Transmission Electron Microscopy for High Resolution Single-Particle Analysis

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Microanalysis of Particles 2009

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Outline

- Why TEM?
  - Introducing the 3010
- Sample preparation (*in the real world*)
- Examples
  - Illustrating an integrated approach to particle identification
- Conclusions

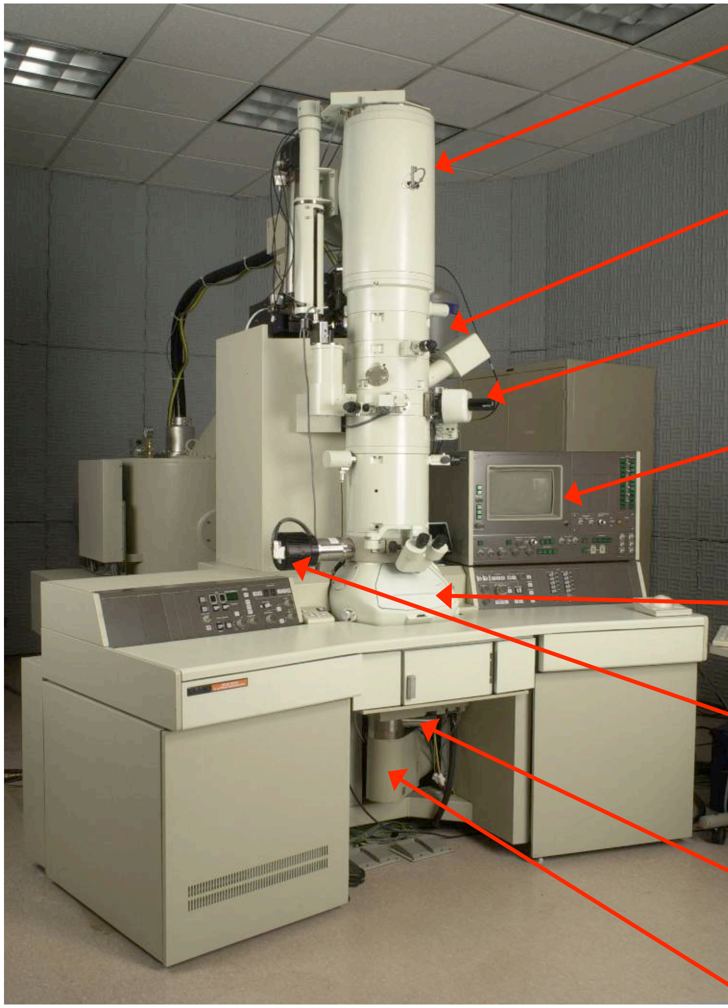
Why TEM for Particle Analysis?

- Sample amount may be very limited.
- Ultimate particle size may be very small.
- Particle may be a mix of:
  - Natural and synthetic components
  - Crystalline phases and amorphous material
  - Elemental compositions
  - Regions with differing electronic properties

Why TEM for Particle Analysis?

- TEM analysis can provide information about size, morphology, texture, elemental composition, crystallinity and electronic state, with sub-nanometer spatial resolution.
- Specialized capabilities include 3D tomography, in situ analysis, aberration correction for sub-Ångstrom resolution, and ultra-fast EM.

Introducing the JEOL JEM-3010 TEM



- Electron beam source (gun), 300 kV accelerating voltage
- X-ray detector for elemental analysis
- Sample holder (single or double tilt, cold stage)
- STEM unit for operation in scanning transmission mode
- Sample viewing chamber (fluorescent screen)
- Anti-blooming CCD camera for diffraction, low magnification imaging
- 2k x 2k high resolution CCD camera
- Electron energy loss spectrometer (EELS)

Some Limitations

- The specimen must be thin enough to transmit electrons; optimum thickness is less than 100 nm.
- The material must be able to withstand heating by the electron beam. Low beam dose conditions or use of a cold stage may be necessary.
- Features of interest must exhibit contrast due to differences in thickness, chemistry or crystallinity.
- Very small amounts of material are examined; use in conjunction with bulk techniques if possible.

