A Closer Look at Gold Bullion Fire Assay

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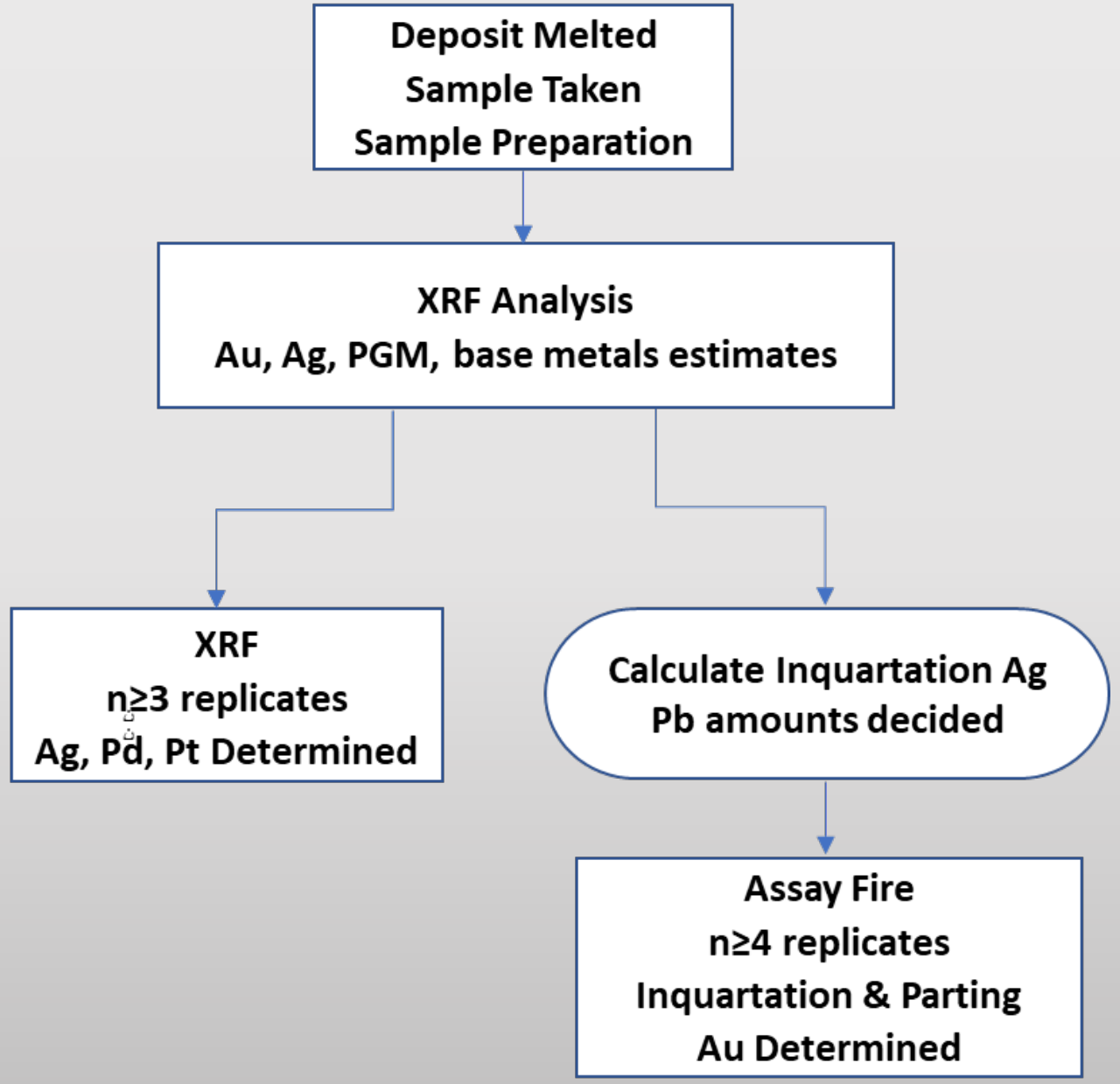
Literature

Paulo Battaini, Edoardo Bemporad, Daniele De Felicis, The fire assay reloaded, Gold Bull., 2014, **47**, 9-20.

I. Ciabatti (2019) Gold parting with nitric acid in gold-silver alloys. Substantia 3(1) Suppl.: 53-60. doi:10.13128/Substantia-606

XRF & Fire Assay

- Fire Assay required for Au settlement
- Parallel determinations
- Ag, Pd, Pt determined by XRF
- Saves time, labour, material
- Frees furnace time
- Can use XRF for provisional settlements

