

Daguerreotype Research

Funded by the National Science Foundation

+

The University of Rochester

George Eastman House International Museum of Photography and Film

Science and the Preservation of Daguerreotypes

Material Science & Technology 2014

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Louis-Jacques-Mandé Daguerre

Daguerreotype by Jean Baptiste Sabatier-Blot: daguerreotype, 1844

George Eastman House Collection

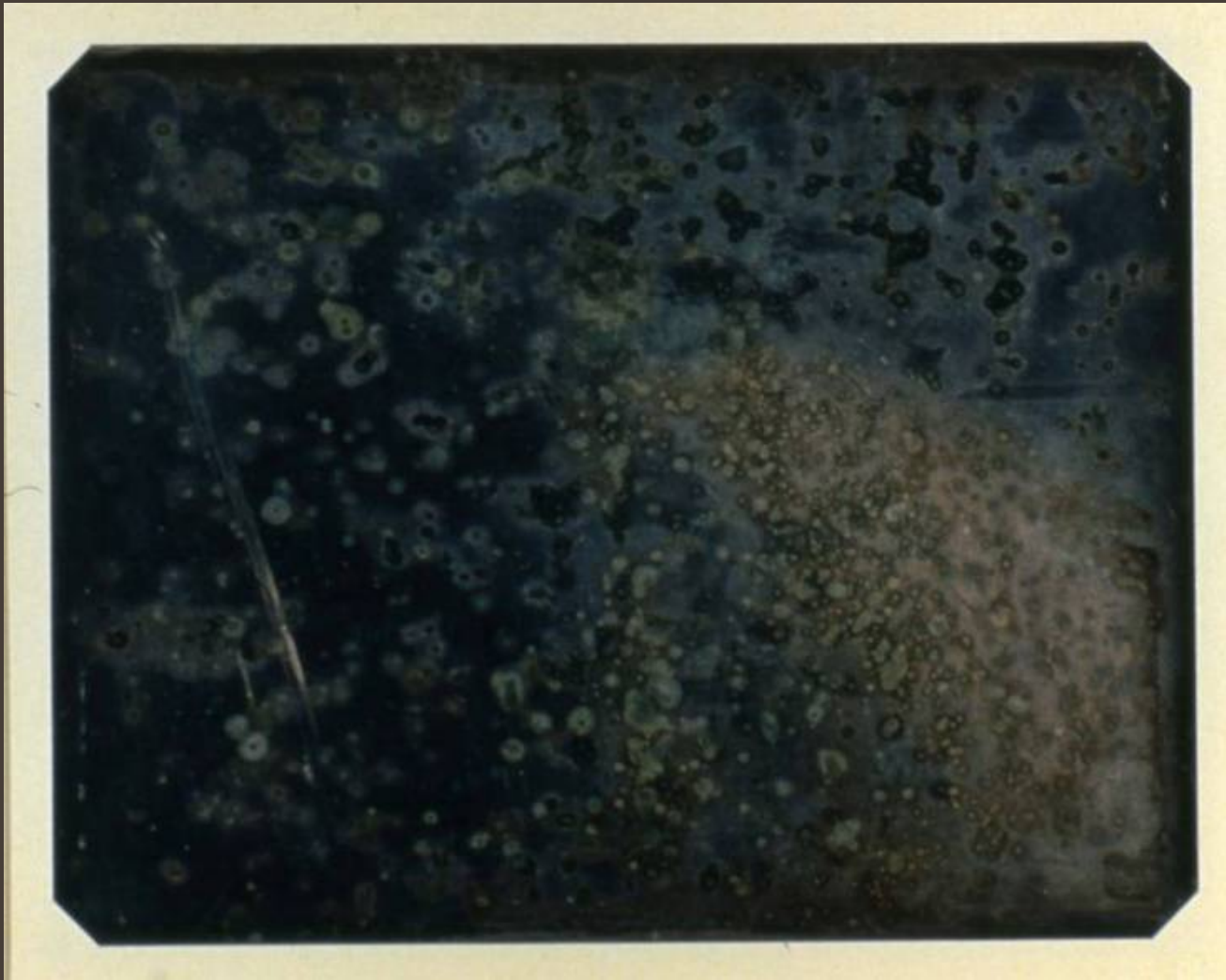
What did people first see?



Bayerisches Museum, Munich; approximately 6" x 8"

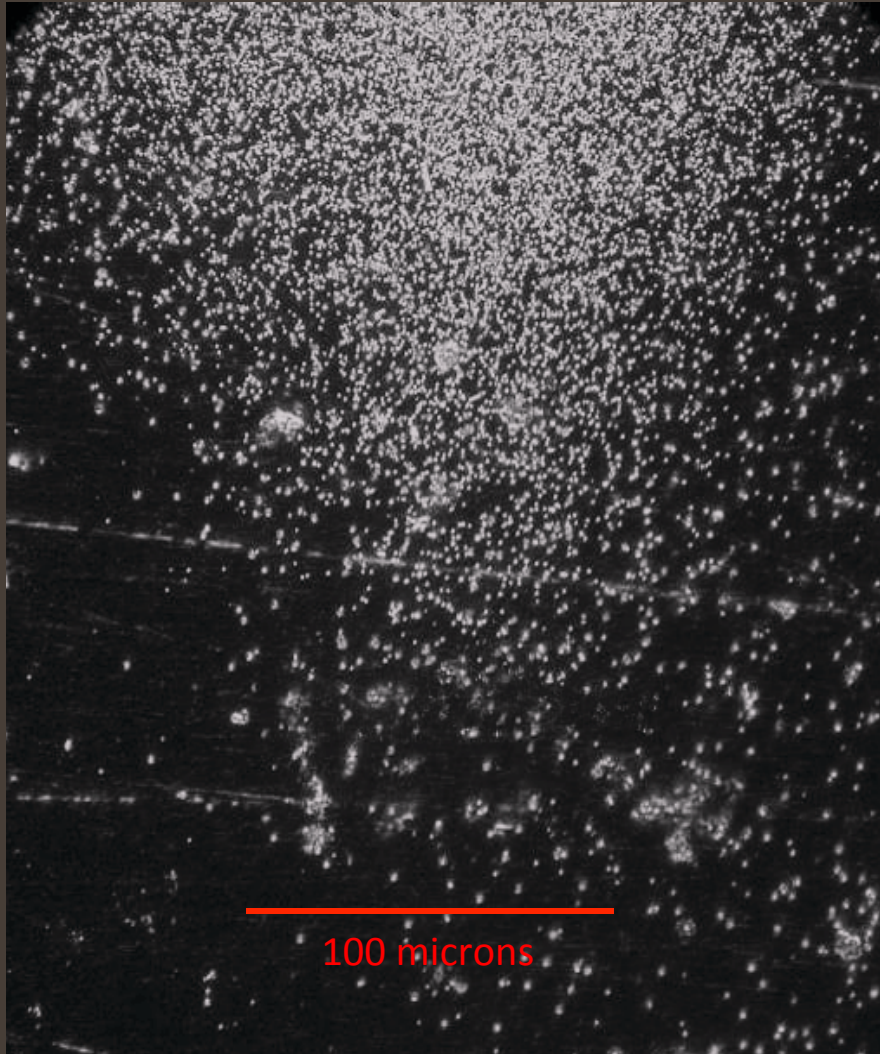
Boulevard du Temple, Paris ca. 1838-39; an authentically named "Daguerreotype"

What do people sometimes see today?



An attributed Daguerre “daguerreotype”: French collection
(2007)

What is a daguerreotype?

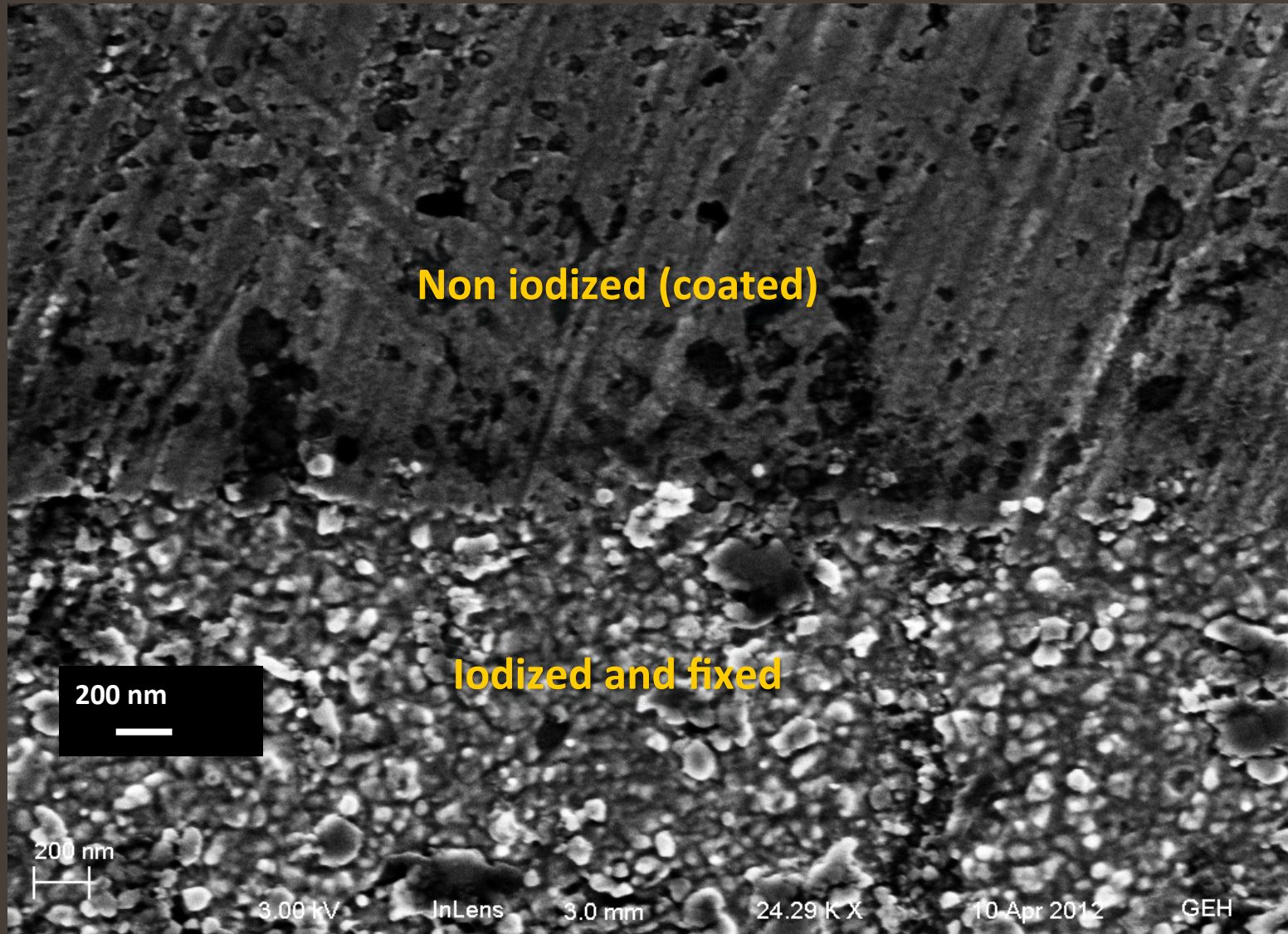


Darkfield microscopy @ 500X magnification



Unidentified Young Girl: Southworth & Hawes: ca 1850
whole plate; George Eastman House collection

The surface effect of sensitization and fixing



Daguerreotypes are iconic first images in extraordinary high native resolution



Panorama of Paris ca. 1845

Friedrich von Martens

78:0168:0136

37.6 cm x 10.6 cm (15" 4.25")

George Eastman House International Museum of Photography & Film

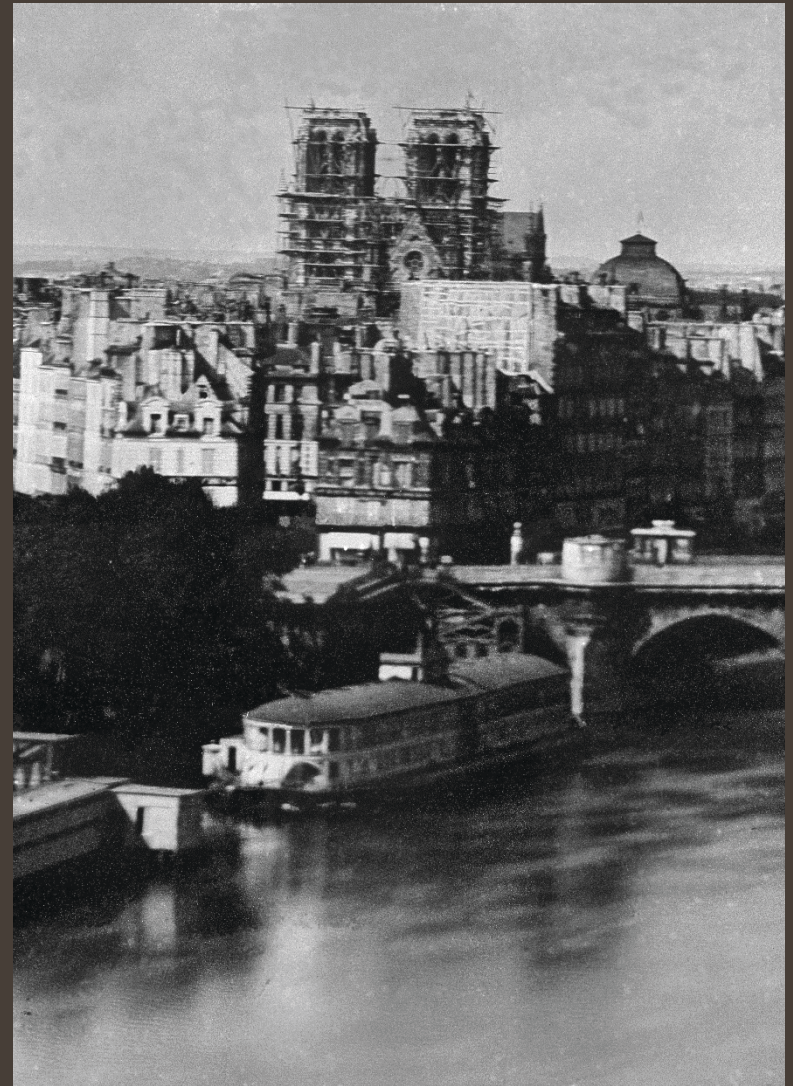
Detail views

Pont des Arts and The Académie



Google Earth Street View 2009

Nôtre Dame



Resolution of the daguerreotype in an American iconic treasure



2 meters

The Cincinnati waterfront daguerreotype panorama

Made by Fontayne and Porter; 1848

Owned by the Library of Cincinnati and Hamilton county



Whole plate format: 6.5" x 8.5" (15.5cm x 21.6cm)



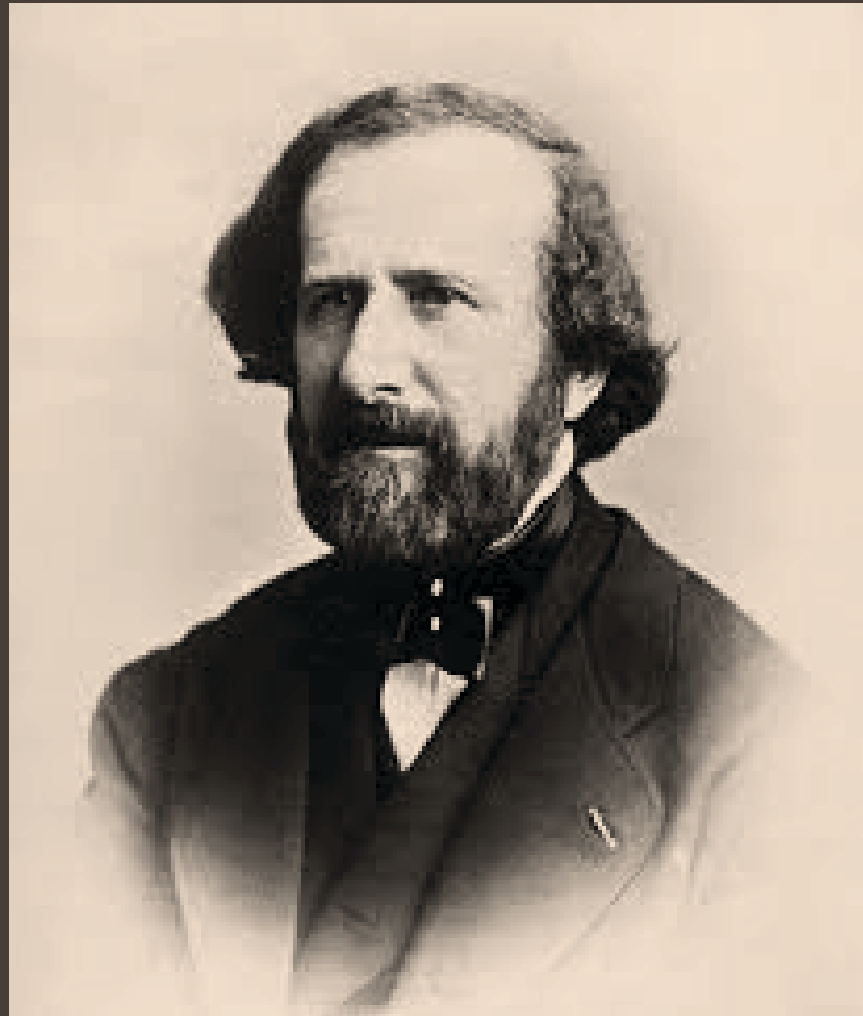
Region approximately 10 mm x 12 mm



1000 μ

3 Research Themes

1. The long-term preservation and conservation of the daguerreotype for its cultural, artistic, and historic value
2. Material science research to serve the above goal and to explain the material science of the daguerreotype process, and its physical responses over time
3. To unlock historical content that is in the material structure of the daguerreotype, and correlate forensic data to the historical record



Armand Hippolyte Fizeau
Chemist, physicist, inventor, visionary

Literary Gazette; and Journal of the Belles Lettres, Arts, Sciences, &c. (London) No. 1231 (22 August 1840): 545. This text appears as part of a column under the header: "PARIS LETTER. Academy of Sciences, August 18, 1840."

M. Fizeau communicated a method of fixing photographic impressions obtained with the daguerreotype, by means of a chlorure of gold. The mixture employed was one gramme of chlorure of gold dissolved in half a litre of pure water (distilled), to be mixed with three grammes of hyposulphite of soda, also dissolved in half a litre of water. The two mixtures to be poured gradually together, and well stirred

Fizeau's recipe rediscovered 170 years later

Tunability and Stability of Gold Nanoparticles Obtained from Chloroauric Acid and Sodium Thiosulfate Reaction

Nanoscale Research Letters 2012, 7:337 doi:10.1186/1556-276X-7-337

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University of Louisville

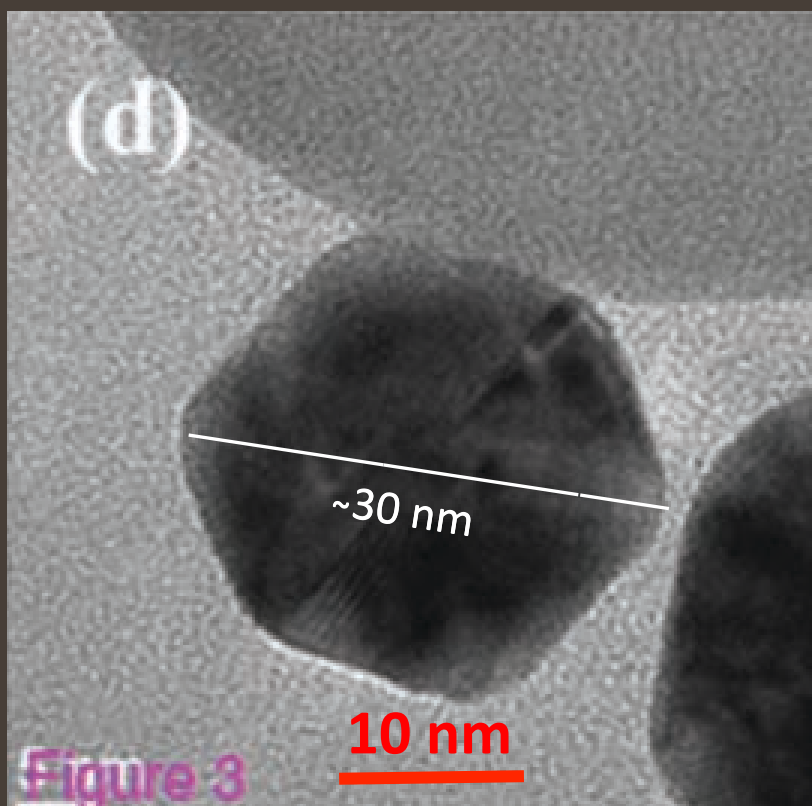
Emission colors of different molar ratio solutions of gold chloride and sodium thiosulfate, indicating different size, shape and stability of gold nanoparticles over 24 hours



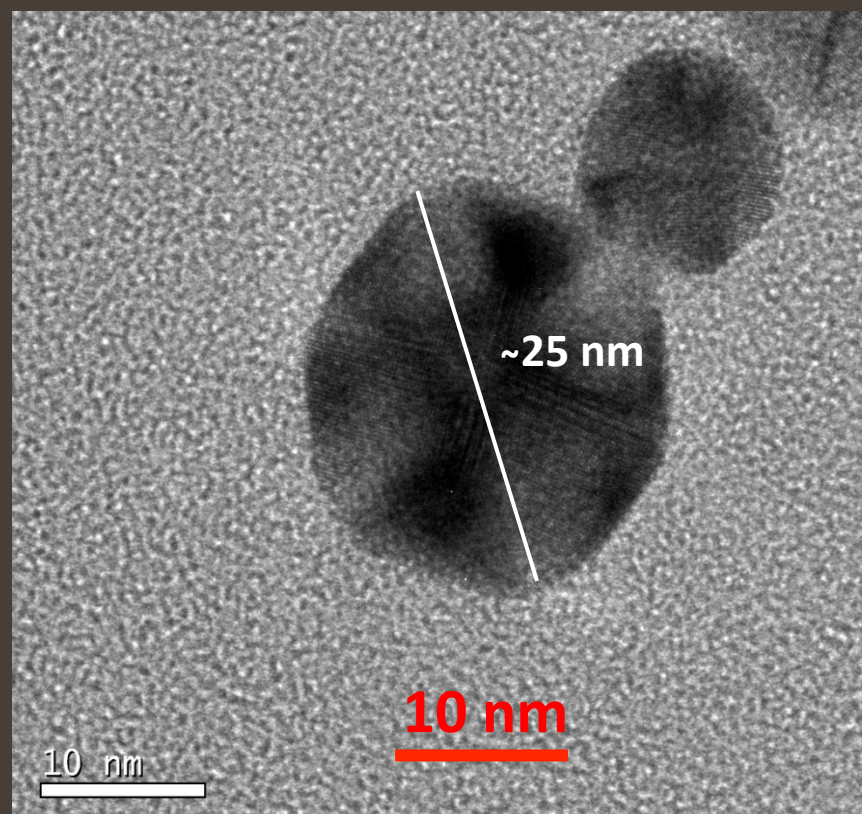
George Eastman House

Fizeau's Recipe

Transmission Electron Microscope



University of Louisville

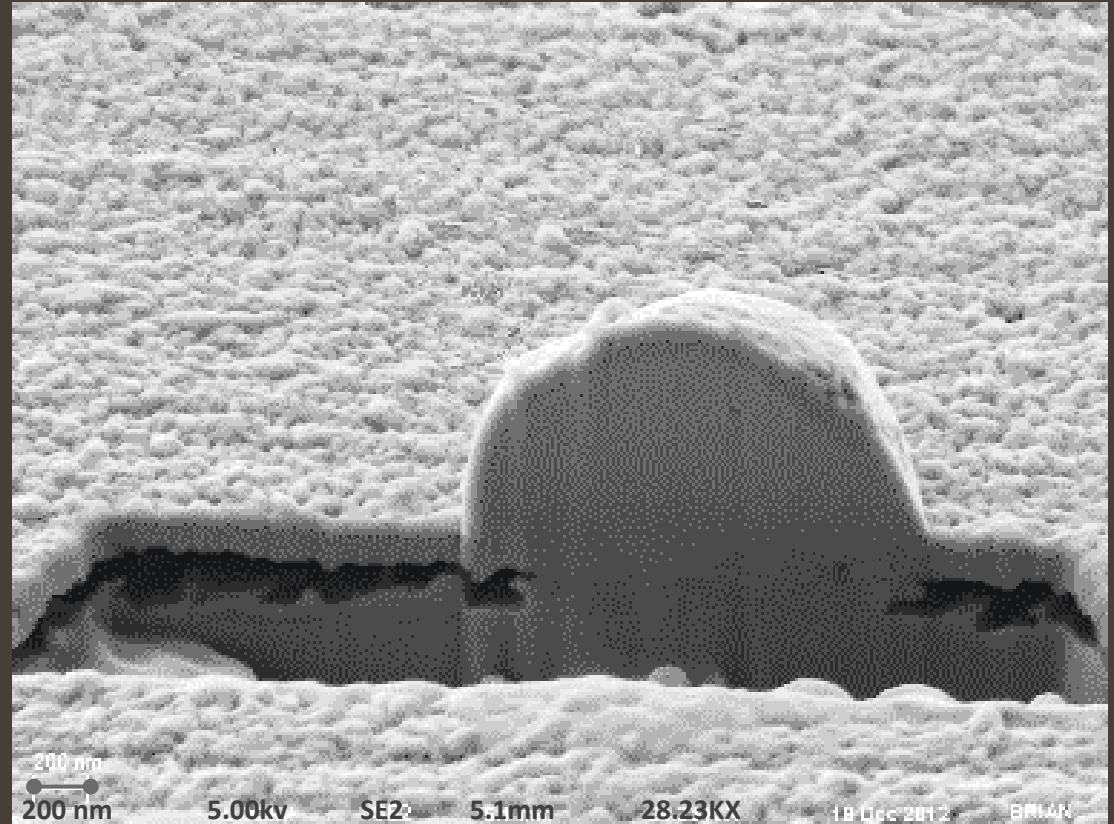


Eastman House

What happens when the solution encounters the silver plate?