Particle Sample Preparation Options

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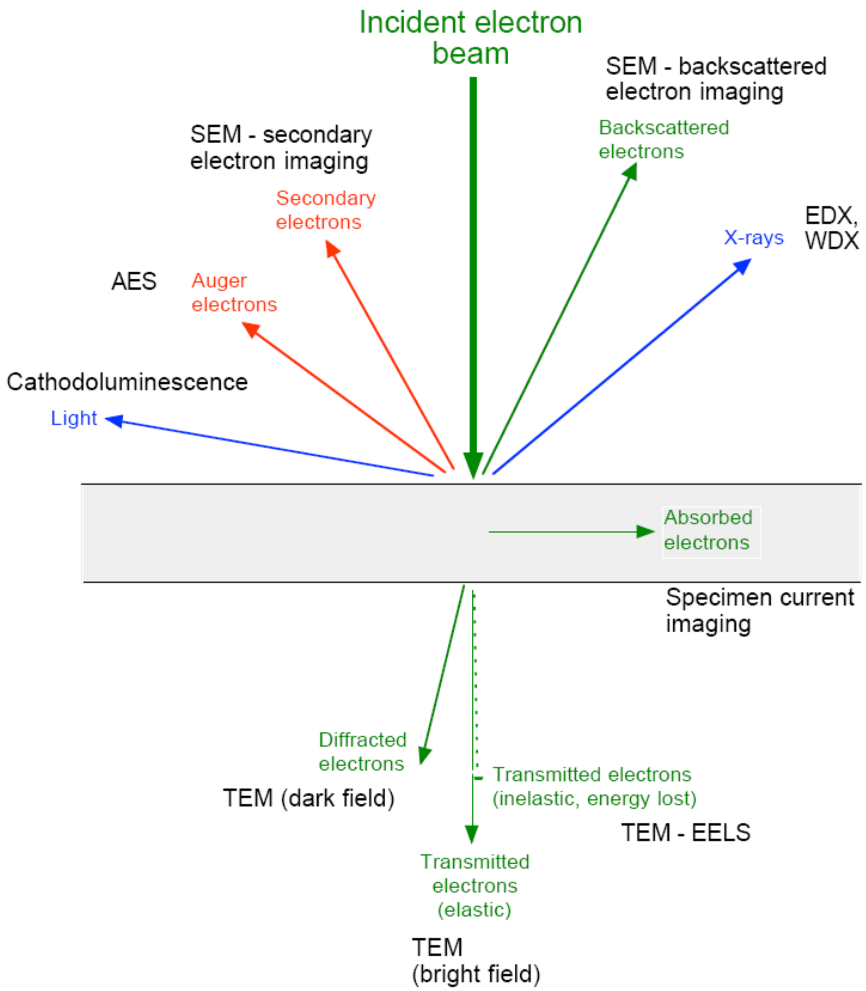
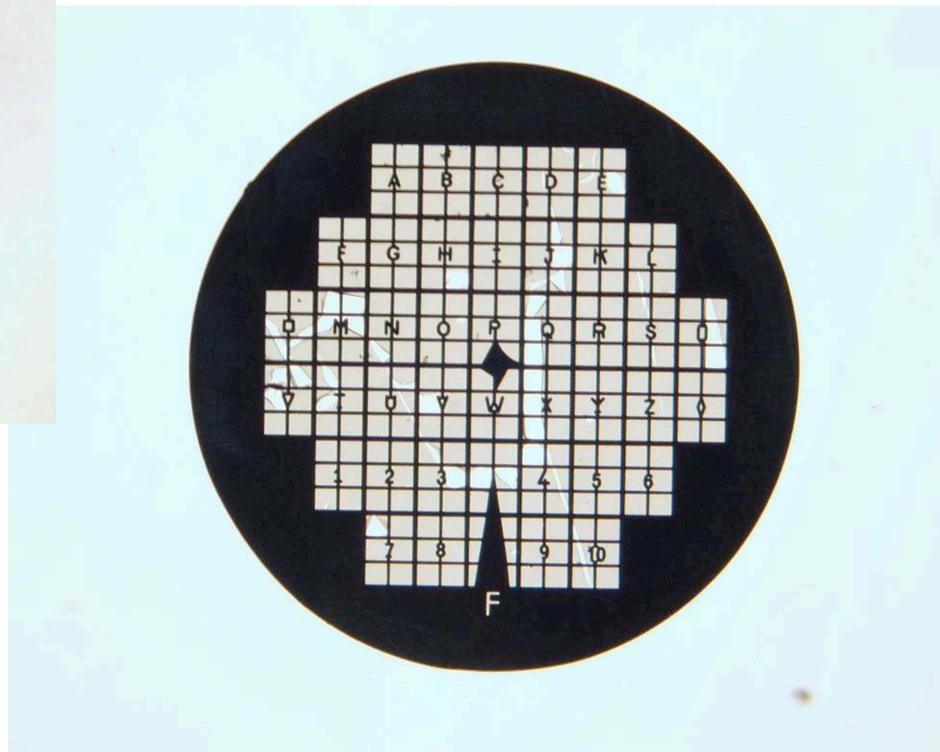
- Analy
  - Em
  - Foc



Standard 3mm Diameter TEM Grid

The copper mesh grid is coated with a thin, amorphous carbon film that supports dispersed particles.



