In-situ XRF analysis as a diagnostic analytical tool in the conservation field

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Outline and the PROMET analytical campaigns across the Mediterranean

Outline

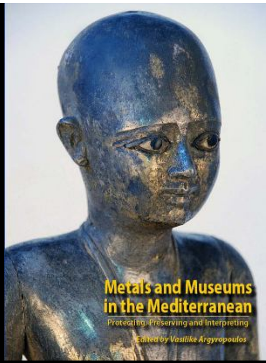
1. The PROMET project
2. The micro-XRF mobile instrumentation

2. Accuracy and pitfalls of micro-XRF analysis

3. PROMET campaigns:

- Ancient Messene (2006)
- Malta, Armoury Palace (2006)
- Damascus National Museum (2007)
- Numismatic Museum, Yarmouk University, Irbid, Jordan

PROMET FP6:2005-2008



Aim:

To develop Prototype innovative and advanced analytical methods to survey large collections of metal objects in-*situ,* making it possible to pinpoint conservation needs without any risk of damaging the artefacts

Efficient, versatile and mobile analytical methodologies: Micro-XRF and Laser Induced Breakdown Spectroscopy

LIBS related tasks were carried out by Prof. D. Anglos FORTH-IESL, Crete

24 partners, including Turkey, Syria, Jordan, Morocco, Italy, France, Spain, Czech Republic

Coordinator: Prof. V. Argyropoulos (TEI, Athens)

Demokritos objectives within PROMET:

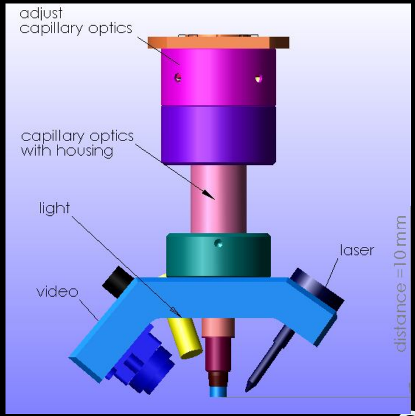
✓ To develop, optimize and calibrate the analytical performance of an innovative portable micro-XRF spectrometer

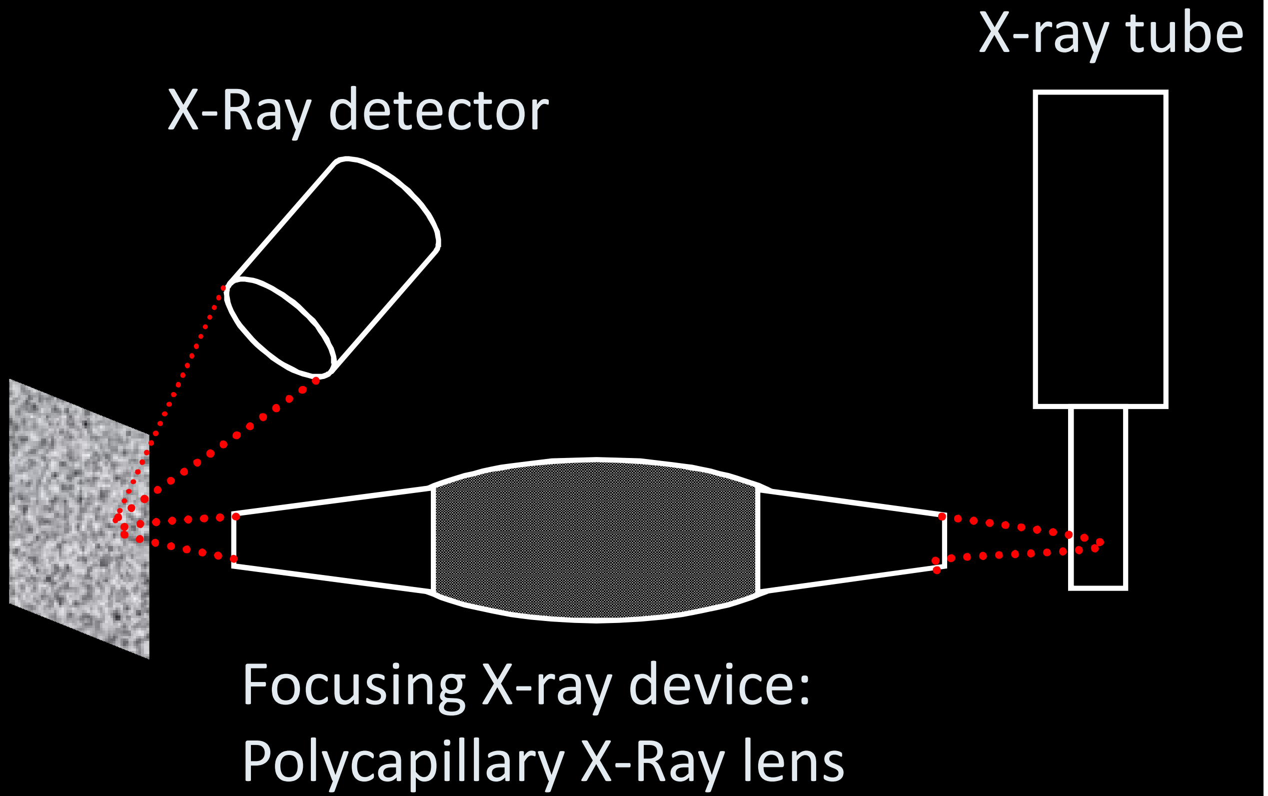
✓ To develop and improve analysis procedures, protocols and the standardization of the method

✓ To apply the micro-XRF spectrometer for systematic technological and conservation related studies of museum metal collections at the Mediterranean region:

- The study of the manufacture technology of metal alloys
- Non – invasive characterization of corrosion products
- Contribution to the assessment of innovative protective coatings

µ-XRF spectrometer: Principle of operation





Development and application of portable micro-XRF unit

ustomized design of ARTAX by Bruker Nano AXS

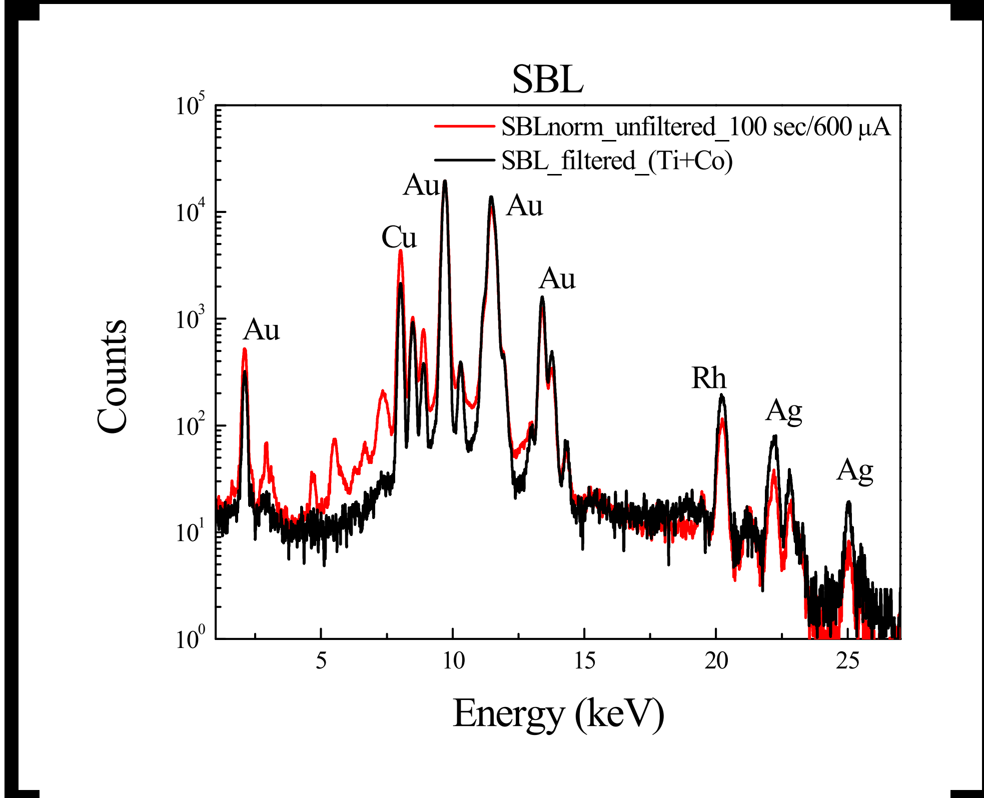
Versatility: *In-situ* Micro-XRF analyses

Damascus National Mus
eum, Syria, October 2007

Laboratory test of TEI coupon

Numismatic Museum of Yarmouk University
Irbid, Nov. 2008

Pitfalls: Interference of XRF signal with diffraction peaks, QC/QA of micro-XRF data



- ✓ Diffraction peaks
- ✓ Heterogeneity at the micro-scale
- ✓ Definition of the scanning area that represents the alloy bulk composition

Alloys	Filters/ Thickness (μm)		
	Ti (23.6 ± 0.2)	Co (17.7 ± 1.3)	Pd (11.3 ± 0.3)
Gold	x	x	
Silver	x	x	x
Copper	x		x

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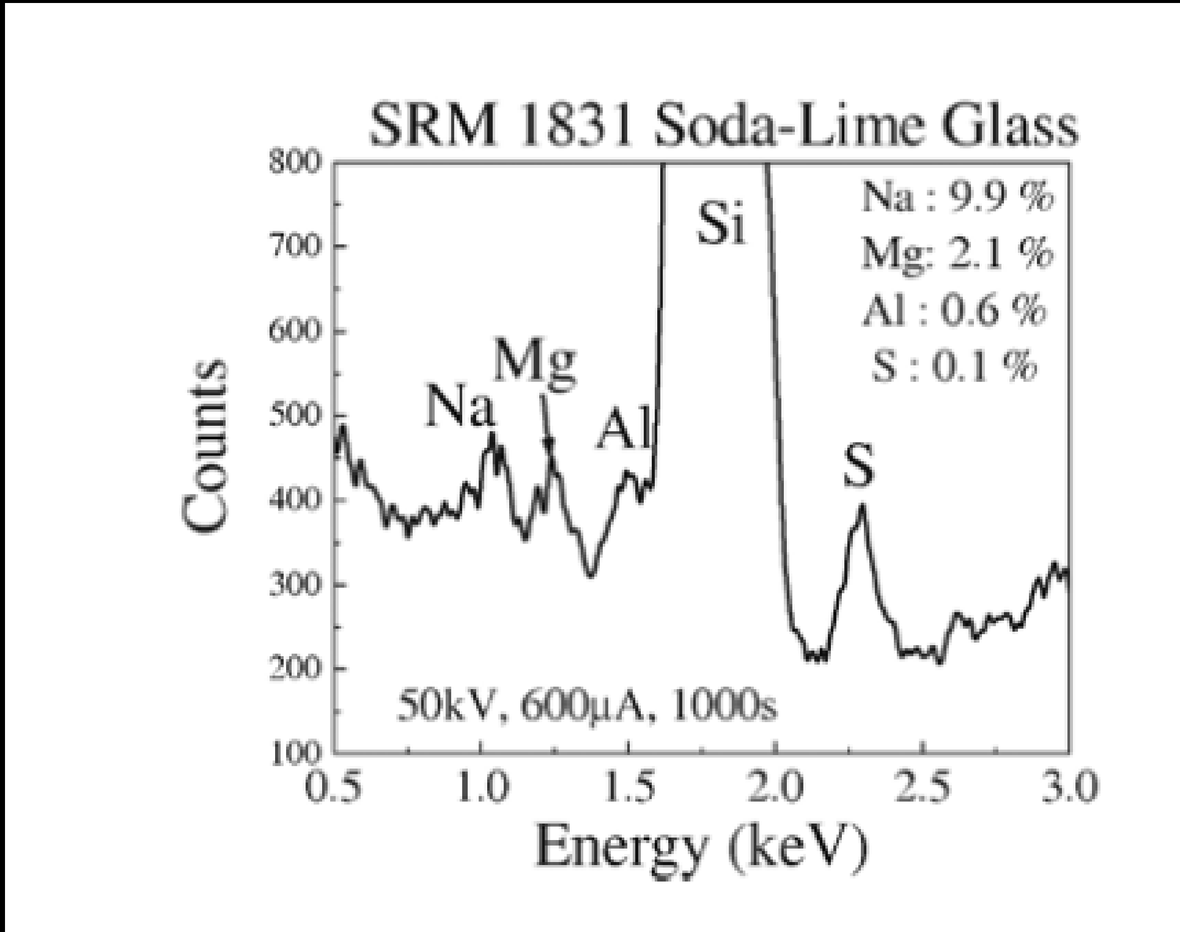
Analytical range using He atmoshpere

50kV, 600mA, 100s



The improvement in the intensity of Al-K and Si-K characteristic X-ray lines is significant, 22 and 7.3 times, respectively.