Unidentified man; George Eastman House Study collection; 6th plate (2.75' x 3.25'') ca. 1850

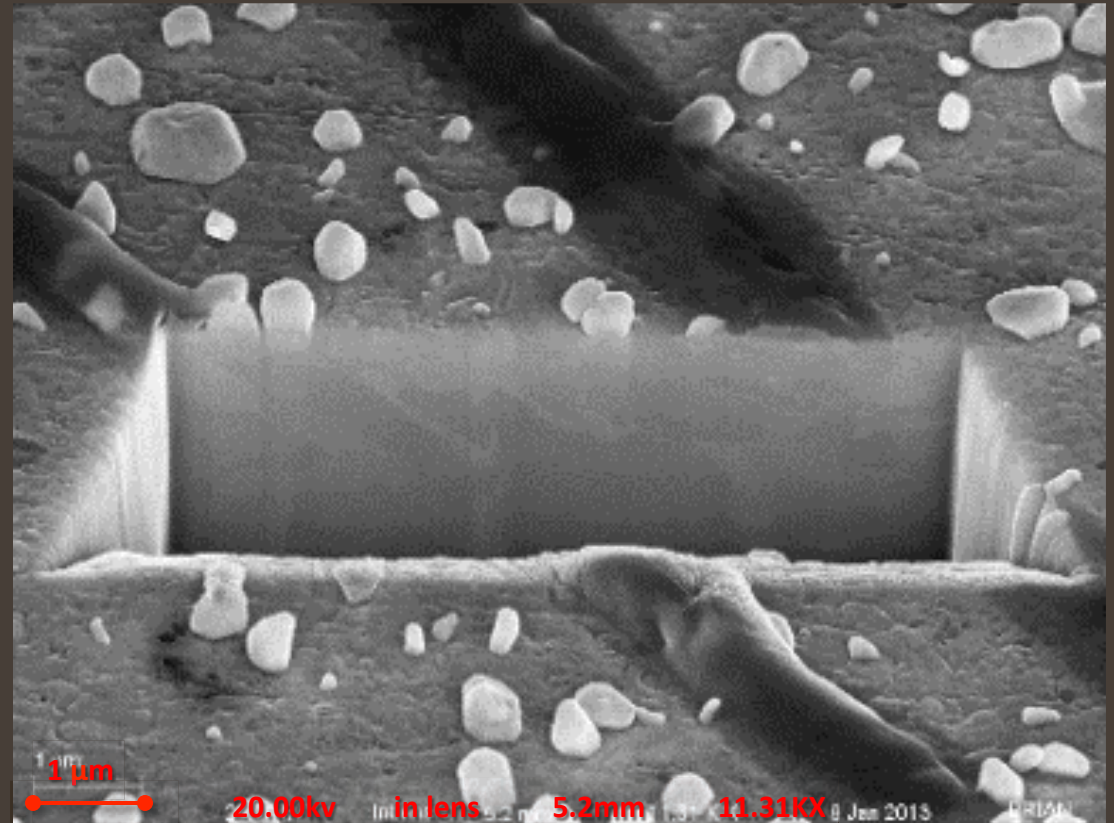


Focused Ion Beam (FIB) cut through an image particle and 500nm of the image surface

An historic un-gilded daguerreotype



Unidentified man; George Eastman House Study collection; 6th plate (2.75' x 3.25'')

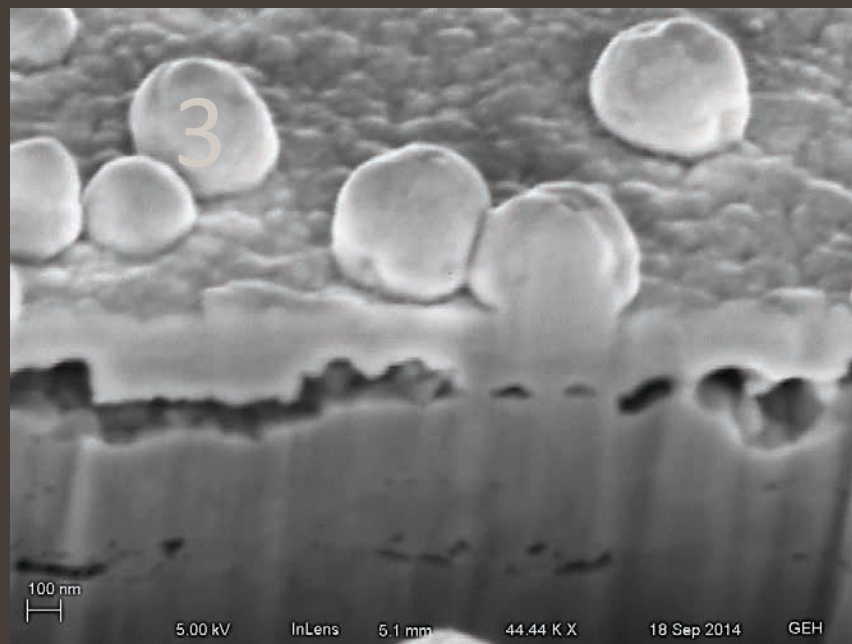


Focused Ion Beam (FIB) cut: the diagonal fibers are biological fibers engaged with the plate surface

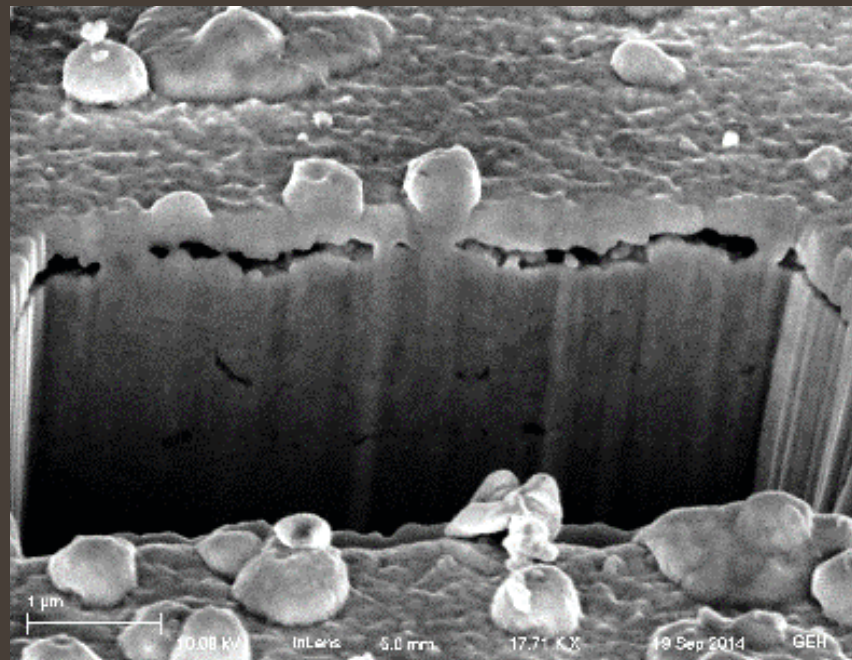


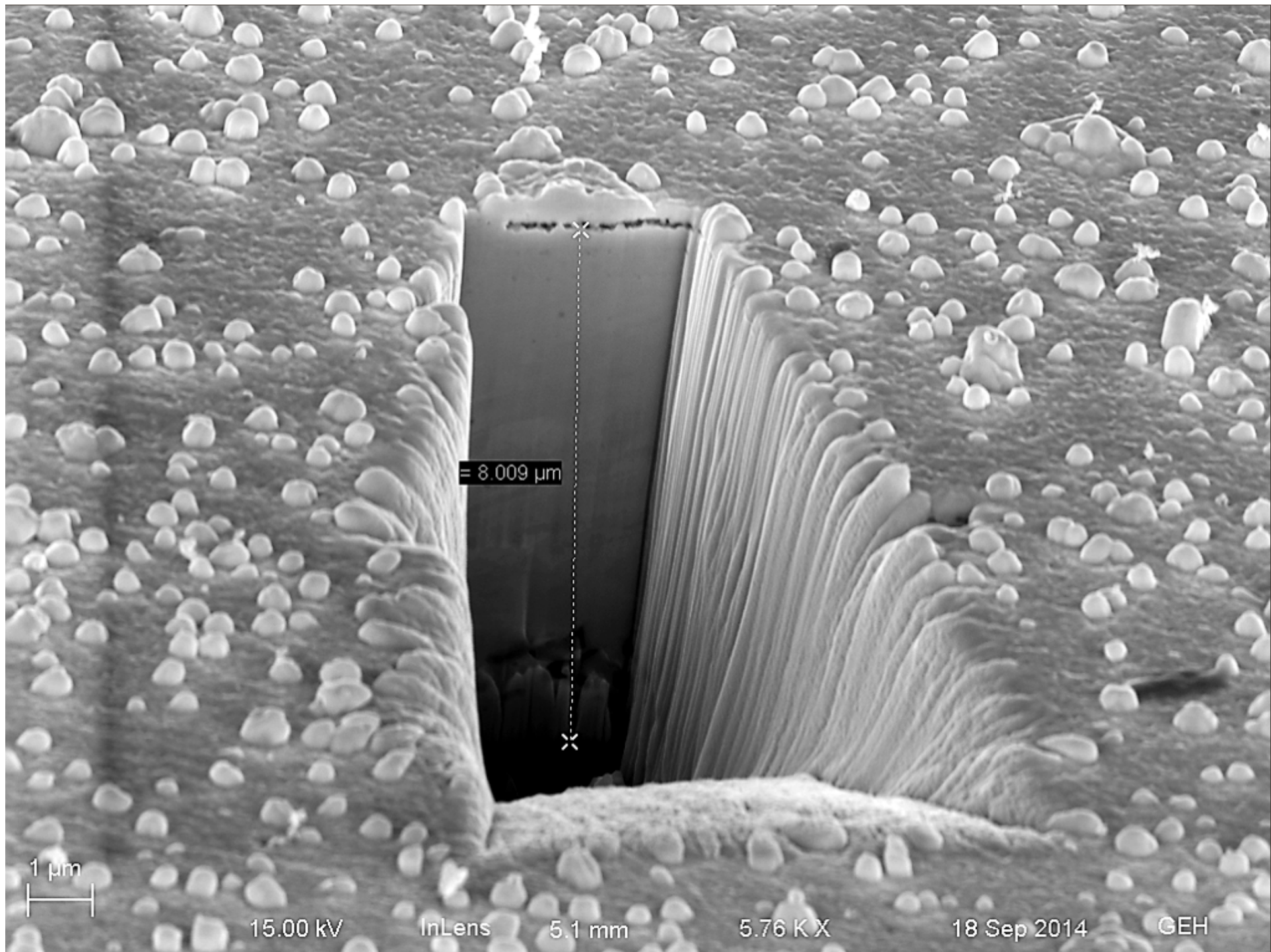


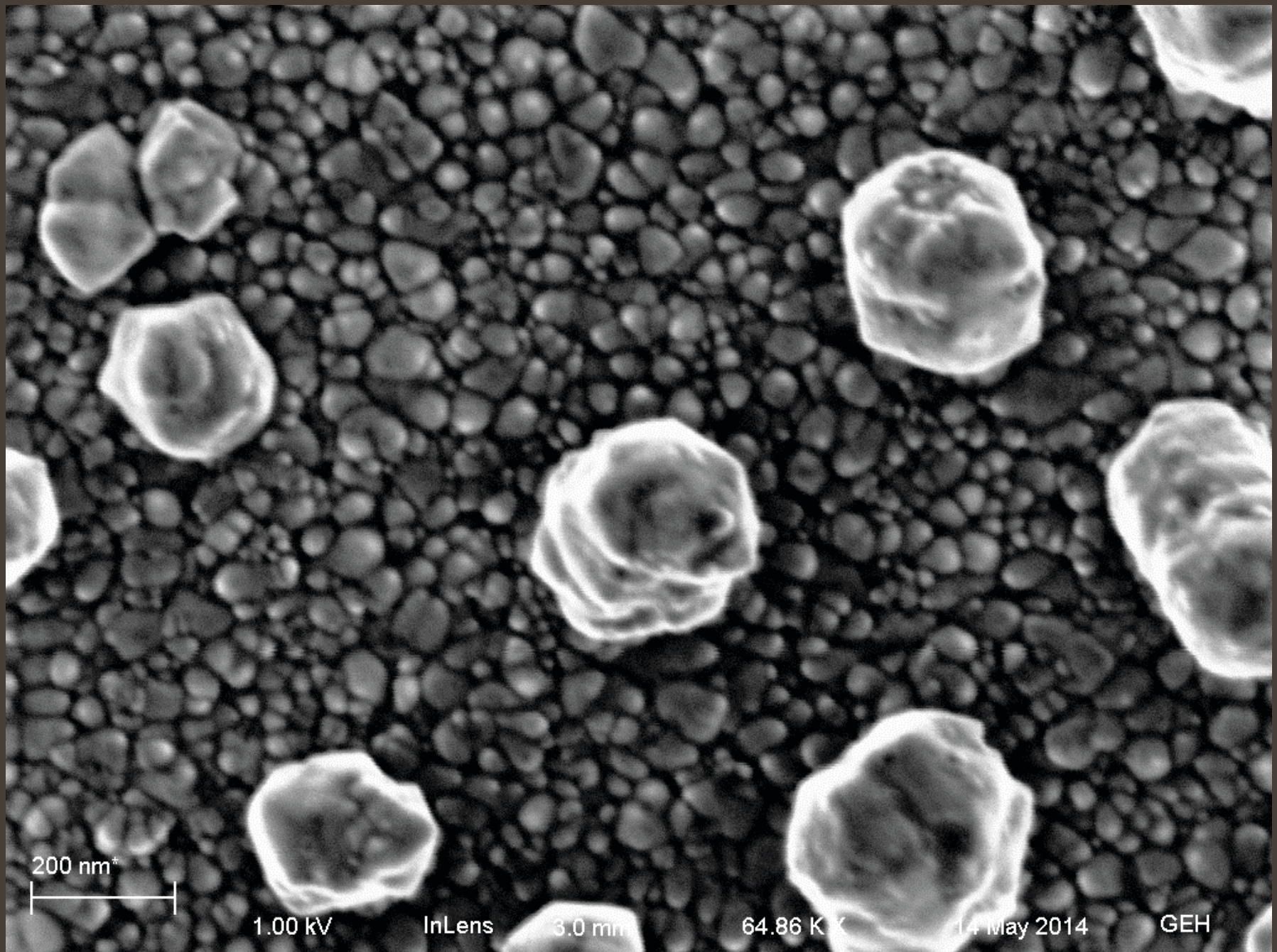
George Eastman House collection
6th plate: 1974:0193:0333



George Eastman House collection
6th plate: 1974:0193:0322







200 nm

1.00 kV

InLens

3.0 mm

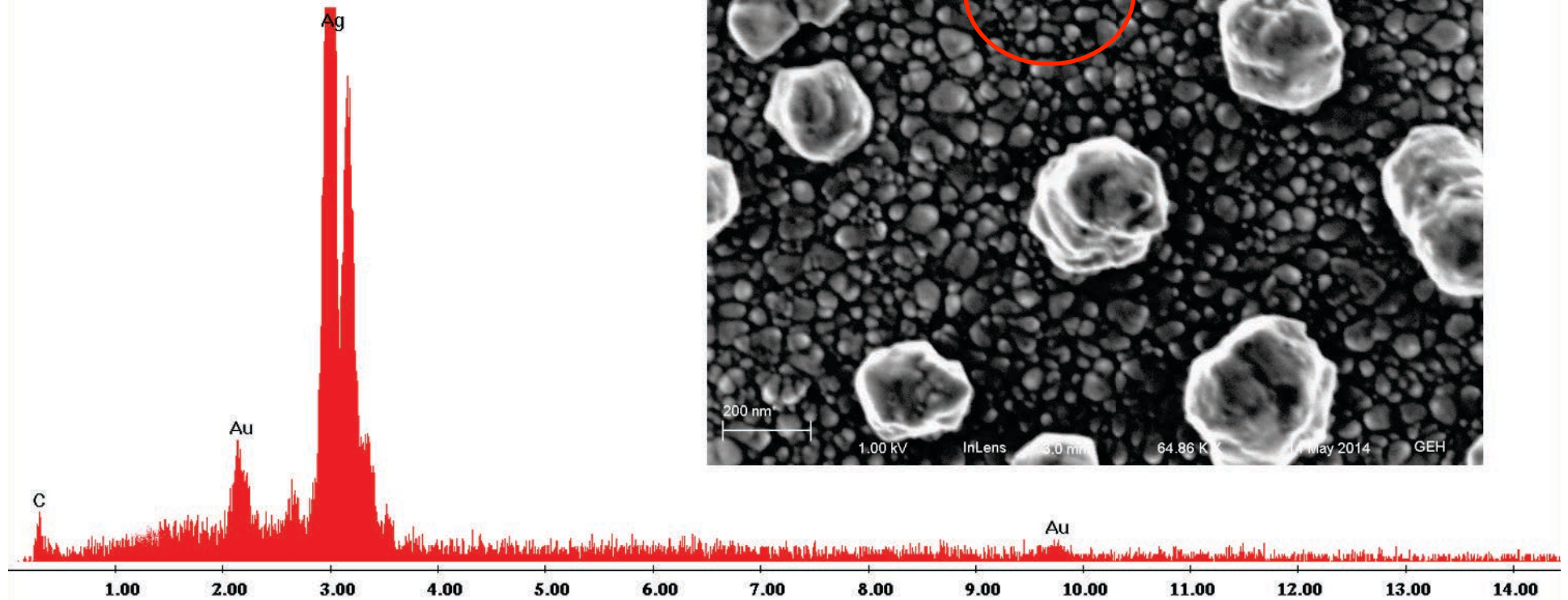
64.86 K X

14 May 2014

GEH

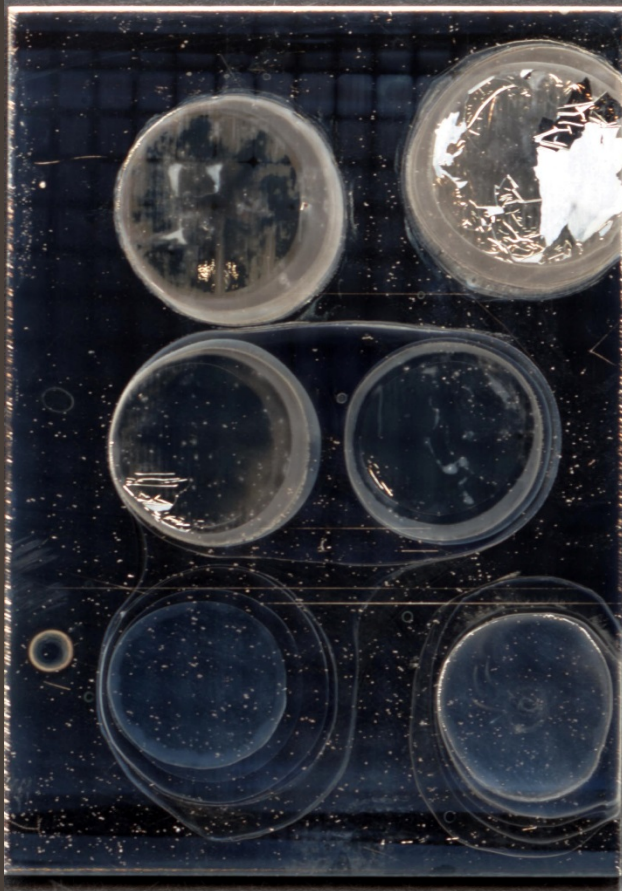
Energy dispersive X-Ray analysis

Label A: SC_D_095

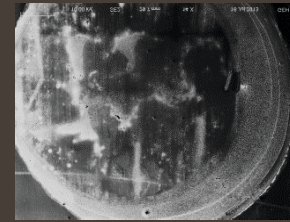


Localized X-Ray beam; accelerating voltage 15 – 20 kilovolts; working distance > 5mm