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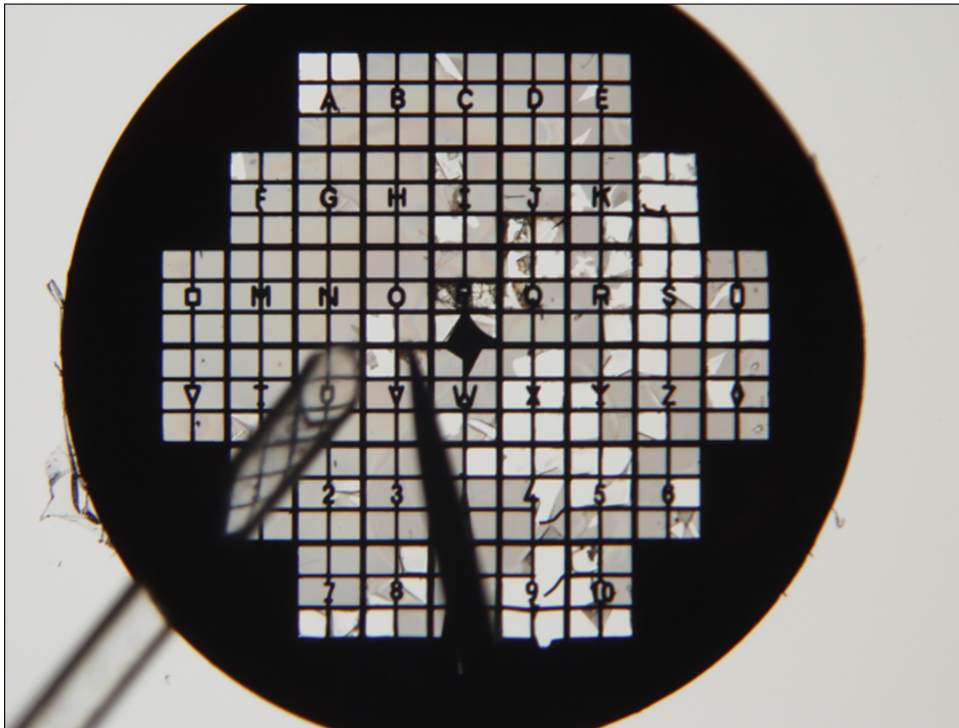
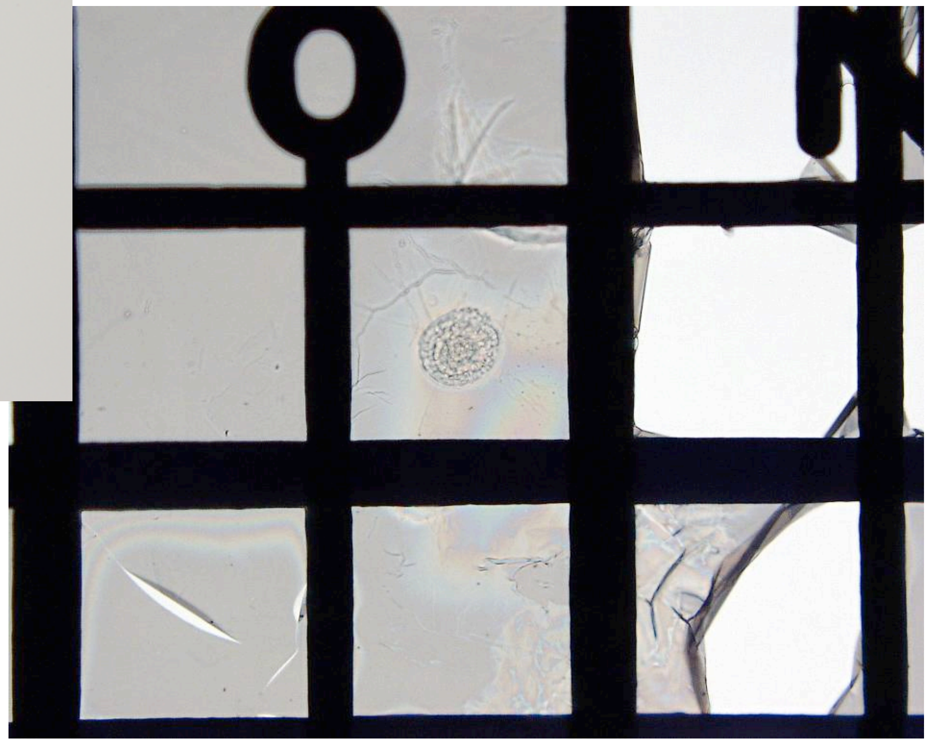
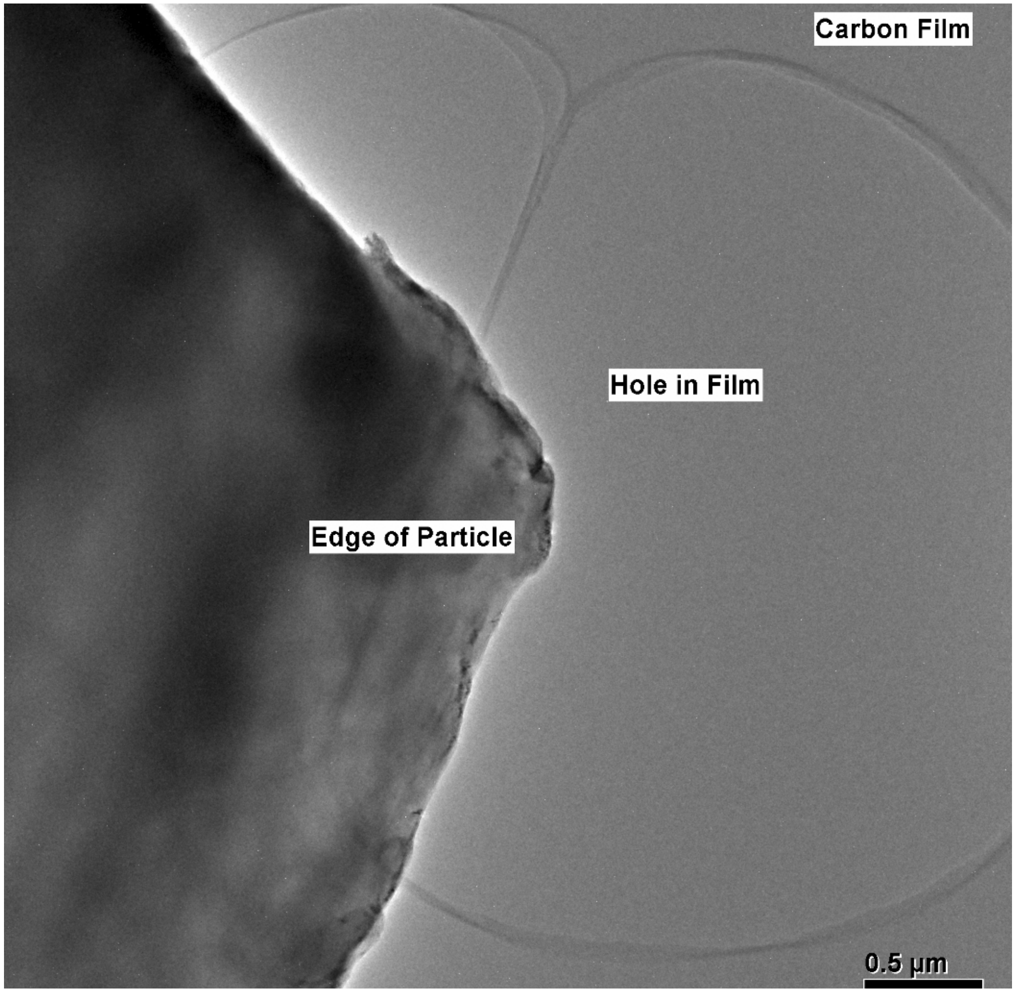
Precision Placement of a Single Spore on a Locator Grid





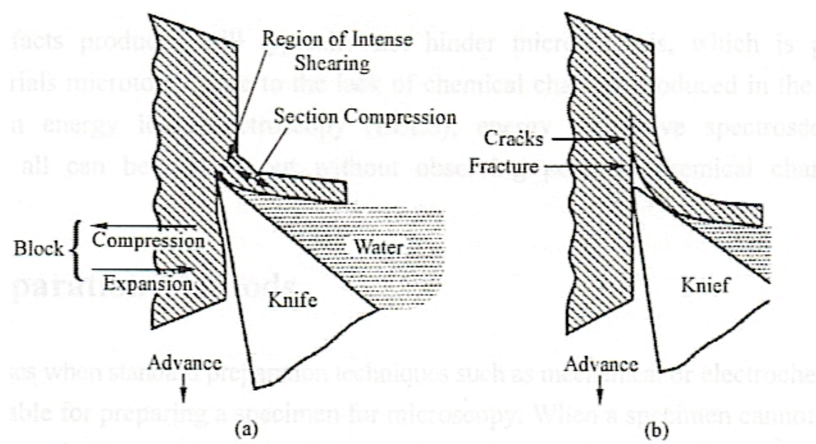
Particle Dispersion on Holey Carbon Film