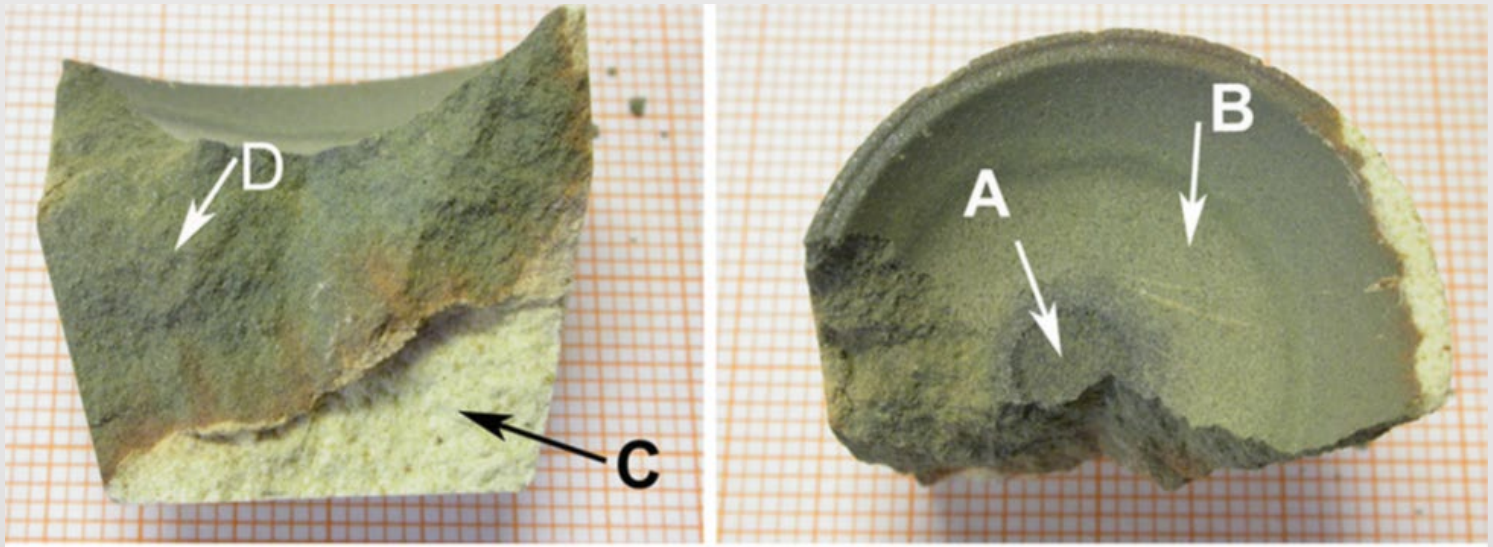


Assay Fire Cupellation – For Determining Au
500 mg sample

Photo courtesy of Rand Refinery, SA

- 50 mg Cu added
- 2.5 x Ag to Au added (Inquartation)
- Wrap in lead foil
- Place in cupel in furnace @ 1060^{o}C
- Pb and sample melt
- PbO & base metal oxides form and absorbed into cupel
- Ag-Au bead remains

Element Determination in Used Cupel by XRF
Cross Sectioned and Top View

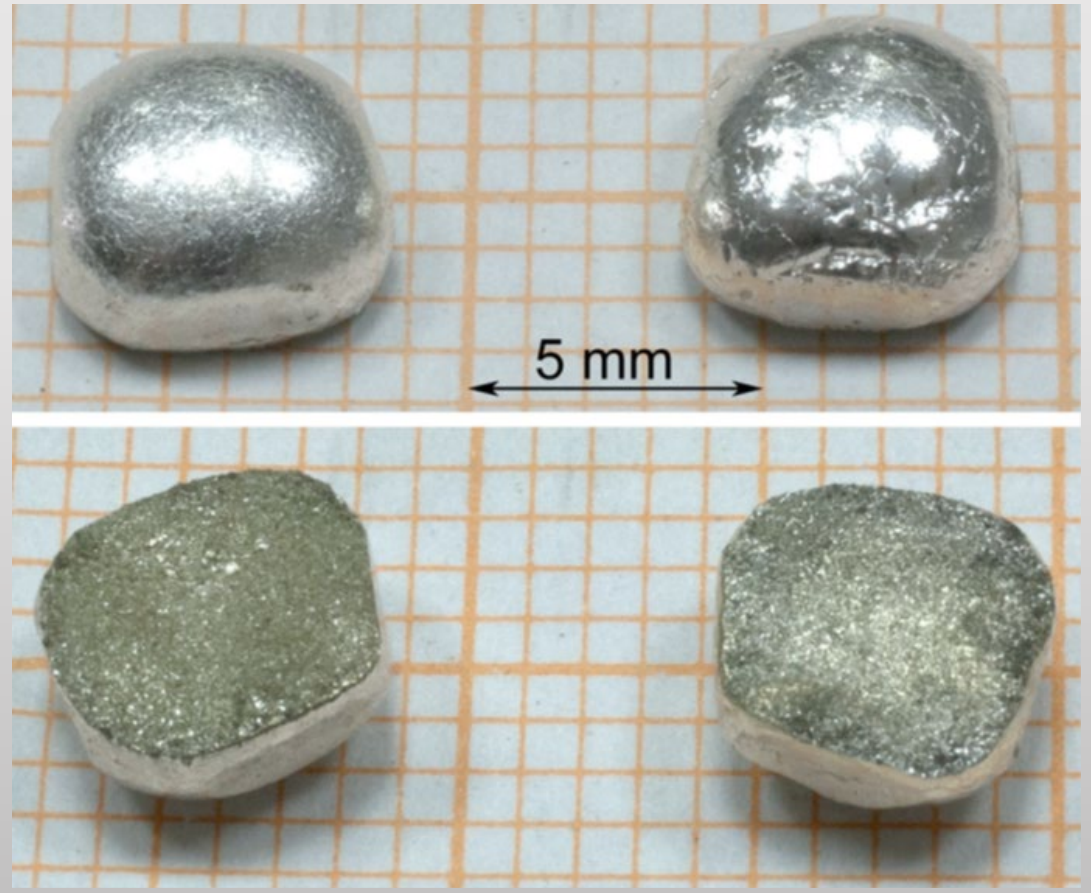


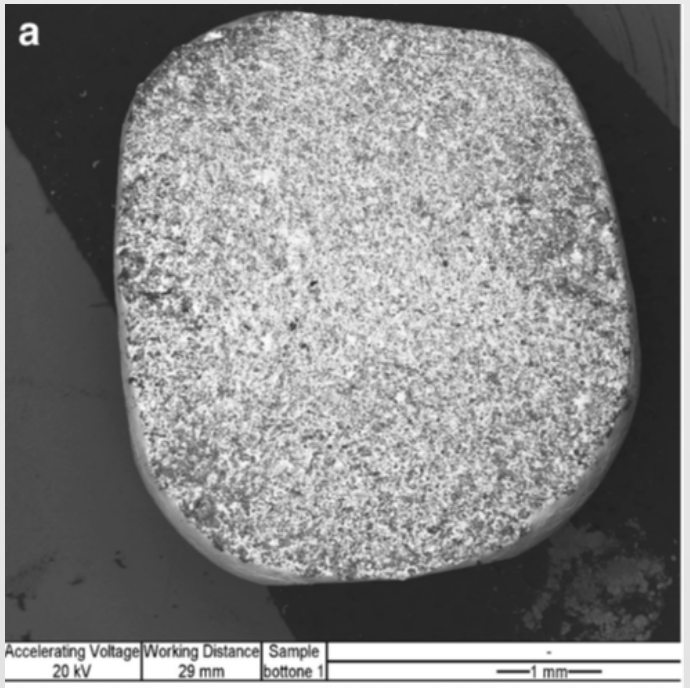
	Weight %			
	Point A	Point B	Point C	Point D
O	35.62	40.87	45.79	36.05
Na	0.17	-	1.22	-
Mg	36.08	52.14	45.43	31.11
Si	1.20	-	6.18	2.80
Fe	0.30	0.37	-	0.18
Cu	0.82	0.62	-	0.83
Ag	0.40	-	-	-
Pb	25.41	6.00	-	28.62
Ca	-	-	1.37	0.42

