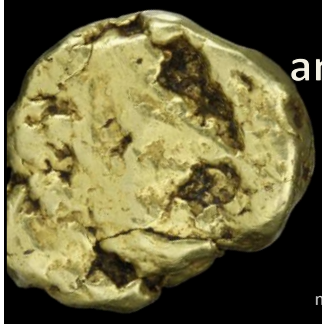
Archaeometallurgy: questions and methods



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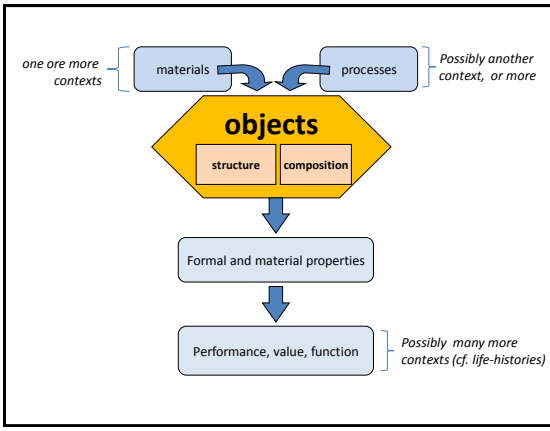
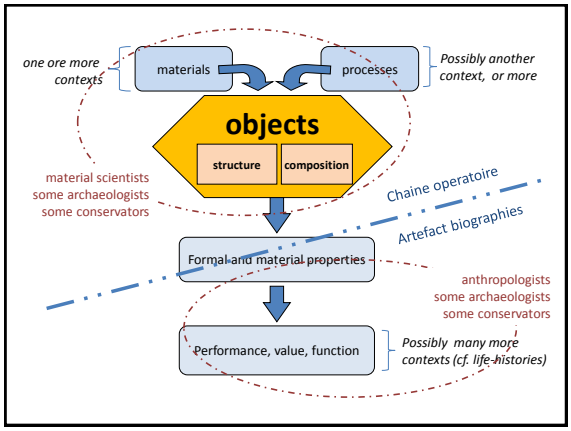
85 mm in diameter
7 mm thick
444 grammes of mass
Cast by lost-wax method
92.50% silver, 6.15% copper, 1.35% gold
6 g of gold
Gold plating 15 µm thick

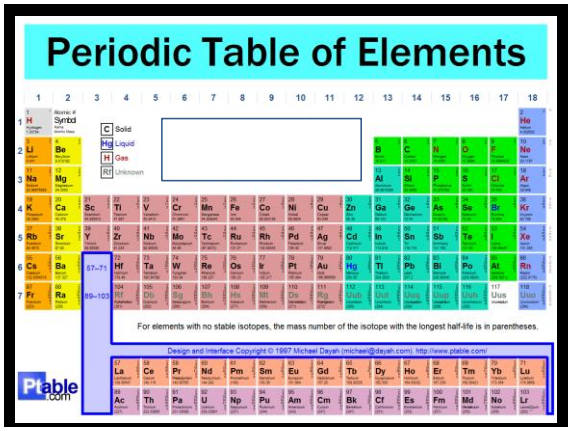




METALS are…

Dense
Tough
Malleable
Shiny / colourful
Sonorous
Recyclable
Rare

These factors, and more, will condition the exploitation and use of metals for different purposes



The 7 metals of Antiquity

	Metal	Planet	Symbol
Au	Gold	Sun	☉
Ag	Silver	Moon	☾
Fe	Iron	Mars	♂
Cu	Copper	Venus	♀
Pb	Lead	Saturn	♄
Sn	Tin	Jupiter	♃
Hg	Mercury	Mercury	☿

Earliest uses: almost invariably trinkets and status-related items (even if shaped like tools and weapons!)

