XRF analysis of ancient and historic metal objects: Examples of applications

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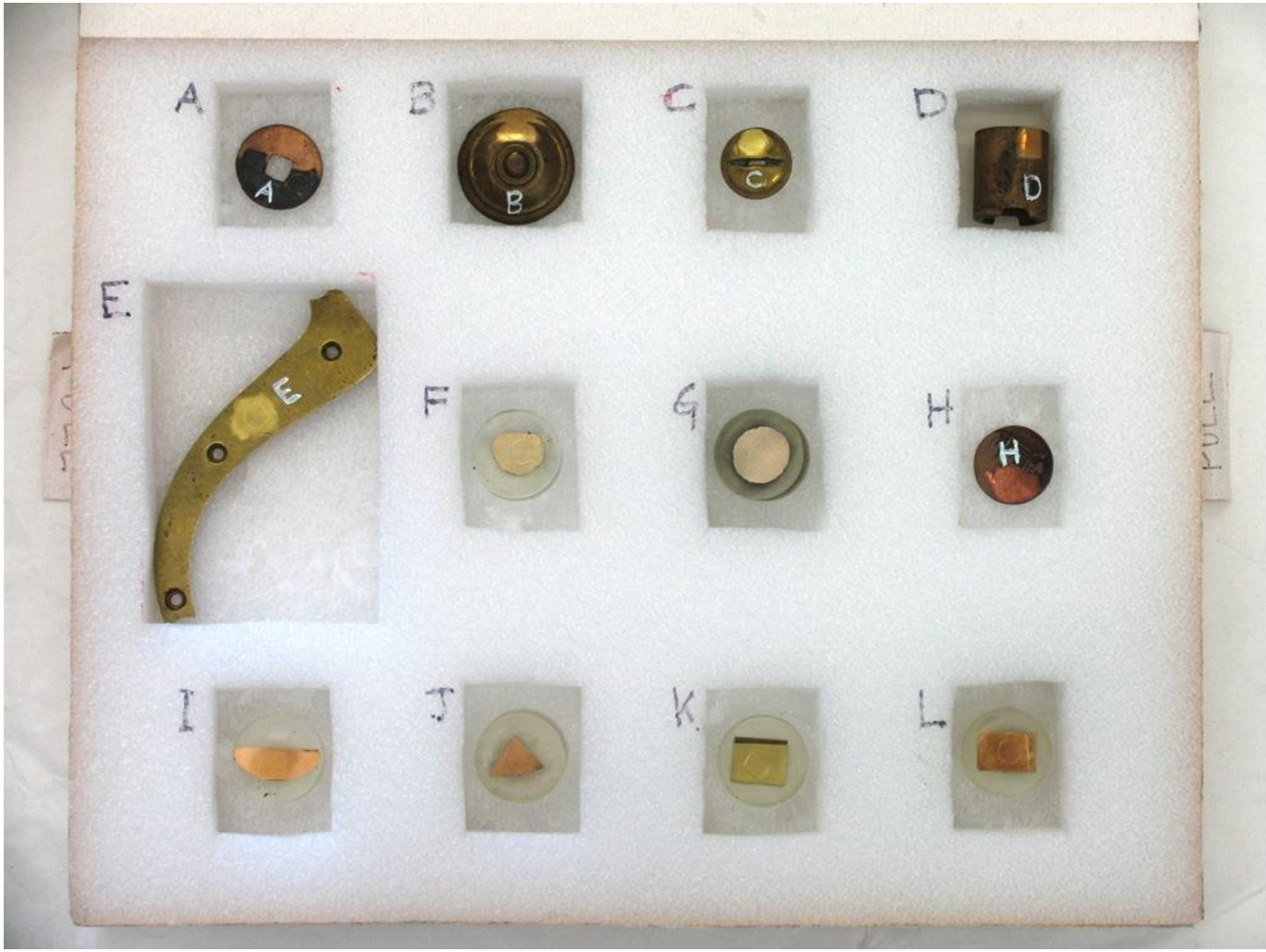
Outline

- General notes, Quantitative XRF analysis of metallic alloys
- Gold alloys (composition, soldering, gilding)
- Silver alloys (composition, corrosion products)
- Copper alloys (composition, corrosion products)

XRF Inter-reproducibility - Historical Metal Alloys

14 institutions,
19 datasets
8 instrument types

- Bruker/Keymaster Tracer,
- Bruker/Roentec Artax,
- EDAX Eagle 3,
- Elva-X light,
- Innov-X XT-260,
- Niton Gold,
- Spectrace Omega 5
- Laboratory-built models.



Coordinated by Arlen Heginbotham, JP Getty, METAL 2010, pp 178-188

Accuracy of Overall Median/Reproducibility

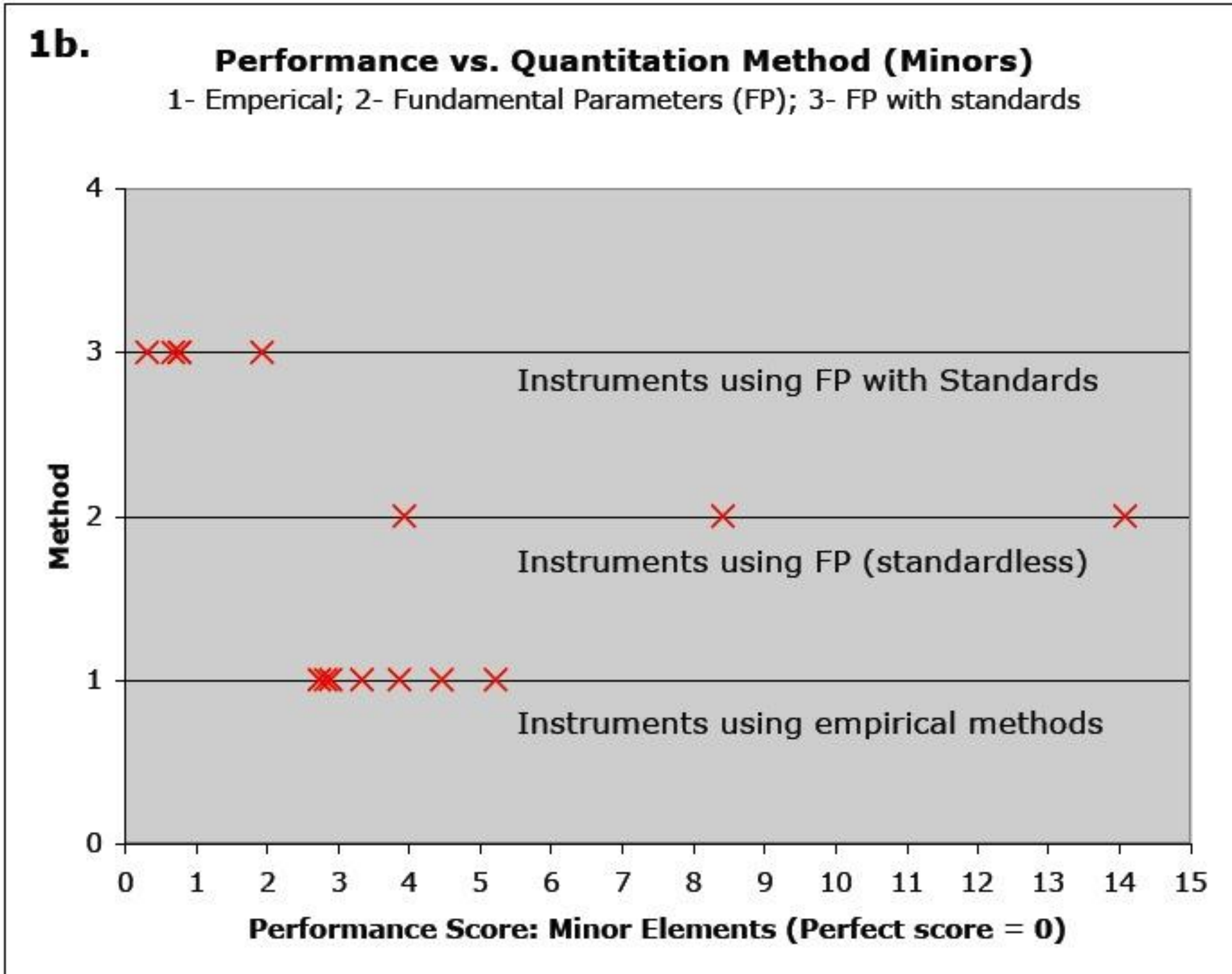
- Tested against 4 reference standards.
- Where the median is above the 'lower limit' …
- Median is accurate with a mean error of 5%.

Sample L (BNF C71.34-3)	# of Labs (p)	Certified Value	Overall Median ($\tilde{x}$)	% error
Mn	12	0.05	0.05	0.0%
Fe	19	0.29	0.25	-13%
Cu	19	87.230	86.592	-1%
Zn	19	1.55	1.62	5%
As	13	0.18	0.17	-6%
Ag	10	0.025	0.038	*
Sn	19	8.20	8.43	3%
Sb	11	0.071	0.119	*
Pb	19	2.47	2.76	12%
Bi	4	0.029	0.025	*
			Mean error (median > L)	5%

* certified value below L

		All Participants
Iron	Calculated Lower Limit (L)	0.165
	Mean $R_{rel\%}$ for $\tilde{X}$>L	121%
Nickel	Calculated Lower Limit (L)	0.354
	Mean $R_{rel\%}$ for $\tilde{X}$>L	61%
Copper	Calculated Lower Limit (L)	n/a
	Mean $R_{rel\%}$ for $\tilde{X}$>L	8%
Zinc	Calculated Lower Limit (L)	0.792
	Mean $R_{rel\%}$ for $\tilde{X}$>L	31%
Arsenic	Calculated Lower Limit (L)	0.246
	Mean $R_{rel\%}$ for $\tilde{X}$>L	110%
Tin	Calculated Lower Limit (L)	0.271
	Mean $R_{rel\%}$ for $\tilde{X}$>L	40%
Antimony	Calculated Lower Limit (L)	0.120
	Mean $R_{rel\%}$ for $\tilde{X}$>L	185%
Lead	Calculated Lower Limit (L)	1.217
	Mean $R_{rel\%}$ for $\tilde{X}$>L	77%

How the reproducibility can be improved?



Cu in Gold (bibliography)

- ✓ Copper can generally be detected in native gold at levels up to a 2.5 % content (Ogden 1992). Typically, it is present in a quantity less than 1% (Craddock 1997)

- ✓ Literature data obtained from gold grains/nuggets, as well as from objects made possibly by native ore indicate that Cu values rarely exceed 1%.

- ✓ If the presence of copper is a result of human intervention, then its content should exceed 2.5% (Ogden 1982) and perhaps even 5% (Scott 1983)

- ✓ Tylecote (1987) considered as a general rule that copper vontents exceeding 3% should be regarded as additions.