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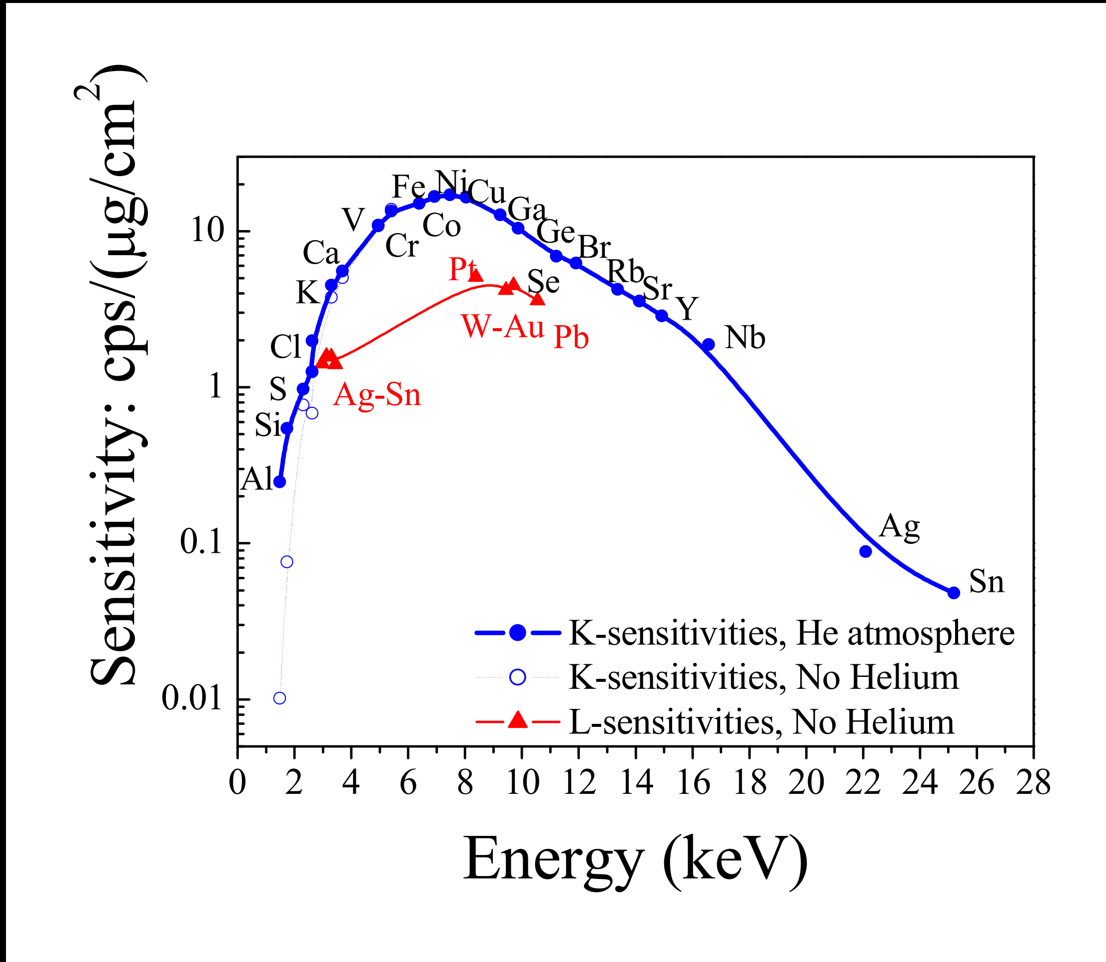
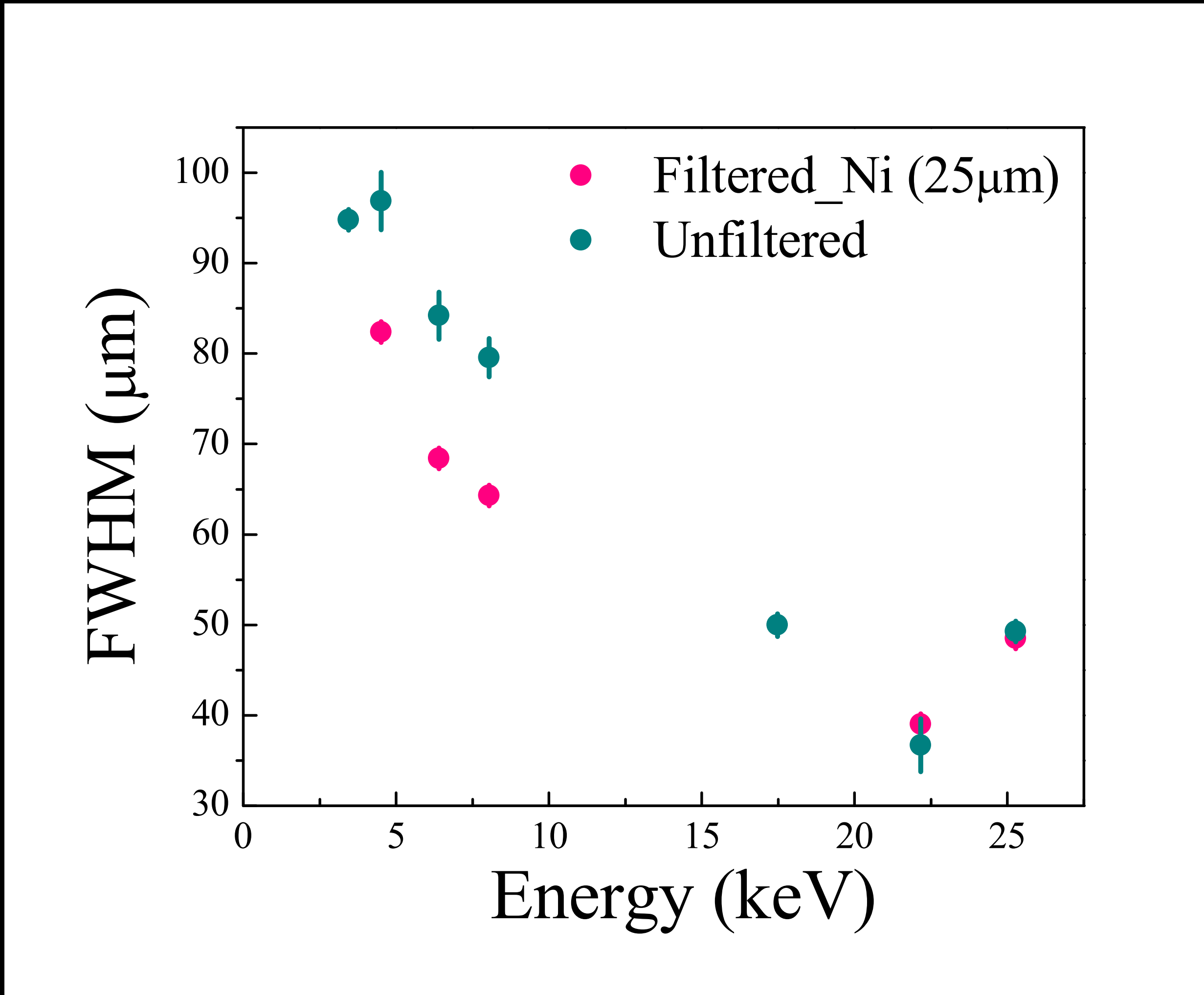
Analytical performance: Elemental sensitivity

Thin Targets ~ 50 μg/cm²



600 μA
50 kV

Analytical performance: Spatial resolution



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Calibration methodology

$$I_i(E_k) = G \cdot w_i \cdot \left(\int I(E) \cdot T(E) \cdot \sigma_i(E, E_k) \cdot A_i(E, E_k) \cdot F_i \cdot dE \right) \cdot f_{air}(E_k) \cdot \varepsilon_d(E_k) \cdot \frac{1}{\sin \vartheta_1}$$

where:

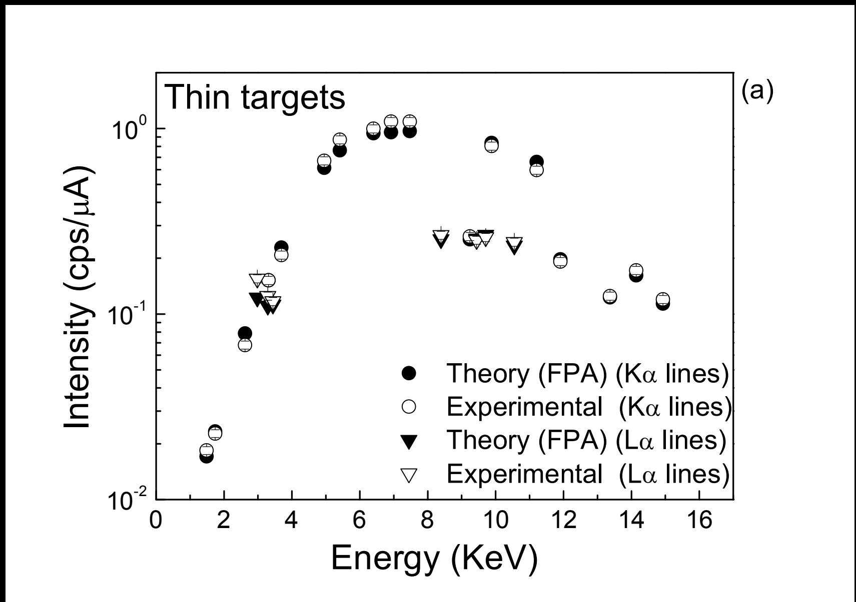
$$A_i(E, E_k) = \frac{1 - \exp[-\mu_{tot}(E, E_k) \cdot \rho X]}{\mu_{tot}(E, E_k)}$$