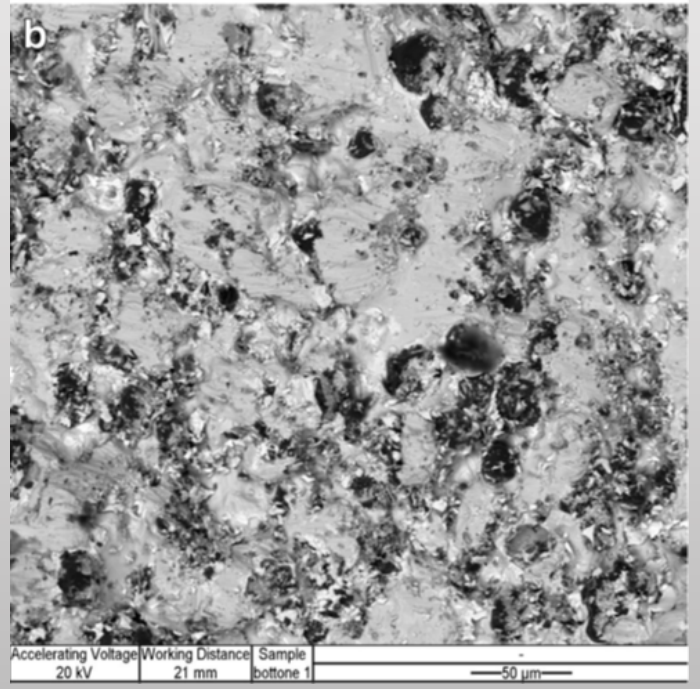
from Battaini, *et al,* 2014

Assay Button (Ag Au alloy)

- Rough bottom surface
- Easy to pick up cupel material
- Cleaning important







(from Battaini, *et al,* 2014)

Annealing Rolled Assay Buttons

Transmission Electron Microscopy (TEM) images of:

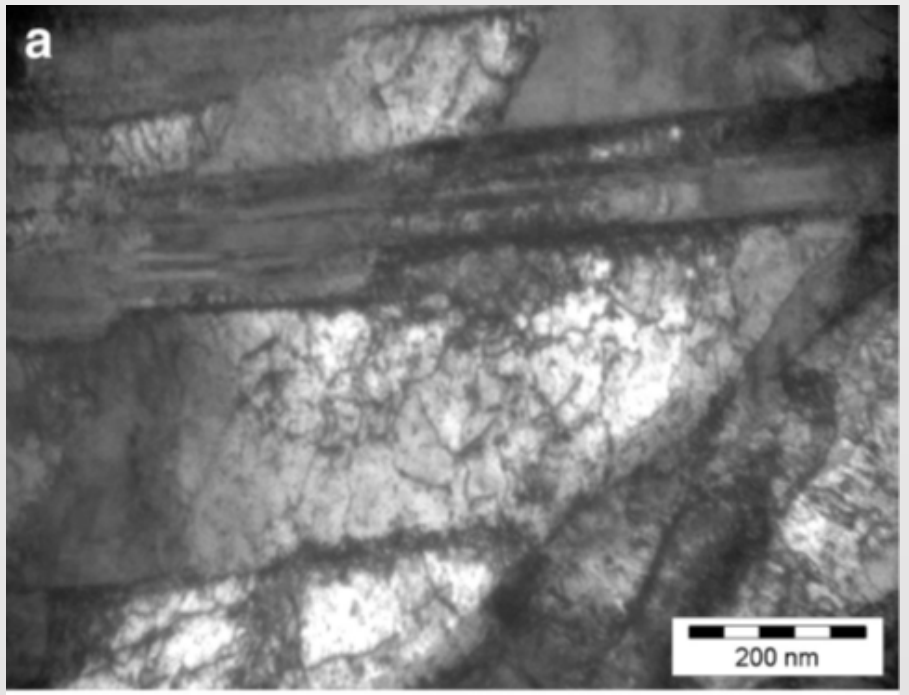
a) Hammered or rolled (work hardened) bead.

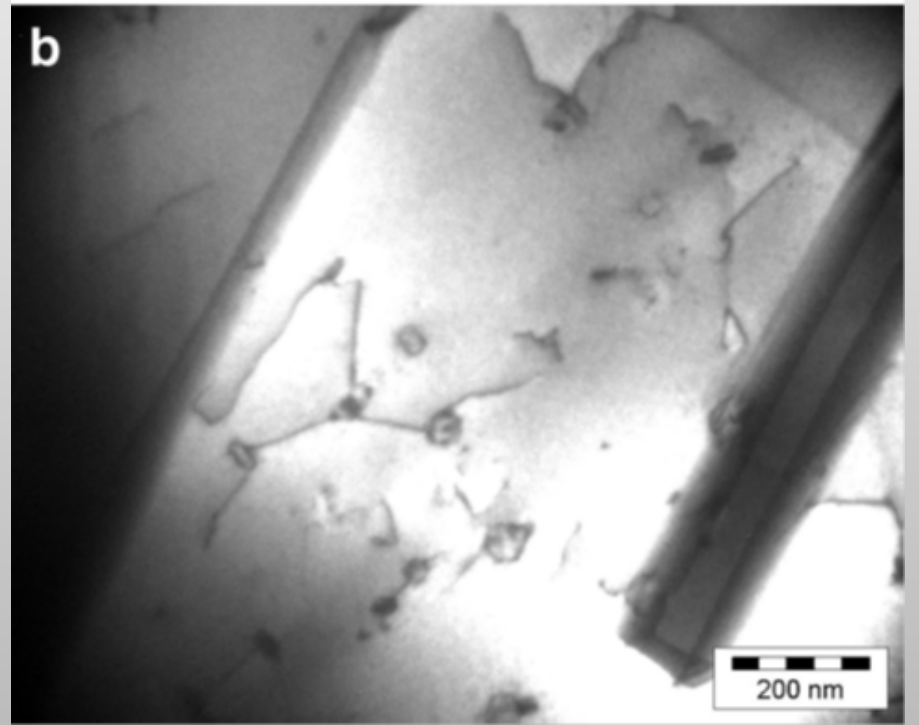
b) The same piece in a) after flame annealing.