Ag, Fe in Gold (Bibliography)

Silver

✓ The initial silver content in native gold can range from less than 1% up to 50% or more (Ogden 1982), but usually ranges between 5 and 30% (Ogden 1982, Scott 1983, Craddock 1997)

✓ In Thassos island, gold grains with Ag between 14-17% have been found, whereas in the St Mandilis river near Nigrita an average 6% Ag content at placer deposits was found. (Michailidis and Vaveldis, 1987)

Iron

✓ Iron concentrations at levels lower than 0.5%, are typical in native gold (chalcopyrite, an iron copper ore), (G. Demortier 1989)

Welding processes (bibliography)

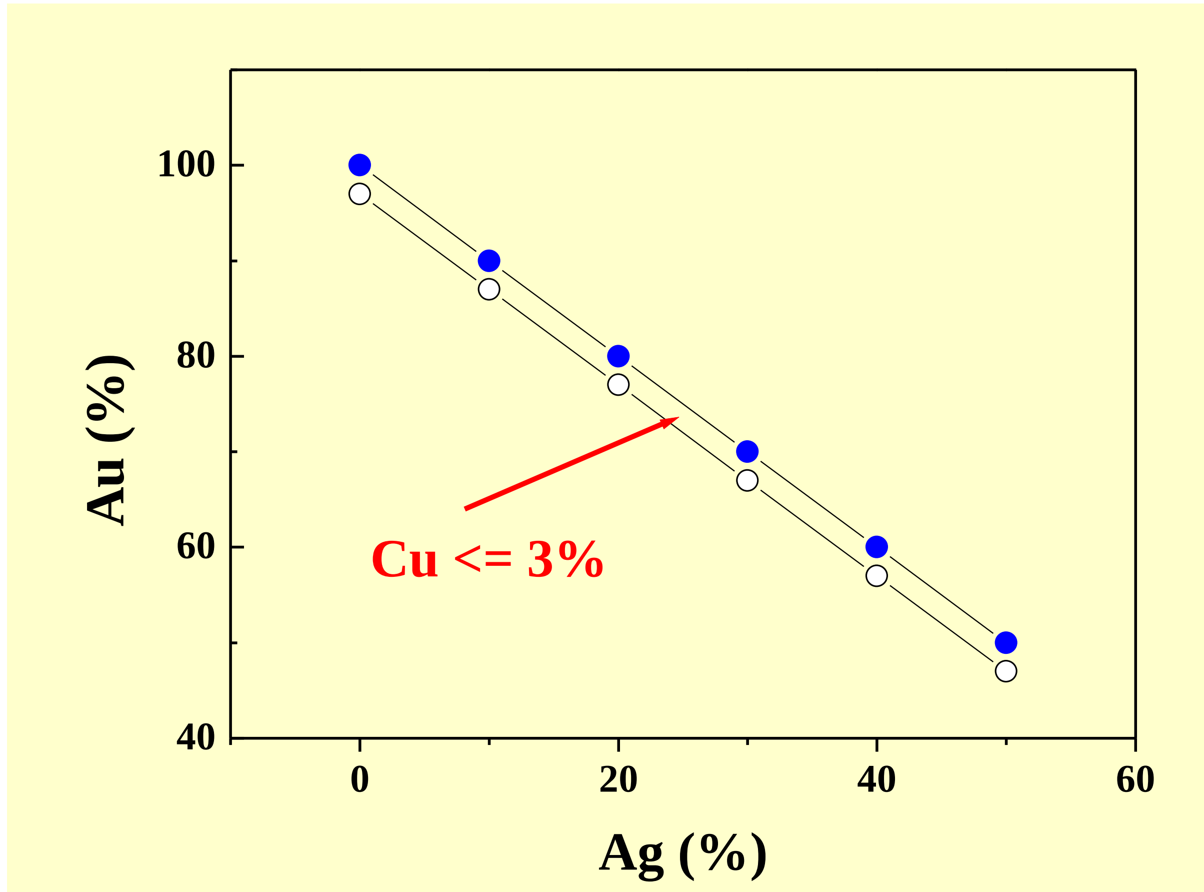
1) Forging by rapid fusion of discrete parts in contact (joined by local heating), without the use of a fusible alloy (autogeneous)

2) Brazing with an alloy or metal with a lower melting point than the gold itself . This usually means a more complex ternary Au-Ag-Cu alloy instead of the binary Au-Ag alloy that forms the major components

3) Heating pure gold with copper powder under reducing conditions a Au-Cu alloy is formed by diffusion, which having a melting point considerably lower than the gold itself, can run into the gap between the two components

Gold Alloys-Chemical composition

Bulk composition-
Au-Ag correlation:
Discriminates
Native or purified



Soldering technique - Criteria:

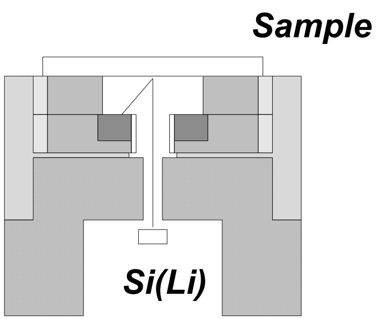
Ag/Au, Cu/Au rations for soldering areas vs bulk metal

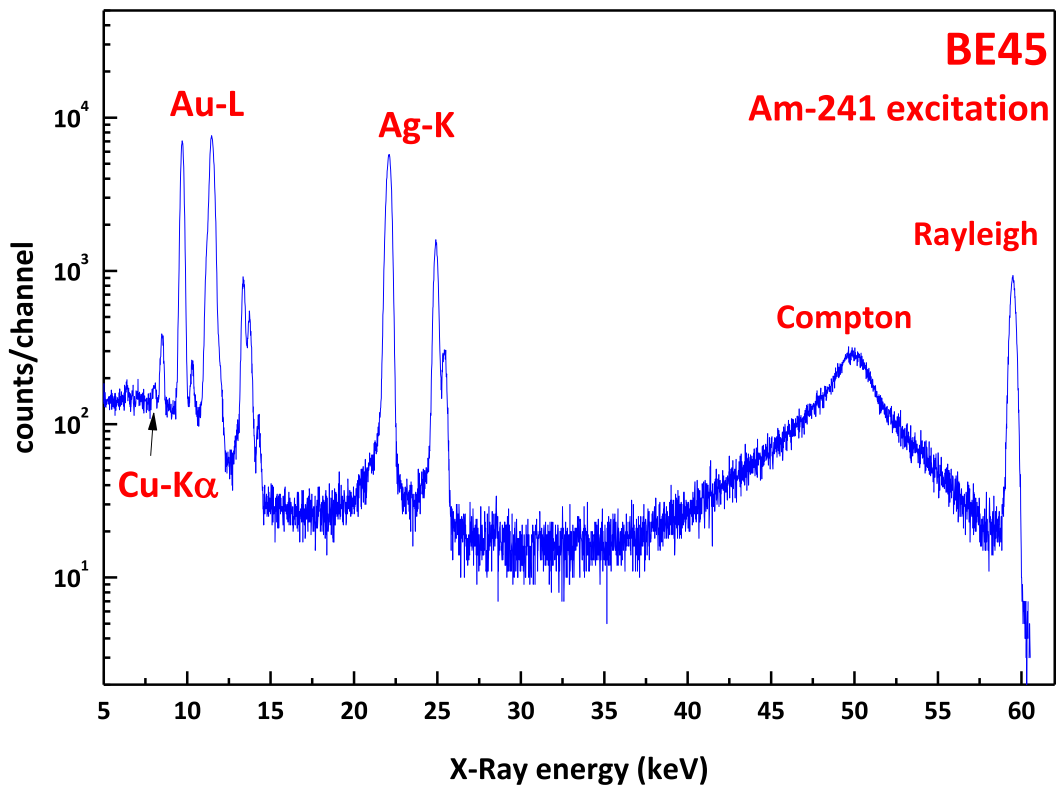
Neolithic artifacts: National Archaeological Museum of Athens

Neolithic gold artifacts

Am-241 XRF spectrum of Neolithic gold artifacts

Annular Cd-109 Radioactive source





Analytical examination of the gold periapts

- ✓ Measurements of dimensions, weight and specific gravity

- ✓ X-ray radiography, for the investigation of interior structural details

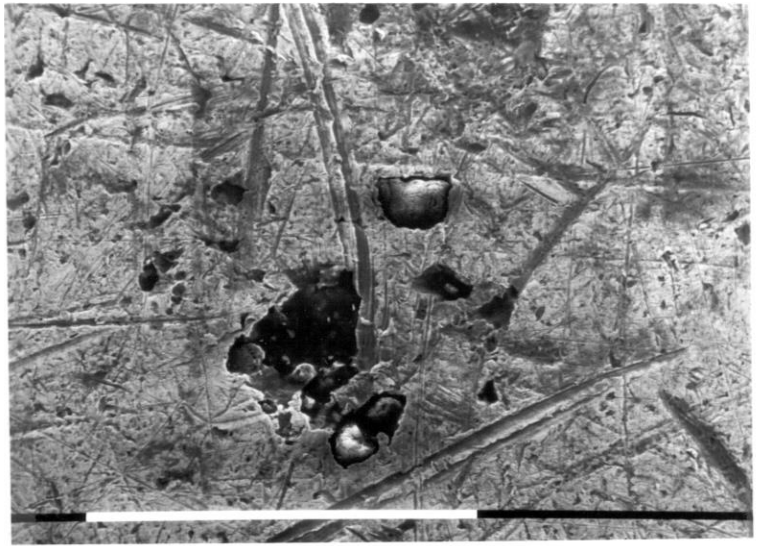
- ✓ Optical Microscopy, for the observation of surface details under magnification up to 80x

- ✓ Scanning Electron Microscopy combined with energy dispersive microanalysis for a detailed examination of the surface micromorphology, under magnifications of up to 3000x, and characterization of the inclusions, admixtures and depositions with spot microanalysis.