Pure metals are very soft, so no great for technical purposes unless mixed to form ALLOYS

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The 7 metals of Antiquity

Gold (Au) and silver (Ag)
Often alloyed together, and with copper (Cu)

Noble (corrosion resistant), very malleable (soft) and rare:
Coins, jewellery, masks, ornaments, wealth stock

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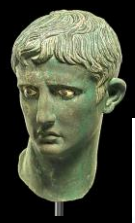
The 7 metals of Antiquity

Copper (Cu), the only orange metal
But typically alloyed to make bronze (with tin, Sn)
Or brass (with zinc, Zn), often leaded (with lead, Pb)
(otherwise not technically superior to stone)

Very versatile alloys:
Tools, weapons, jewellery, ornaments, statues, everyday life implements, coins…



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The 7 metals of Antiquity

Iron (Fe), the democratic metal
Very abundant, great for tools and weapons
BUT only when alloyed with carbon (C) to form STEEL
(otherwise not technically superior to bronze)

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The 7 metals of Antiquity

Lead (Pb) and tin (Sn), white metals

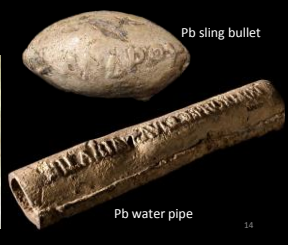
Pb: quite abundant, very dense, easy to extract:
weights, bullets, plumbing… and alloys

Sn: quite rare.
main use: making bronze (with Cu)

Pb and Sn alloyed together: pewter


Pewter


Pb anchor


Pb sling bullet

Pb water pipe

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Main analytical approaches to metals

Microscopy (manufacture and use)
(light (OM) or electron-based (SEM))
- On whole artefacts/surfaces
- On polished cross-sections (metallography)

Chemical analysis (alloy selection and provenancing)
- Bulk (XRF, ICP, NAA), or phase (SEM-EDS, EPMA)
- Surface or core

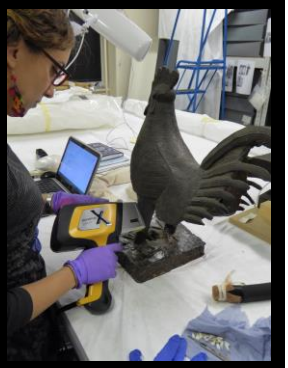
Isotope analysis (Pb, Sn…)(for provenancing)
(great, but problems of alloying, recycling, reference data…)

Mineralogical/crystallographic (XRD, FTIR, Raman)
(esp. on patinas and corrosion products rather than metals proper)

POTENTIALS,
PROBLEMS
& APPLICATIONS

pXRF analysis of archaeological Metals

(portable X-ray fluorescence)



Why should I care about the chemistry of metals?

'Conscious' aspects (typically major elements, i.e. ≥1%):

Selection of metals and alloys: cultural preferences, availability, knowledge, (date)…

'Unconscious' aspects (geological 'impurities')

An indication of source, grouping…
(often supplemented by isotopic analyses)

Why should I care about the chemistry of metallurgical products?

Furnace charge, nature of metals being processed, efficiency, operating parameters (by looking at relevant phase diagram)… BUT almost always microstructural analysis required too

And if I analyse a used crucible?

You get a mixture of the composition of the crucible and the composition of the residue: useful QUALitatively, but NOT QUANTitatively

Methods of chemical analysis

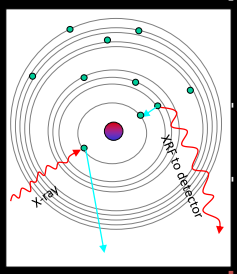
ICP, NAA, AAS, SEM-EDS, PIXE, EPMA, XRF…

Which one should I use?

