XRF analysis of pigments on marble, easel and mural paintings

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Outline

Polychromy on marble, wall-paintings , stone materials, easel painting

General approach

- ✓ Detection of at least one fingerprint pigment element – Pigment identification is modest. **XRF is performing elemental analysis!**

Single at millimeter scale XRF measurement

- ✓ Detection of two or more fingerprint pigment elements at the same spot – Pigment identification is strong (narrow list of candidates)

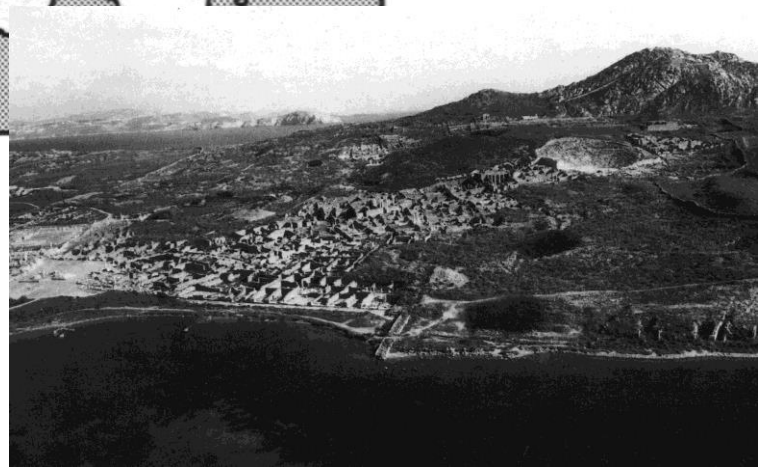
Scanning micro-XRF or Macroscopic XRF analysis

- ✓ Local association of two or more fingerprint pigment elements – Pigment identification is strong (narrow list of candidates)

Trace element detection may help to discriminate pigments of the same type or to address provenance issues

In-situ XRF analyses. Delos

Archaeological site of Delos 1873 -



Papposilène, Délos, Musée

Actual state

Strategy of the *in-situ* analyses

Observation

Recording

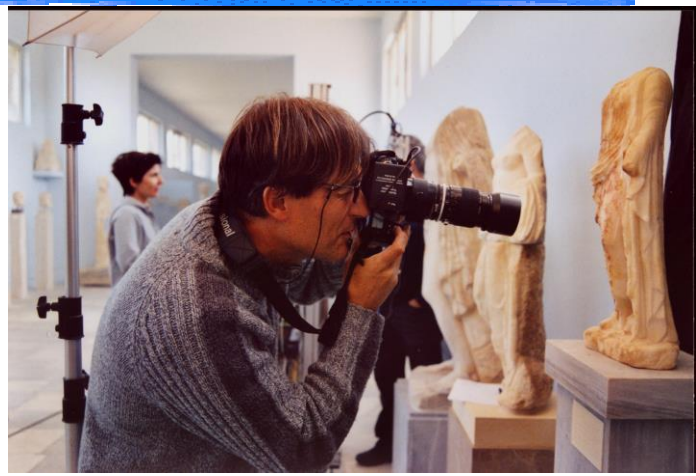
Mapping

Delos Archaeological Museum
National Archaeological Museum in Athens

XRF analyses

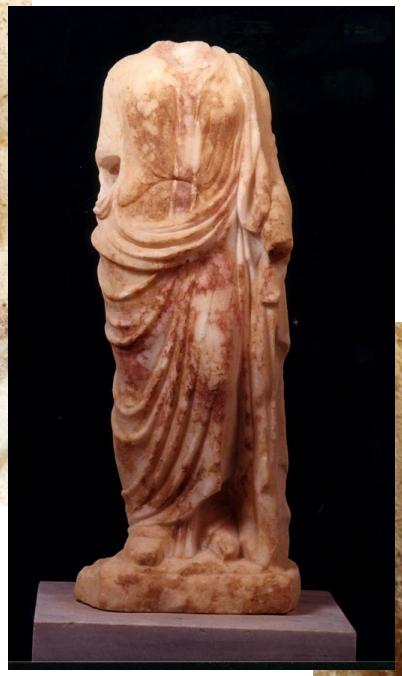
Photographic Techniques

- ✓ Raking Light
- ✓ Macrophotography
- ✓ Infra-red photography
- ✓ Ultraviolet photography