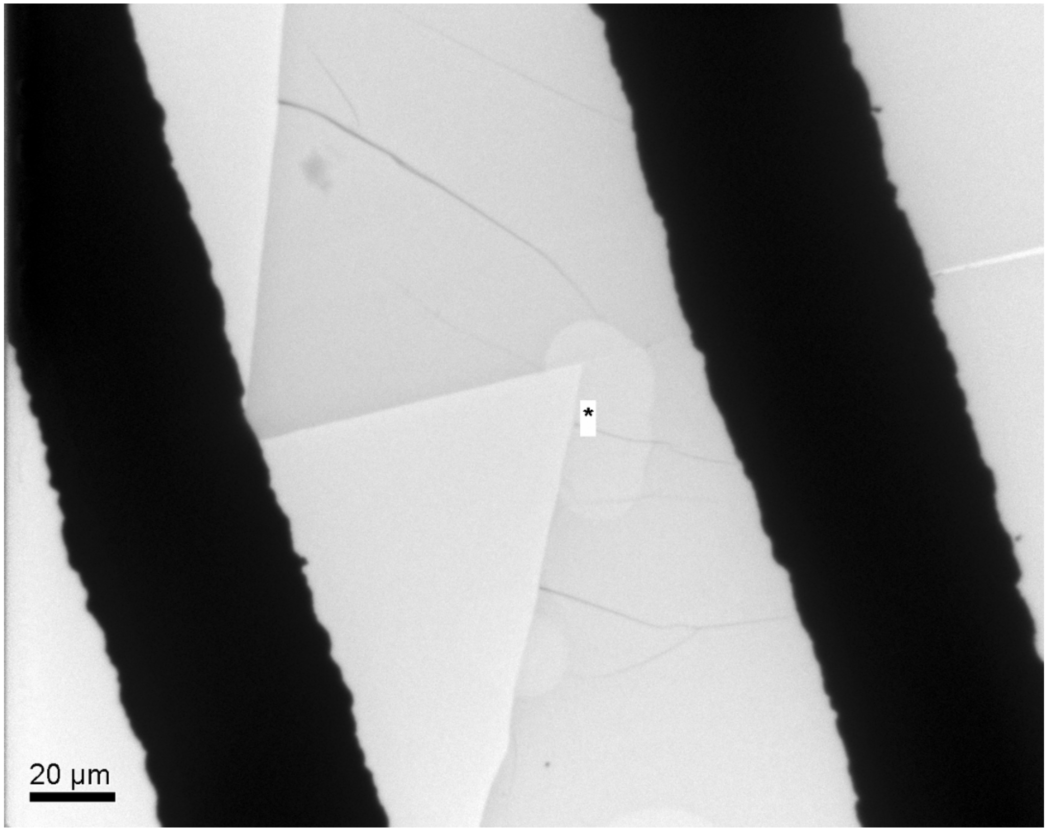
The holey carbon film is supported on a copper mesh grid. Thin particle edges suspended over holes are ideal locations for analysis, because beam electrons are transmitted only through the sample. There is no additional scattering from the support film, and resolution is improved.

Ultramicrotomy

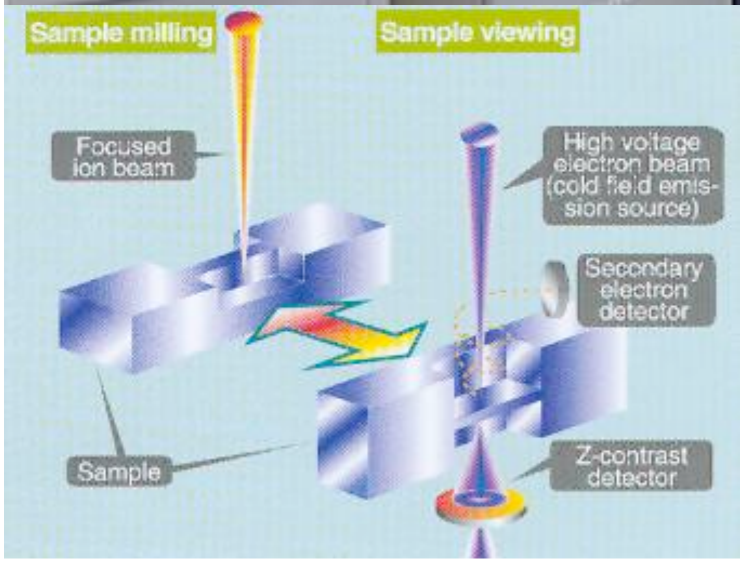
Makes use of a diamond cutting knife to slice a thin portion of the specimen as it is advanced by as little as 5nm per revolution. More regularly used for life science specimens, it has some advantages for materials science prep – in particular, chemistry changes do not occur using ultramicrotomy, unlike ion milling and electropolishing. However there is severe mechanical deformation.



Microtomed Polymer Sections on a Slotted Grid



Focused Ion Beam Milling (FIB)



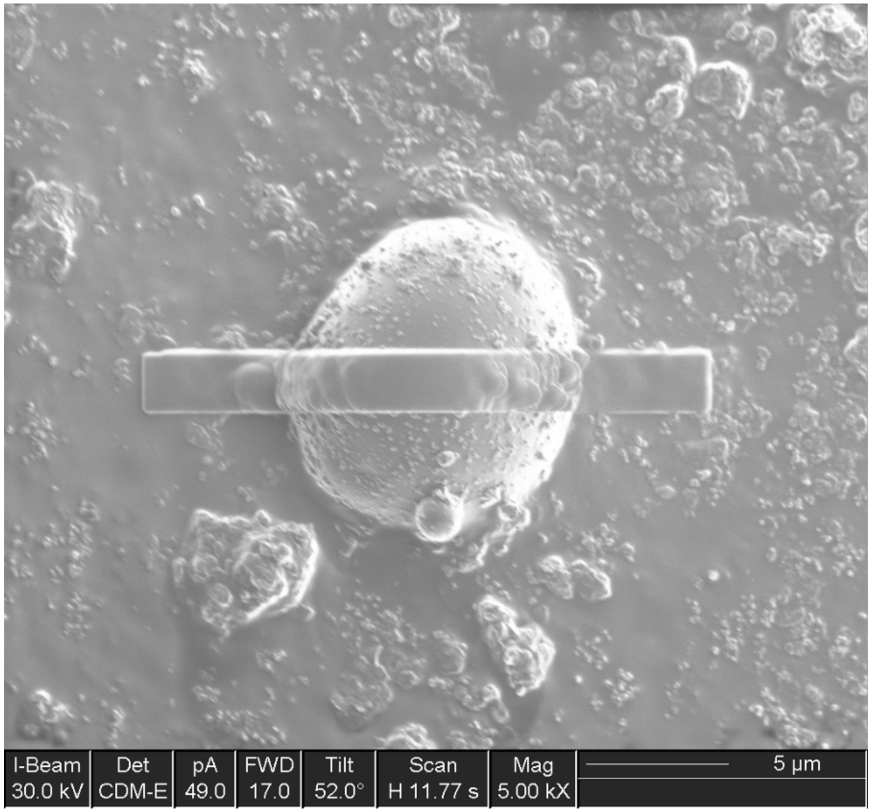
- Operation is similar to an SEM.
- Ga ion beam is used at low current to form images using secondary ions or secondary electrons produced by interaction with the sample (~5nm).
- At high current, the beam sputters material from the sample; this can be controlled to carry out precision milling on a micro scale (up to several nA; probe size up to 500nm).
- Dual beam instruments incorporate an electron beam for imaging and an ion beam for milling.

