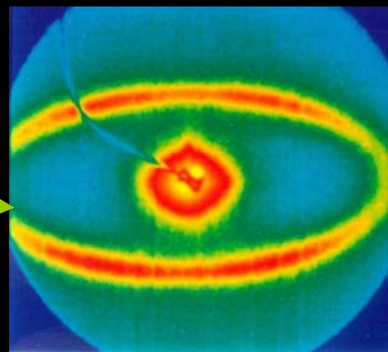




Light

Bright

Wavelength tunable



Data

Fast collection

Large volume

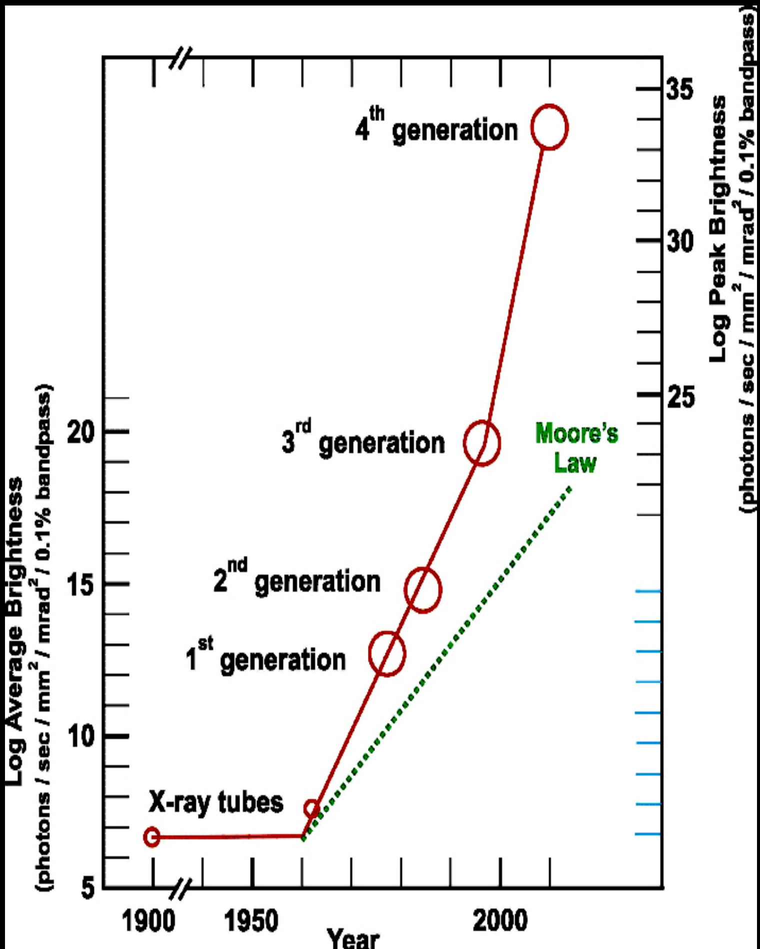
What would <u>You</u> like to do at a Synchrotron?

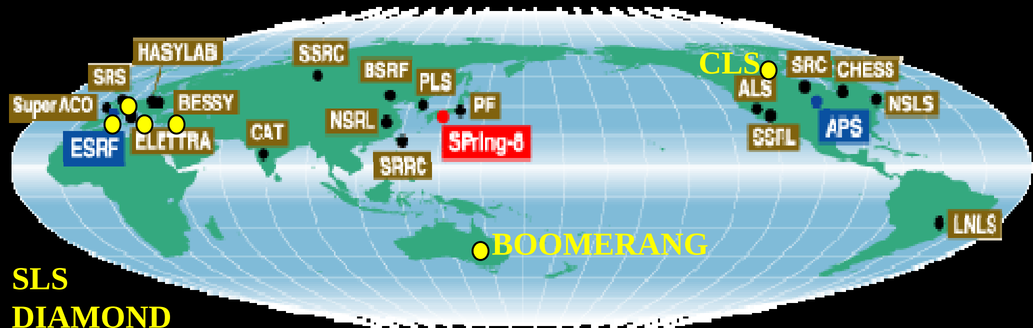
The Three Key SR Features

Brilliance: Fast data collection, Small sample size

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

Tunability: Choice of energy region to suit the problem





SLS
DIAMOND
SOLEIL
ALBA
SESAME
BOOMERANG

- Planned sources

SR sources around the world

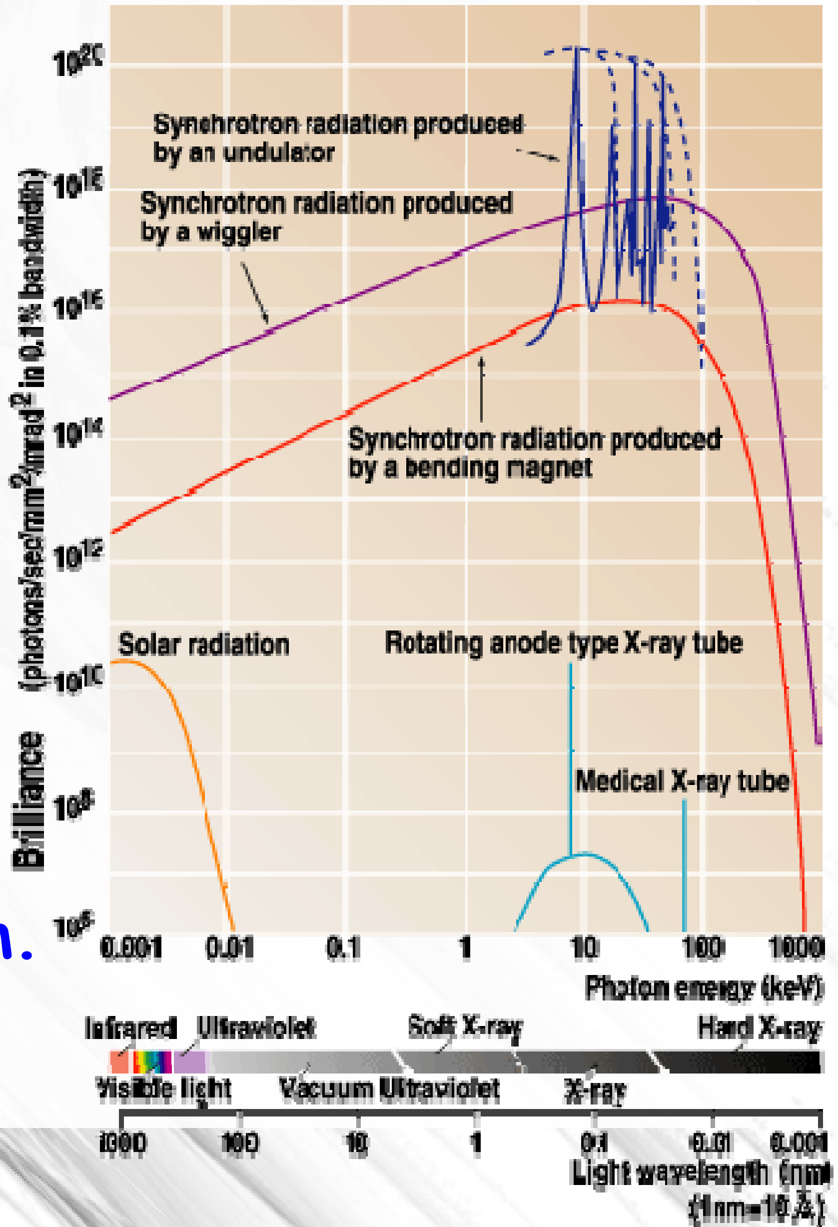
http://www.spring8.or.jp/ENGLISH/general_info/overview/sr.html

SR has enabled the development of techniques for Advanced Materials Science

Archaeology is about People

Properties of materials can be probed by the interaction of light with matter.

The properties of materials that can be probed by light map directly onto the synchrotron radiation spectrum.

