Radioactivity

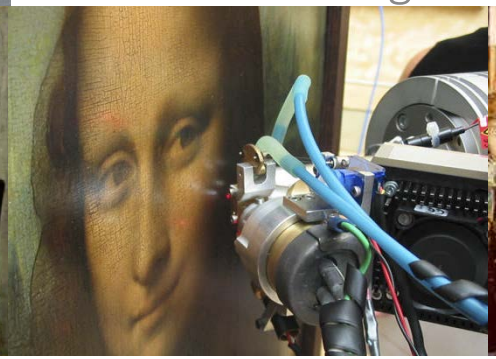
Lecture 25

Radioactivity and Art Analysis

Modern Tools for Ancient Art

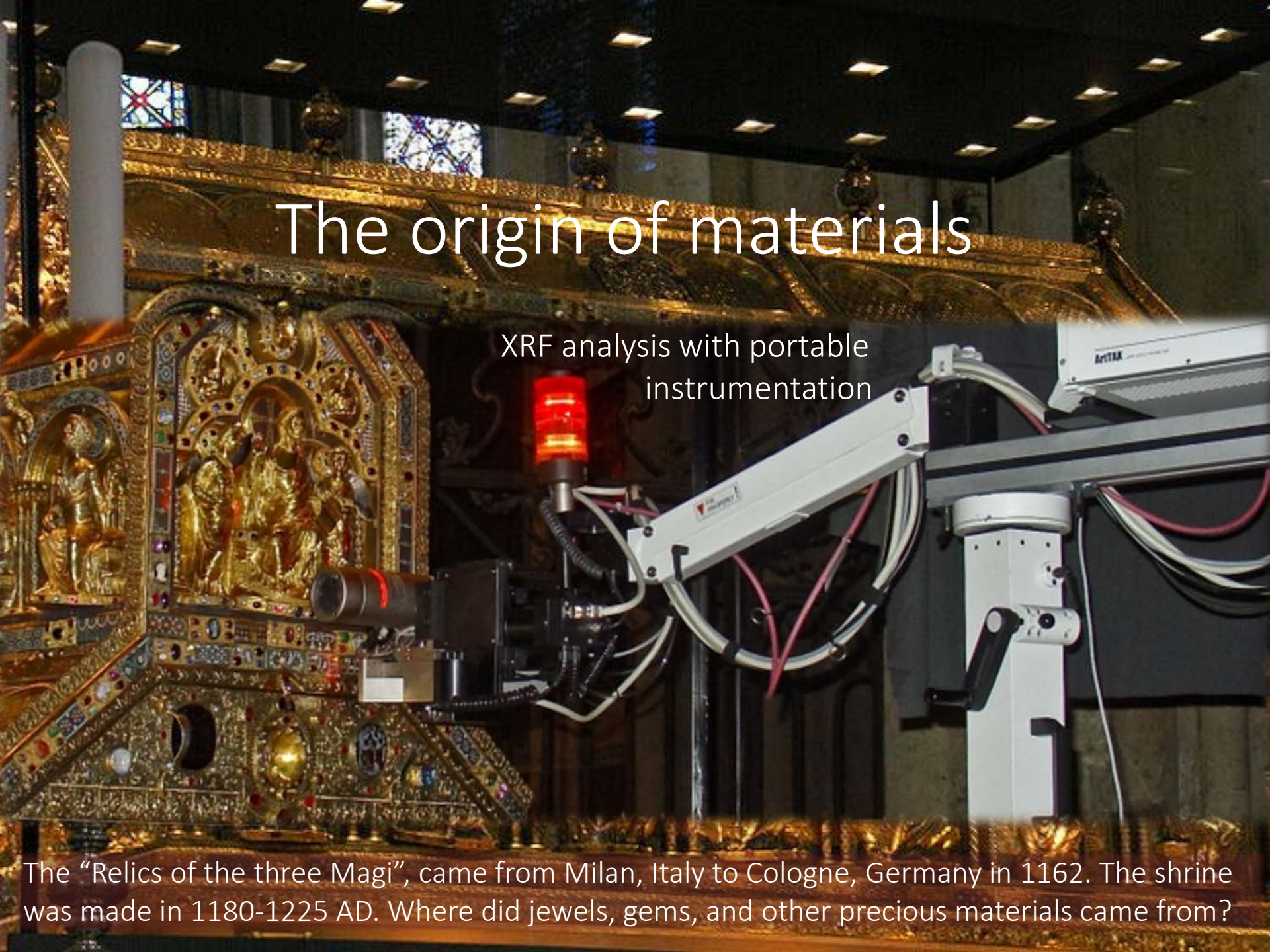
Modern art analysis techniques rely on the quantum nature of matter to determine providence, age, techniques, and forgeries.

The most frequently used methods are x-ray analysis such as PIXE and XRF, coupled with atomic analysis techniques such as Raman spectroscopy, and nuclear physics techniques such as Neutron activation analysis. This is complemented by radioactive dating taking the half-life as time scale.



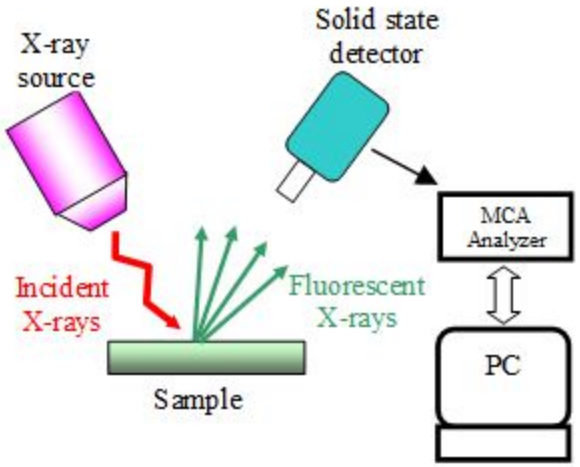
The origin of materials

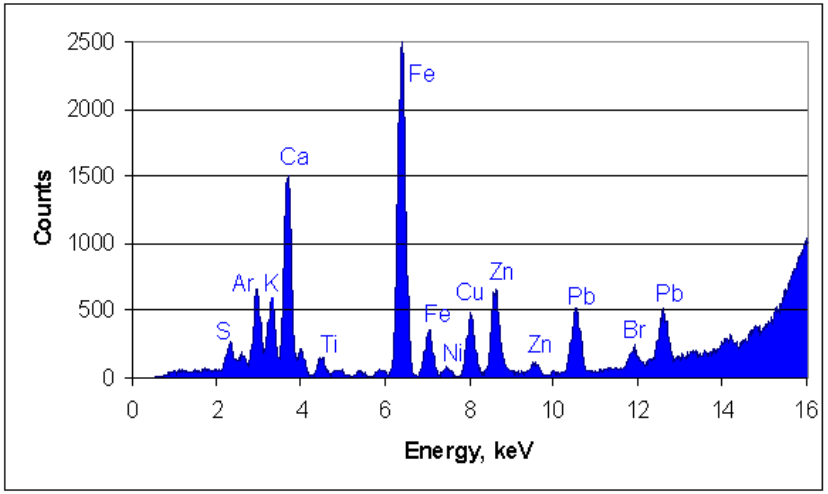
XRF analysis with portable instrumentation



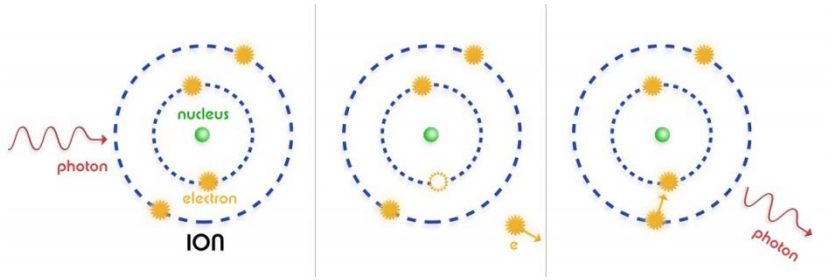
The “Relics of the three Magi”, came from Milan, Italy to Cologne, Germany in 1162. The shrine was made in 1180-1225 AD. Where did jewels, gems, and other precious materials came from?

X-ray Analysis by XRF and PIXE





Each element emits its own characteristic line due to the quantum transition of electrons to lower excited orbits in the atomic shell.



$$E_x = (Z-1)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right)$$

for S: $Z = 16$; $E_x = (15)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 2.29\,[eV]$

for Ca: $Z = 20$; $E_x = (19)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 3.68\,[eV]$

for Ti: $Z = 22$; $E_x = (21)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 4.50\,[eV]$

for Fe: $Z = 26$; $E_x = (25)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 6.37\,[eV]$

for Zn: $Z = 30$; $E_x = (29)^2 \cdot 13.6\,[eV] \cdot \left(1 - \frac{1}{2^2}\right) = 8.58\,[eV]$

Analysis of paint pigments

Pre 1800 oil paintings contained specific pigments prepared from naturally available materials to achieve color effects. After 1850 these pigments were gradually replaced by organic (Carbon based) pigments provided by the chemical industry.

White pigments	
Antimony white	Sb_2O_3
Lithopone	$ZnO + BaSO_4$
Permanent white	$BaSO_4$
Titanium white	TiO_2
White lead	$2PbCO_3 \cdot Pb(OH)_2$
Zinc white	ZnO
Zirconium oxide	ZrO_2
Chalk	$CaCO_3$
Gypsum	$CaSO_4 \cdot 2H_2O$

Yellow pigments	
Auripigmentum	As_2S_3
Cadmium yellow	CdS
Chrome yellow	$2PbSO_4 \cdot PbCrO_4$
Cobalt yellow	$K_3[Co(NO_2)_6] \cdot 1.5H_2O$
Lead–tin yellow	$Pb_2SnO_4/PbSn_2SiO_7$
Massicot	PbO
Naples yellow	$Pb(SbO_3)_2/Pb_3(SbO_4)_2$
Strontium yellow	$SrCrO_4$
Titanium yellow	$NiO \cdot Sb_2O_3 \cdot 20TiO_2$
Yellow ochre	$Fe_2O_3 \cdot nH_2O$ (20–70%)
Zinc yellow	$K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$

Red pigments	
Cadmium red	$CdS + CdSe$
Cadmium vermilion	$CdS + HgS$
Chrome red	$PbO \cdot PbCrO_4$
Molybdate red	$7PbCrO_4 \cdot 2PbSO_4 \cdot PbMoO_4$
Realgar	As_2S_3
Red lead	Pb_3O_4
Red ochre	Fe_2O_3 (up to 90%)
Vermilion	HgS

Green pigments	
Basic copper sulfate	$Cu_x(SO_4)_y(OH)_z$
Chromium oxide	Cr_2O_3
Chrysocolla	$CuSiO_3 \cdot nH_2O$
Cobalt green	$CoO \cdot 5ZnO$
Emerald green	$Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$
Guignent green	$Cr_2O_3 \cdot nH_2O + H_3BO_3$
Malachite	$CuCO_3 \cdot Cu(OH)_2$
Verdigris	$Cu(CH_3COO)_2 \cdot nCu(OH)_2$

Blue pigments	
Azurite	$2CuCO_3 \cdot Cu(OH)_2$
Cerulean blue	$CoO \cdot nSnO_2$
Cobalt blue	$CoO \cdot Al_2O_3$
Cobalt violet	$Co_3(PO_4)_2$
Egyptian blue	$CaO \cdot CuO \cdot 4SiO_2$
Manganese blue	$BaSO_4 \cdot Ba_3(MnO_4)_2$
Prussian blue	$Fe_4[Fe(CN)_6]_3$
Smalt	Co-glass ($K_2O + SiO_2 + CoO$)
Ultramarine	$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$