Re-crystallization reduces dislocations

Easier to roll out

(from Battaini, *et al,* 2014)



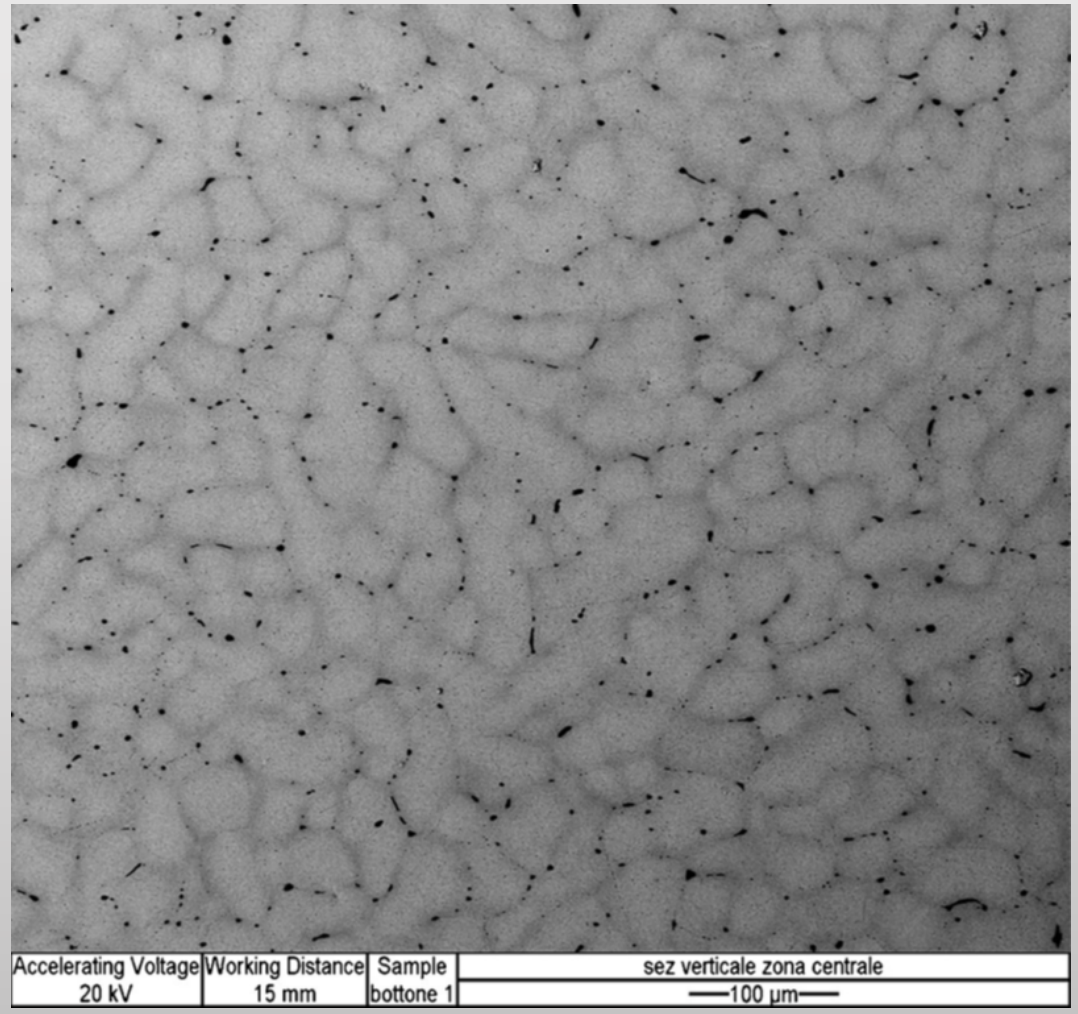


After Cupellation Assay Fire Button

SEM backscattered electron image of a cross sectioned button after cupellation.

- Fine grain structure due to micro-segregation of the silver.
- The concentration of silver along the grain boundaries is 75%. The black spots are Cu and Ag oxides.

(from Battaini, *et al,* 2014)



Copper in Silver Button After Cupellation (Assay Fire)

- All procedures add Cu with Inquartation Ag
- No Copper – Silver Button Cracks during rolling → X
- Addition of Copper required for good rolling ✓

Is Cu retained in sample after cupellation?