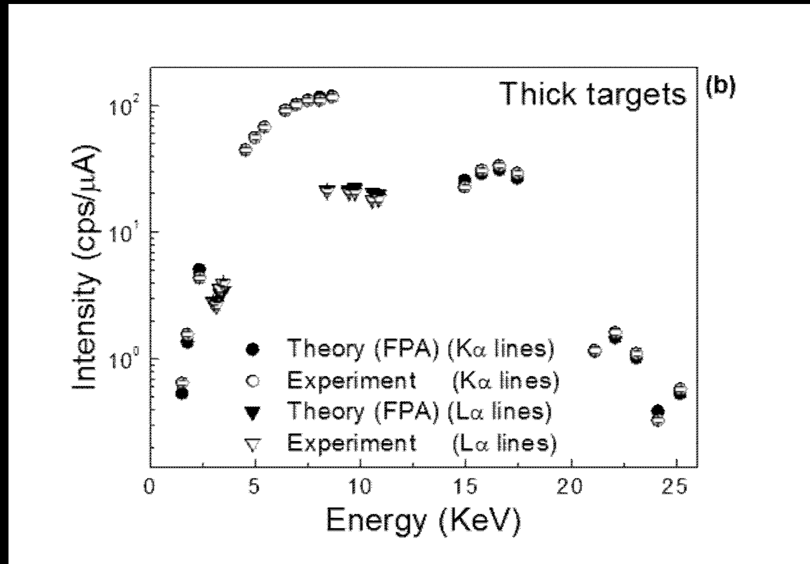
$$\mu_{tot}(E, E_k) \equiv \sum_{i=1}^{N} w_i \cdot \left(\mu_i(E) / \sin \vartheta_1 + \mu_i(E_k) / \sin \vartheta_2 \right)$$

$$F_i = 1 + \sum_{j=1,n} SF_{ij} \left(1 + \sum_{k=1,n} SF_{jk} \right)$$

$$T(E) = \left(\sum_{i=0,5} A_i \cdot E^i \right) \cdot \exp(-c \cdot E)$$

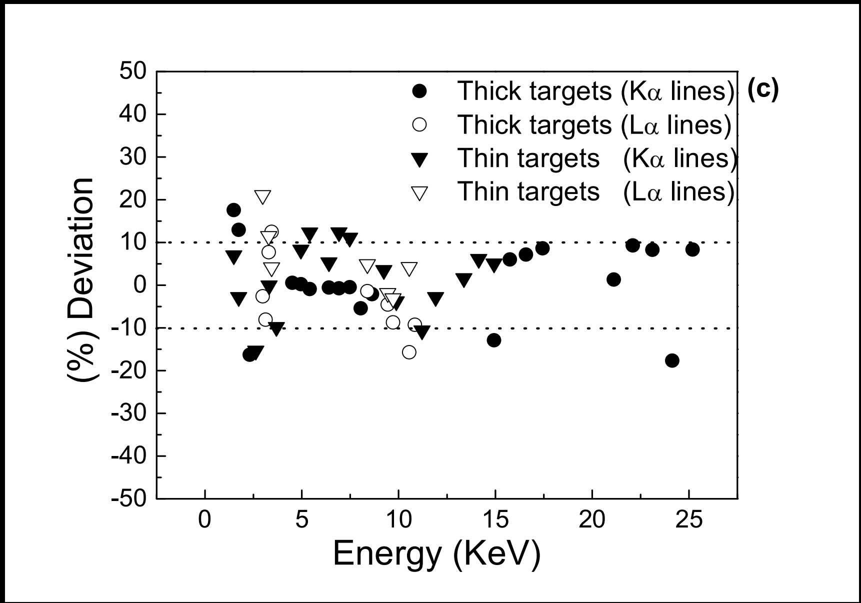
Experimental/simulated pure element thick/thin elemental intensities



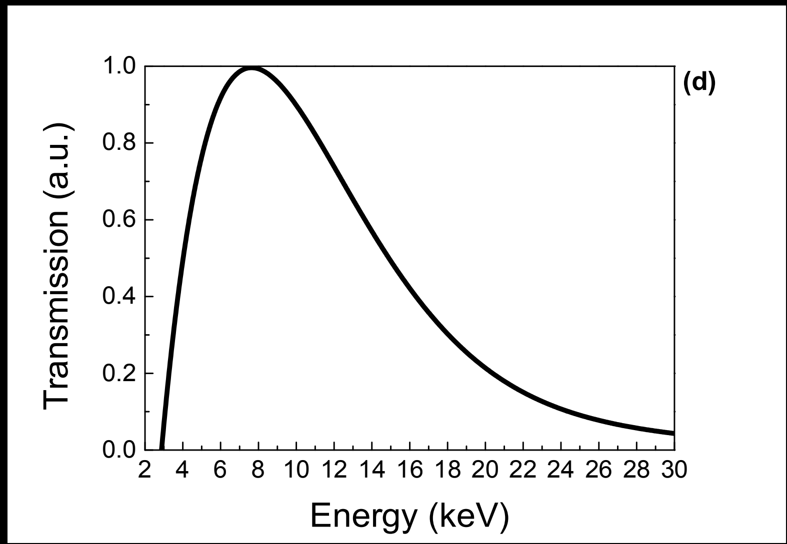


Kantarelou et *al.*, XRS, 2015

Results of the fitting procedure

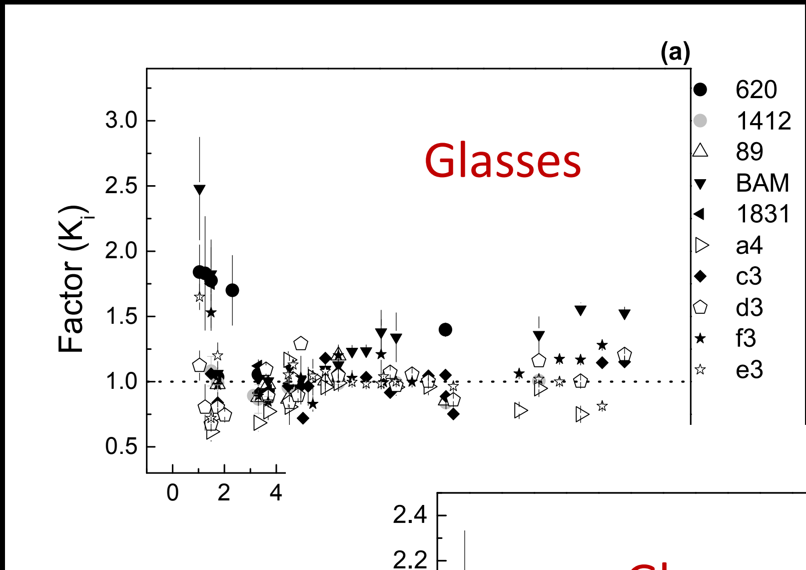


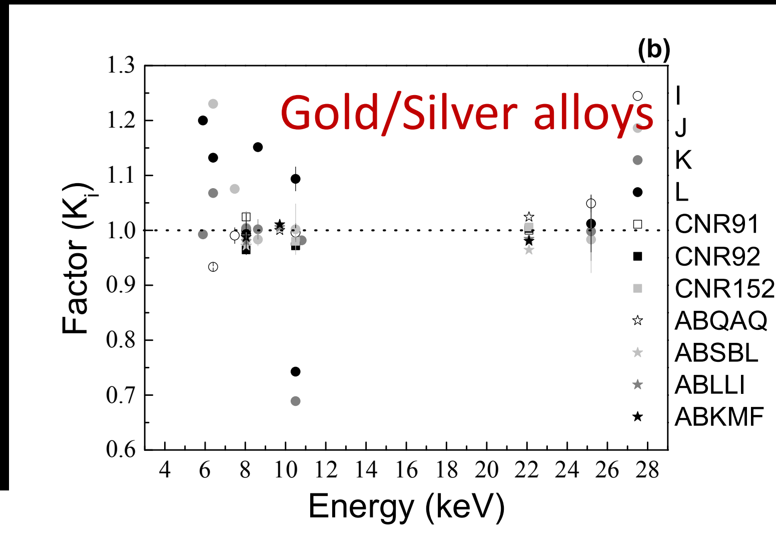
Estimated Lens transmission efficiency

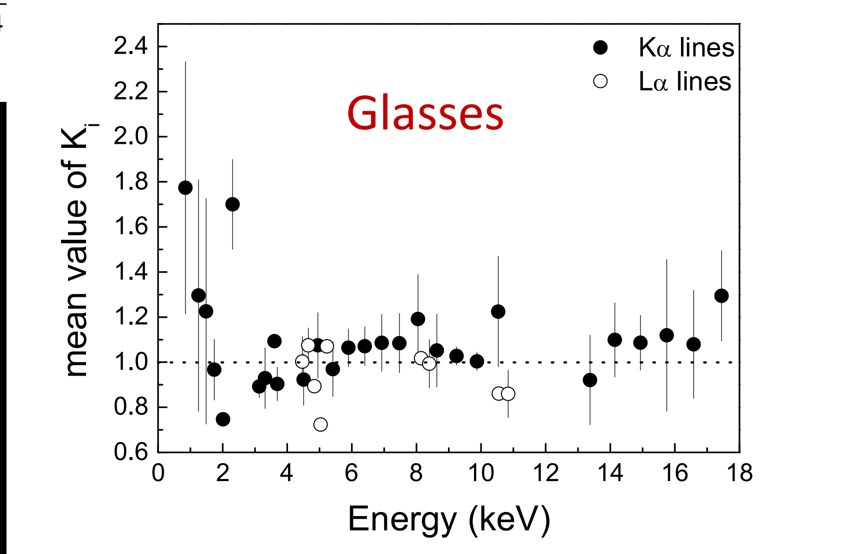


Kantarelou et *al.*, XRS, 2015

Accuracy/Quantification of CH related materials



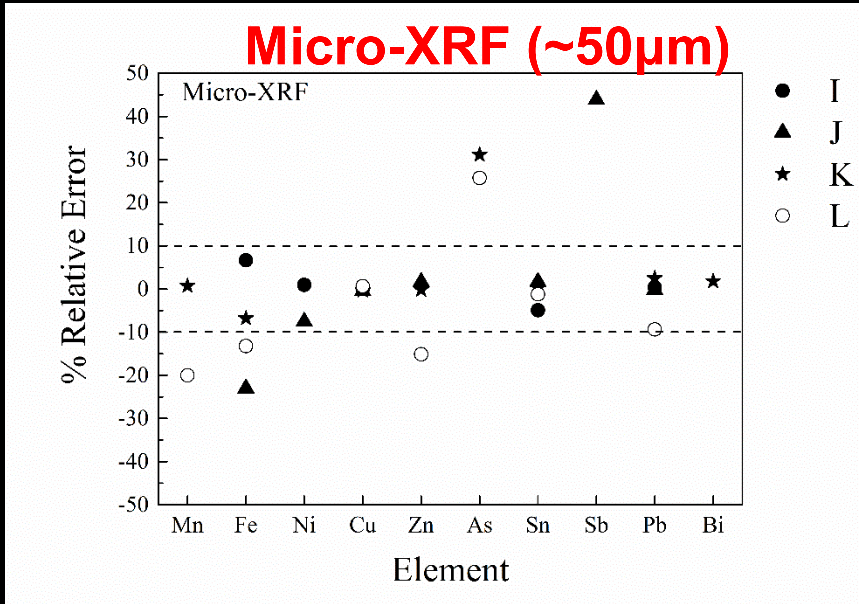


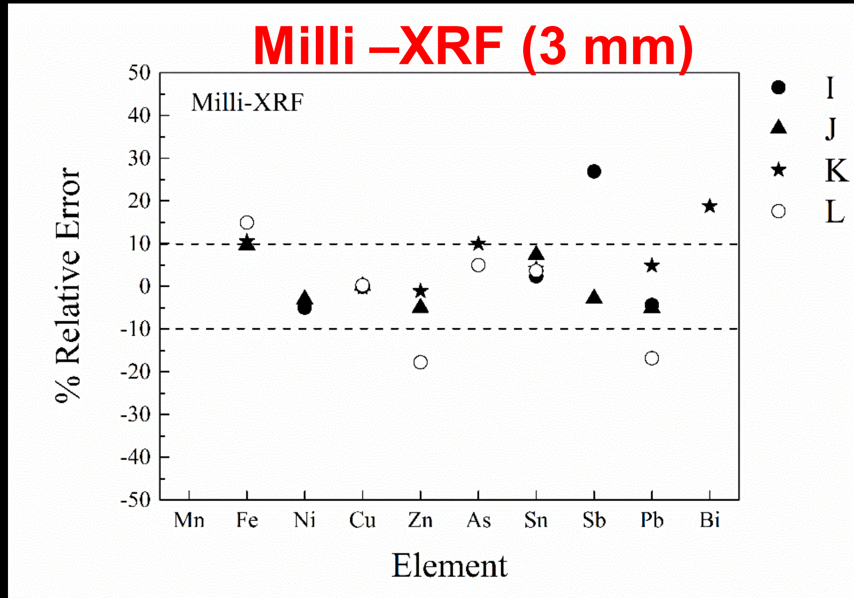


Andreas Karydas, ICTP, 14th of July 2015

Assessment of micro-XRF analysis accuracy

Validation with respect to Cu based RMs





A. Heginbotham et *al*., An Evaluation of Inter-Laboratory Reproducibility for Quantitative XRF of Historic Copper Alloys, Proceedings of the International Conference on Metal Conservation, **METAL 2010, pp 178-188**, Edited by Paul Mardikian, Claudia Chemello, Cristopher Watters and Peter Hull, 11-15 October 2010, Charleston, South Carolina, USA

Semi-QA and Diagnostic Micro-XRF Analysis

Methodology:

Variation of the K/L or L/M elemental intensity ratios in single spot, line or area scan measurements

Filtered excitation

Analysis of corroded area vs corrosion free area

Line and area scans to obtain in reasonable measuring time (1x1 mm^2, 50 μm step, 10s/step,~1.5h) intensity maps of the detected characteristic X-ray lines

Semi-QA and Diagnostic Micro-XRF Analysis

Results obtained:

- Identification of the spatial coexistence of different elements, fingerprints of certain corrosion products or of manufacture techniques.