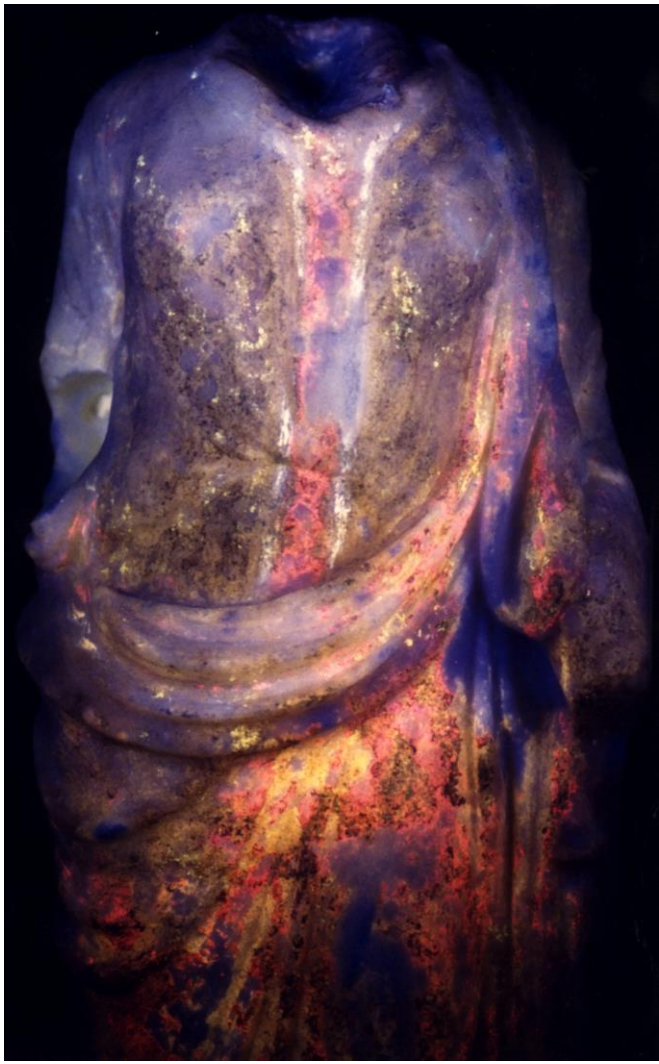
Philippe Collet

Macro-photography

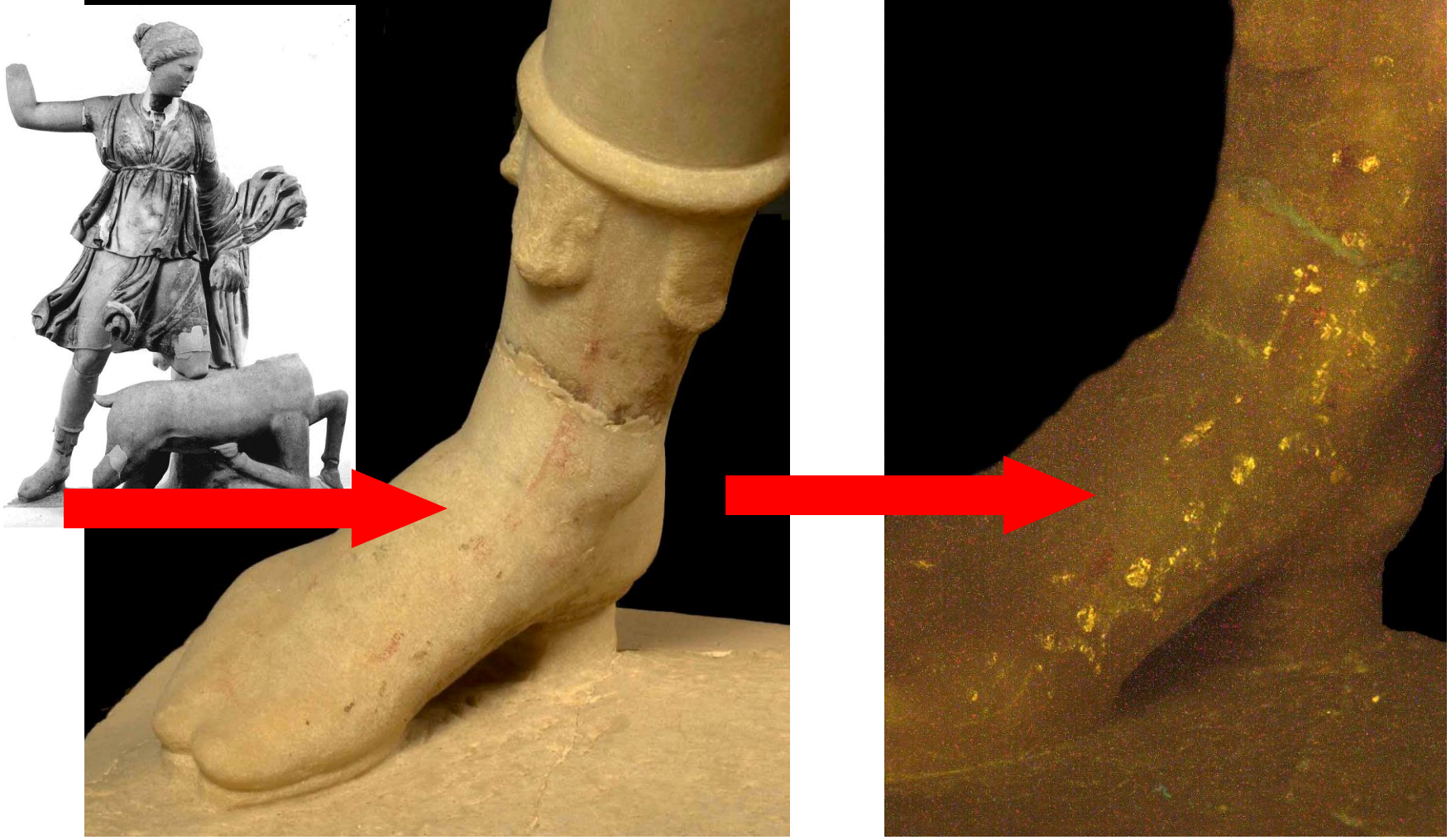


Délos, Musée, Aphrodite

UV Photography



UV Photography



Artémis Elaphébole, Délos, Musée

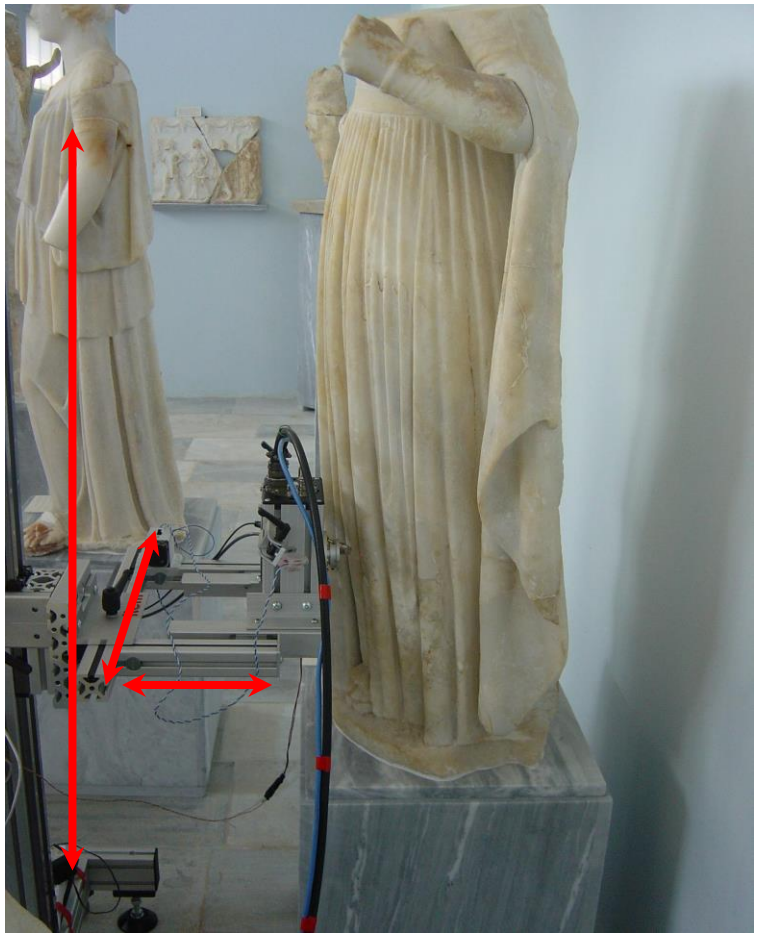
Video-microscope examination

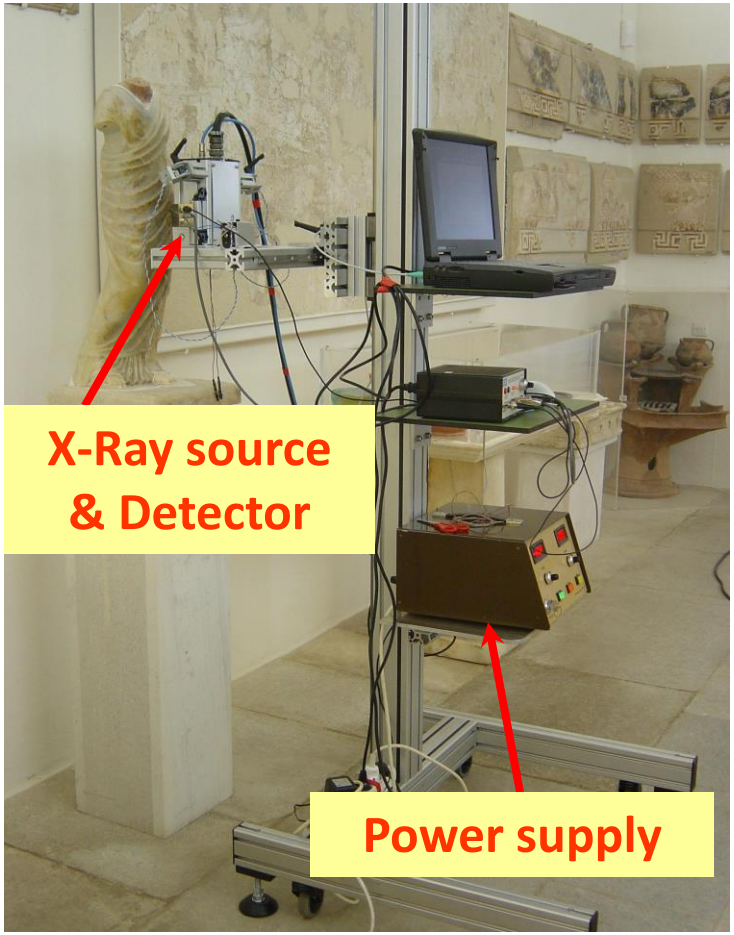
Brigitte Bourgeois, CNRS, Louvre Museum

Inherent difficulties for the XRF analyses

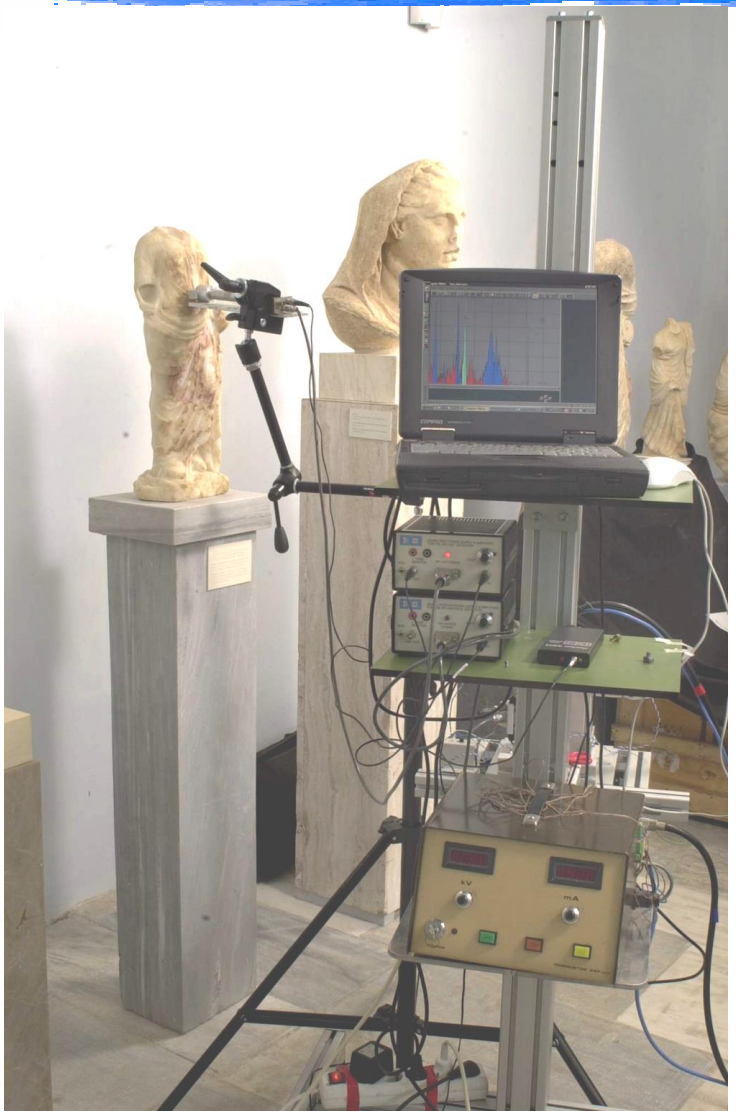
➢ to the structure of the statues' draperies, which often obstructed the access of the beam on the interior parts of their folds, where colour was preserved in larger and more homogeneous areas

XRF portable instrumentation @Delos





Probe with radioisotope source



Inherent difficulties for the XRF analyses

- to the excessive abrasion of pictorial layers and therefore the insufficient quantity of pigment to be analysed.

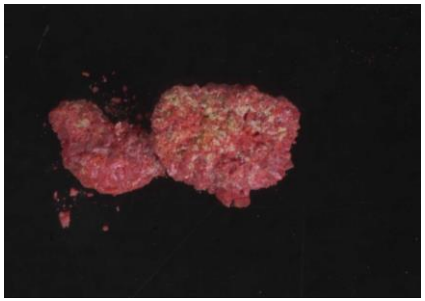
Complementarity of the Applied analytical techniques

The accurate documentation of traces of polychromy on the status' surfaces by video optical microscopy allowed for the detection of pigments even in areas where they were entirely invisible macroscopically. In thes cases, the combination of the two techniques (XRF and optical microscopy) applied *in-situ* proved to be highly efficacious.

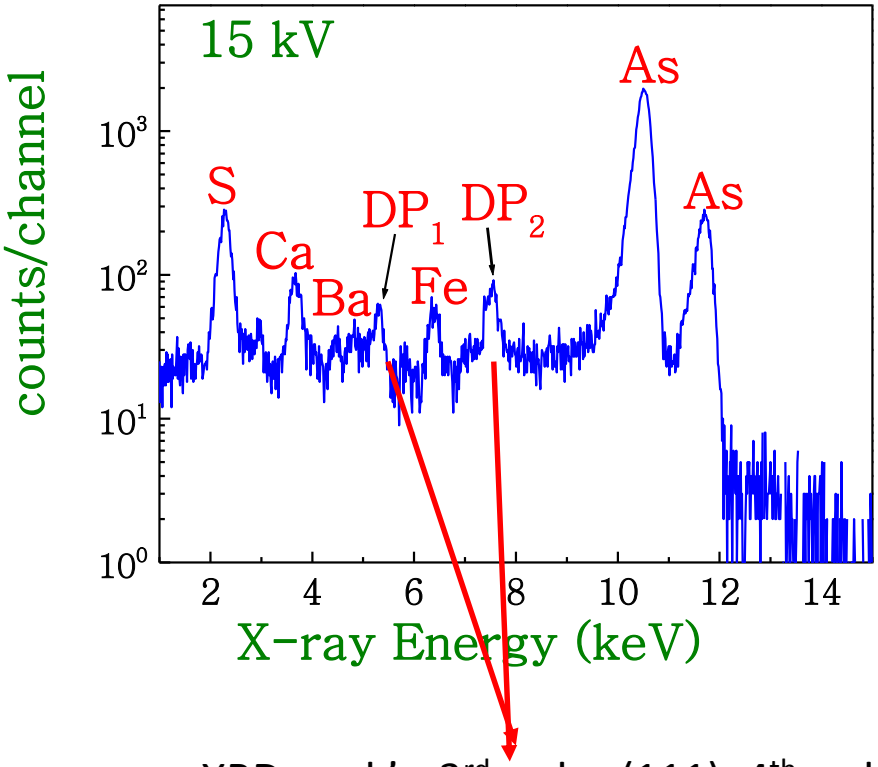
Delian Raw Pigments

Orpiment (As_2S_3) vs Realgar (α-As_4S_4)

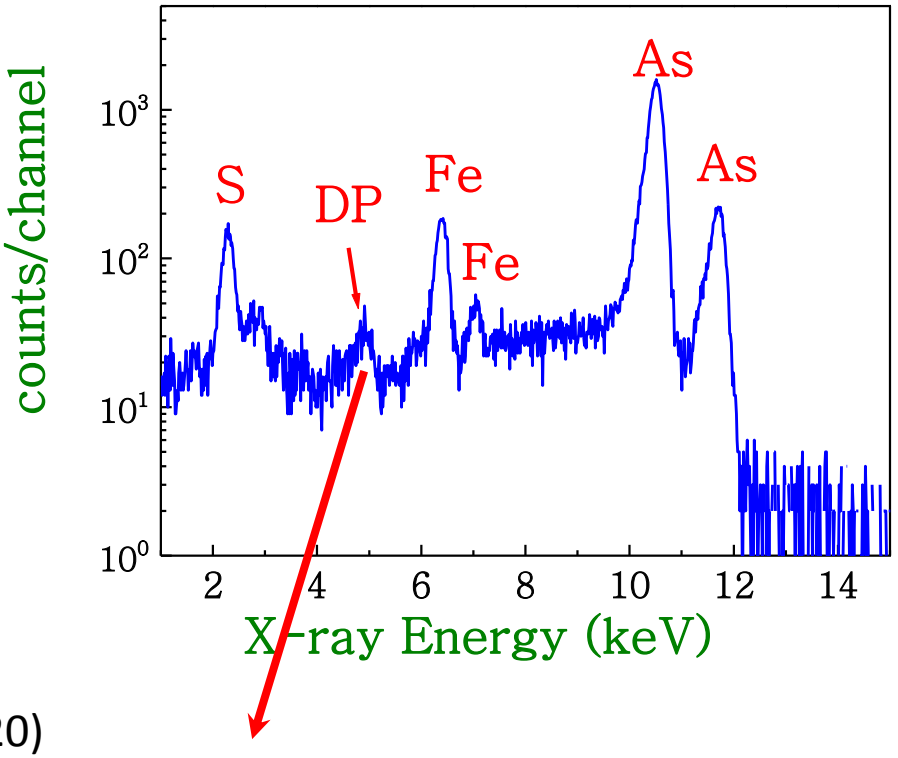
As: 64.6%
S: 32.8%
Ca: 2.3 %
Fe: 0.30 %



As: 71.7 %
S: 26.7 %
Fe: 1.6 %

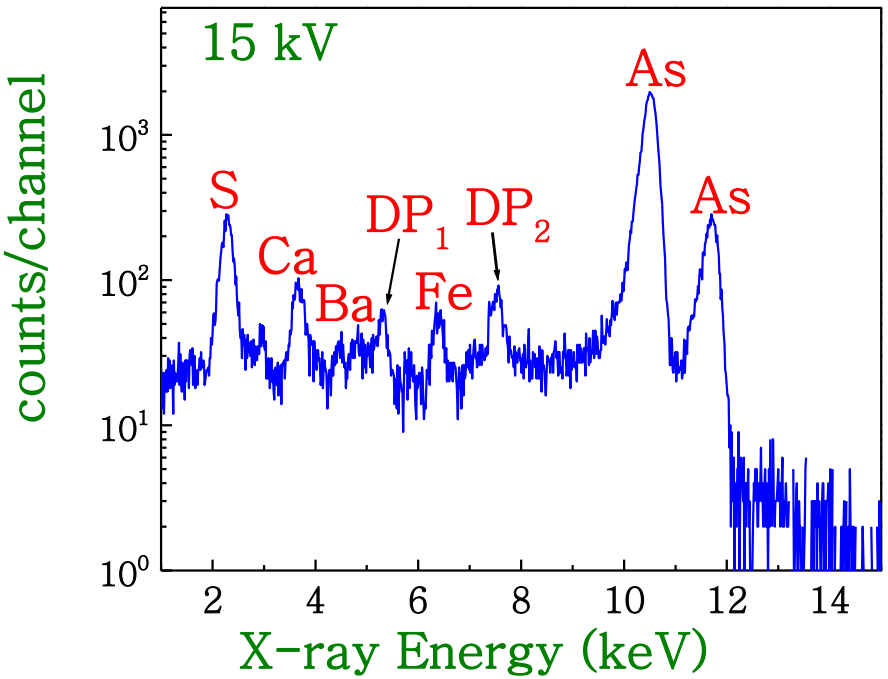


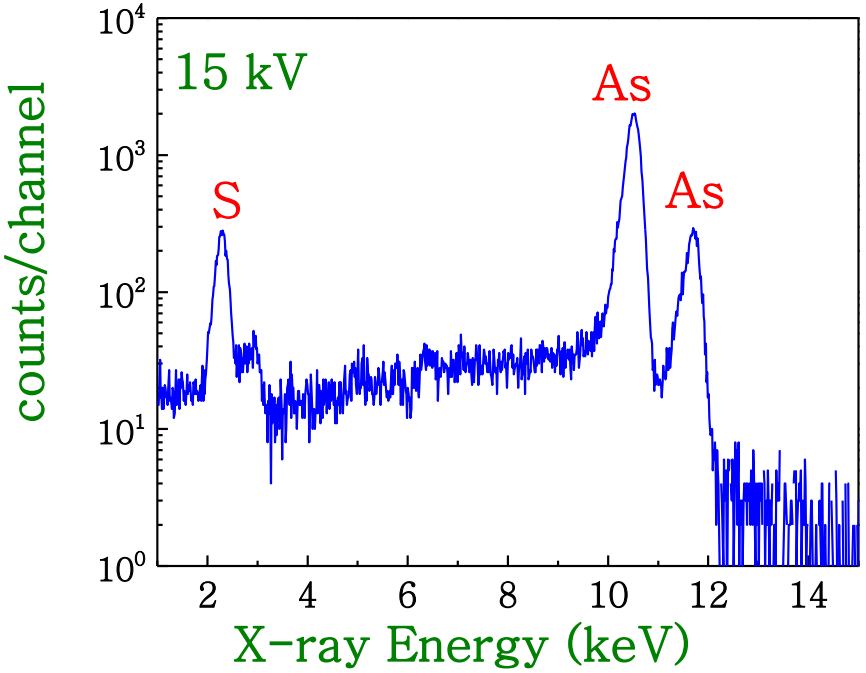
XRD peak's: 3rd order (111), 4th order (020)