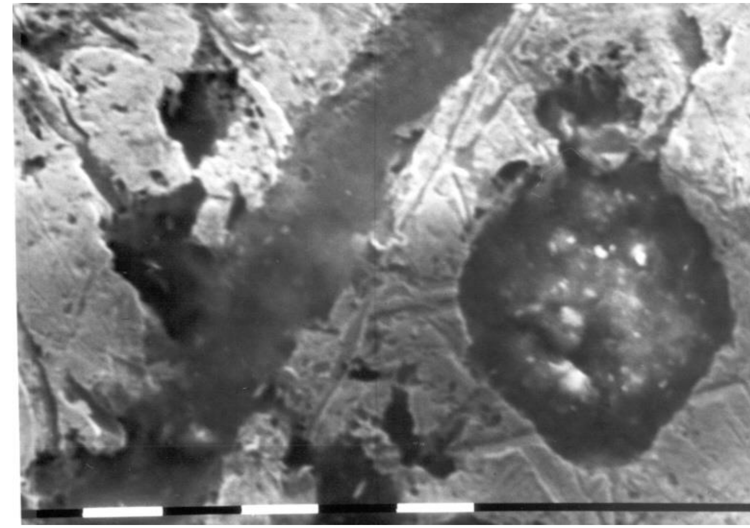
- ✓ Radioisotope induced

s

Inclusions/Surface depositions



Magnification : 573 x

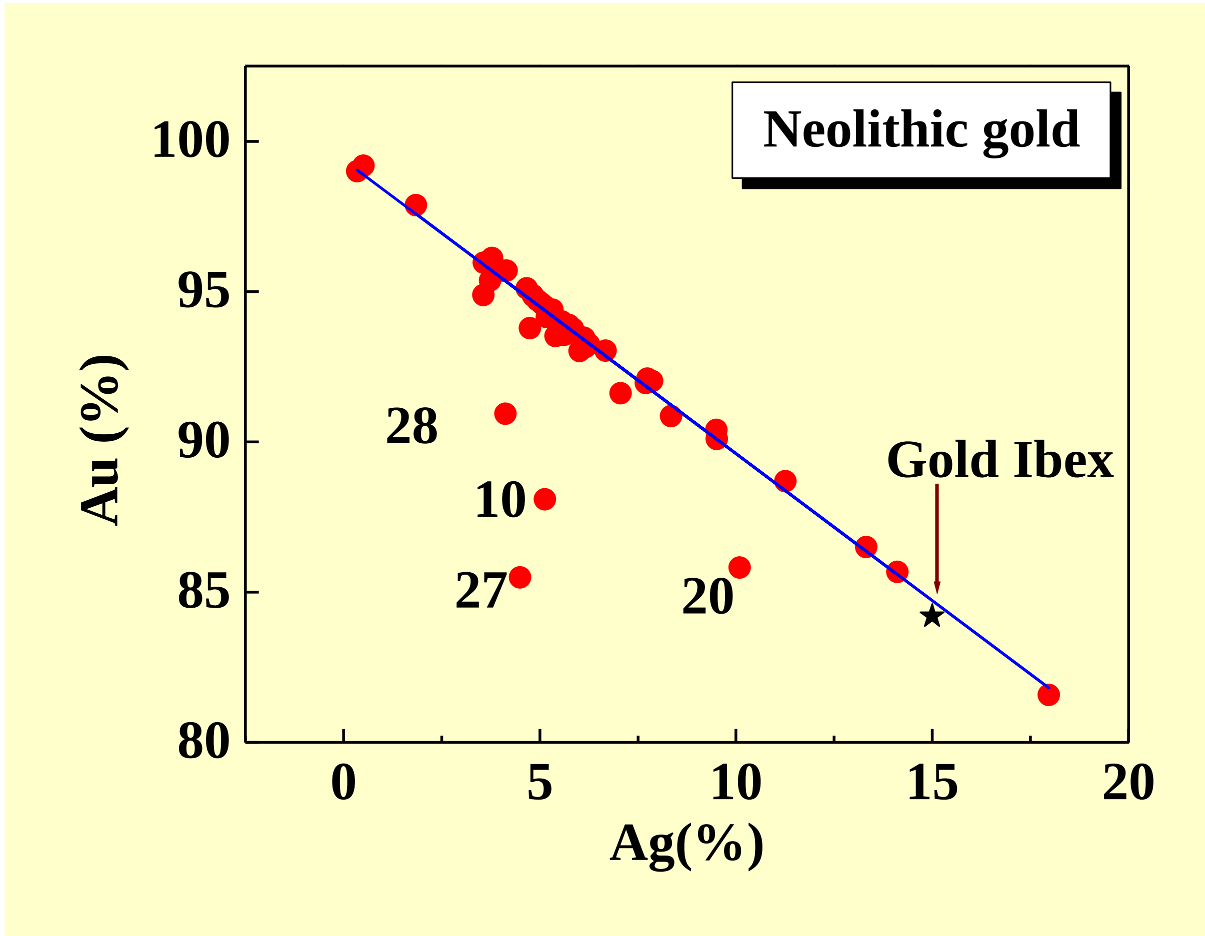


Magnification 1250 x

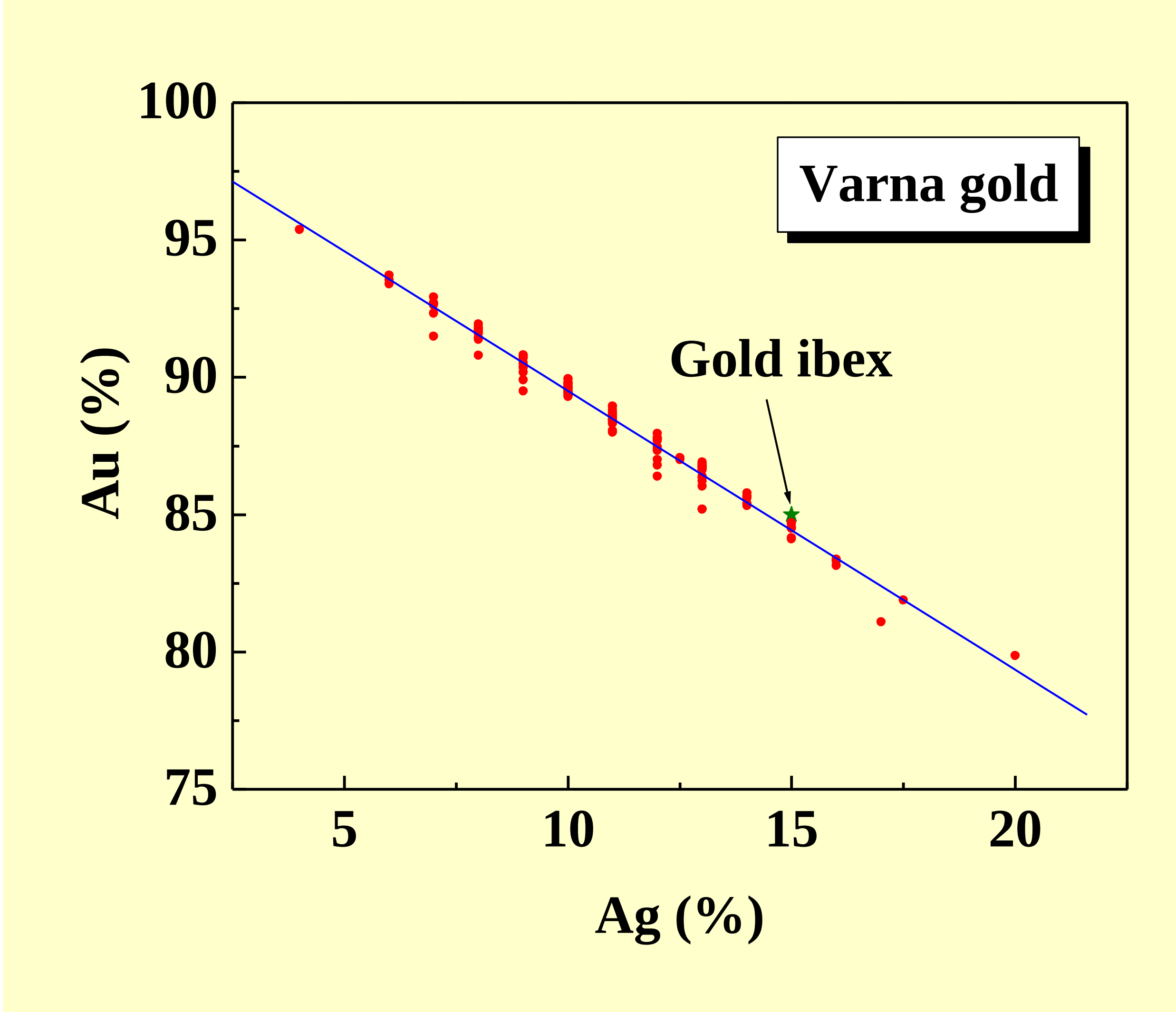
✓Typical feature of all objects: Natural openings on the surface in which quartz grains (2-20 μm) and in some cases of feldspars are embedded.

✓Clay depositions are traced mainly in channels, scratches and cavities and therefore have occurred after the use of the object and during burial

Neolithic gold – XRF results



Literature Data: Neolithic gold from Varna



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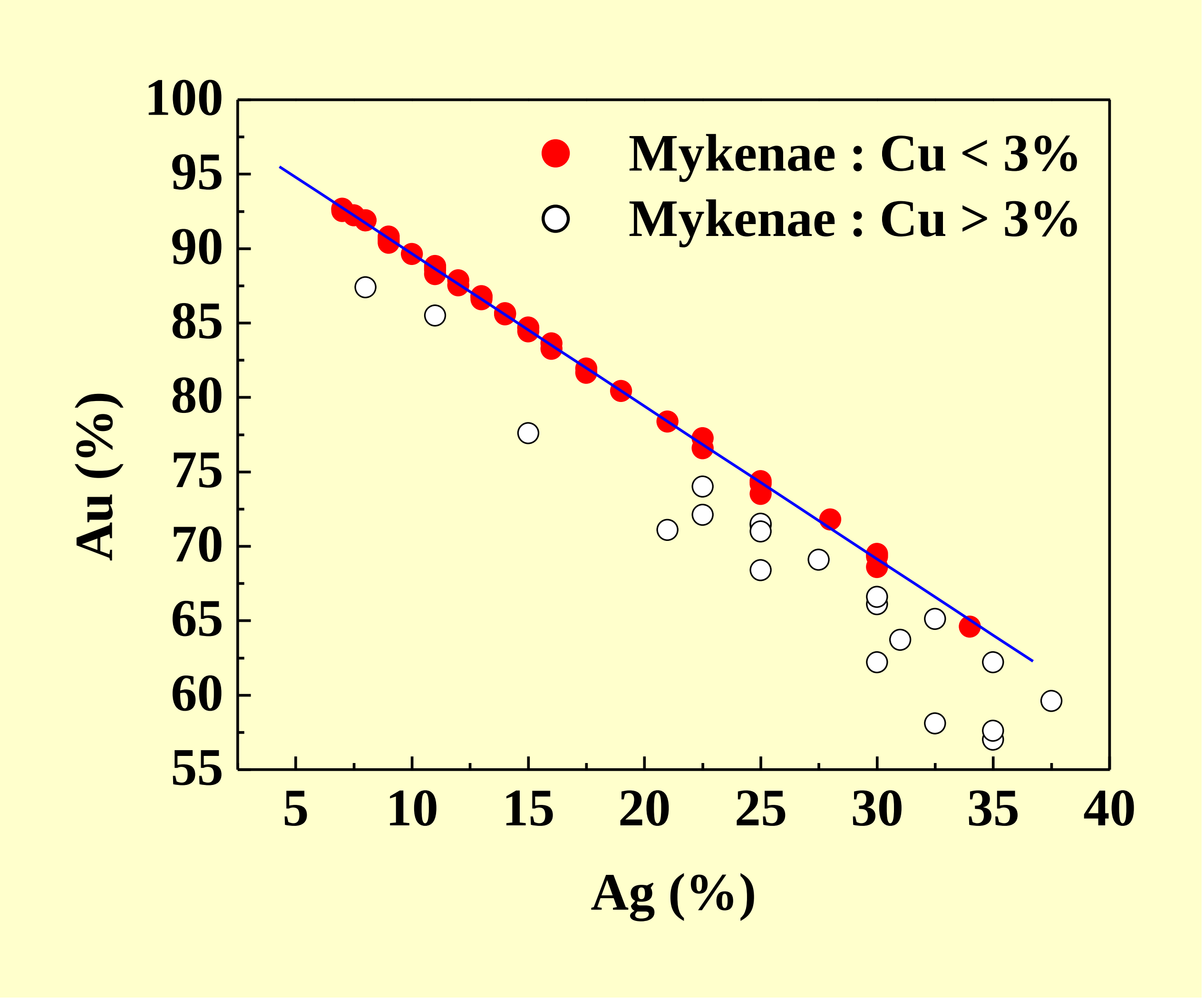
Literature Data : Mycenean Gold



Conclusions - Neolithic gold artifacts

- The XRF and SEM results indicate that the raw material is native gold from alluvial depositions, since all objects contain embedded sand grains.

- The general characteristics of the chemical compositions is the very high gold content and very low copper concentrations

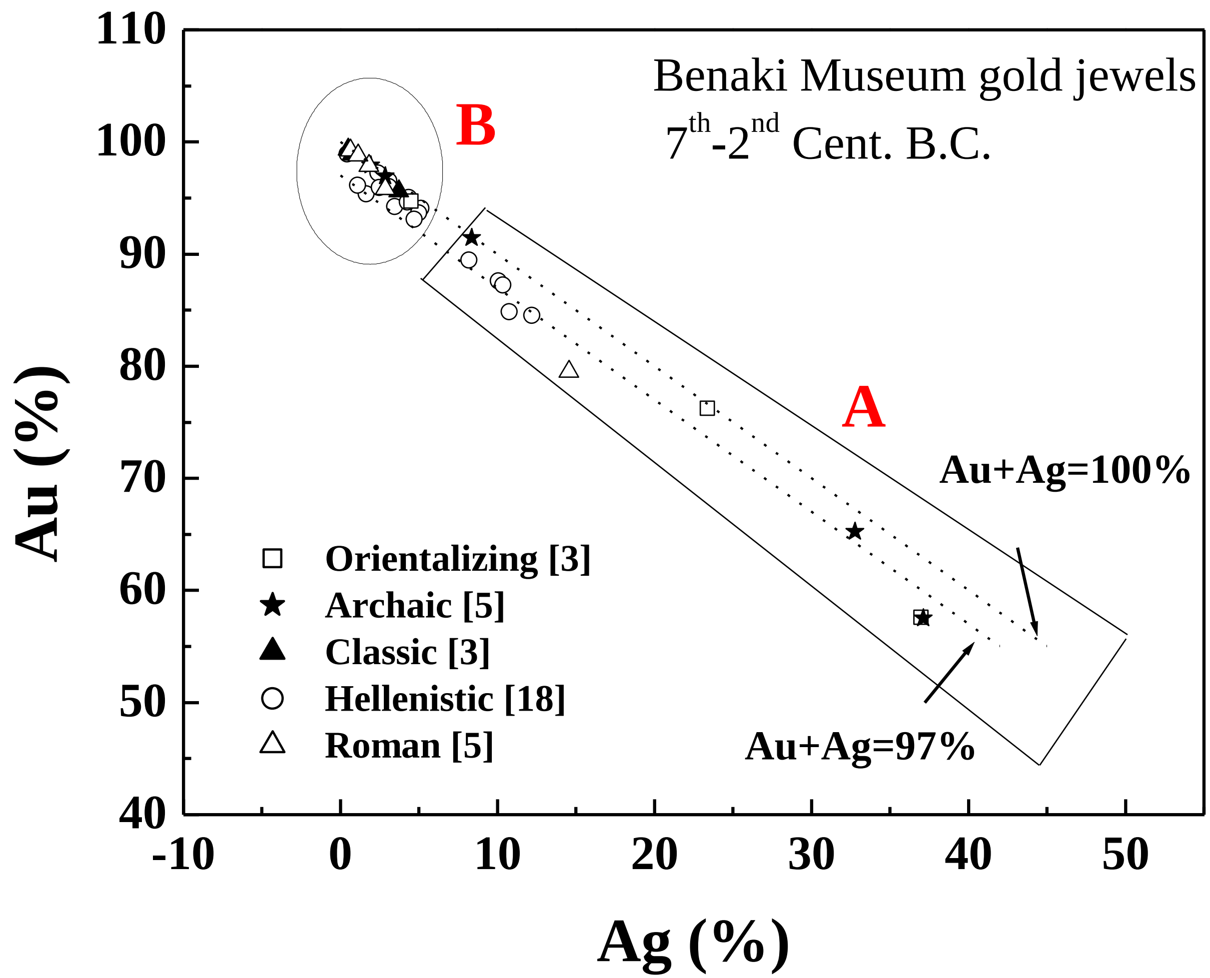
- The high copper content in few (4/50) of the samples could indicate alloying