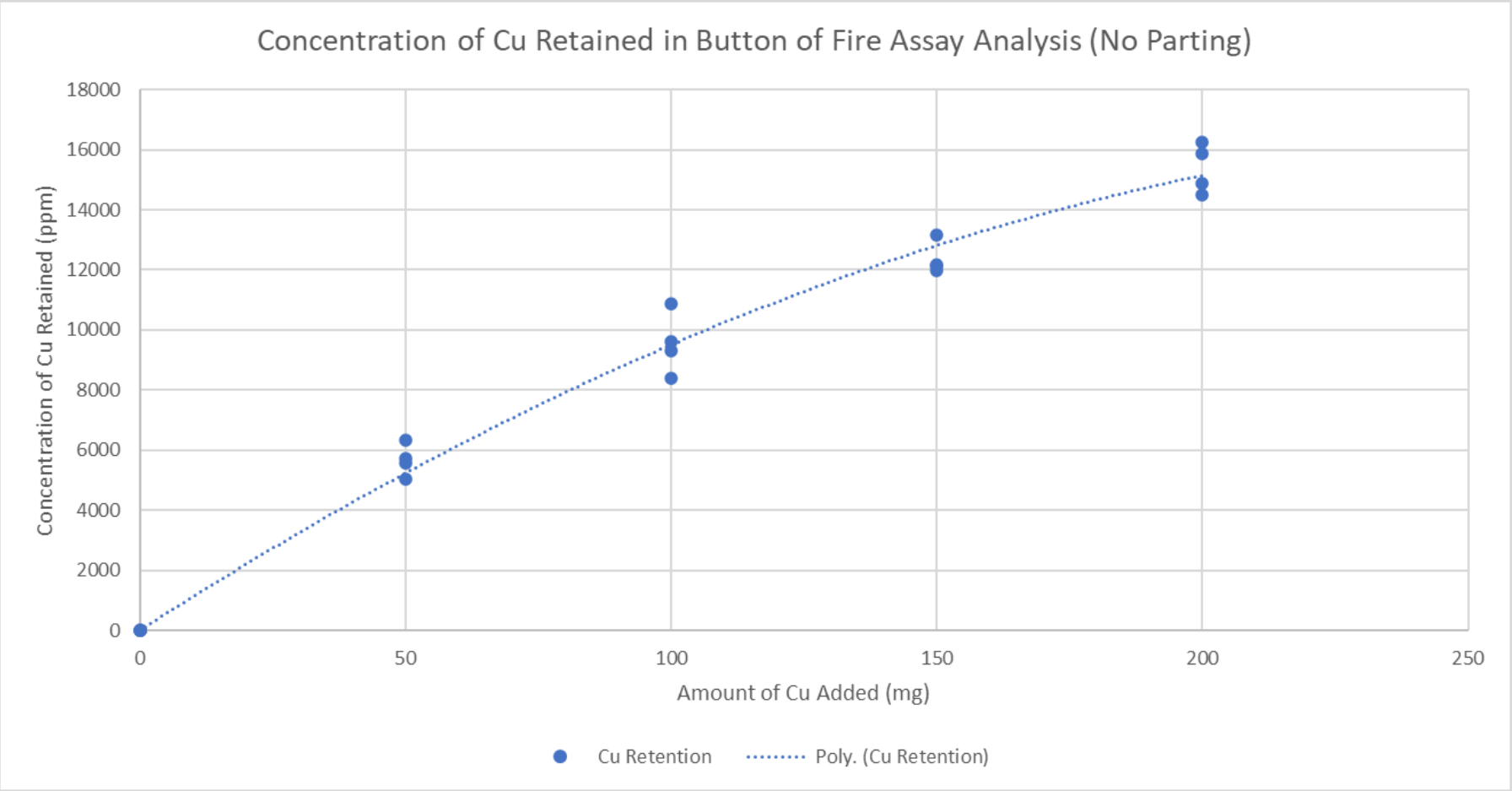
Photo from Pankaj Deshmukh, MMTC PAMP, 2021 LBMA A&R Conference

Determine Cu retained in Ag Button After Cupellation

- Sample:
  - 500 mg Proof Au (999.99‰) or Sample X; 1250 mg Ag (999.9 ‰); 10 g Pb foil
  - Vary added Cu: 0, 50, 100, 150, 200 mg
  - 4 replicates
- Cupel at 1060^{o}C for 25 minutes
- Dissolve each sample; 10 ml 50% HNO_3 then 10 ml HCl
- Ag precipitates as AgCl; Au & Cu dissolve
- Determine Cu in Ag Button by ICP-OES (after cupellation)

Cu Retained in Ag Button After Cupellation

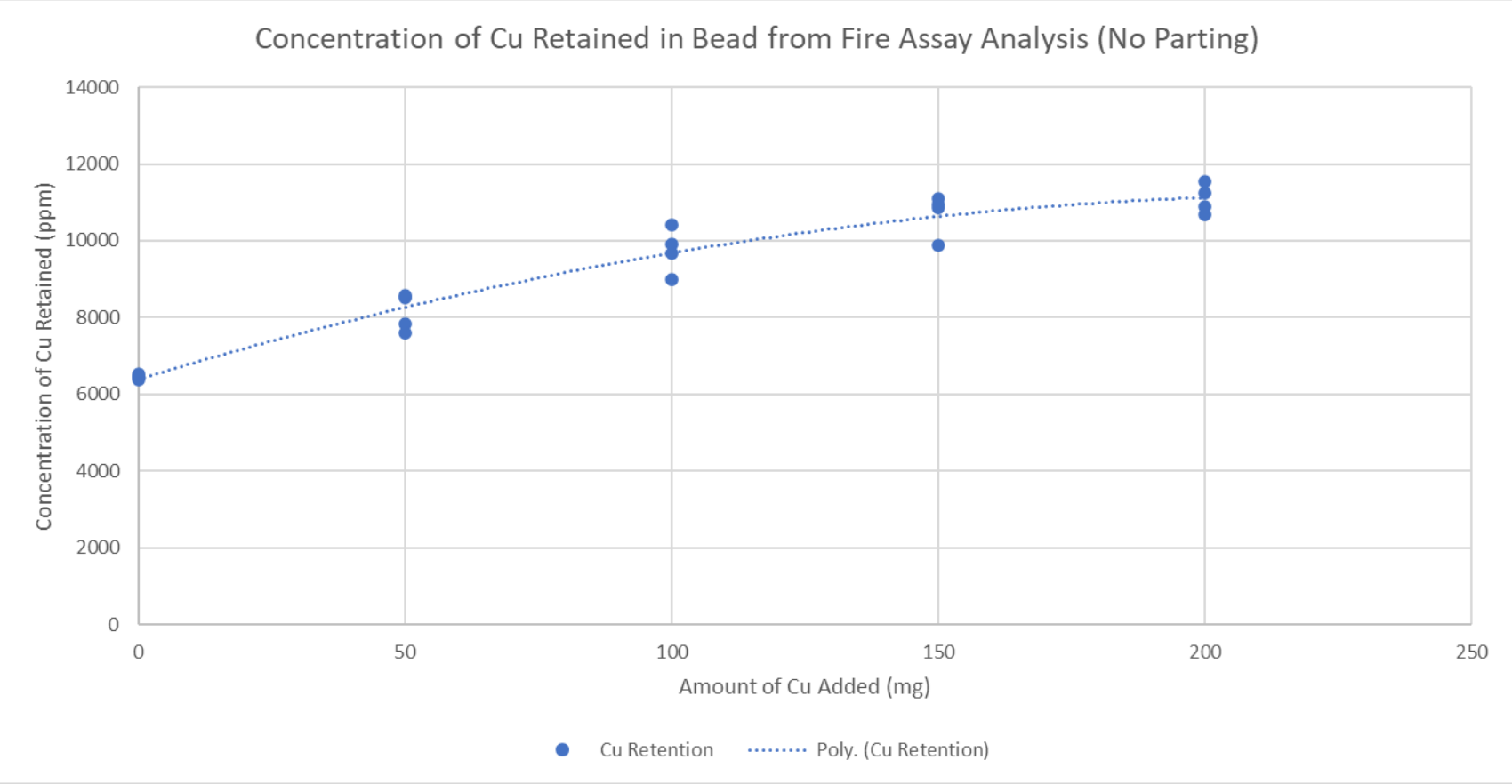
Cu added to 500 mg Proof Au



(no Cu in dissolved cornets after parting)

Cu Retained in Ag Button After Cupellation

Cu added to 500 mg Au Deposit X



Element	Concentration, ‰
Ag	72.21
Au	670.72
Cd	2
Cu	***212.6***
Fe	0.9
Ni	2.2
Pb	7.7
Pd	0.4
Pt	0.2
Sn	1.3
Zn	29.8

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Other elements retained in Assay Button?