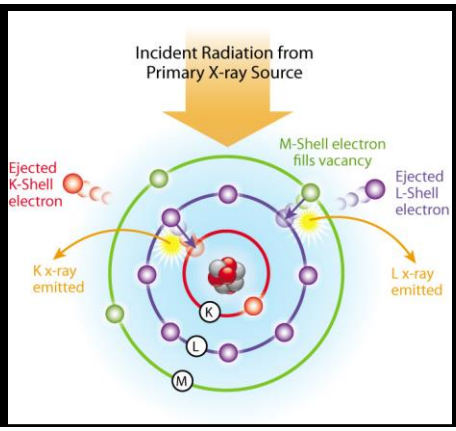
Some issues to consider

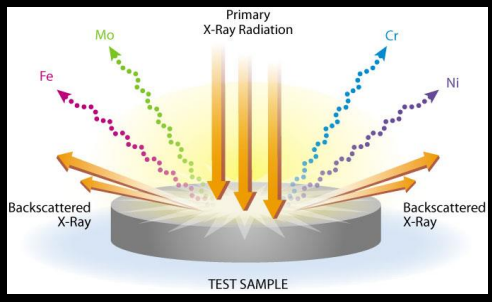
- Accuracy
- Detection limits
- Sensitivity
- Precision
- Cost
- Speed
- Invasiveness
- What do I want to know?
- What have others used before?
- Do I know what I'm doing?

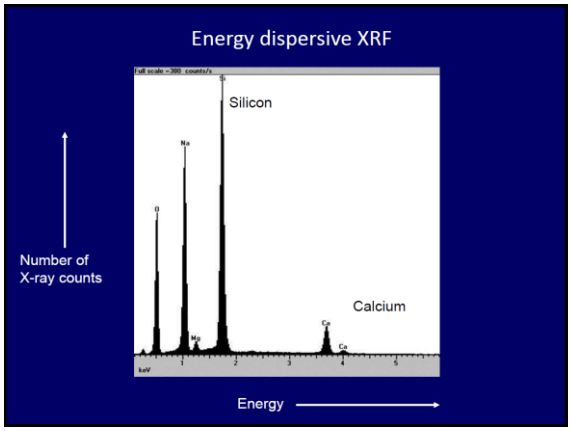
XRF foundations

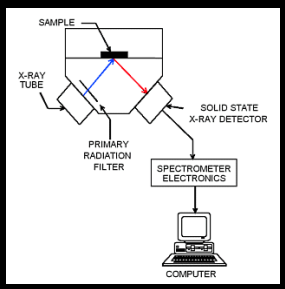


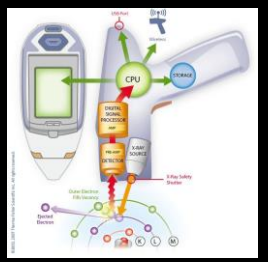
- A source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected from the atom.
- Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent X-rays .
- The energy of these rays is characteristic to each element; their intensity is relative to their concentration
- For elemental analysis of Na - U.











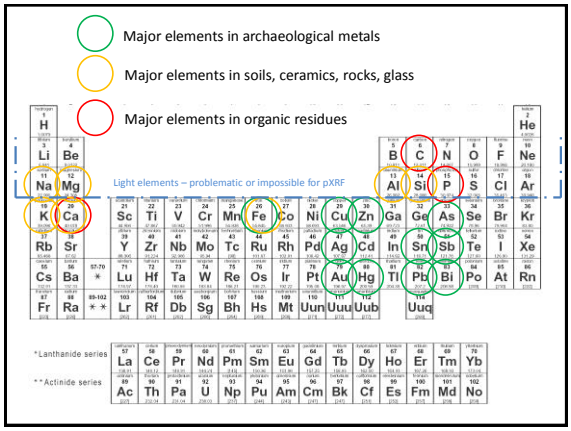
pXRF of metals: problems and potentials

Most of the issues discussed today affect *any* XRF

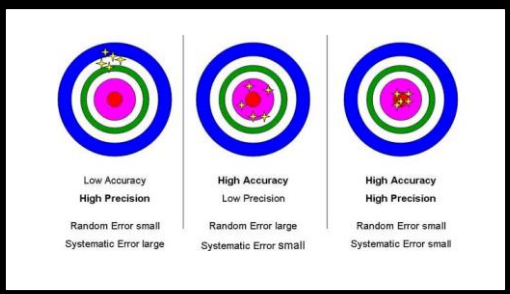
Specific advantages of pXRF
- Portable
- Fast
- Cheap
- Almost anyone can use it

Specific problems of pXRF
- Difficulties detecting light elements (signal absorbed by air)
- Almost anyone can use it

The main problems are not to do with the instrument but with its users!