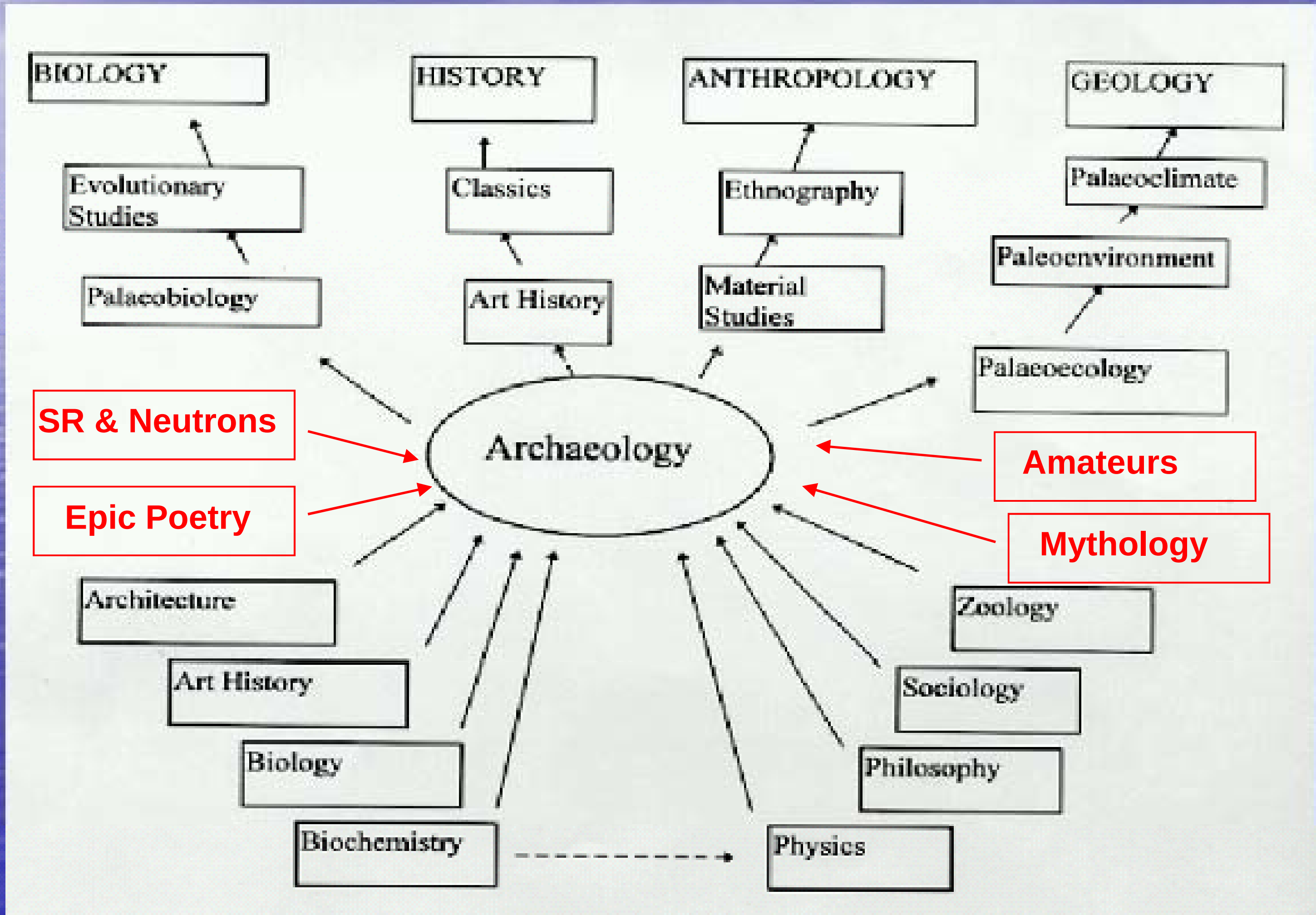


Traditional Materials Science Questions in Archaeology

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

From A.M.Pollard, SR2A Conference, 9-12Feb 05, Grenoble

Academic Links in UK Archaeology

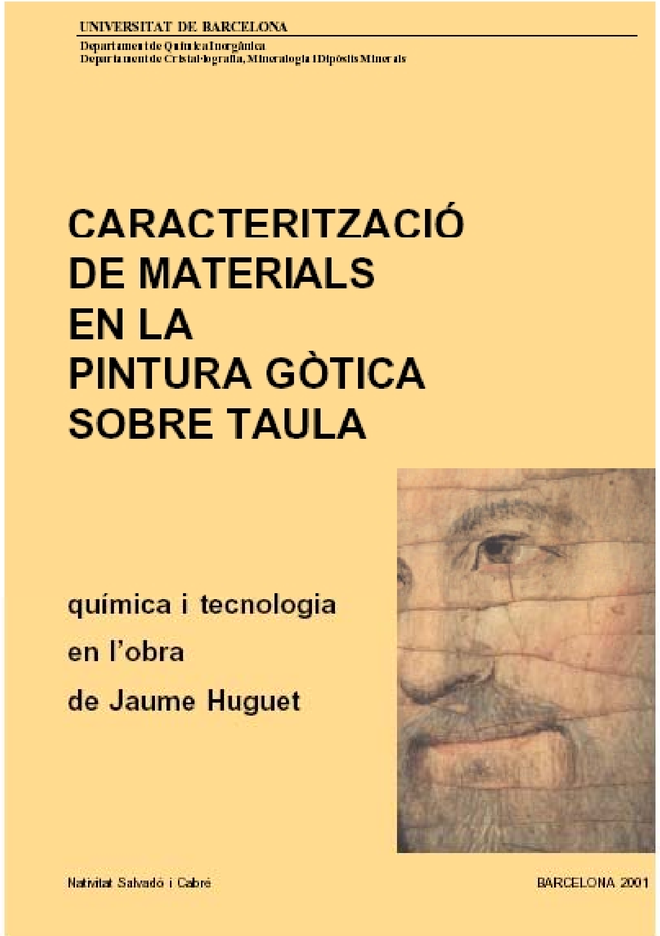


From A.M.Pollard, SR2A Conference, 9-12Feb 05, Grenoble

Gothic Catalan Paintings

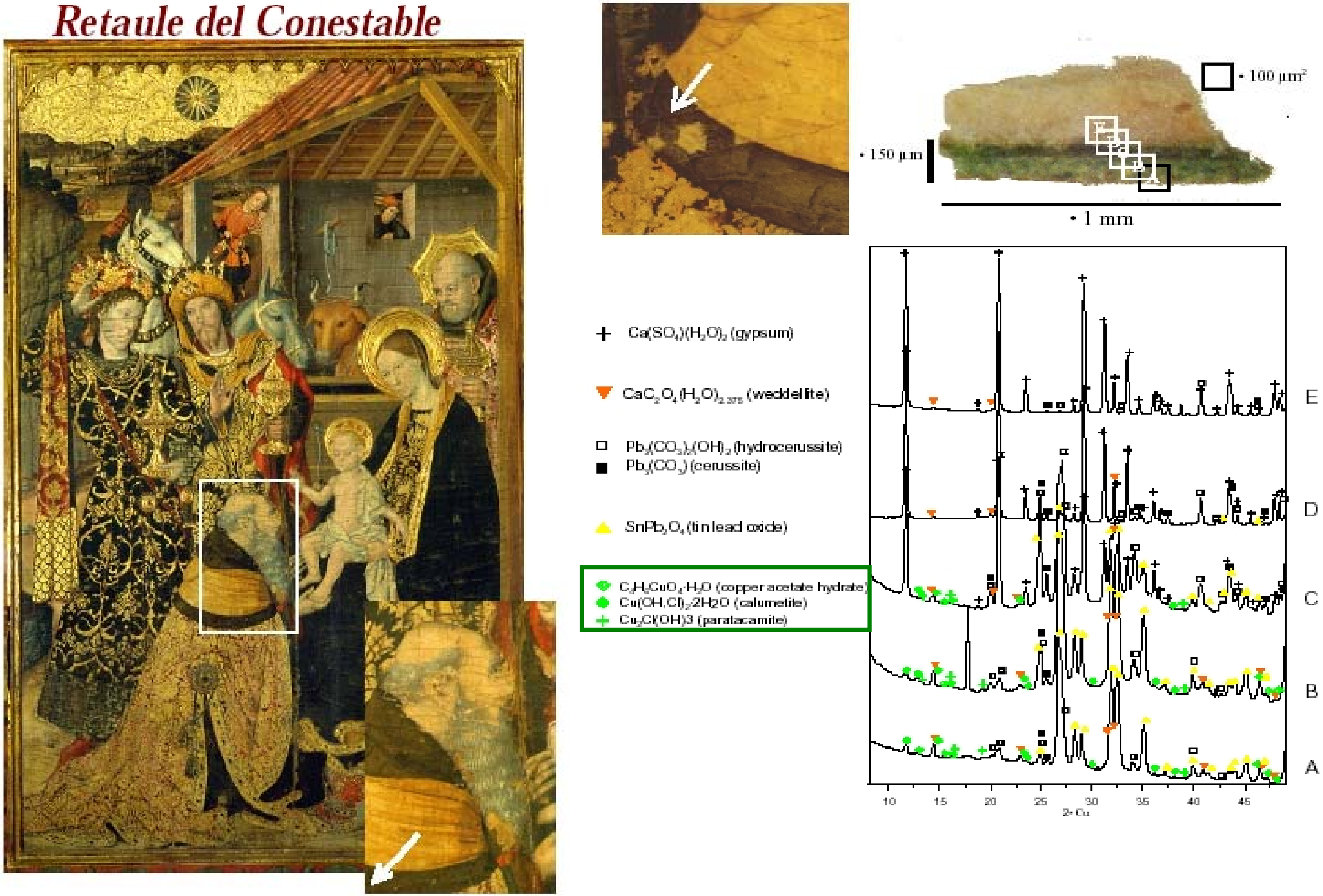
Chapel of St Agatha, Barcelona, Catalunia

Jaume Huguet
1415-1492
Barcelona



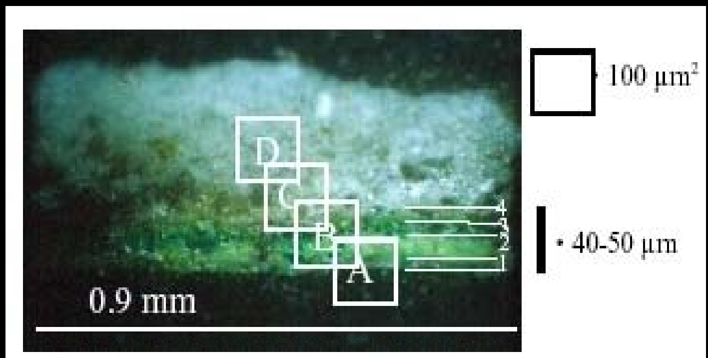
green pigments from Gothic altarpieces

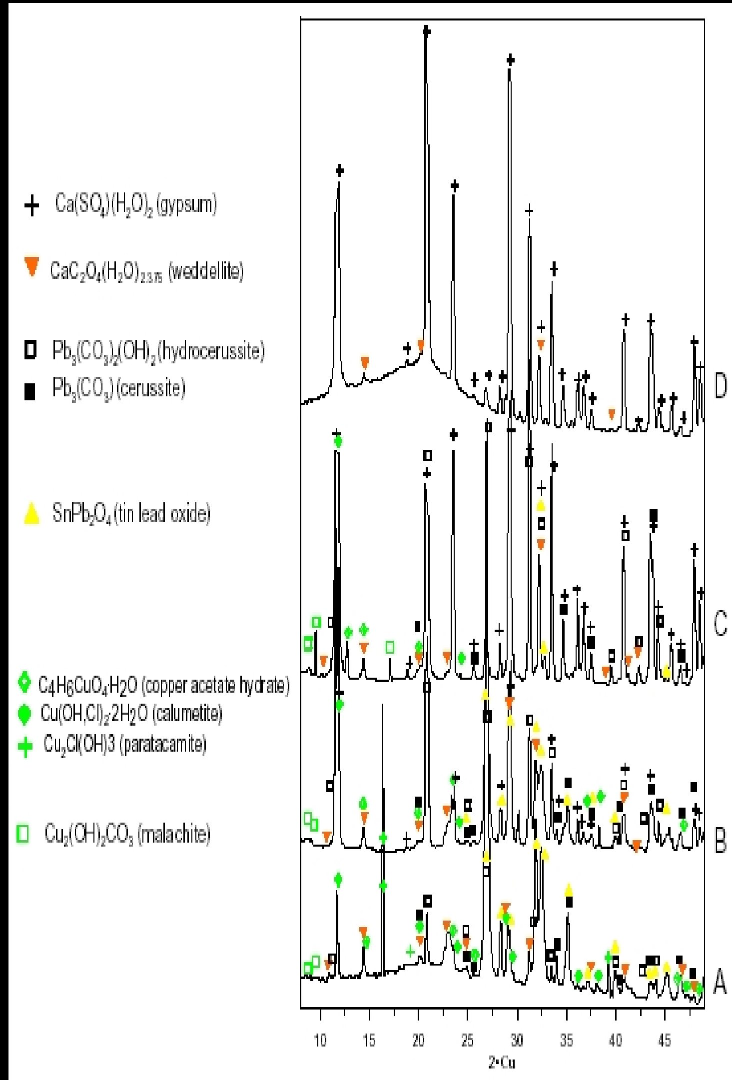
Retaule del Conestable



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

Thin Section XRD





The diffraction data reveal the composition of Jaume Huguet's green paints and the preparation layers as well as the presence of alteration products. **The copper chlorides were selected intentionally.**

N. Salvadó, T. Pradell, E. Pantos, M.Z.Papiz, J. Molera, M. Seco and M. Vendrell-Sa , *Identification of copper based green pigments in Jaume Huguet's Gothic altarpieces by Fourier transform infrared micro-spectroscopy and synchrotron radiation X-ray diffraction*, J. Sync. Rad. (2002) Vol. 9, pp. 215-222.

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.

Museum of Ceramics, Palau Real, Barcelona

al 15th century lustre decorated dish from de
Moresque workshop of Paterna.

Technology Transfer

When was lustre pottery first produced ?

- Irak 9th AD : Abbasid court of Samarra.

The collapse of the Fatimid dynasty in Egypt (end of 12th AD) resulted in the emigration of the potters to safer areas first to Syria, Iran and then through Sicily, Mallorca and Tunis to the islamic kingdoms in the Iberian Peninsula.

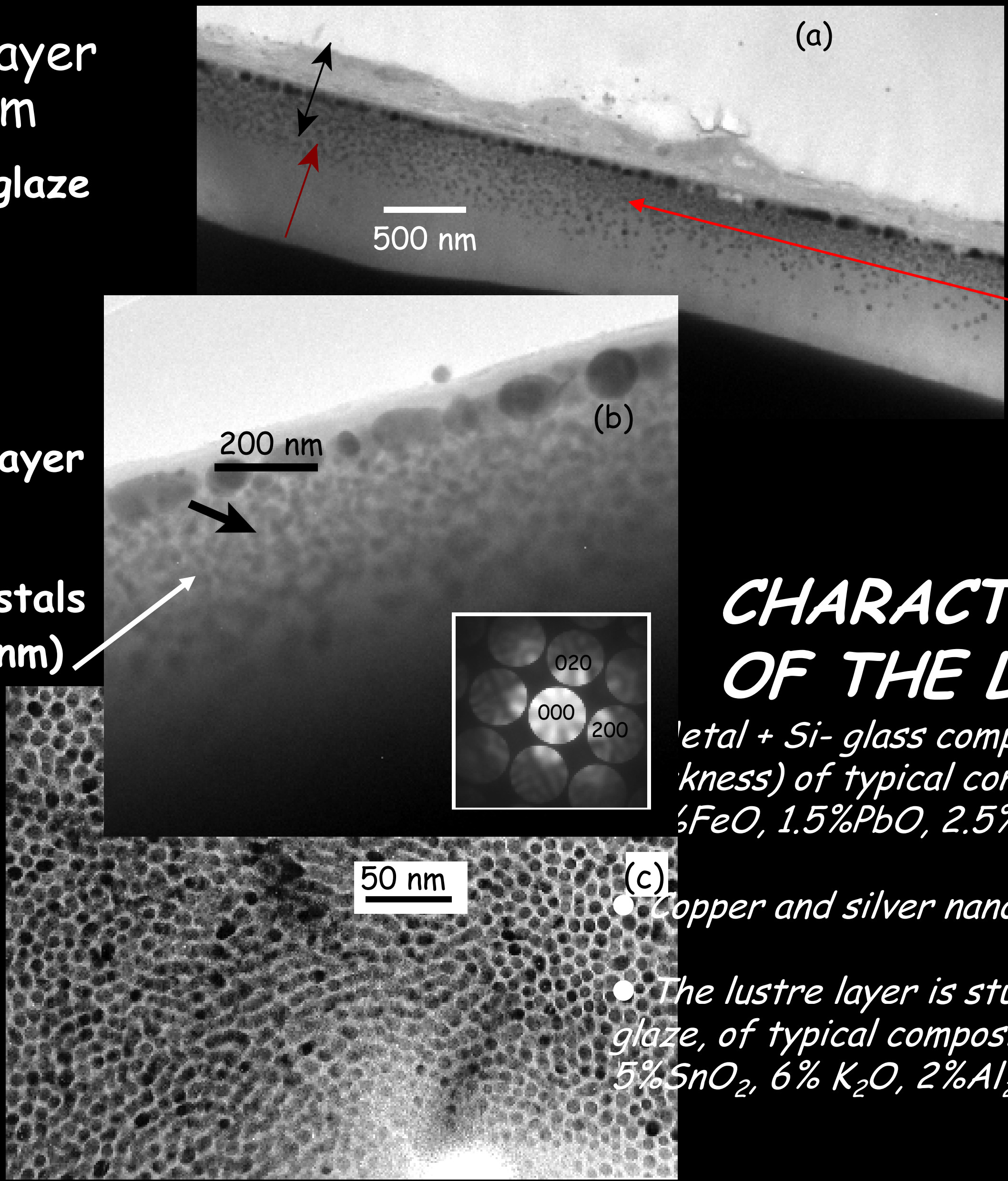
Composite layer
200-500 nm

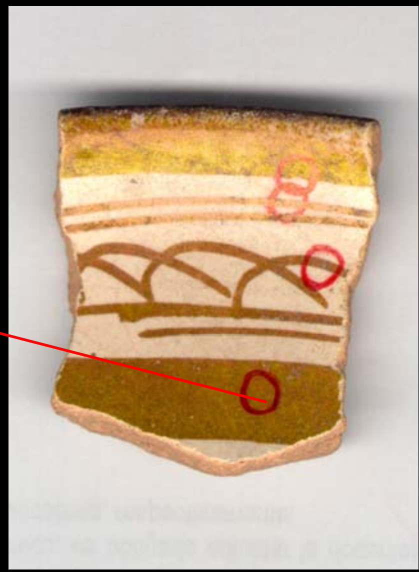
tin glaze

Glassy layer

Copper
nanocrystals
(10-50 nm)