- The surface examination indicates burial of the objects in a rich in clay and organics deposit

- Selective surface polishing suggests recent human intervention

Chemical composition of jewelry: Benaki

34 gold jewels
Benaki Museum



A.G. Karydas et al. Nucl. Instr. Methods B, 2004

Compositional results of the Benaki jewels

Group A:

Bulk composition typical for native gold (except one jewel with Cu: 4.7% and Ag 14.7% which indicates alloying). The four items belonging to the Orientalizing and Archaic period were made possibly by electrum

Group B:

The low percentage of Ag and Cu, or the high Au percentage (97 +- 1)% indicate that the metal originates from native gold that had however undergone some refining process, in other words separation of the precious metals from the base metals and then a second stage of parting the gold from the silver silver

Technology for the Gold Leaves

- The refining process of the primary metal was a common practice over Classic to Hellenistic and Roman periods

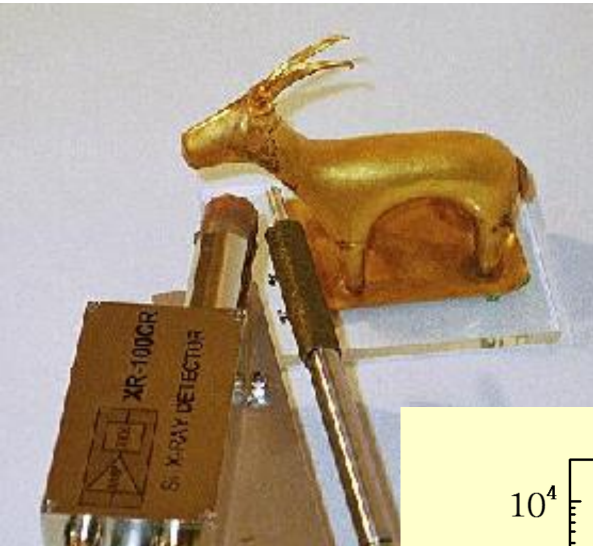
- The refining process includes two steps: separation of the precious metals from the base metals and then a second stage of parting the gold from the silver.

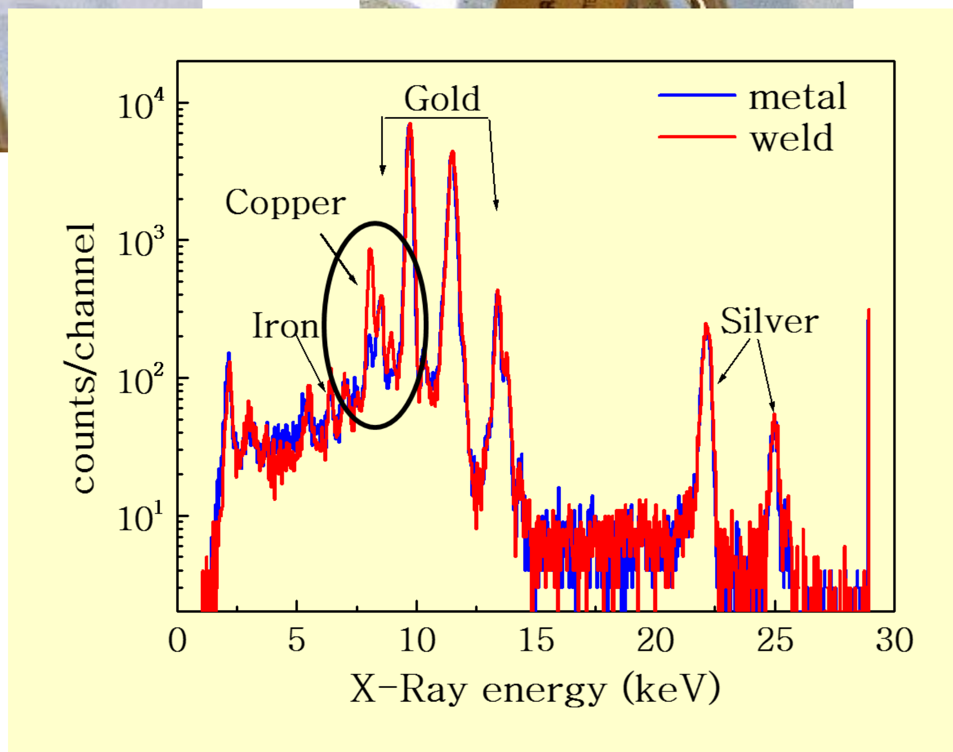
	Hellenistic-Roman Jewelery (Benaki museum)		
Number	Au (%)	Ag (%)	Cu (%)
16	96.2 ± 1.8	2.7 ± 1.5	0.8 ± 0.8

Summary - Ancient Gold composition

Site	Period	Source	Number	Ag (%)	Cu (%)
Varna	Neolithic	Hartmann 1978	125	11 ± 2.6	0.50 ± 0.37
?	Neolithic	COST-2000	44	6.2 ± 3.2	0.35 ± 0.33
Mycenaean	Mycenaean	Hartmann 1982	40	16.5 ± 7.5	0.51 ± 0.34
Benaki jewels	7th- 1st BC	NIM B' 2004	31(45) Group A	2.4 ± 1.4	0.63 ± 0.11
Ibex	Thera	Metron	1	15.0	0.55

Gold Ibex, Akrotiri- Thera





left part.

Pantazis et al., Metron 2003

Chemical analysis of the gold-ibex

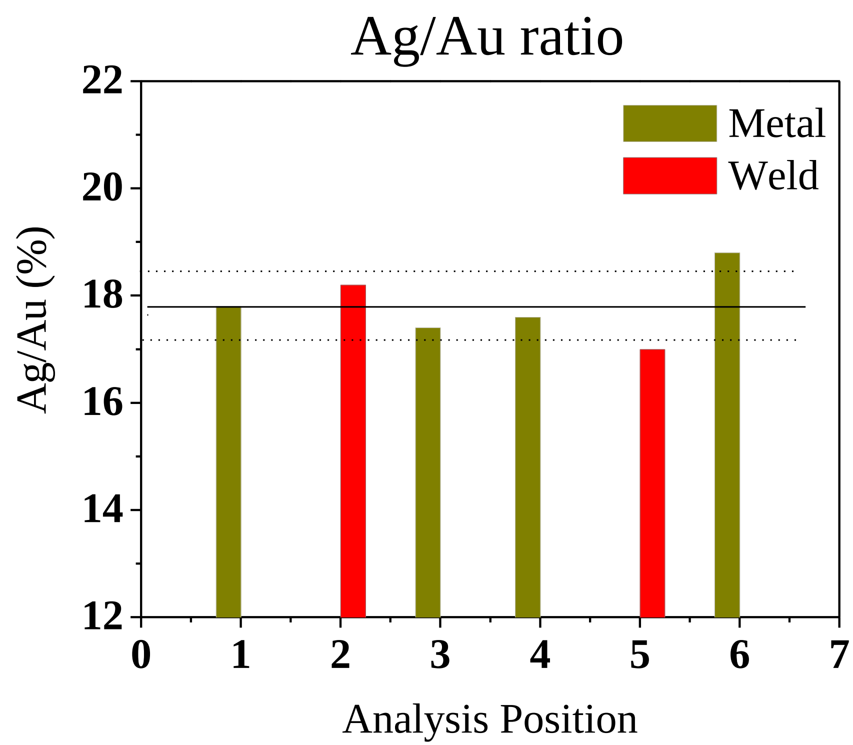
Position	Gold %	Silver %	Copper %	Iron %	Description %
metal	84.2	15.0	0.49	0.32	Main body
metal	84.4	14.7	0.51	0.38	Rear left leg
metal	84.7	14.4	0.55	0.37	Right horn
metal	83.4	15.7	0.66	0.29	Bottom
welding	82.5	15.0	2.25	0.30	Weld under the neck
welding	82.5	15.0	2.25	0.30	Weld under the neck
metal	84.2	15.0	0.55	0.34	Average
welding	82.5	14.9	2.53	0.34	Average