Black pigments	
Antimony black	Sb_2O_3
Black iron oxide	$FeO \cdot Fe_2O_3$
Carbon or charcoal black	C (95%)
Cobalt black	CoO
Ivory black	$C + Ca_3(PO_4)_2$
Manganese oxide	$Mno + Mn_2O_3$

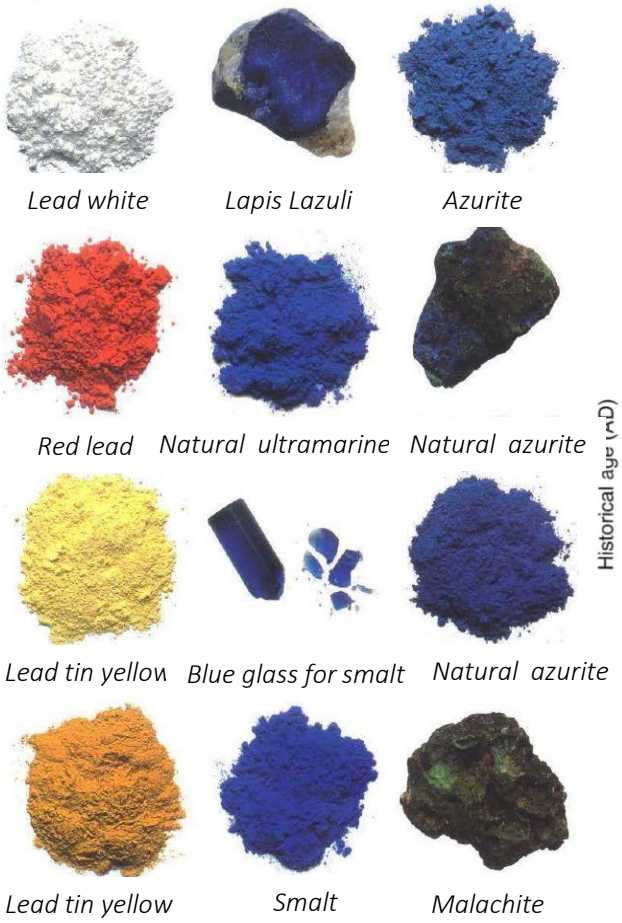
Pigments available until 1800 AD

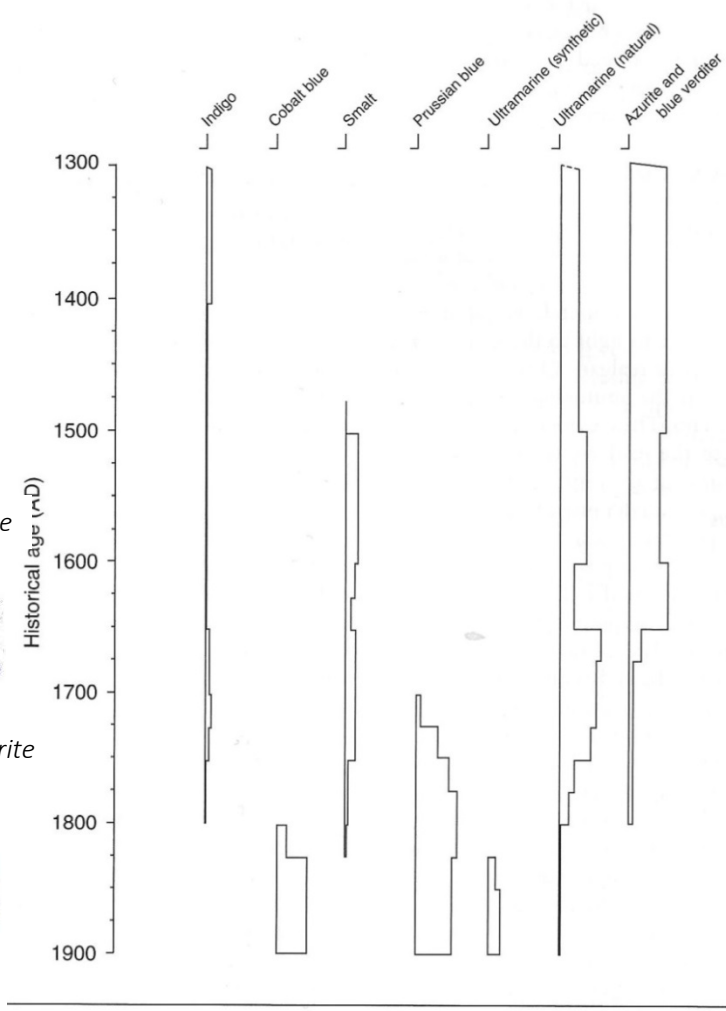
Paint is composed of a colored pigment and a binder substance

Pigment: colored powdered substance grinded from minerals salts, or dyes

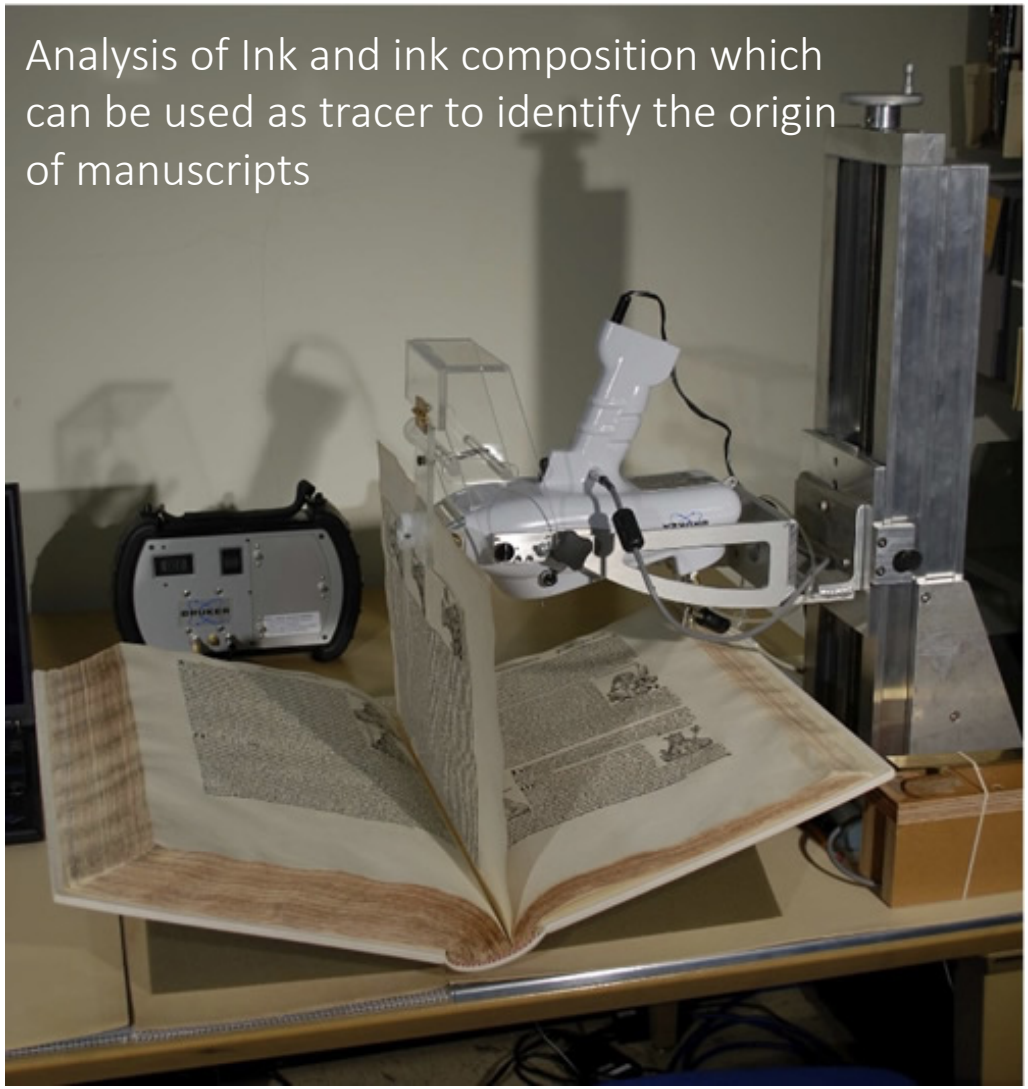
Binder: Material that evenly disperses the pigment, adheres to surface when paint applied and then dries.

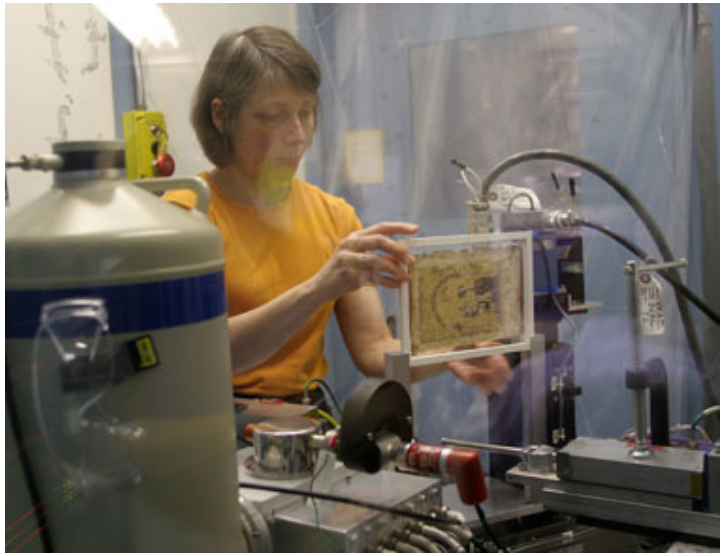
Paints are throughout uniform homogeneous mixtures.