Silver
nanocrystals
(5-10 nm)





CHARACTERISTICS OF THE LUSTRE LAYER:

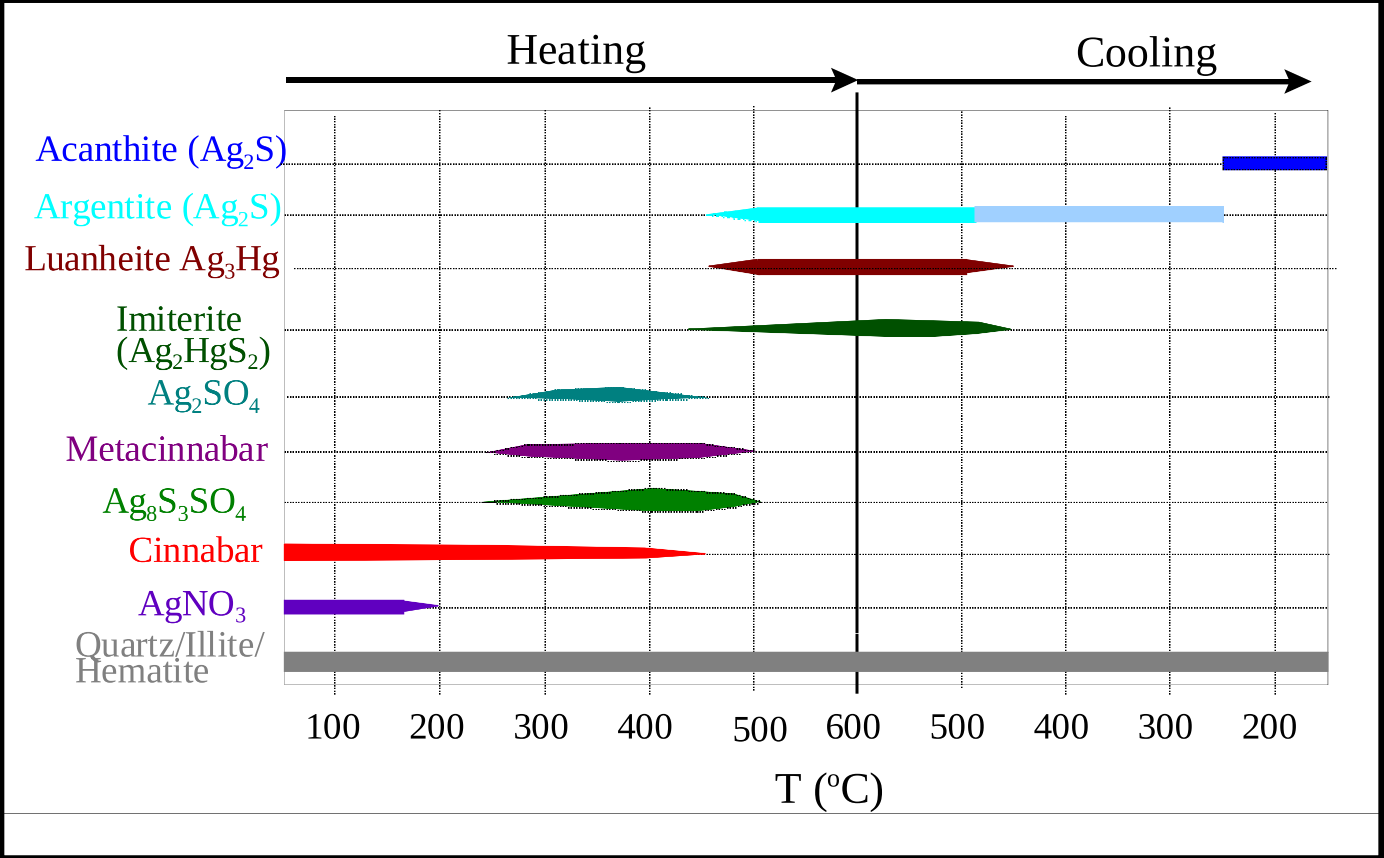
etal + Si- glass composite layer (200-500 nm kness) of typical composition 13%Al_2O_3, 71%SiO_2, FeO, 1.5%PbO, 2.5%K_2O, 5%CaO and 4.5%Na_2O.

- *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.*

Luster pottery from the 13th to the 16th century: a nanostructured thin metallic film.
J.Pérez-Arantegui, J.Molera, A.Larrea, T.Pradell, M.Vendrell-Saz, I.Borgia, B.G.Brunetti,
J. American. Ceramic Society, **84 [2],** 442-446 (2001).

Hard X-rays for time resolved studies

High penetration, non-destructive.
Mineralogical and texture information in seconds.
Ideal for time-temperature studies.

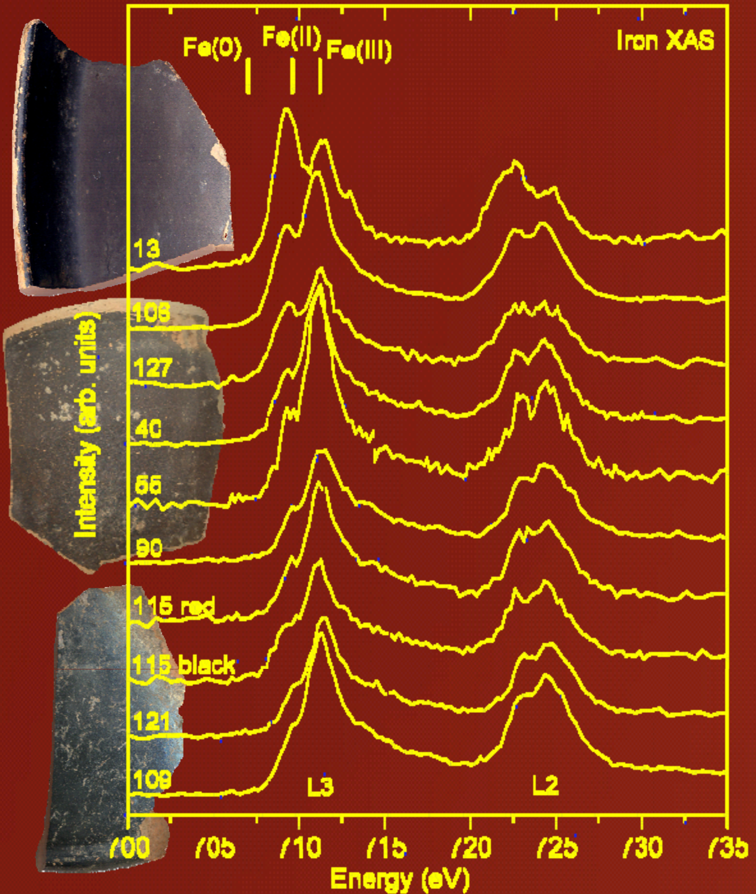


90keV SR-XRD of on-line heated ceramic powders have revealed the technological processes involved in the production of lustre ware from medieval Spain.

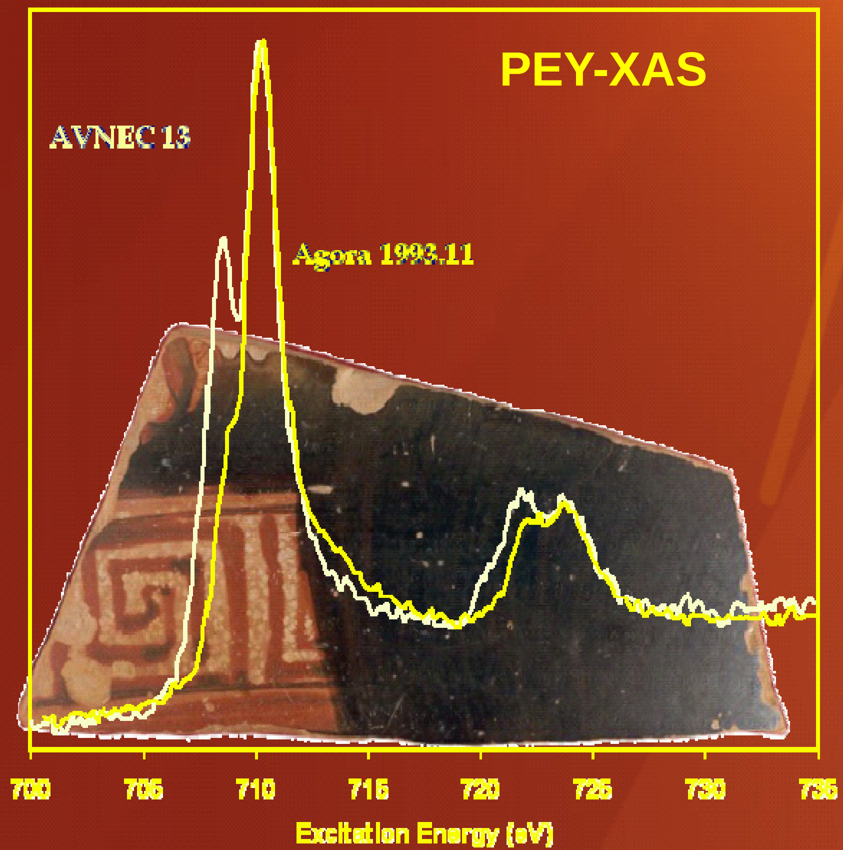
T. Pradell , J. Molera, M.Vendrell, J. Perez-Arantegui, E. Pantos, M. Roberts, and M. M. DiMichiel, (2004),
The role of cinnabar in lustre production, J.Am.Ceram.Soc. 87(6), 1018-1023 (2004)

Fluorescence and Electron Yield XAS

Partial Electron Yield (PEY) measurements in the L-edge of iron (700-740eV region), probe the top 10nm of the surface of the gloss. Unlike fluorescence XAS, electron emission is a first-order process, more sensitive to the local environment of the absorbing atom.



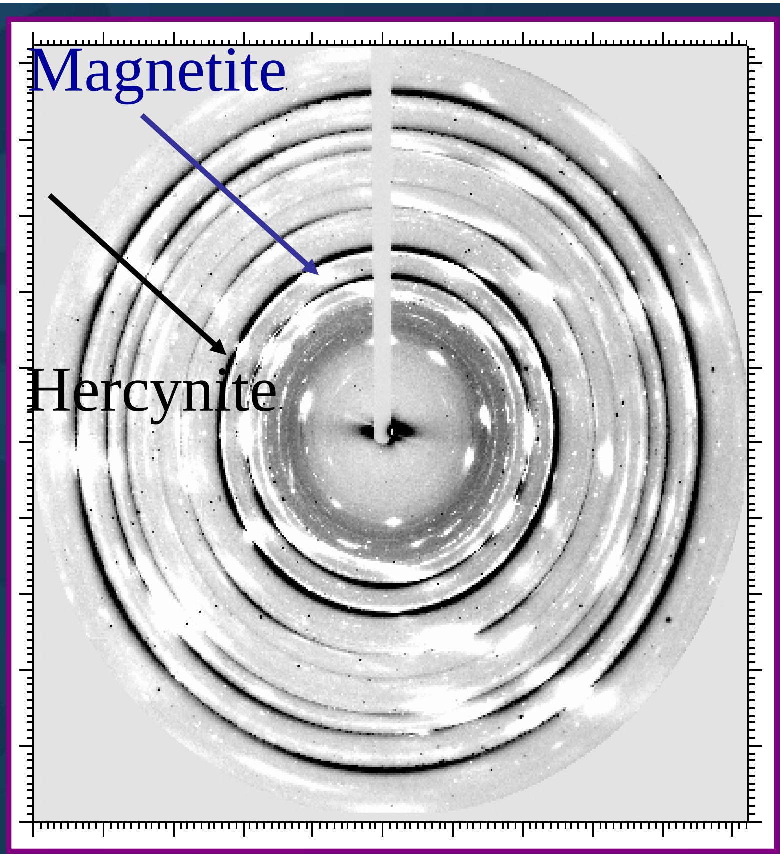
Colour correlates with content in iron oxide type at the top surface layer.