Focused Ion Beam Milling

Features

- Multiple beams for coating and sputtering (Ga, Pt, W)
- Multiple ion and electron detectors for monitoring milling process and for high quality SEM imaging
- EDS, WDS and EBDS detectors for chemical analysis and phase identification
- STEM detector to monitor sample thickness during TEM specimen preparation, and for transmission imaging in FIB
- Sample manipulators; thin sections can be transferred to TEM grids *in situ*

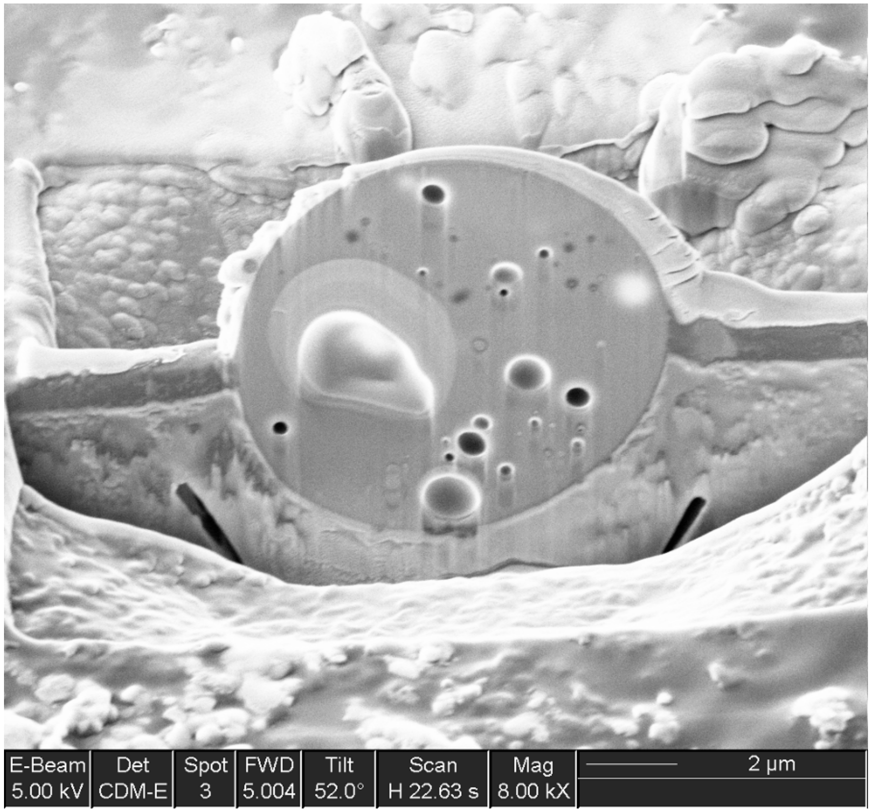
Focused Ion Beam Milling



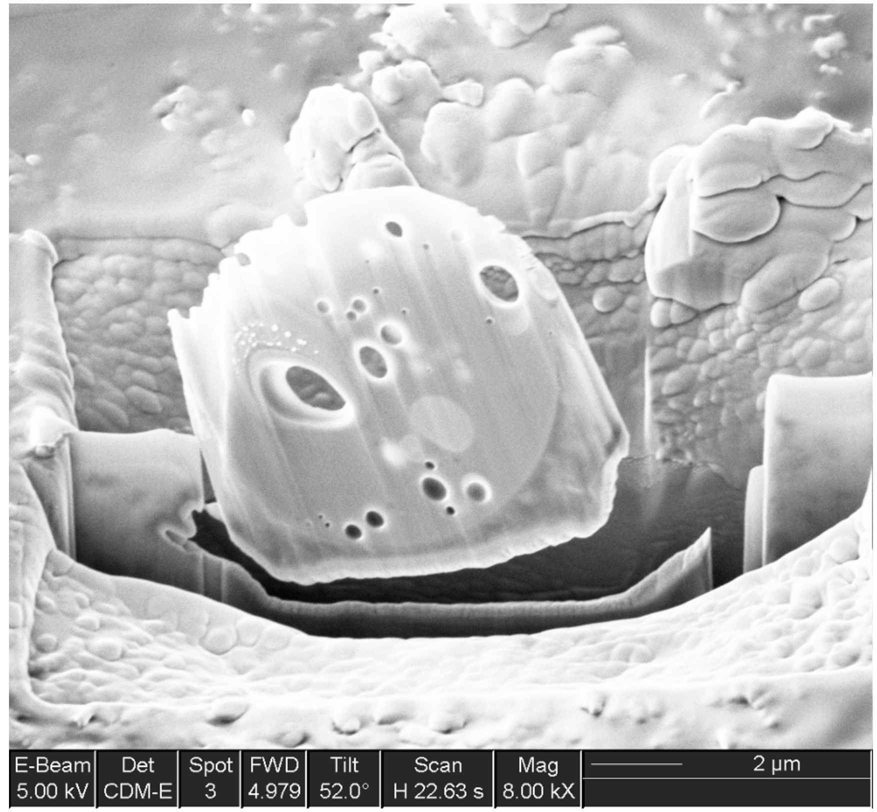
Ion image after coating specimen with Pt