- Estimation on a semi-quantitative basis of the elements enriched or depleted from the surface

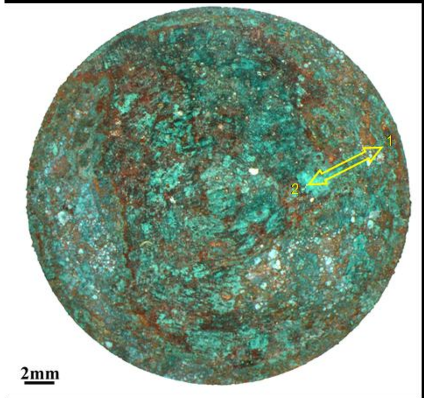
- Rough estimation of the depths that a certain element is located, namely, on the surface, near surface (~2-10 μm) or below ~10 μm.

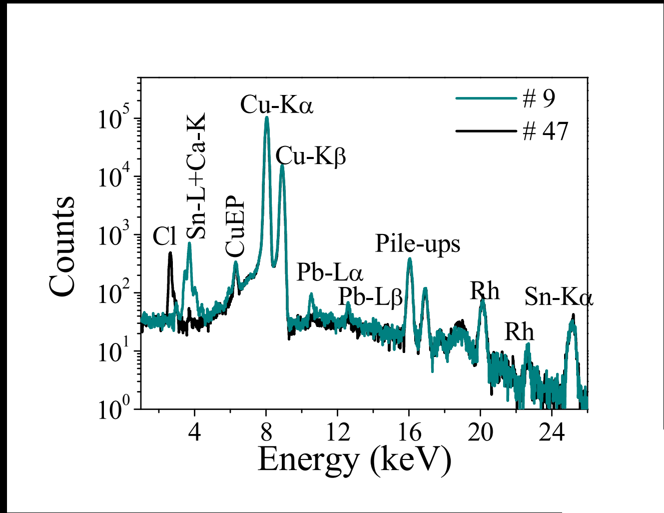
- Spatial distribution of individual elements

- Identification of the presence of certain minor to trace elements that may support provenance and manufacture studies of the metal

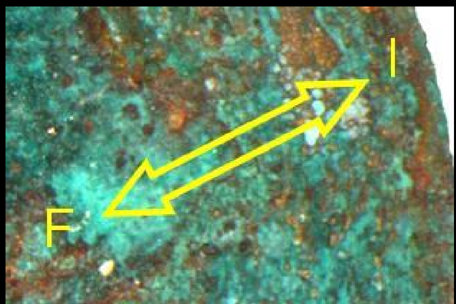
Analysis of Copper coupon corrosion products

Artificially and naturally aged bronze coupon: **(Cu: 91.3%, Sn: 7.5%, Pb: 1.0%)**

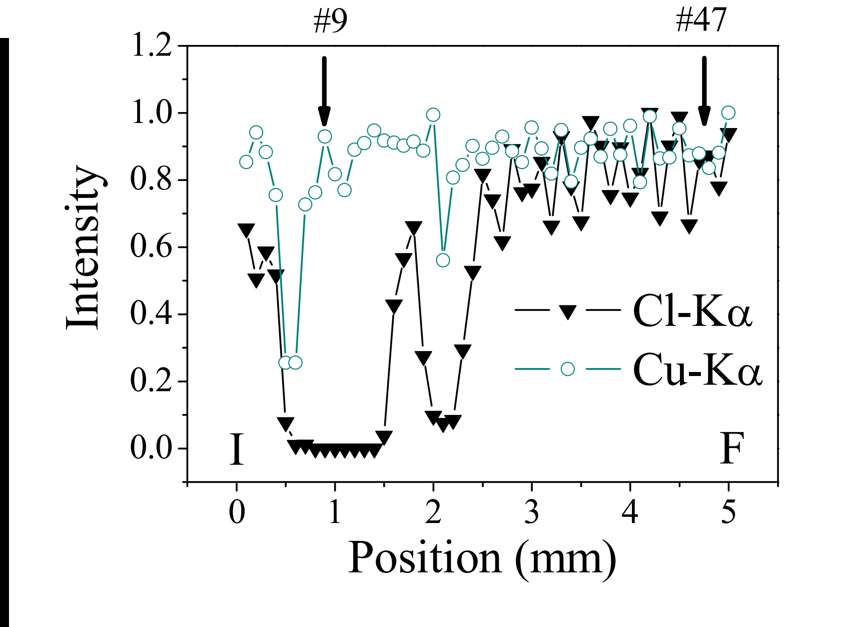




#9 : green area
#47: pale green area



50kV, 600μA,
30s/step,0.1mm/step,
50 measurements

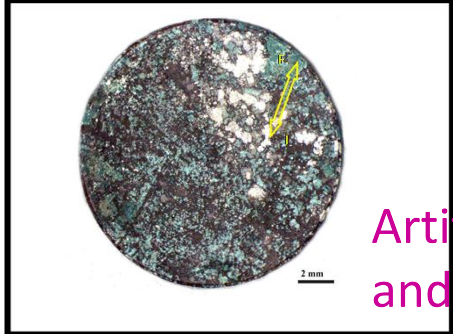


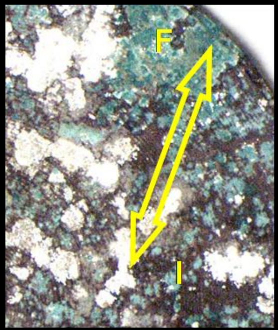
Analysis of metal corrosion products

Silver coupon (prepared-characterized by Prof. G. M. Ingo, Polytechnico of Milano)

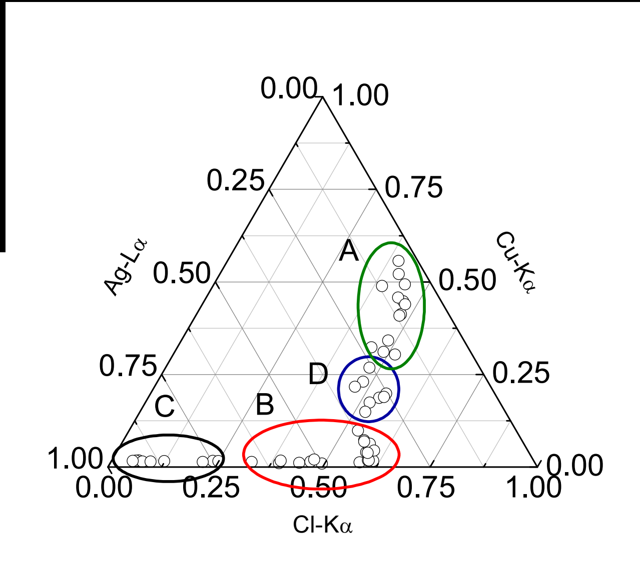
A – Green
B - White
C - Black

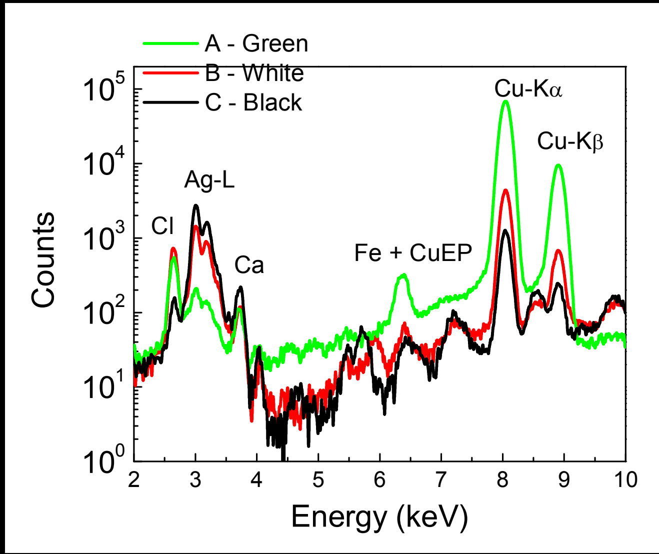
A - Paratacamite
B - Chloroargyrite
C - Silver (oxide)

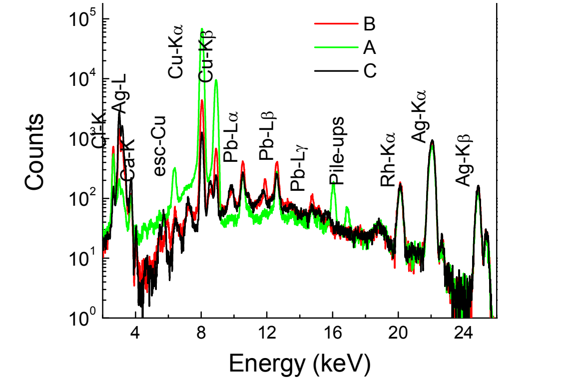




Artificially and naturally aged silver coupon:
Ag: 92%
Cu: 6.5%
Pb: 1.5%







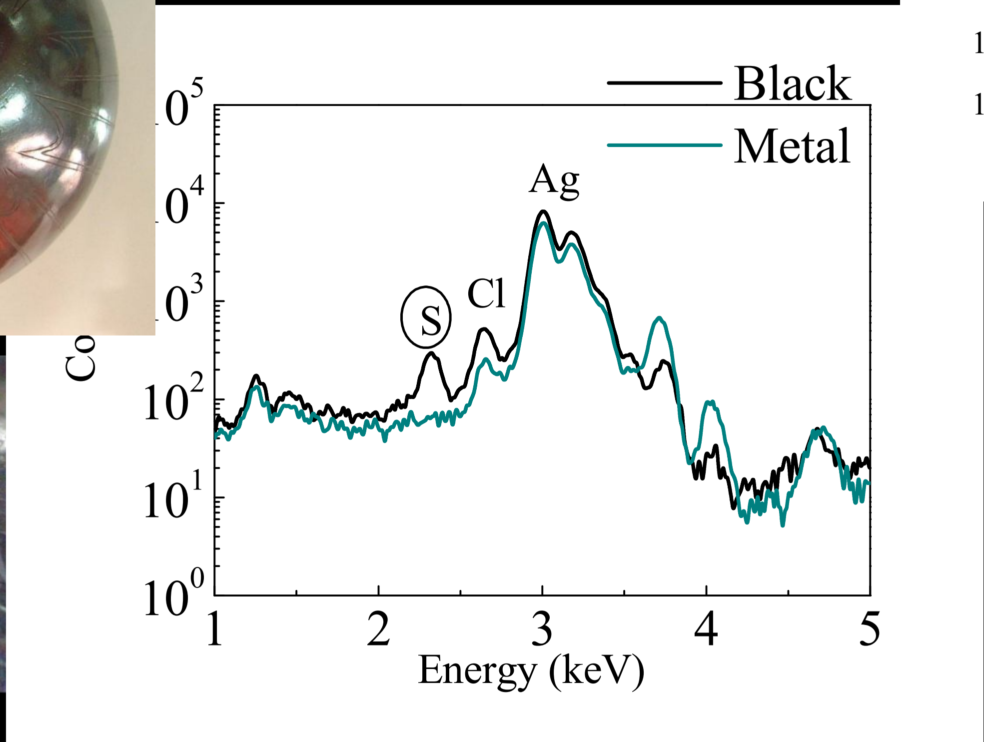
50kV, 600μA, 30s/step, 0.1mm/step, 50 measurements