Pantazis et al., Metron 2003

Soldering technique: Thera - ibex

❖An increased Cu concentration was measured at the welding areas

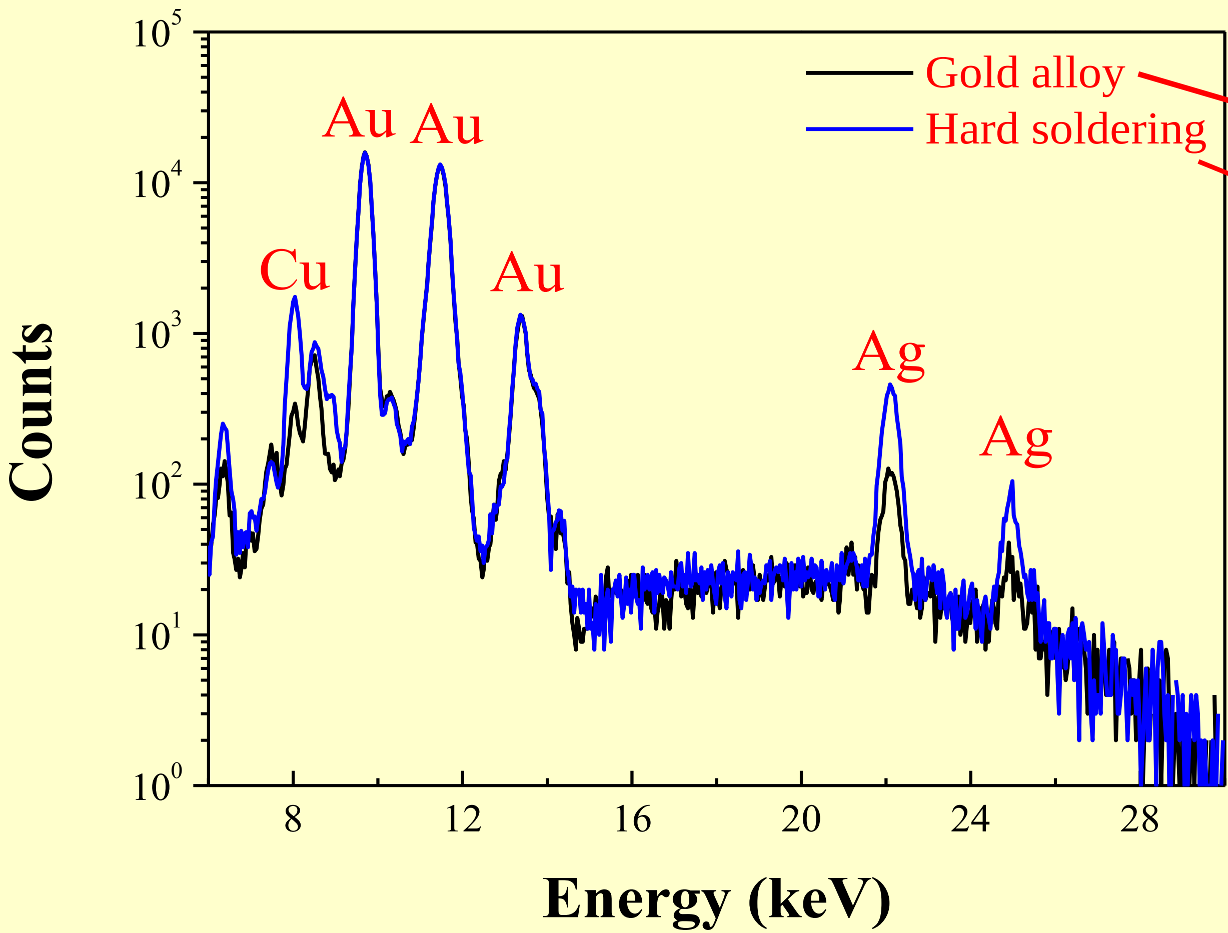
❖No change in the Ag/Au ratio

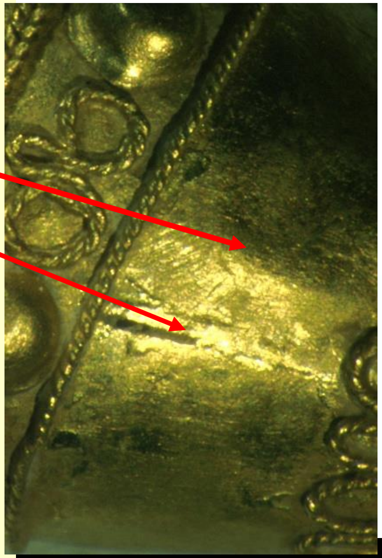


➢ A copper compound, probably chrysocolla, a hydrated copper silicate mineral was used for the welds, although the possible use of malachite, a green copper mineral, can not be rejected.

Pantazis et al., Metron 2003

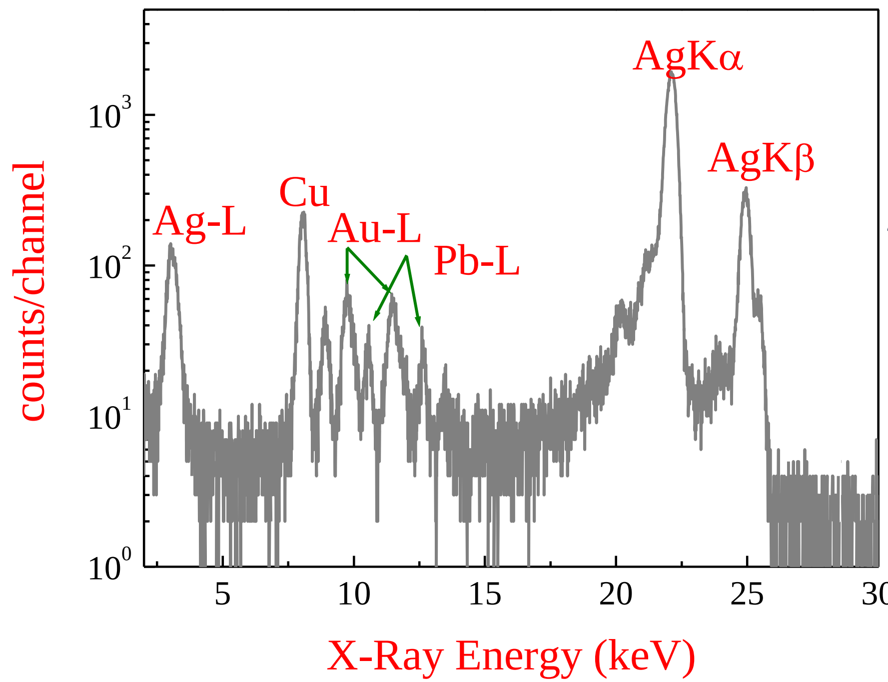
Soldering technique: Hellenistic Jewel





Ch. Zarkadas et al., Spectroch. Acta B, 2004

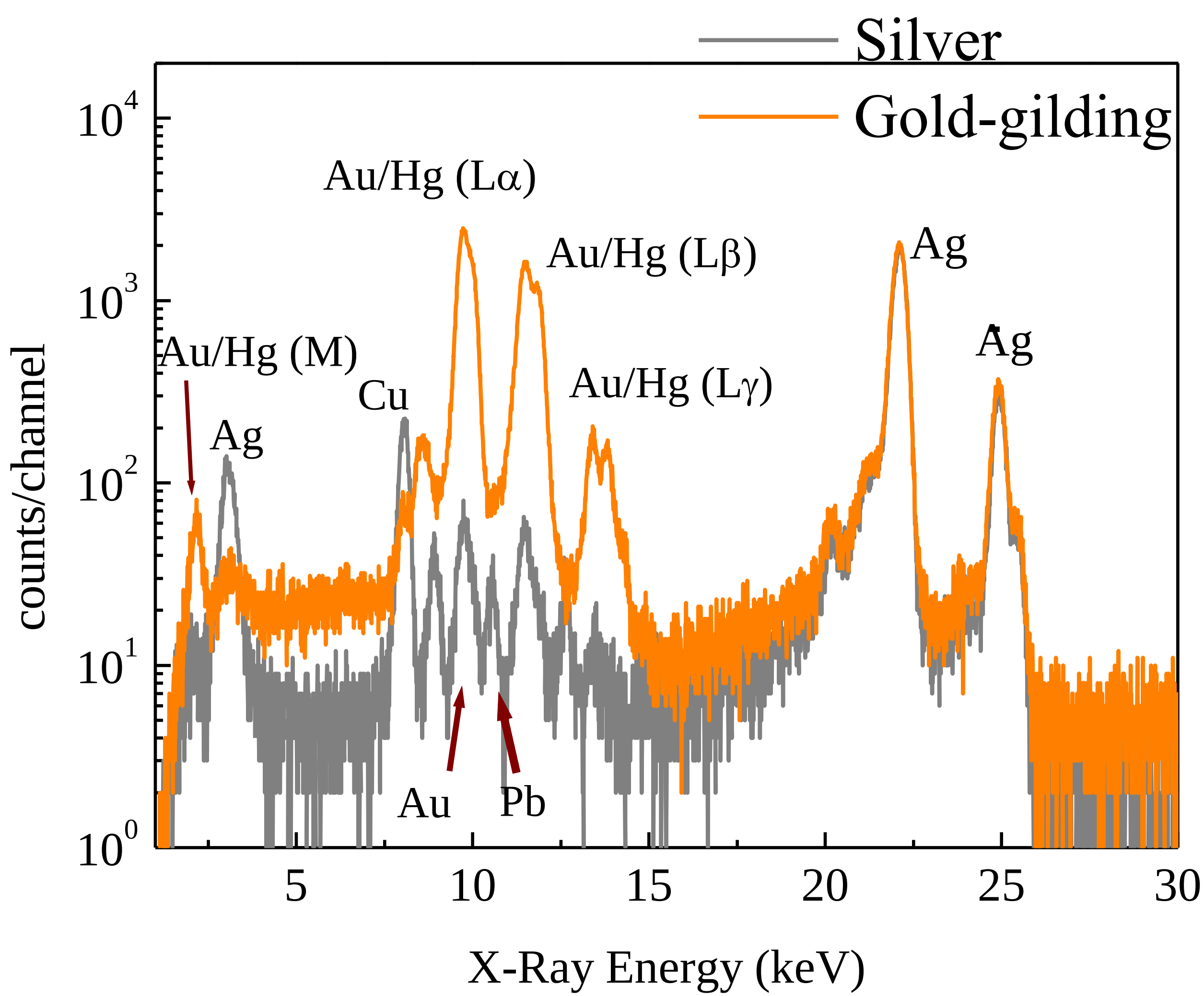
Silver dishes (Byzantine period)