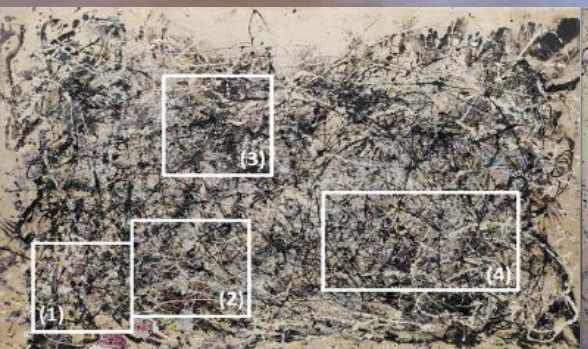
X-Ray Fluorescence of Manuscripts



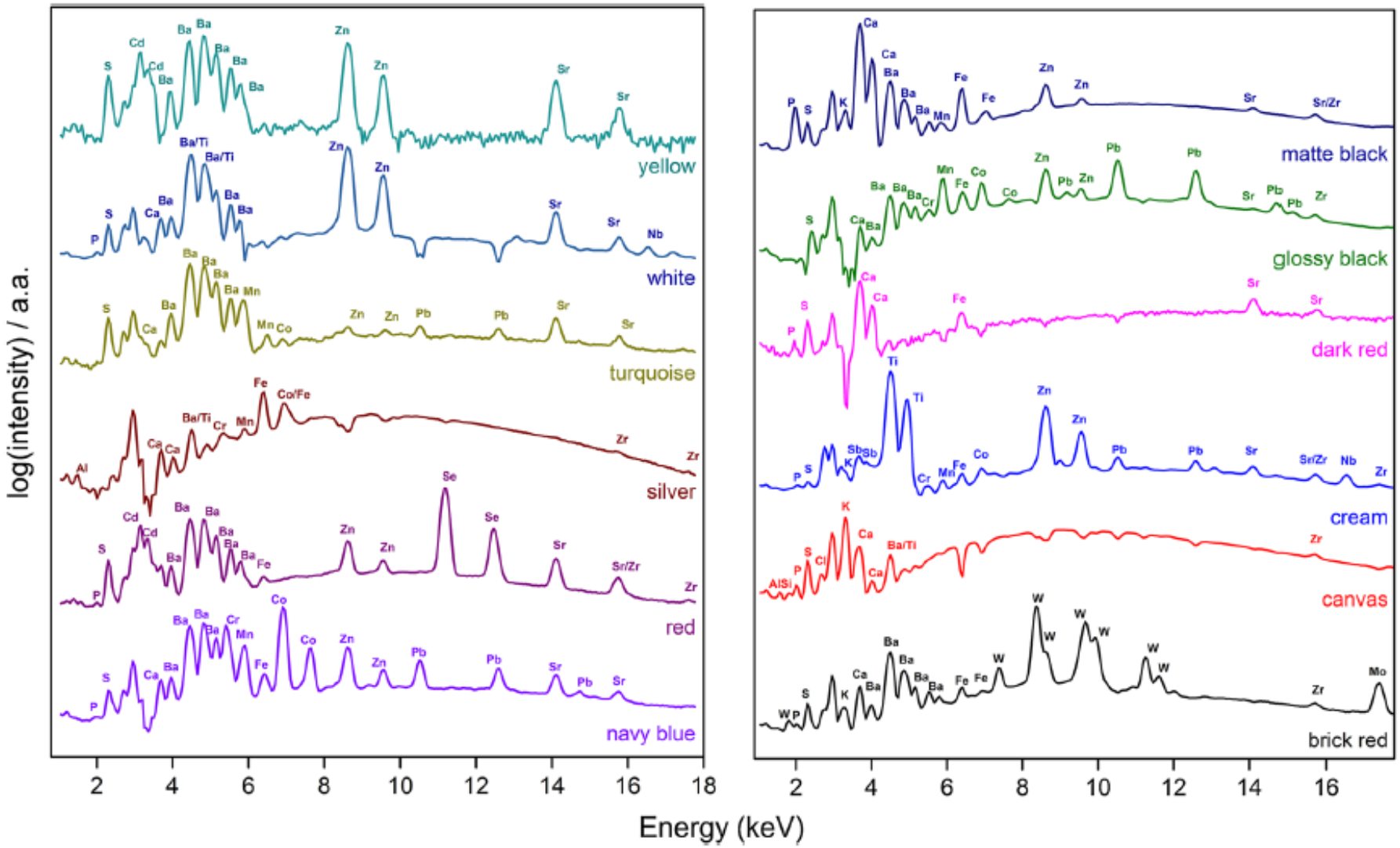


Painting techniques on the example of Pollock

Jackson Pollock's Number 1A (1948)



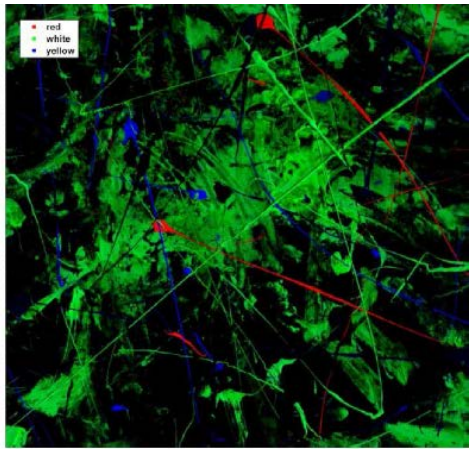
XRF spectra for different color combinations



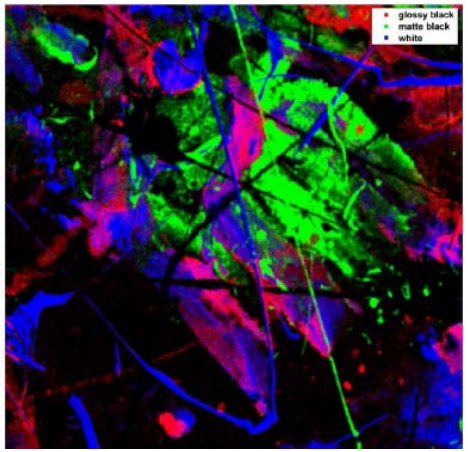
Signature spectra for the twelve components (11 paints and canvas) identifying the characteristic x-ray *lines* for the elements present.

XRF analysis of use of overlaying colors

Overlapped distribution maps of the *white*, *red* and *yellow* paints for area (1) and image of that area. The sequence in which they were applied can be established by examining how the paints overlap: *white*, *red*, *yellow* and *white* again.



Overlapped distribution maps of the *white*, *glossy* and *matte black* paints for a section in area (1) showing that the gray paint was made by mixing the *white* paint and the *black glossy* paint and not the *matte black*



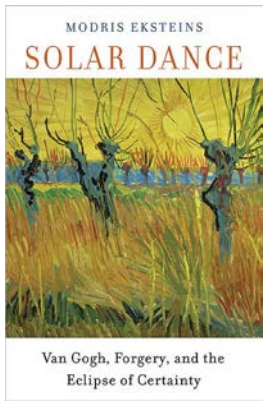
Pollock mostly applied each paint straight out of the tube or can, and with a specific gesture, brushstroke (matte black and white), dripping (cream, glossy black and silver gray), thrusting (turquoise, matte black and white), squeezing the tube (red and yellow) or splattering (cream and silver gray), and using a specific tool, brush or stick. Some of the paints were applied wet on wet like the thinner cream and glossy black house paints creating a marbling look by overlapping the corresponding distribution maps for the area . He used his hands to apply the red brick and matte black paints leaving clear handprints, or creating large stains by dragging his hands or pressing his palms against the canvas.

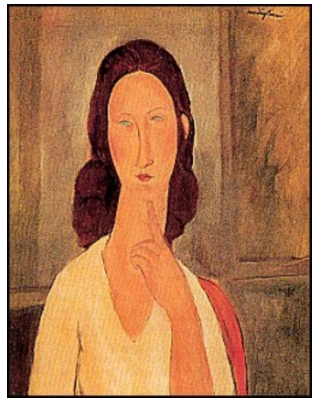
Identification of Art Forgery

Science techniques are an emerging tool for:

- Forgery analysis by nuclear forensic techniques in a competitive art market (Vermeer, Van Gogh, Modigliani, Rothko, etc)

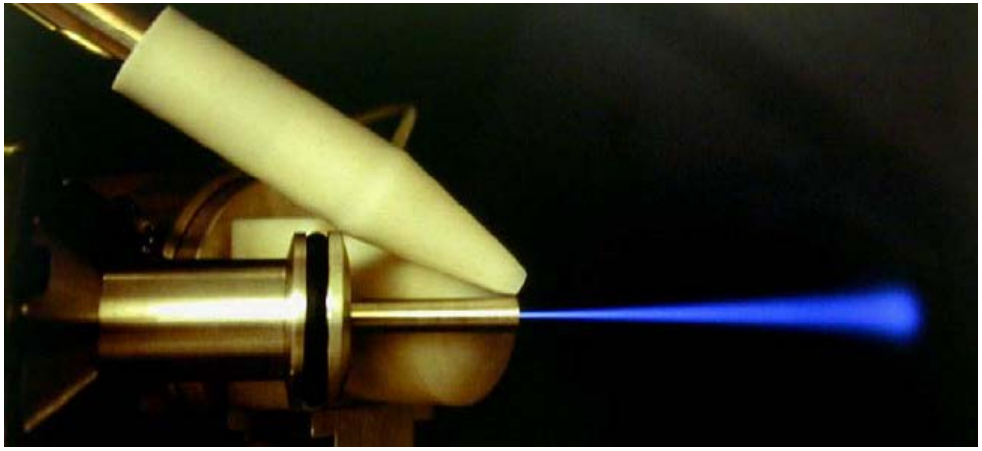
e.g. Vermeer forgeries by Hans van Meegeren
Van Gogh forgeries by Otto Wacker
>1000 Modigliani fakes by Elmyr de Hory
New York galleries sold Mark Rothko, Jackson Pollock and Willem de Kooning forgeries; damage unknown
Recent forgeries by Wolfgang Beltracchi of German expressionists such as Heinrich Campendonk and Max Ernst caused a major art scandal in Europe.

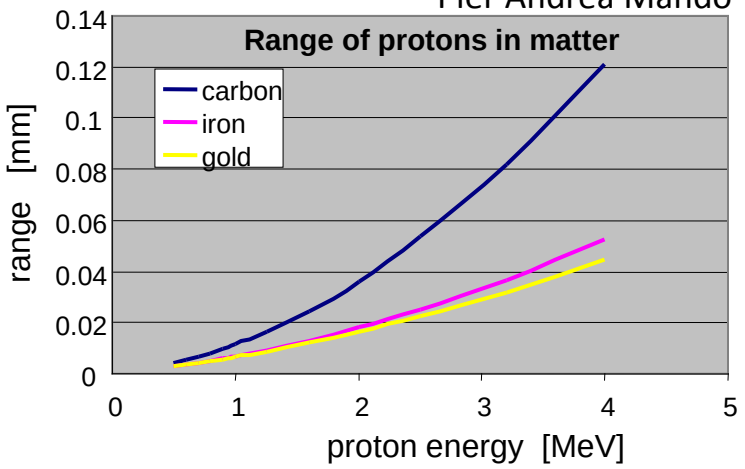




Proton Induced X-ray Emission (PIXE)

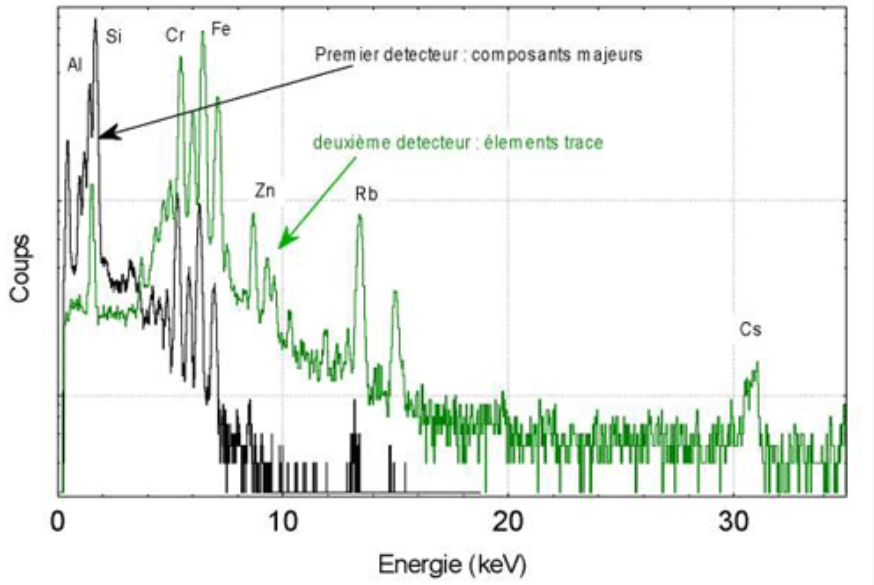
Pier Andrea Mandò





Tracing Material Origins

The red stone eyes of the statue of the Parthian goddess of love Ishtar were originally thought by Louvre curators to be made of colored glass