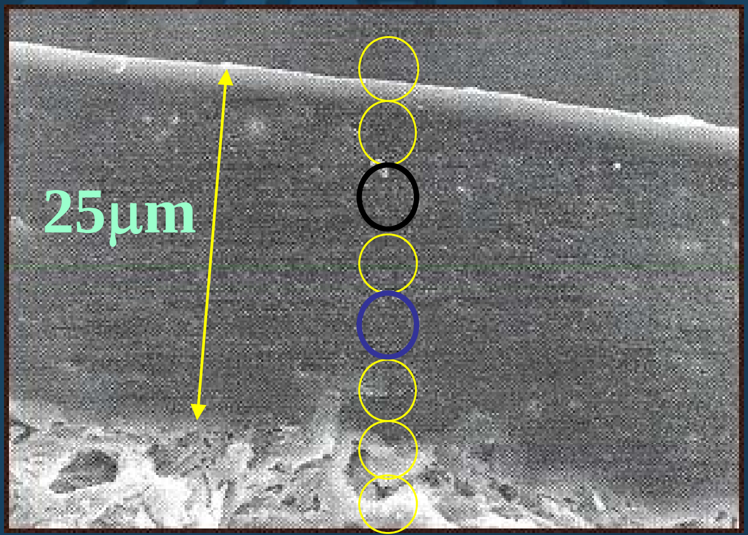
PEY-XAS results on BG previously studied with fluorescence XAS tell the same story.

Question: Any concentration gradients?

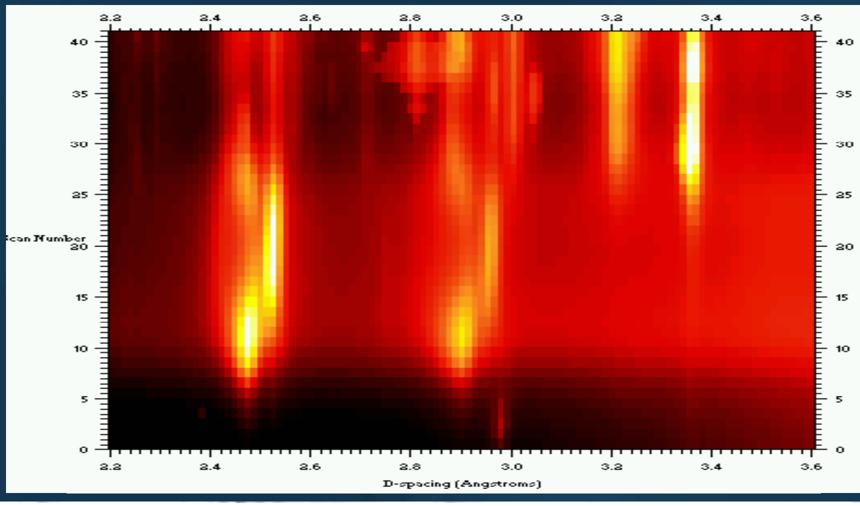
Spatially resolved micro-XRD



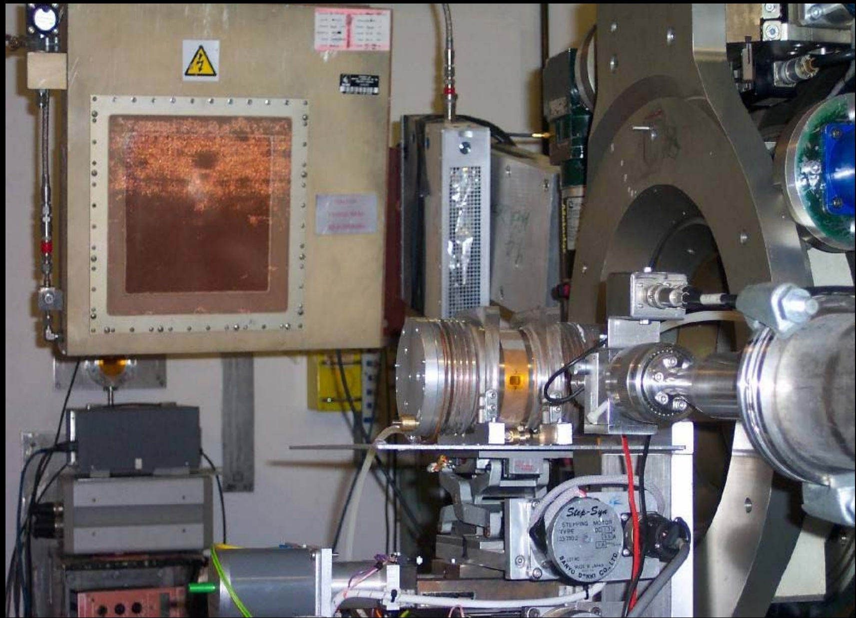
Above: Difference pattern at 10 and 20 μm from the surface



Microfocus beamline ID13
European Synchrotron Radiation Source, Grenoble.



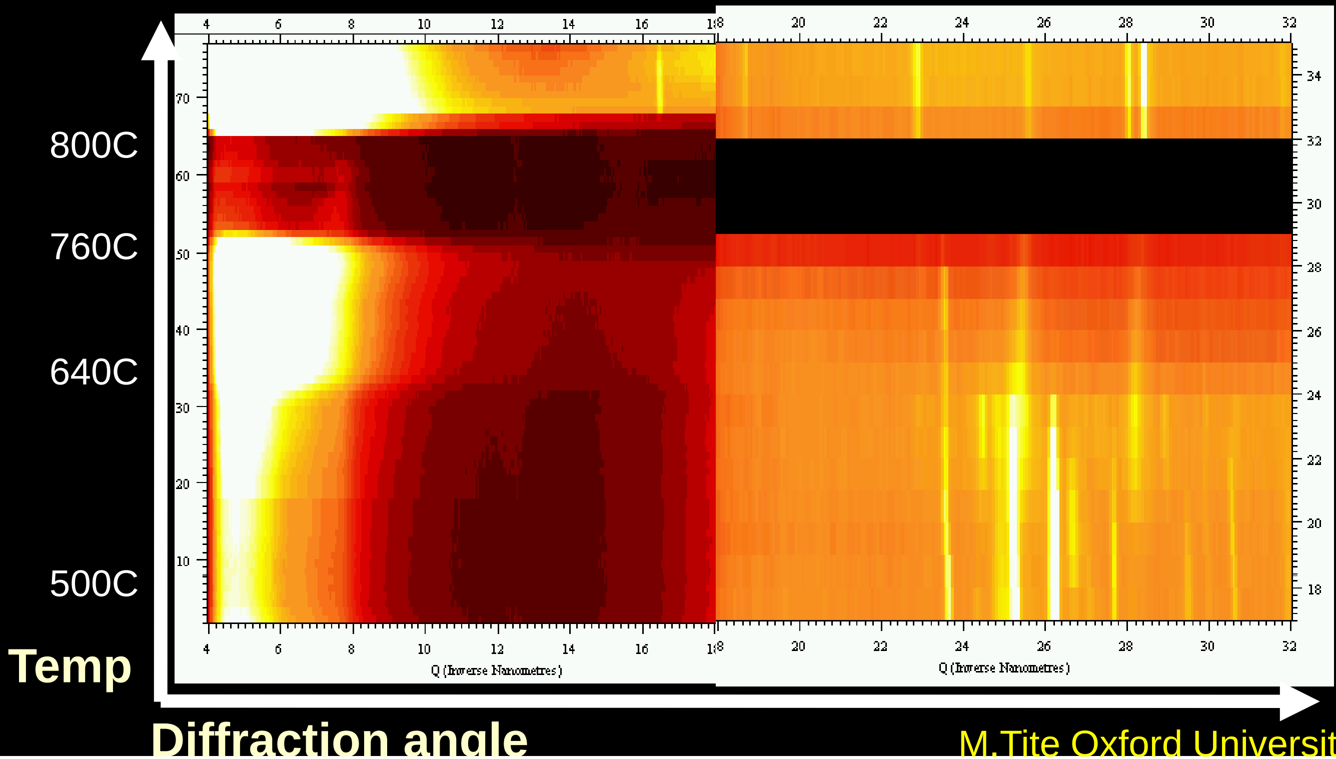
Right: The sequence of diffraction patterns shows a variation in hercynite/magnetite ratio across the gloss.



The Art and Science of Glaze Making

SR modalities offer the opportunity for time-resolved experiments, in –situ, at high angular and time resolution.

The role of process parameters such as slip composition, kiln atmosphere and firing protocol need to be studied at will.



SAXS and WAXS of glaze mixtures heated at 5ºC/min from 25 to 1000ºC.

Diffraction patterns recorded every 1min.

M.Tite Oxford University, T.Pradell Barcelona University

Corinthian type helmets

Low resolution images of helmets from http://www.hellenic-art.com/armour/helmets.htm and http://www.ncl.ac.uk/shefton-museum/

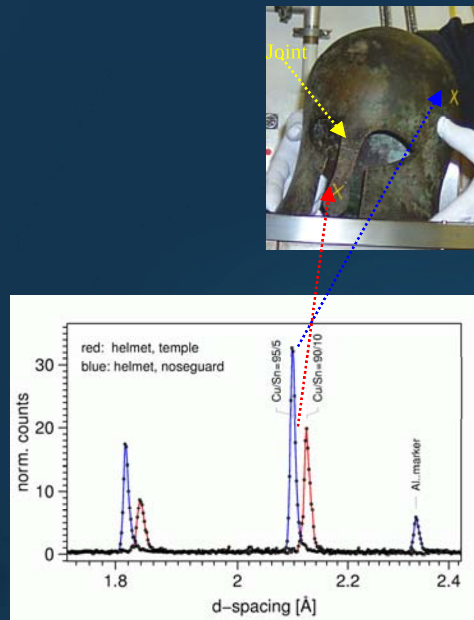
First Aias son of Telamon, bulwark of the Achaians, brake a battalion of the Trojans and brought his comrades salvation, smiting a warrior that was chiefest among the Thracians, Eussoros' son Akamas the goodly and great. Him first he smote upon his thick-crested helmet ridge and drave into his forehead, so that the point of bronze pierced into the bone; and darkness shrouded his eyes. Homer, *Iliad* VI 5-11. (transl. by Andrew Lang, Walter Leaf and Ernest Myers, Macmillan 1912).

The object is a battle helmet of Corinthian type - the only one for which we know the ancient Greek name. Along with his shield, corslet and greaves, it formed part of the armour of the Classical Greek infantryman: such men formed the core of the citizen armies of the Greek city-states, and had to be rich enough to provide their own equipment.

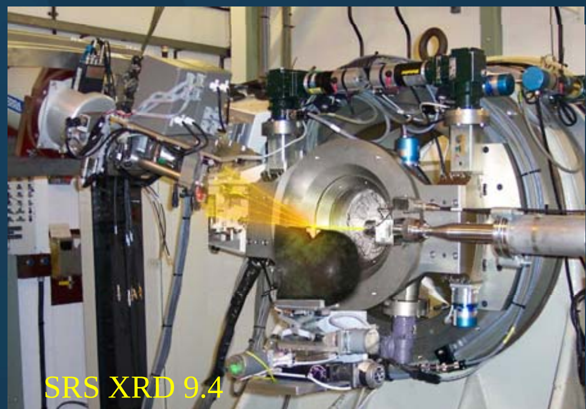
The fact that the metal on this helmet is rather thin and that it lacks the common crest suggests that our man may have been rather limited in his means. Padded with a leather or felt lining whose fixing holes can still be seen along the edges, the helmet protected the head, face and neck of the wearer very effectively (A.Jackson, Annual of the British School at Athens, in preparation). However, he could see little and hear almost nothing.

The Corinthian helmet has been called "one of the great independent achievements of early Greek technology”. It was beaten out of a single sheet of bronze, probably on a rod-anvil, and like all body-armour it was made to measure: this required exceptional skill on the part of the smith, but once discovered the design was so efficient that it was still being used in fifteenth-century Italy, more than 2000 years after its invention around 700 BC. However, by the seventeenth century the art had been lost and had to be re-invented for modern replicas.

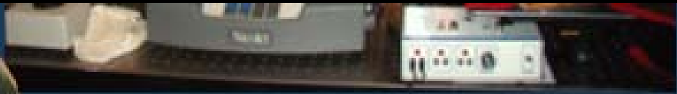
The technology of the Corinthian-type Hoplete Helmet

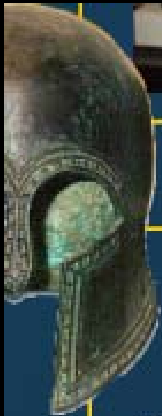


Key objective: To check whether the repaired noseguard end-piece is of the same material as the rest of the helmet.