Electron image after first rough cut to remove bulk of particle

Focused Ion Beam Milling



Electron image showing undercut



Electron image showing final cuts to loosen section

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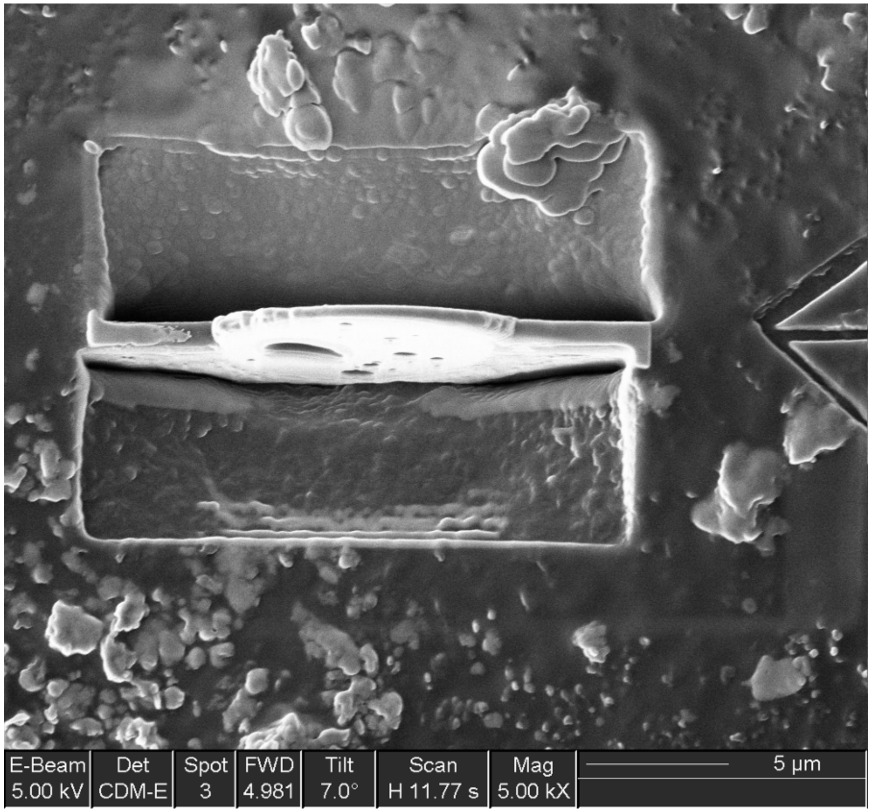
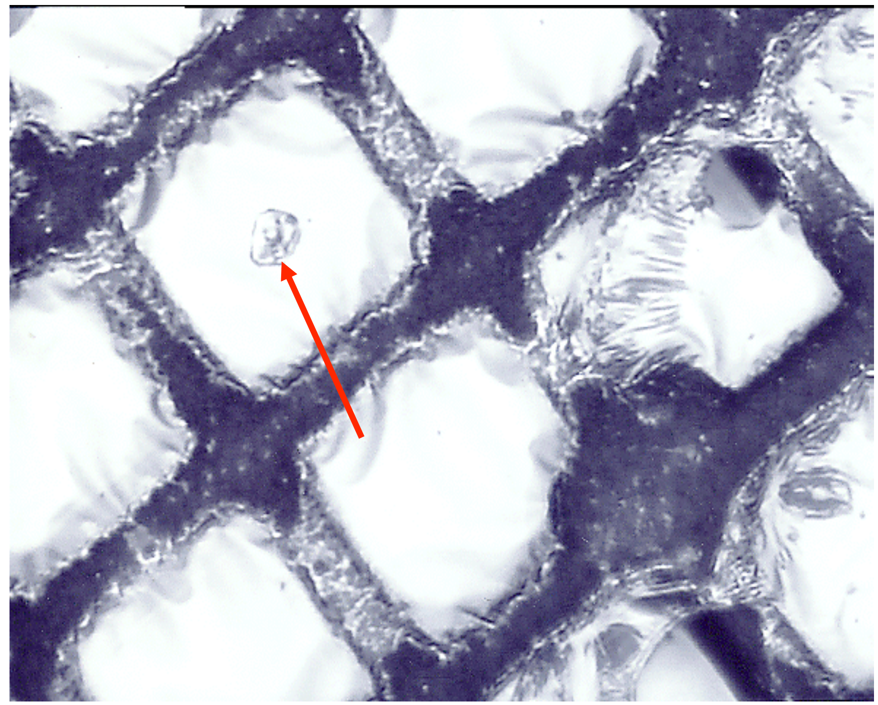
Focused Ion Beam Milling