Progressive gilding test



GILDING DENSITY



5



6



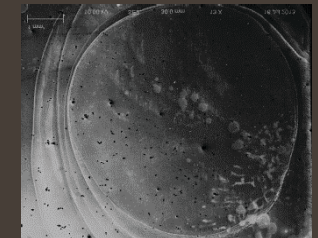
3



4



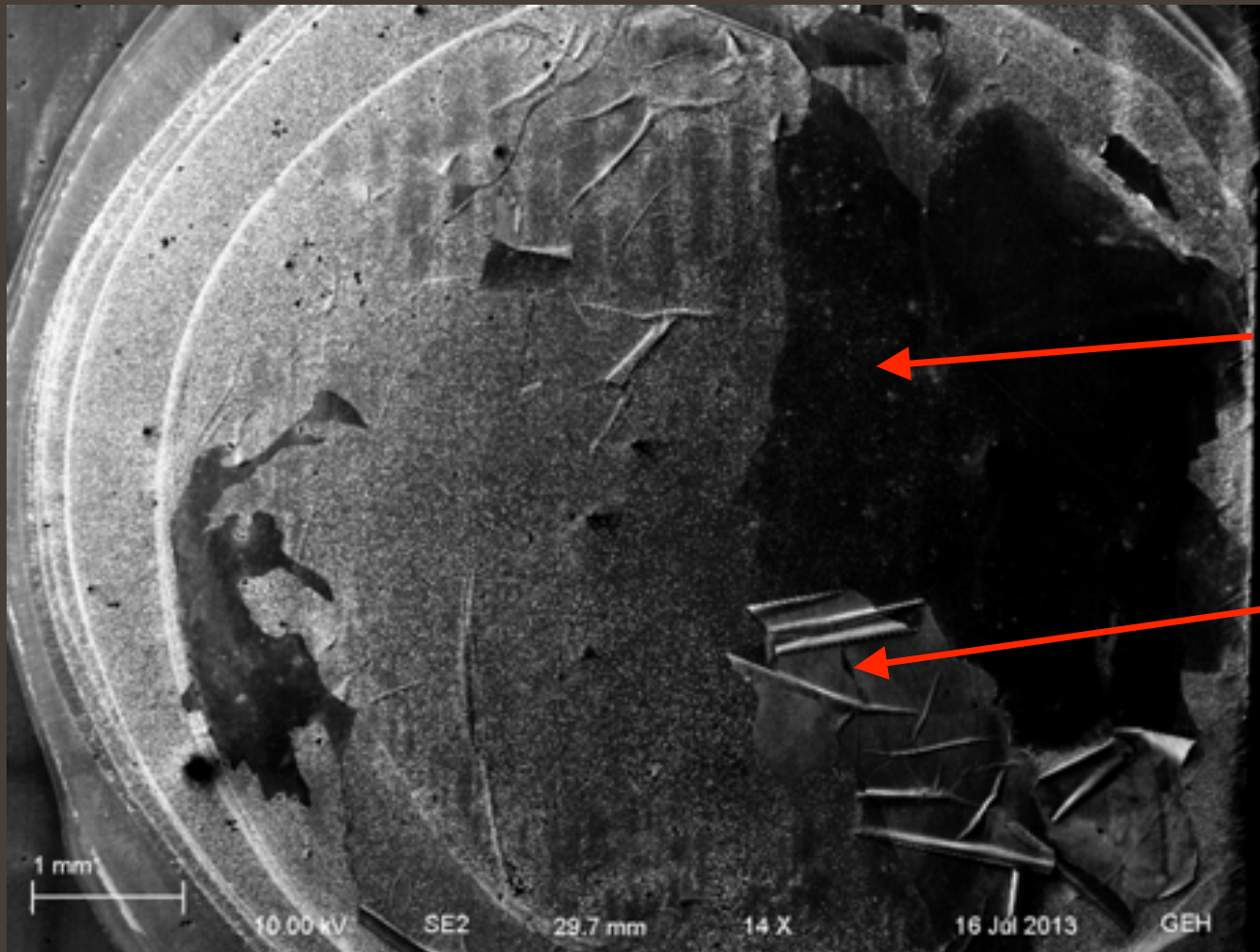
1



2

This test was conducted under the NSF Research Undergraduate (REU) Program at the University of Rochester by Emily Thompson in 2013

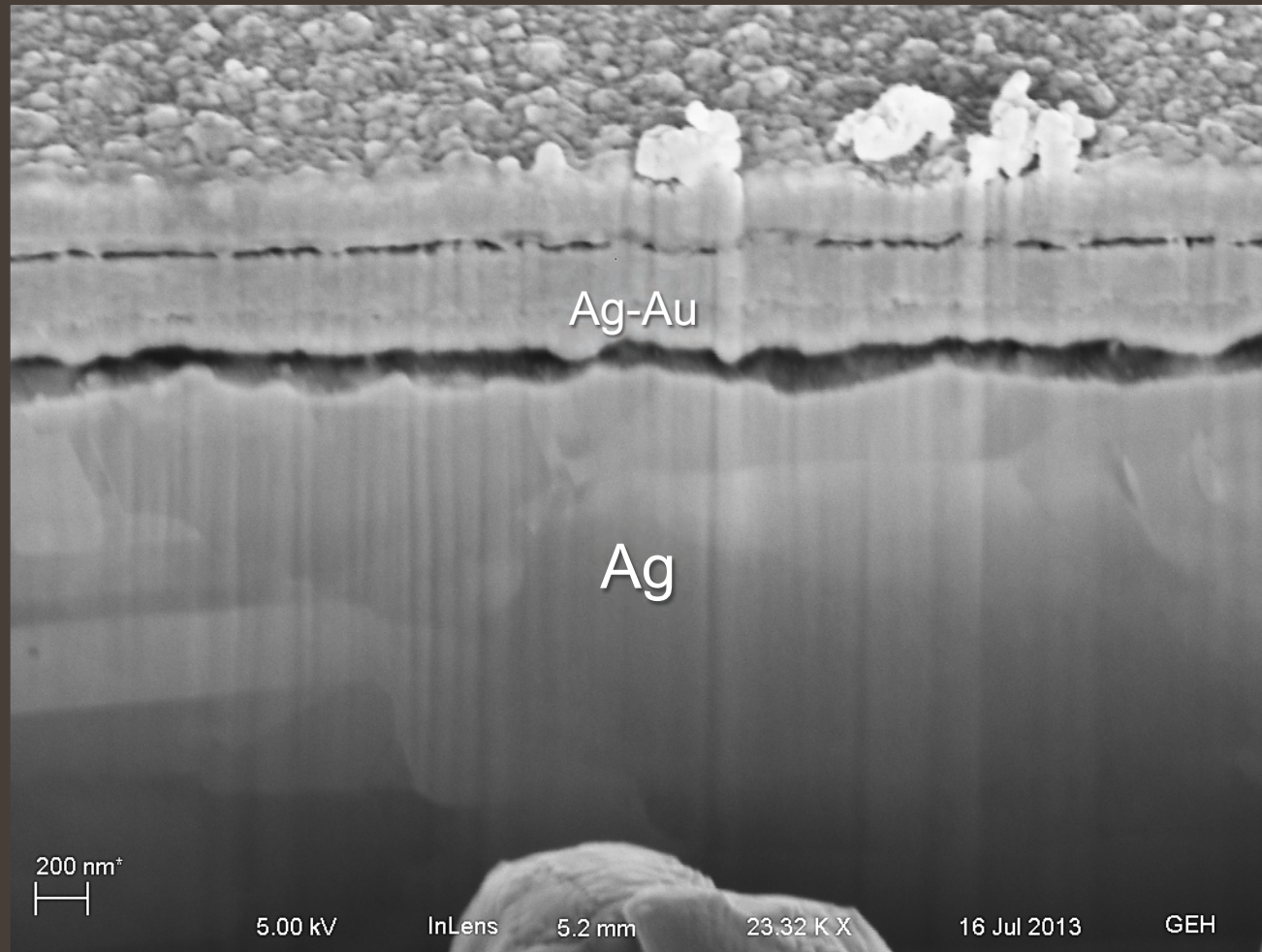
#6: 8 drops gilding solution over 8 minutes, over heat
–then immersed in distilled H₂O, rinsed and dried



Loss of superlayers exposing sub-surface Ag

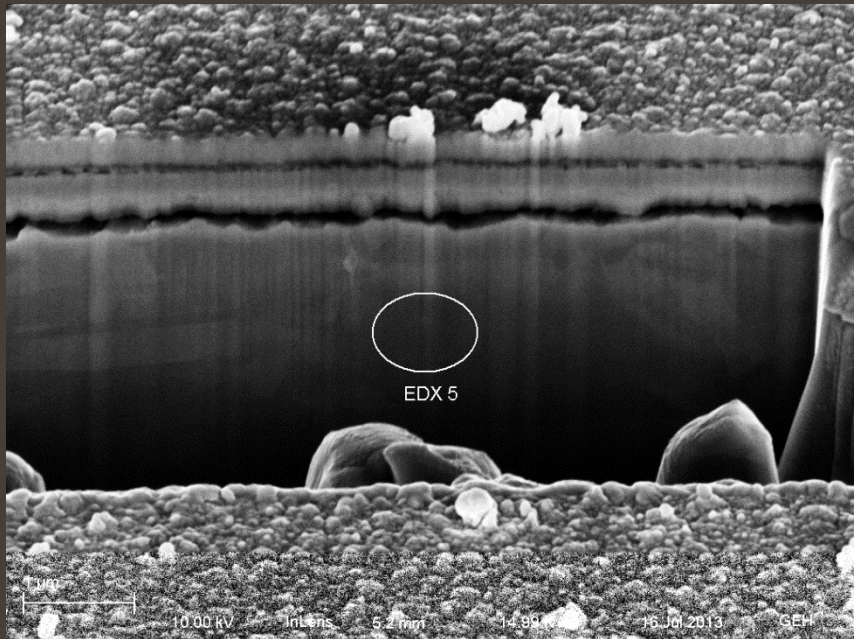
Curled up superlayer – often termed exfoliation

FIB Section of Region 6

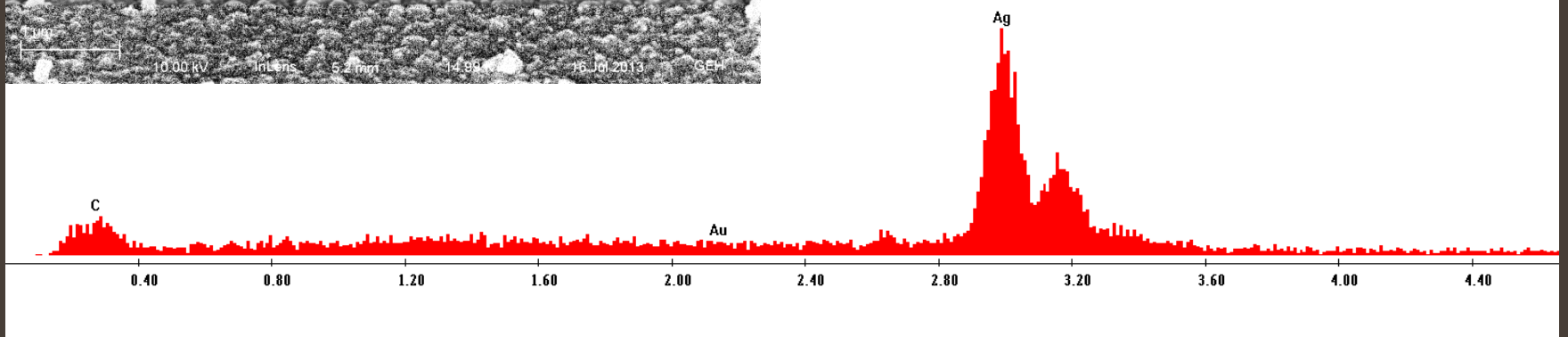


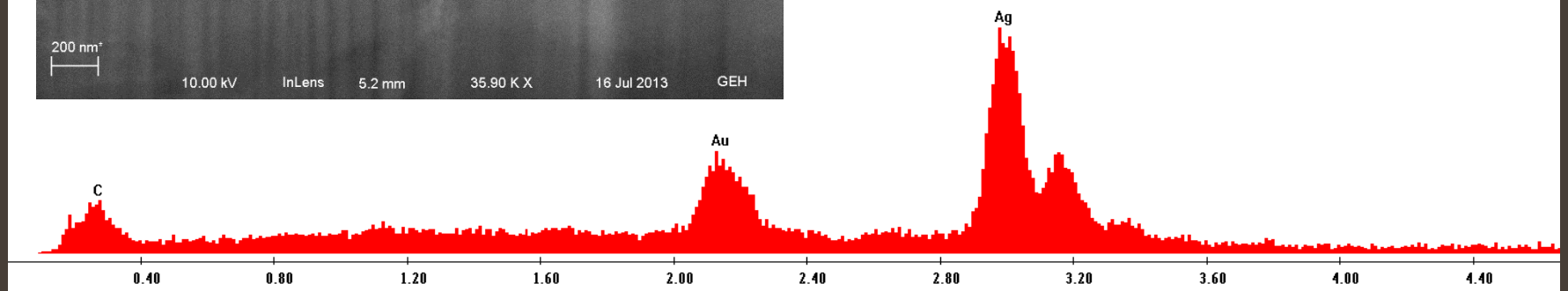
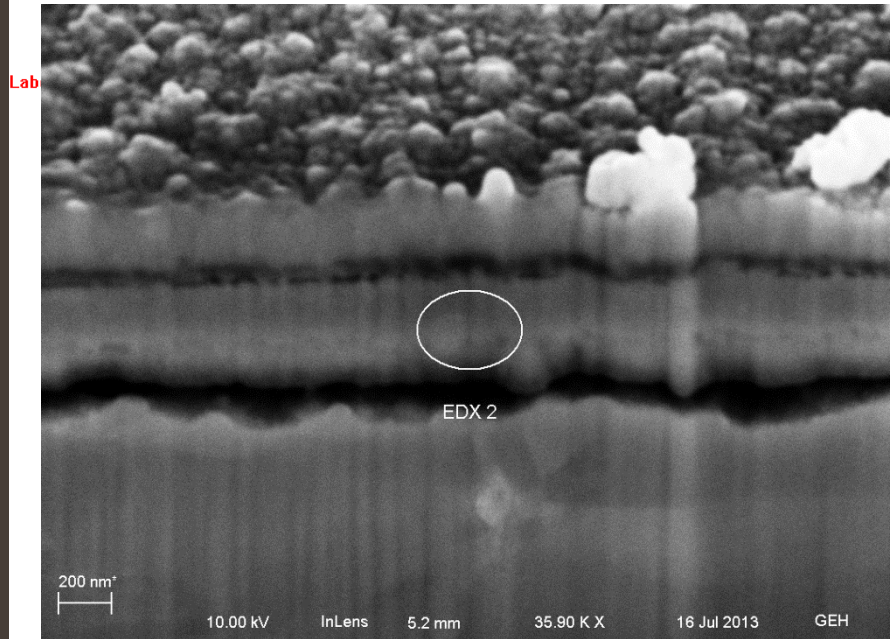
Note the full separation of superlayer 1 between the base silver layer and the Ag-Au layer above. Superlayer 2 with separation shows a possible repeat of the same phenomenon –with an increase in the Au content.

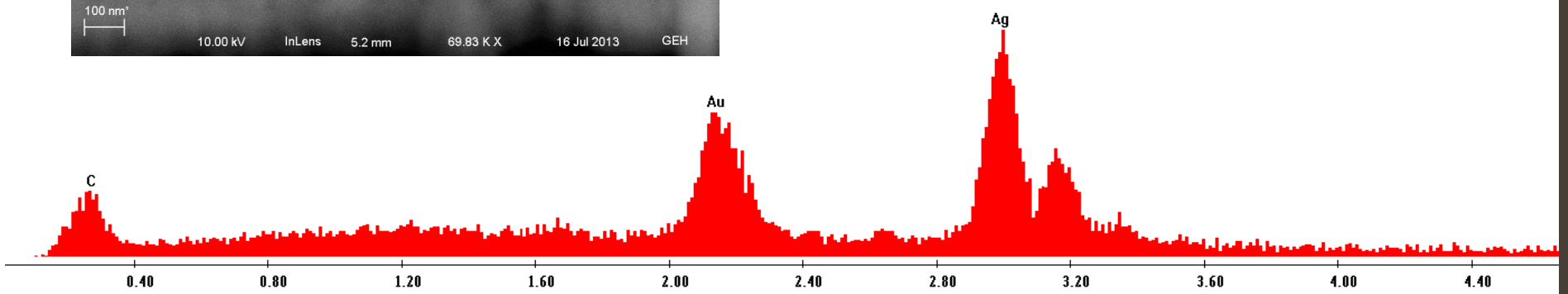
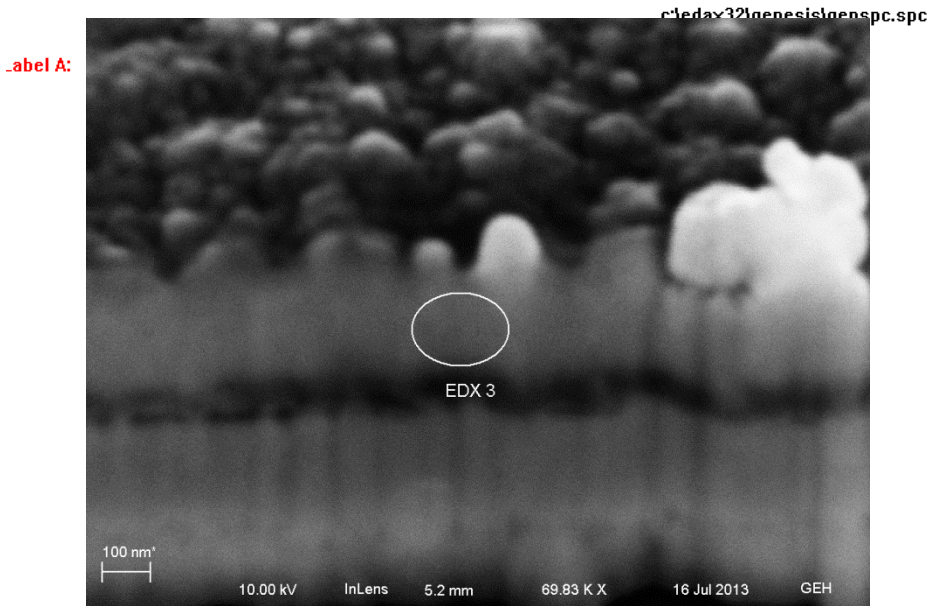
FIB –EDX analysis of ROI 6



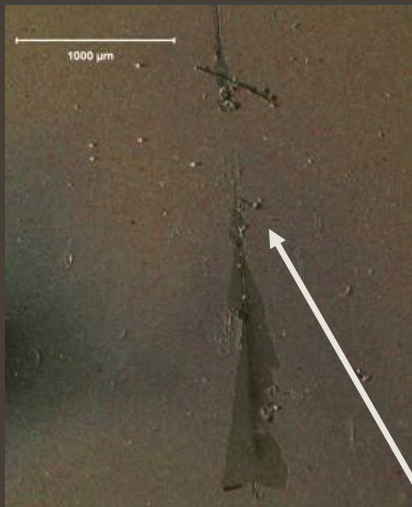
Location of FIB cut







Conservation Implications of this research: new explanations



Miss Hodges of Salem
Southworth & Hawes

Quarter plate daguerreotype
George Eastman House
1974:0193:0389

Photomicrographs courtesy of Taina Meller

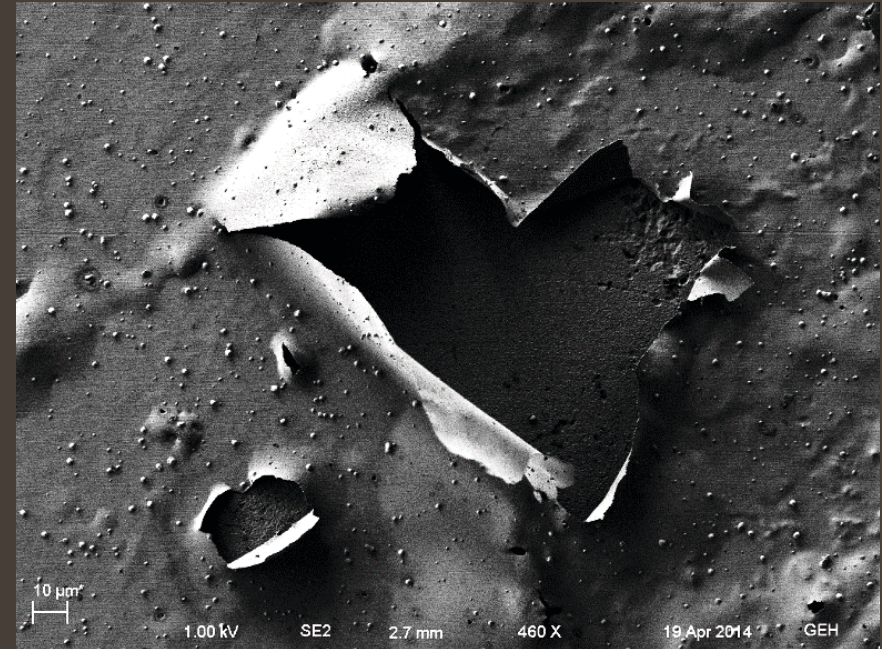
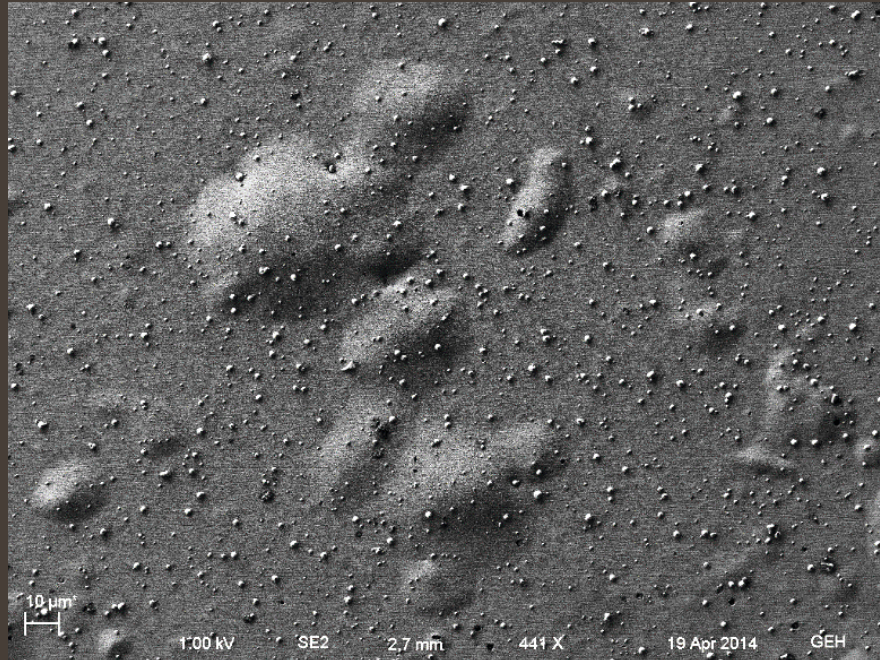
Reproduction image courtesy of Michael Shuter