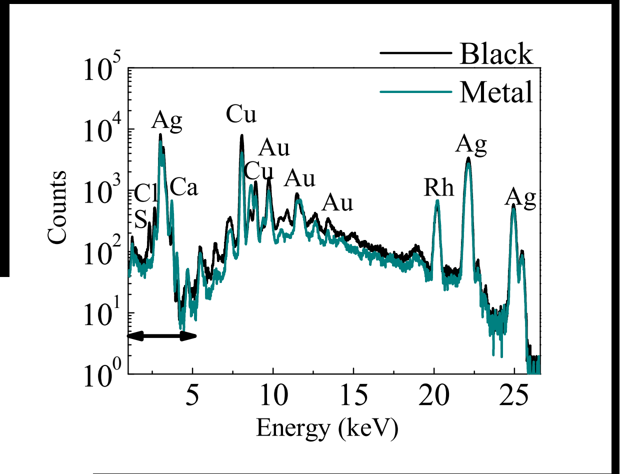
A.G. Karydas et *al*, PROMET Book, 2008

Damascus Archaeological museum: Analysis of silver tarnishing

Silver Bowl 1400 -1300 BC   Late Bronze Age

Thickness of the layer: ~ 0.5 µm





Tarnish: corrosion mainly caused by the sulfur in the air

PROMET, Damascus, Syria:
Gilded Bronze figurines

Late Bronze Age, 1400 B.C. Ugarit site: Issues addressed

- ✓ Manufacture technology (compositional analysis, raw materials)
- ✓ Gilding technique
- ✓ Identification of corrosion products

Baal Gods

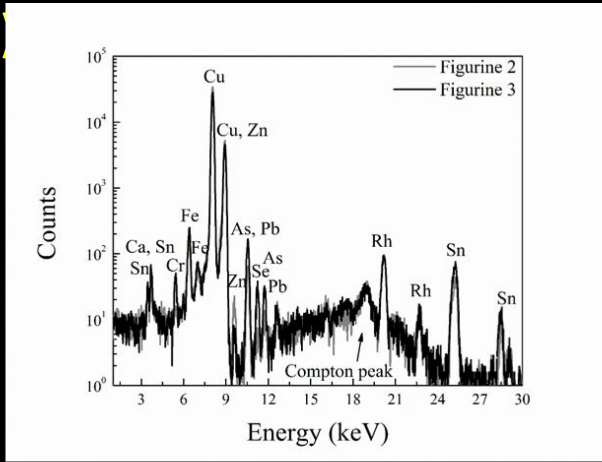
El God

Kantarelou et al., JAAS, 2015

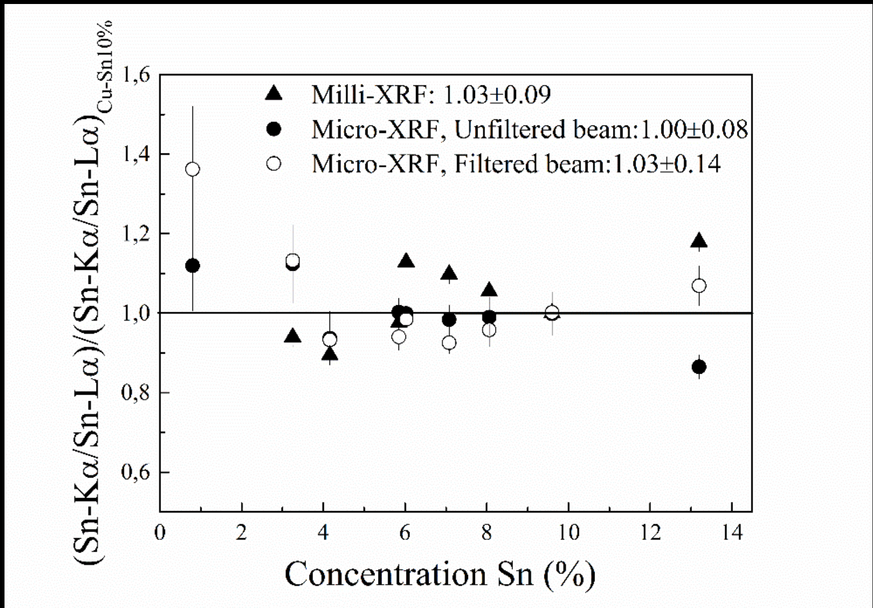
Compositional analysis of bronze metal

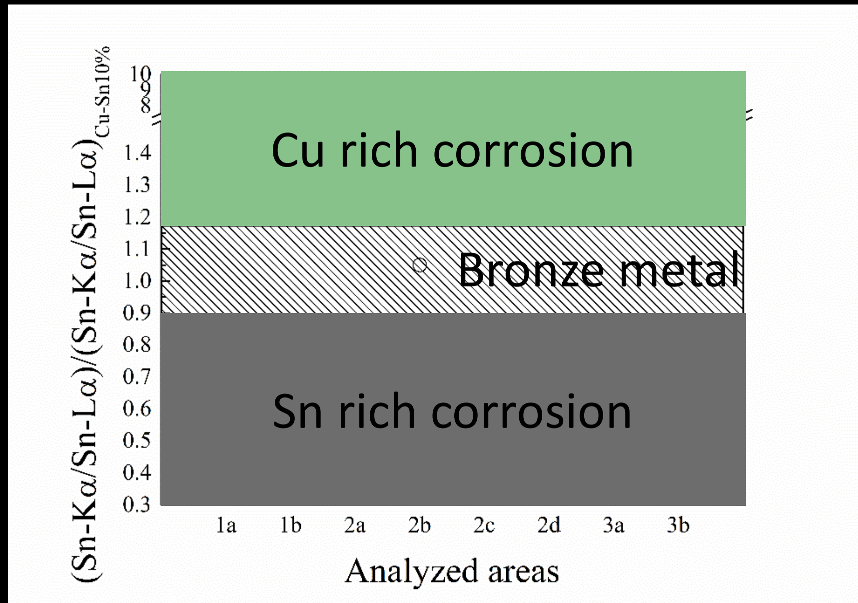
Concentrations (wt. %)

Fe: 0.26 ± 0.03
Cu: 92.5 ± 1.0
Zn: 0.60 ± 0.06
As: 0.10 ± 0.01
Sn: 6.32 ± 0.30
Pb: 0.040 ± 0.004

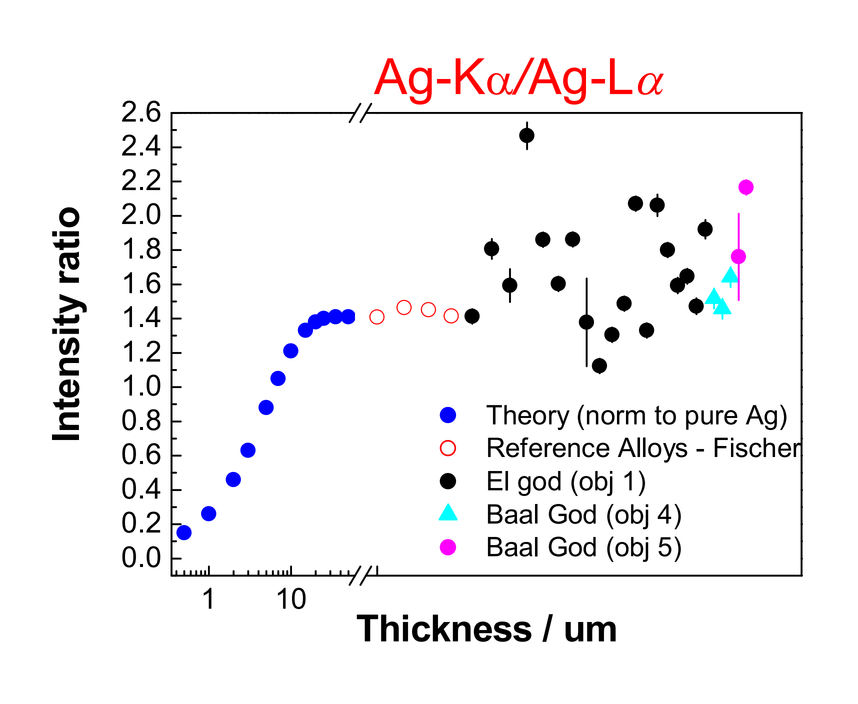


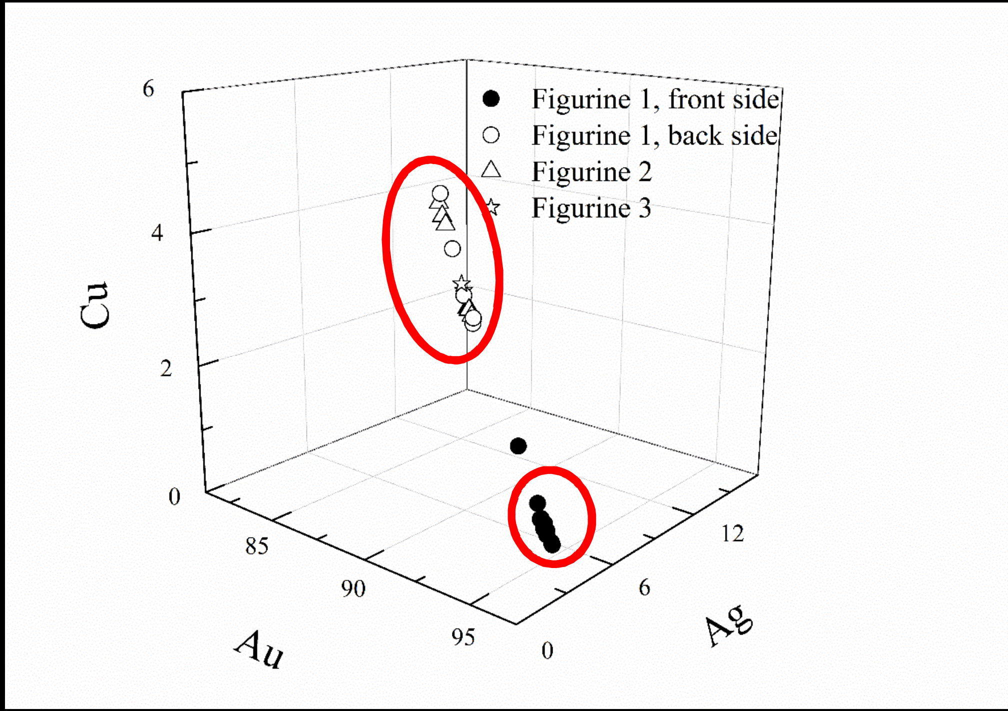
$$G_{Sn}=\frac{\left(\frac{I_{Sn}(K_\alpha)}{I_{Sn}(L_\alpha)}\right)_S}{\left(\frac{I_{Sn}(K_\alpha)}{I_{Sn}(L_\alpha)}\right)_R}=\frac{\mu_R(E_1,E_{K\alpha})}{\mu_s(E_2,E_{K\alpha})}\times\frac{\mu_S(E_3,E_{L\alpha})}{\mu_R(E_4,E_{L\alpha})}\times\frac{(1+SE_T)_R}{(1+SE_T)_S}$$