XRD peak: 4th order (120), 2nd order (320, 141)

Crystallized vs "Amorphous" orpiment





As: 64.6%

S: 32.8%

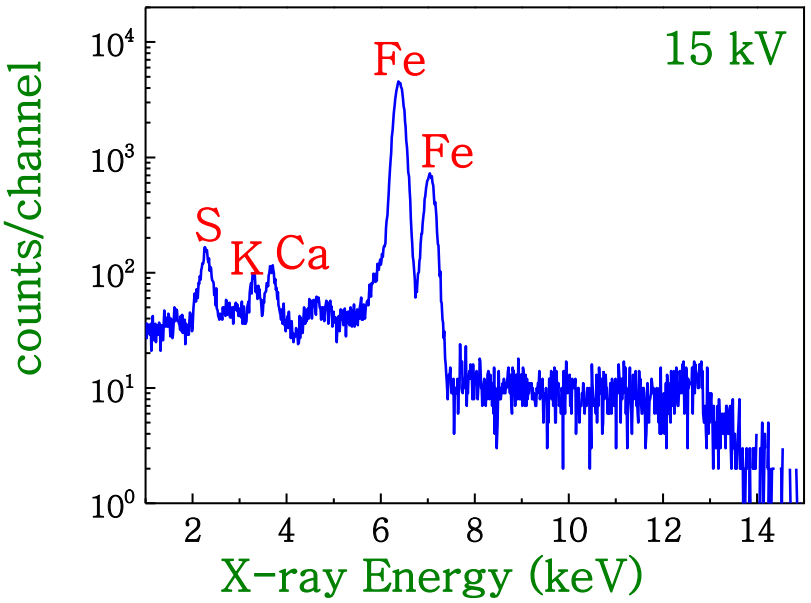
Ca: 2.3 %

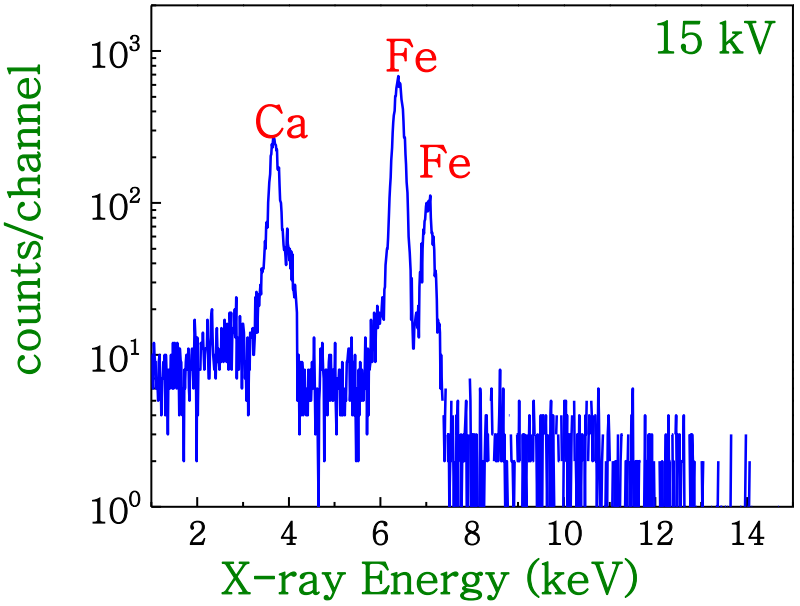
Fe: 0.30 %

As: 64.7 %

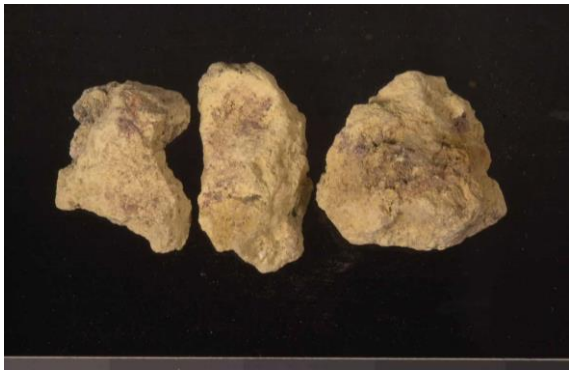
S: 35.3 %

Yellow Raw pigments: Jarosite vs Yellow ochre





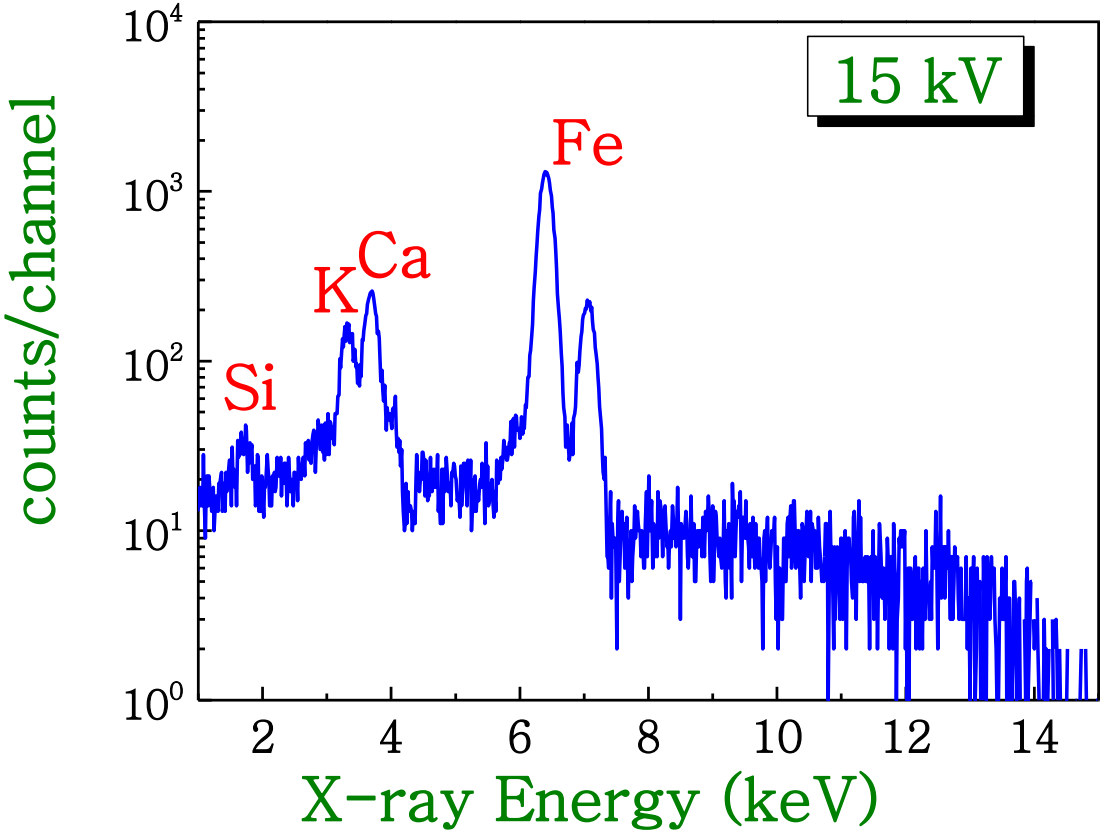
Fe_2O_3: 53.5 %
SO_3 : 27.9 %
K_2O : 2.0 %
CaO : 1.9 %



$KFe_3(SO_4)_2(OH)_6$ + Ca-comp + geothite?

αFeO-OH+Ca-comp

Green Raw Pigment: Celadonite



$K(Mg,Fe)(Fe,Al)Si_4O_{10}(OH)_2$

+ Ca-compound

SiO_2 : 53.1 %

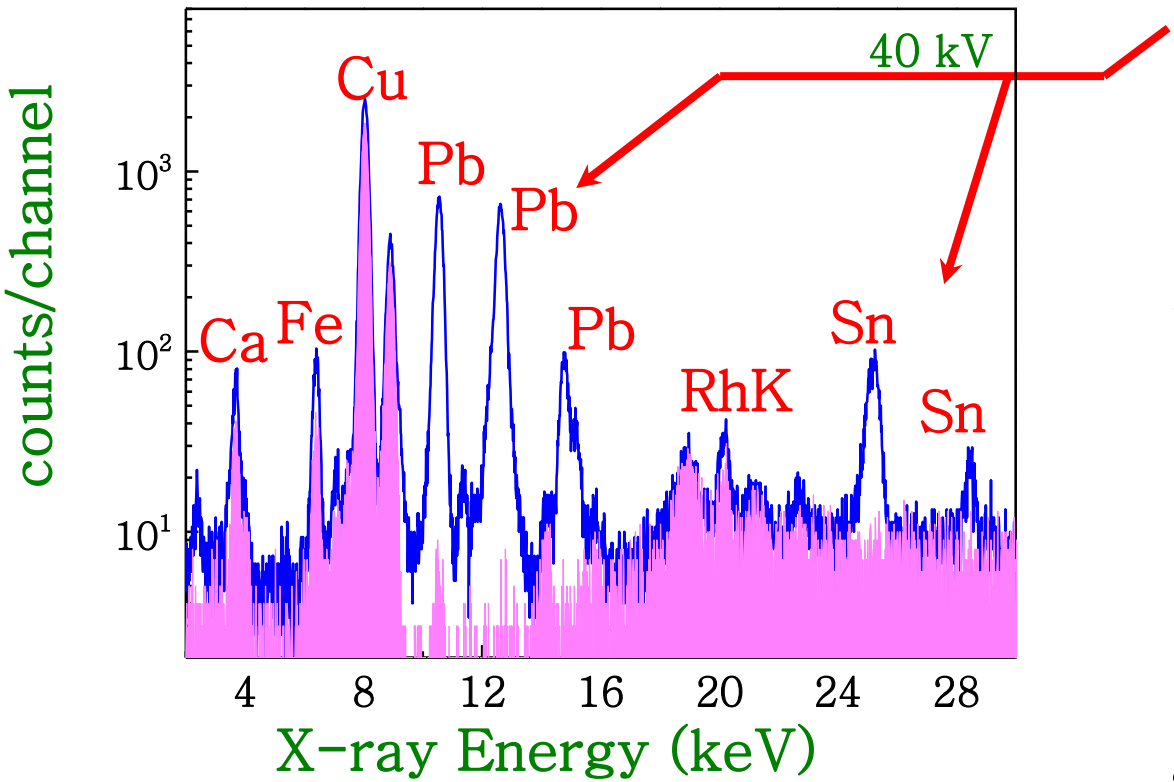
Fe_2O_3: 16.9 %

K_2O : 7.1 %

CaO : 8.8 %

Egyptian Blue raw pellets

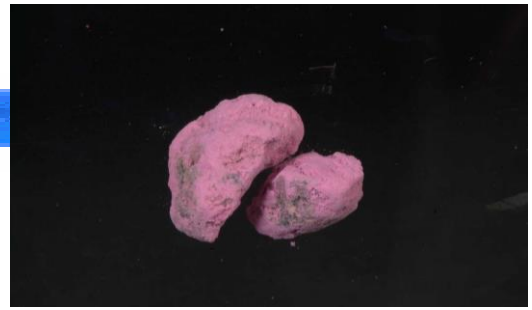
$CuCaSi_4O_{10}$ + interstitial glass + residual glass