The well known condition concern of “exfoliation” Southworth & Hawes is likely due to their gilding “to the limit” by enhancing the image at the risk loss due to the gilding “superlayer”

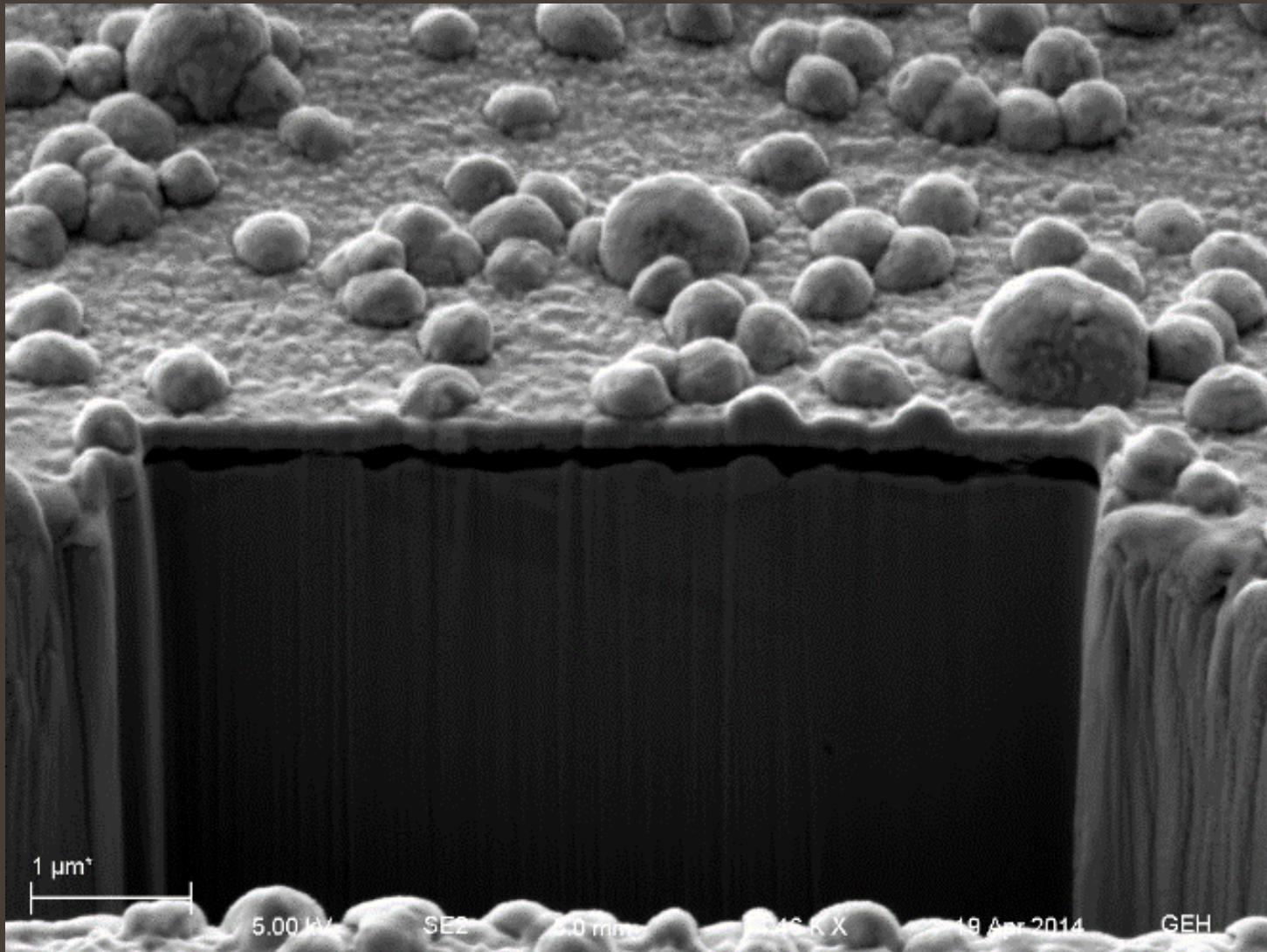
Research on the cause of exfoliation, as seen on Southworth & Hawes plates, and many others....



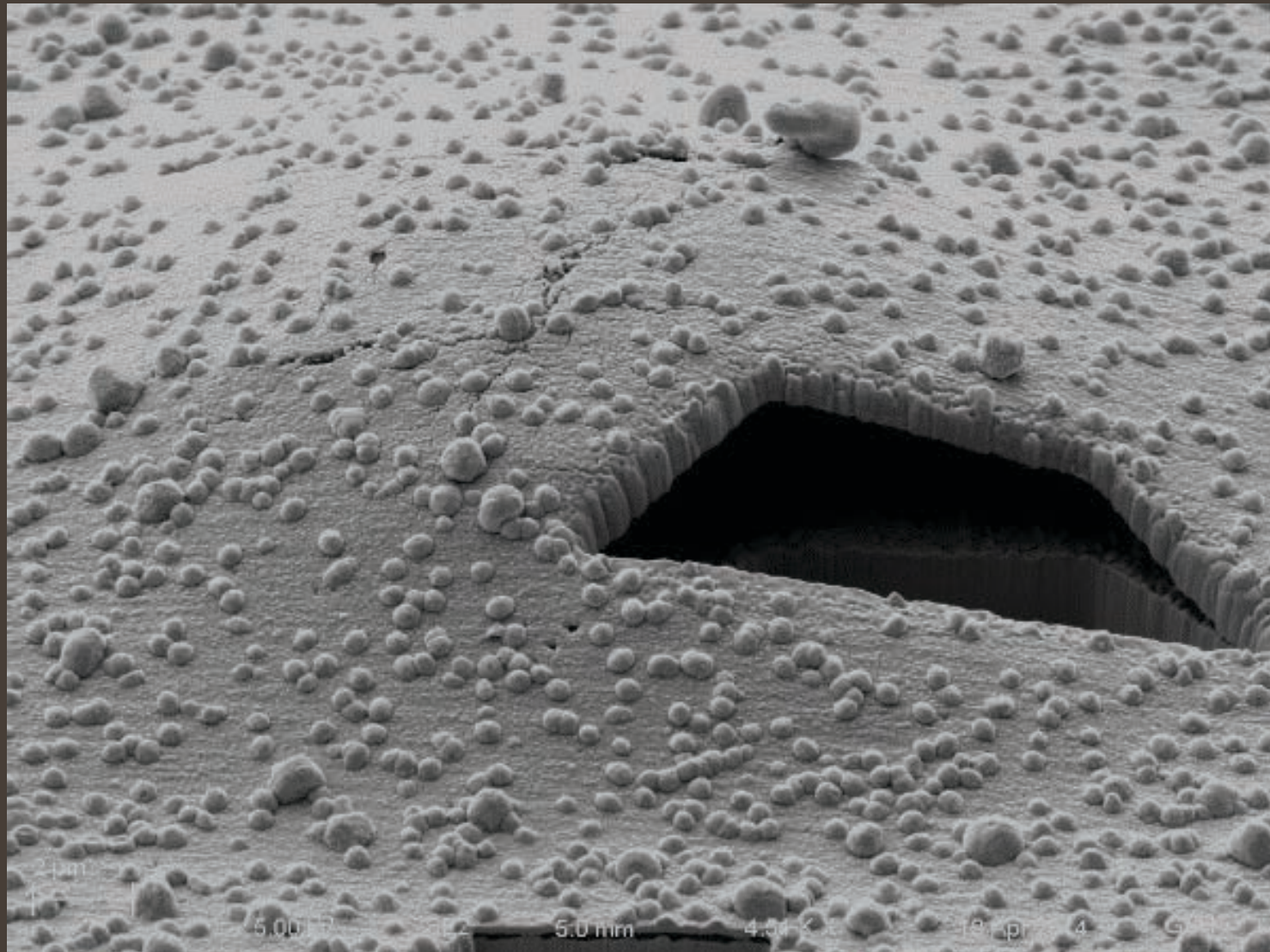
Surface disruptions at low magnification SEM

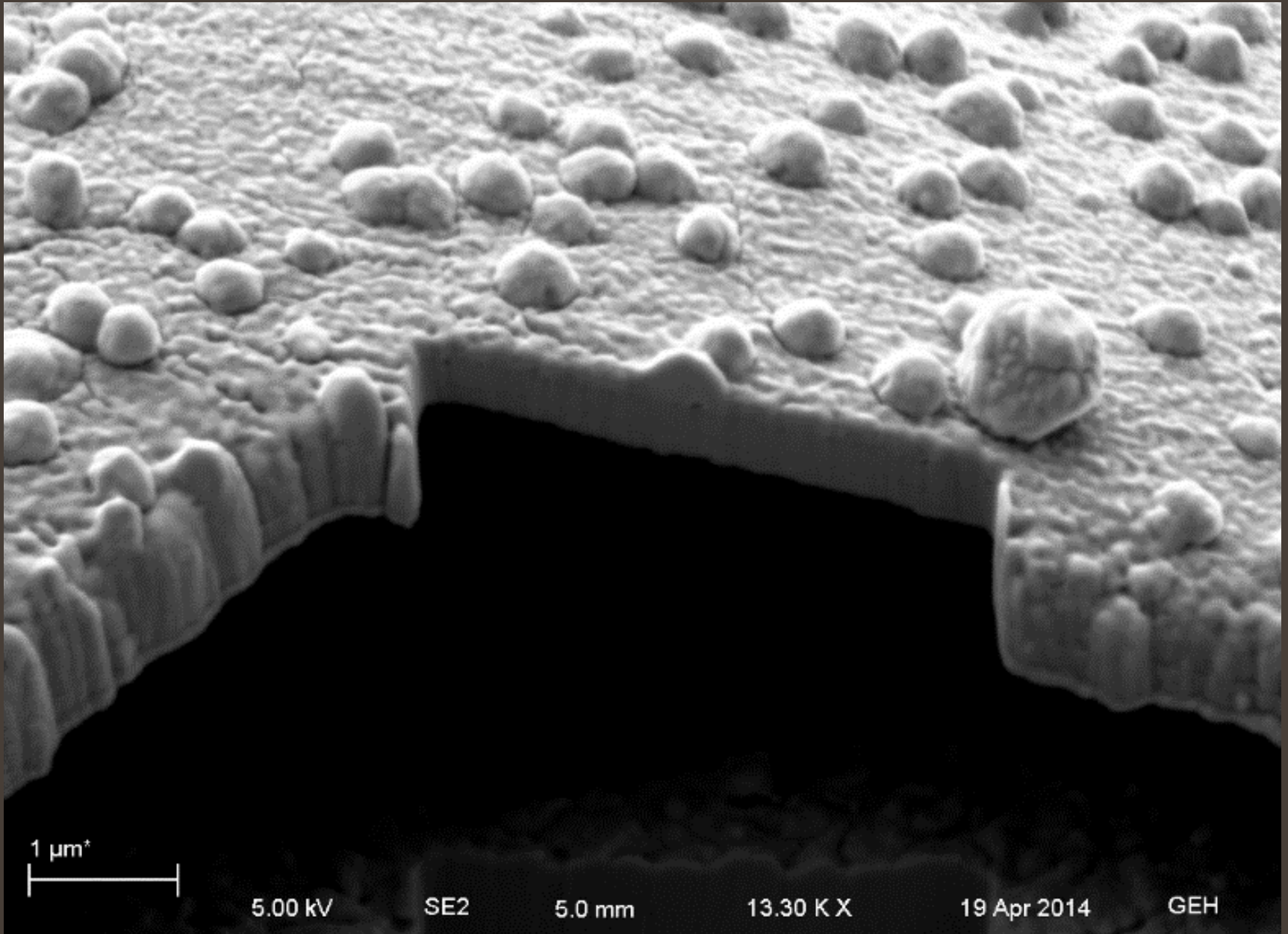


The superlayer is completely disassociated from the silver base



SEM-FIB dramatically shows the condition of surface disruption –likely caused by excessive gold





1 μm

5.00 kV

SE2

5.0 mm

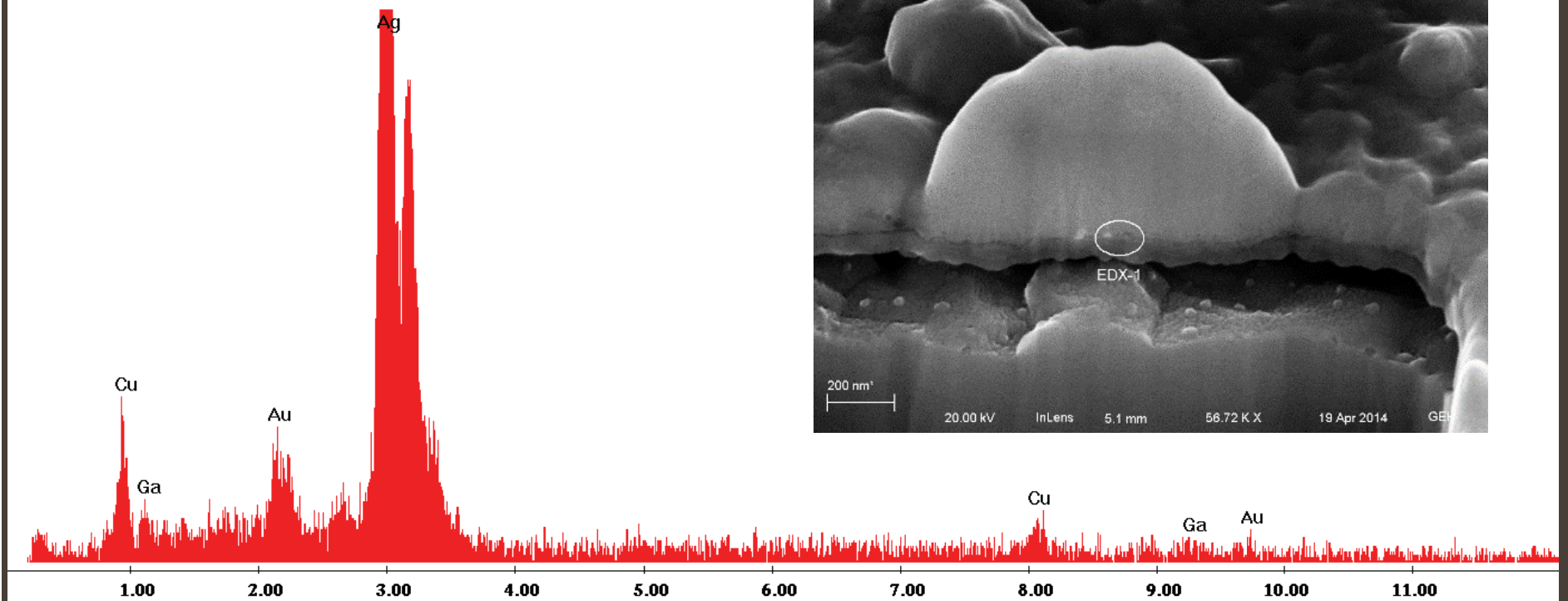
13.30 K X

19 Apr 2014

GEH

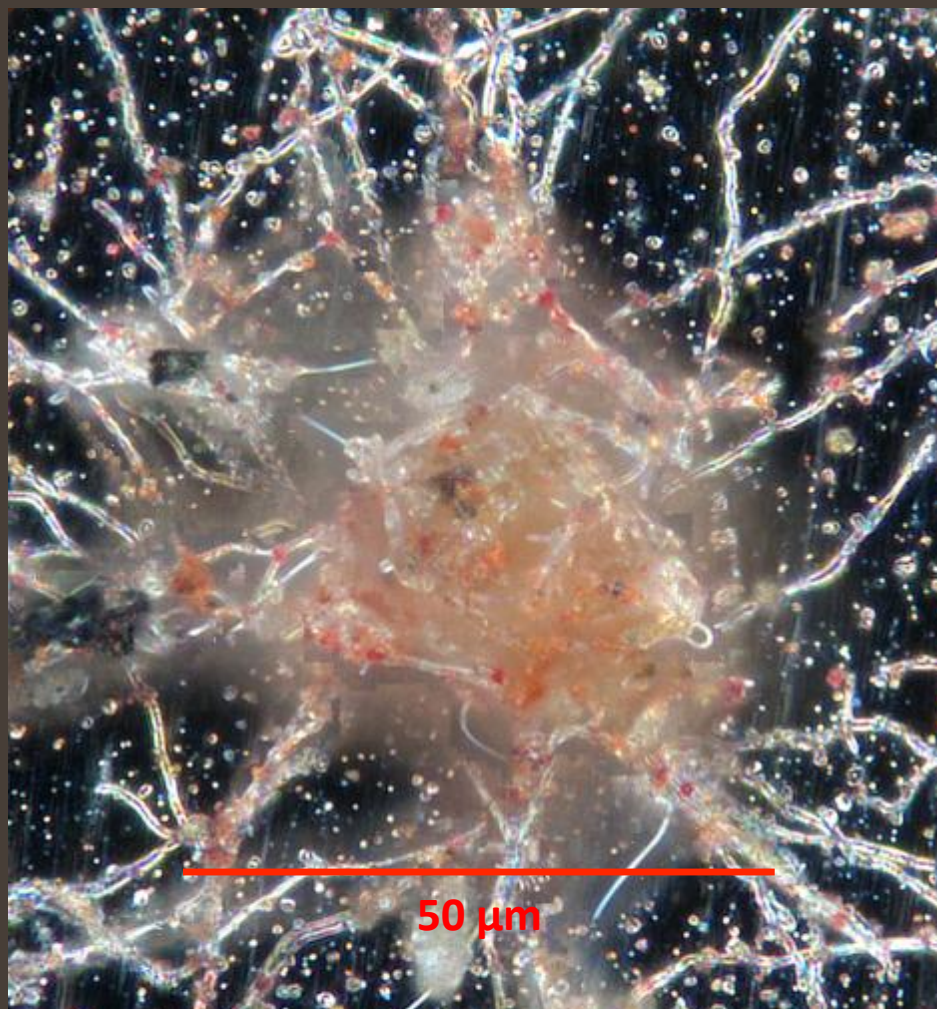
c:\edax32\genesis\genspc.spc

Label A: SC_D_220_4-19-14



The Cu signal is unexpected; possibly indicative of an immersion treatment that plated Cu at the Ag-Au interface –or that the gilding solution was contaminated with copper salts

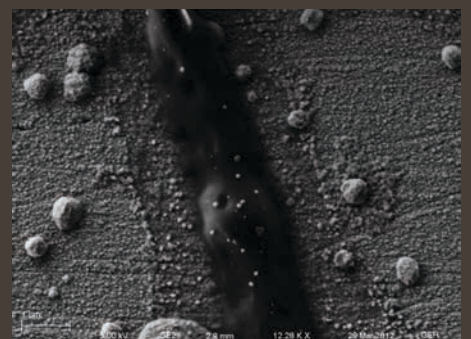
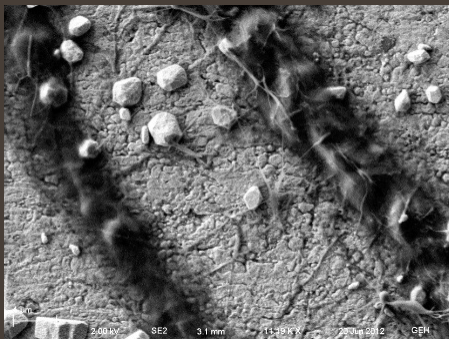
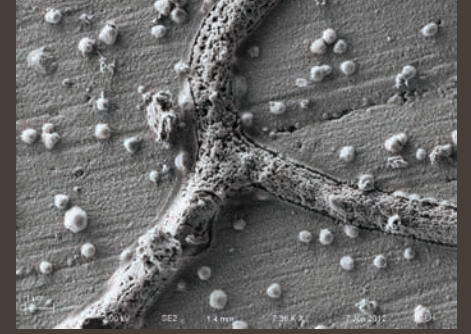
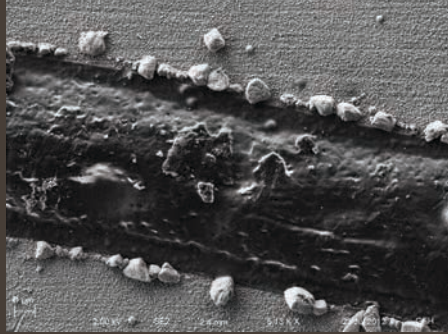
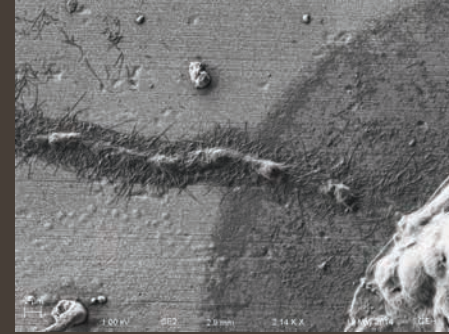
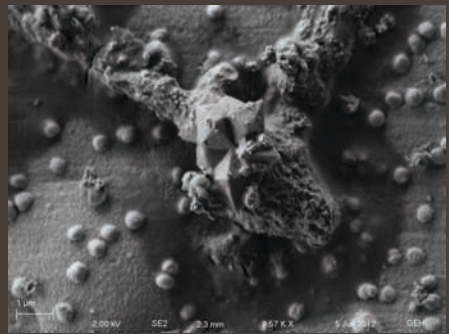
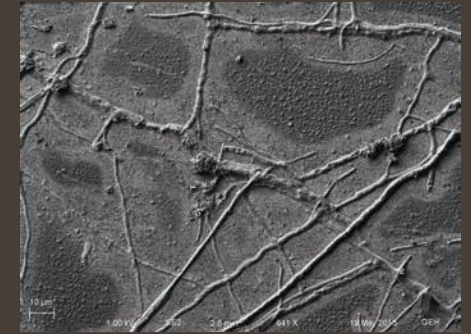
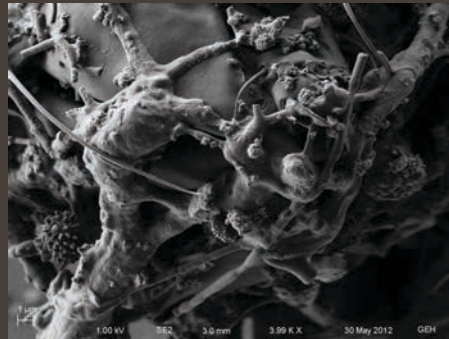
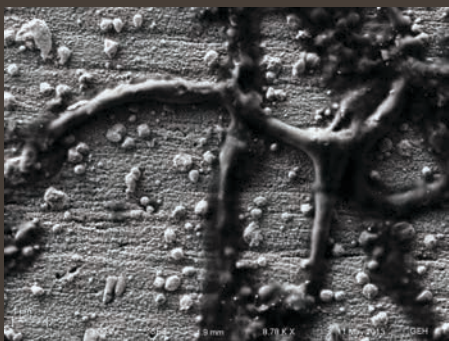
The gold-silver-sulfur complex as a substrate for self assembling organo-metallic structures



