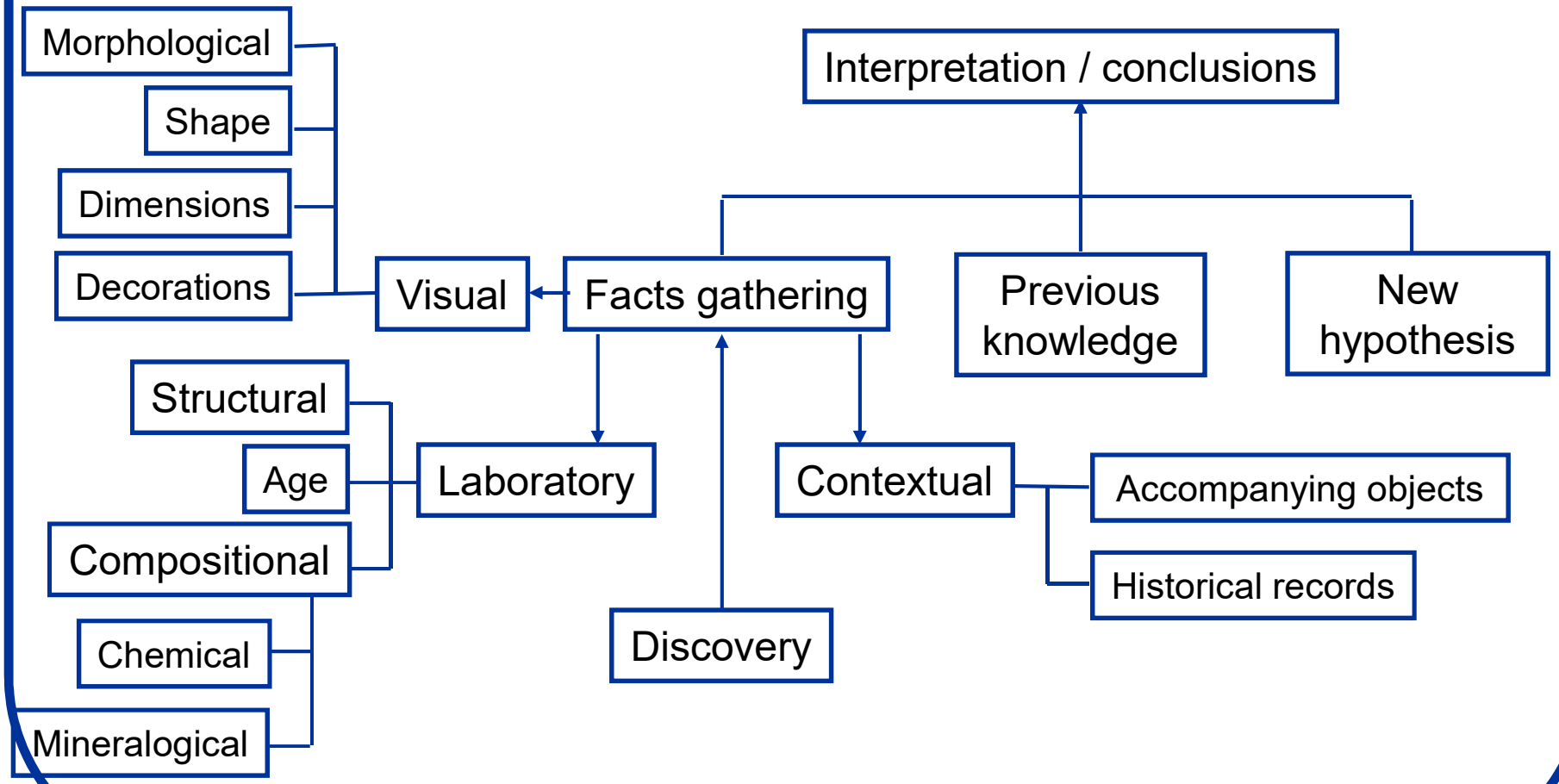
XRF in support of study and preservation of Cultural Heritage

Román Padilla Alvarez
Alessandro Migliori
International Atomic Energy Agency

Outline:

- Object characterization
- NSIL analytical capabilities
- X-ray Fluorescence: Principle
- XRF techniques and applications

Object characterization implies, among other actions…

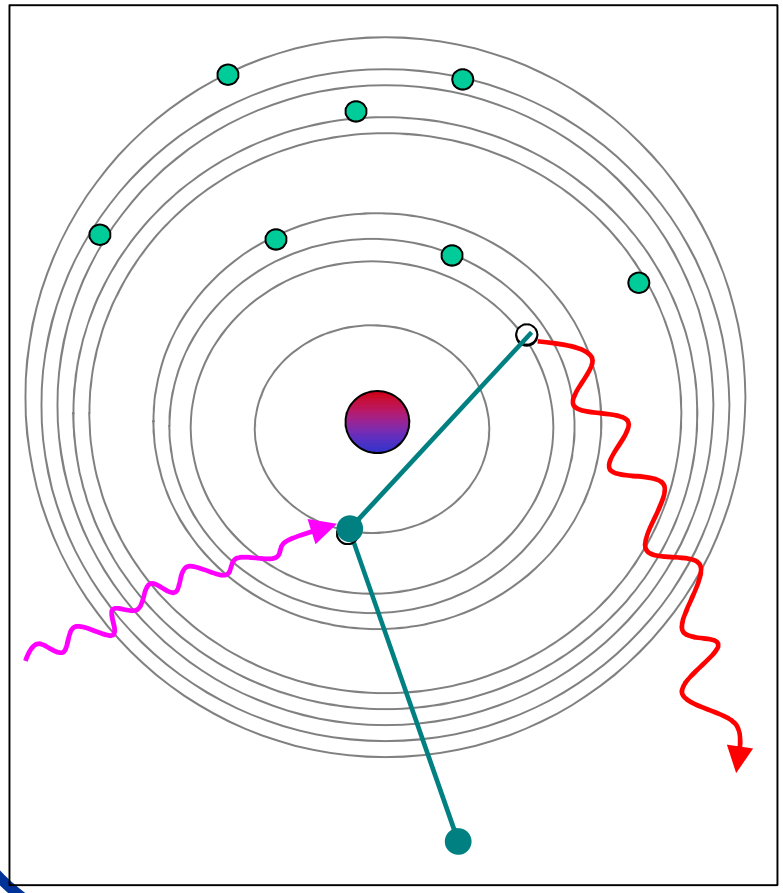


NSIL: Analytical facilities

- Energy Dispersive XRF
  - 2 x Secondary Target Excitation (SPECTRO2000, EPSILON 5)
  - Direct/filtered x-ray tube excitation (MiniPAL3)
  - Micro-XRF and confocal-XRF setup (own development)
  - Transportable XRF (Collimated / micro-XRF, own development)
  - Handheld XRF (NITON Xlt)
  - TXRF
  - FFXRF
- SEM-EDS (FEI)
- Transportable XRD (InXitu)
- Multipurpose HVC (GIXRF, XRR, XAS)
  - At ELETTRA Synchrotrone, Trieste
  - At Seibersdorf (for training)
- IBA end station (PIXE, RBS, at IRB, Zagreb, Croatia)