Ag: 93.6-95.0 %
Cu: 3.11-4.72 %
Au: 1.26-1.49 %
Pb: 0.37-1.15 %

Benaki Museum Athens, GR

XRF analysis of gilded silver dishes

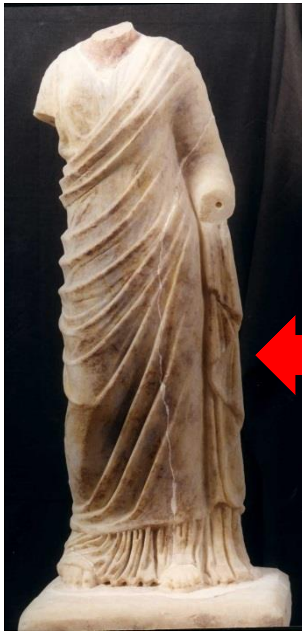


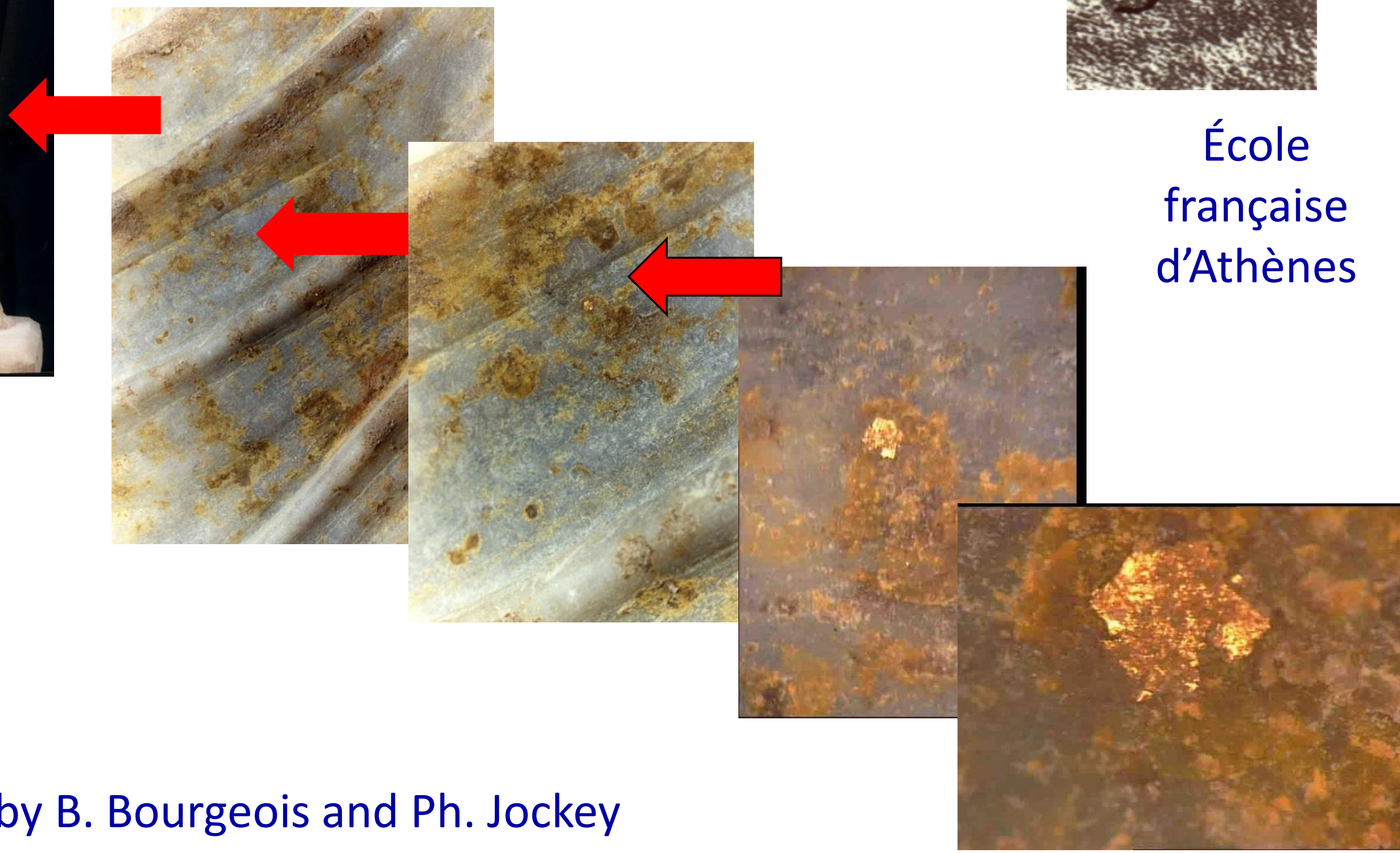
Au/Hg: 1.3-3.5

Thickness:
3.0-4.6 μm

Au: 61%
Hg: 39 %

Microscopic gold leafs on marble



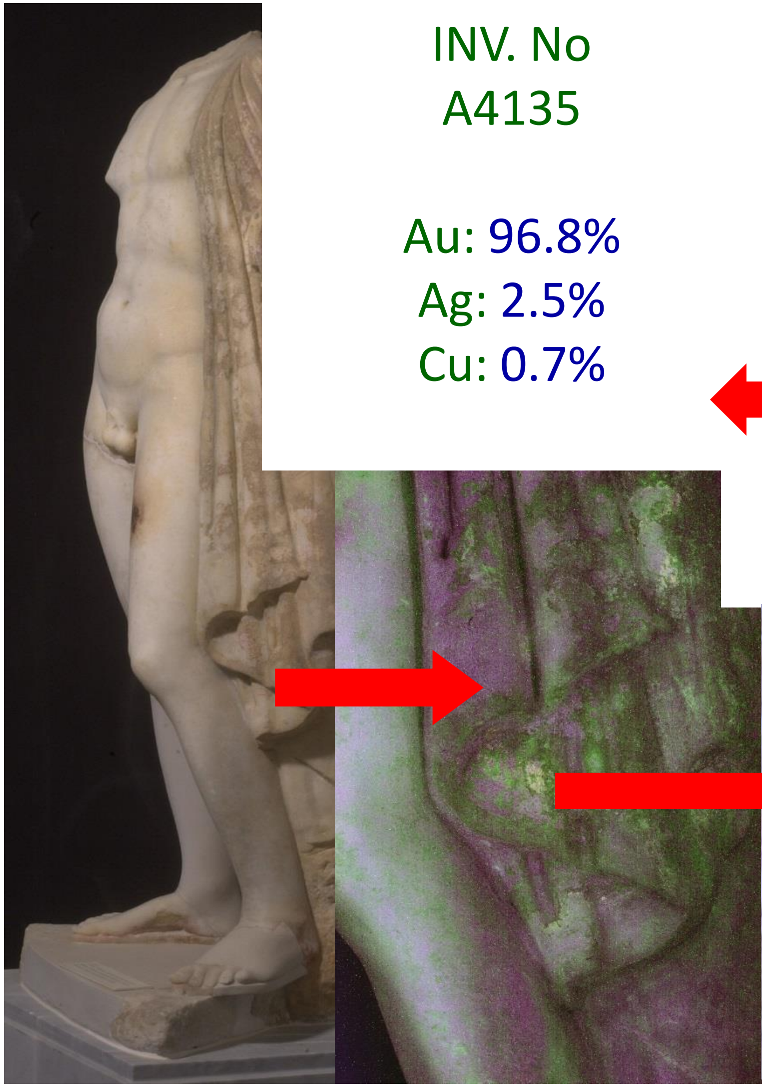


École française d’Athènes

Delos, Musée, Aphrodite dorée

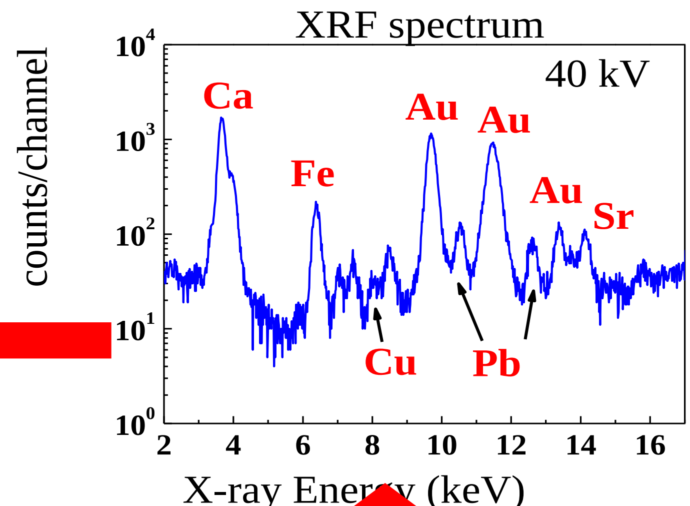
Video Microscope by B. Bourgeois and Ph. Jockey

Microscopic gold leafs on marble



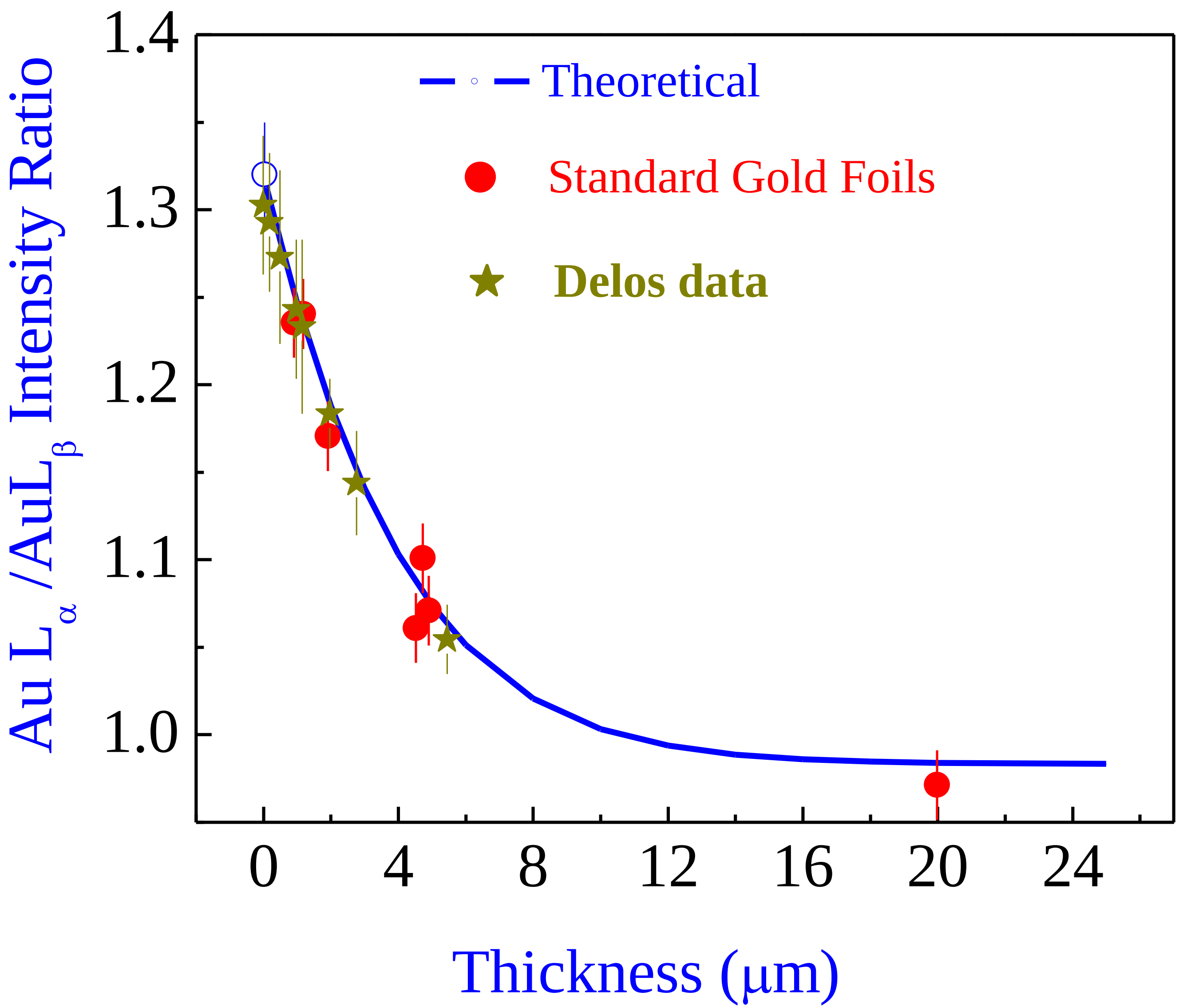
INV. No
A4135

Au: 96.8%
Ag: 2.5%
Cu: 0.7%



Video Microscope by B. Bourgeois, Ph. Jockey

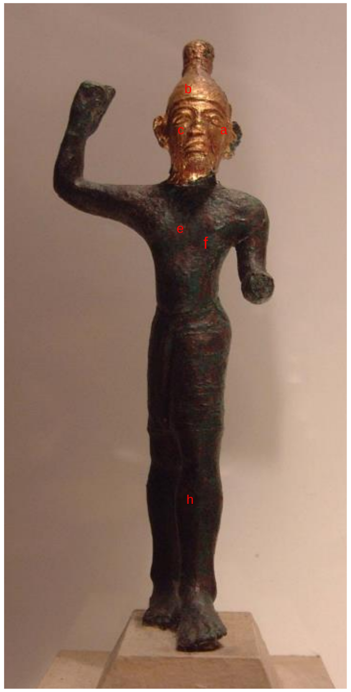
ND Analysis of the Gold Leafs



Thickness of the Gold Leafs

Statue	Au %	Ag %	Cu %	Thickness (μm)
A5280	97.5 ± 1.3	< 2.6	1.2 ± 0.1	2.0 ± 0.3
A4134	95.5 ± 3.0	< 6.2	1.5 ± 0.2	5.5 ± 0.7
A4135	96.8 ± 0.8	2.5 ± 0.8	0.7 ± 0.2	> 12
MN1827	98.2 ± 1.5	< 3.1	0.23 ± 0.05	2.8 ± 0.5
A5357	96.8 ± 2.7	< 5.5	0.44 ± 0.09	< 1.3
A394	97.5 ± 2.5	< 3.5	< 1.6	< 1.3
A312	96.4 ± 1.8	< 3.6	1.6 ± 0.2	< 1.3
A3473	96.2 ± 2.8	< 5.7	0.95 ± 0.1	1.0 ± 0.6