- A web of bio-organic growth 500X darkfield microscopy
- Note the reflective fibrous structures due to internal organo-metallic mediation
- The strong color emissions are localized plasmon resonance effects of Ag/Au nanoparticles incorporated into biofibers

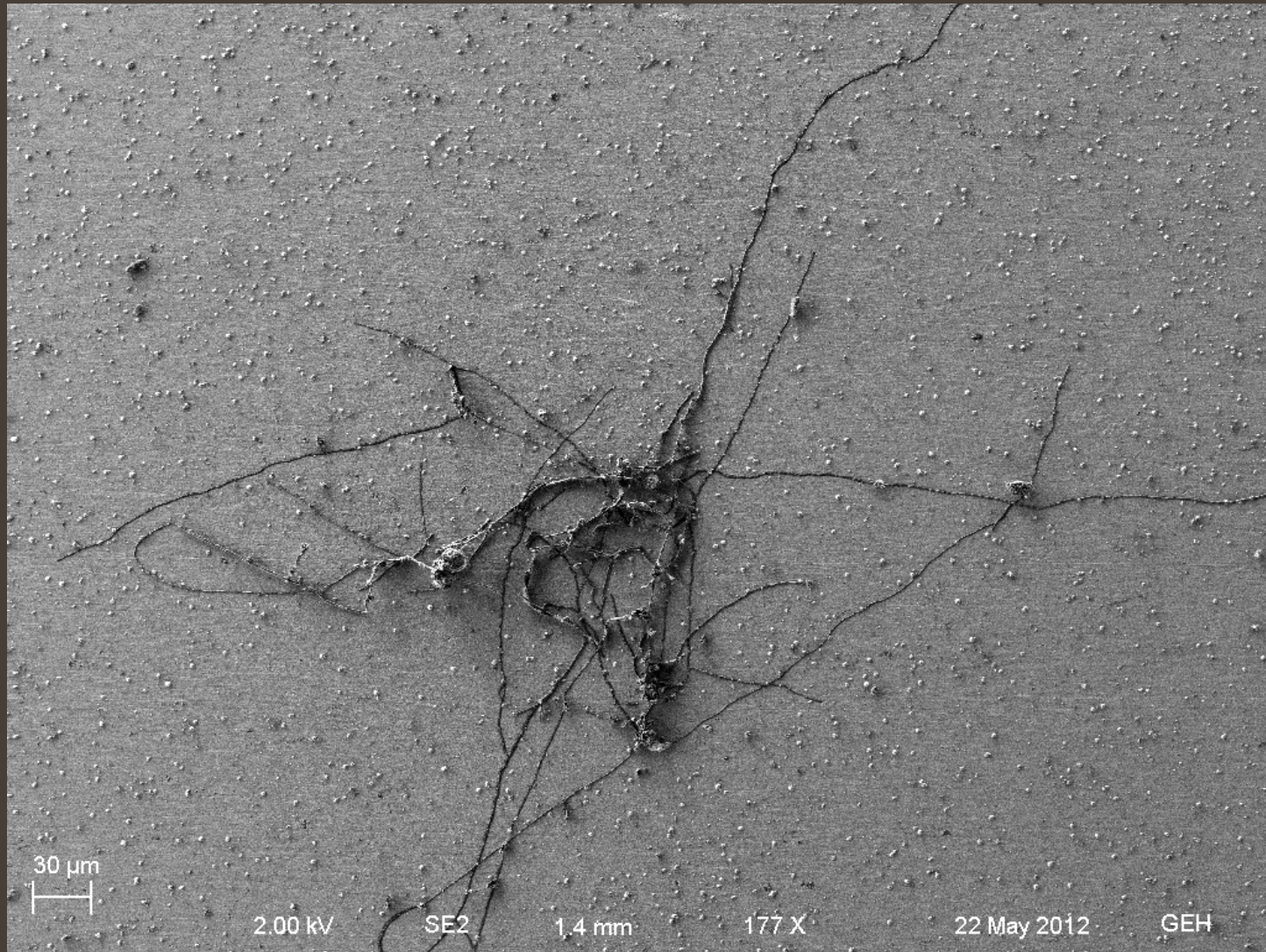


Examples of diverse biological forms documented during SEM examinations

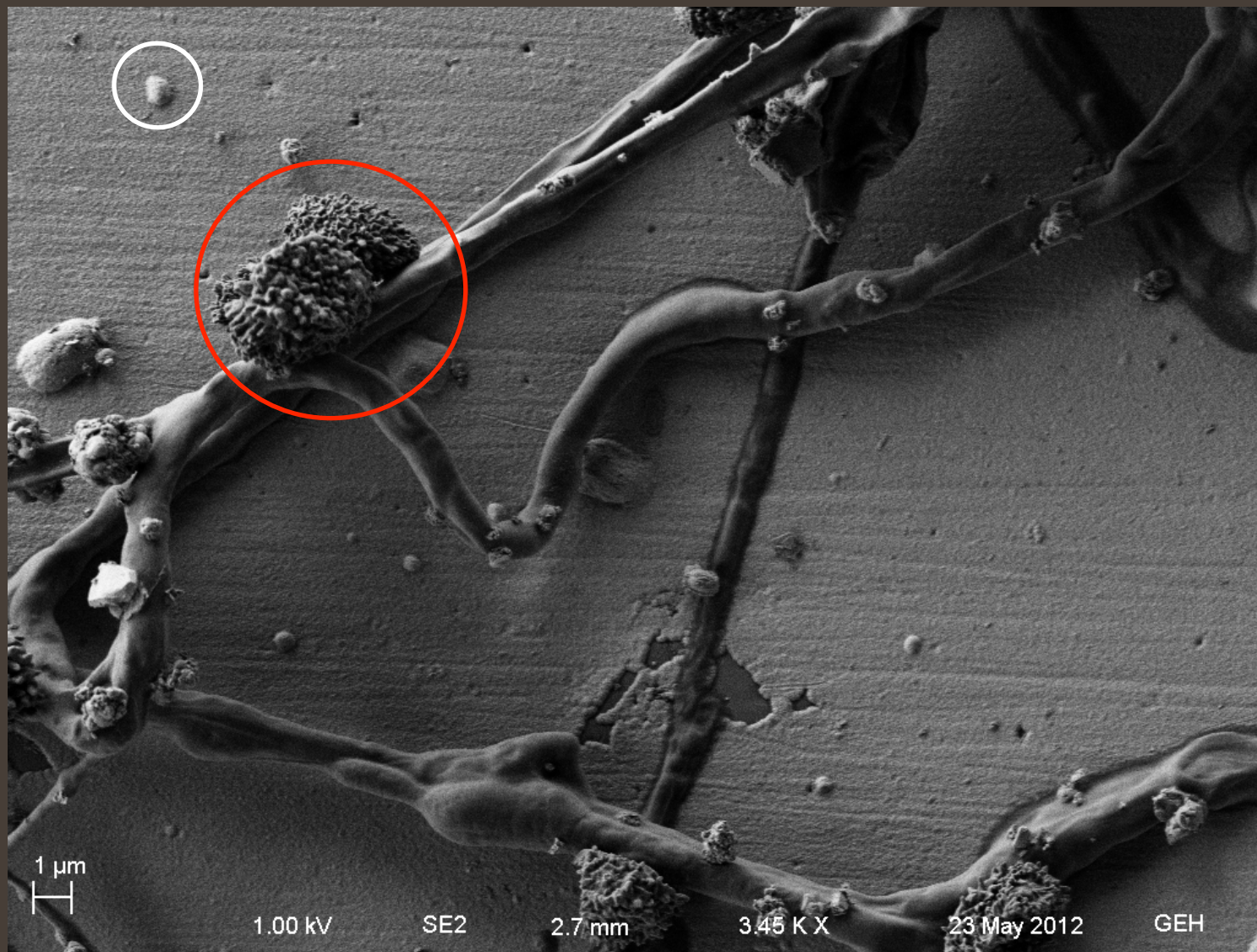




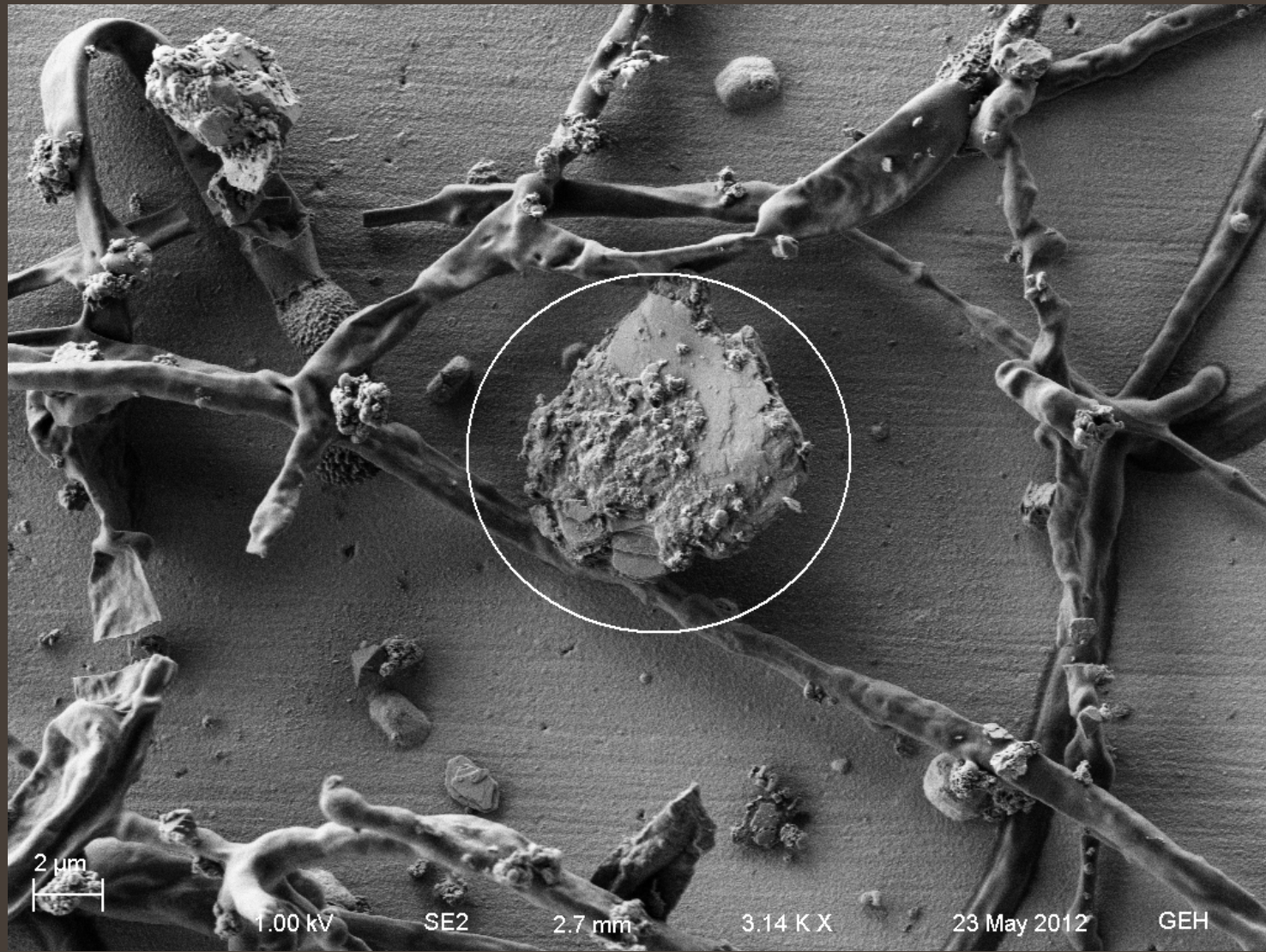
Area of biological growth and interactions with the gold-silver-mercury plate nano structure



SEM image of a bio-formation within ROI



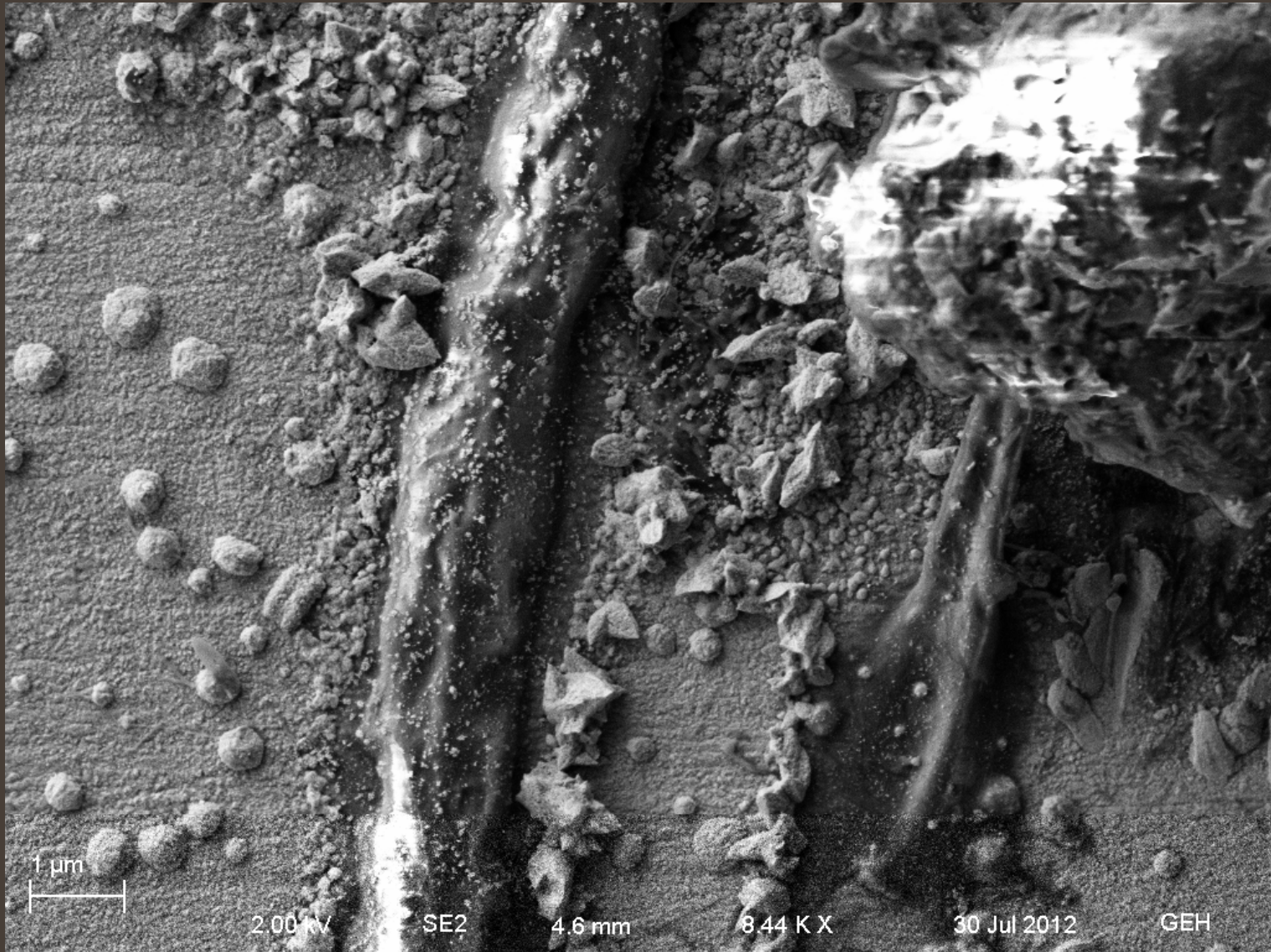
Detail view of structure –note distinctive bio-forms; white circle is an image particle



Large (micro) flat laminate crystalline structure populated with nano-features on surface; appears joined between two bio-fibers

Evidence of biological interaction has been documented on every daguerreotype examined by SEM