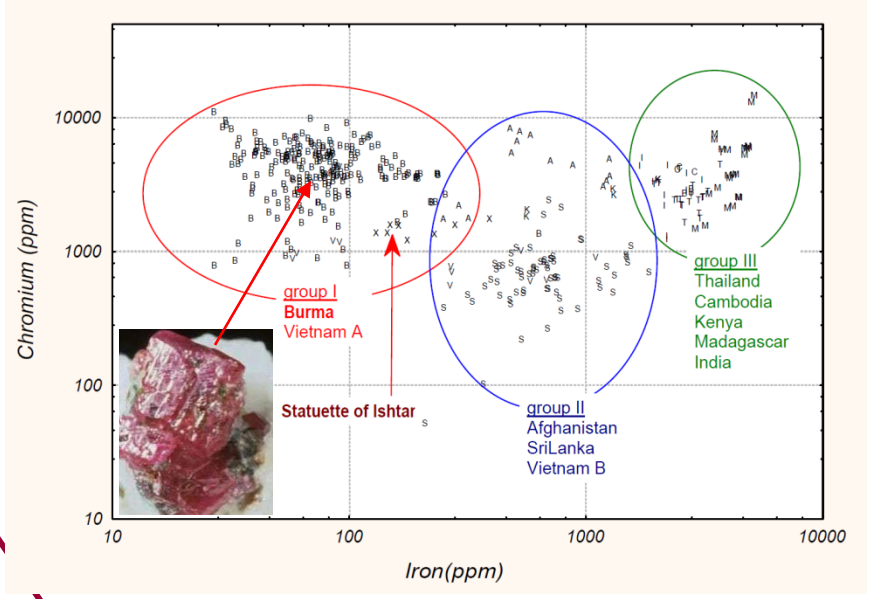
PIXE analysis showed that the inlays were rubies. $AL_2\ SIO_4\ (F,OH)_2$+(Cr,Fe rich)

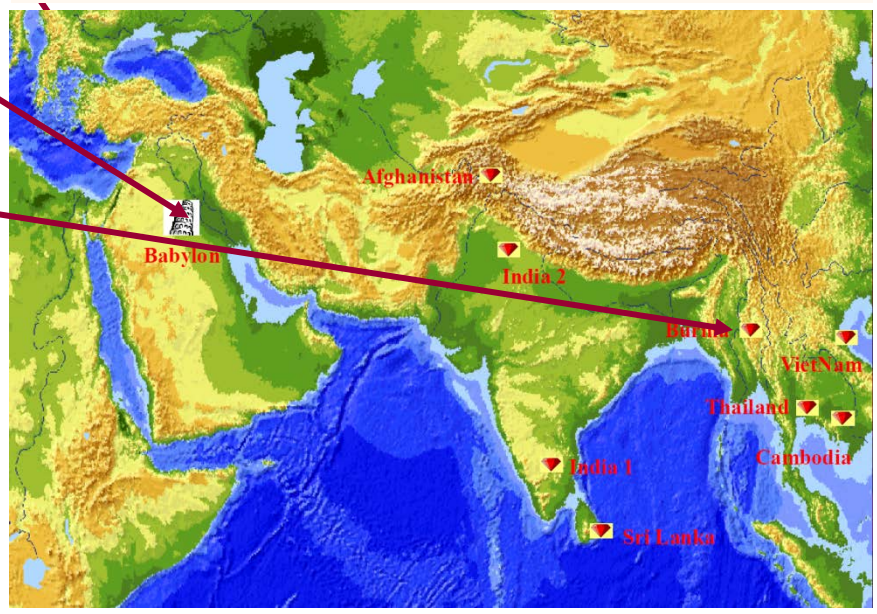
T. Calligaro et al. Nucl. Instr. Meth. B 136 (1998) 846-850

Provenance, or where did the rubies come from?

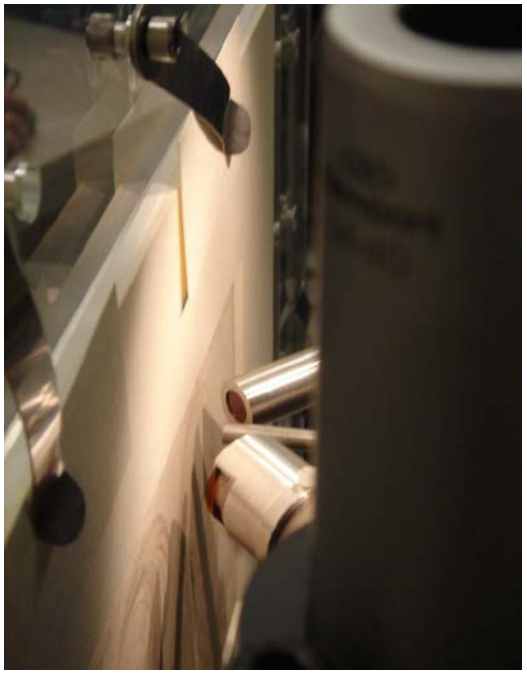
The trace element content provides the fingerprint of provenance in archaeology

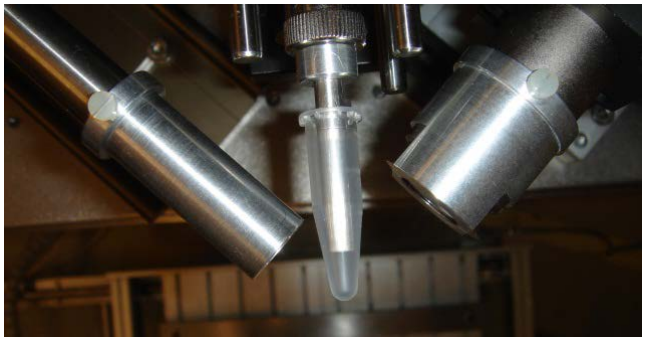
Comparison of Fe versus Cr content in the Ishtar rubies found in Mesopotamia with rubies from various provenances shows strong indication that rubies did originate from Burma. Ancient trade connections (silk road) between near and far east empires!

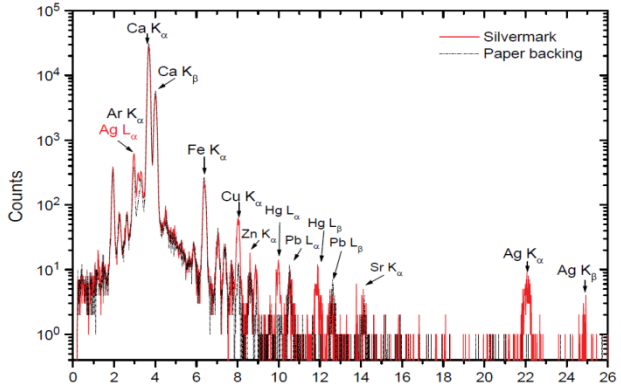


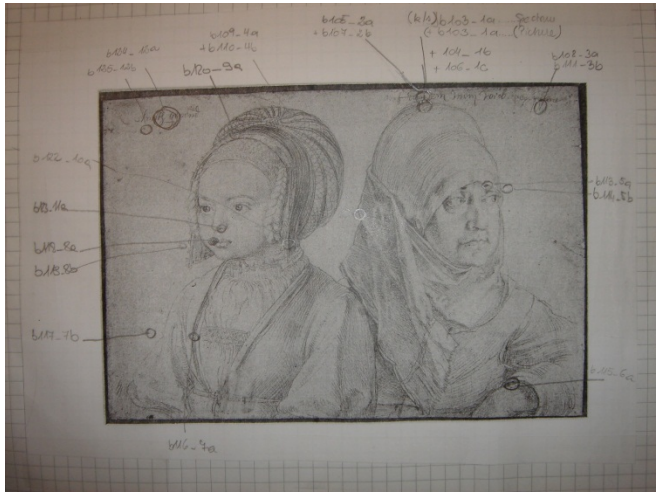


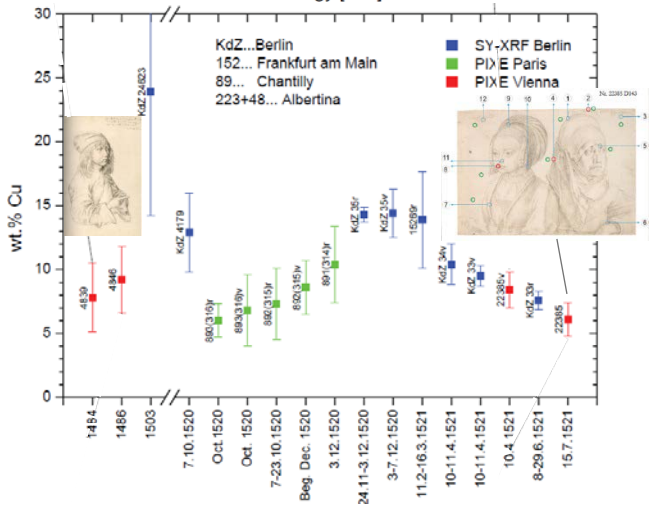
PIXE and Dürer travels





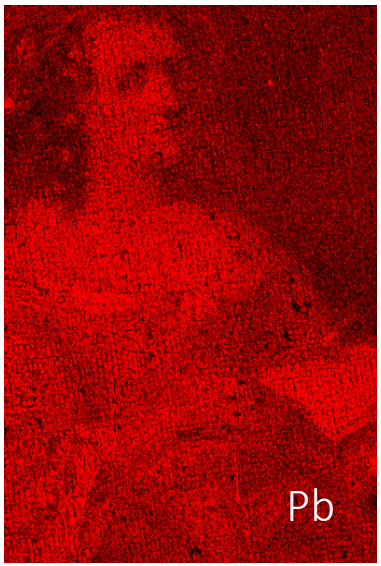


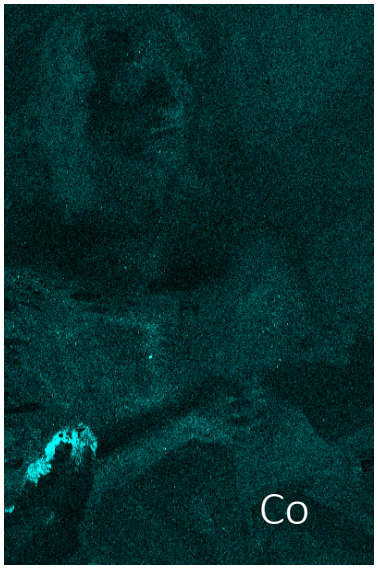


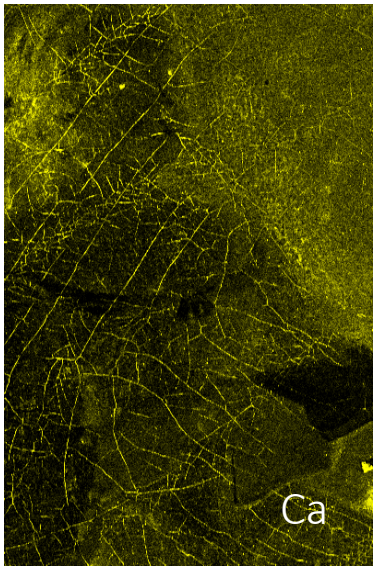


Albrecht Dürer silverpoint drawings

Meet my Great-Great-Great-Great-Grandmother







Test of the imaging homogeneity by using argon in air

Ar

$PbCO_3$ (lead-white) white pigment for preparing the backing (canvas, wood) and for highlighting bright areas, today TiO (titanium oxide)

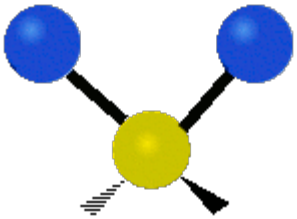
C_xH_y+ FeO + $CaC0_3$) (calcinated Van Dyke Brown) – a local product from the region near Cologne, which was used for the toning of darker brownish areas.