Some important parameters



Precision and accuracy

Some important parameters

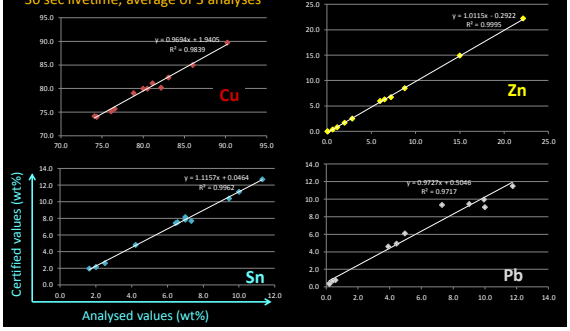
Use (certified) reference materials, aka 'standards'

Their composition should be as similar as possible to that of your analysed materials

Precision and accuracy

Olympus InnovX Alpha
Ag anode, SiPIN detector, 6mm window
Resolution ca 180 eV FWHM at 5.9 keV on AISI 316
40keV, 30.5 µA, 2mm Al filter, FP
30 sec livetime, average of 3 analyses

Portable XRF



XRF is a surface analytical technique

The Kanaya-Okayama range (i.e. penetration depth)

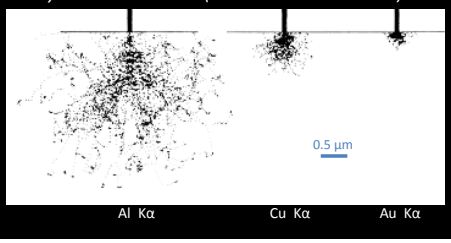
$$r(\mu m) = \frac{2.76 \times 10^{-2} A E_0^{1.67}}{\rho Z^{0.89}}$$

r = range (penetration)
ρ = density of the material (g/cm^3)
Z = atomic number
A = atomic mass
E_0 = accelerating voltage

XRF is a surface analytical technique

Archaeological metals are generally denser than any other materials so this problem is particularly relevant

X-ray excitation at 20 kV (Monte Carlo simulations)



XRF is a surface analytical technique

Typical accelerating voltages

- SEM-EDS 10-20 kV
- XRF 35-50 kV
- PIXE 500-1700 kV

So XRF is better than SEM-EDS, but still not great if you need bulk analysis

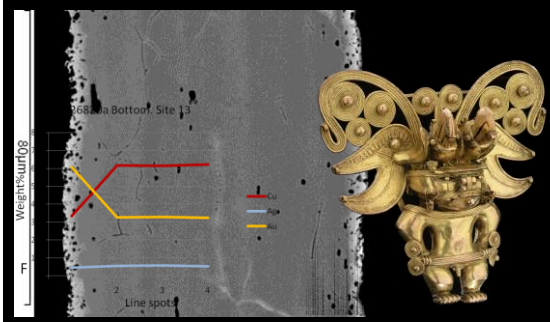
Is your surface composition representative of the bulk?

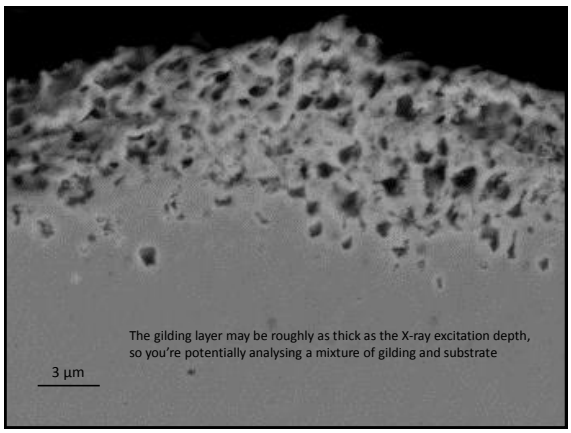
Two main factors may be affecting it:

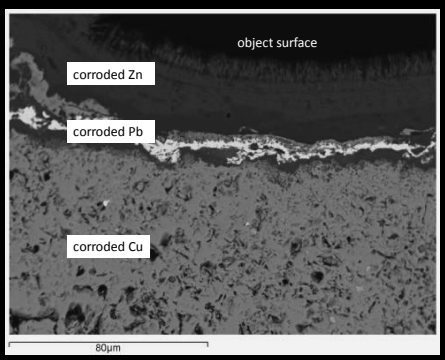
Intentional processes
ancient (e.g. gilding) or modern (e.g. conservation)

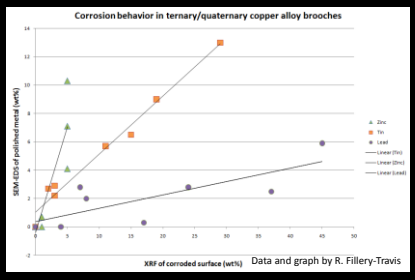
Post-depositional processes
hard to predict or model

Depletion gilding







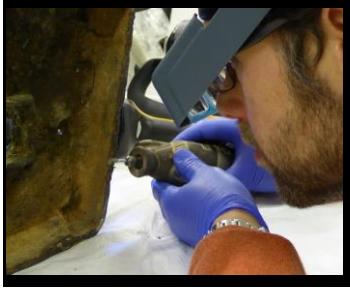


Data and graph by R. Fillery-Travis

Pb and Sn tend to appear enriched on corroded bronze surfaces
Zn tends to appear depleted ("dezincification")

BUT this is not always the case, and
the extent of this phenomenon is not predictable

Can I overcome this problem by cleaning the corrosion products from the surface?



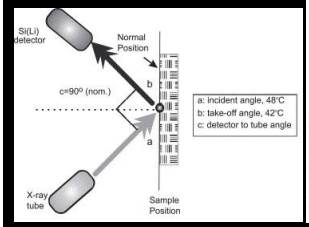
Can I overcome this problem by cleaning the corrosion products from the surface?

Potentially yes – but how can you be sure?

More factors to consider:

- Analytical geometry
- Analytical spot size
- Metal homogeneity

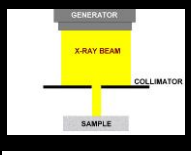
Analytical geometry



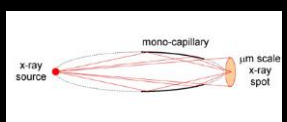
XRF is designed for flat analytical surfaces, at fixed analytical distances and at fixed angles

Analytical spot size: COLLIMATORS

By default, spot size in most pXRFs I know is around 5-10 mm in diameter, but this can be collimated down to a few micrometers



A mask that 'blocks' part of the X-rays.
Results in a loss of beam intensity



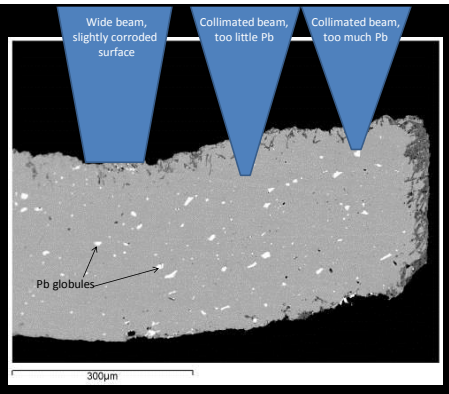
One of more glasses where the X-rays are reflected so that they can be focused in a smaller spot. Can result in an increase of beam intensity

So I'm analysing a clean flat spot with a focused beam – is this ok?

Potentially yes – but how can you be sure?

Metal homogeneity

Collimated beam on clean spot, reasonably good results



What's best?