1 μm

2.00 kV

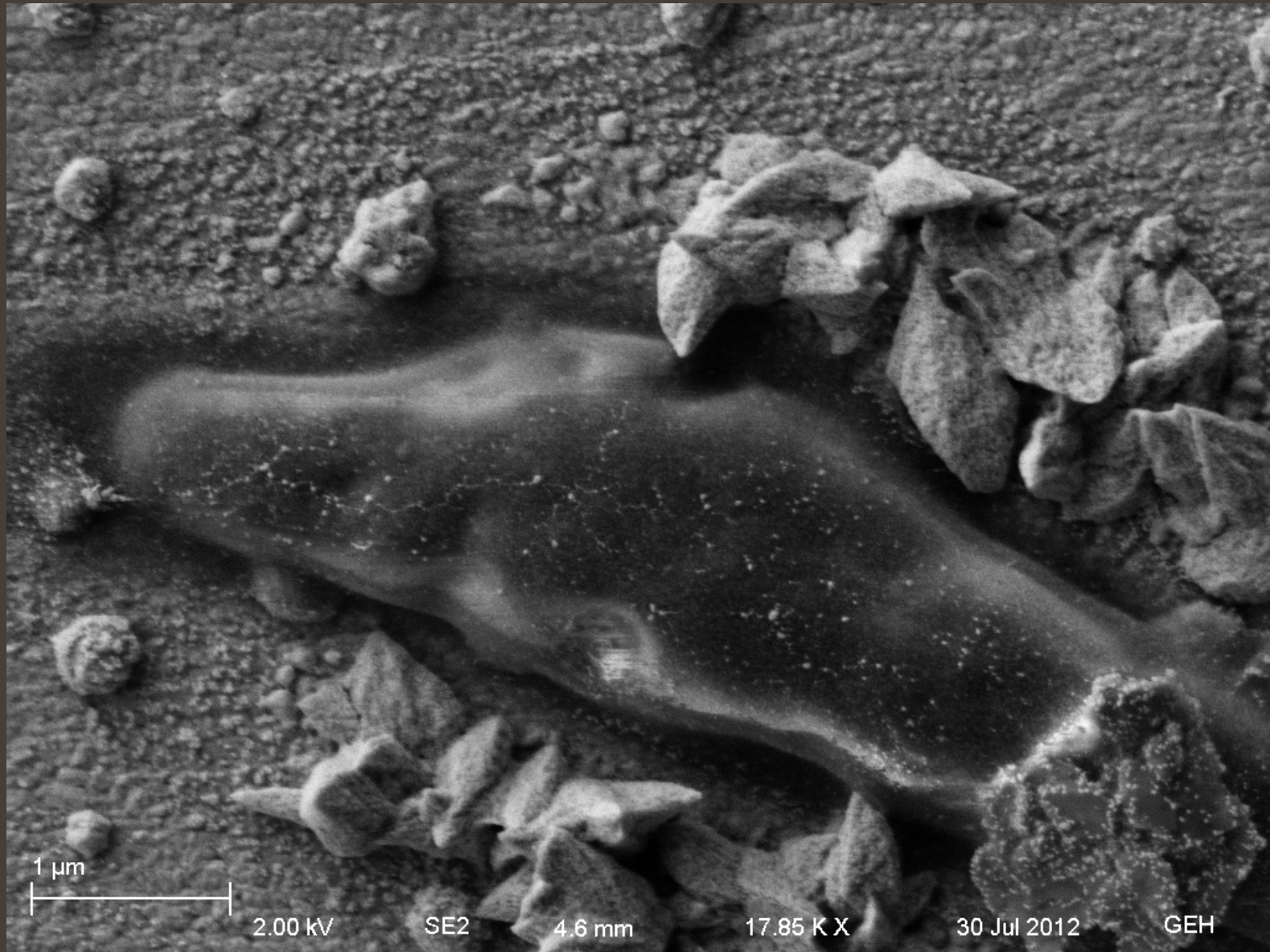
SE2

4.6 mm

8.44 K X

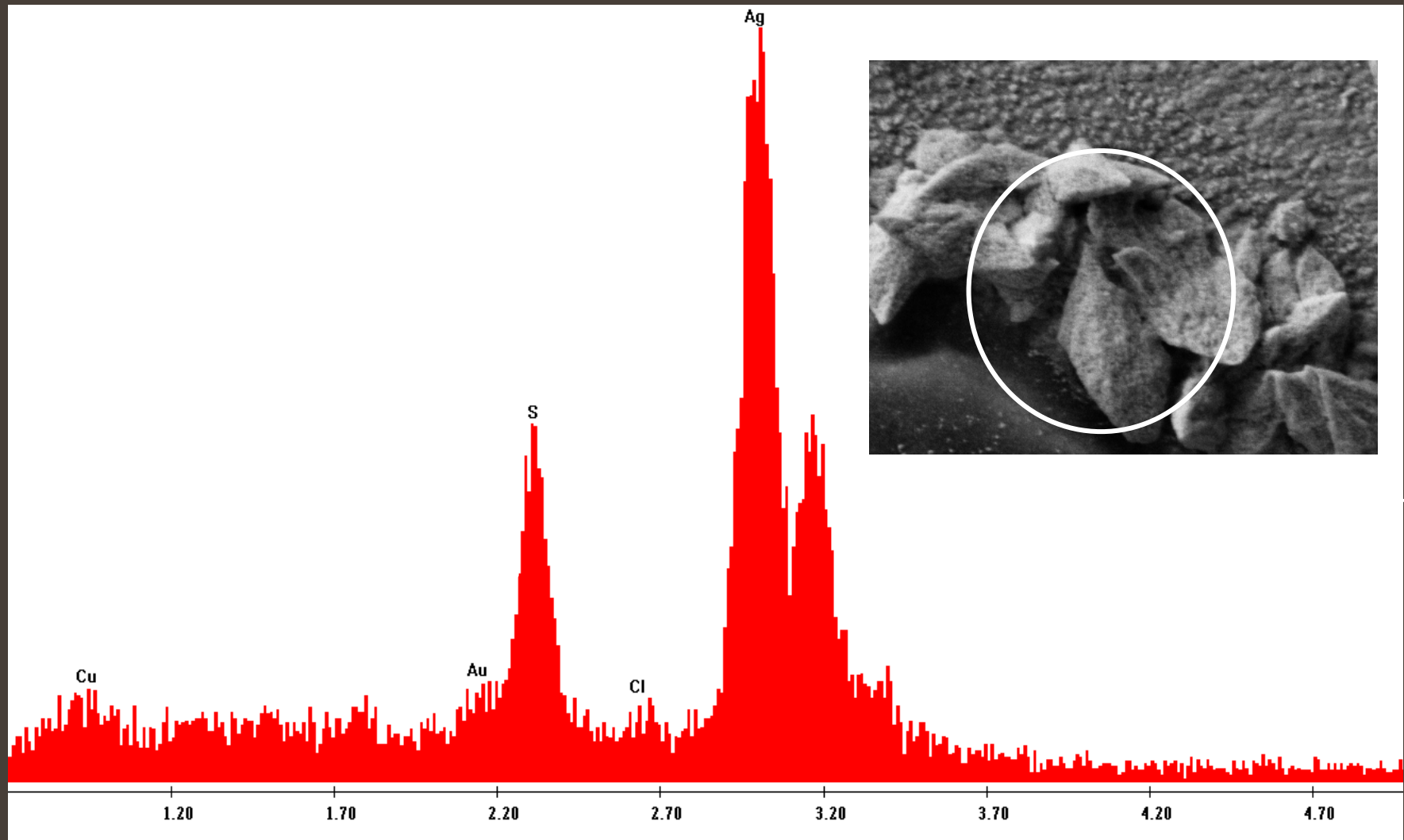
30 Jul 2012

GEH

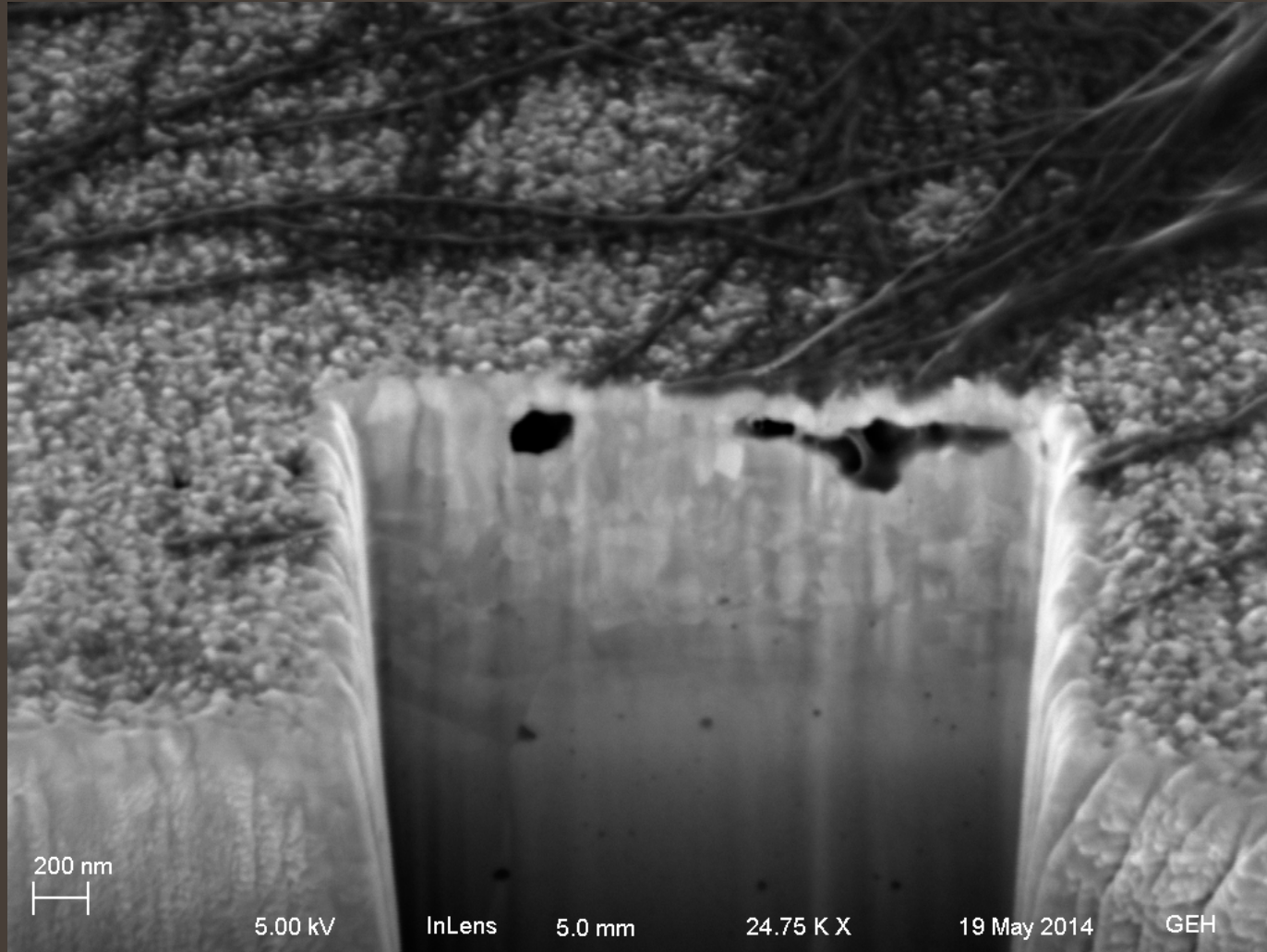


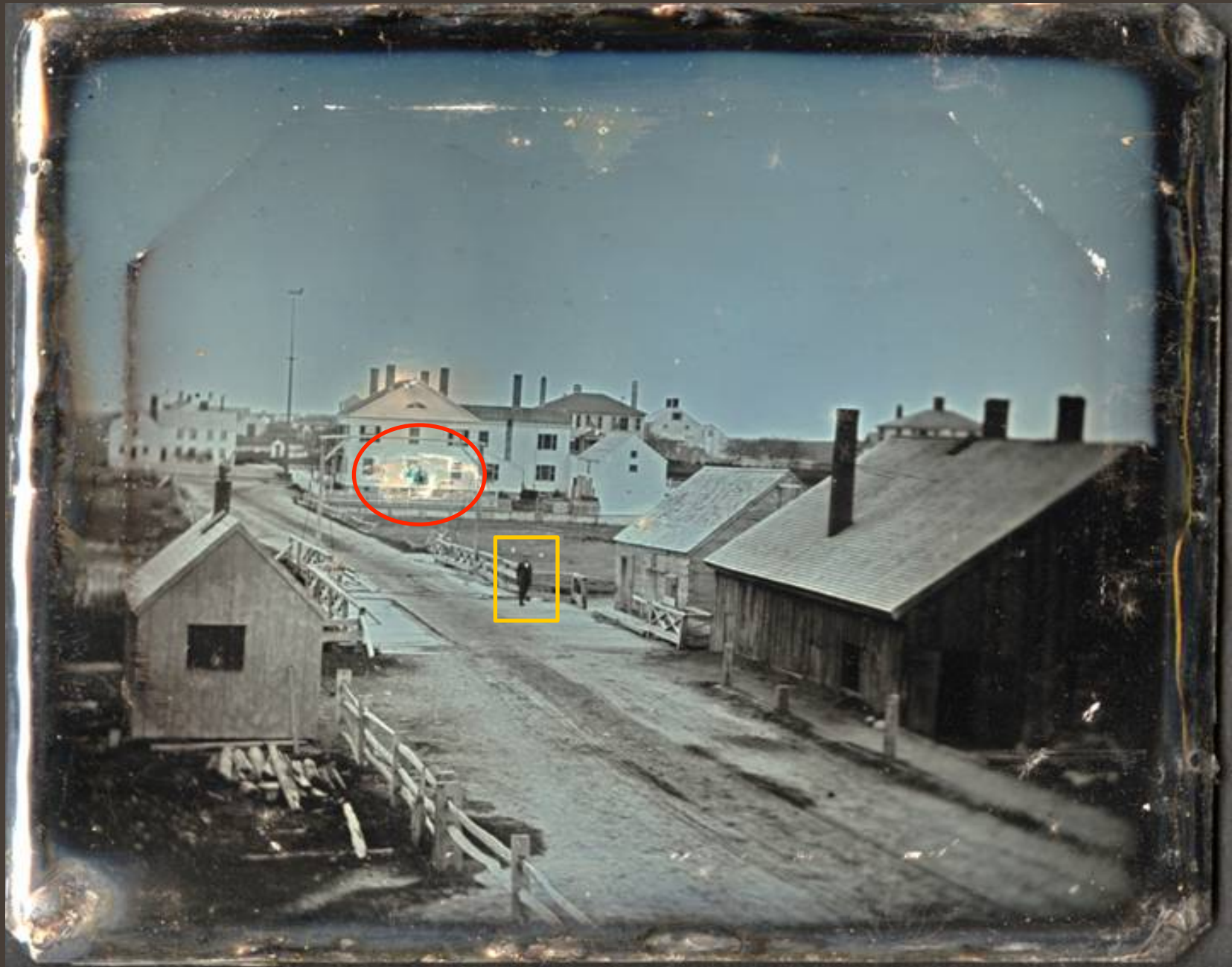
Fiber terminus; note the large aggregate particles and the extending surface bio-film , perhaps indicative of the linear propagation of the bio-fiber.

Large sulfur rich particles accumulate at the bio-fiber perimeter



Subsurface biological interactions



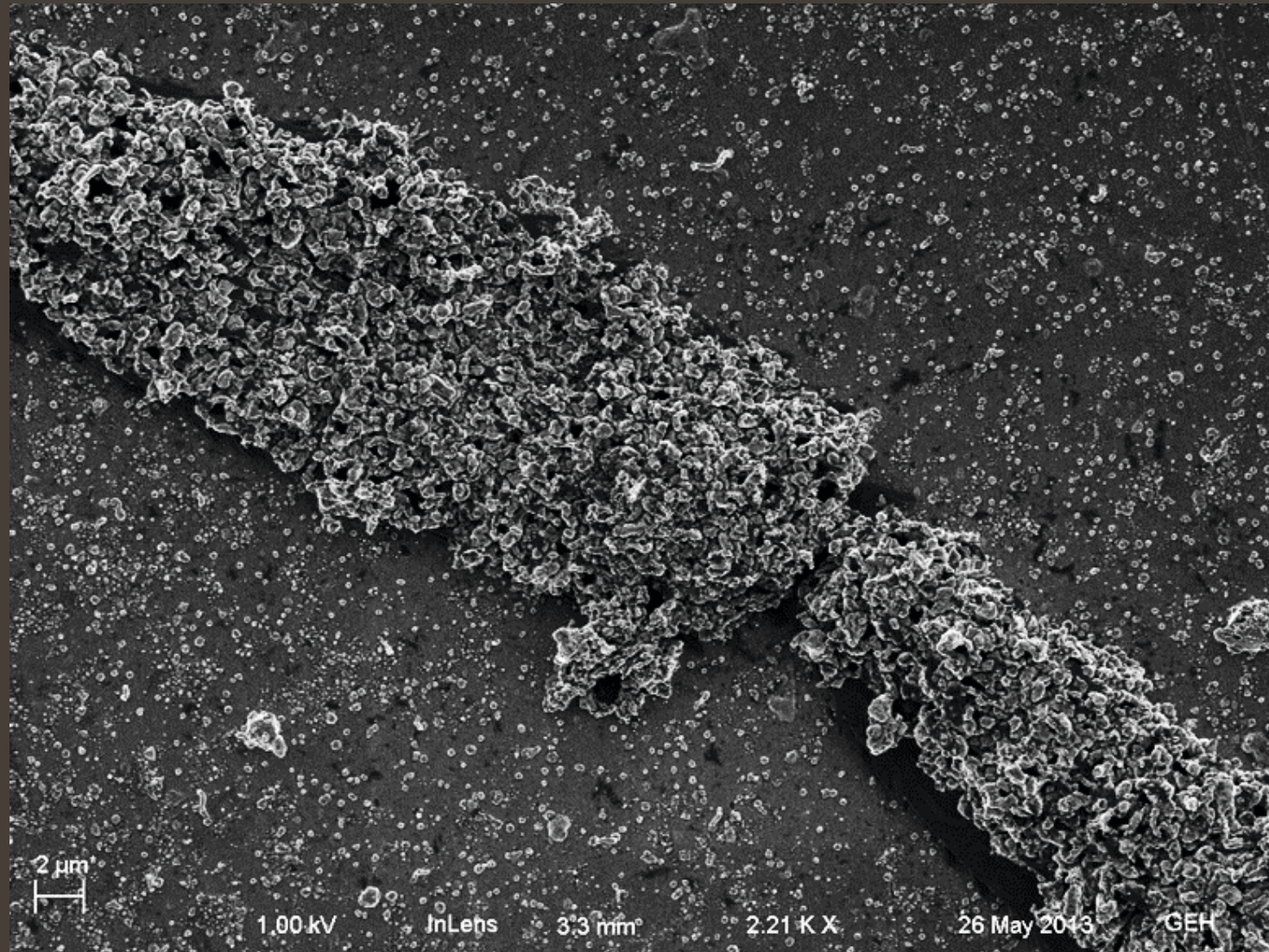




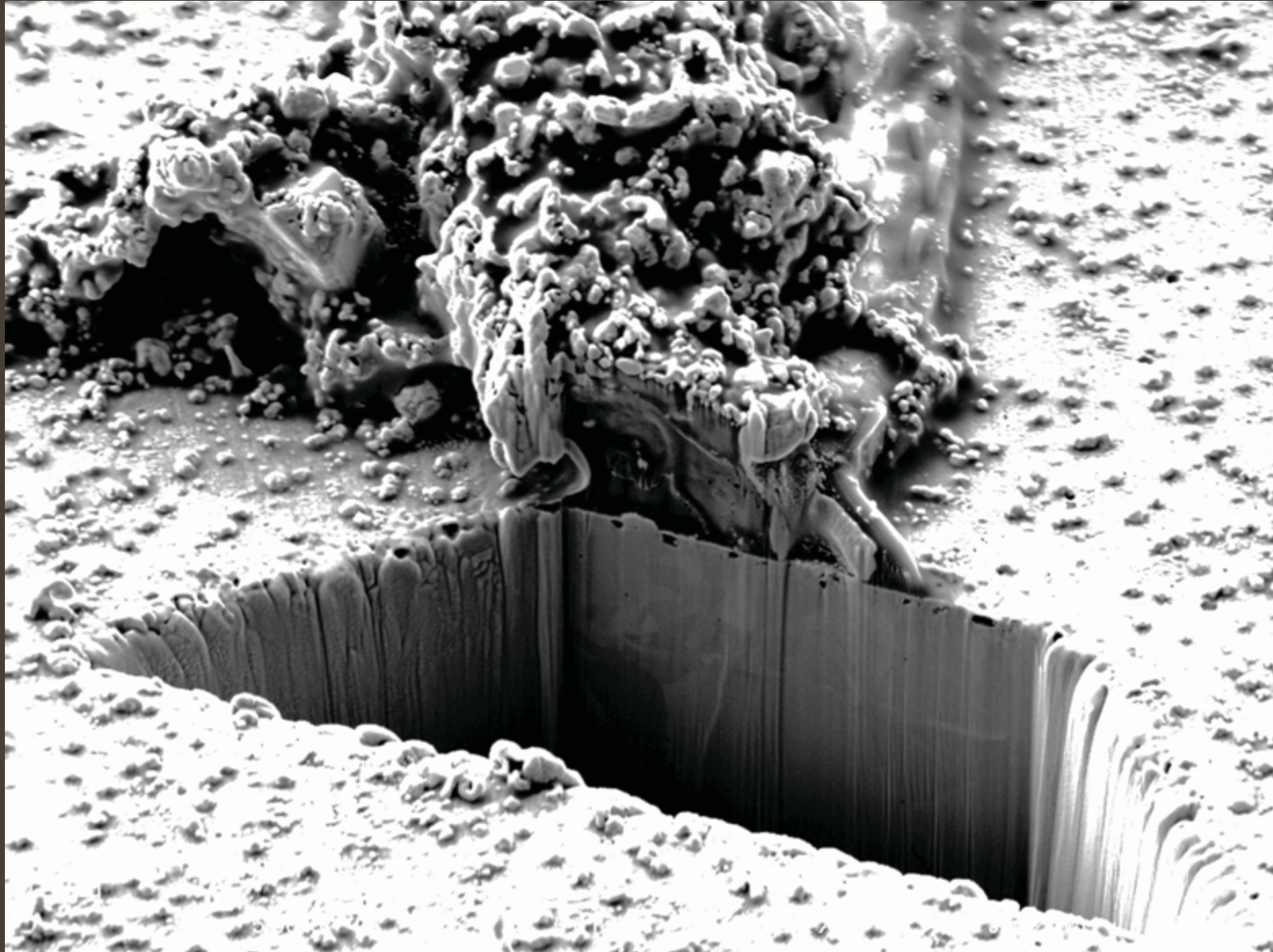
Arthropod interaction



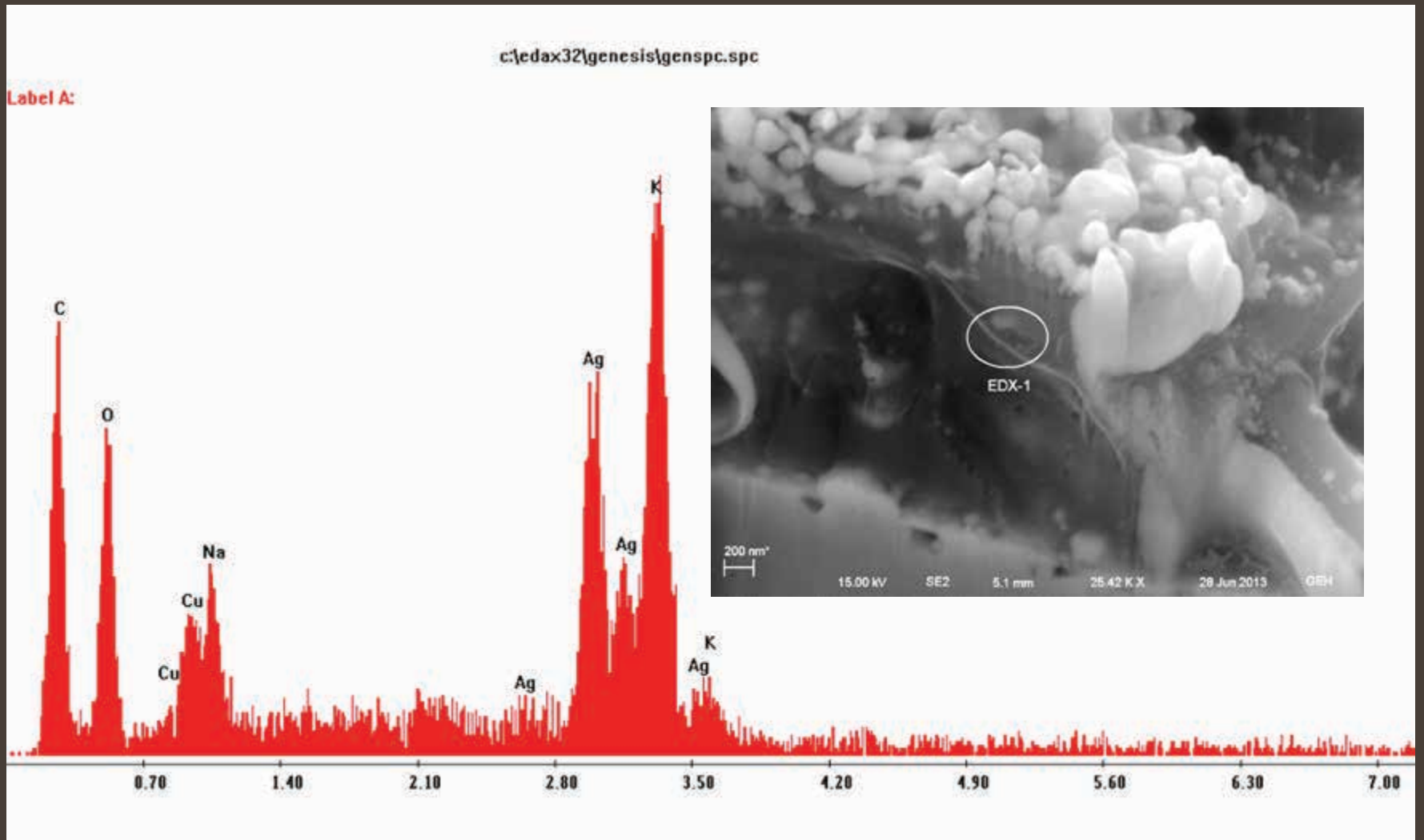
Diverse complexes of organo-metallic species encrusted on antennae



FIB X-section of antenna



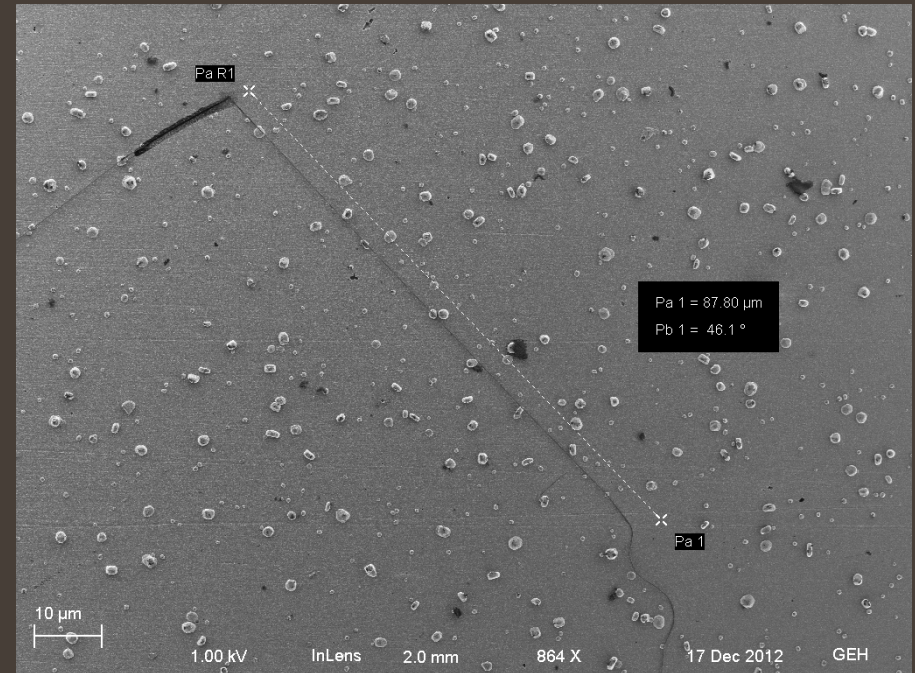
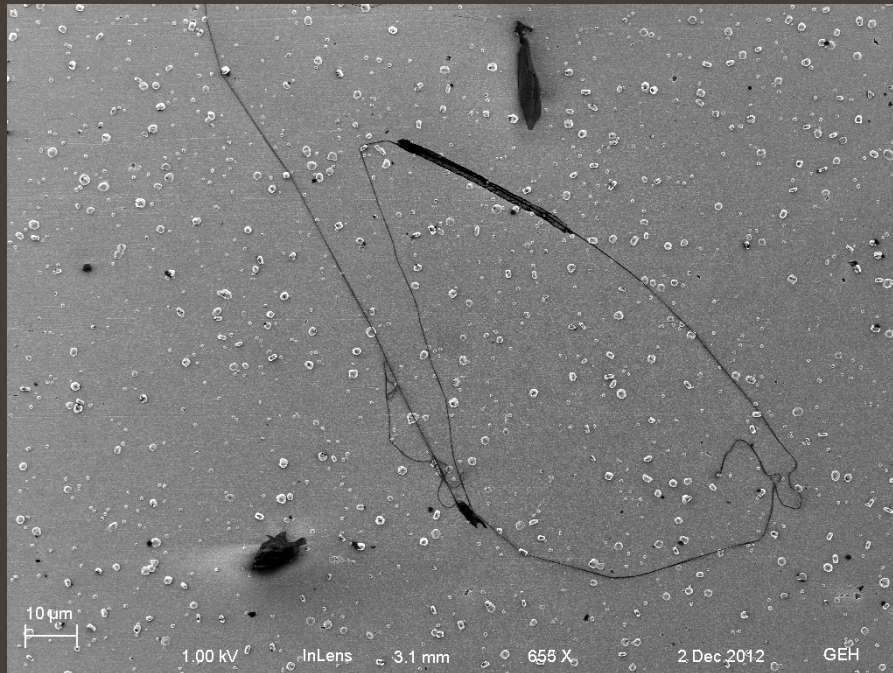
Analysis confirms the copper oxygen transport system of arthropods