$(Fe_4[Fe(CN)_6])_3$ (Prussian Blue, based on Fe)- was used for the blue tones of broche – no Cu (Azurite) was observed. $CoAlO_4$ (Cobalt Blue or Smalt) was used for sleeve.

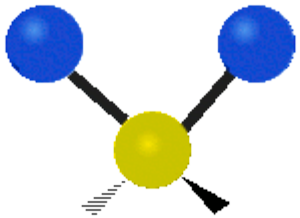
C_xH_y+ FeO + $CaC0_3$) (calcinated Van Dyke Brown) – a local product from the region near Cologne, which was used for the toning of darker brownish areas.

Raman Spectroscopy of Molecules

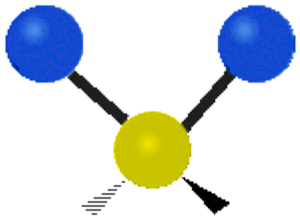
Provides a spectroscopic tool for analyzing molecular components in pigments by looking for signals corresponding to molecular excitation modes (vibration, rotation and combinations of such. Raman Spectroscopy is therefore also tool for analysis of modern organic chemistry based pigments.



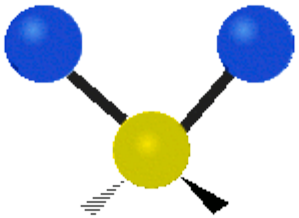
stretching



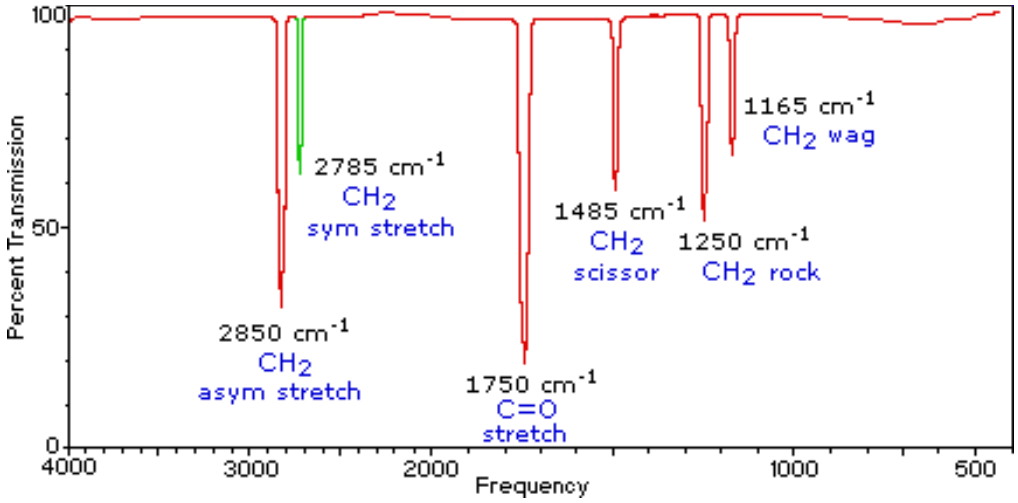
bending



scissoring



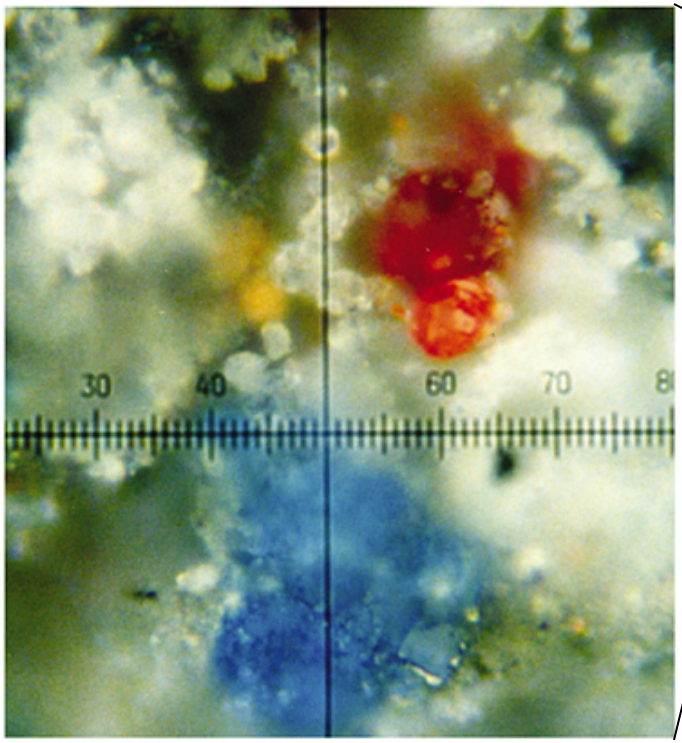
twisting

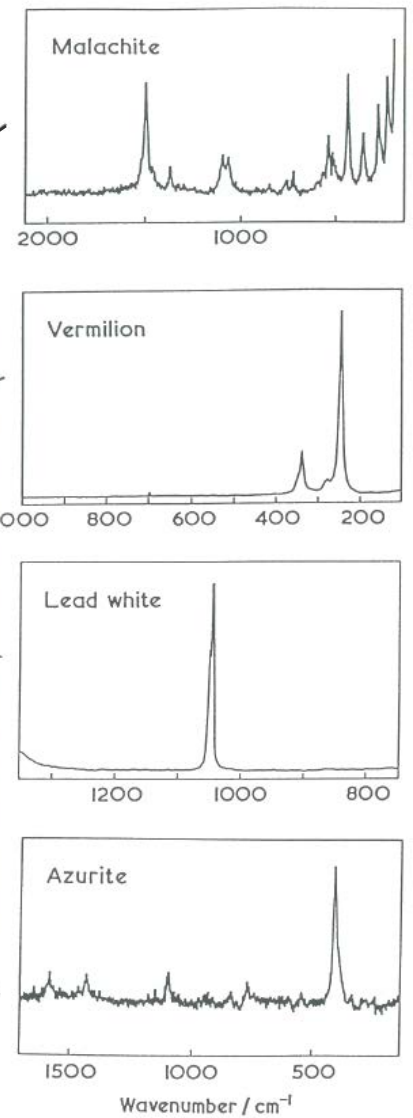


Excitation source for excitation process is a monochromatic laser. Raman Spectroscopy works in the infrared since molecular excitations are less energetic than atomic or nuclear excitations.

Testing ink pigments of medieval monastery handwriting of letter ℜ

Lead white: k=1050 cm^{-1} ($PbCO_3$)
Malachite: ($Cu^{2+}{}_2(CO_3)(OH)_2$)
Azurite: ($Cu^{2+}{}_3(CO_3)_2(OH)_2$)
Vermillion: k= 253 cm^{-1} 285 cm^{-1}, 343 cm^{-1} (HgS) (cinnabar)
Minium: k=226 cm^{-1}, 313 cm^{-1}, 390 cm^{-1}, 549 cm^{-1} (Pb_2O_3)



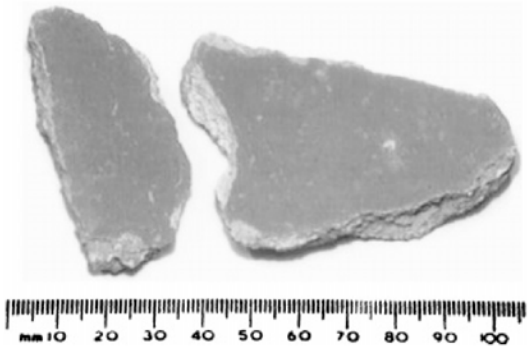


Best et al. Endeavour, New Series 16 (1992) 66-73

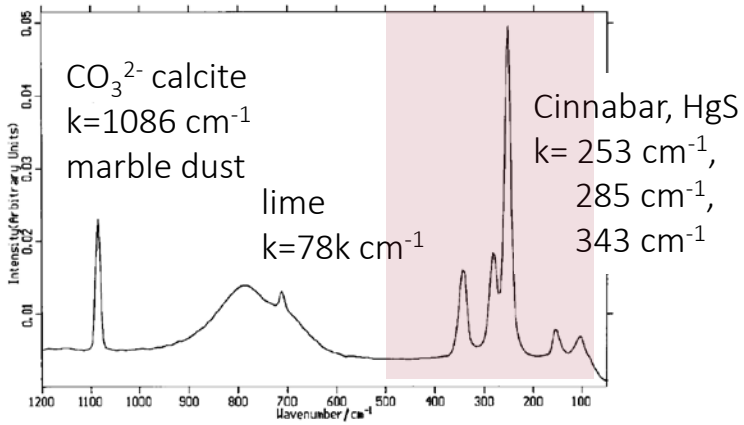
Frescoes in Herod's Tomb in Jericho

Roman fresco technique: lime wash, followed by pigment application

Analysis of fragments with Raman spectroscopy

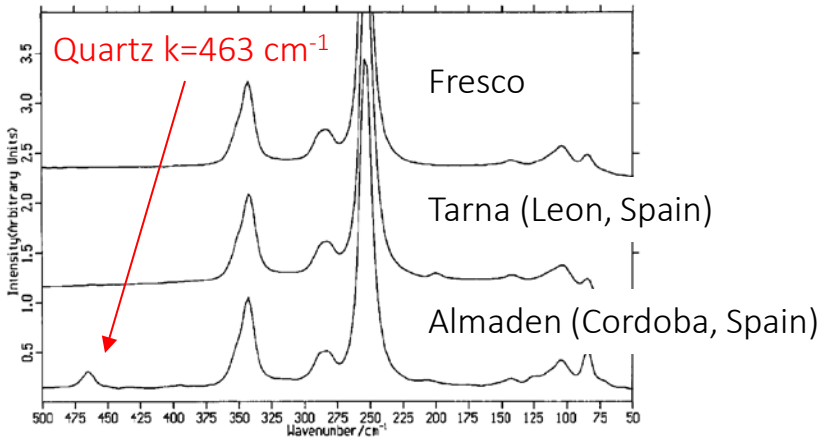


Cinnabar (Persian Dragon's blood): HgS (vermilion)



1064 nm excitation

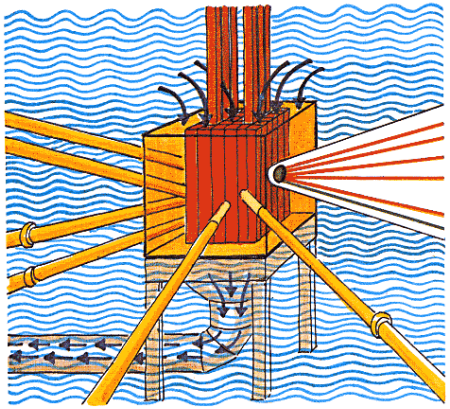
Provenance of HgS pigment (Pliny & Vitruvius claim Spain)

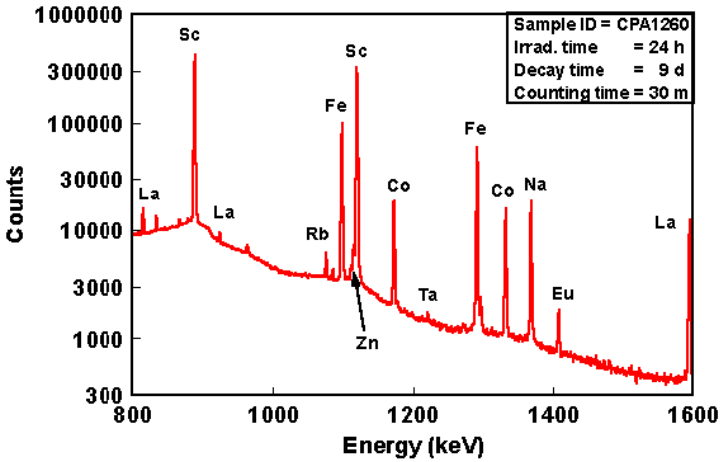


H. G. M. Edwards et al. J. Raman Spectrosc. 30 (1999) 361-377

Neutron Activation (NA)