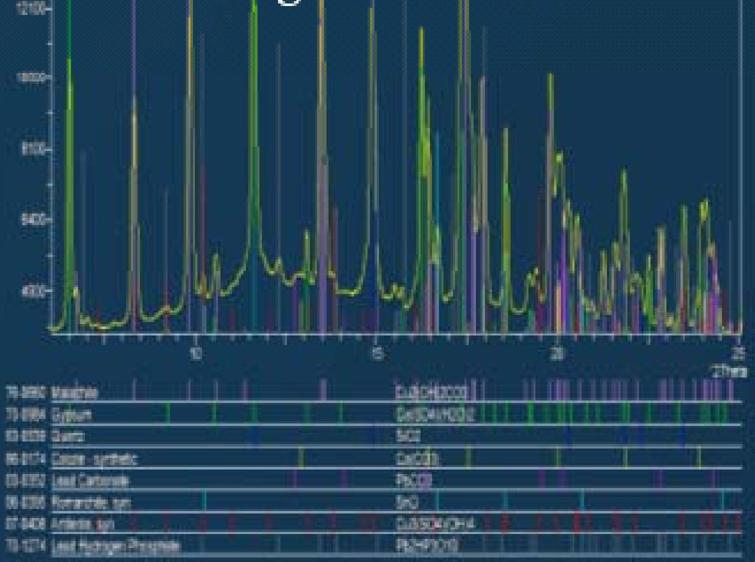
The helmet will be studied with SR-mFTIR in reflection mode and with XRF and surface SR-XRD at the SRS beamlines 13.3, 16.1 and 9.4 (photo-montage by G.A.Pantos). The objective is to characterise the corrosion products and the elemental composition.





Corrosion products - XRD

Tiny flakes (ca. 100µm) extracted from the corrosion layers inside the helmet were examined with SR-XRD using a CCD detector.



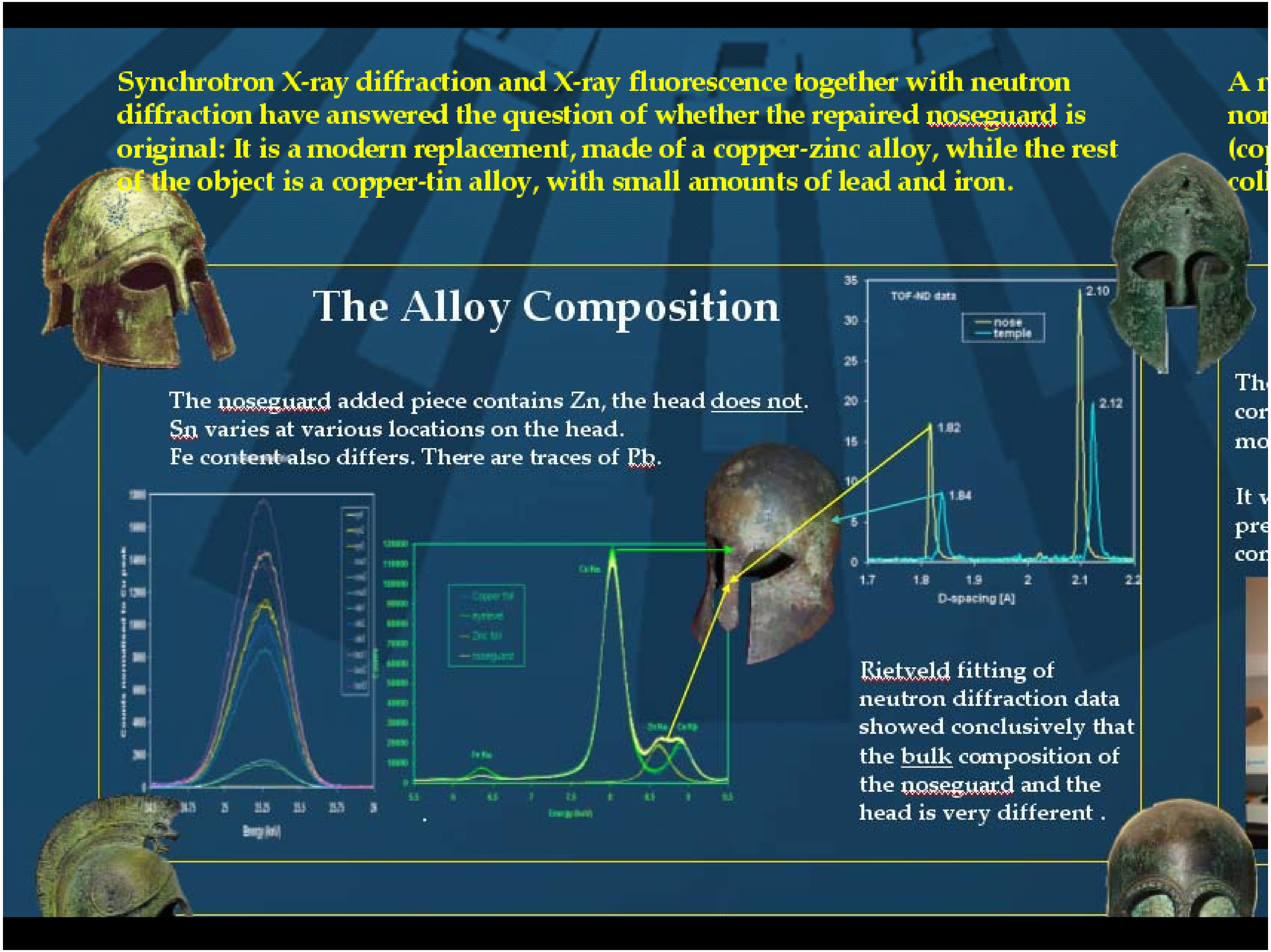
Example of phase id from one of the corrosion flakes.

Corrosion phases identified

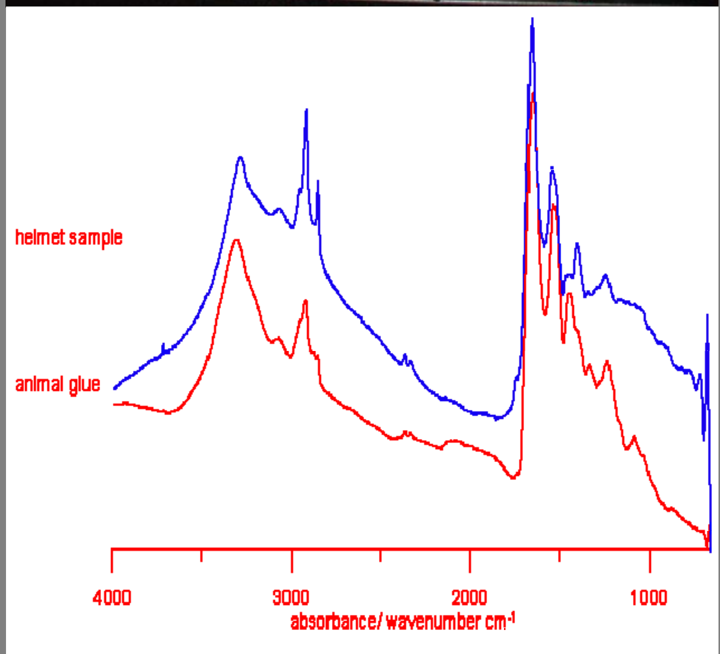
Malachite $Cu_3(CO_3)_2(OH)_2$
Cerusite $PbCO_3$
Romarchite SnO
Anglesite $PbSO_4$
Cuprite Cu_2O
Antlerite $Cu_3(SO_4)(OH)_4$
Brochantite $Cu_4SO_4{\cdot}(OH)$
Chalcocite Cu_2S
Digenite $CuS_{1.8}$
Azurite $2CuCO_3{\cdot}Cu(OH)_2$
Hydroxided Nitrate of copper and zinc $Zn_3(OH)_4(NO_3)_2$ and $Cu_2(OH)3NO_3$

Soil minerals

Quartz, Calcite, Gypsum, Hematite, Illite, Feldspars.


Synchrotron X-ray diffraction and X-ray fluorescence together with neutron diffraction have answered the question of whether the repaired noseguard is original: It is a modern replacement, made of a copper-zinc alloy, while the rest of the object is a copper-tin alloy, with small amounts of lead and iron.
The Alloy Composition
The noseguard added piece contains Zn, the head does not.
Sn varies at various locations on the head.
Fe content also differs. There are traces of Pb.
TOF-ND data
nose
temple
2.10
2.12
1.82
1.84
D-spacing [A]
Rietveld fitting of neutron diffraction data showed conclusively that the bulk composition of the noseguard and the head is very different .

Micro-FTIR in reflection mode



It was possible to identify the chemical nature of corrosion products in reflection mode, and with a beam cross-section of **10μm**.

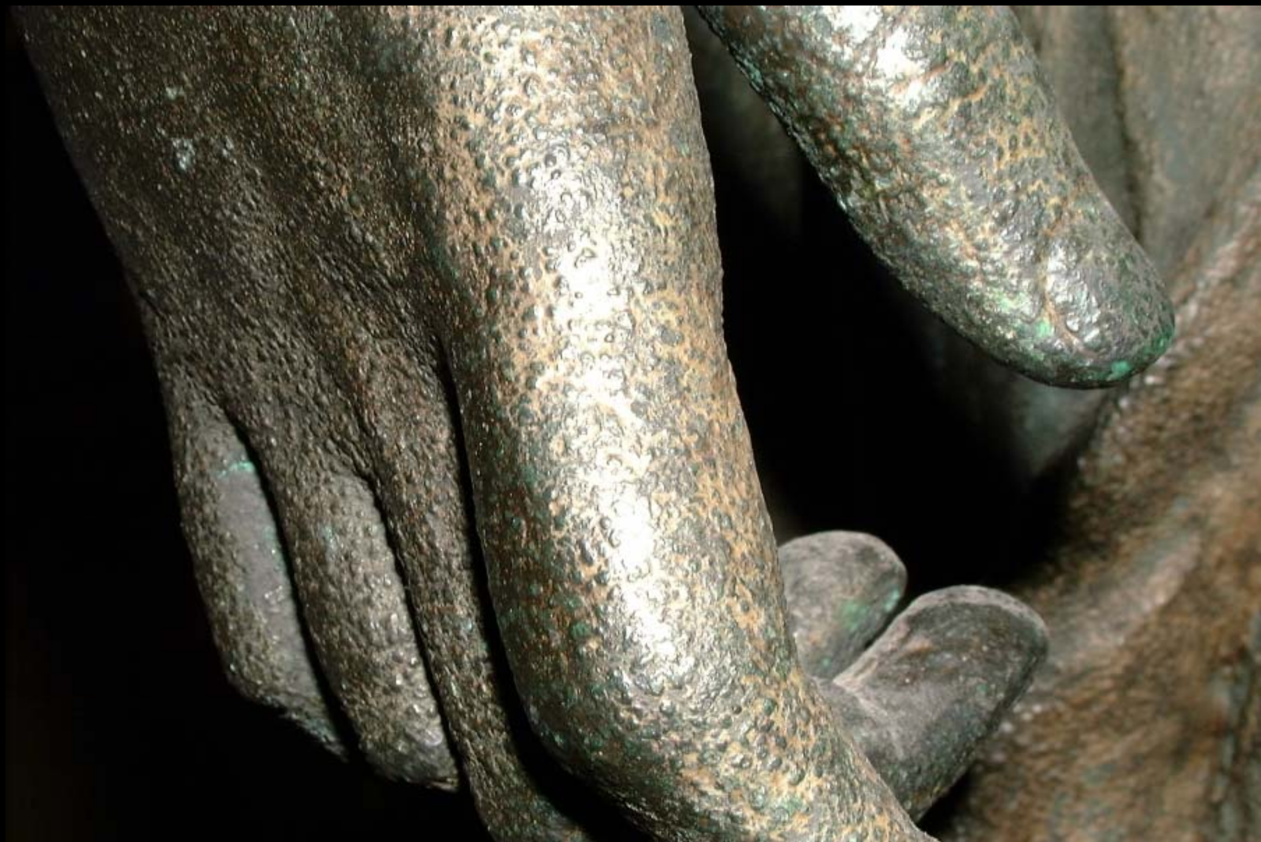
It was quickly established that the helmet had been coated (by a previous owner) with an animal glue. In glue-free locations, the composition of some of the surface deposits could be identified.

Small flakes of corrosion products were extracted from the inside of the helmet and were studied in a diamond cell.

Several corrosion products have been identified, none of them chlorides, which in the long run would initiate reactions tha can turn the metal into a heap of dust.