All of these hard-to-control factors affect your

sampling uncertainty

(see brief, very useful information by the Analytical Reports Committee of the Royal Society of Chemistry at www.sc.org/amc)

Some of the main potentials

Analyses *in situ*
(selecting what your questions require, not what you are given; adapting sampling to initial results and new questions)

Fast screening analyses
(e.g. qualitative classification copper/bronze/brass)

Large sample sizes
(e.g. 'trends' as opposed to individual samples)

BUT
The use of qualitative or 'screening' analyses is no excuse for the lack of a robust assessment of data quality and sampling uncertainty

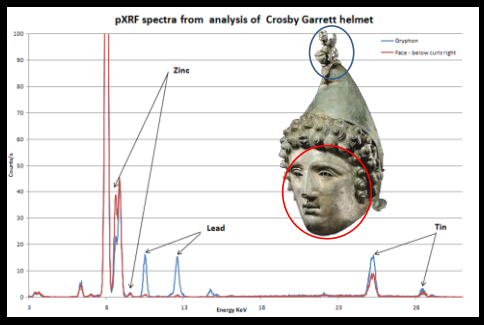
Is there no hope then?

The main problems are not to do with the instrument but with its users!

An example of fast screening analysis

Work by Ruth Fillery-Travis

Crosby Garrett helmet



Showing spectra rather than actual figures – good enough for these purposes and it prevents people from misusing your data

SEM-EDS of archaeological metals

(scanning electron microscopy with energy dispersive spectroscopy)

POTENTIALS,
PROBLEMS
& APPLICATIONS

SEM-EDS of archaeological metals

(scanning electron microscopy with energy dispersive spectroscopy)

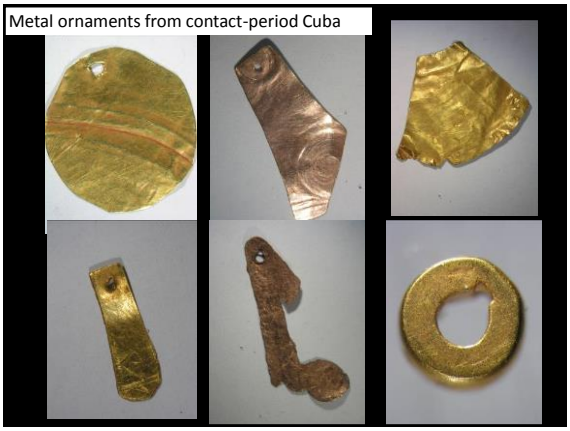
Some advantages

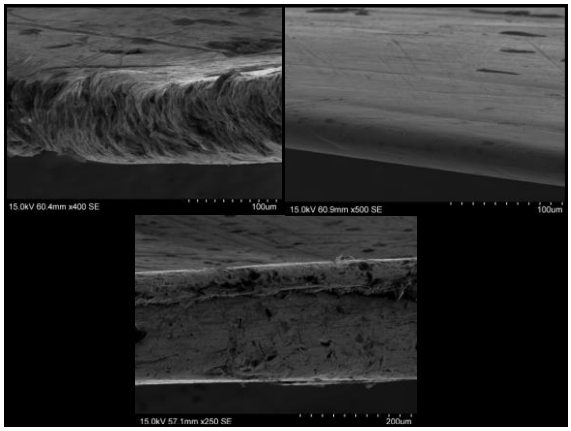
High magnification
Focus
Depth of field
High quality images
Chemical information