X-ray Fluorescence: Principle

- Ionization of atoms followed by characteristic emission
  - High selectivity

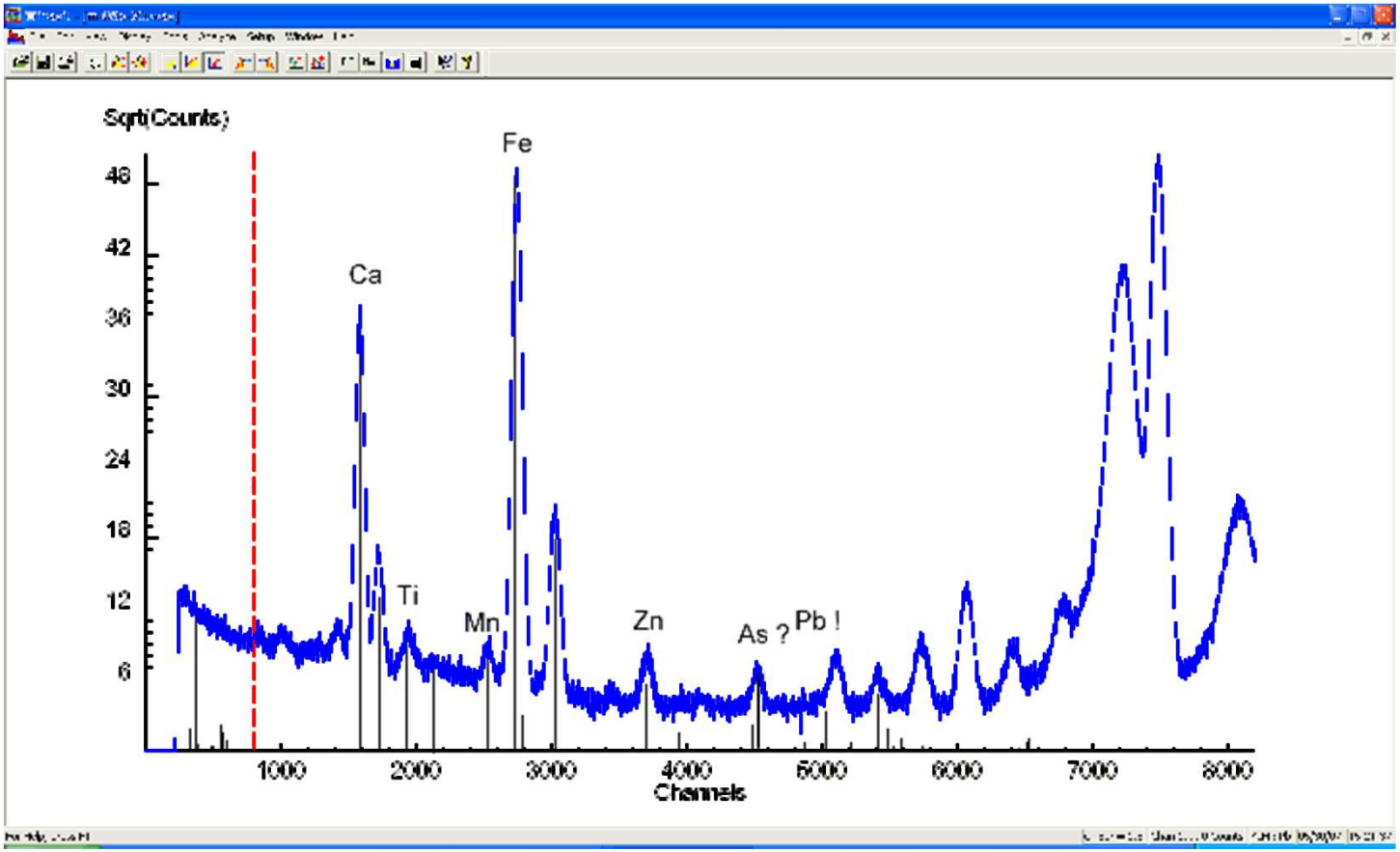


- A particle/photon interacts with an inner-shell electron. If its energy is larger than that of the shell binding energy, the electron is expelled
- An electron from any of the outer shells takes the vacancy recently created
- The excess of energy is released in the form of x-ray

  ➔ Such transitions are allowed by compliance with the principle of exclusion of Pauli

  ➔ CHARACTERISTIC RADIATION

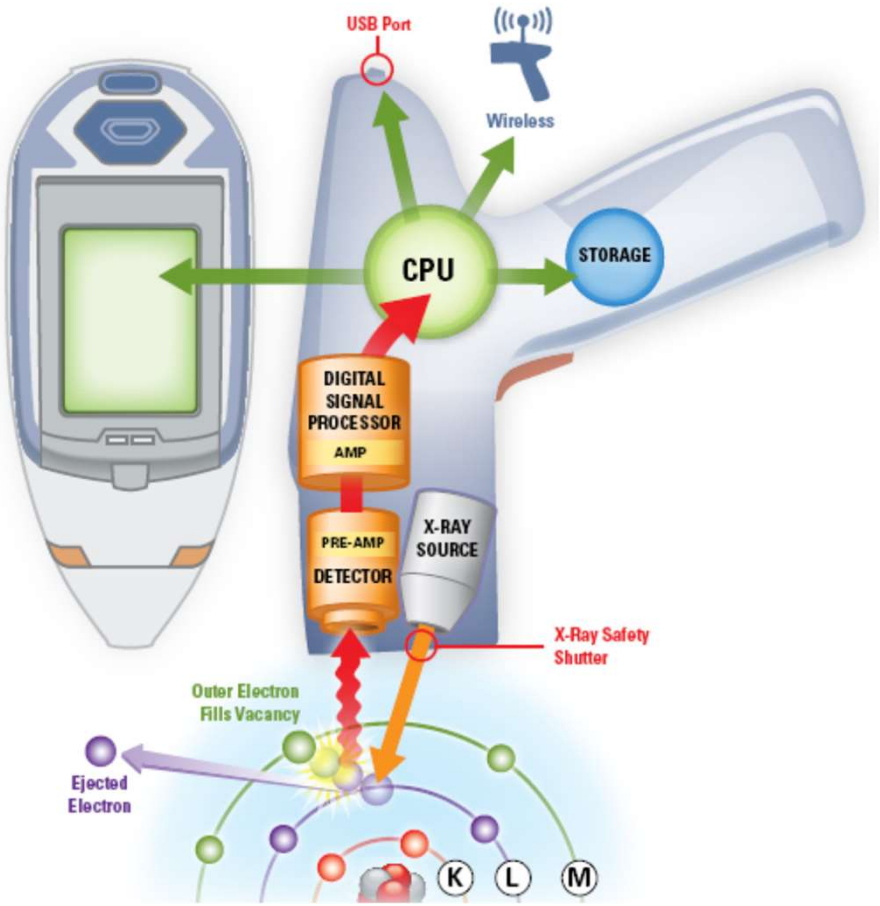
XRF selectivity



Ideal technique for qualitative analysis

XRF advantages

- Non-destructive
  - Even portable
- Multiple configurations allow increasing sensitivity and improving DLs
- Possible use of x-ray optics / focusing elements
- Relatively low investment and operation costs
- Attenuation corrections required



Case of study 1: Portable XRF
Identification of pigments in frescoes

Pigments used by the painter:

Red and orange: ochre in a fresco mode. Rarely cinnabar in a secco mode.

Yellow: yellow ochre and giallolino, lead tin yellow, of the second type ($PbSn_{1-x}Si_xO_3$). Giallolino is used in a secco mode mixed with biacca or San Giovanni white.

Green: green earth and malachite.

Blue: for the sky blue of azurite over a base of dark blue. Lapis over a base of ochre red for the dress of Saint John.

Black: carbon black

Brown: ochre and carbon black (note no Mn burnt earth).

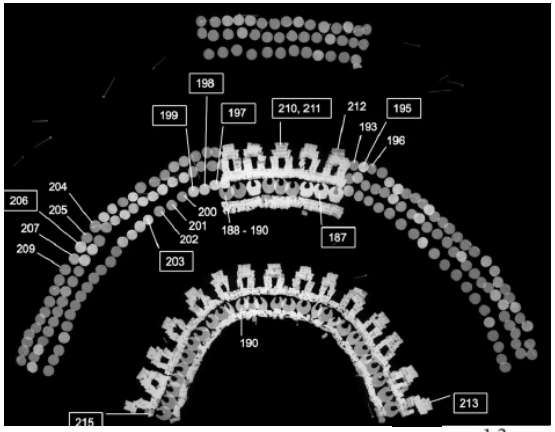
White: San Giovanni while. Lead only mixed with yellow giallolino.

Gilding: base of bolo (red earth) and fine gold.

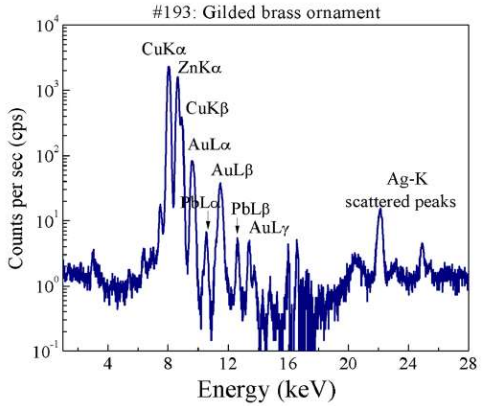
Courtesy of S. Ridolfi, Ars Mensurae

Case of study 2: PXRF Study of gold decorations

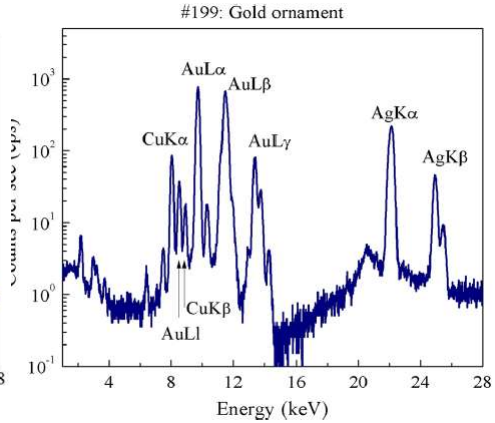
XVI century Mexican feather headdress



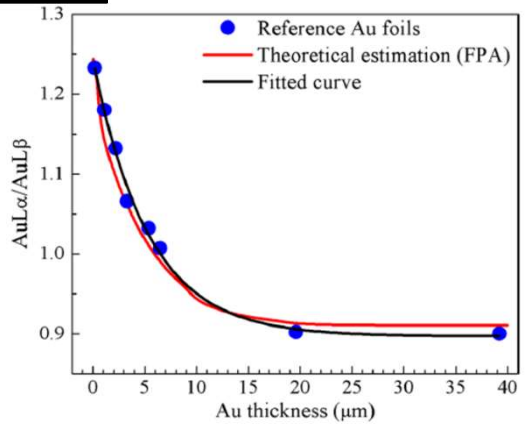
Radiography did not allow to discern superimposed golden scales PXRF was used