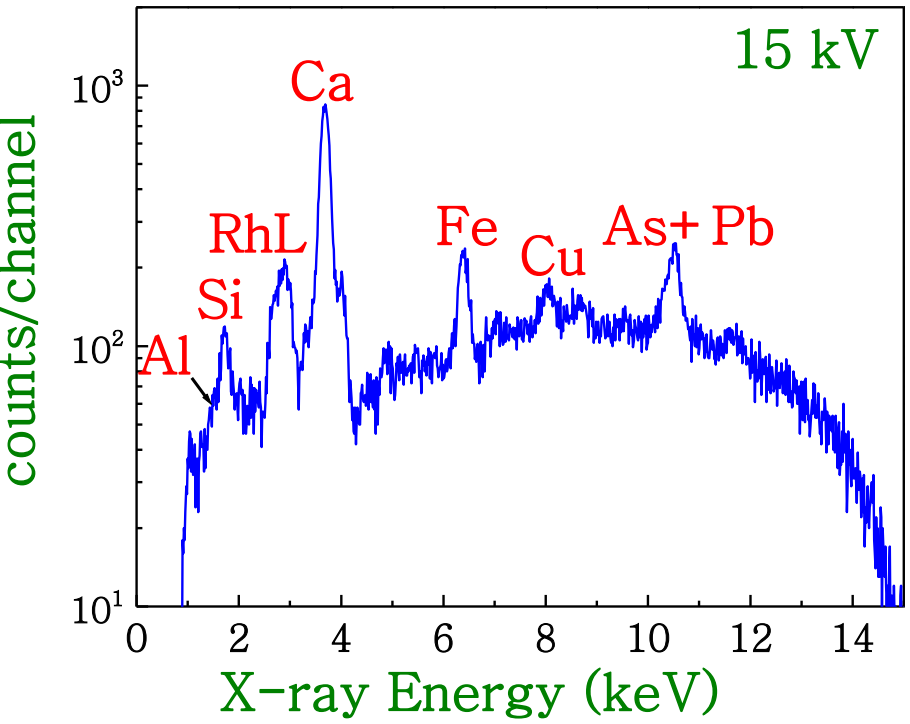


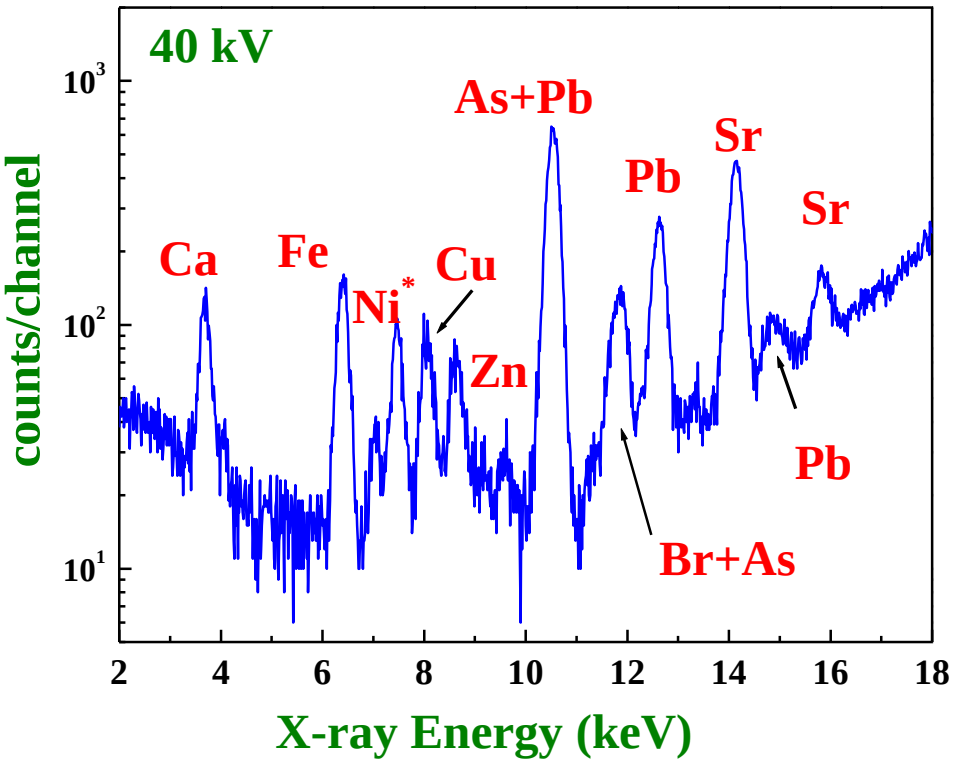
Very interesting the presence of Pb and Sn. Leaded bronze as a source of copper?
Using SEM with back scattered electron imaging Pb and Sn were found in association with a second phase (apart the pure Egyptian Blue phase) consisted of interstitial glass. (Kakouli, 2002)

The inclusion of leaded glass in the pellets is a unique feature that chronologically agrees with the first occurrence of Ptolemaic leaded glass and glazed faience

Organic Pink Raw Pigment







Organic Pink Raw Colorant

✓ The presence of Al and Si, the absence of any other inorganic mineral pigment provide enough evidence's in order to characterise it as an organic colorant.

✓ Trace elements (except Sr) exhibit large inhomogeneities

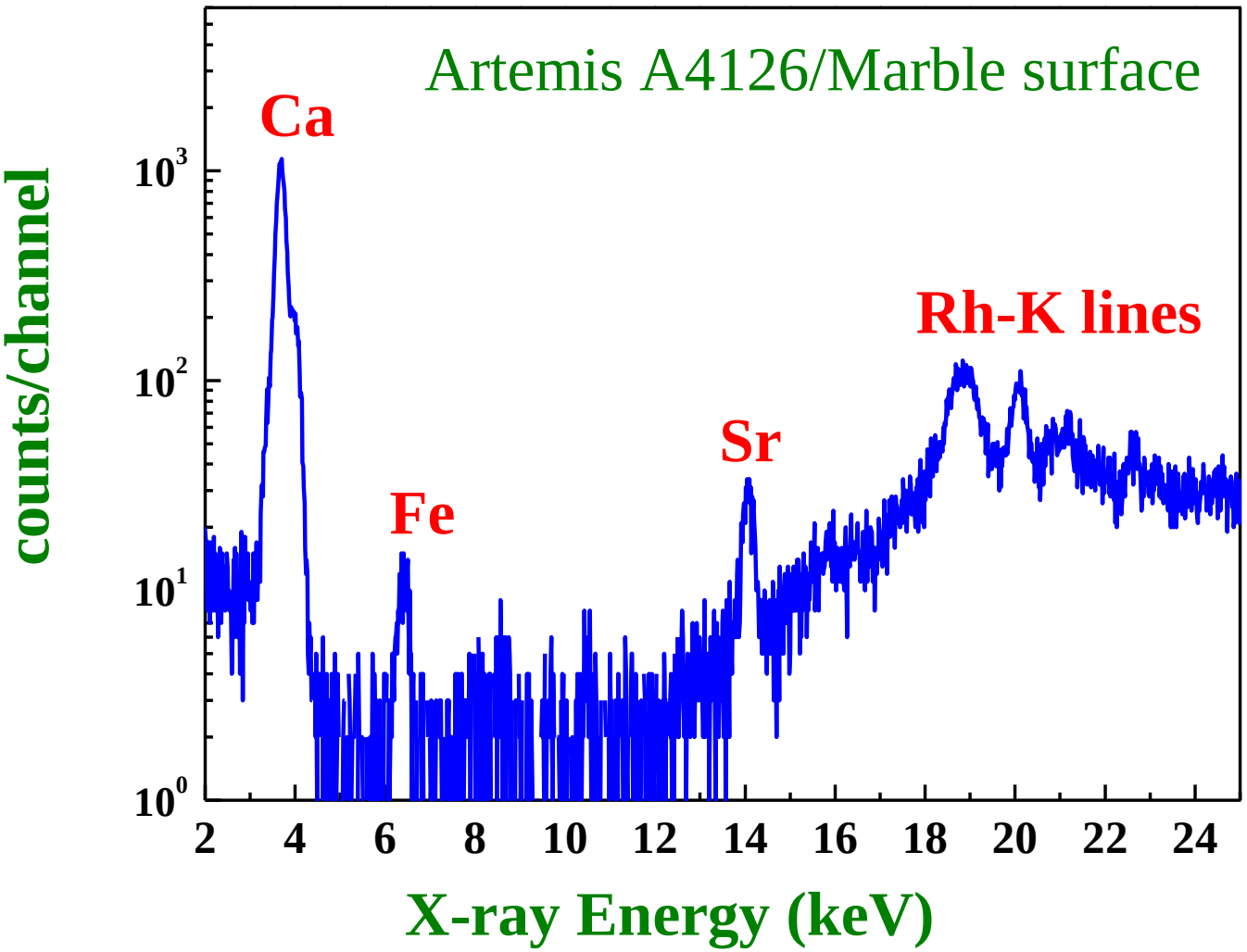
Concentrations are expressed in μg/g:

Fe: 1140 ± 380	Cu: 220 ± 100	Zn: 109 ± 50
As: 555 ± 253	Br: 95 ± 60	Sr: 276 ± 26
Pb: 643 ± 114		

Large variations between elements (etc, As/Pb: 0.5 – 1.6)

✓ The presence of Bromine which may support an hypothesis for the dye's possible origin from shellfish-murex purple

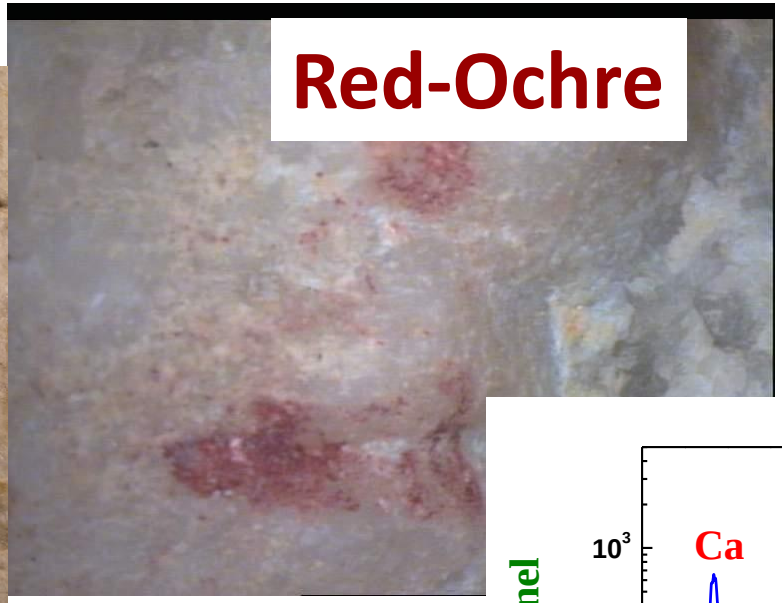
XRF spectrum of the marble substrate

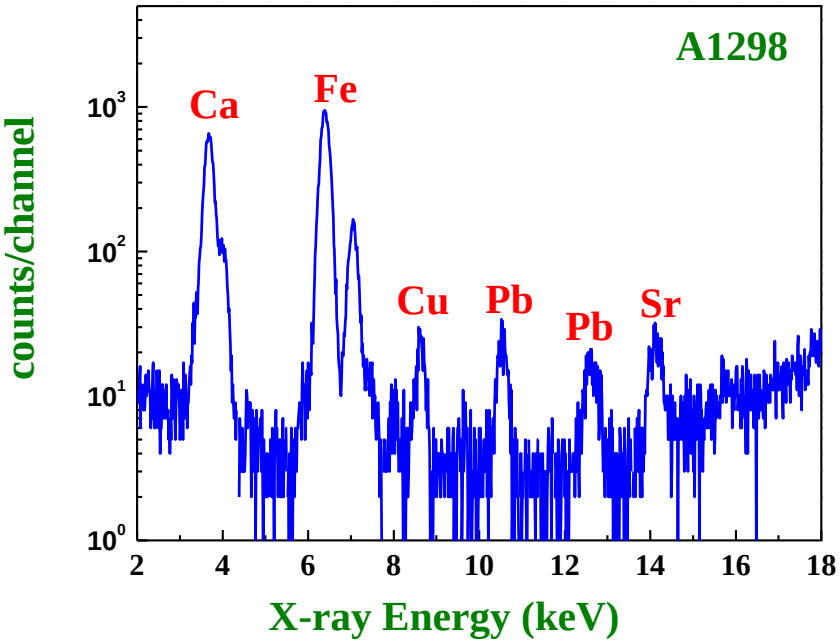


Polychromy on marbles: The “palette’s”

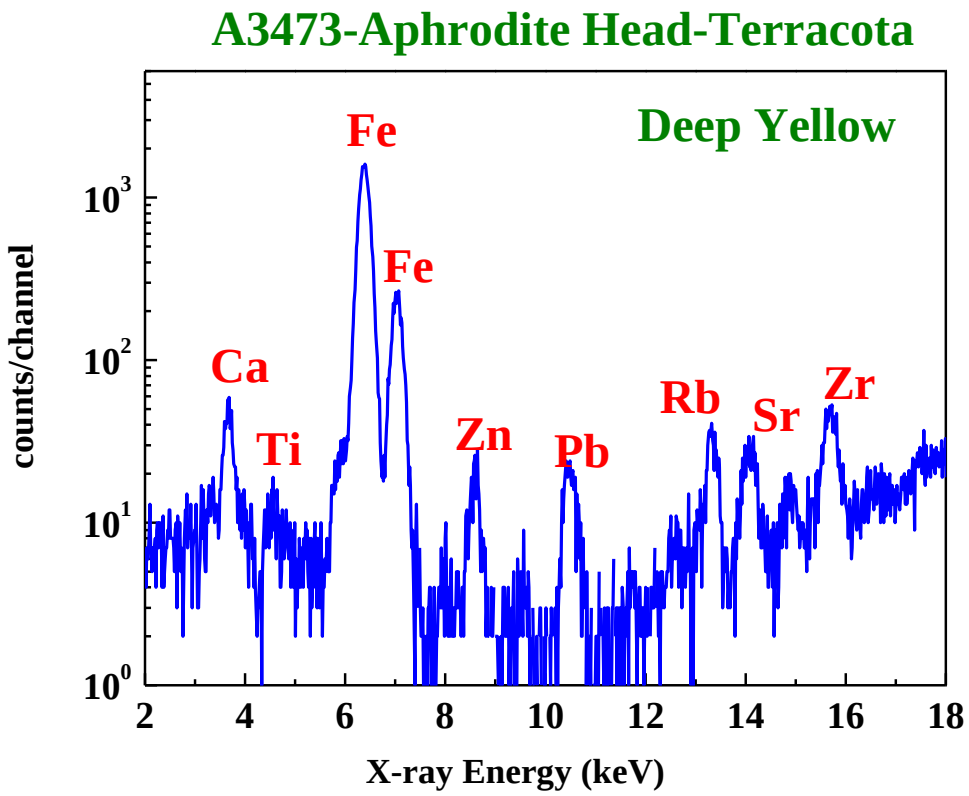
1. Pure pigments
   - Natural inorganic
   - Synthetic inorganic
   - Organic based colorants
2. Mixture of pigments
3. Superimposition of different pictorial layers