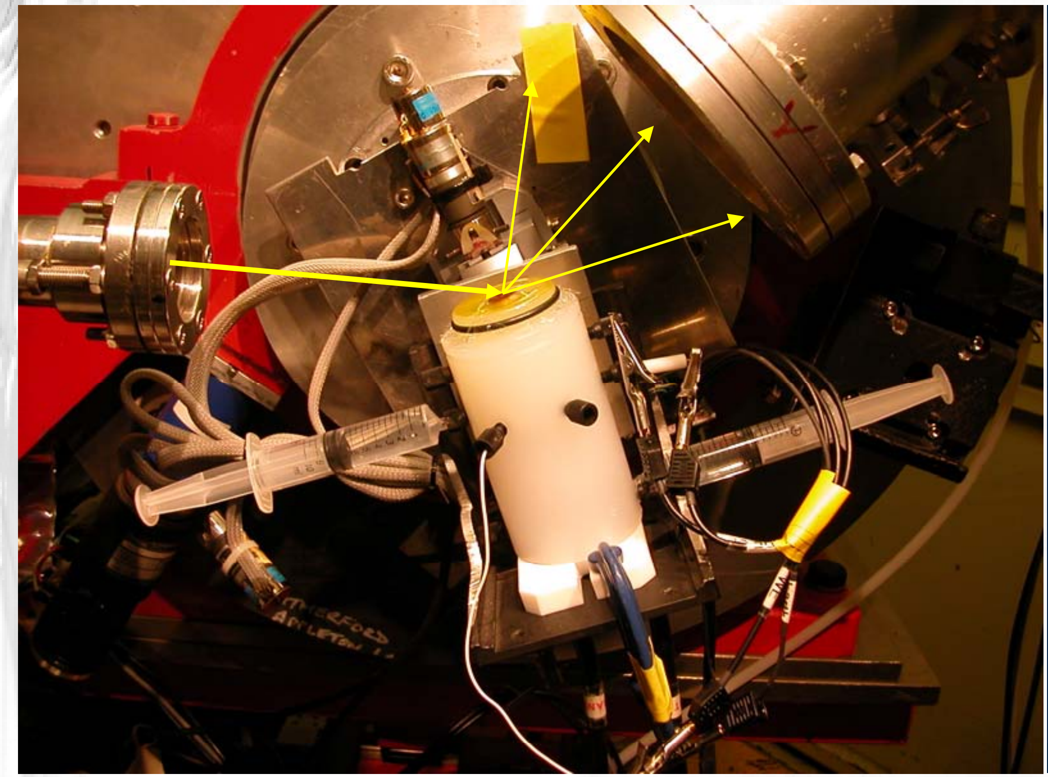
N.Salvadó, S.Butí, M.Tobin, E.Pantos and T.Pradell, The nature of medieval synthetic pigments: The capabilities of SR-Infrared spectroscopy , Anal.Chem. 2005

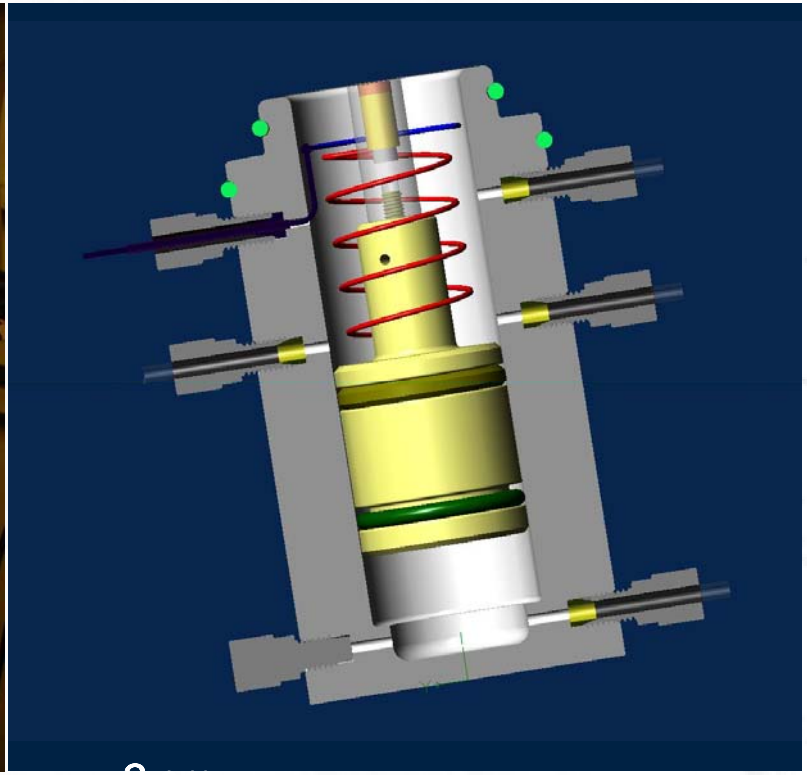
Preservation of cultural heritage



Dancing Nymph, Merseyside Museum

In-situ time-resolved
easurements

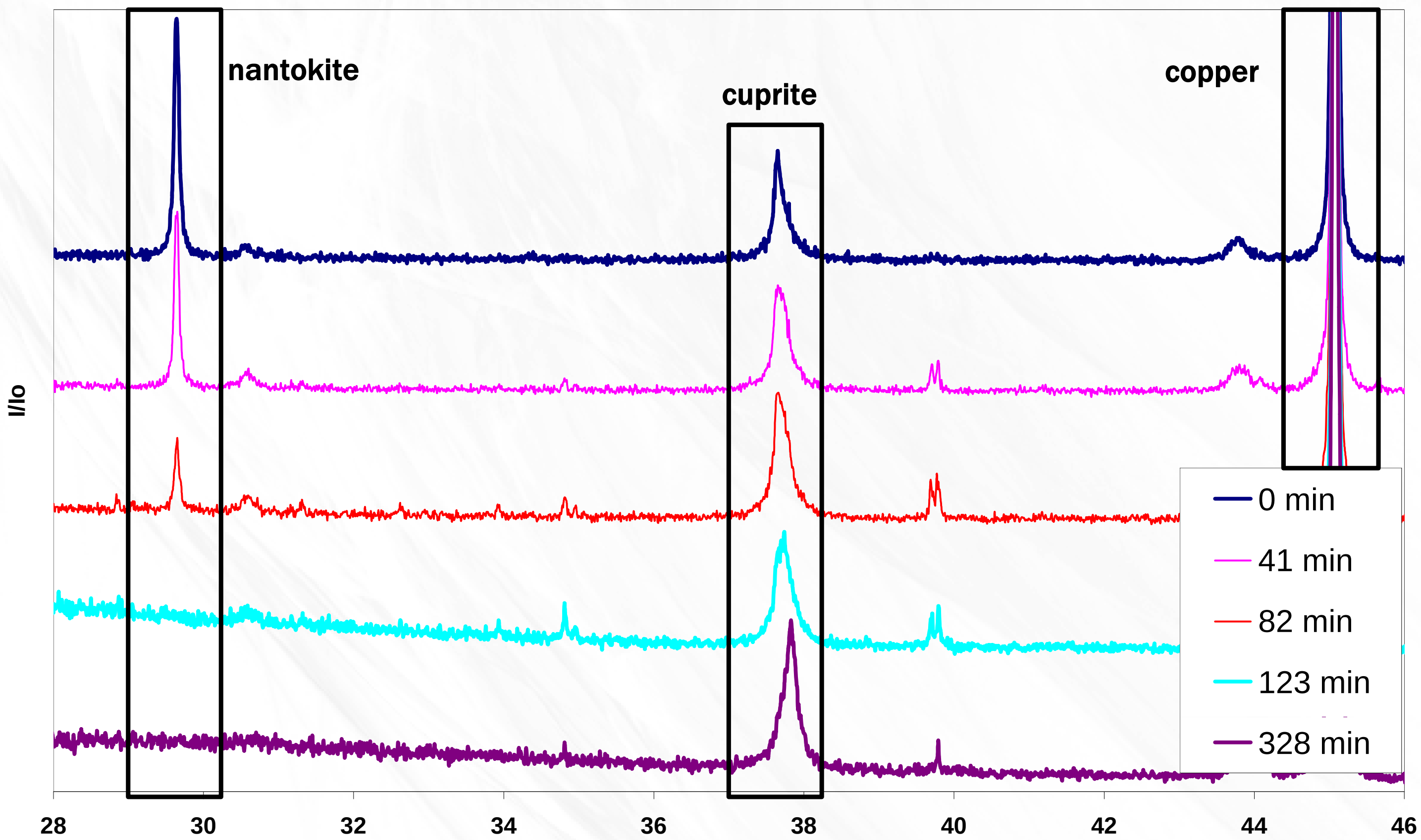




Daresbury **SRS, station 2.3**

SRS, station 2.3, Daresbury

In-situ time resolved measurements – XRD data



Data collected 5 Feb 05

A.Adriaens, K.Layssens Ghent University, M.Dowset Warrick University
UNIVERSITEIT GENT

Sulphur damage to waterlogged wo

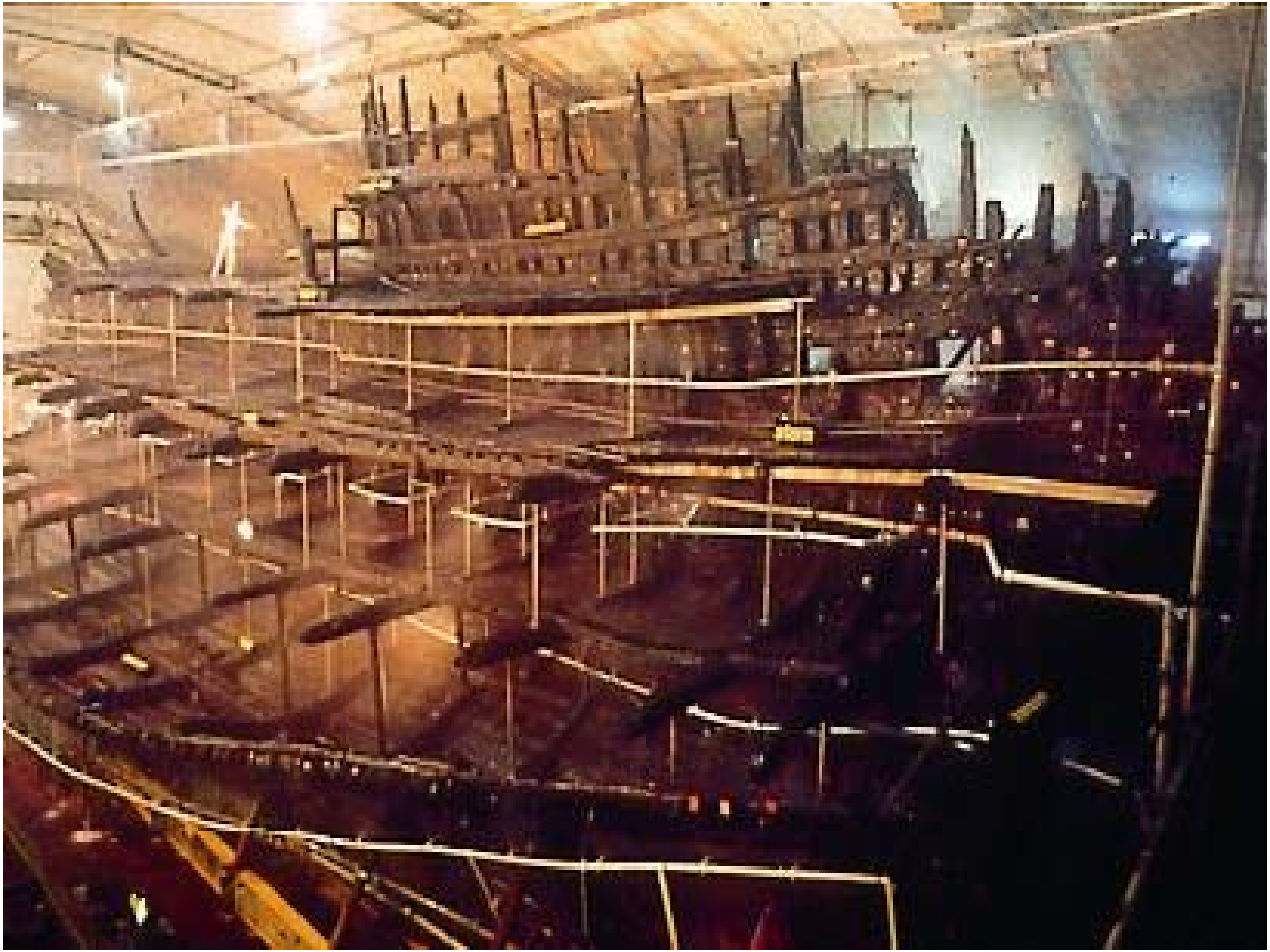
Mark Jones, Glenn McConachie
Mary Rose Trust, Portsmouth
Theo Skinner
National Museums of Scotland, Edinburgh