Gilded brass



Gold

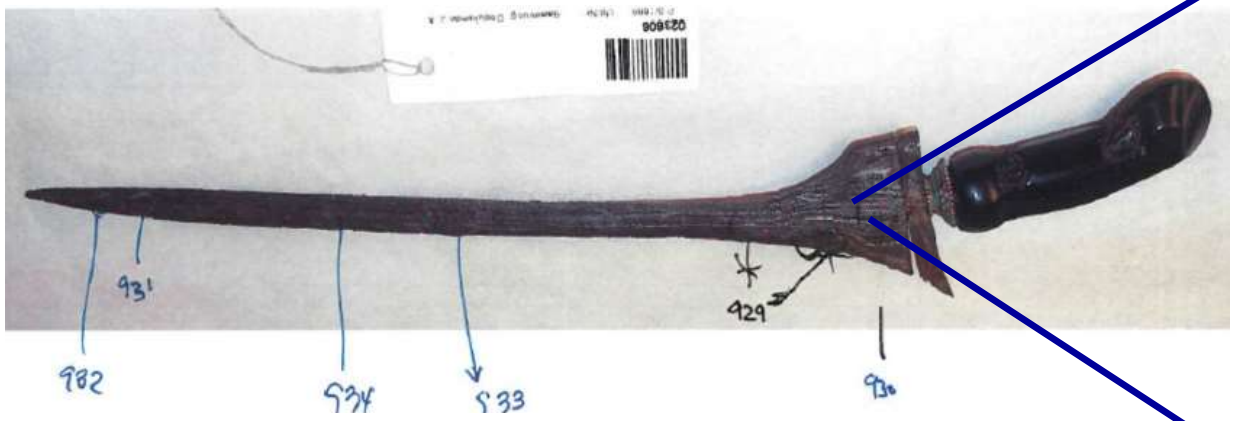


Thickness of gild from Au-La/Au-Lb ratio

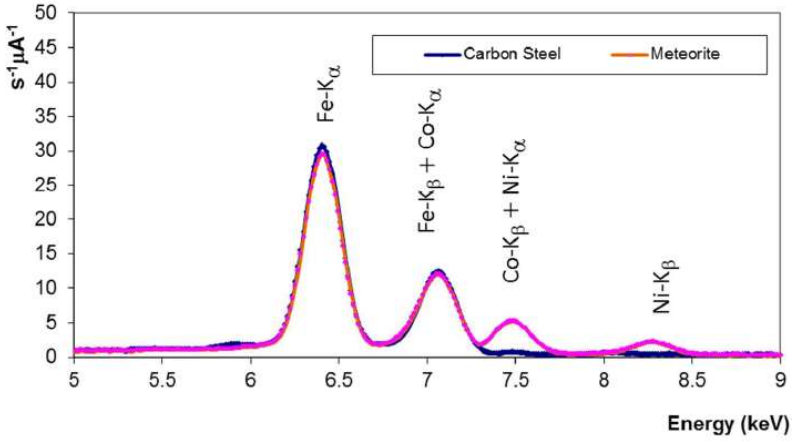
X-Ray Spectrometry 43 (2014), 138–145

Case of study 3: PXRF Study of Keriss daggers

Meteorite origin iron used in hammered successive layers



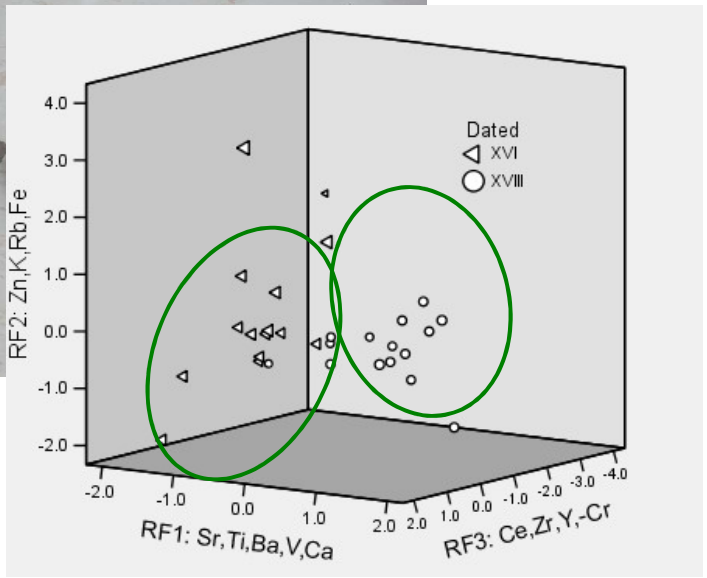
Spectra measured with Handheld XRF spectrometer (Main mode)