The palette, 1 : “Pure” colours





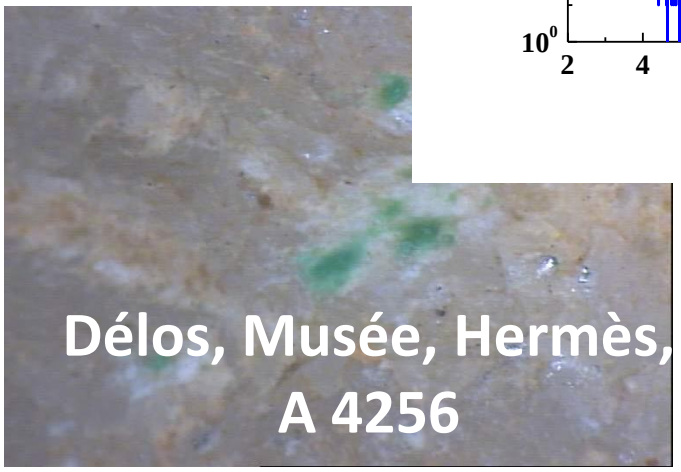
The palette, 1 : “Pure” colours

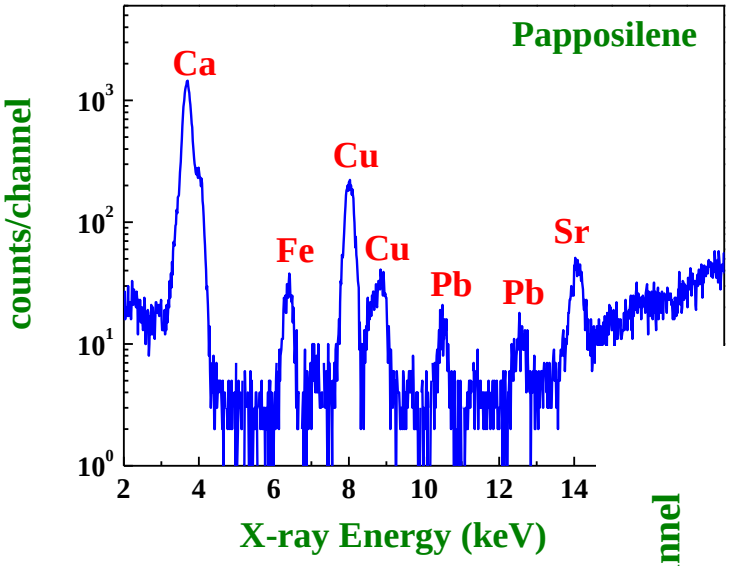


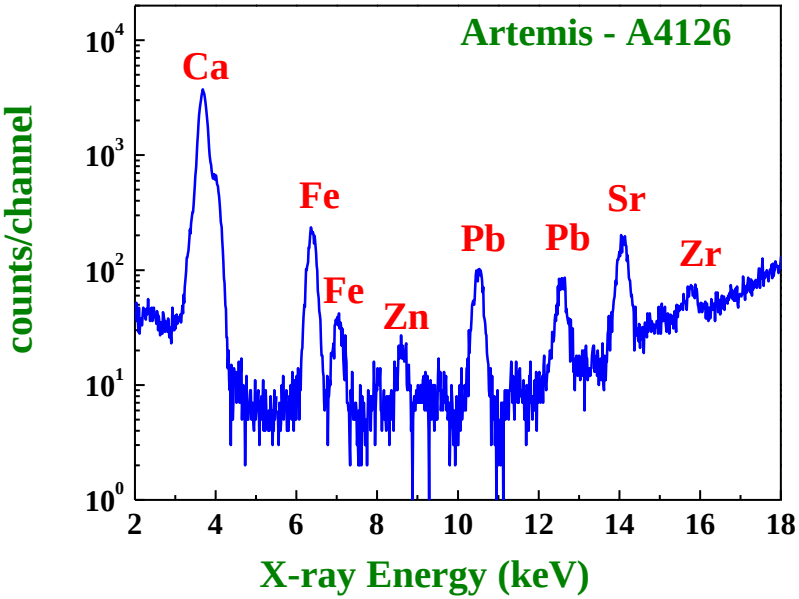
Délos, Musée,
Stèle de Kerdon

The palette, 1 : “Pure” colours

Natural occurred pigments, Malachite/Green Earth

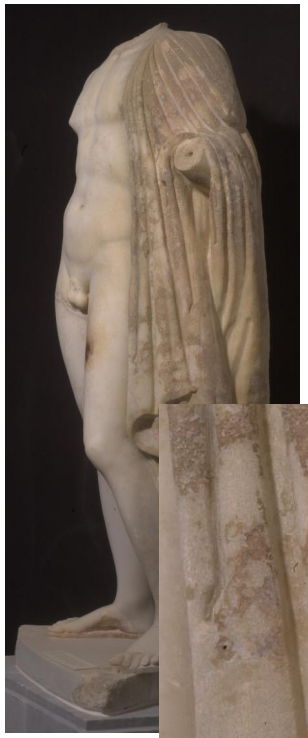


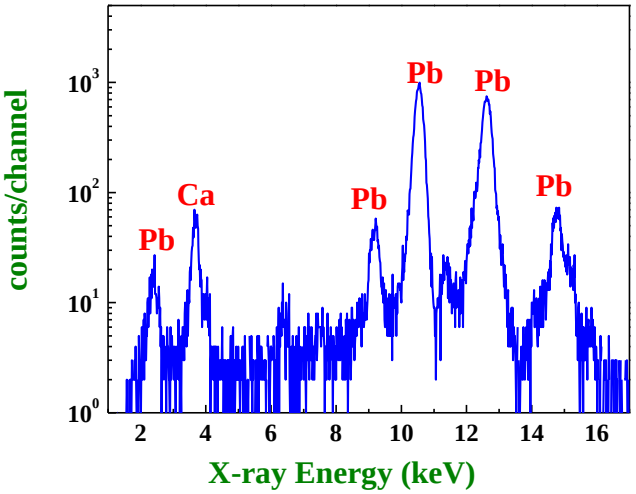




Malachite is characterized by its angular particle form. The colour of the coarser particles show high relief and dark edges, while the finer particles are nearly colourless

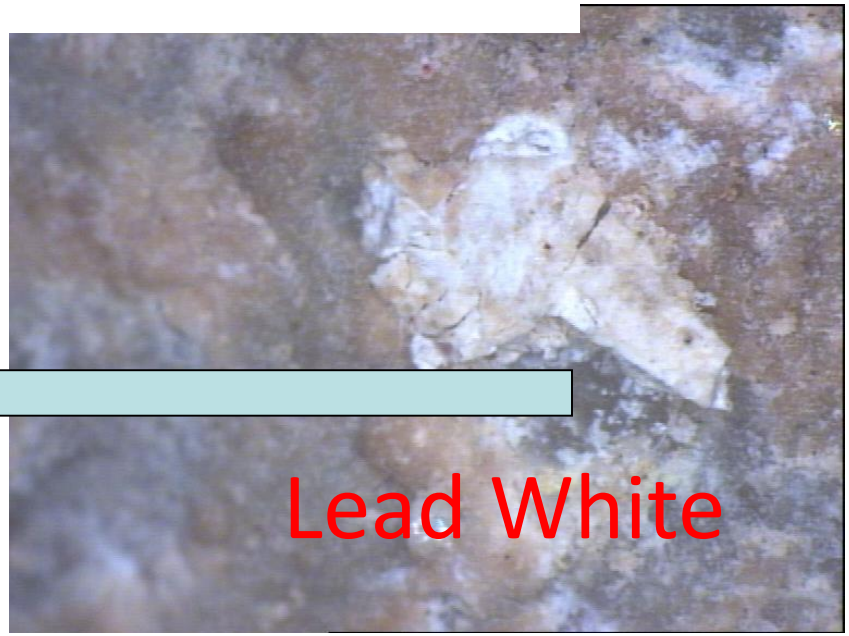
The palette, 1 : “Pure” colours





Artificial pigment

(PbCO3)2·Pb(OH)2



Function of Lead White

✓To create a homogeneous and non porous undercoat which serves as a substrate to the pictorial layers

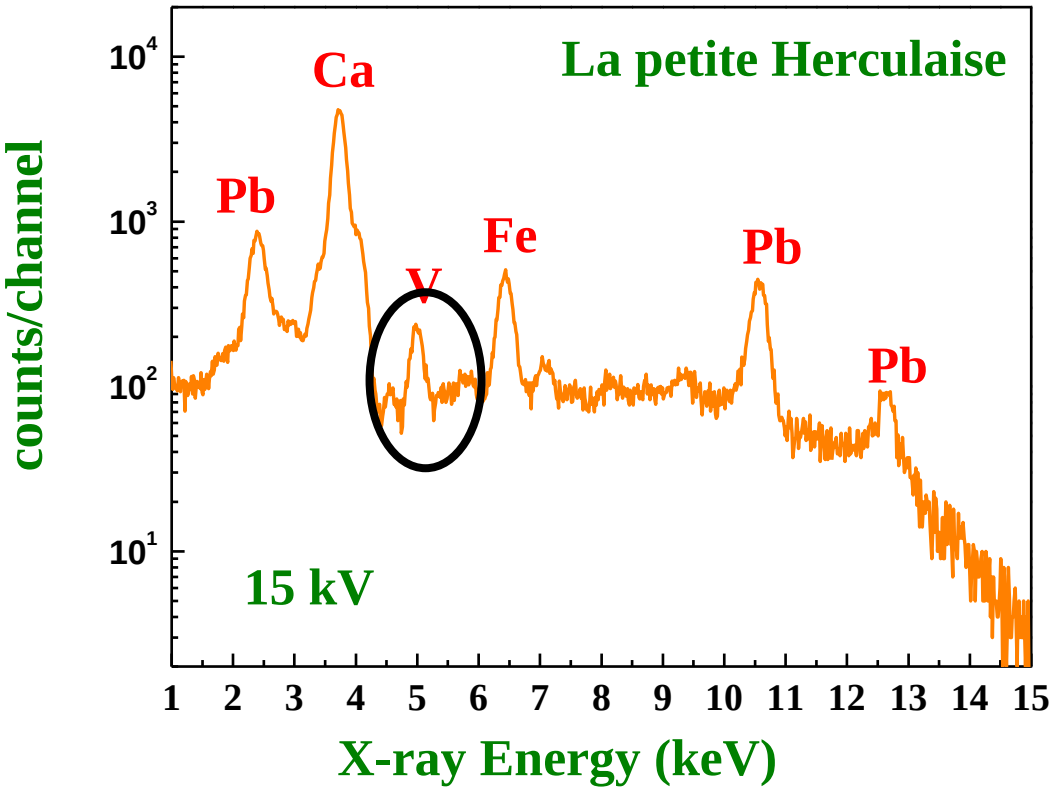
✓To increase the colours' luminosity, thanks to its hiding properties and high refractive index, compared to other whites used in antiquity.

✓ To be used in mixtures with other colours to achieve tonal variations

✓ To be used as a filler mixed with other pigments

❖Its use is attested on other stone monuments of the late Classical and early Hellenistic period

The palette, 1 : “Pure” colors



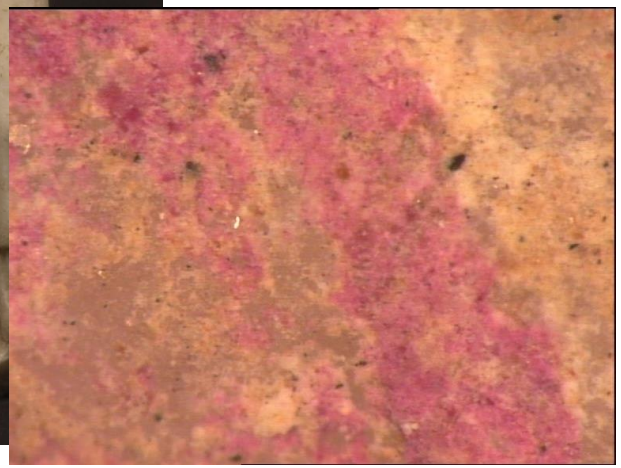
Vanadinite

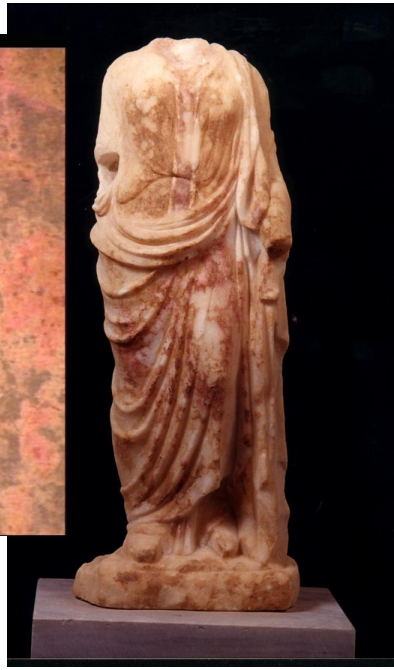
$Pb_5(VO_4)3Cl$,
V:10.8%
Cl: 2.5%
Pb : 73.1%

Vanadinite has been also found on Alexandria stele’s, Louvre Museum.