Gilding techniques

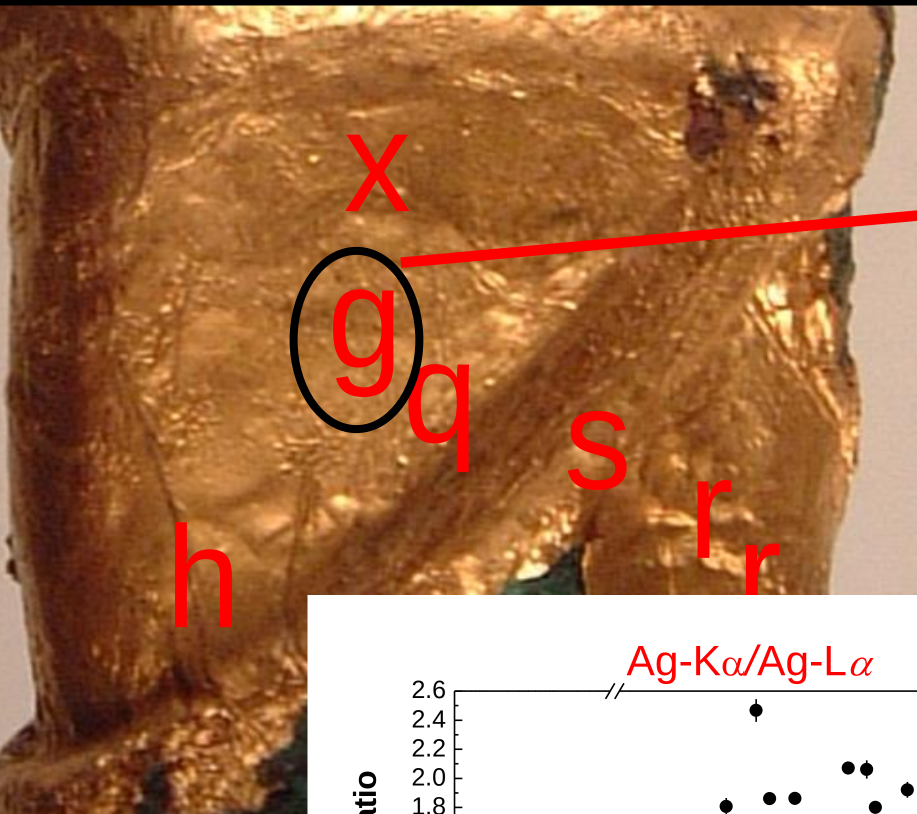


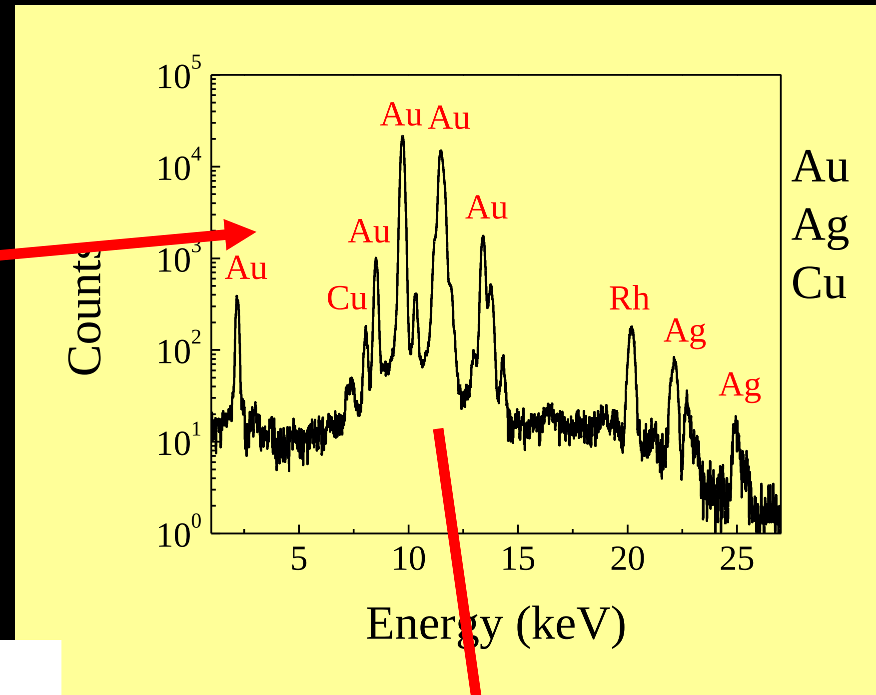
Archaeological Museum of Damascus
Eail God, Baal God 1, Baal God 2
Late Bronze Age 1400-1300 B.C.

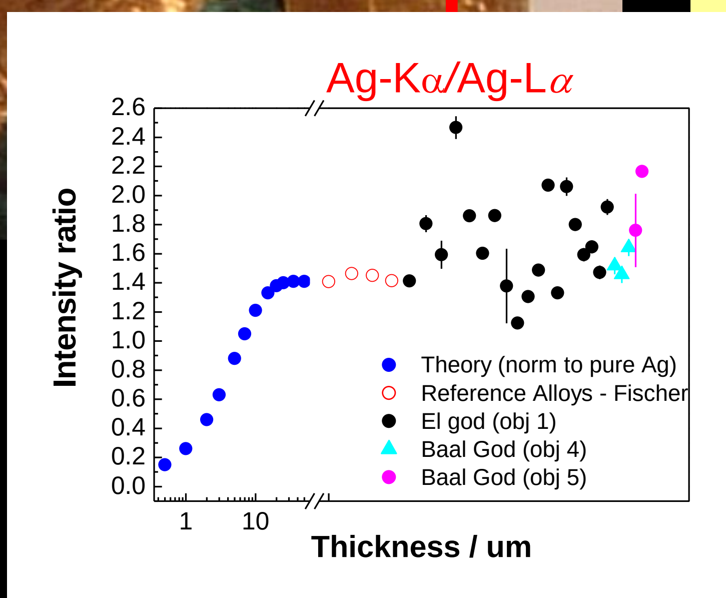
Eail God, Late Bronze Age 1400-1300 B.C.
Museum No. 3573
Very corroded Bronze statue, gilded with golden leaves
Height 15.3 cm

Damascus National Museum, October 2007, PROMET Group

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







Au: 94.7%
Ag: 4.9%
Cu: 0.4%

Composition of the gold foil

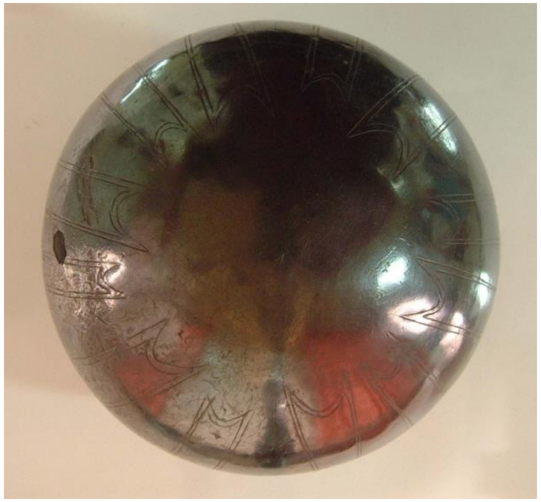
Analysis of silver corrosion

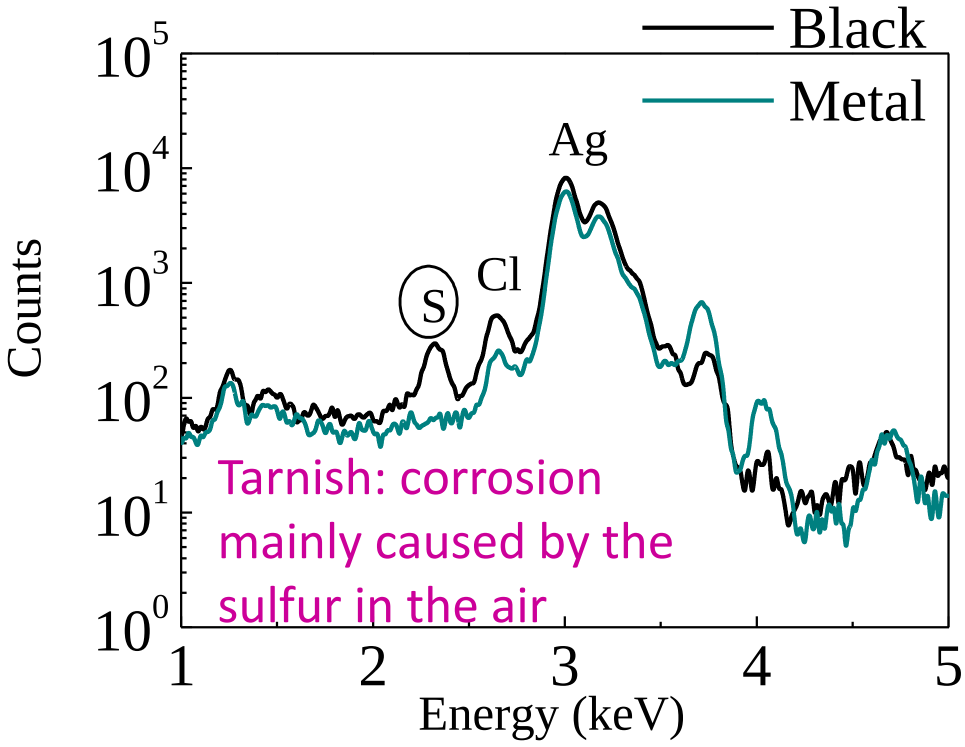
Damascus Archaeological museum

Silver Bowl 1400 - 1300 B.C.   Late Bronze Age

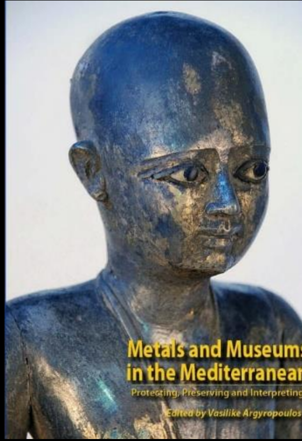
Thickness of the layer: ~ 0.5 μm.

DL's from about 20 nm

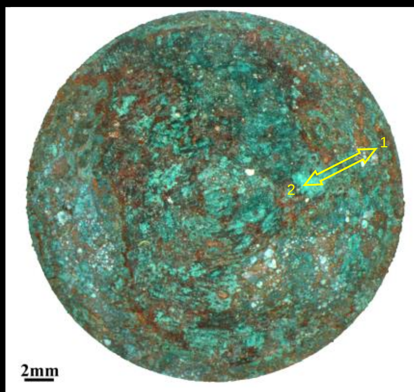




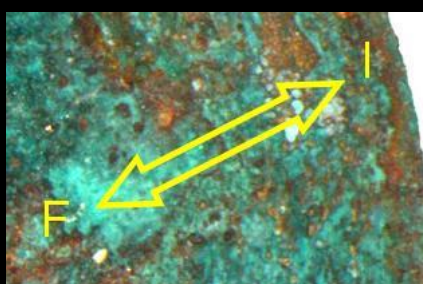
Analysis of Cu corrosion products

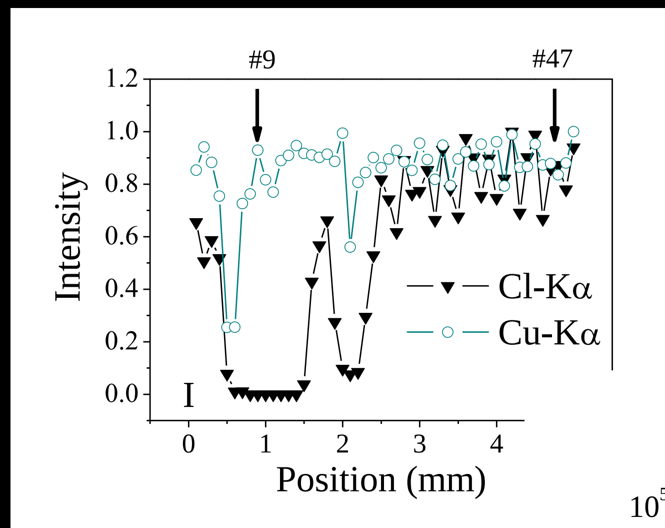


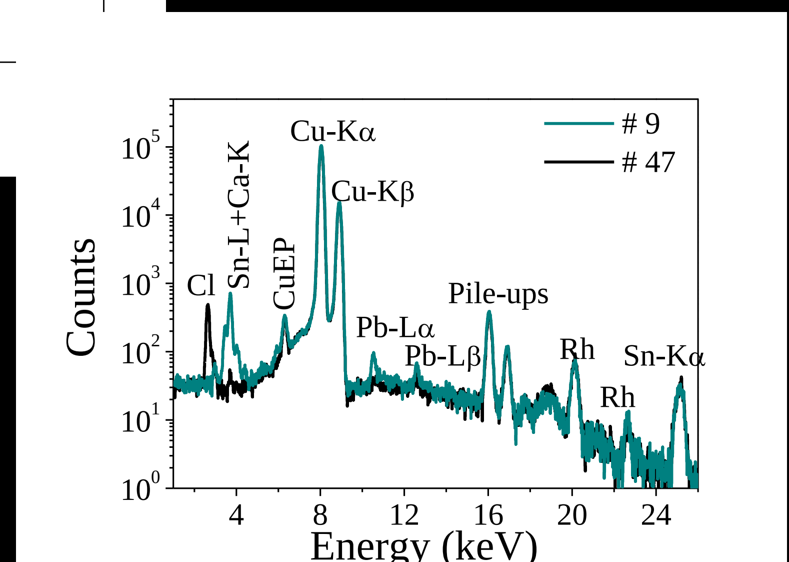
Artificially and naturally aged bronze coupon:
Cu: 91.3%, Sn: 7.5%, Pb: 1.0%)