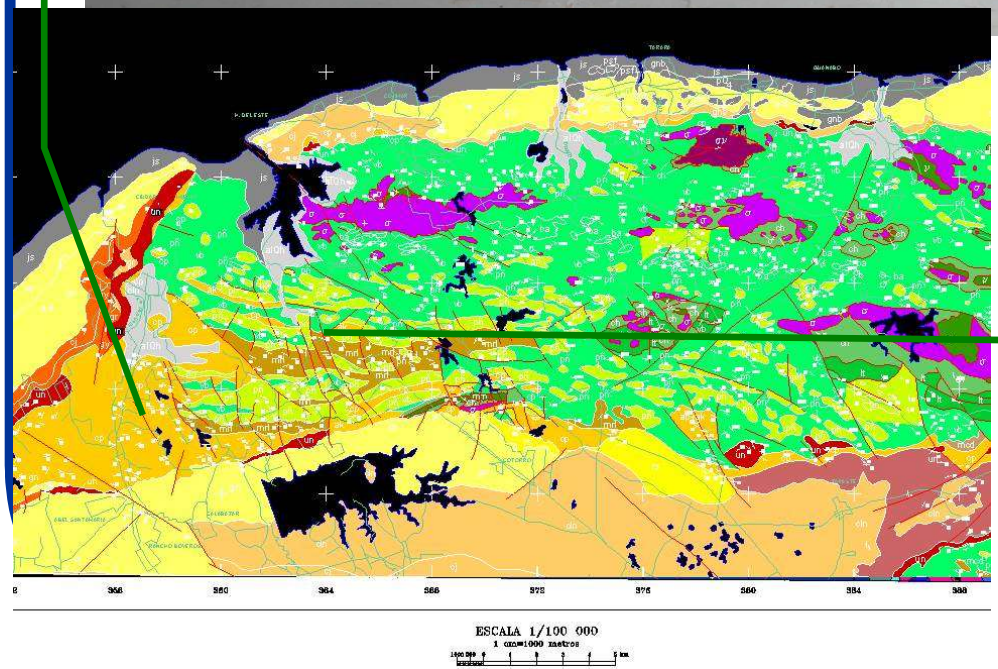


High contents of Ni and Co

Case of study 4: XRF classification of aboriginal found in colonial sites

Sand silt, siltstone, marga, grauwacka

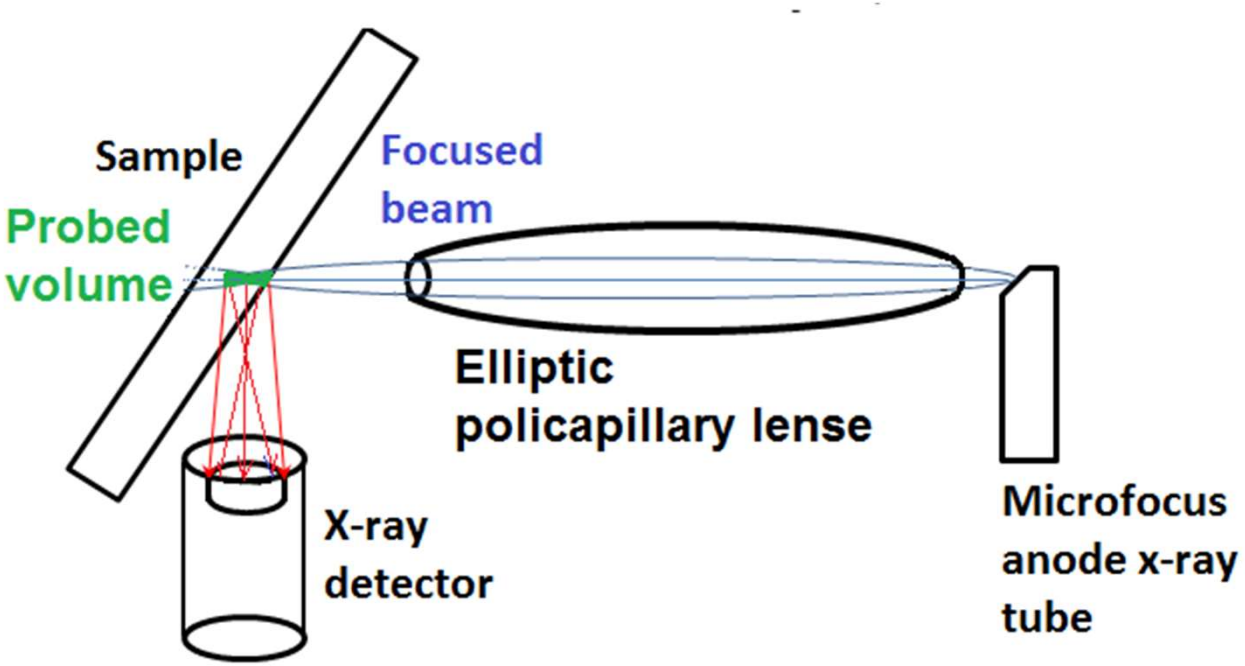




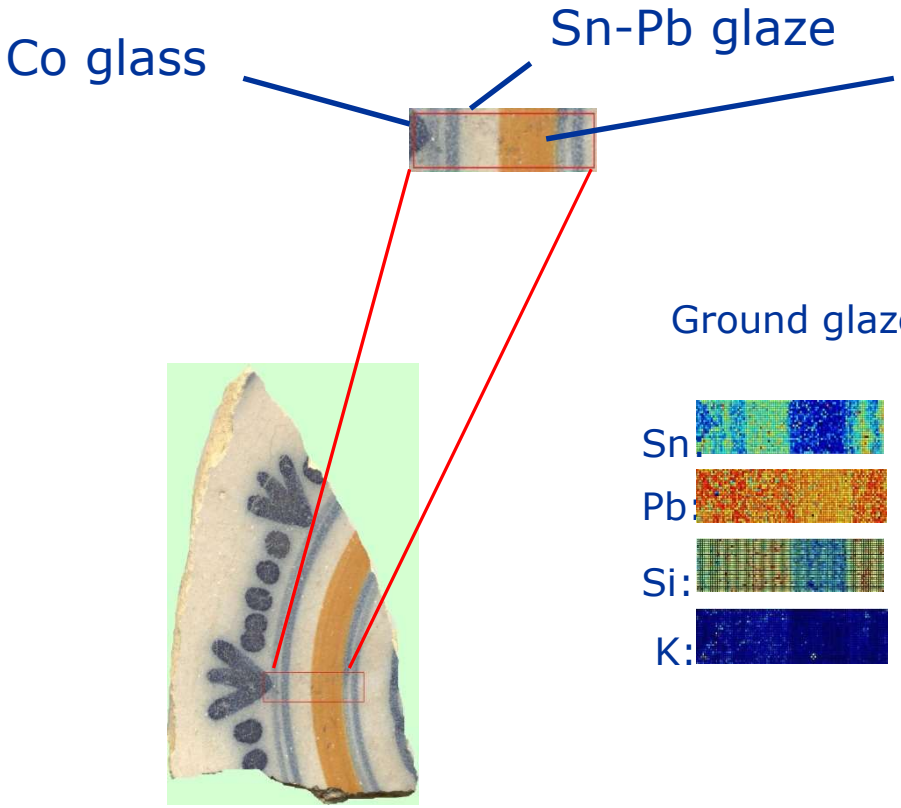
Limestone, limonite

μXRF: 2D elemental maps

- Poly-capillary lens
  - Either sample or excitation – detector module is translated in XY



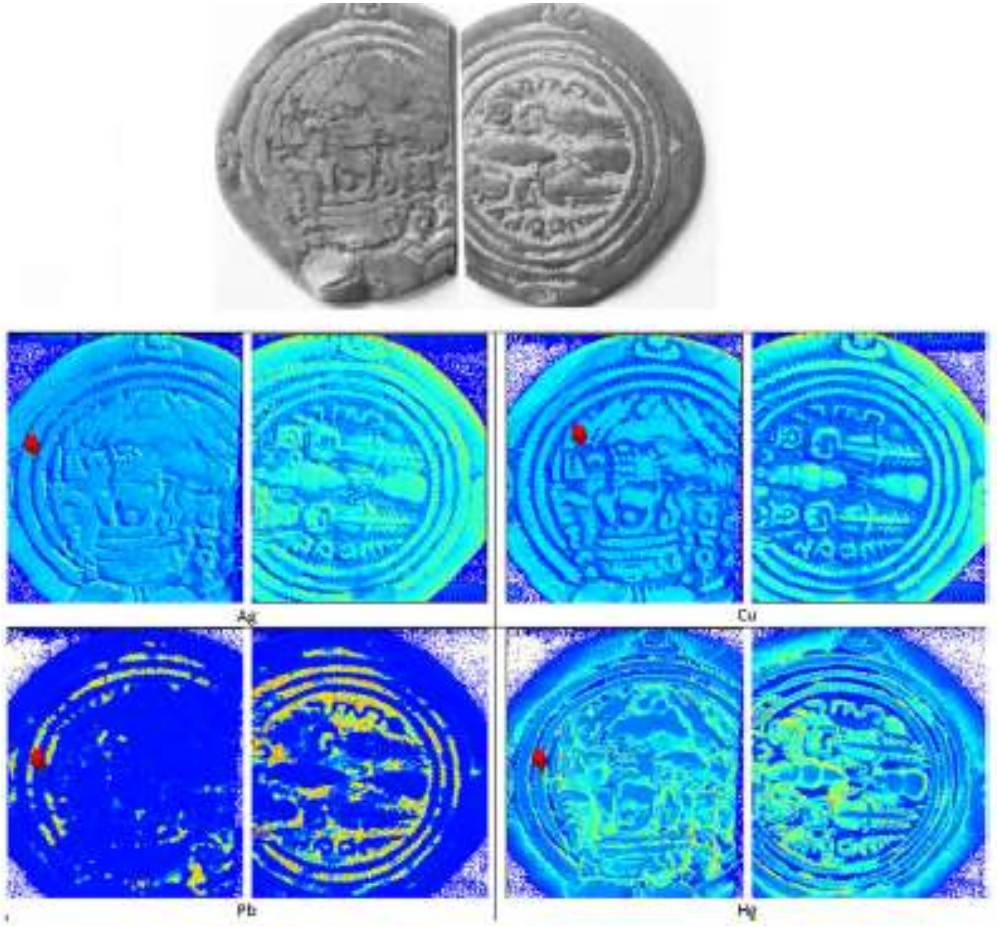
Case of study 5: μ-XRF identification of pigments in Majolica glazes (XVIII)