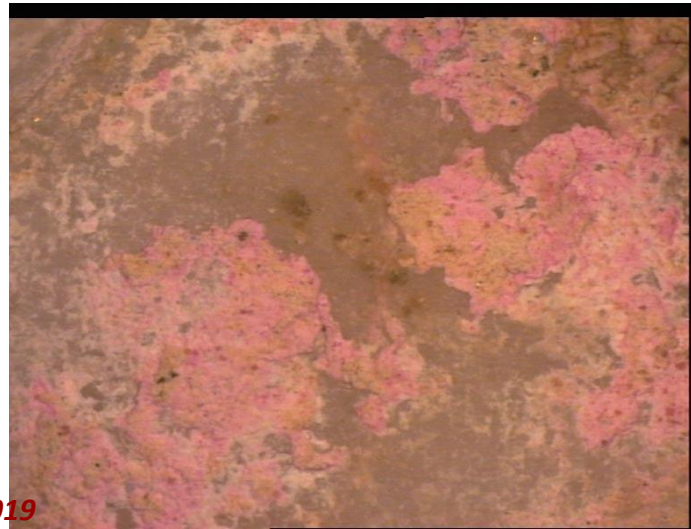
Natural occurred pigment!

The palette, 1 : “Pure” colours



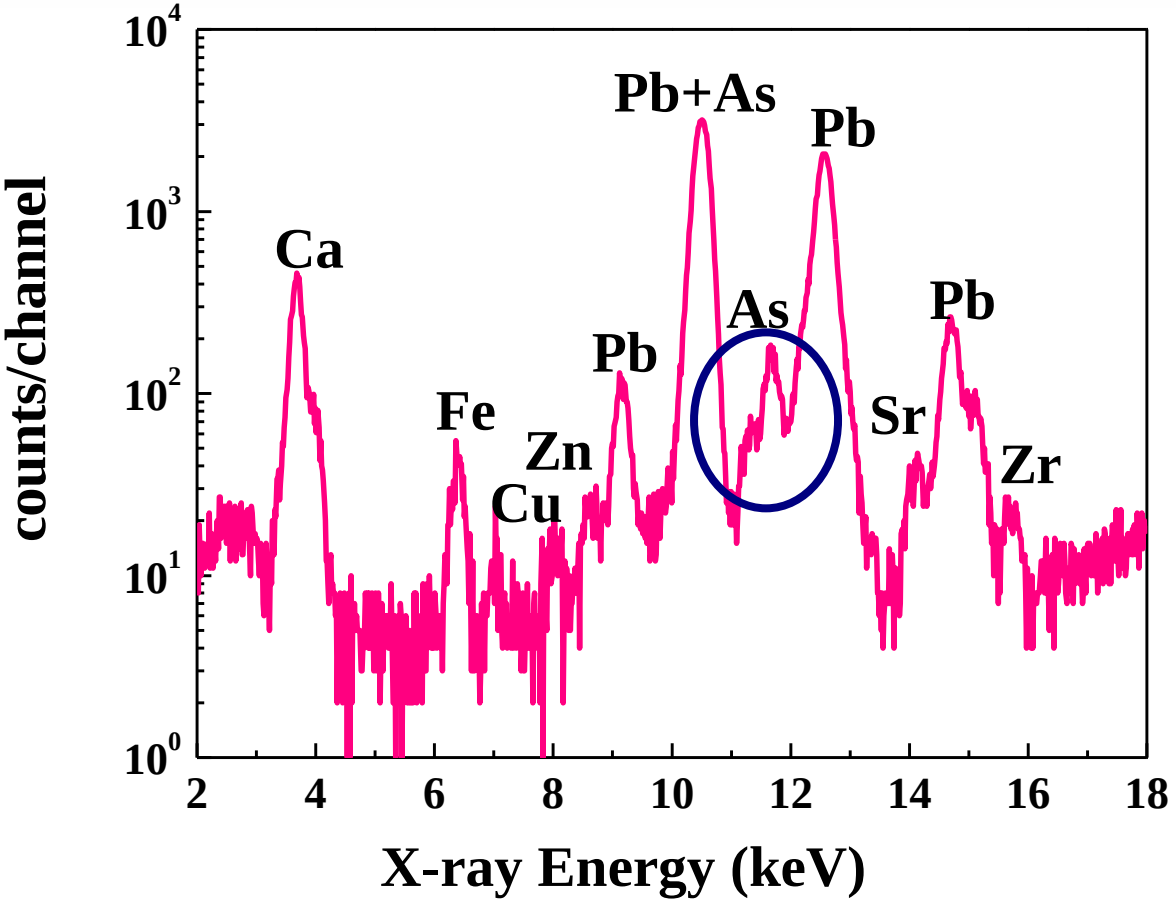


Organic colorant



The palette, 1 : “Pure” colours

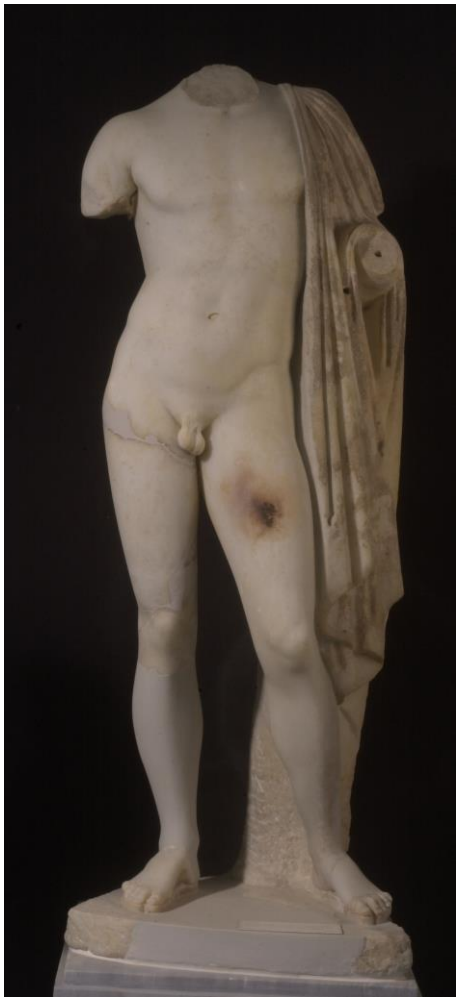
Pink organic colorant

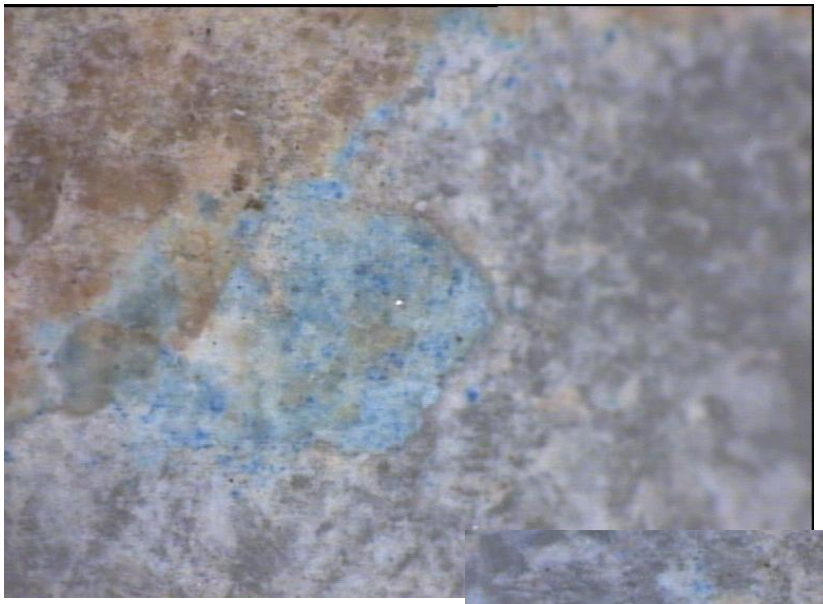


Presence of As: Indicates common origin for pigment lump and pinkish areas on the sculptures

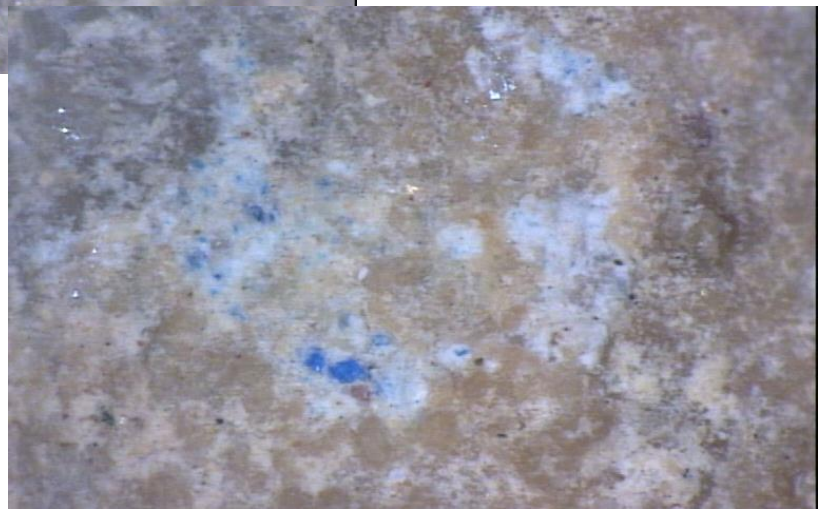
The palette, 1: “Pure” colors

Egyptian Blue





Délos, Musée
Apollon,
Inv. A 4135



Artificial pigment

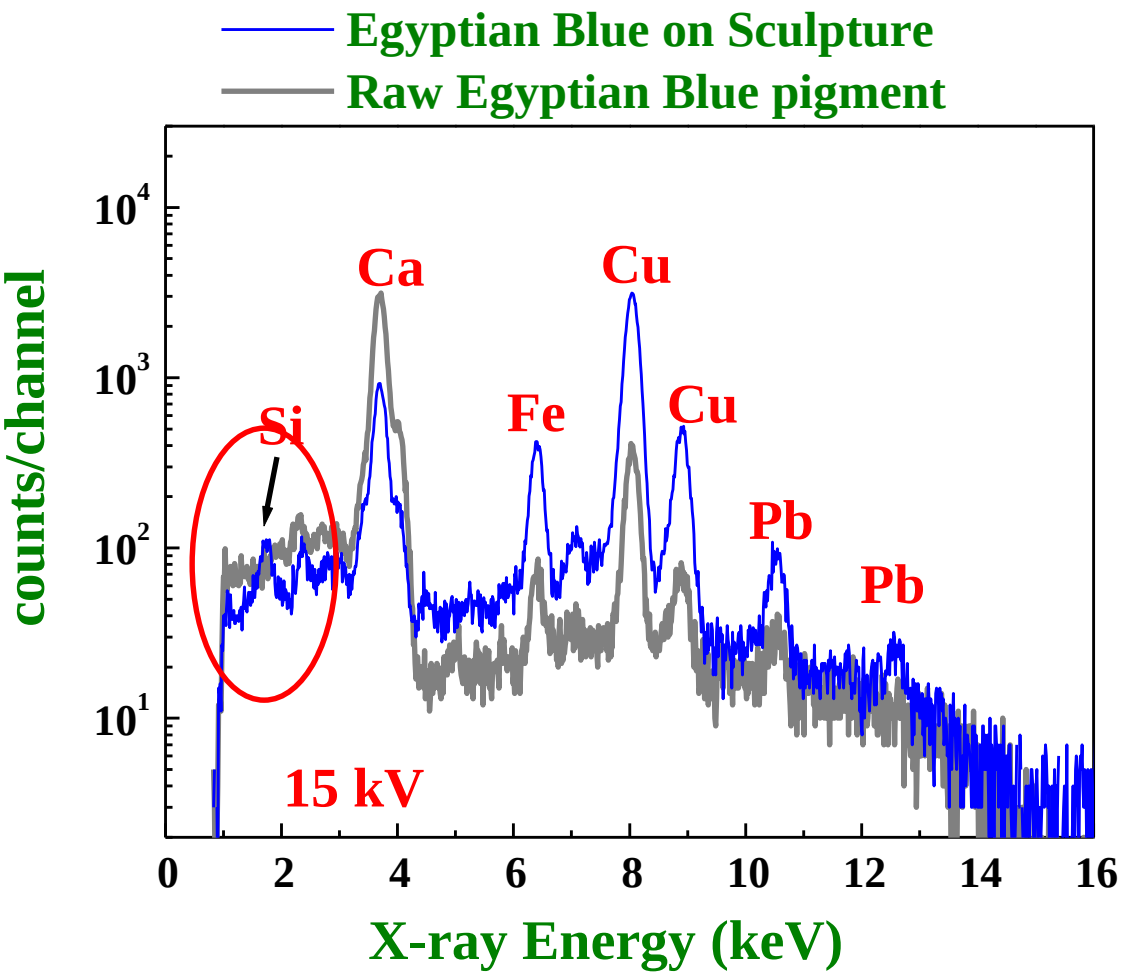
Identification of Egyptian Blue in Ancient pictorial surface's