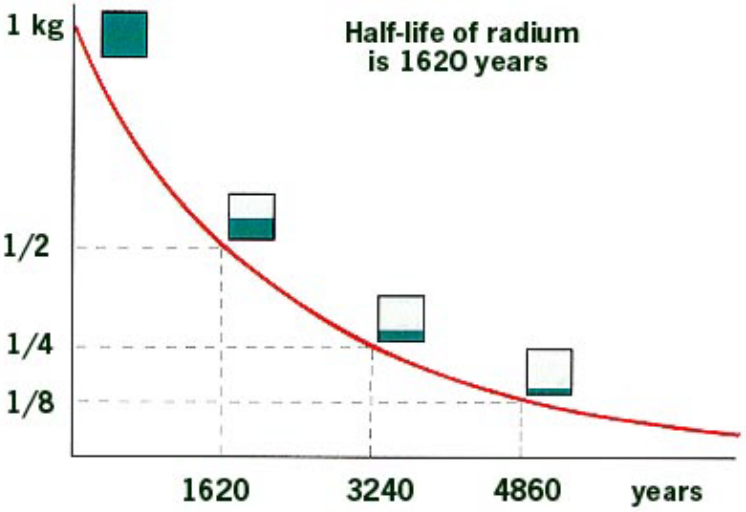
Expose material to high neutron flux and add neutrons to nuclei to produce an radioactive isotope with subsequent analysis of its characteristic radioactive decay pattern.





Timescale and Radiation Sensitivity

Signatures are either characteristic radiation or characteristic decay time, which is different for each radioactive isotope



Chemical element	Associated pigment	Radioactive isotope formed during activation and its half-life	Time period after activation during which best images in autoradiographs are produced
manganese	umber, dark ocher	Mn^{56}, 2.6 hours	0–24 hours
copper	malachite, azurite, verdigris	Cu^{66}, 5.1 minutes Cu^{64}, 12.8 hours	0–20 minutes 1–3 days
sodium	glue, medium, canvas, ultramarine	Na^{24}, 15.0 hours	1–3 days
arsenic	smalt, glass	As^{76}, 26.5 hours	2–8 days
phosphorus	bone black	P^{32}, 14.3 days	8–30 days
mercury	vermilion	Hg^{203}, 48 days	more than 25 days
cobalt	smalt, glass	Co^{60}, 5.3 years	more than 25 days

Table 1. Chemical elements and associated pigments most frequently observed in autoradiography of seventeenth-century Dutch and Flemish paintings.
The following pigments generally do not cause distinct images in autoradiographs: chalk, lead white, ocher, lead-tin yellow, lakes, madders, and indigo.

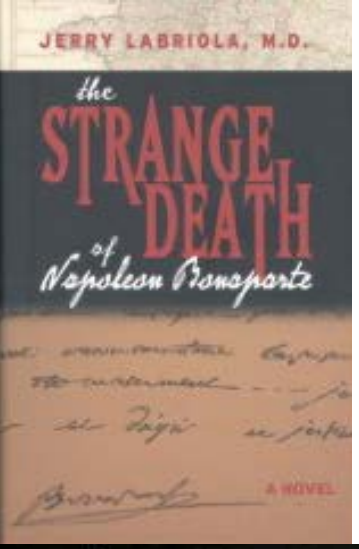
Taking advantage of radioactive decay

The Man with the Gold Helmet

by Rembrandt van Rijn?

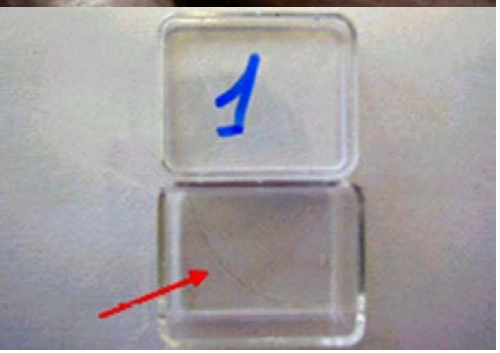
Was Napoleon murdered by the British?

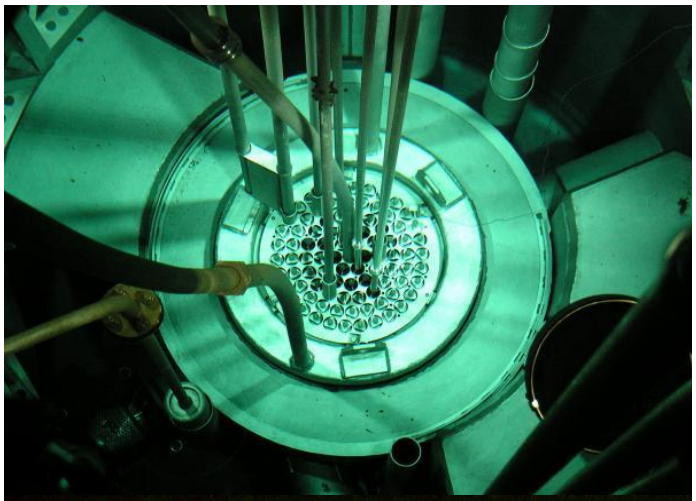
Neutron activation comes handy



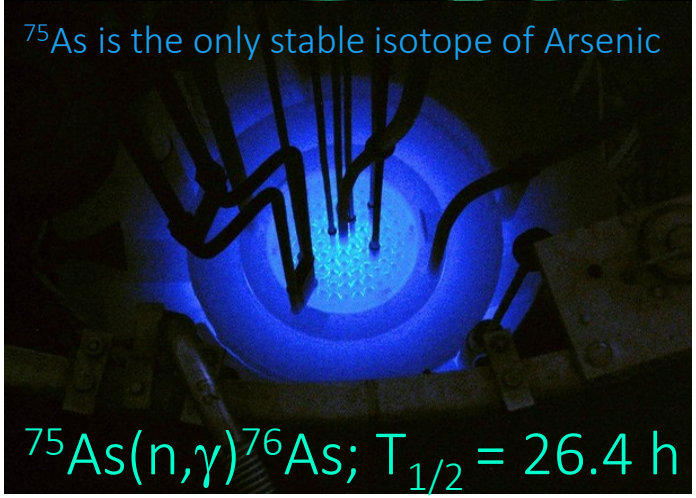
Napoleon's Death

poisoned by Arsenic?????





^{75}As is the only stable isotope of Arsenic



$^{75}As(n,\gamma)^{76}As$; $T_{1/2} = 26.4$ h

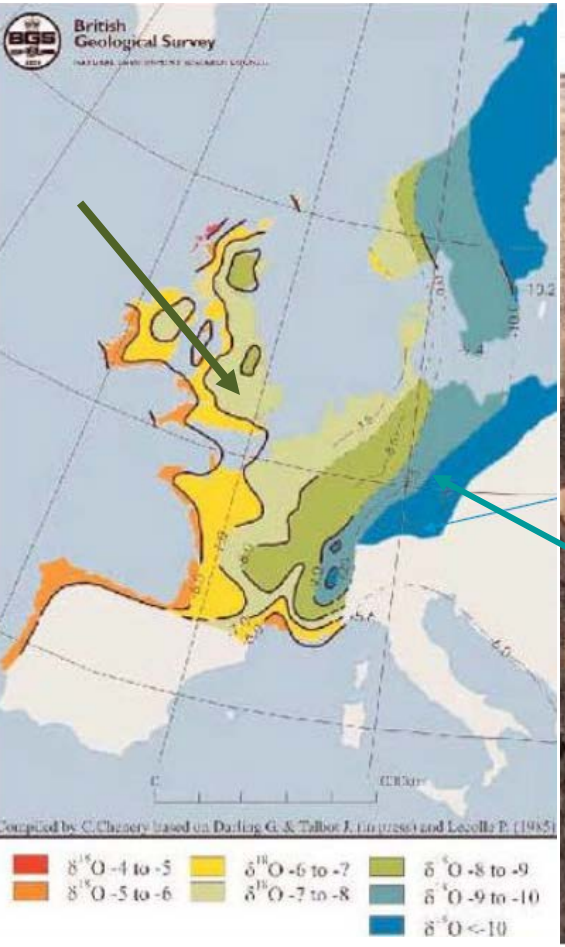
The Emperor's hair had an average arsenic level of around 10-15 ppm, whereas the arsenic level in the hair samples from currently living persons is around 0.1 ppm. But surviving relatives had similar levels!

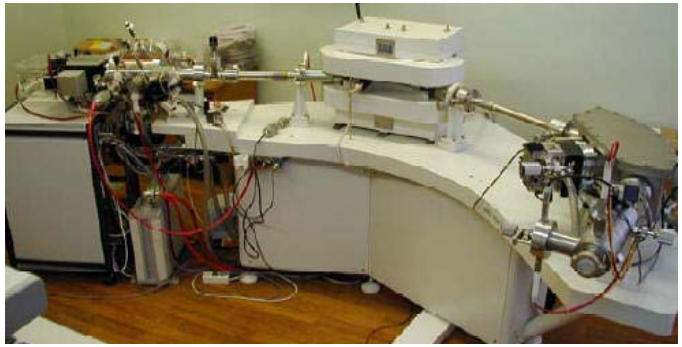
May 5 1821

Napoleon has declared in his will that 'I die before my time, murdered by the English oligarchy and its hired assassin'.