Analytica Chimica Acta 535(2005) 201-211

Case of study 6: Silver coin surface alterations

- μXRF surface measurements were made and elemental maps created



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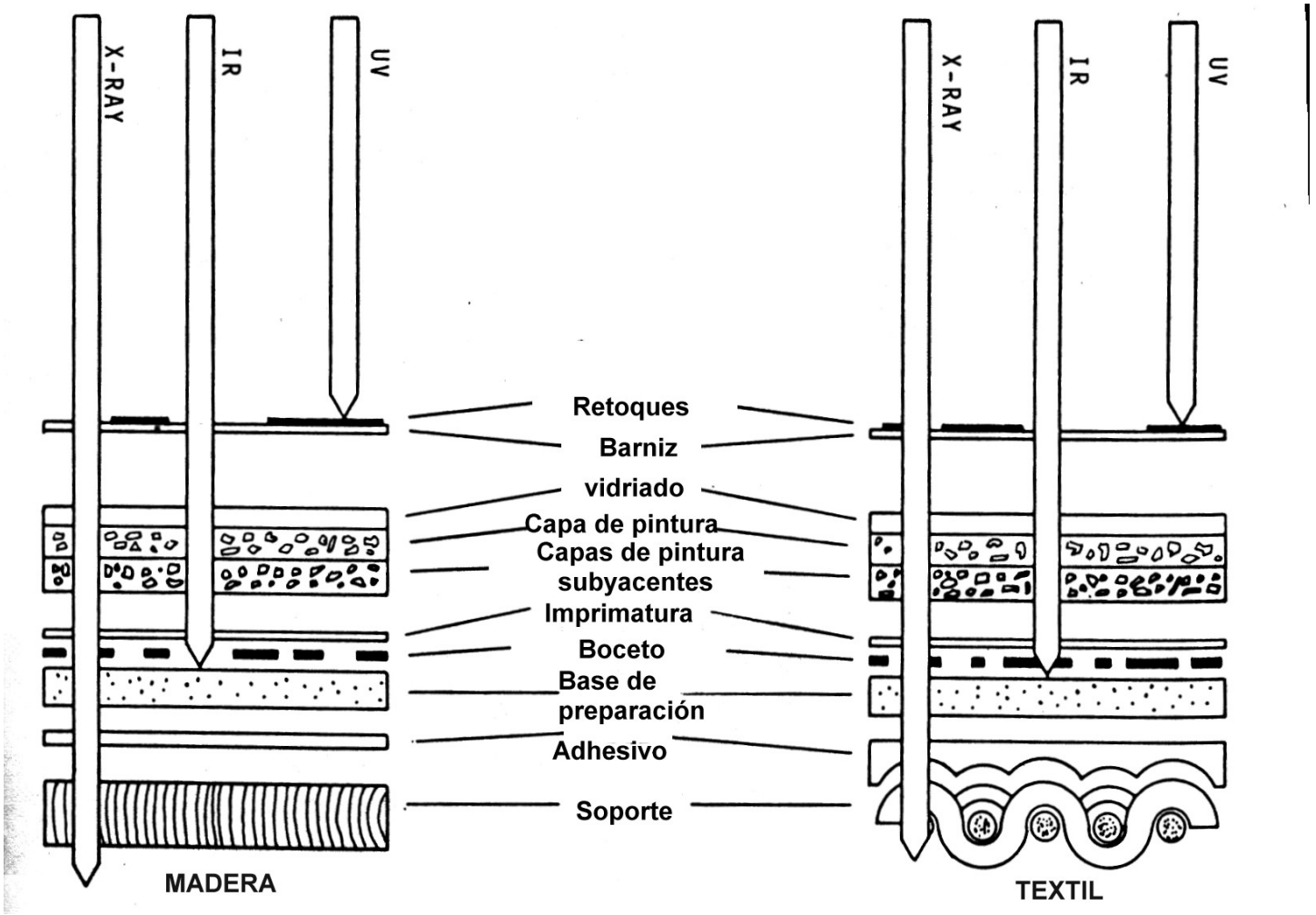
Paintings: Features



Common pigments

- White:
  - Gypsum - $CaSO_4.2H_2O$
  - Chalk - $CaCO_3$
  - Titanium White - TiO_2
  - Zinc White - ZnO
  - Zirconium Oxide - ZrO_2
  - Lithopone - $ZnO + BaSO_4$
  - Permanent White - $BaSO_4$
  - Antimony White - Sb_2O_3
  - White Lead - $2PbCO_3.Pb(OH)_2$

Common pigments

- Yellow:
  - Cobalt Yellow - $K_3[Co(NO_2)_6]x1.5H_2O$
  - Yellow Ochre - $Fe_2O_3.nH_2O(20\text{-}70\%)$
  - Zinc Yellow - $K_2O.4ZnO.4CrO_3.3H_2O$
  - Titanium Yellow - $NiO.\ Sb_2O_3.20TiO_2$
  - Strontium Yellow - $SrCrO_4$
  - Auri-pigmentum - As_2S_3
  - Cadmium Yellow - CdS
  - Chrome Yellow - $2PbSO_4PbCrO_4$
  - Lead-Tin Yellow - $Pb_2SnO_4/PbSn_2SiO_7$
  - Naples Yellow - $Pb(SbO_3)_2/Pb_3(SbO_4)_2$
  - Maasicot - PbO

Common pigments

- Red:
  - Red Ochre - Fe_2O_3 (up to 90%)
  - Realgar - As_2S_3
  - Cadmium Red - CdS+ CdSe
  - Cadmium Vermillion - CdS+ HgS
  - Molybdate Red - $7PbCrO_4.2PbSO_4.PbMoO_4$
  - Chrome Red - $PbO.PbCrO_4$
  - Red Lead (Minium) - Pb_3O_4
  - Vermillion - HgS

Common pigments

- Green:
  - Chromium Oxide - Cr_2O_3
  - Malachyte - $CuCO_3.\ Cu(OH)_2$
  - Emerald Green - $Cu(CH_3CoO)_2.3Cu(AsO_2)_2$
  - Cobalt Green - $CoO.5ZnO$
  - Chrysocolla - $CuSiO_3.nH_2O$
  - Verdigris - $Cu(CH_3CoO)_2.nCu(OH)_2$
  - Basic Copper Sulphate - $Cu_x(SO_4)_y.\ (OH)_z$
  - Guignet Green - $Cr_2O_3.nH_2O+H_3BO_3$
  - Veridian - $Cr_2O(OH)_2$
  - Brunswick Green - $CuCl_2+ Cu(OH)_2$

Common pigments

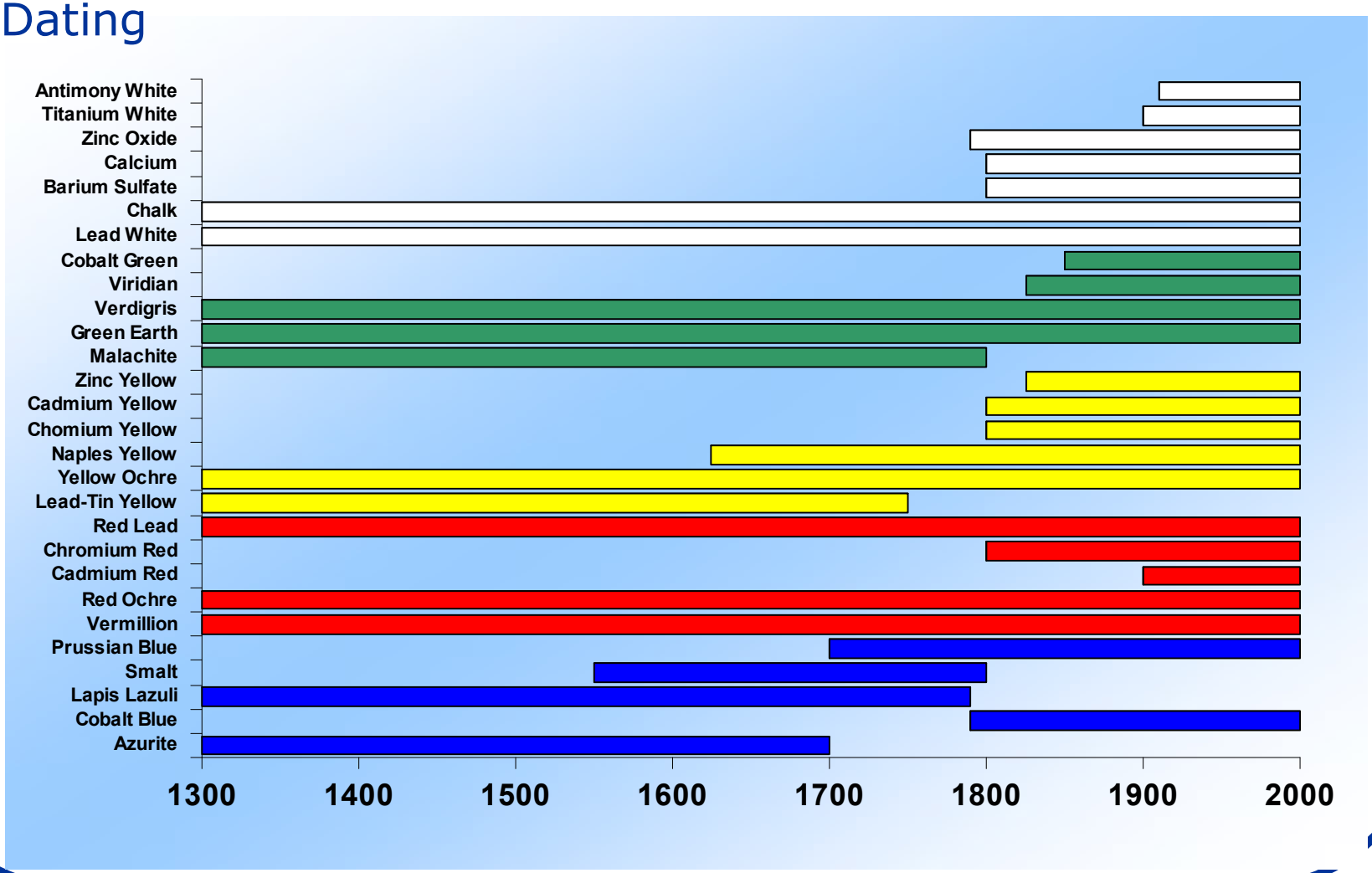
- Blue:
  - Cobalt Violet - $Co_3(PO_4)_2$
  - Egyptian Blue - $CaO.CuO.4SiO_2$
  - Prussian Blue - $Fe_4[Fe(CN)_6]_3$
  - Cobalt Blue - $CoO.\ Al_2O_3$
  - Smalt (Cobalt Glass) - K_2O+SiO_2+CoO
  - Azurite - $2CuCO_3.Cu(OH)_2$
  - Manganese Blue - $BaSO_4.Ba_3(MnO_4)_2$
  - Cerulean Blue - $CoO.nSnO_2$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