Scientific rationale to pursue the nano-biological research of self-assembling organo-metallic structures

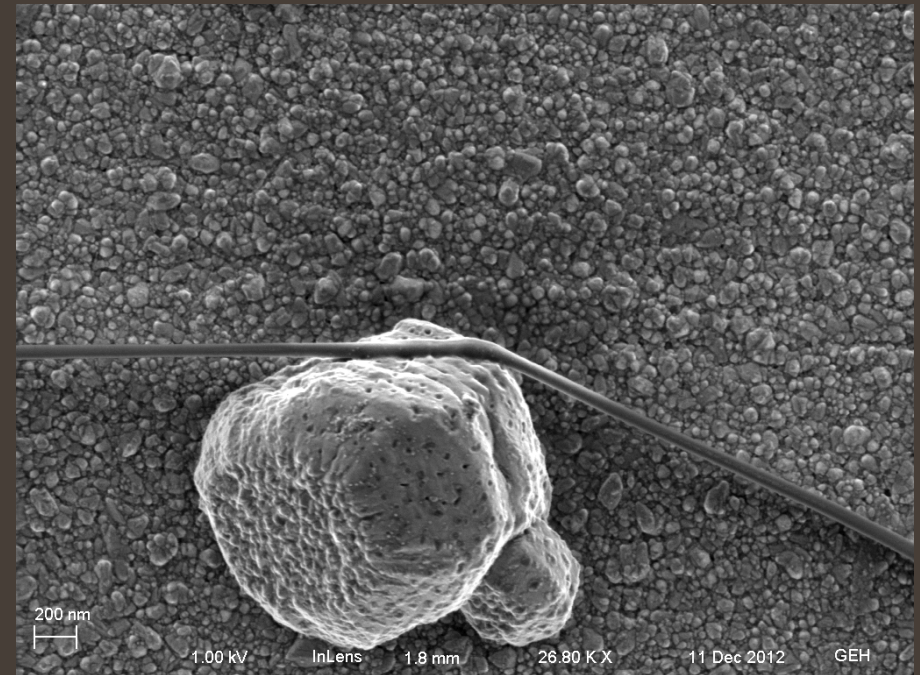
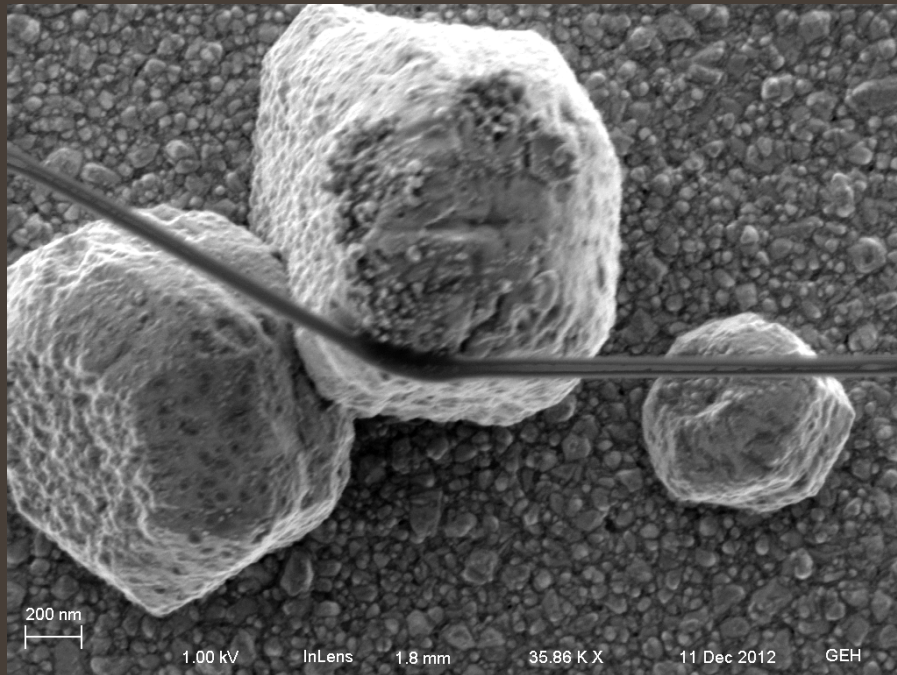


Single organism nano-metallic formation

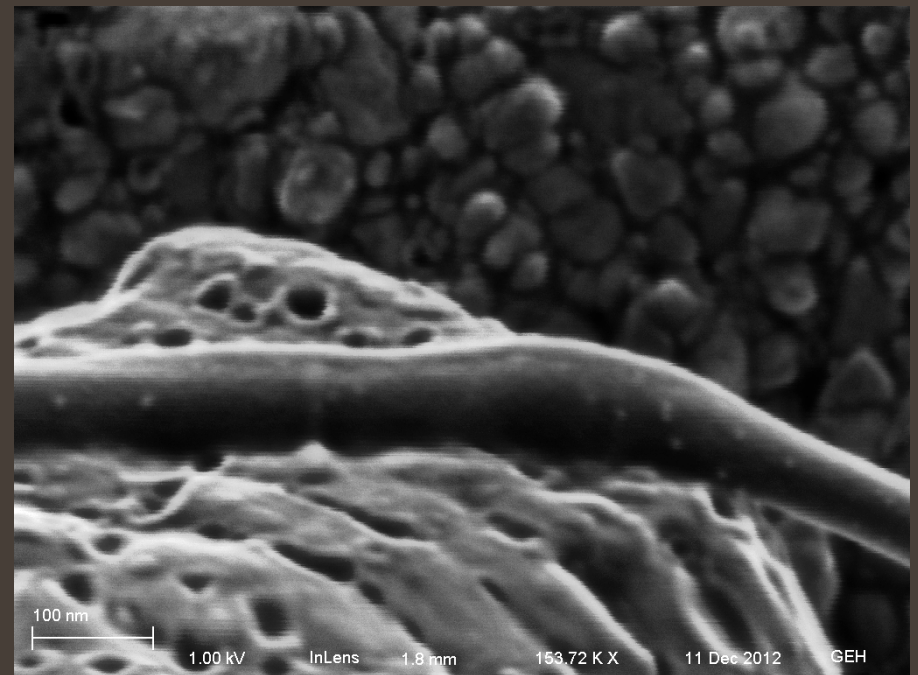
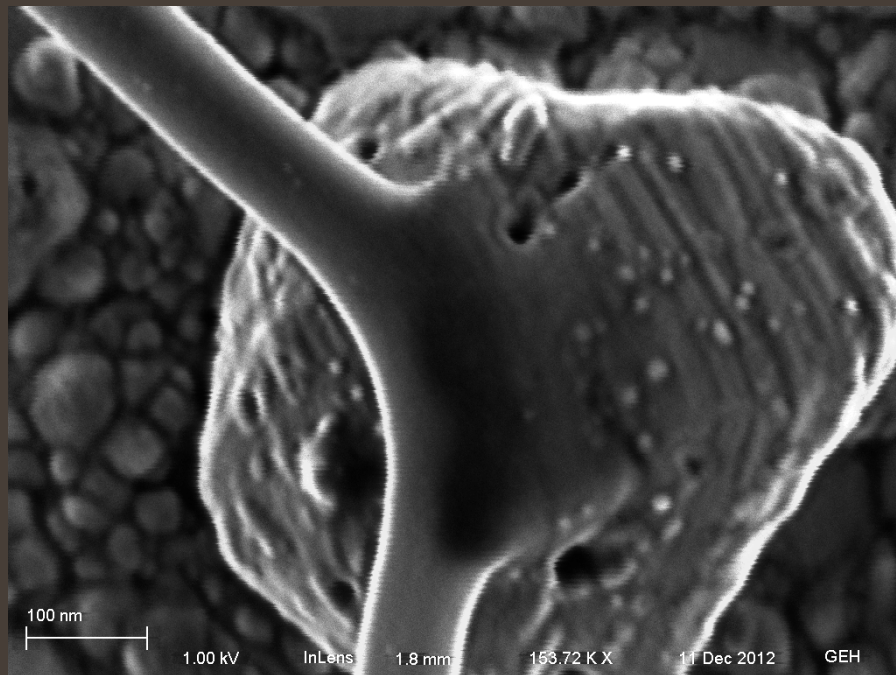


Approximate aspect ratio of 1:1760

Maintains a preferred distance above the daguerreotype surface of $\sim 250\text{nm}$

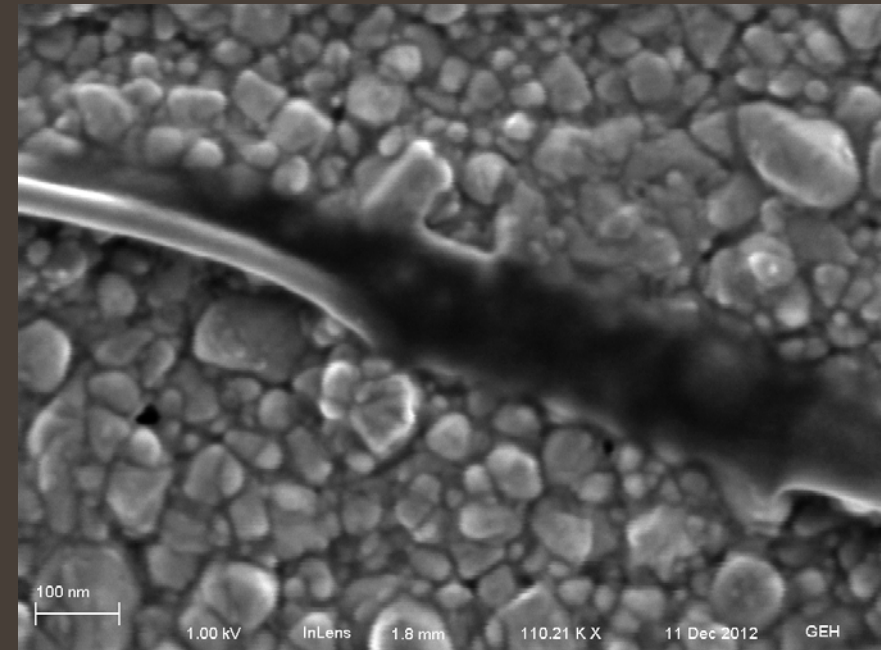
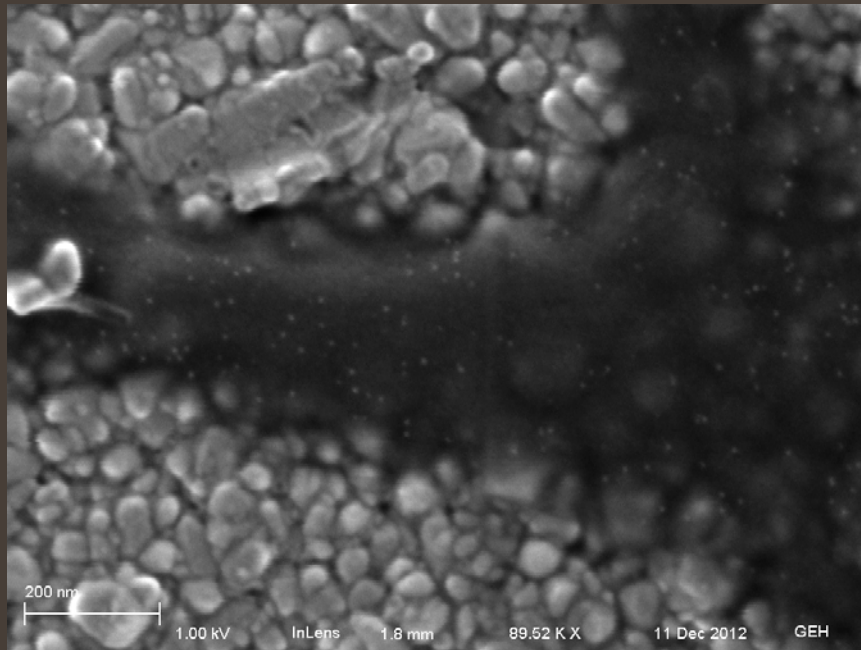


Appears to have macro mechanical properties



Magnification = 153Kx

Nano-fiber encounters surface



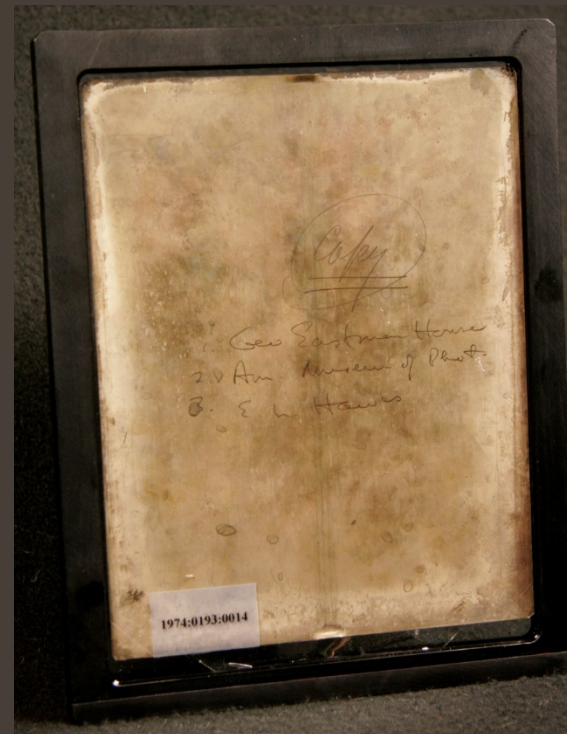
Dispersion of cytoplasmic contents –and then re-emergence and continuation of the 50nm diameter linear formation

Promising new methods to preserve daguerreotypes

Daniel Webster

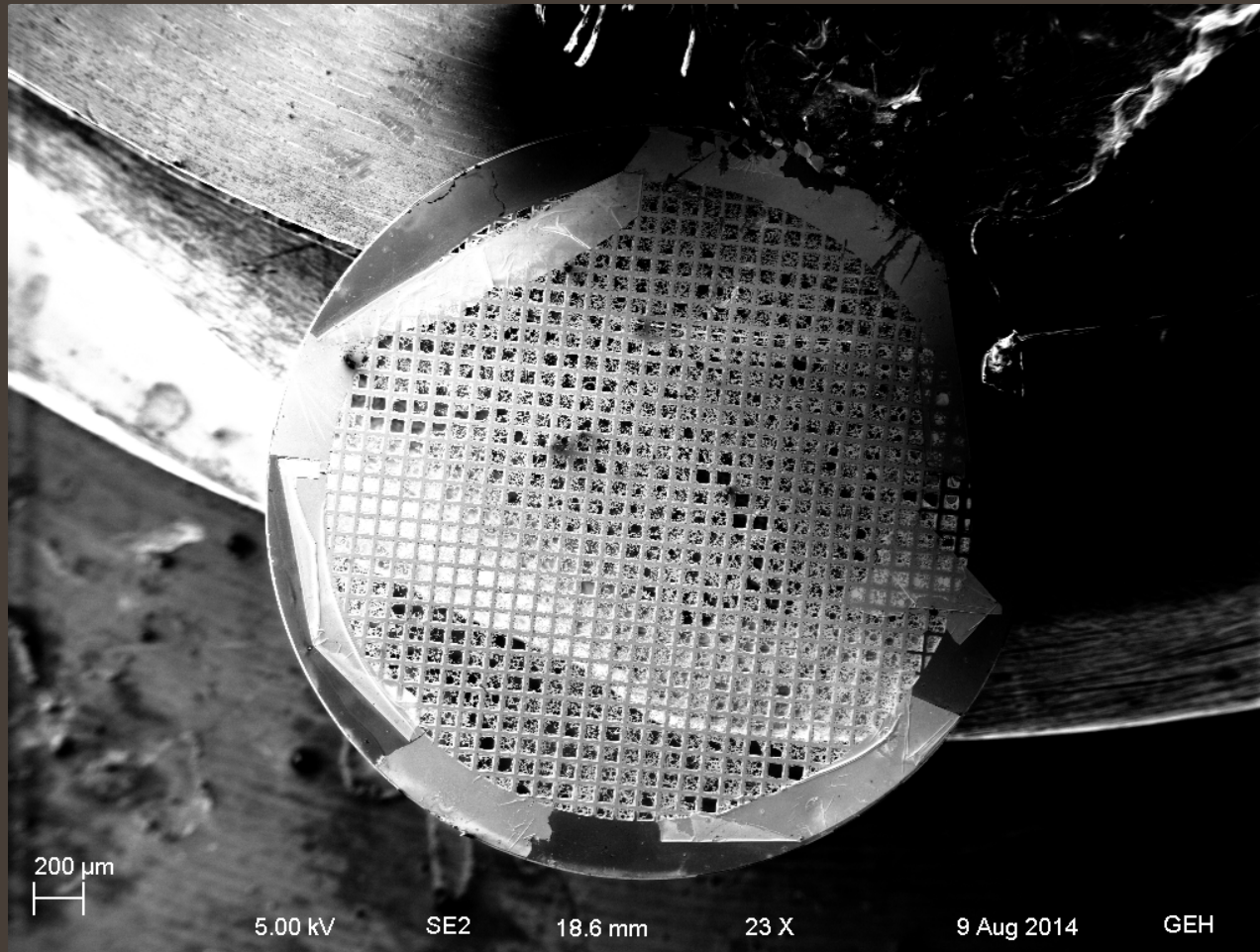
Albert Southworth & Josiah Hawes

George Eastman House International Museum of Photography & Film



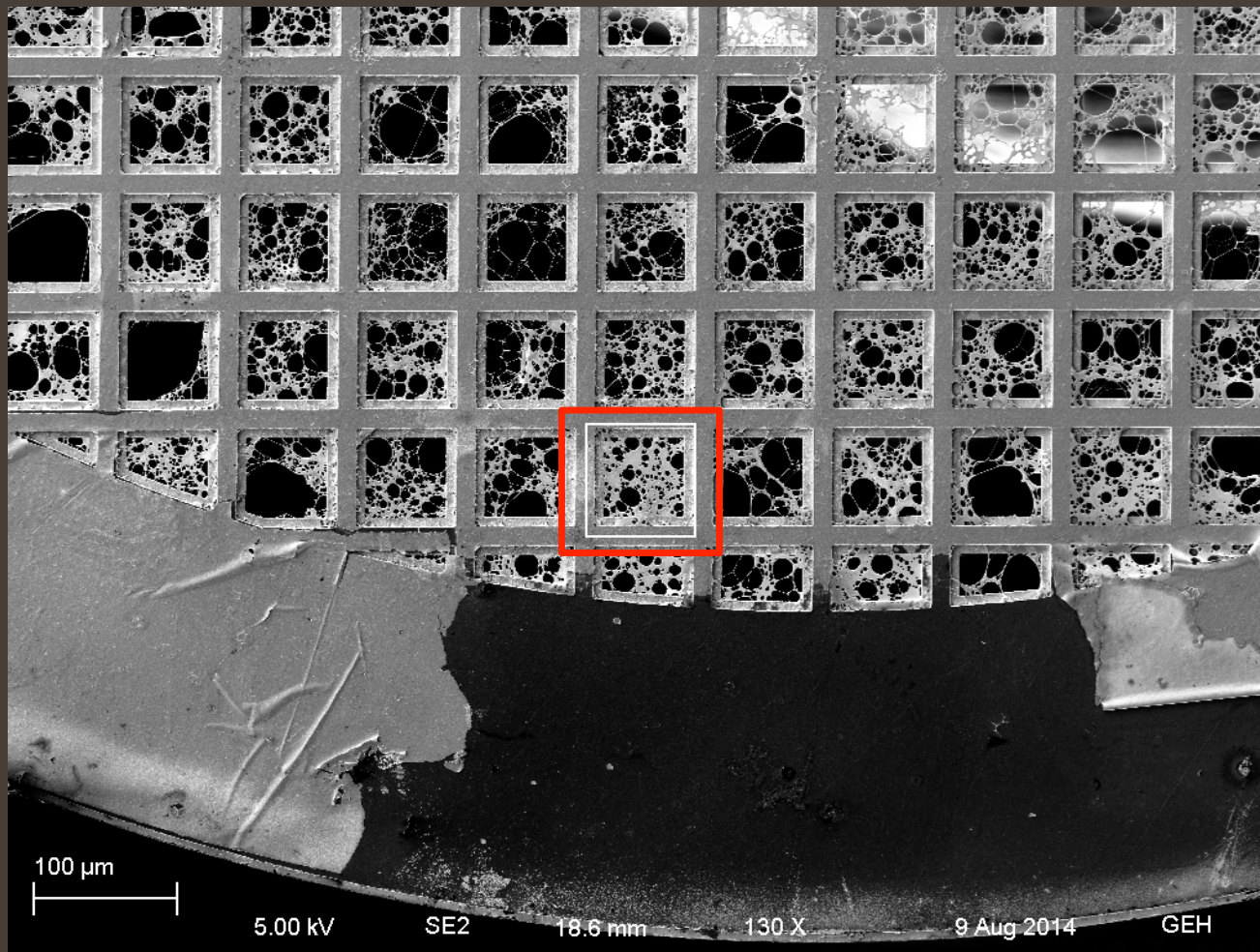
Whole plate daguerreotype: 8.5" x 6.5" in hermetically sealed argon enclosure