Top view of thin section before final cuts



Optical photomicrograph of thin section after placement on TEM grid

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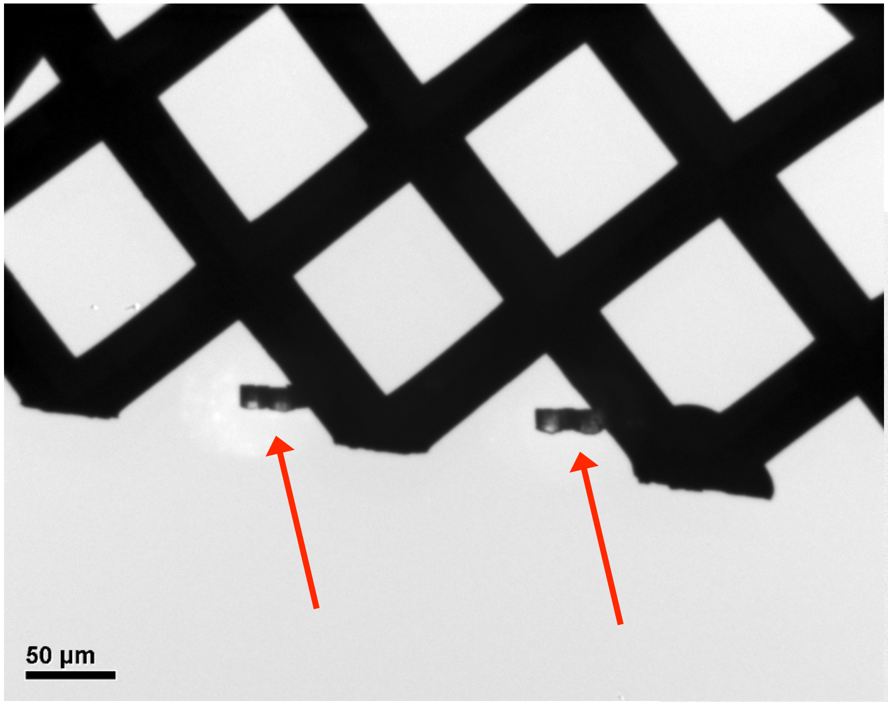
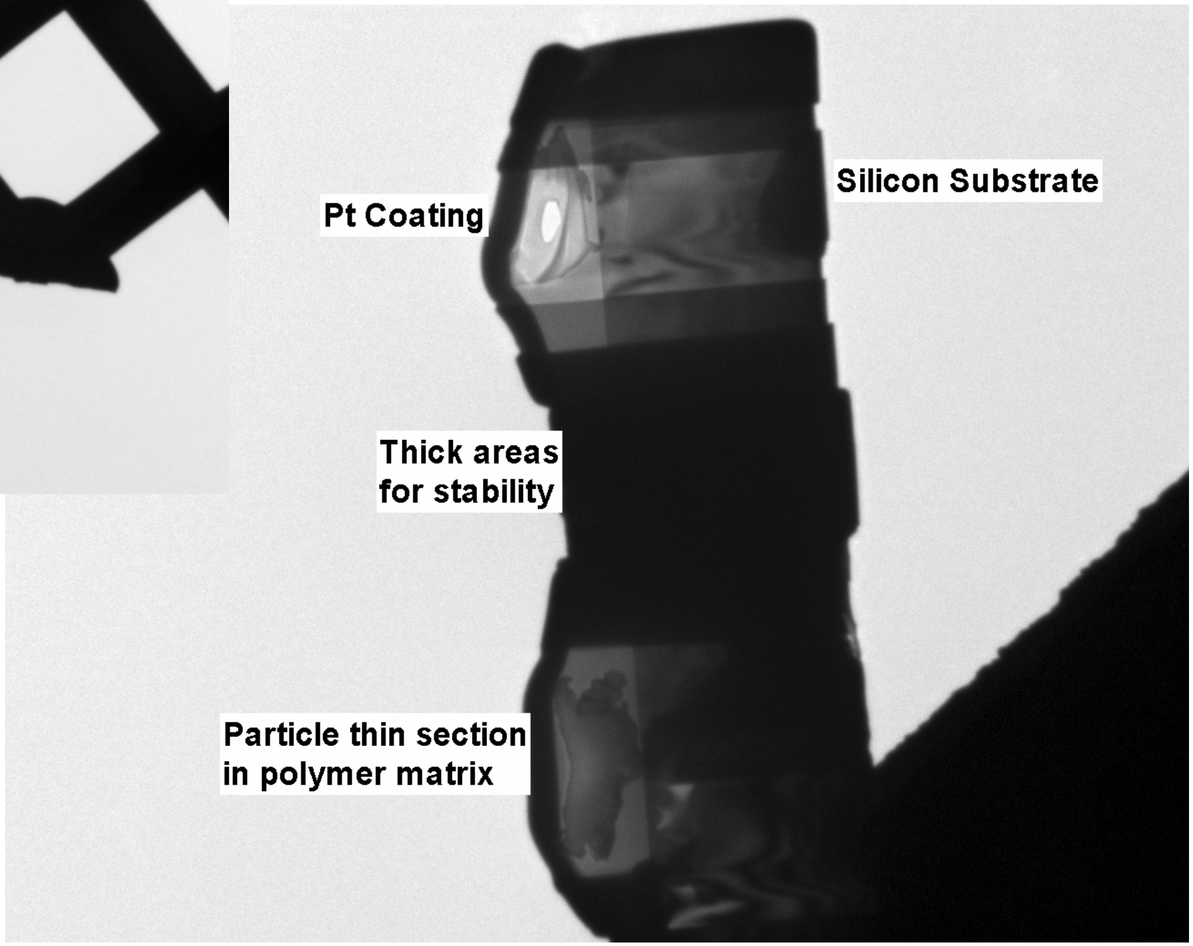
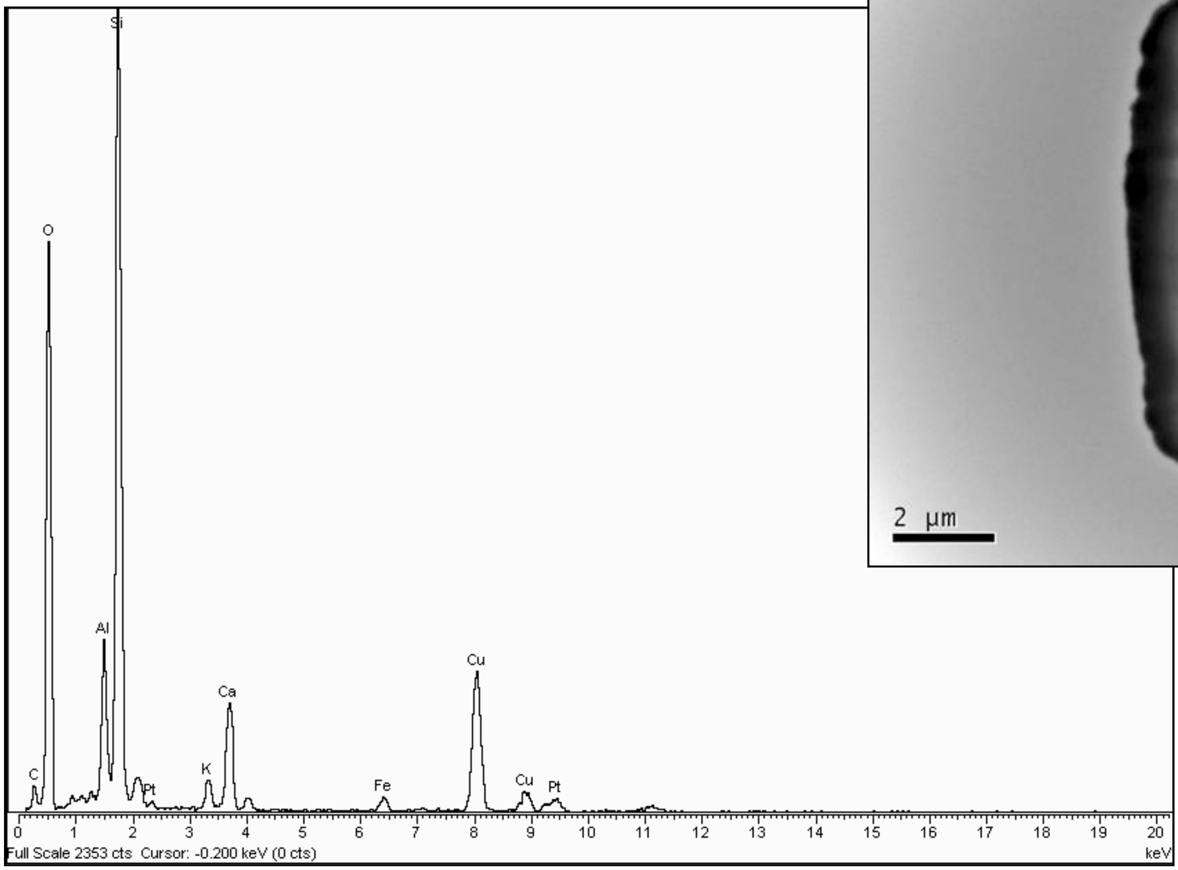
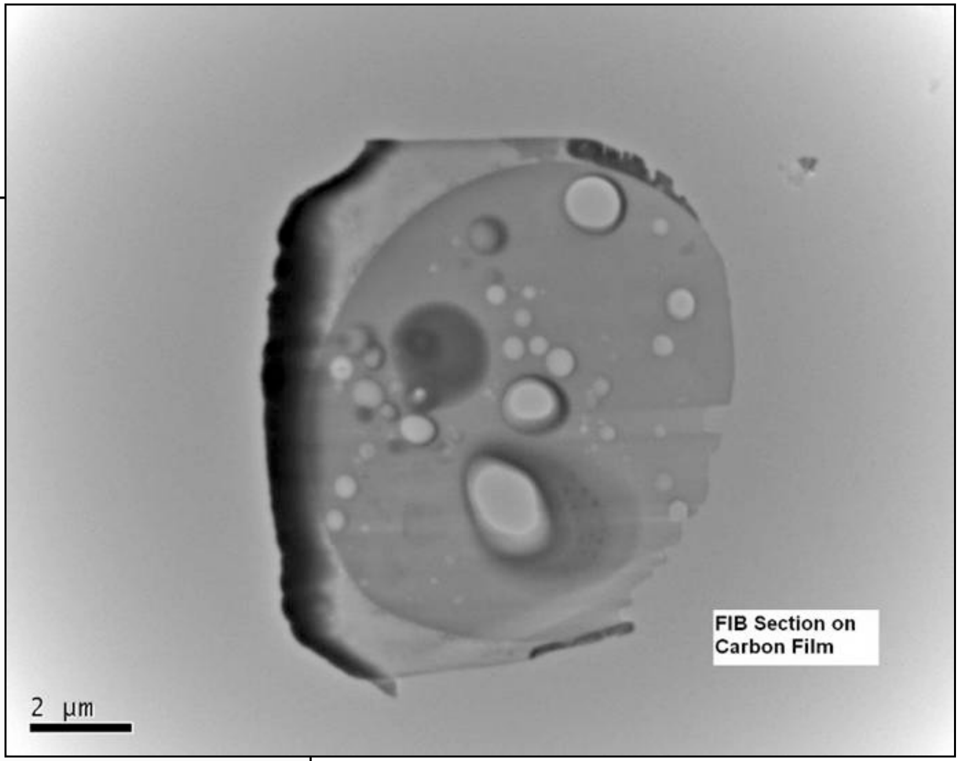
FIB Sections Welded to a Copper Grid