Common pigments

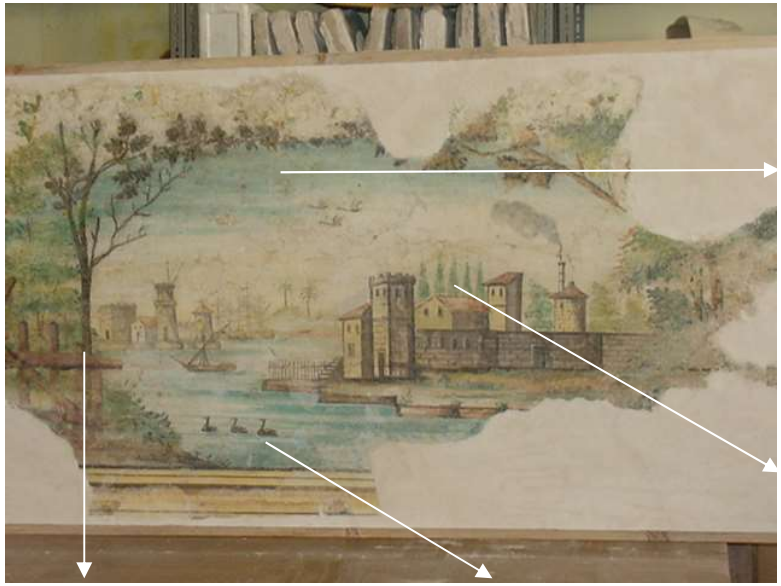
- Black:
  - Antimony Black - Sb_2O_3
  - Black Iron Oxide - $FeO.Fe_2O_3$
  - Carbon (Charcoal Black) - C
  - Cobalt Black - CoO
  - Ivory Black (Bone Black) - $C+Ca_3(PO_4)_2$
  - Manganese Oxide - $MnO.Mn_2O_3$