No added Cu; Au Deposit X

	Dore (XRF)	Retained in Ag Button
Element	Concentration, ‰	Concentration, µg/g
Ag	72.21	
Au	670.72	all
Cd	2	
Cu	212.6	6450
Fe	0.9	
Mg		3860
Ni	2.2	12
Pb	7.7	2780
Pd	0.4	370
Pt	0.2	125
Se	0	
Sn	1.3	
Te	0	
Zn	29.8	925

Retained Elements in Assay Button

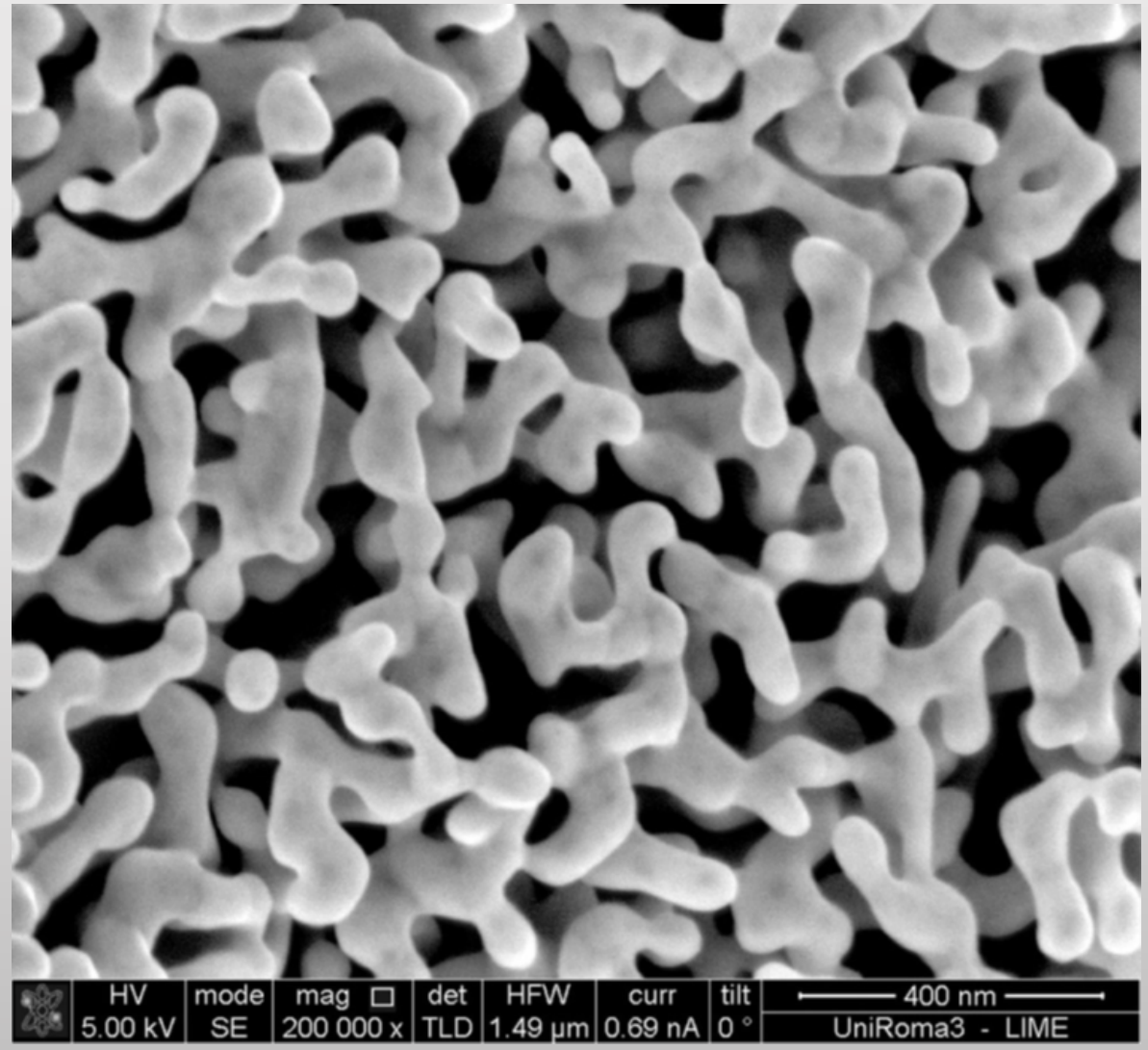
- Base elements not completely removed by cupellation Assay Fire
  - Cu – good for rolling the button!
  - Base metals when at high concentrations in sample
  - Pd, Pt, other platinum group metals
- Magnesium absorbed from cupel material

- Nitric acid parting removes retained elements from Au except PGMs

After Parting

SEM image: Gold cornet microstructure.