Henry VIII 1509–1547

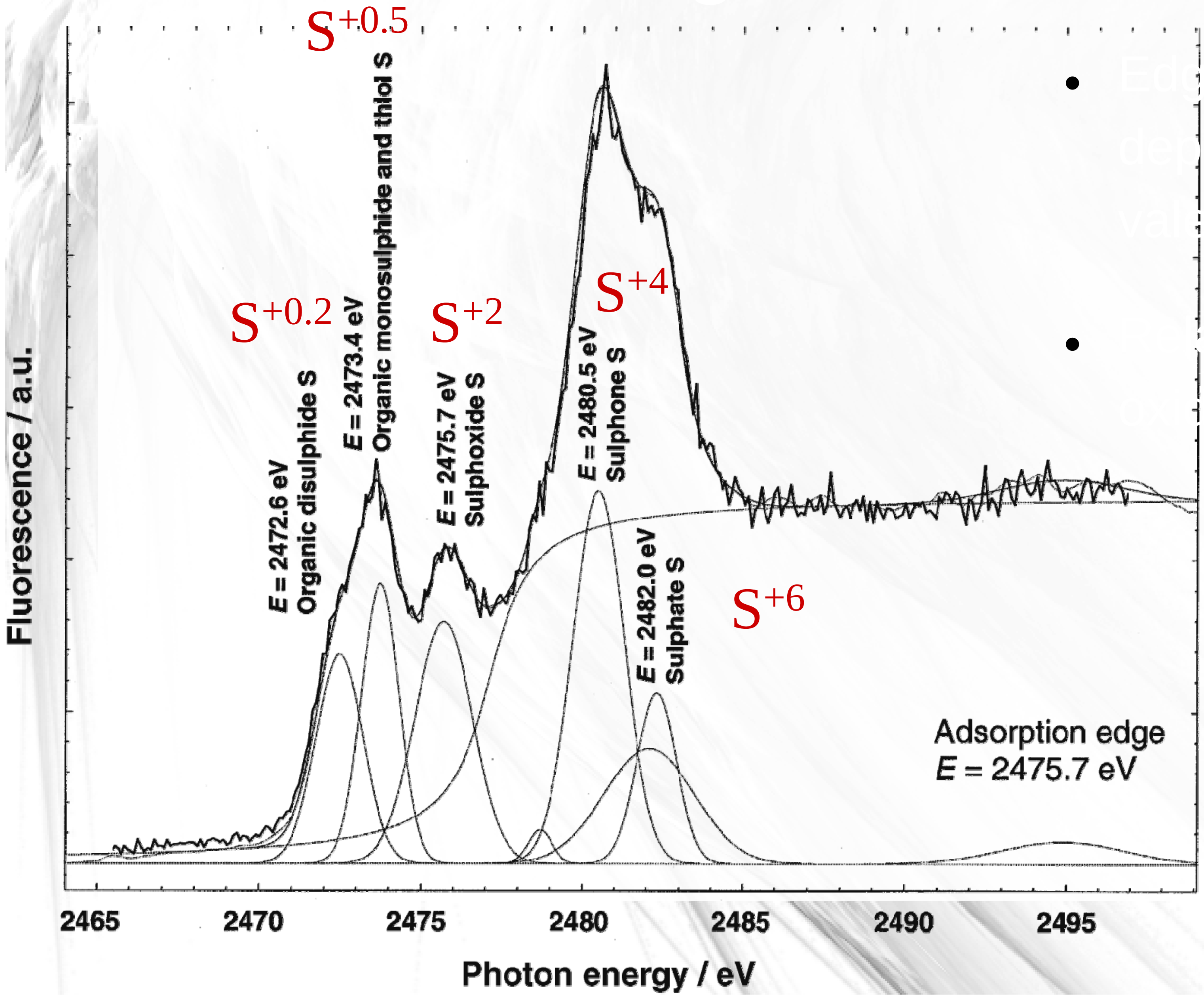
Mary Rose

Launched – 1511
Sunk – 1545
Wreck found – 1971
Wreck raised – 1982

Battle of Southsea 1545



S K-edge XANES



Prietzel *et al*
Euro.J.Soil.Sci.(2003)
54 *pp.423–433*

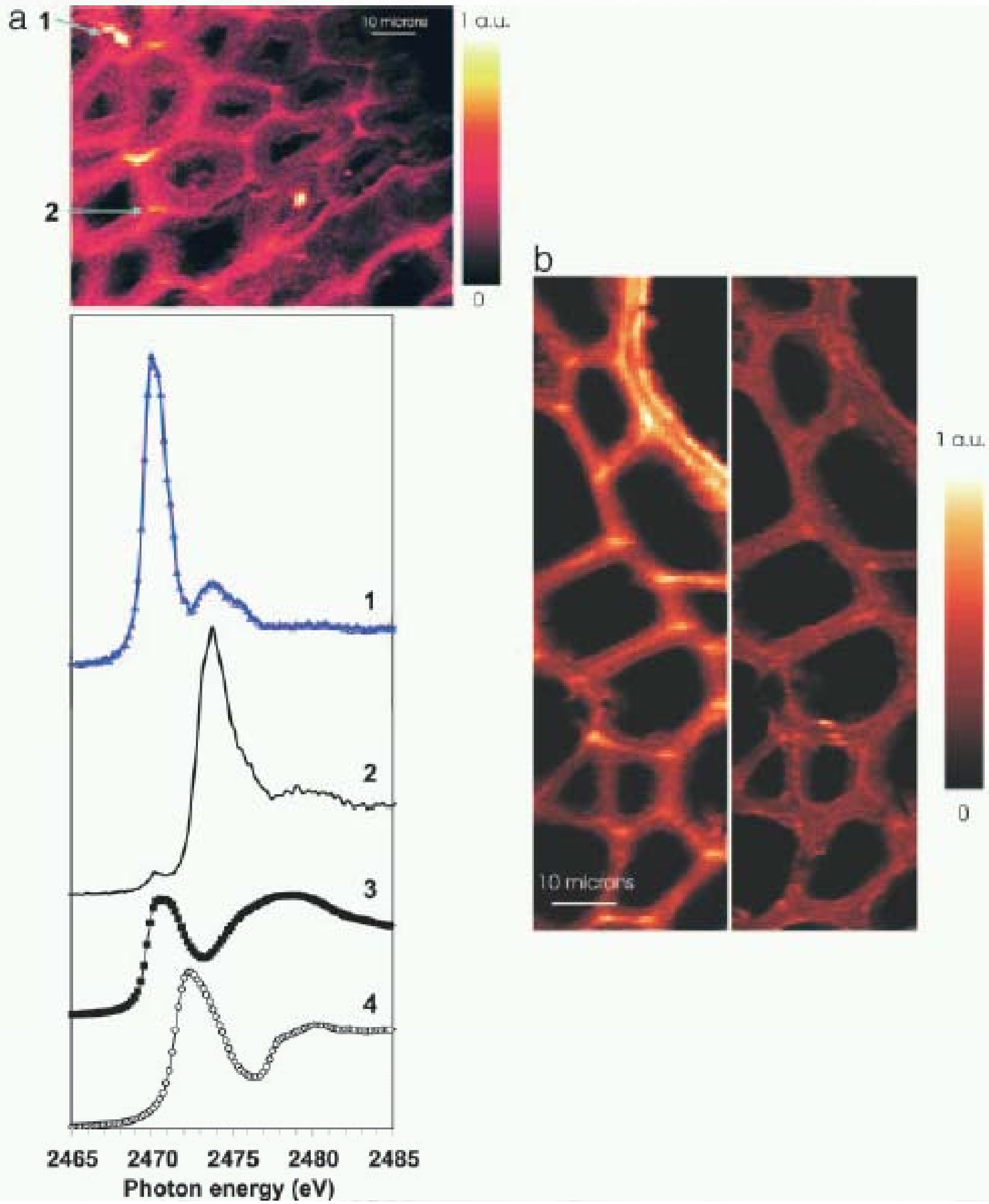
Micro-speciation of Sulphur in marine timber

Hull timber under spray treatment

Soft X-ray microscopy of reduced sulphur in cellular structure of wood from the Mary Rose.

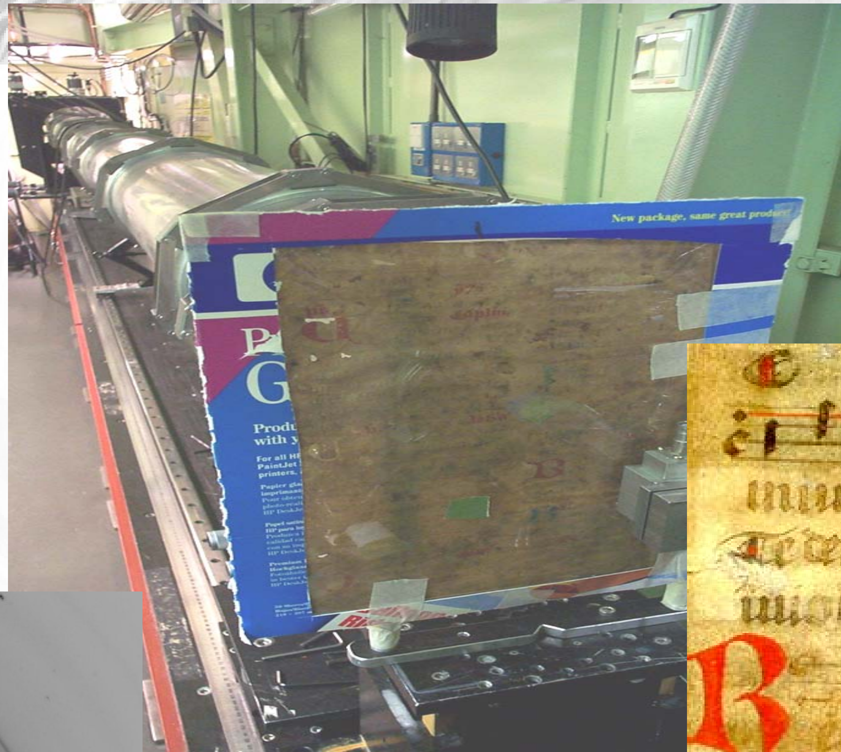
From points 1&2

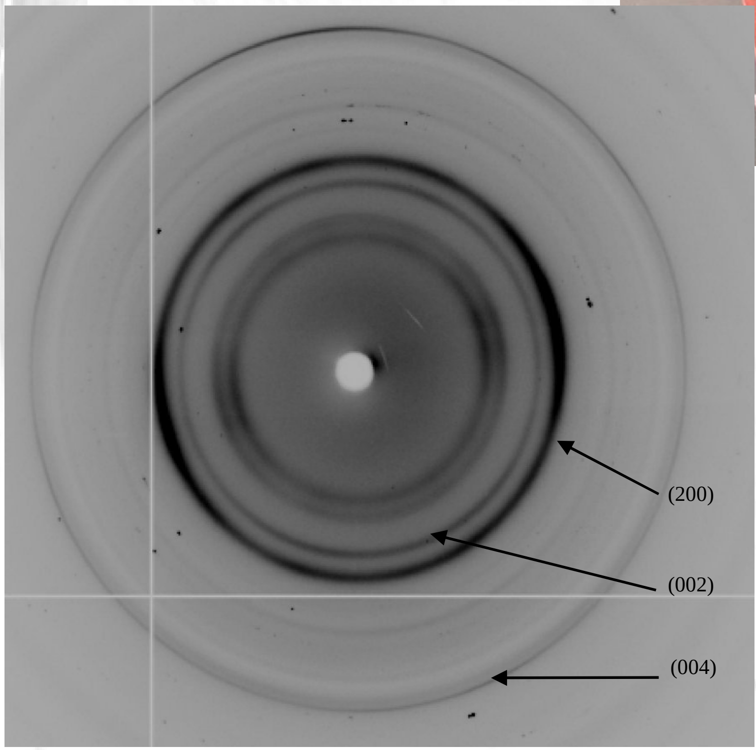
Pyrrhorite $F_{1-x}S$ and pyrite FeS_2 standards



X-rays interact weakly with organic matter.

SR gives strong scattering signal.





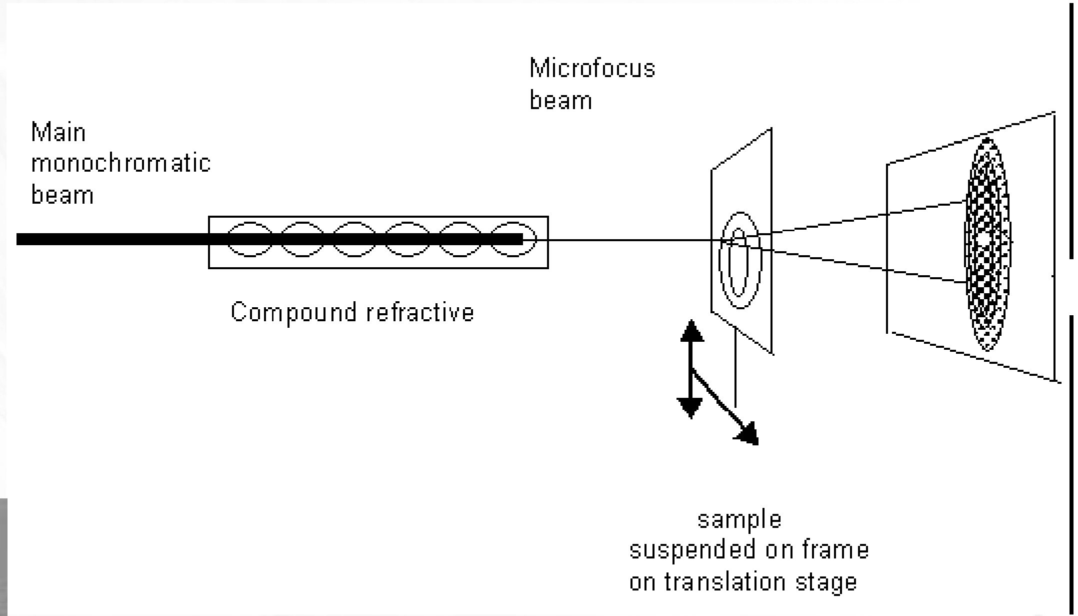
An X-ray diffraction image of historical paper from the Museums of Scotland, taken at beamline 14.1 at the Daresbury synchrotron.