#9 : green area
#47: pale green area



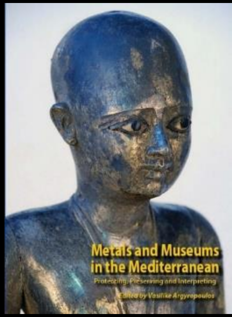


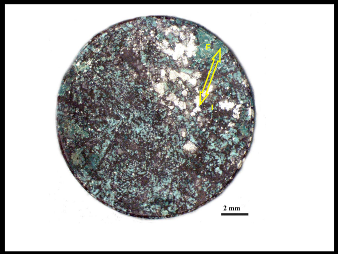


50kV, 600μA,
30s/step,0.1mm/step,
50 measurements

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

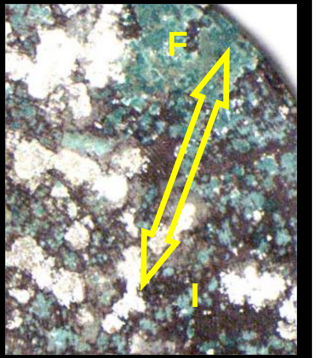
Analysis of Ag corrosion products

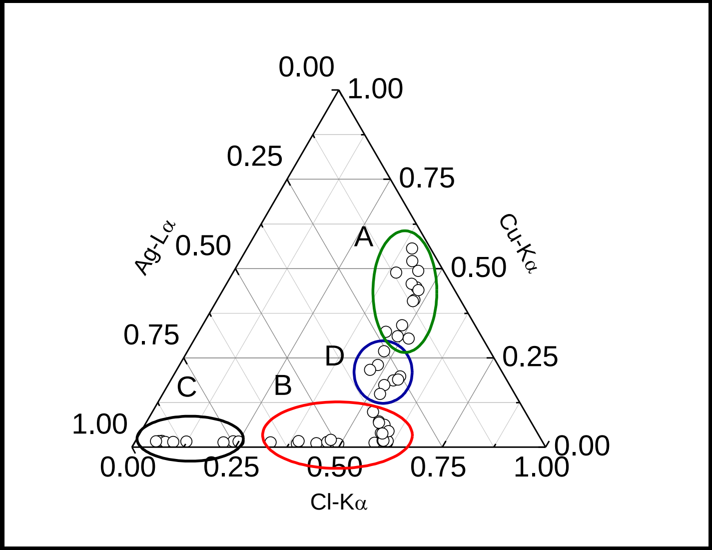


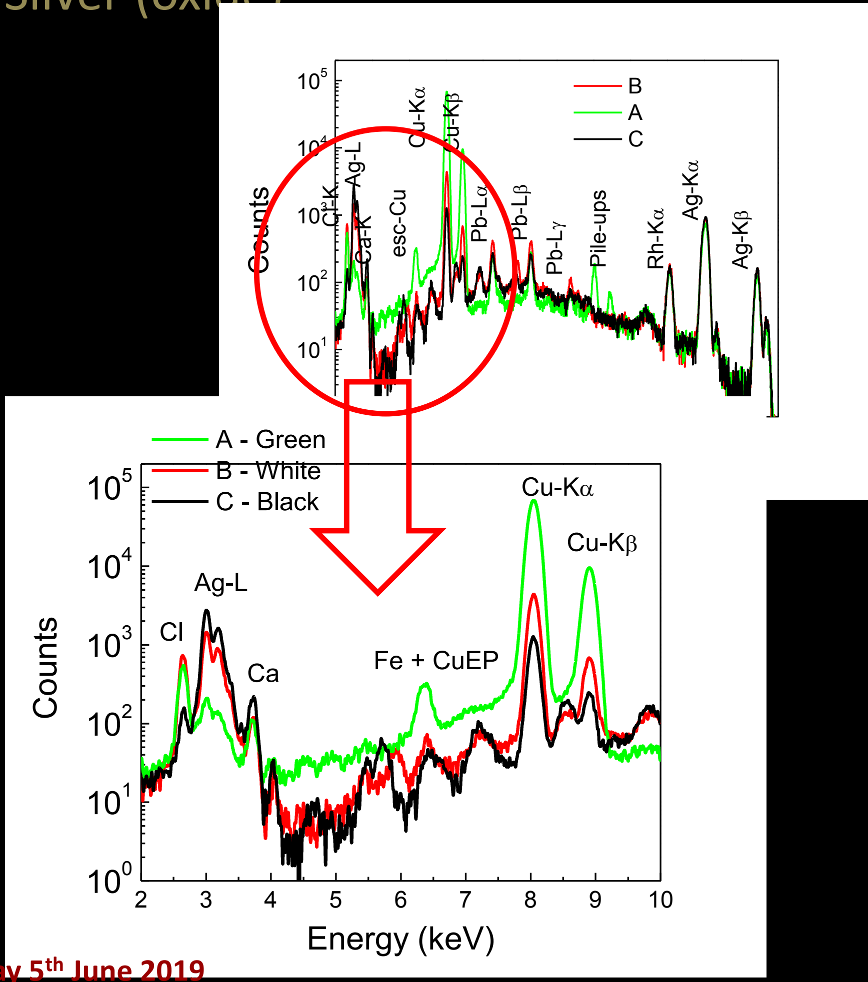


Artificially and naturally aged silver coupon:

Ag: 92%	A – Green	A – Para/Atacamite
Cu: 6.5%	B - White	B - Chloroargyrite
Pb: 1.5%	C - Black	C - Silver (oxide)





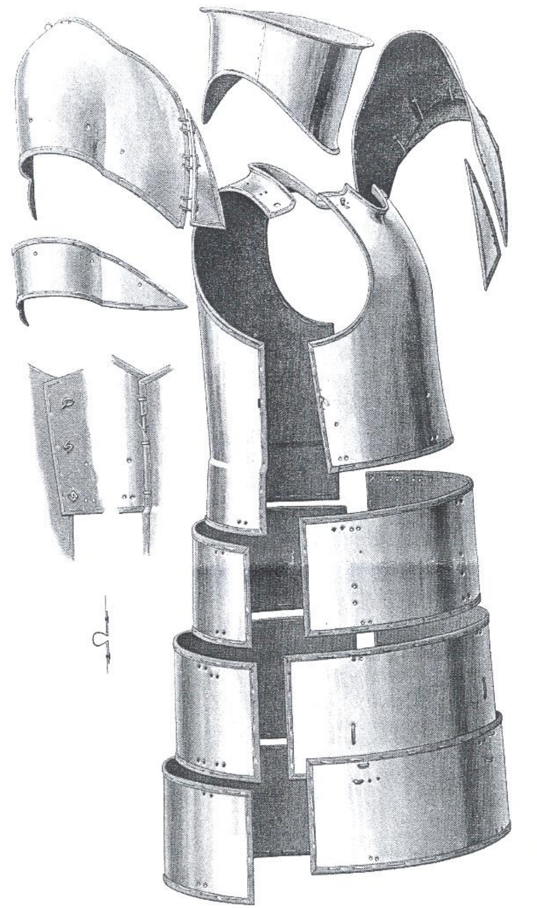


50kV, 600μA,
30s/step, 0.1mm/step,
50 measurements

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

In-situ XRF analysis, Mycenaean Armory

15th Cent BC

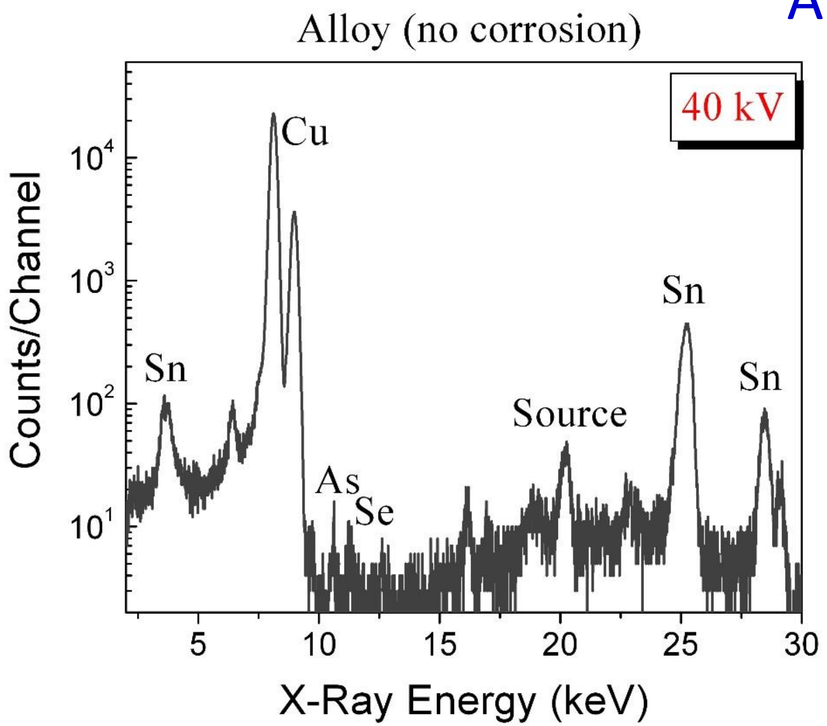


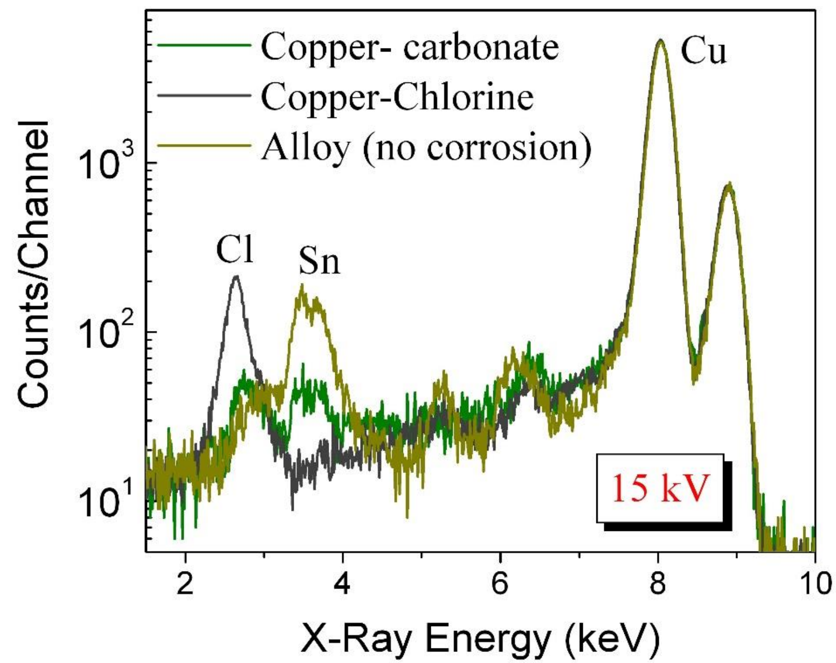
Taratori et al., 2010

Alloy composition, Corrosion layers

Malachite

Atacamite, Para-atacamite, Nantokite?





	Cu (%)	Sn (%)	Fe (ppm)	As (ppm)	Se (ppm)
Belt #1, cleaned area	89.5	10.5 ± 0.5	≤ 300	239 ± 79	275 ± 55

Thank you for your attention!