- The magnification is 200,000x
- Au nanoporous morphology observed throughout the cornet.
- Very large surface area



(from Battaini, *et al,* 2014)

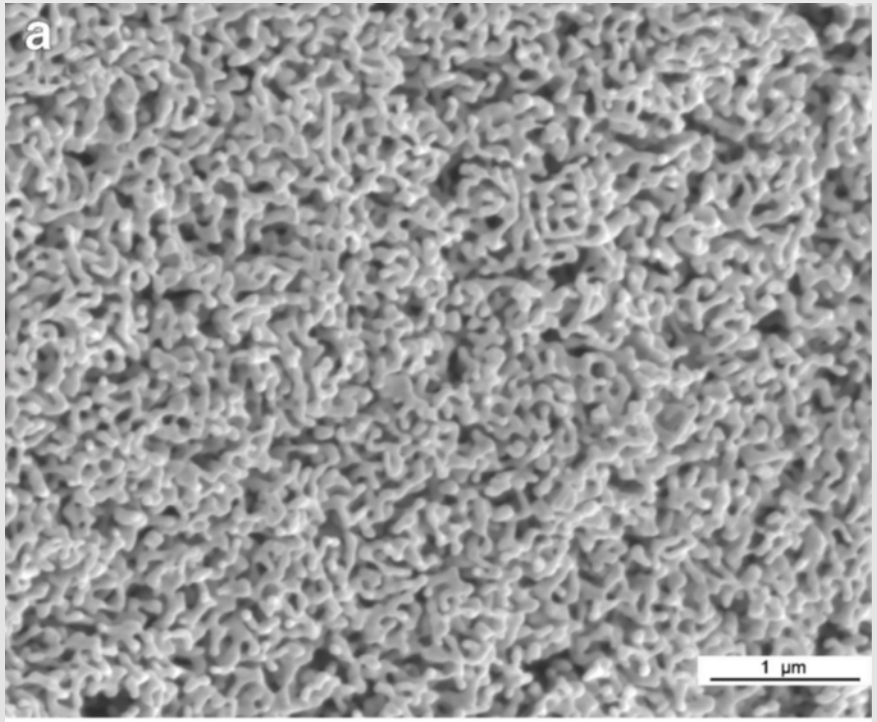
Effect of Annealing Gold Cornet

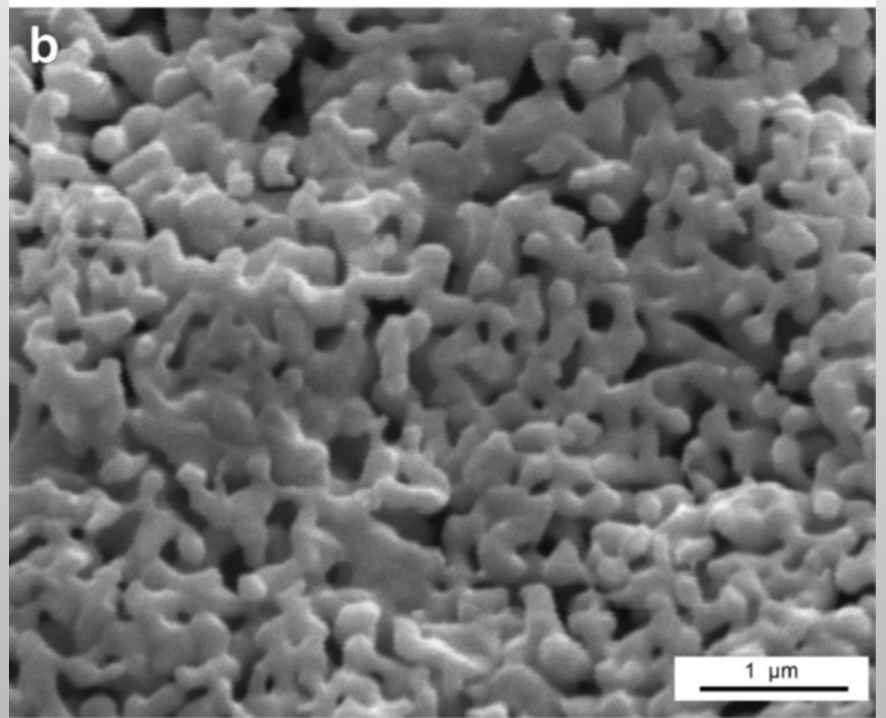
Two SEM images of the same gold cornet area under the same magnification.

Image a) Au cornet structure after parting

Image b) after heating to a temperature of 450°C.

- annealing drives coarsening of Au nanostructures
- Strengthens cornet (doesn't fall apart)
- Smaller size