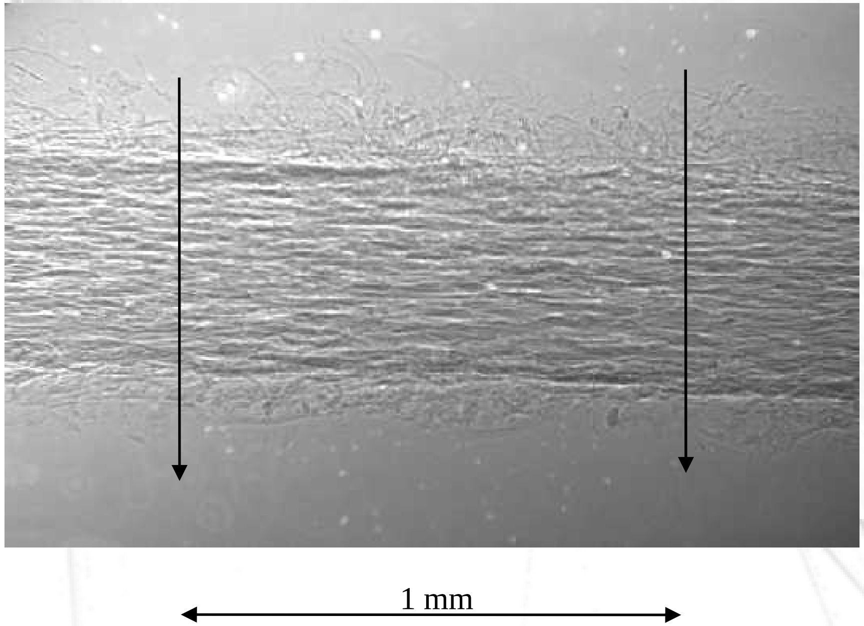
Kennedy C.J., Hiller J.C., Lammie D., Drakopoulos M., Vest M., Cooper M., Adderley W.P., Wess T.J. (2004) Microfocus X-ray diffraction of historical parchment reveals variations in structural features through parchment cross sections. *Nano Letters*, **4**, 1373-1380

Microfocus X-ray Diffraction

ESRF ID18F: Very small beam size (1.5µm x 15µm).

Allows surface-to-surface scans of the parchment to be taken (up to 200 images).





Localised (e.g. surface) effects can thus be monitored.


19/07/2005


19/07/2005

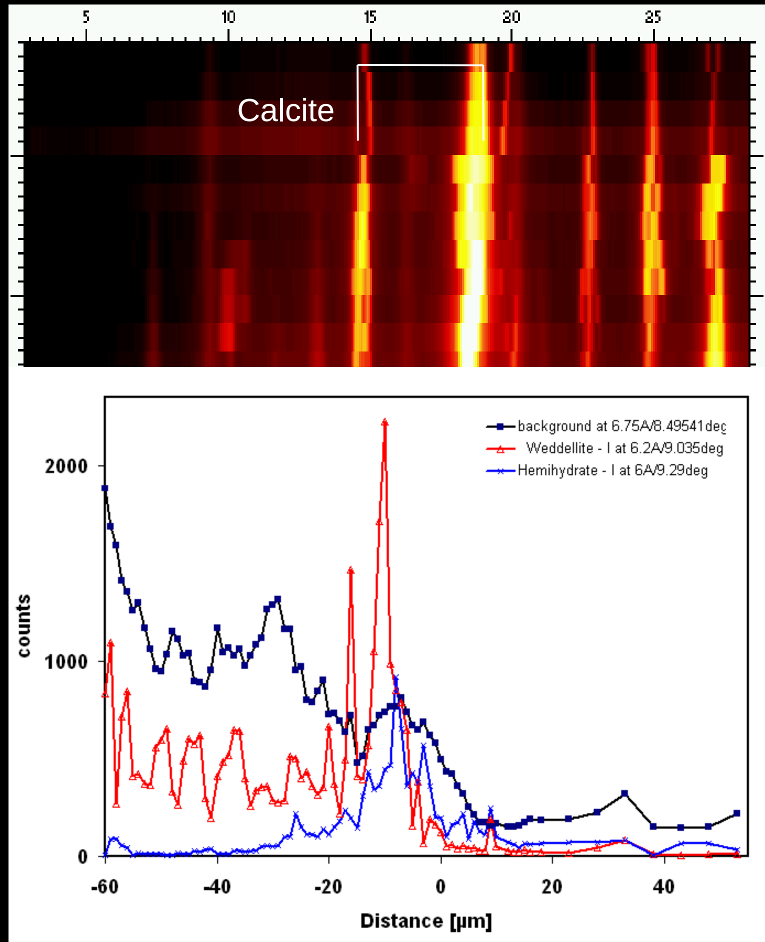

19/07/2005

Stone weathering and bioremediation

Biodeterioration includes several mechanisms such as surface formation called patina (consisting in films or crusts); organic pigment production, salt precipitation and recrystallization, corrosive and oxidative processes caused by cell excretion of inorganic and organic acids.

Bioremediation techniques can use bacteria to link the mineralization processes which remove stone crusts to the consolidation phenomenon of calcification.

SR micro-imaging modalities can be used to characterise mineral changes in stones during bioremediation treatment in laboratory studies and the extent of penetration into the stone.



Diffraction map across Duomo marble in 100 micron steps

L.Depero, R.Petrazani, E.Bontempi, Brescia University – Lucia Toniolo, Milan Polytechnic

Trends

Characterisation of painting pigments and ceramic glazes

Issues of manufacture and evolution of techniques

Deterioration studies – paper, stone, ink, metals

Time-resolved studies for reproduction or monitoring ageing/alteration effects

Special objects: authenticity, provenance

Overlap with conventional techniques

Overlap with other “big” techniques involving use of large scale facilities

80% of applications address cultural heritage area – 20% archaeology

Interest in SR-CH growing both from sources and future users

Challenges

Engaging archaeologists and archaeological scientists
museum curators and conservation scientists
Relations of trust over long time

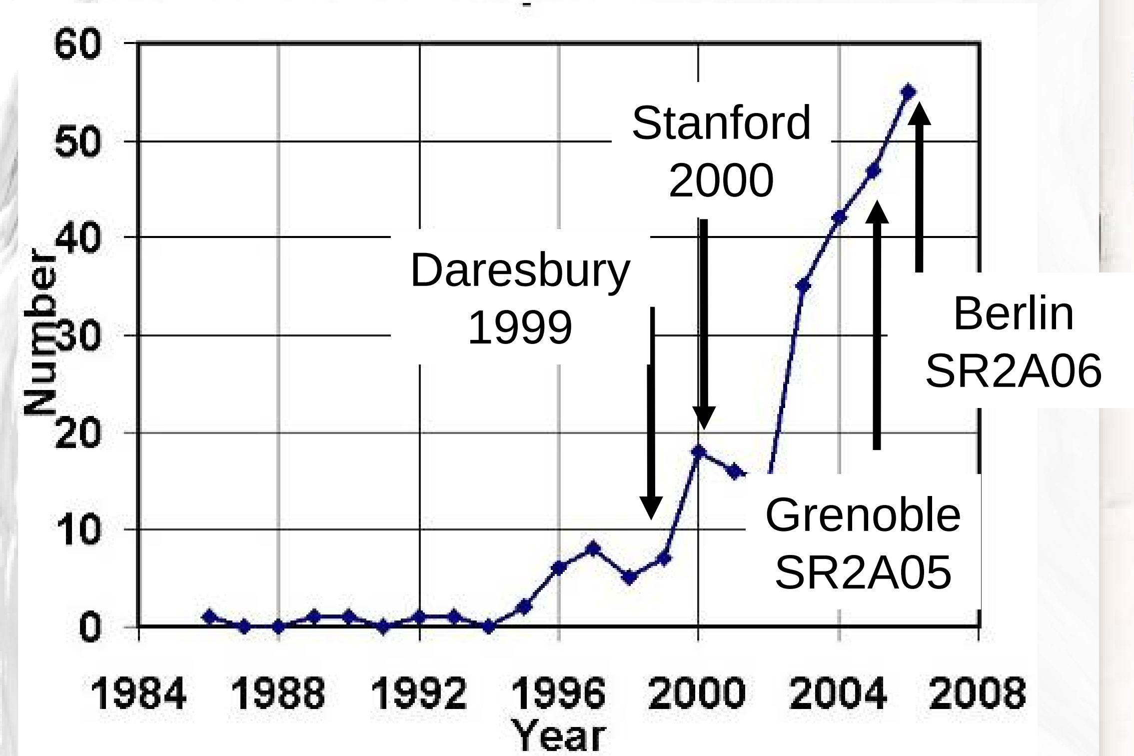
Funding from diverse sources. CH not frontline science
PR of high interest to SR sources

Access to beamline facilities and resident personnel
on a long-term basis

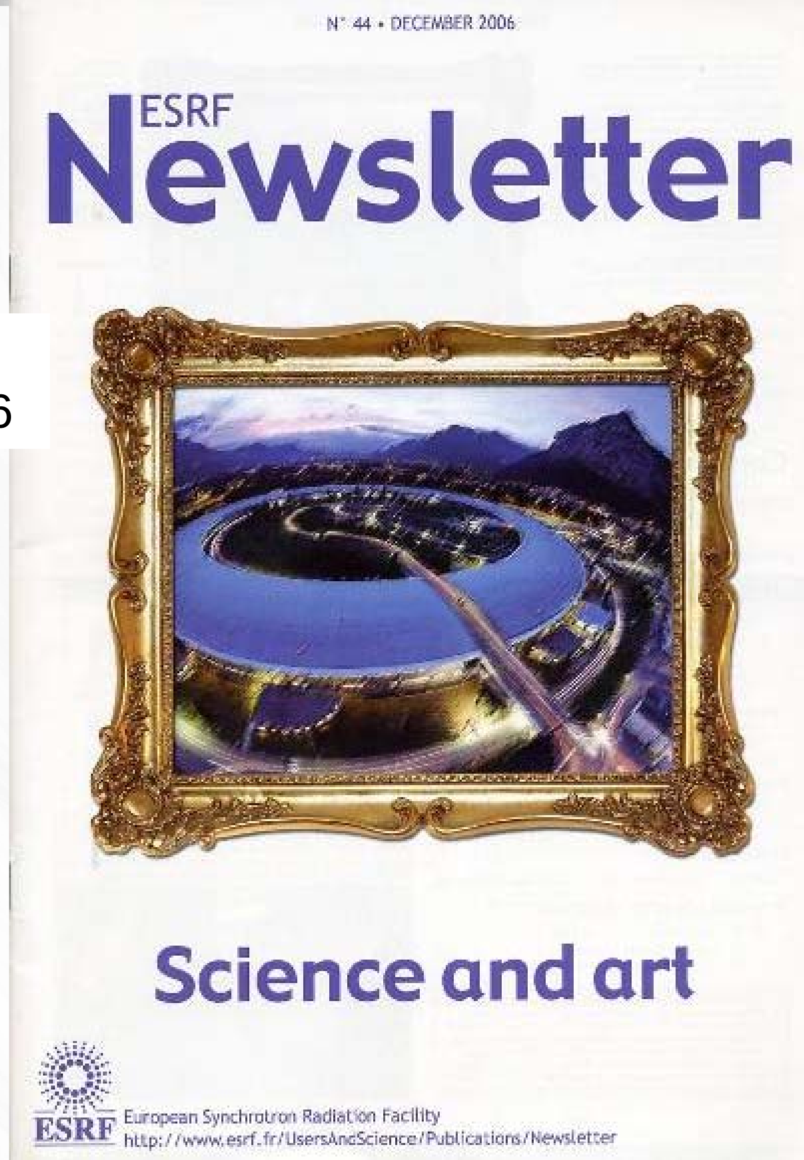
Sample preparation handling – very small or large objects

Space-resolved measurements can produce large datasets
Problems of interpretation

Time-resolved studies require a lot of beamtime
Processes can not be rushed



Nothing succeeds like success



ootprint as
Probing the Past
Vegetable, Animal or Mineral
µXRD
PEY-XAS
High
Temperature-resolved XRD