Problems : Detection of Si and Sn in Egyptian Blue

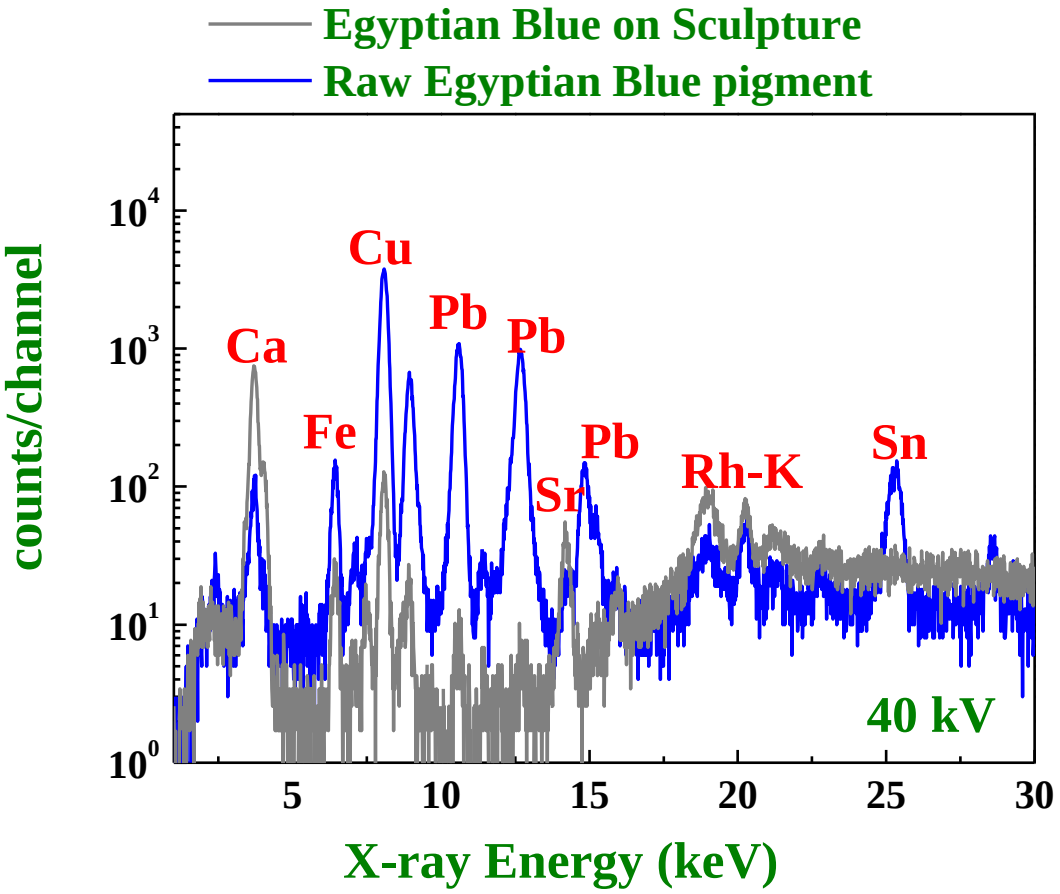
✓The poor preservation of Egyptian Blue, due to its high grain size and sandy texture, often enhances the pulverisation of the pictorial layer.

➢ The relatively large spot area of the exciting beam results to small contribution in the XRF spectrum by the pigment characteristic X-rays of pigment elements.

Identification of Egyptian Blue



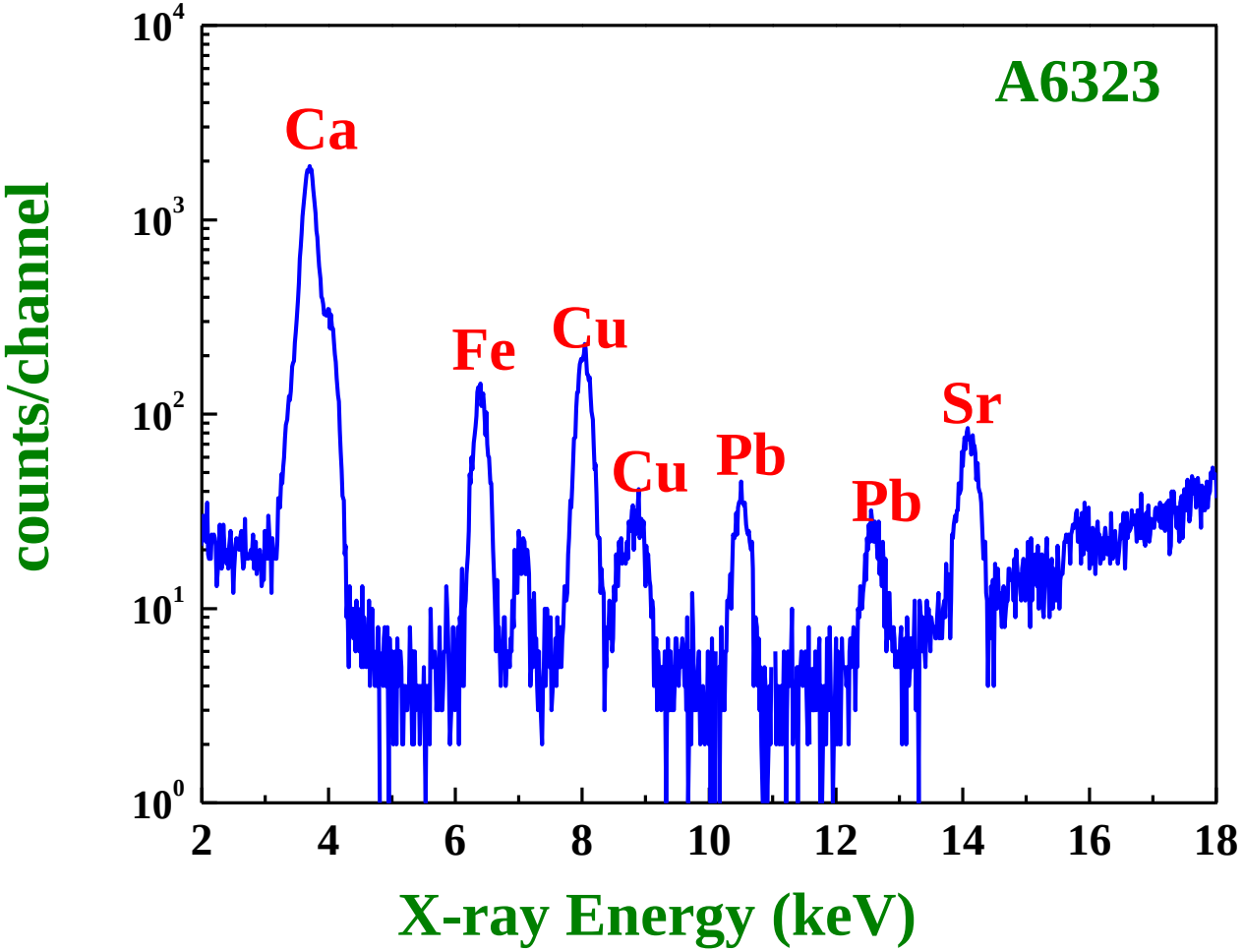
What Egyptian Blue pigment was applied?



❖ Cu/Pb Ratio approach: The ratio Cu/Pb is varied between 2.5 - 6 (for the four raw samples)

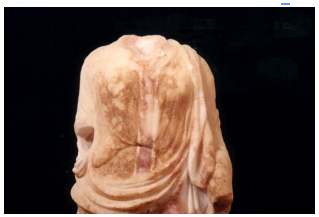
➢ The high Cu/Pb ratio value that was measured, despite the presence of lead white, suggests that raw Eg. Blue pellets with leaded glass were not used on the sculptures.