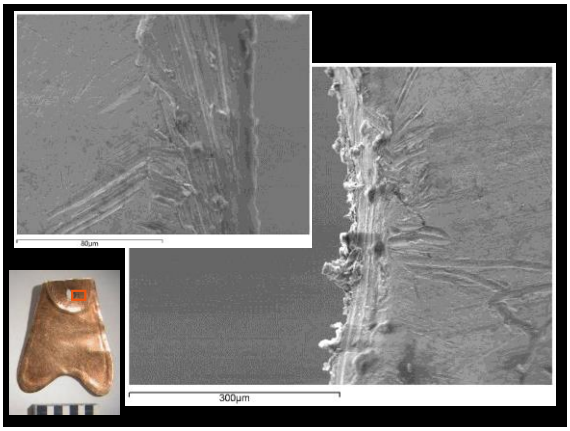
Some shortcomings

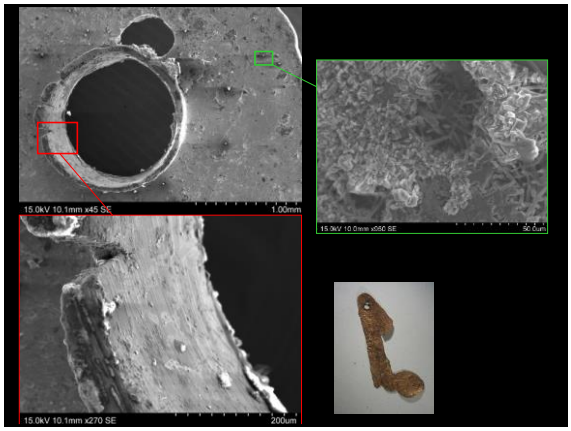
Limited sample size
High detection limits
(no trace elements)

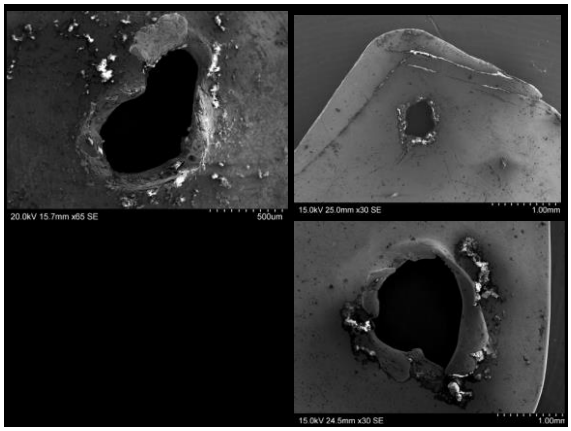
Metal ornaments from contact-period Cuba