Compositional analysis of gold foil

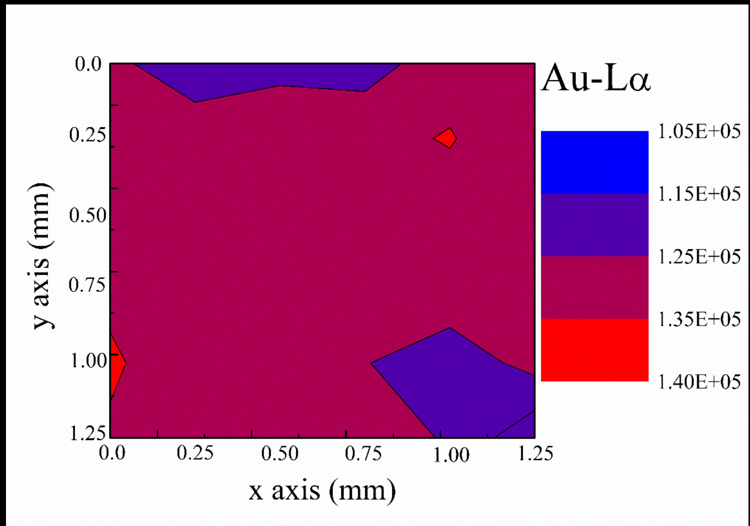


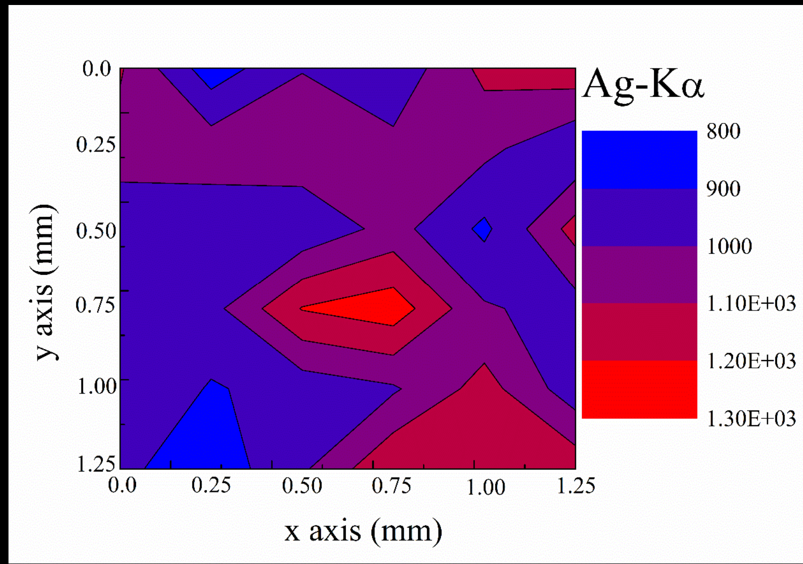


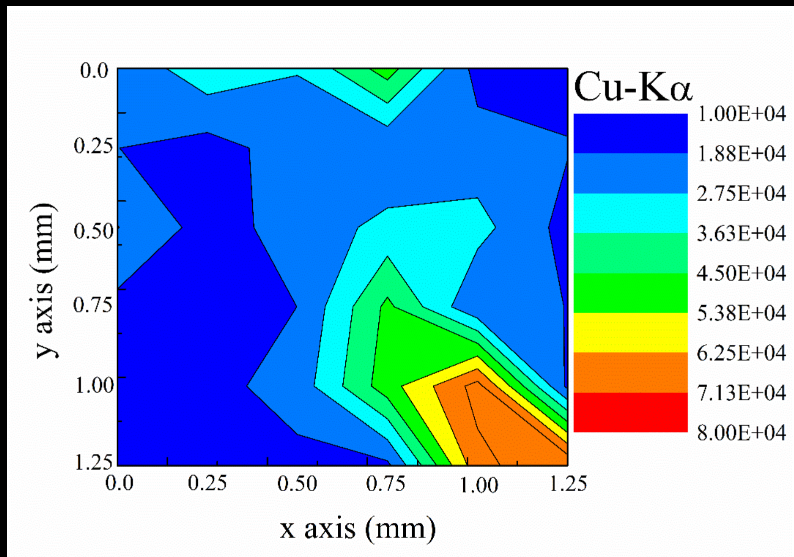
Thickness of the gold foil > 10 micrometers

Two (2) main compositional groups:
Ag: **14-15%** or **4-5%**
Cu: generally **<2-3%**

Imaging of the elements distribution on the gold foil

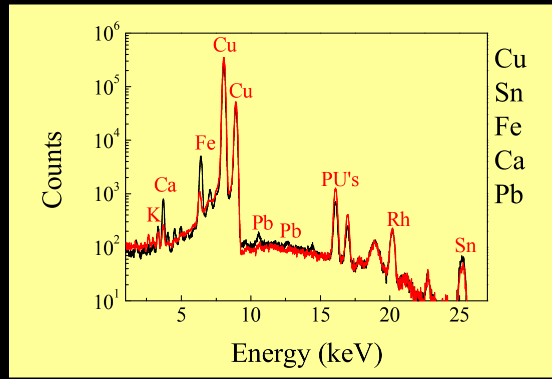


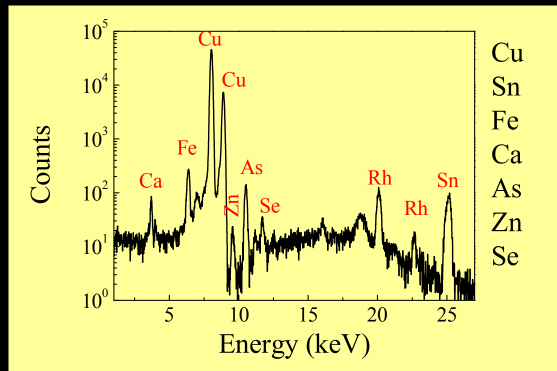


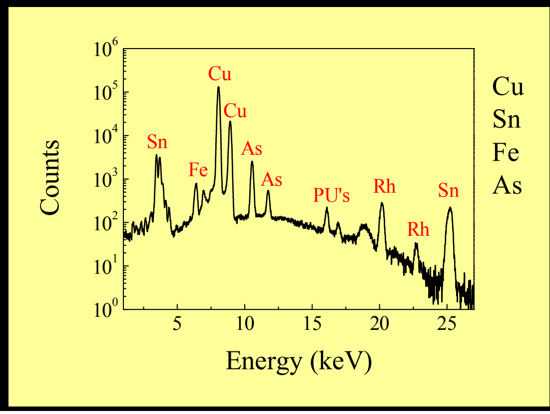


PROMET, Damascus, Syria: Corrosion products

Eail God, Late Bronze Age 1400-1300 B.C.







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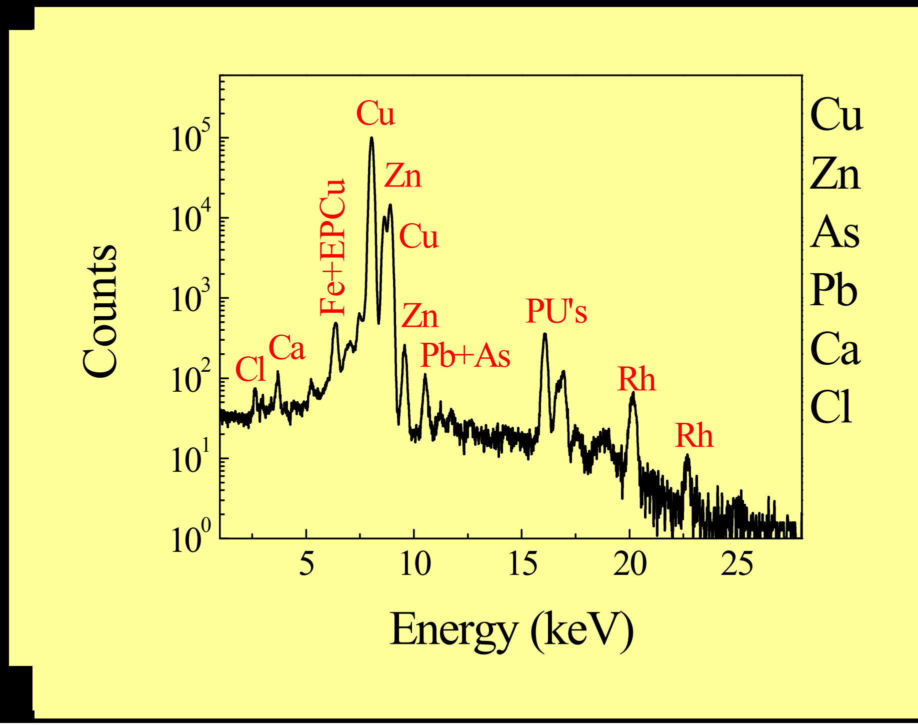
PROMET at Irbid, Jordan

Umm Qais artefacts

Cu: 76.08%
Zn: 21.7%
Ni: 0.80%
Sn: 0.43%
Pb: 0.43%
Fe: 0.39%
As: 0.17%

Copper-base bracelet, #216, (Ottoman Period), General + Pitting + Crevice Corrosion, Active corrosion have caused serious crack

A. Arafat et al., Journal of Cultural Heritage, http://dx.doi.org/10.1016/j.culher.2012.07.003, 14 (3), (2013) 261-269



PROMET in Ancient Messene - Objectives:

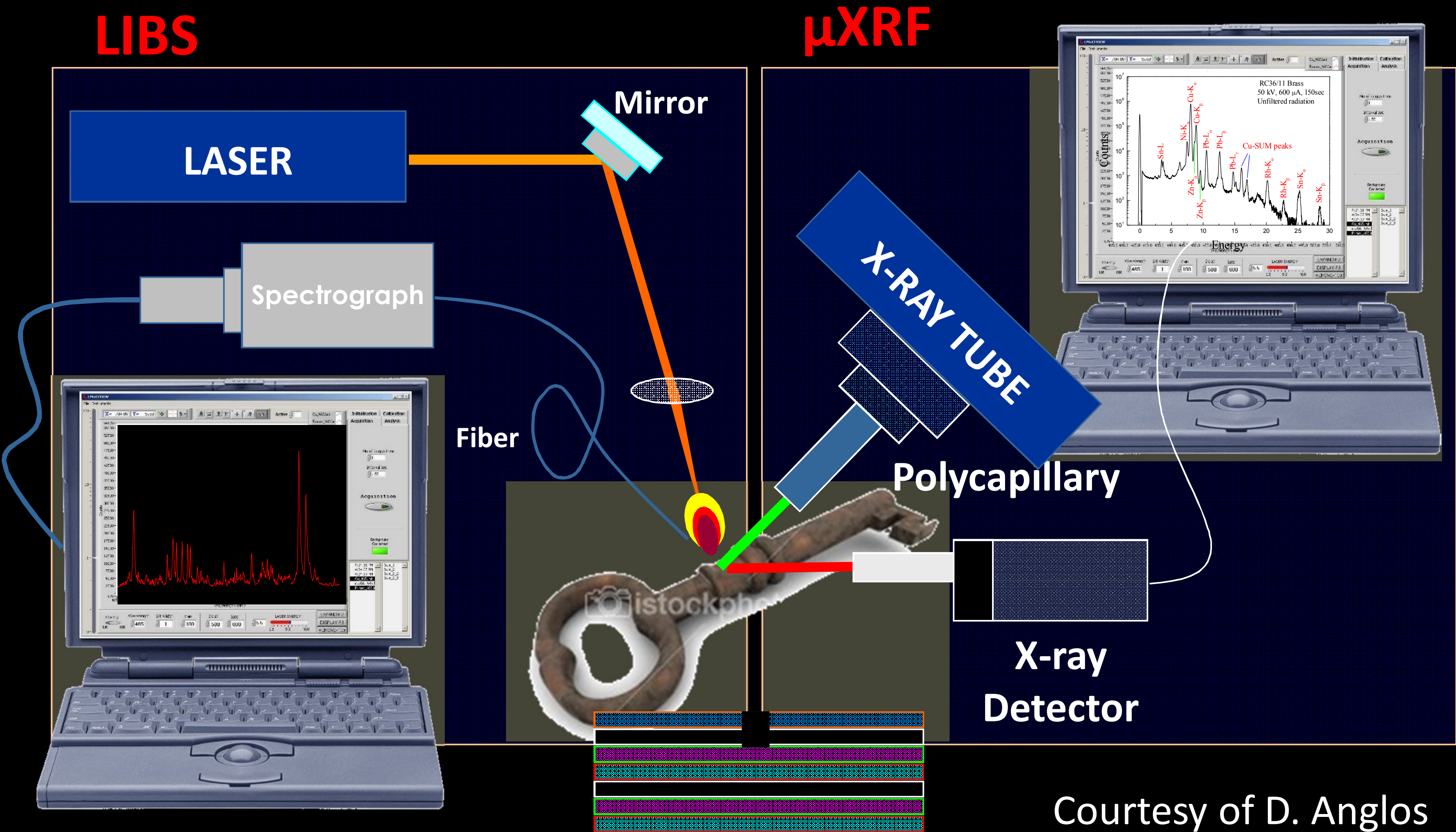
Compositional analysis of different typology copper based artifacts through time