The palette, 2 : Mixtures

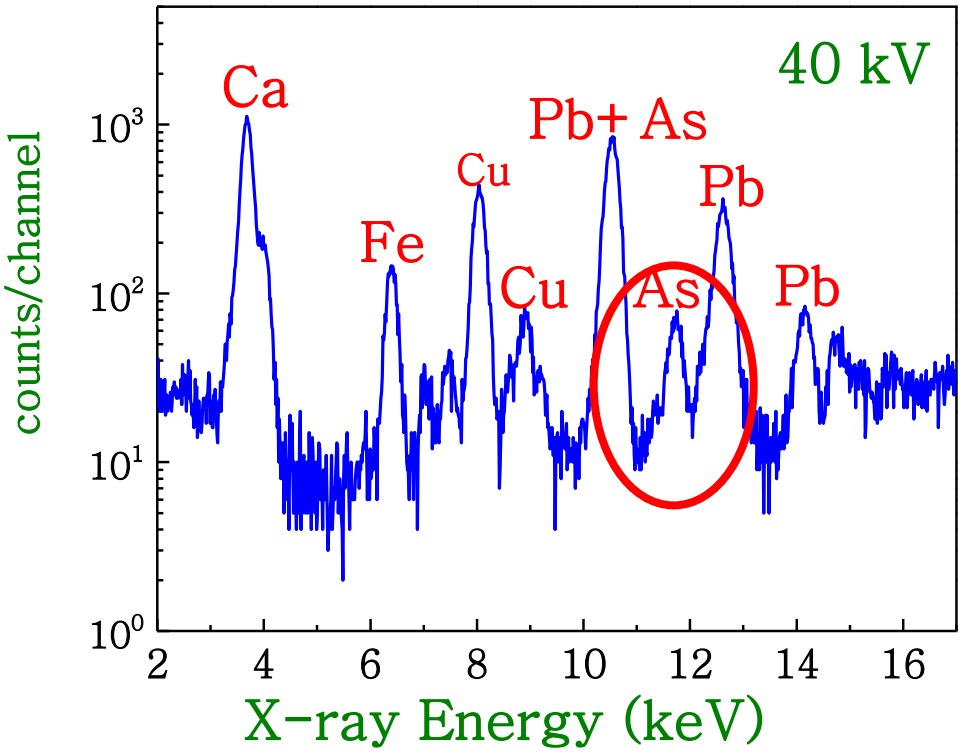


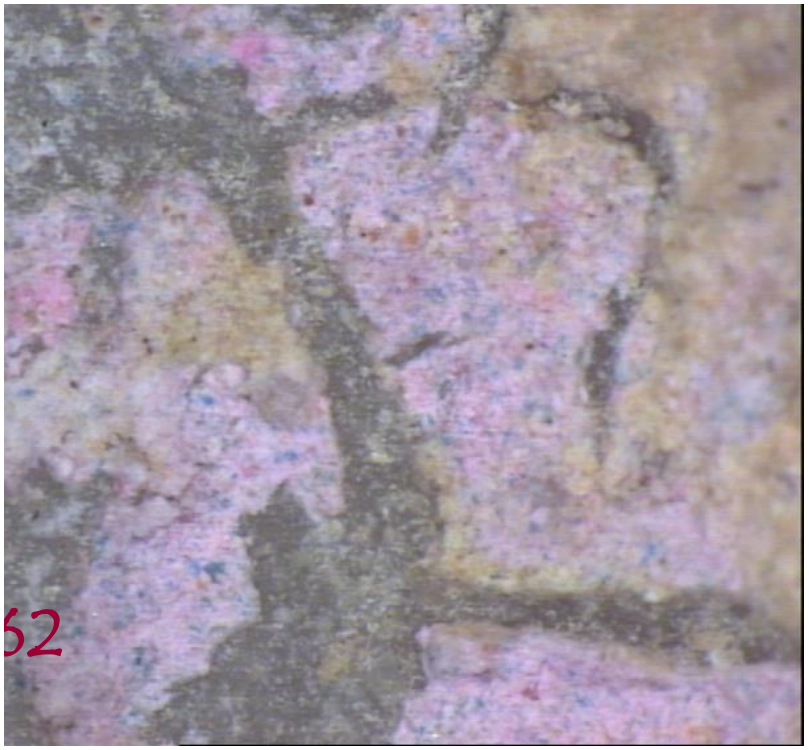
Green-Blue

The palette, 2 : Mixtures



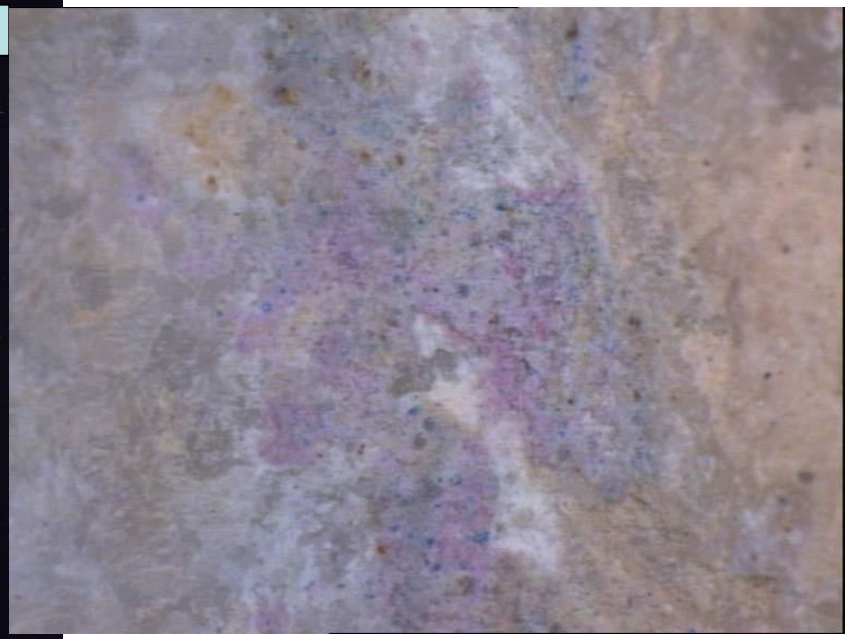
Mauve





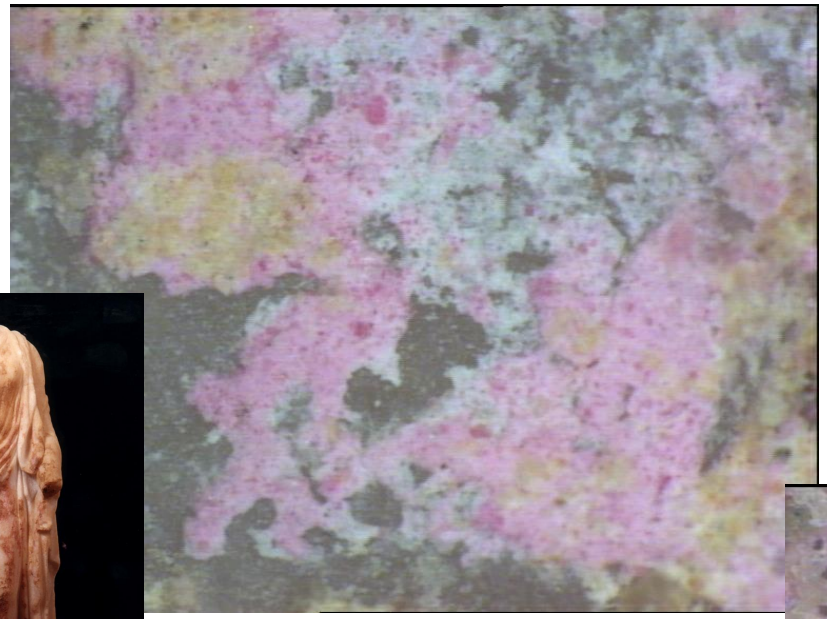
Pink Organic colorant + Egyptian Blue

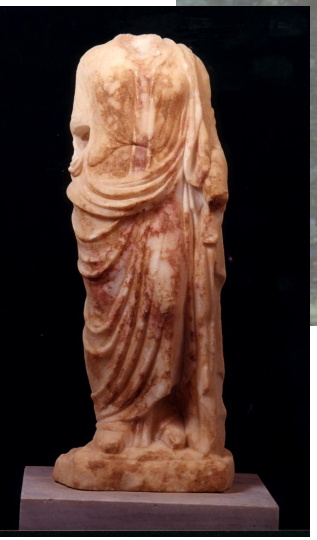
Papposilène



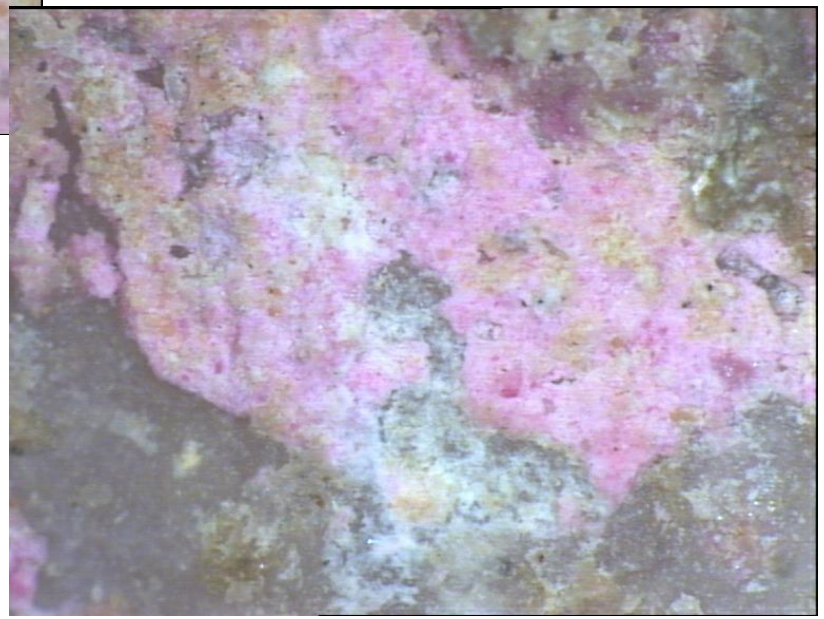
Délos, Musée, Inv. A 4123

The palette, 3 : Superimposition of pictorial layers

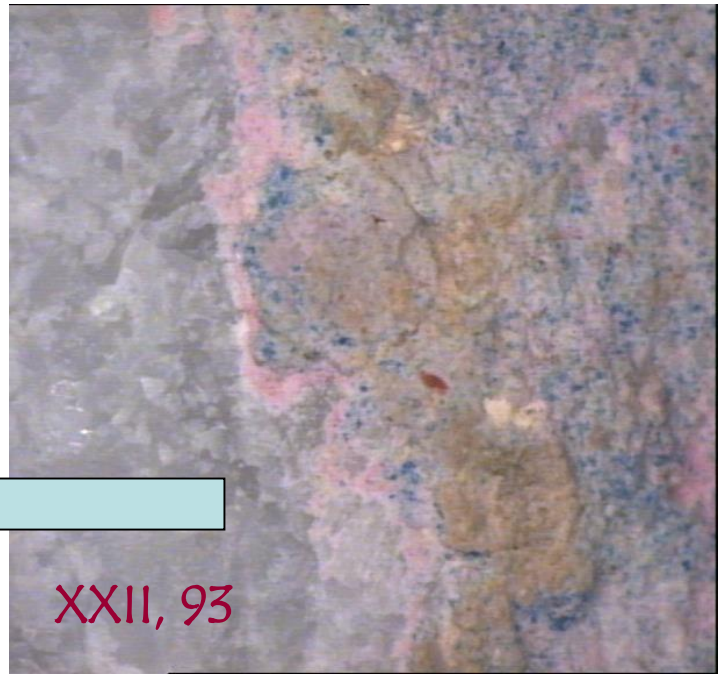




Organic colorant onto Lead White



The palette, 3 : Superimposition of pictorial layers

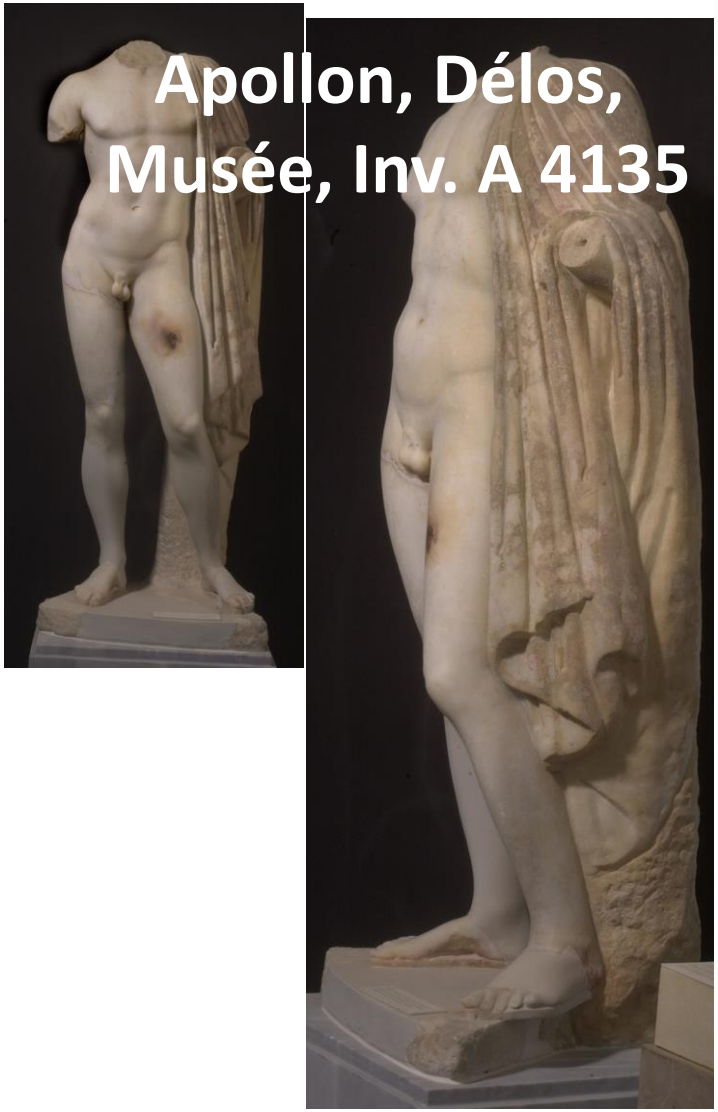


Tychè, Délos, Musée, Inv. A 4129

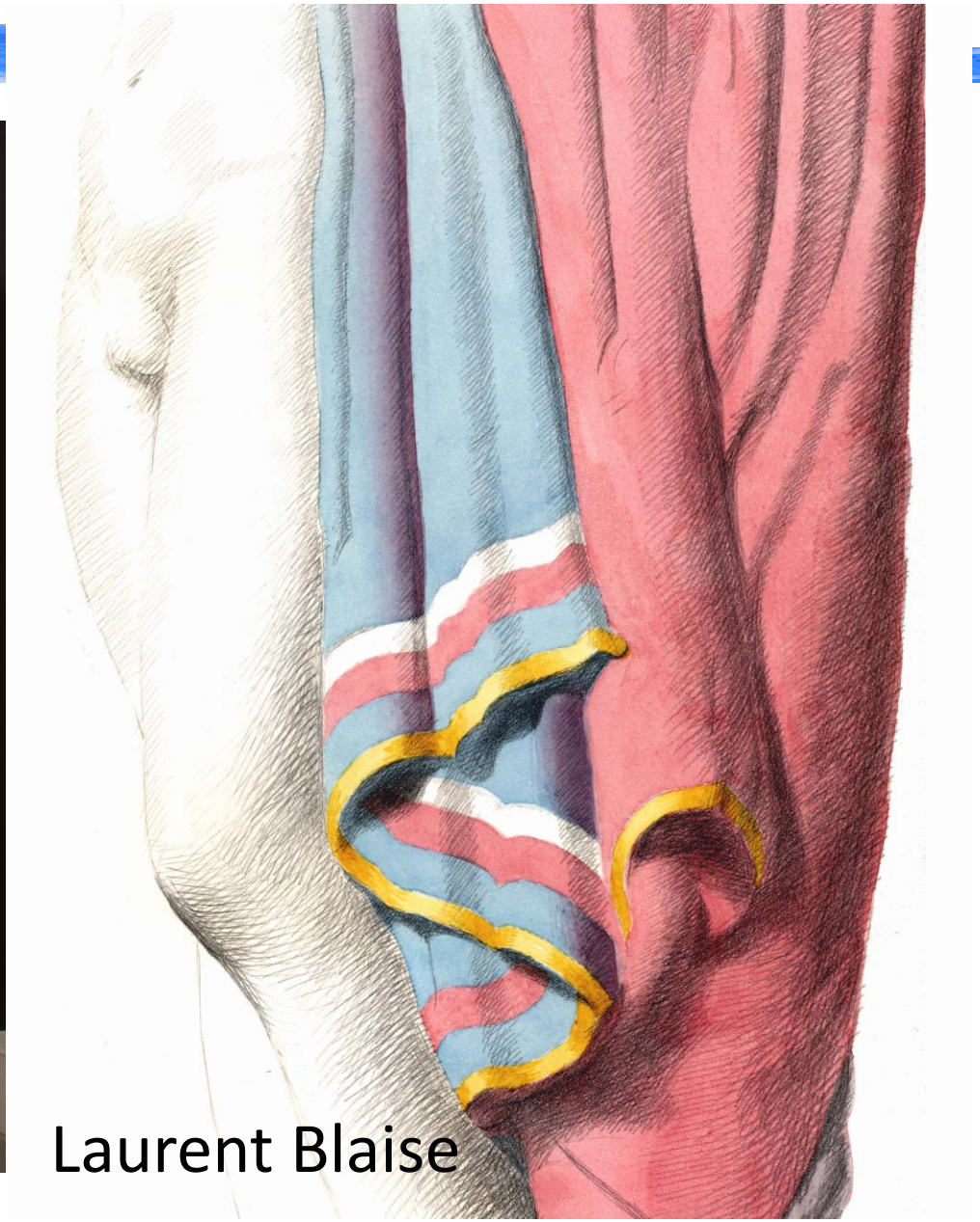
Egyptian Blue onto
Organic colorant onto
Lead White

Summary of results

Type/ Description	No of Samples	No of Samples	Pigments Materials identified
Raw materials	23	23	Yellow/Brown//Red/Orange Ochre, Egyptian Blue, Orpiment, Realgar, Jarosite, Celadonite, Pink organic, Organic black
Sculptures	28	184	Egyptian Blue, Lead white, Yellow/Red/Orange/Brown ochre's, Vanadinite, Organic colorant, Malachite, Celadonite, Gold
Terracotas	3	20	Egyptian Blue, Lead white Yellow/Red/Orange ochre's, Oragnic colorant, Gold, Carbon Black



Apollon, Délos, Musée, Inv. A 4135



Laurent Blaise

Artémis Elaphébole,
Délos, Inv. A 449

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Thank you for your attention!