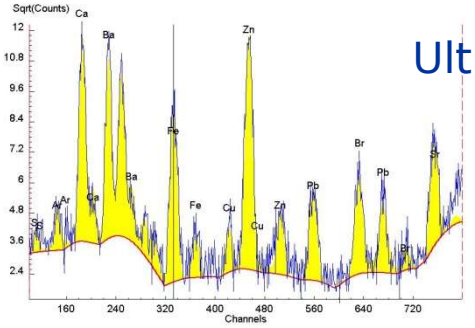
Paintings: Relative dating

- Dating

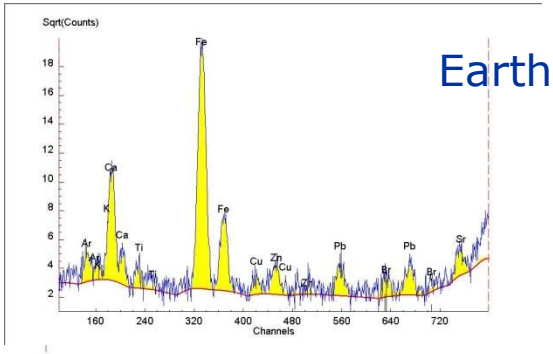


Case of study 7: TXRF
Identification of pigments in mural restoration

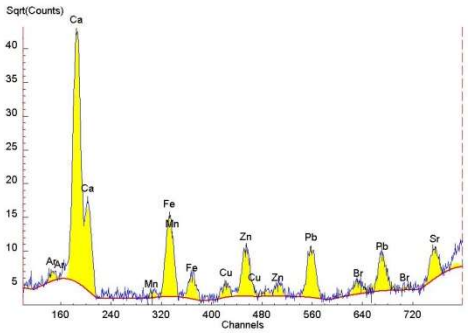




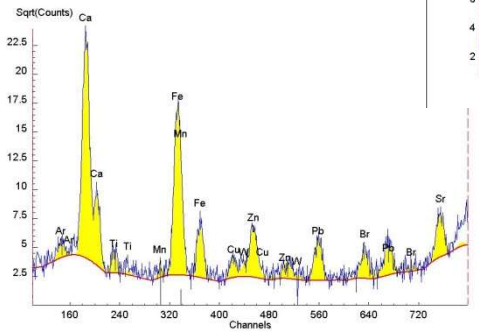
Ultramarine blue



Earth green



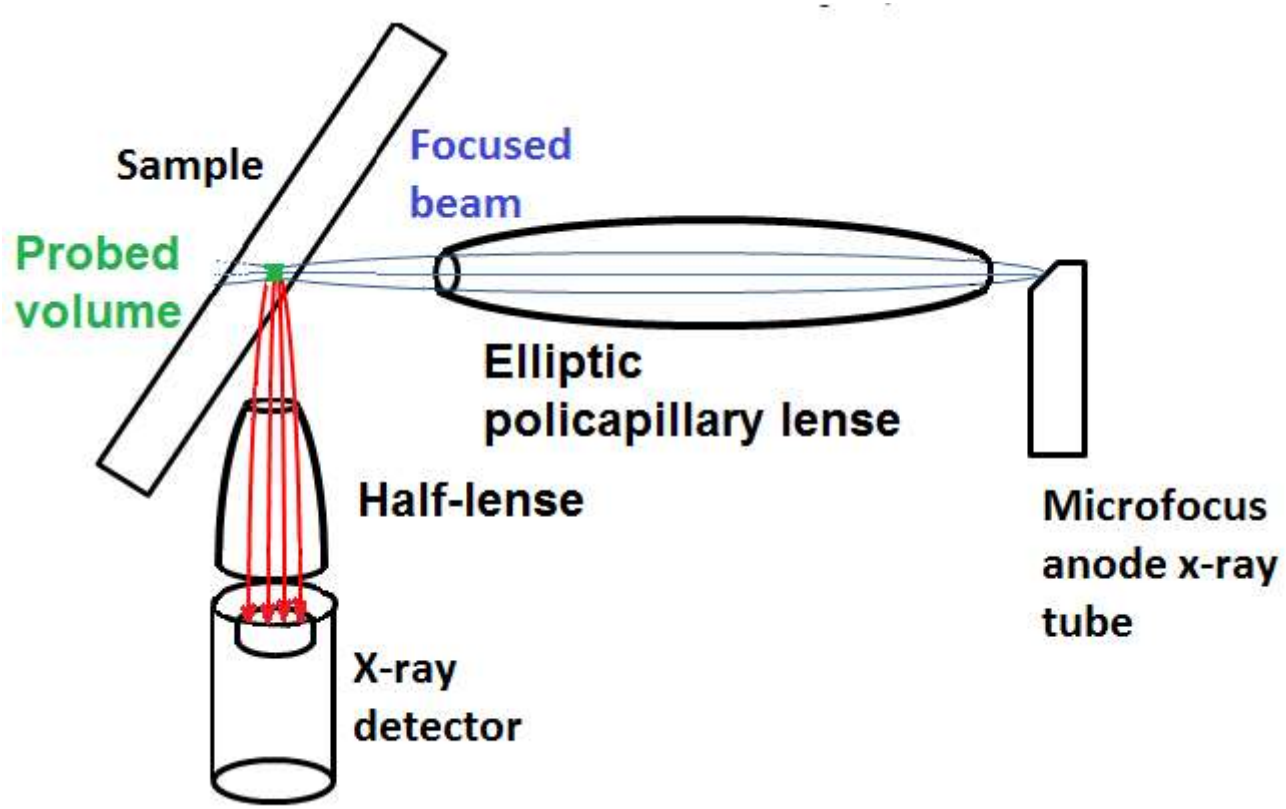
Earth ochre



Black iron oxide

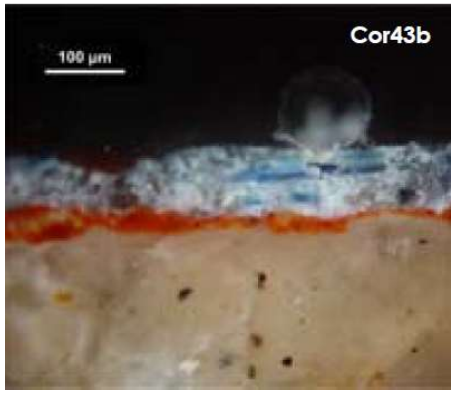
Confocal XRF: 3D elemental maps

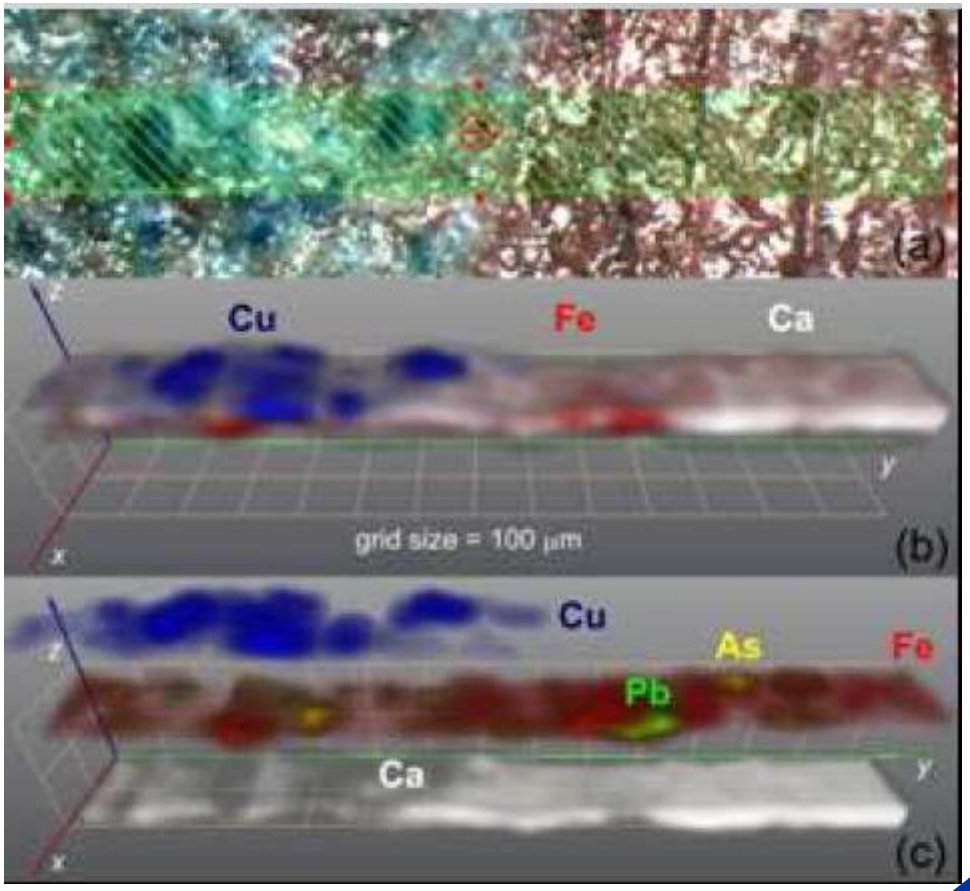
- Either sample or excitation – detector module is translated in XYZ
- Sample must be light attenuating



Case of study 8: CXRF
Identification of pigments in cross sections

Roman Corinth plasters





Egyptian blue

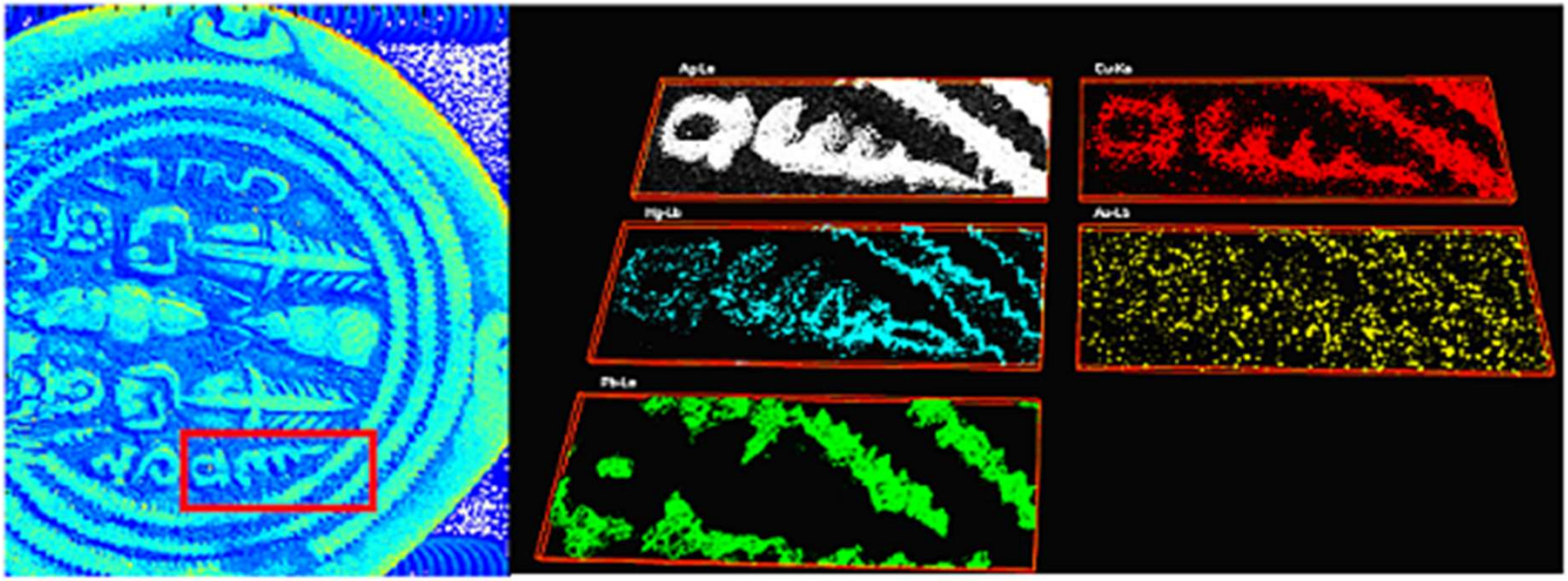
Red ochre

White plaster

TECHNART (2011) Poster

Case of study 9: Silver coin surface alterations

- CXRF volumetric scans were made on coin surfaces



Micro XRF image

Confocal XRS images

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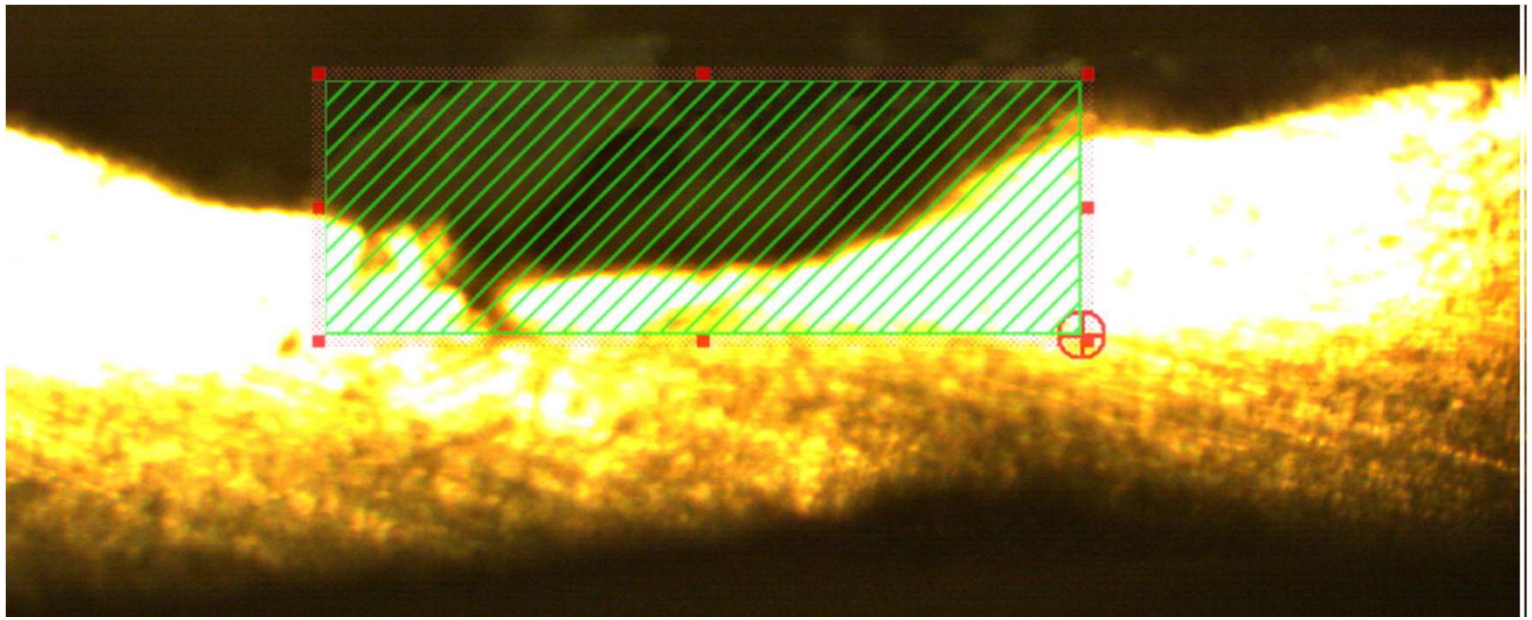
Case of study 9: Silver coin surface alterations