Surface characterization of high tin bronze mirrors

Combined microXRF and LIBS analysis for enhancing in-depth elemental distribution

Dynamic combination of micro-XRF and LIBS

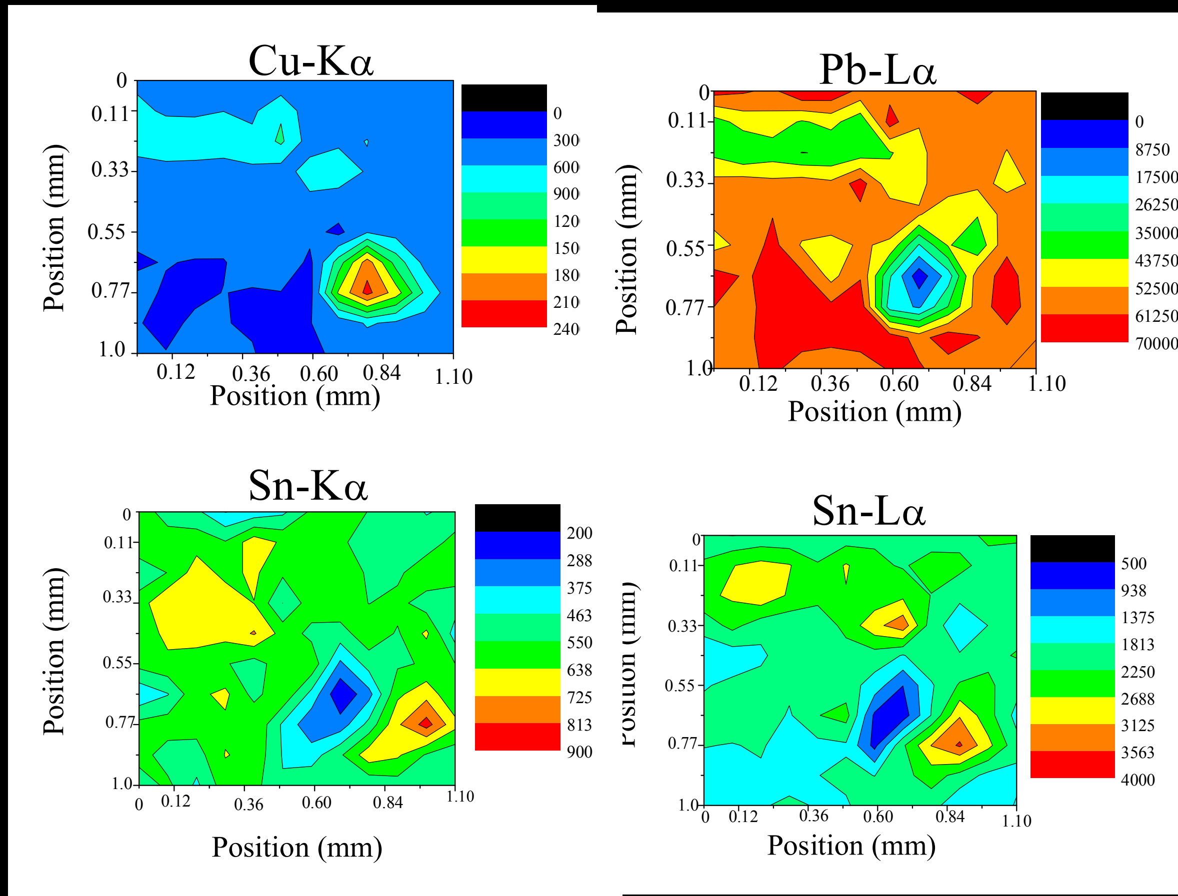
V. Kantarelou et al., METAL-07, Vol. 2, Innovative investigation of metal artifacts, pp. 35-41, (2007)



Courtesy of D. Anglos

PROMET at Ancient Messene

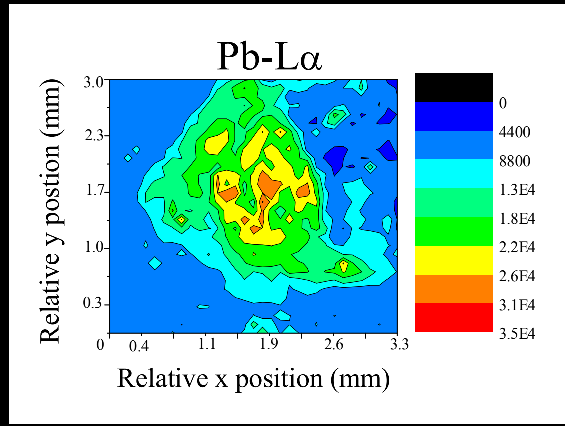
Micro-XRF elemental mapping of the LIBS ablated area

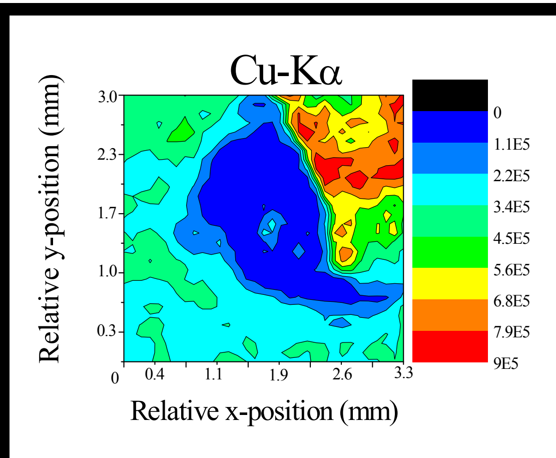


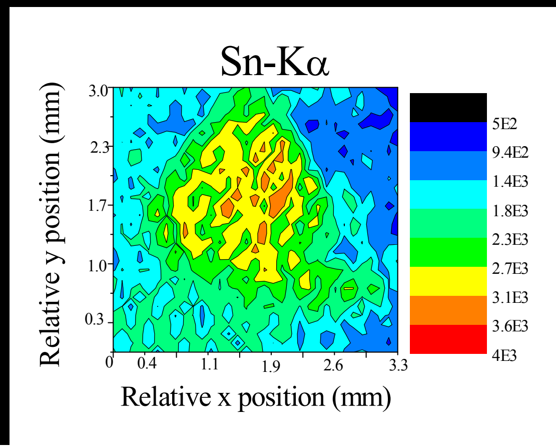
W2 (%): Cu: 82.1, Sn: 6.9, Pb: 10.7

PROMET at Ancient Messene

μ-XRF analysis of High Tin Bronzes

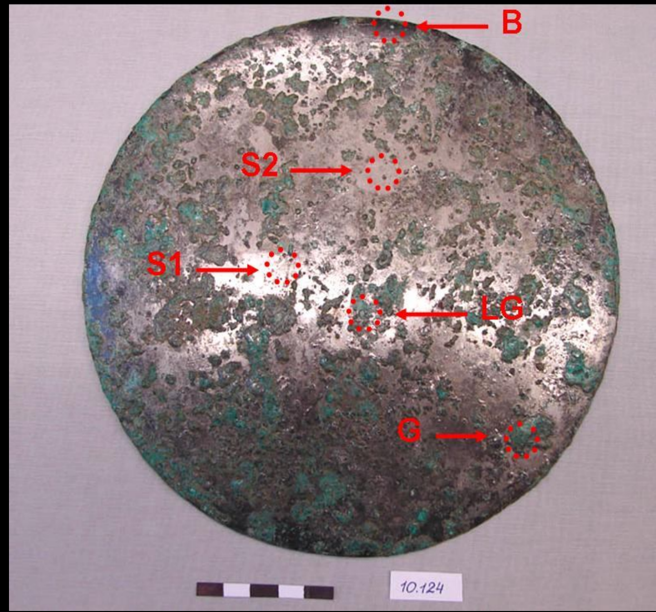






Ancient Messene, Greece: Manufacture of high tin bronze mirrors

2nd c. BC



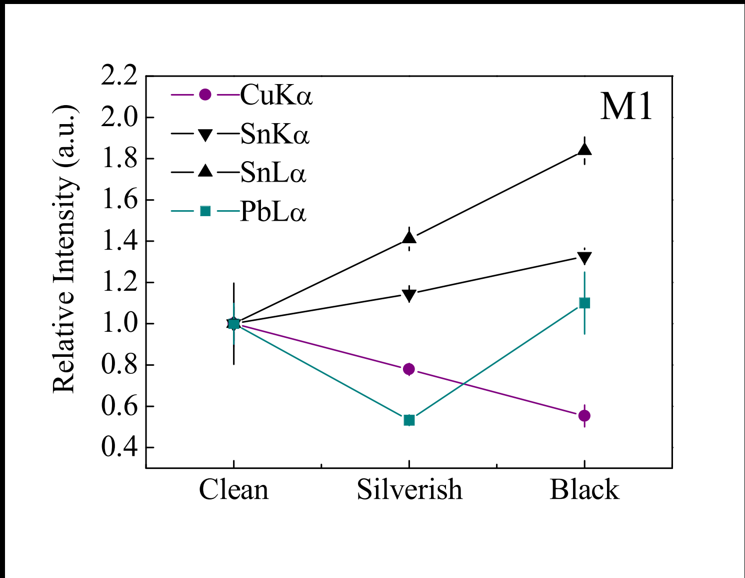
Mirror 1 (M1)

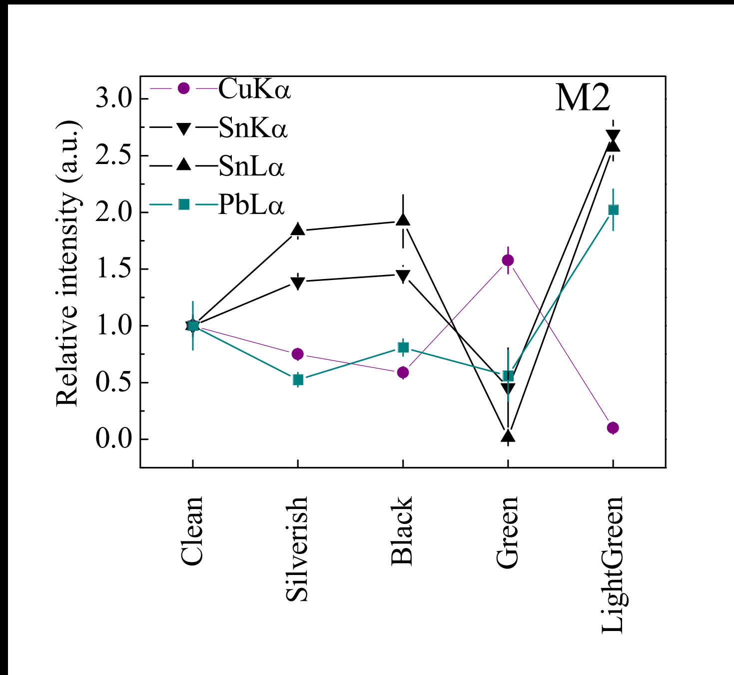
(Cu: 70.6%, Sn:26.0%, Pb:3.4 %)
Examined areas : metal, black, silverish