Stable Isotope Analysis (SIA),
the King of Stonehenge at 2300 BC

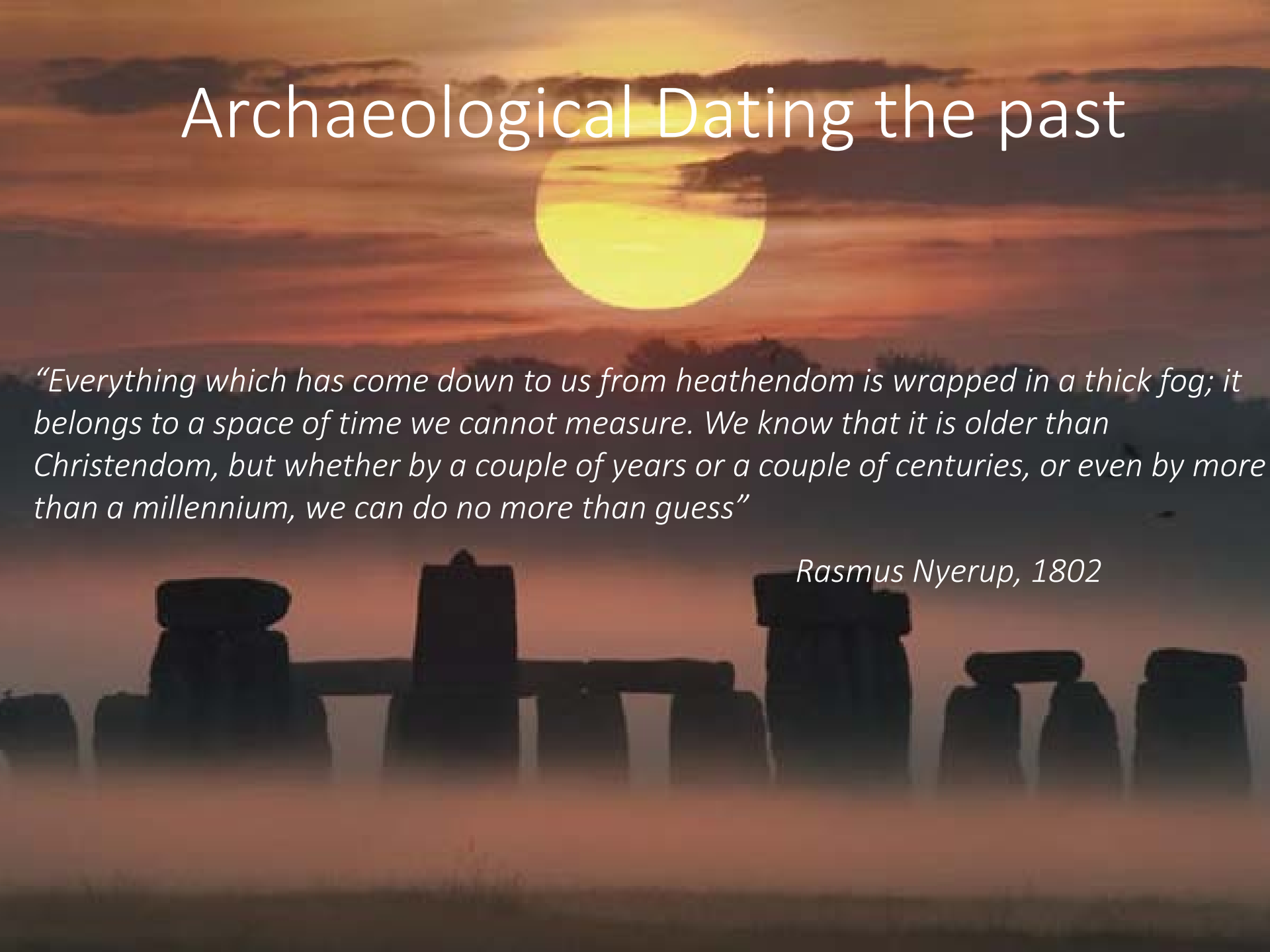
Chemophysical fractionation of isotopes cause local changes in abundance ratio.
Climate and rain pattern influence the ^{18}O to ^{16}O isotope ratio from sea to land.





The Daily Express expressed the opinion
"This is as shocking as the discovery that the first cricket players wore leather pants and ate Bratwurst with their tea".

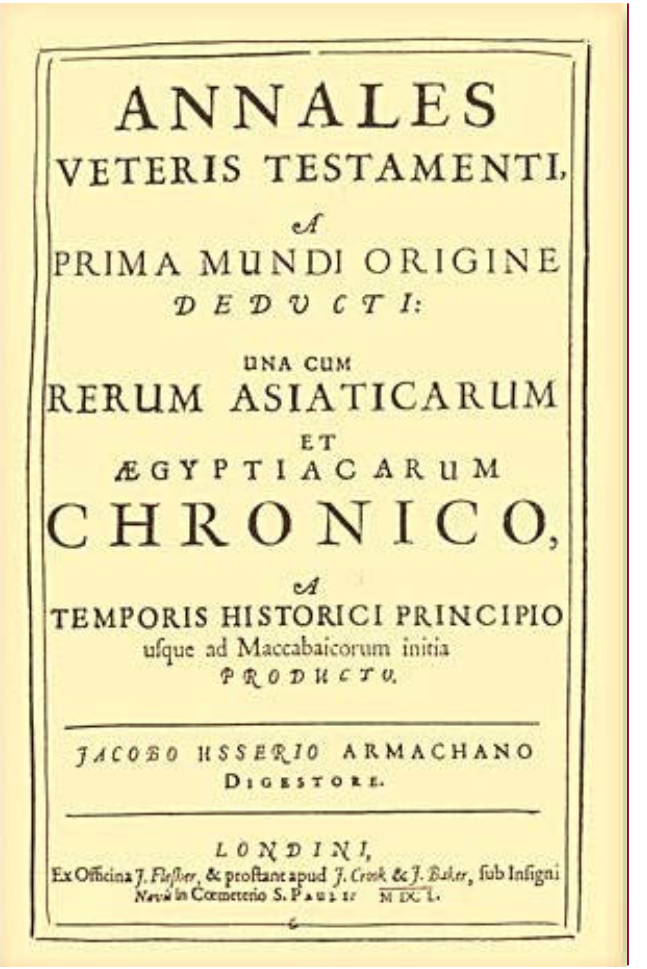
Archaeological Dating the past



"Everything which has come down to us from heathendom is wrapped in a thick fog; it belongs to a space of time we cannot measure. We know that it is older than Christendom, but whether by a couple of years or a couple of centuries, or even by more than a millennium, we can do no more than guess"

Rasmus Nyerup, 1802

Archaeological clocks



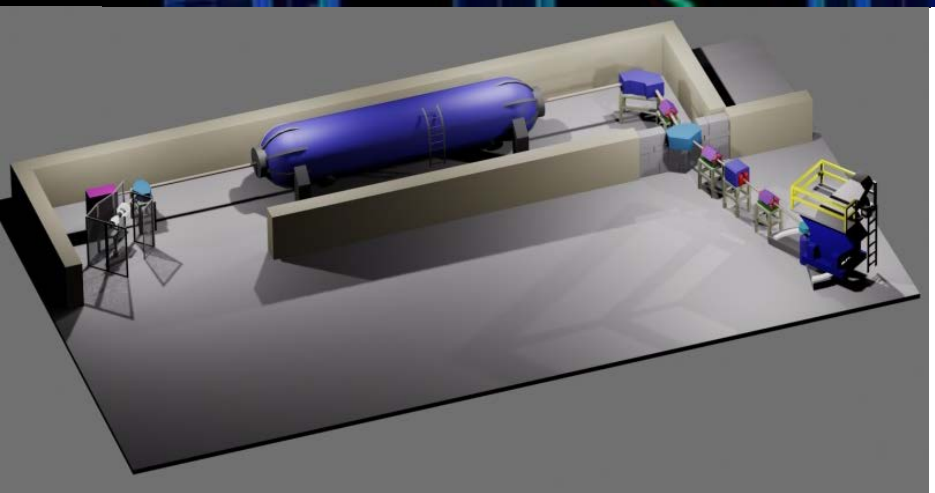
ANNALES
VETERIS TESTAMENTI,
A
PRIMA MUNDI ORIGINE
DEDUCTI:
UNA CUM
RERUM ASIATICARUM
ET
ÆGYPTIACARUM
CHRONICO,
A
TEMPORIS HISTORICI PRINCIPIO
usque ad Maccabaicorum initia
PRODUCTO.

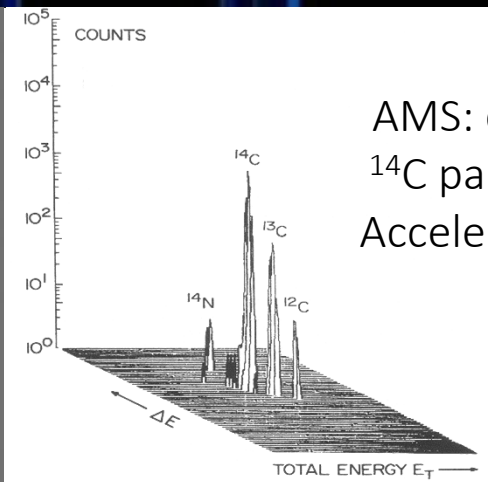
JACOBO USSERIO ARMACHANO
DIGESTORE.

LONDINI,
Ex Officina J. Flesher, & proftant apud J. Crook & J. Baker, sub Insigni
Navis in Cœmeterio S. Pauli. MDCL.

How to measure the time and age of things?

^{14}C dating with AMS

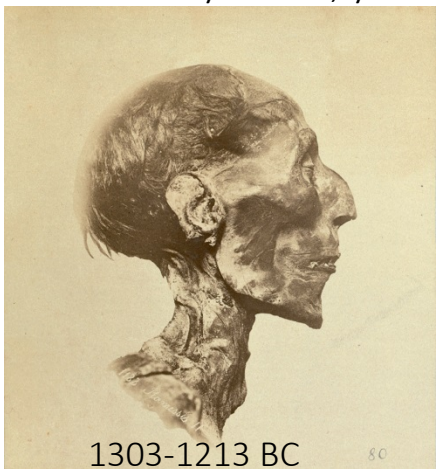


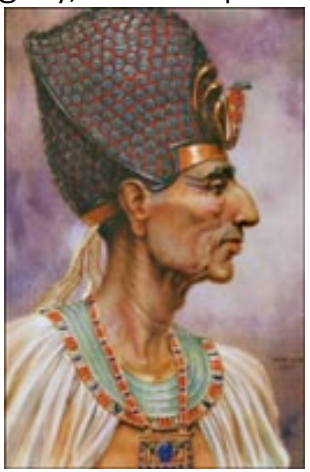


AMS: counting the radioactive ^{14}C particles with accelerators: Accelerator Mass Spectrometry

Dating Mummies

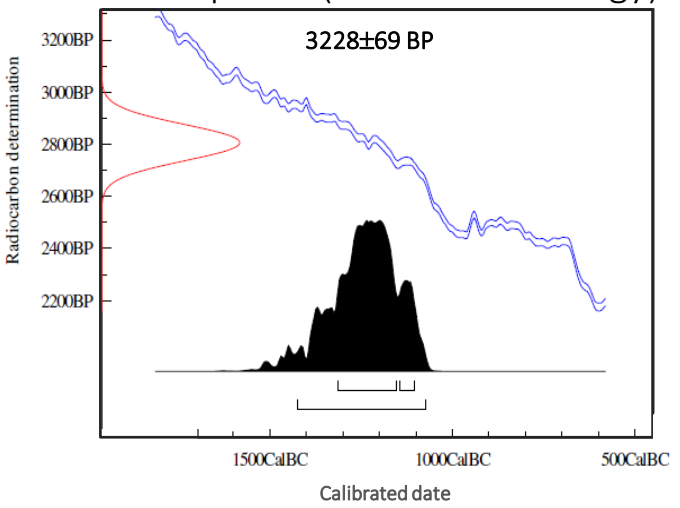
'My name is Ozymandias, king of kings:
Look on my works, ye Mighty, and despair!'

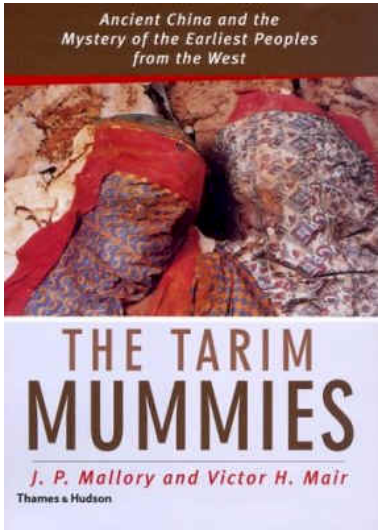


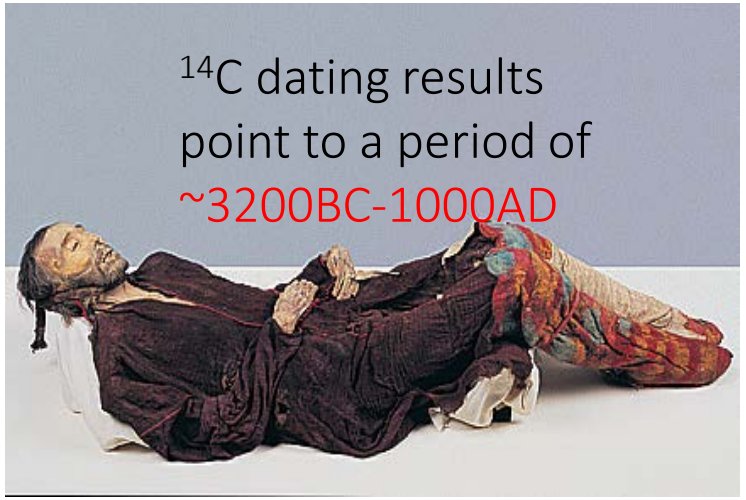


The mummy of Ramses II was one of the first samples tested by the new ^{14}C radiocarbon method to check the reliability of Egyptian dynasty counting versus biblical counting.