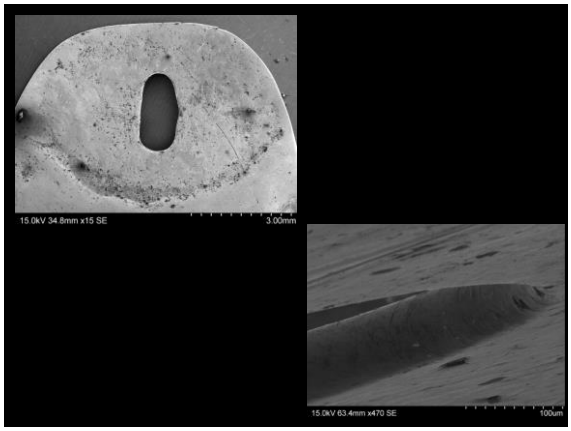


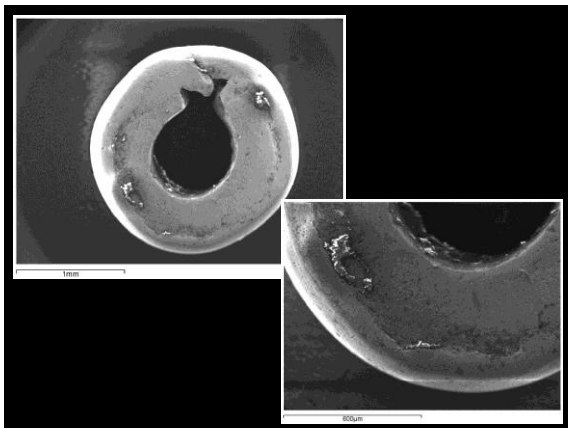


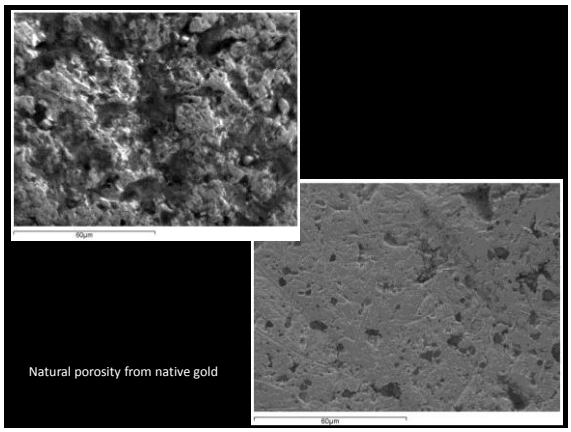


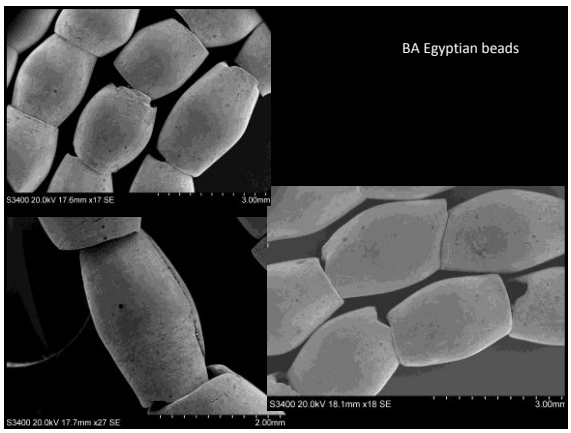




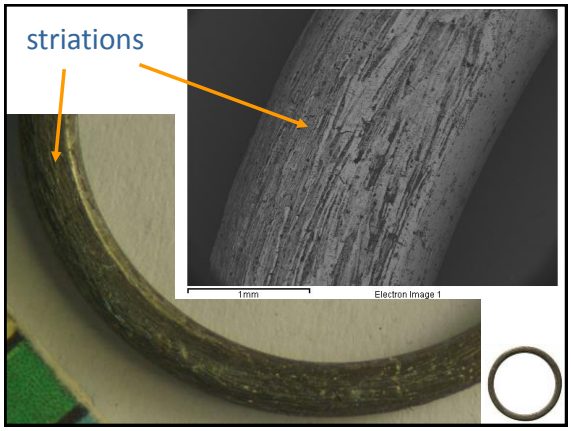


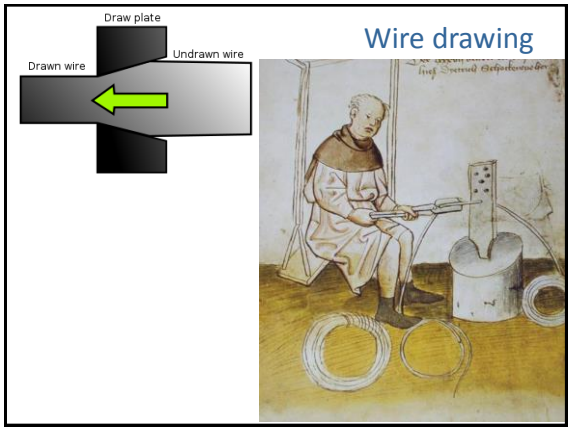




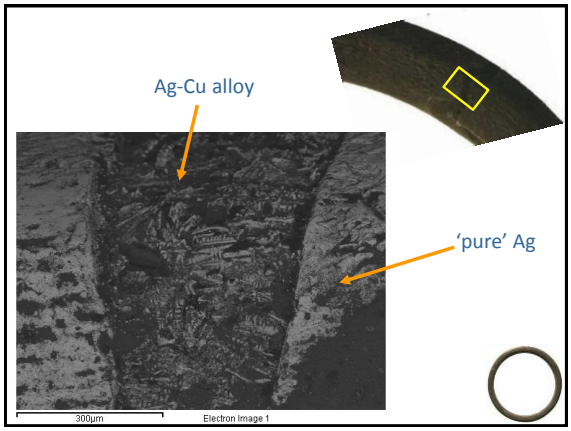


Silver rings from Iron Age Spain


striations
1mm
Electron Image 1


Draw plate
Undrawn wire
Drawn wire
Wire drawing


solder


Ag-Cu alloy
'pure' Ag
300µm
Electron Image 1