- CXRF volumetric scans were made on coin cross sections



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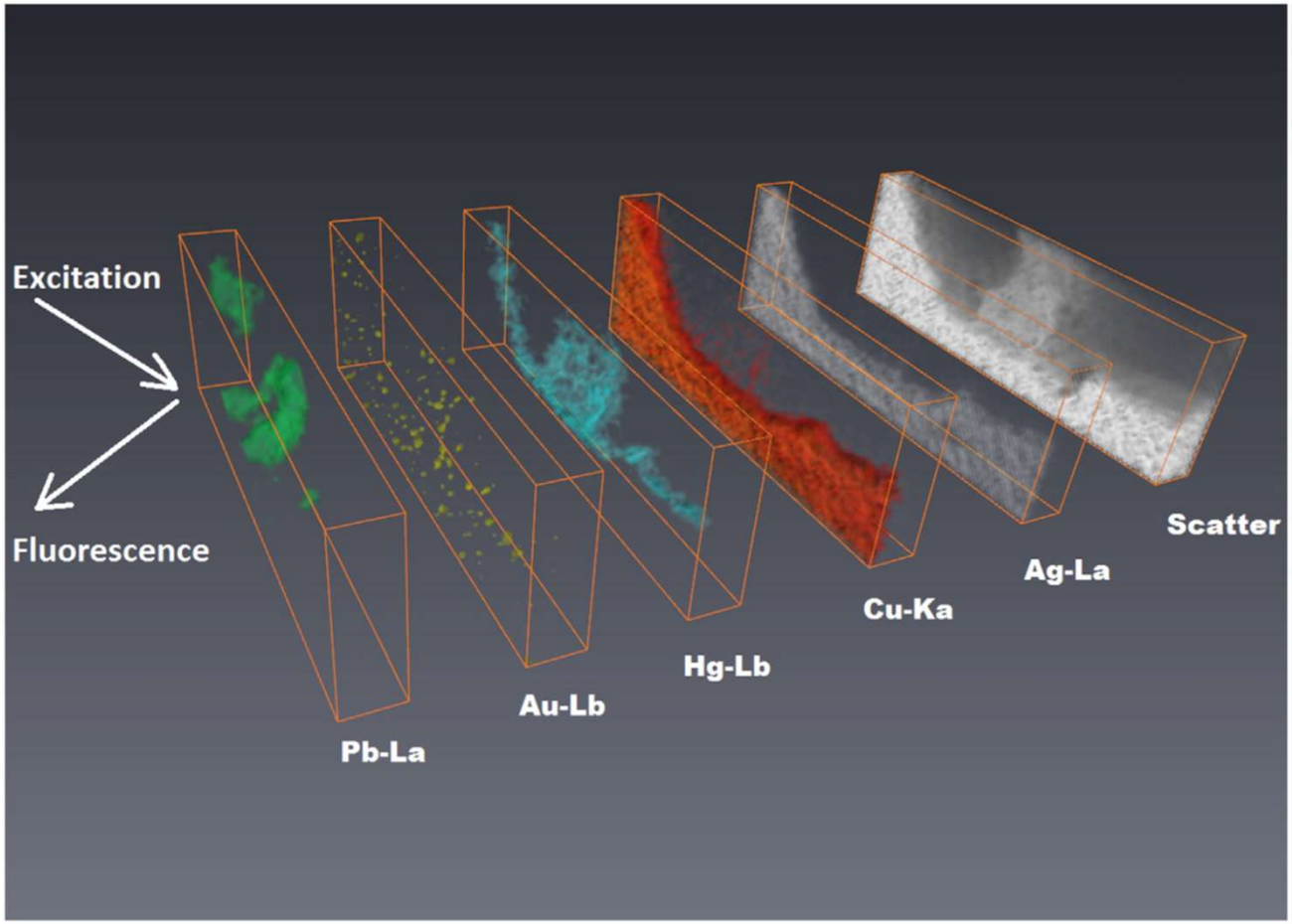
Case of study 9: Silver coin surface alterations

- CXRF volumetric scans were made on coin surfaces and cross sections



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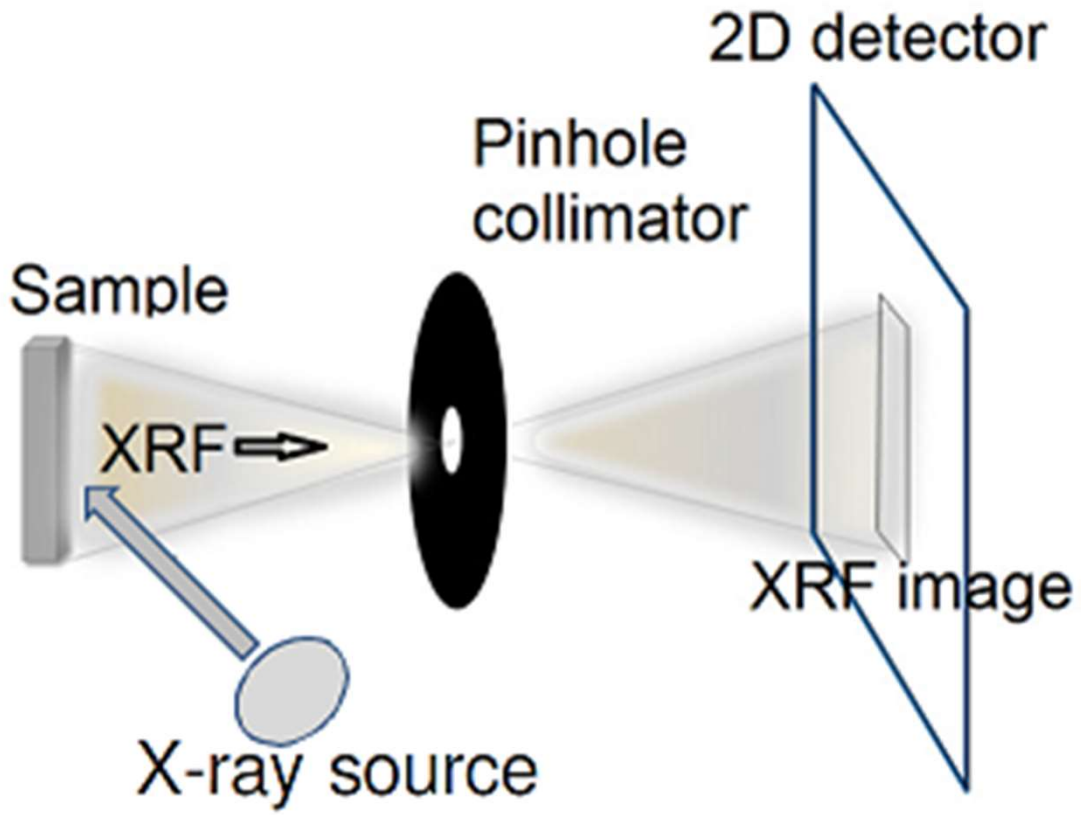
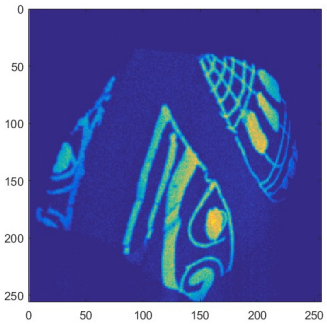
Full Field XRF

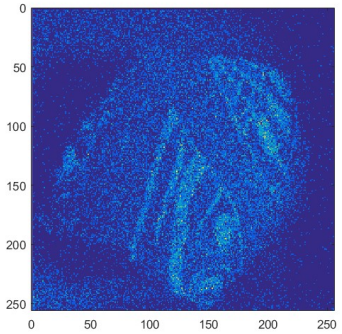


(Courtesy of Dr Paolo Romano
IBAM-CNR, Catania, Italy.)

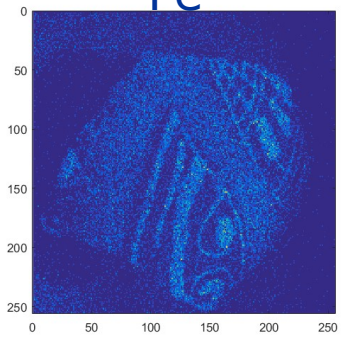
Case of study 10:
Identification of pigments in ceramic glaze



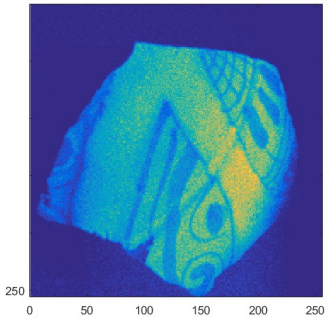
Fe



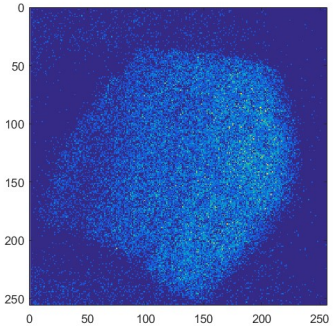
Ti



Co



Pb



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Thanks for your time and attention…