New research techniques for studying daguerreotypes

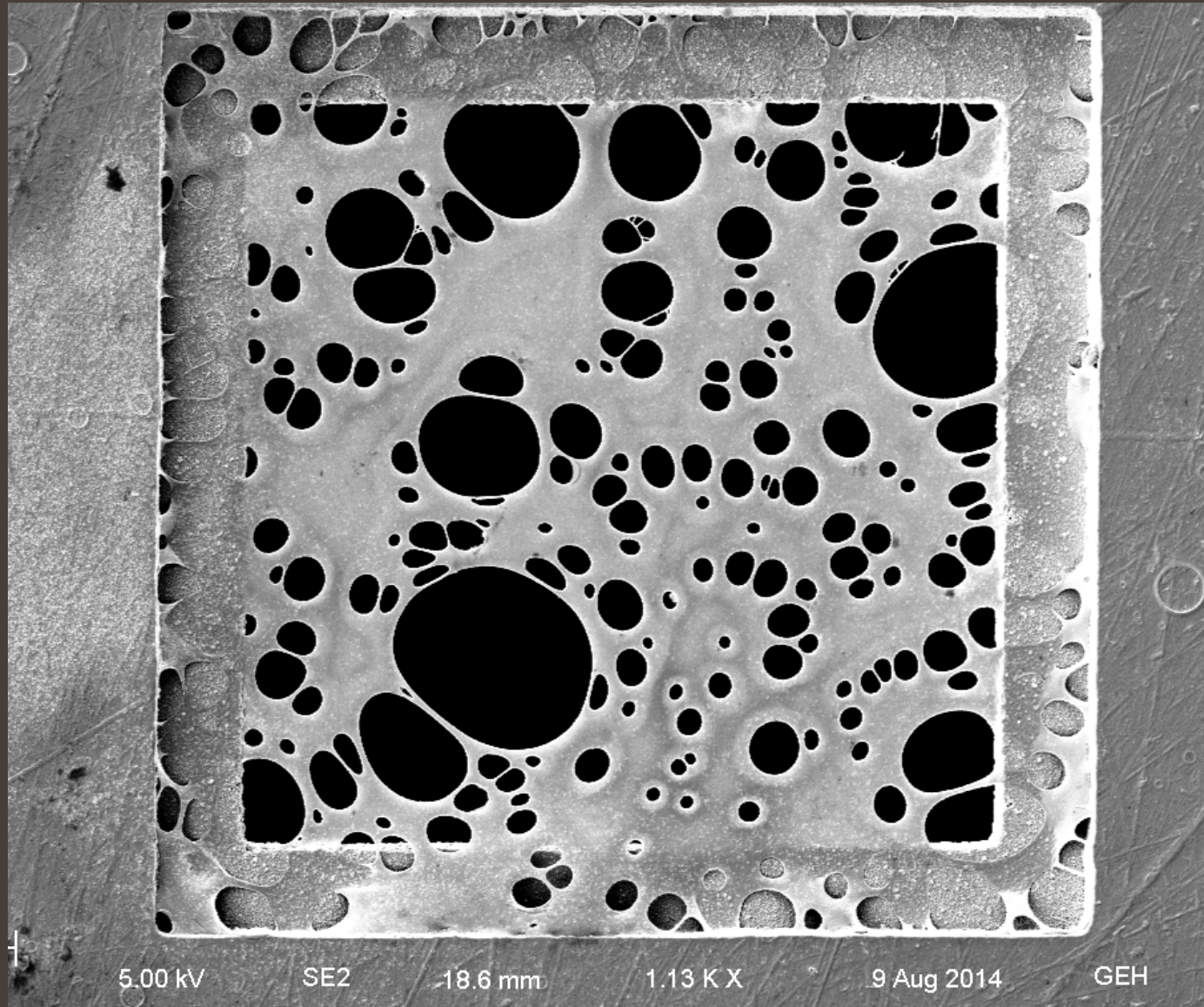


Making daguerreotypes directly on a transmission electron (TEM) microscope grid

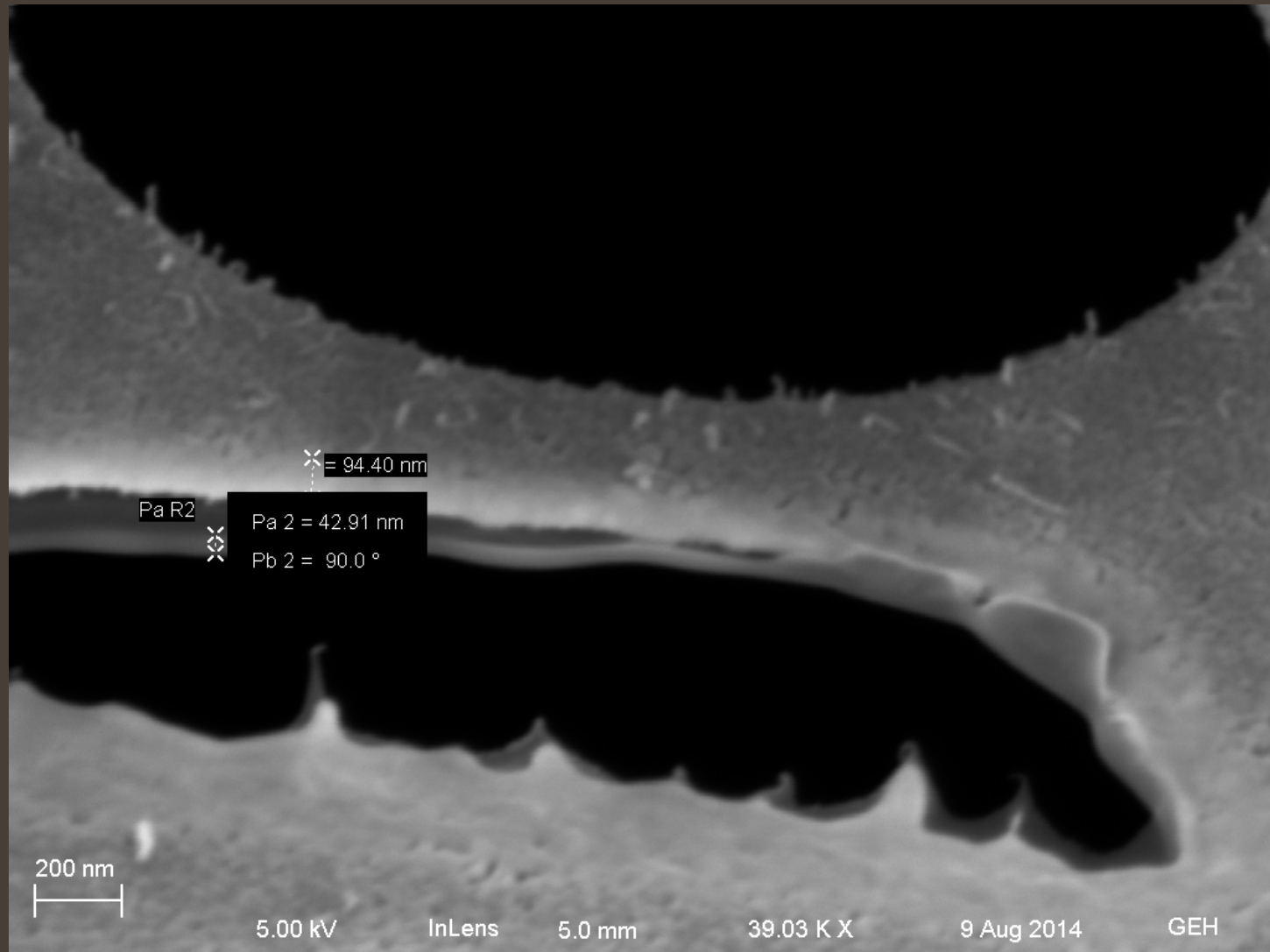
Grid square chosen for FIB analysis



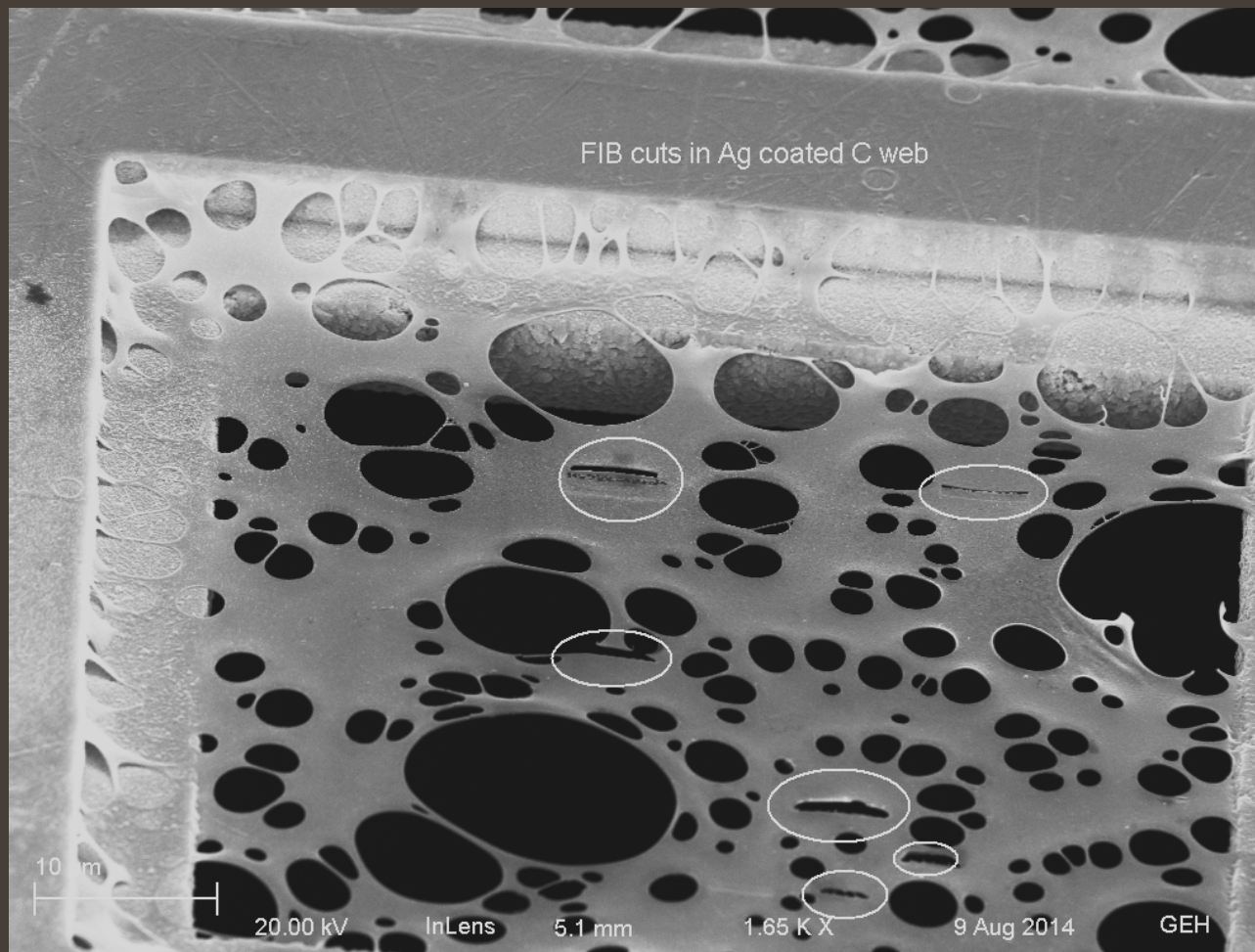
100 nm Ag vacuum sputter coated onto a “lacey carbon” TEM grid



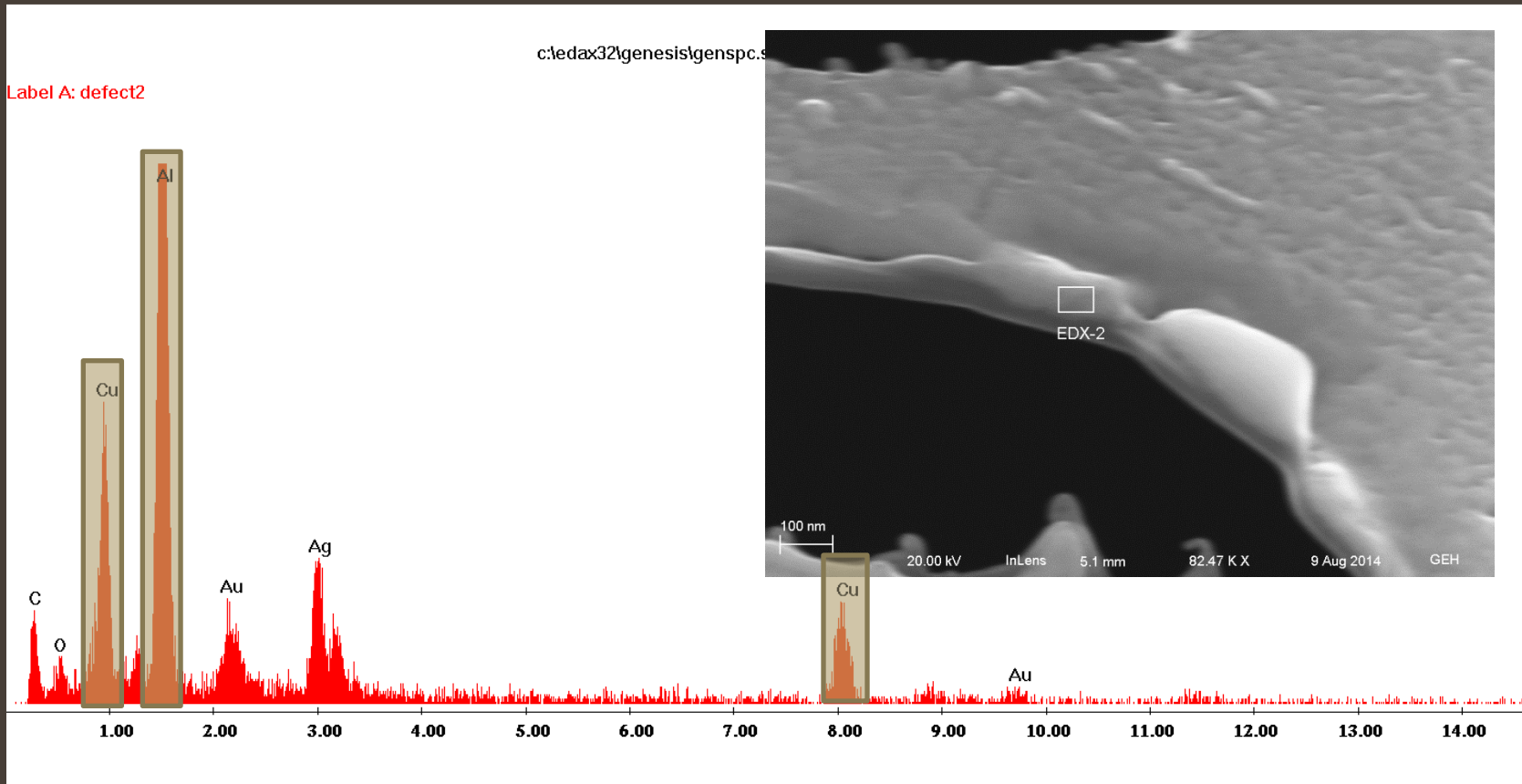
Thickness of the silver deposition after gilding: 92.40 nm
The lower stratum is a section of the carbon grid,
measuring 42.91nm



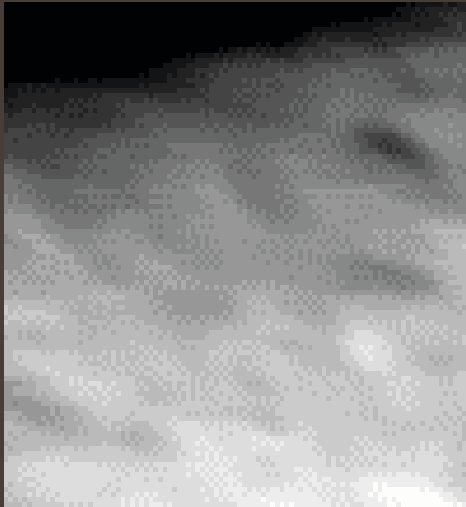
Location of FIB cuts into the iodized, fixed, and gilded “Tem-grid-otype”



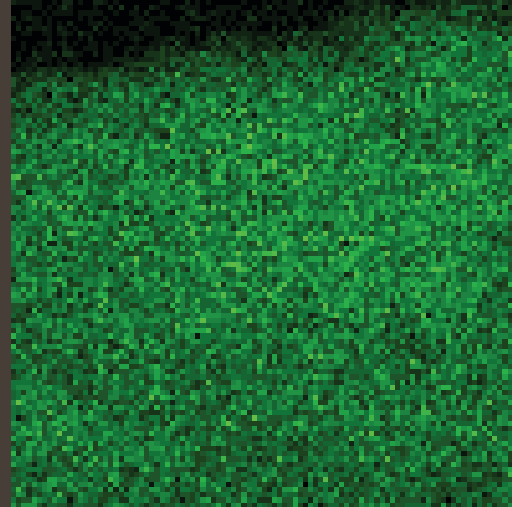
SEM-EDX spectrum shows an expected proportion of Ag to Au in a gilded daguerreotype. The Al signal is a result of scatter from the mounting stub, and the Cu signal is from the grid structure. Both the Al and Cu are to be discounted.



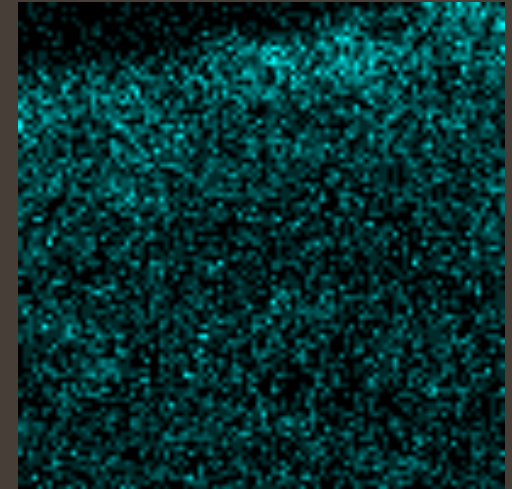
FIB section edge in Transmission Electron Microscope: high resolution elemental mapping nearly at the atomic level



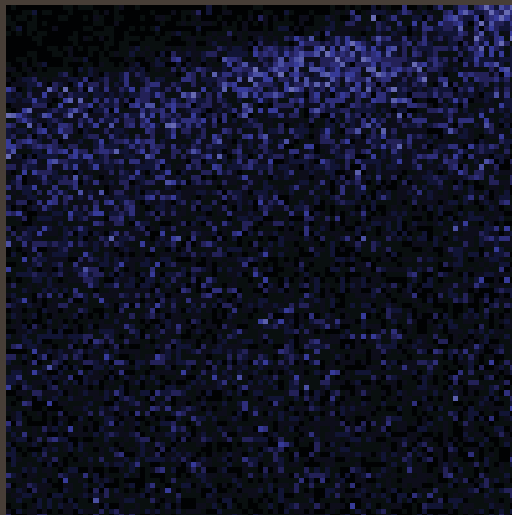
Detector image



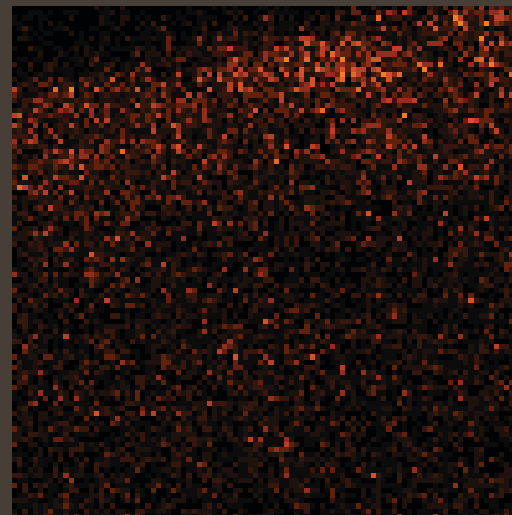
Ag-L



Au-L



Au-M



S-K

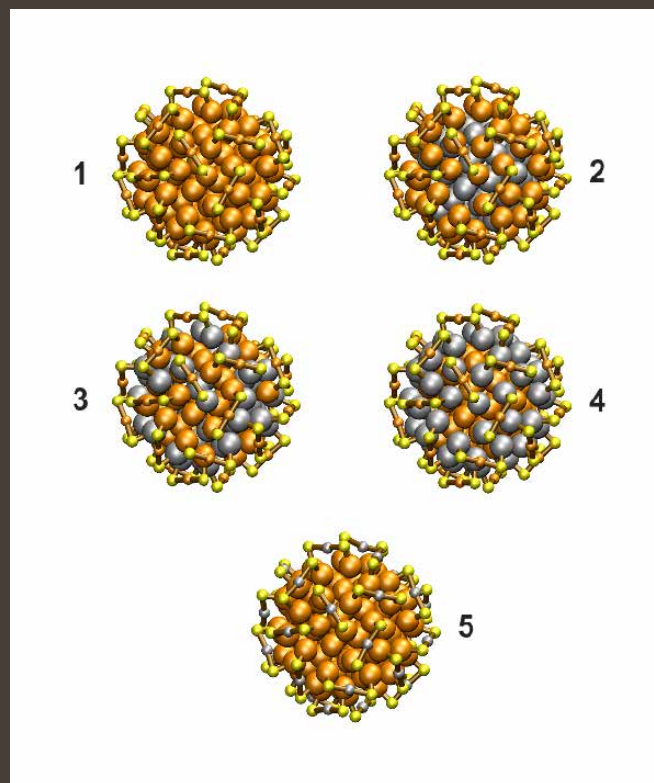
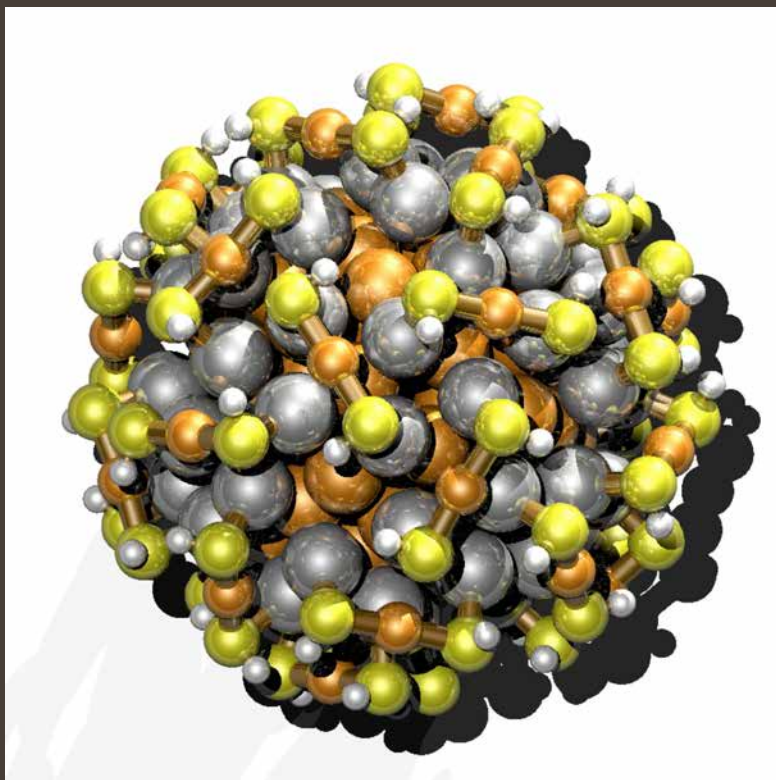
These first results of directly mapping the elemental distribution within the gilding layer by TEM is a breakthrough technique.

In this mode we will be able to control variables and measure results with great precision

Application of new analytical tools to characterize the daguerreotype; good for the daguerreotype – good for science!

- XPS is the newest instrument in the URNanocenter. It has the capacity to analyze the top few nanometers of a surface elementally and compositionally by determining binding energies that characterize the molecular structures
- XPS (which is a destructive technique), gathers tomographical data by progressive plasma etching and layer by layer analysis
- Using TEM grids as surrogate daguerreotypes we will be able to collect spatially resolved elemental data by TEM at the molecular level, and analyze the molecular structures by XPS

Research into the properties of gold and silver complexes, or superclusters for their extraordinary optical and electronic properties, may help our research into gilding.



Electronic Structure and Bonding of Icosahedral Core-Shell Gold-Silver Nanoalloy Clusters $\text{Au}_{144-x}\text{Ag}_x(\text{SR})_{60}$

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