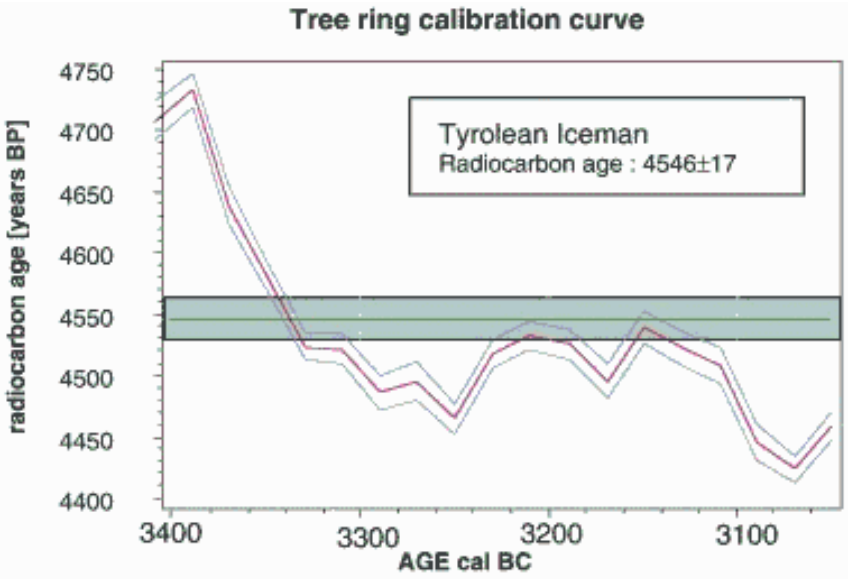
Calibration against ^{14}C variations in the atmosphere (dendrochronology)

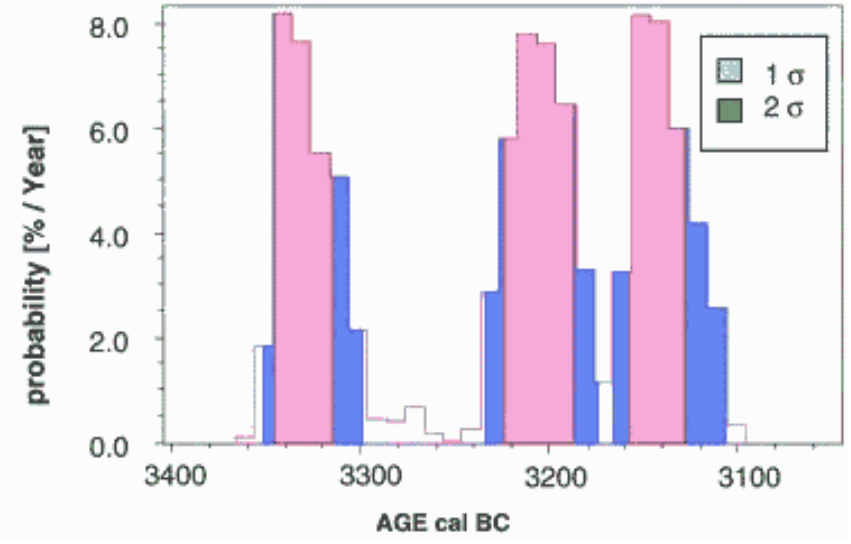




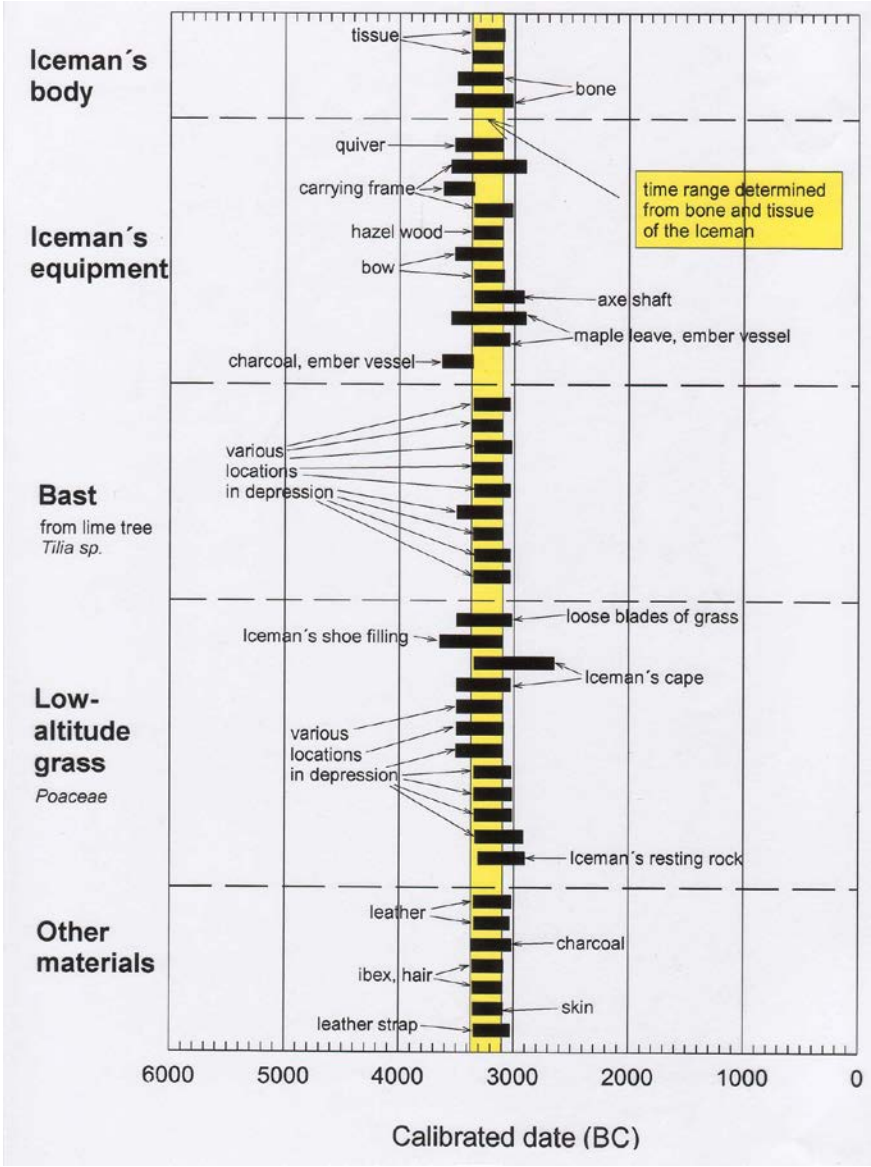


Conserved by ice - Oetzi, the iceman



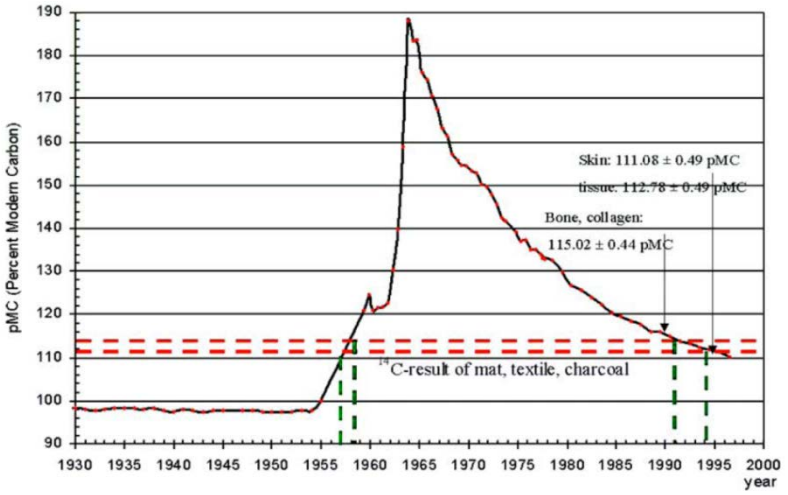


Murder 5000 years ago



The big business with (false) artifacts

Police raid of an art dealer in Karachi, Pakistan in October 2000 found a mummy, supposedly Rhodugune the daughter of Persian King Xerxes I (519-466 BC). The asking price of the dealer was $ 11 Million. An offer for $1.1 Million was out.



Owner claims were filed by the governments of Pakistan, Iran, Afghanistan (Taliban).

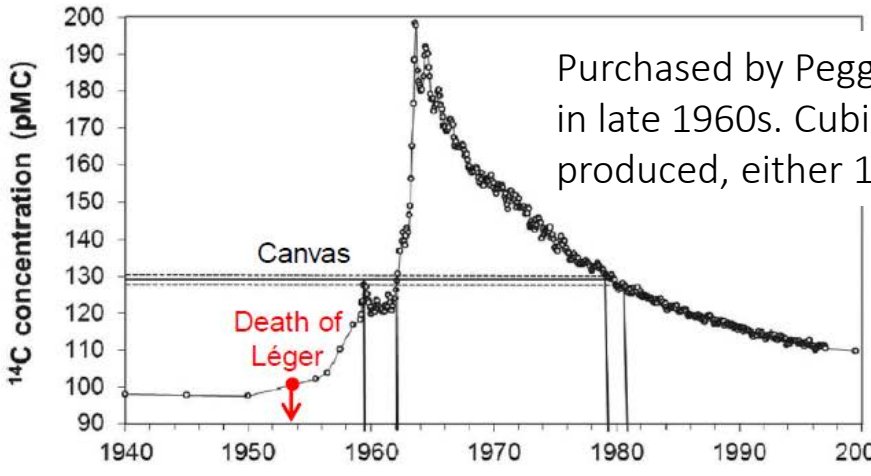
AMS analysis determined a large ^{14}C amount in the mummy and dated her death to ~1993 !

Fernand Léger purchased by Guggenheim Collections

Contraste de formes, Fernand Léger (?)
Peggy Guggenheim Collection, Venice

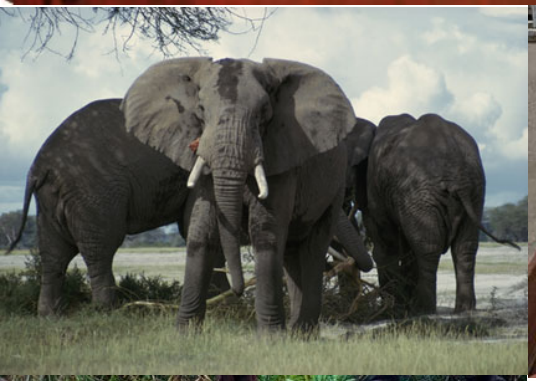
Contraste de formes, Fernand Léger (1881-1955), 1913,
Solomon G. Guggenheim Foundation, New York

Detail of the canvas sample



Purchased by Peggy Guggenheim in late 1960s. Cubist forgery was produced, either 1959 or 1962

Tracking Illegal Ivory Trade



- Increasing slaughter of elephants since 1970 with increased use of automatic weapons.
- Ivory trade ban in 1989 to protect elephants from becoming extinct.
- Growth in poaching and smuggle leading to local decline of elephant population as high as 90%.