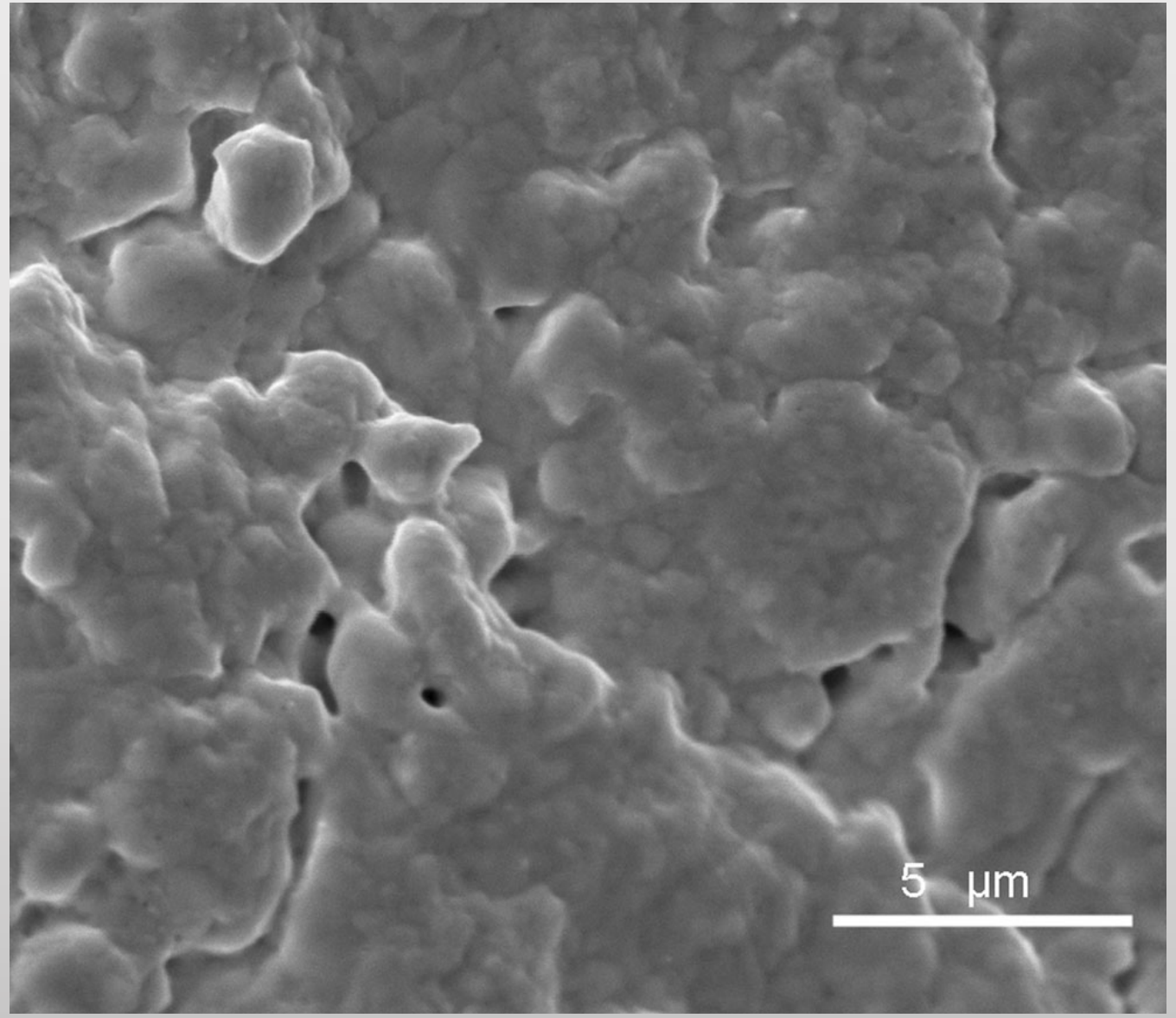




(from Battaini, *et al,* 2014)

Effect of Annealing

- Annealing at 500^{o}C
- Au Nanoporous microstructure gone
- Au microstructure fused together
- Stronger; will not fall apart



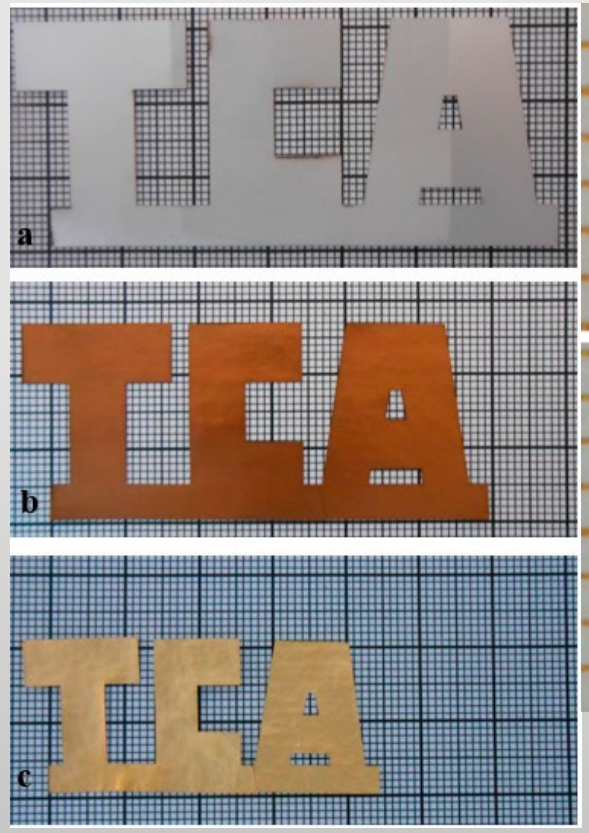
(from Battaini, *et al,* 2014)

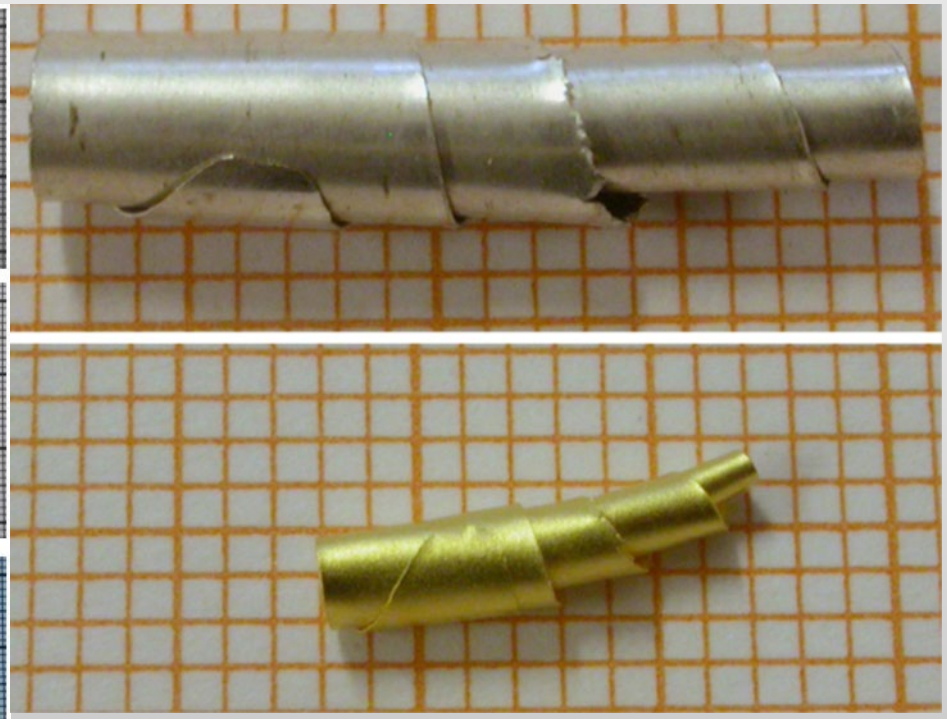
Gold cornet after parting and annealing

Before parting

After parting

After annealing





Before parting

After parting
After annealing

Ciabatti, 2019

from Battaini, *et al,* 2014

Takeaways:

- Images shown provide a better understanding of Fire Assay process
  - Cupellation
  - Annealing
  - Parting
- Copper retained in Au-Ag alloy during cupellation
  - Beneficial for rolling large silver-gold bead in the Assay Fire
- Cupellation of Inquarted samples: base elements not 100% removed
- Parting dissolves retained base elements, except PGMs

Acknowledgements

- Royal Canadian Mint, Canada
- Rand Refinery SA