Mirror 2 (M2)

(Cu: 70.2%, Sn:22.9 %, Pb: 6.8 %)
Examined areas : metal, black, silverish, green and light grey

Ancient Messene, Greece: Surface examination of high tin bronze mirrors





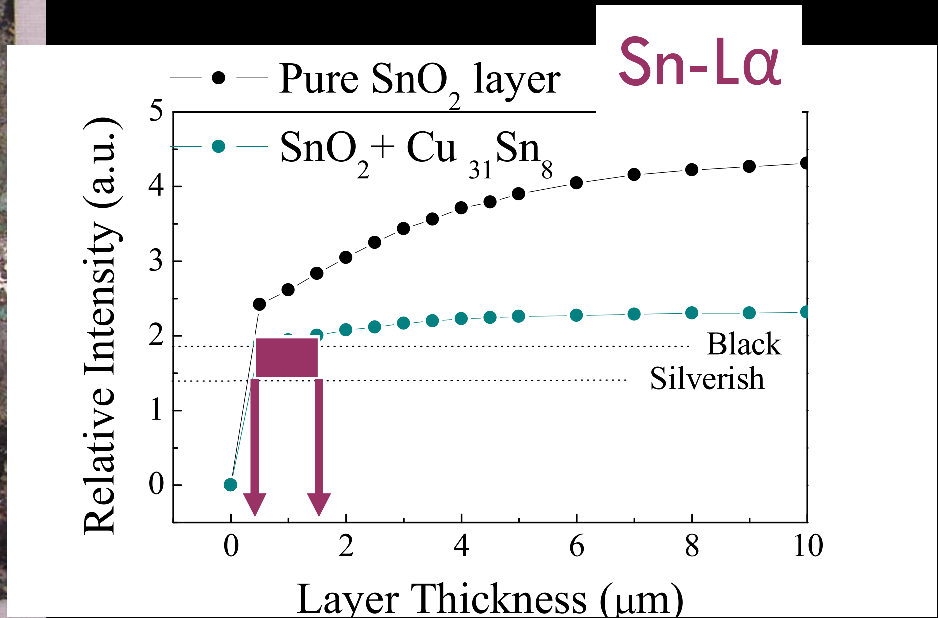
Silverish: Increase of SnLα, decrease of CuKa and PbLa : Sn surface enrichment

Black : Significant increase of SnLα (Cassiterite?)

Green : Increase of CuKa, Cu corrosion products (malachite?)

Light green : Increase of PbLα, SnLα, decrease of Cu-K, (Lead-white? Cassiterite?)

Ancient Messene, Greece:
Black patina on high tin bronze mirrors



Silverish < 1 μm

Black layer with a thickness of very few micron

PROMET at Armoury Palace, Malta

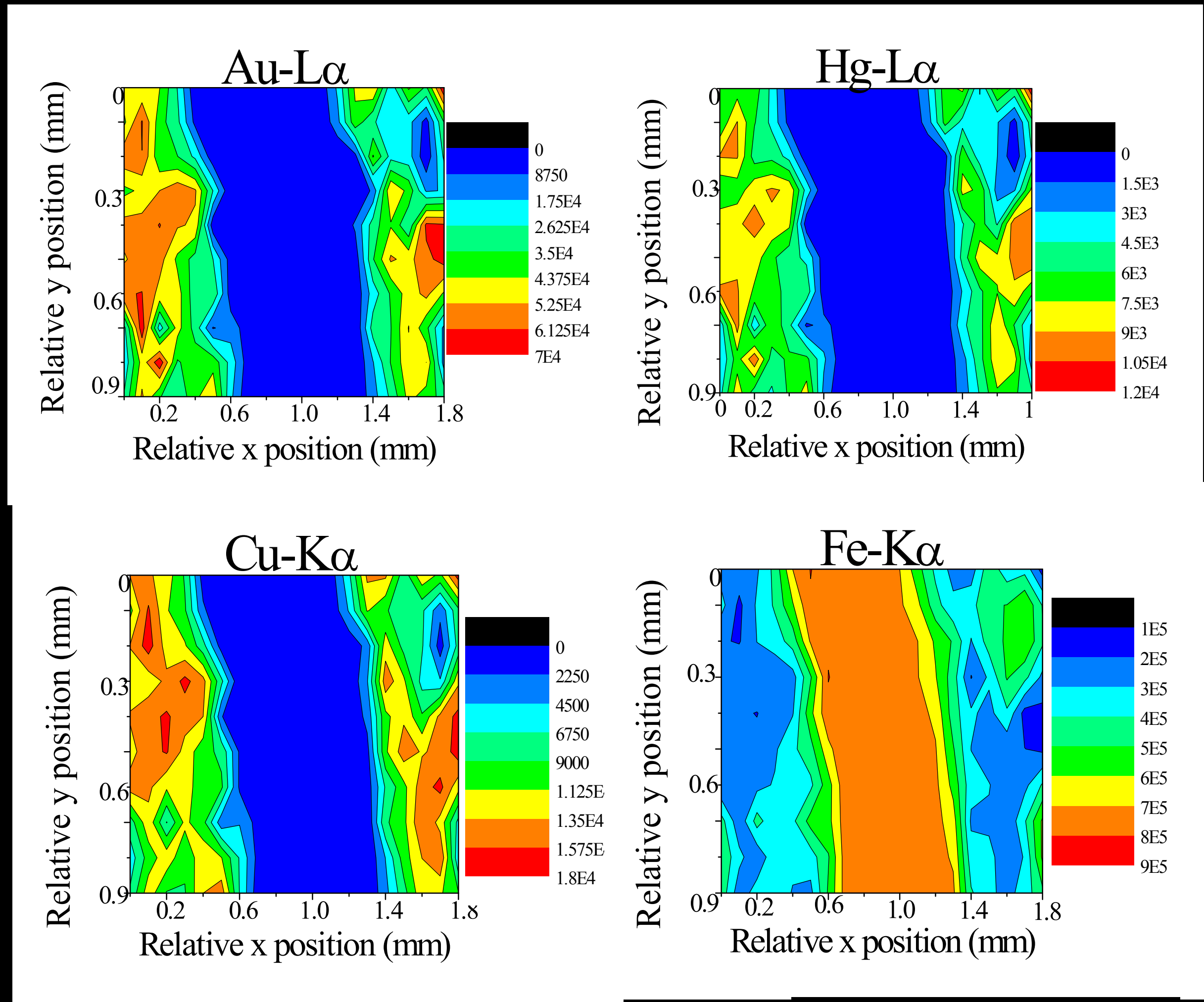
Conservation related issues addressed:

- ✓ Authenticity issues
- ✓ Gilding technology
- ✓ Compositional analysis of armory components (rivets)
- ✓ Identification of surface corrosion products

PROMET at Armoury Palace, Malta

Gilded Iron Alloy Falling Buff

μ-XRF analysis of gilding areas

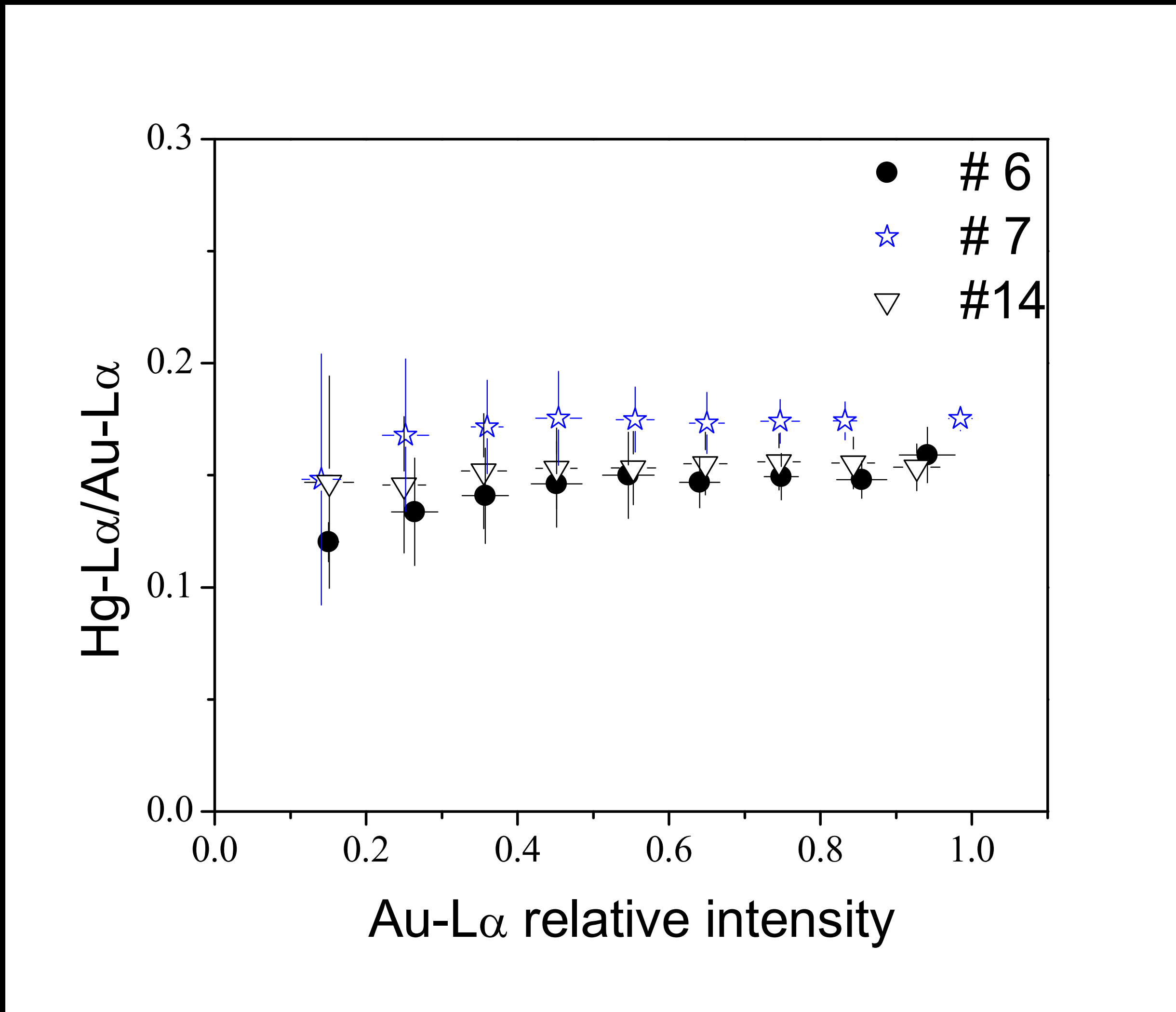


Andreas Karydas, ICTP, 14th of July 2015

Fire-Gilding technique: Hg to Au ratio

Palace Armoury, Malta

The mean Au/Hg values were deduced among a subgroup of the area map spots, where the Au intensity varies between 0-10%, 10-20%, 30-40% etc with respect to its maximum value



C. Degrigny et *al*. , Metal-07, pp. 26-34, (2007)

Conclusions

Micro XRF analysis can offer fast elemental distribution maps, contributing thus both towards the identification of surface corrosion products and manufacture techniques as well

The operating conditions of the micro-XRF spectrometer require careful optimization per type of samples analyzed, that it is in many cases not a trivial and straightforward procedure.

PROMET Impact

- The results of the project offer a cost effective approach in identifying the conservation problems and needs of a metals collection using portable diagnostic techniques

- The achieved results can easily be applied to any museum setting world-wide due to the portability of the instruments developed whereas analytical methodologies are easily transferable.

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