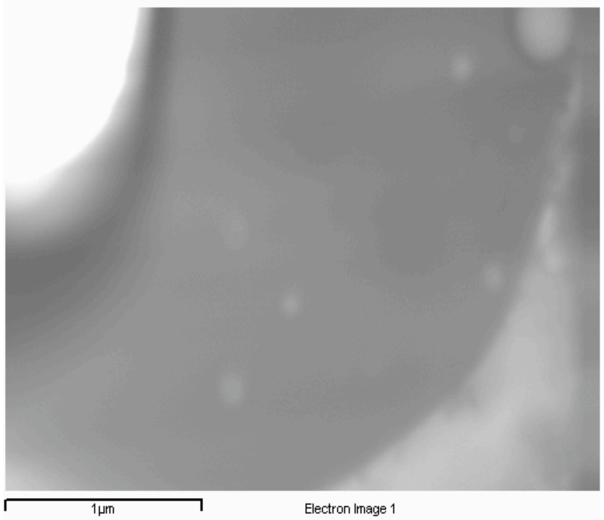


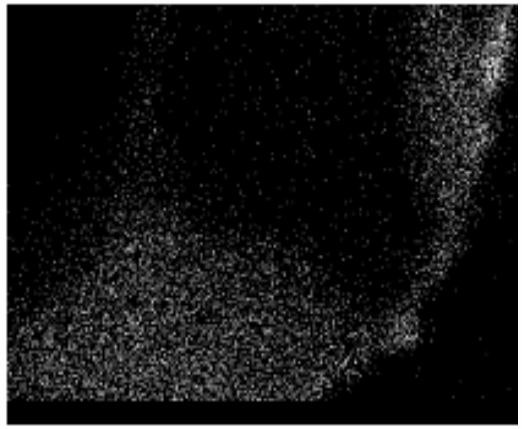
TEM Characterization of FIB Section – Imaging and EDS Spot Analysis of Matrix



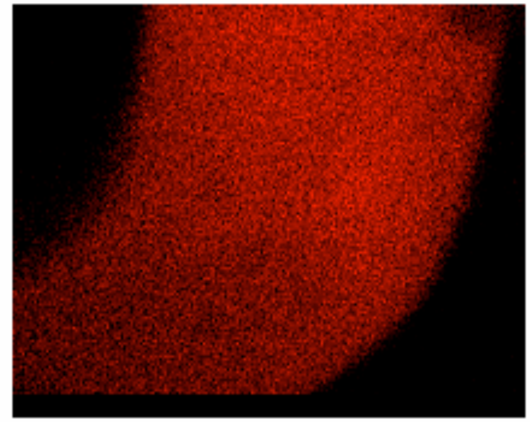


FIB Section – EDS Mapping of Matrix Region

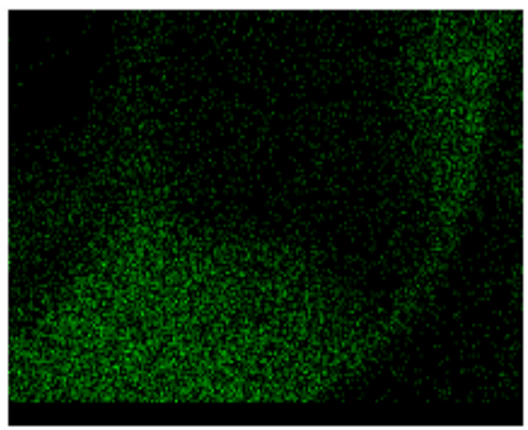




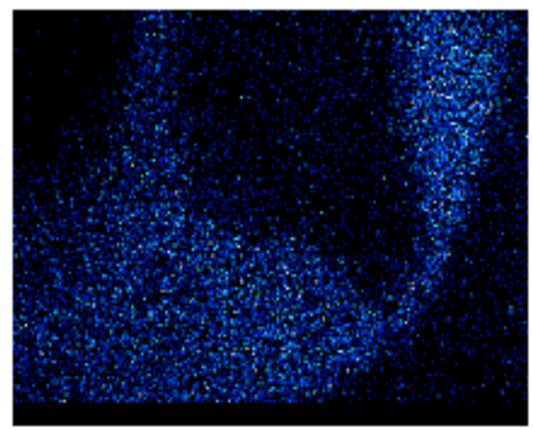
Al Ka1



Si Ka1

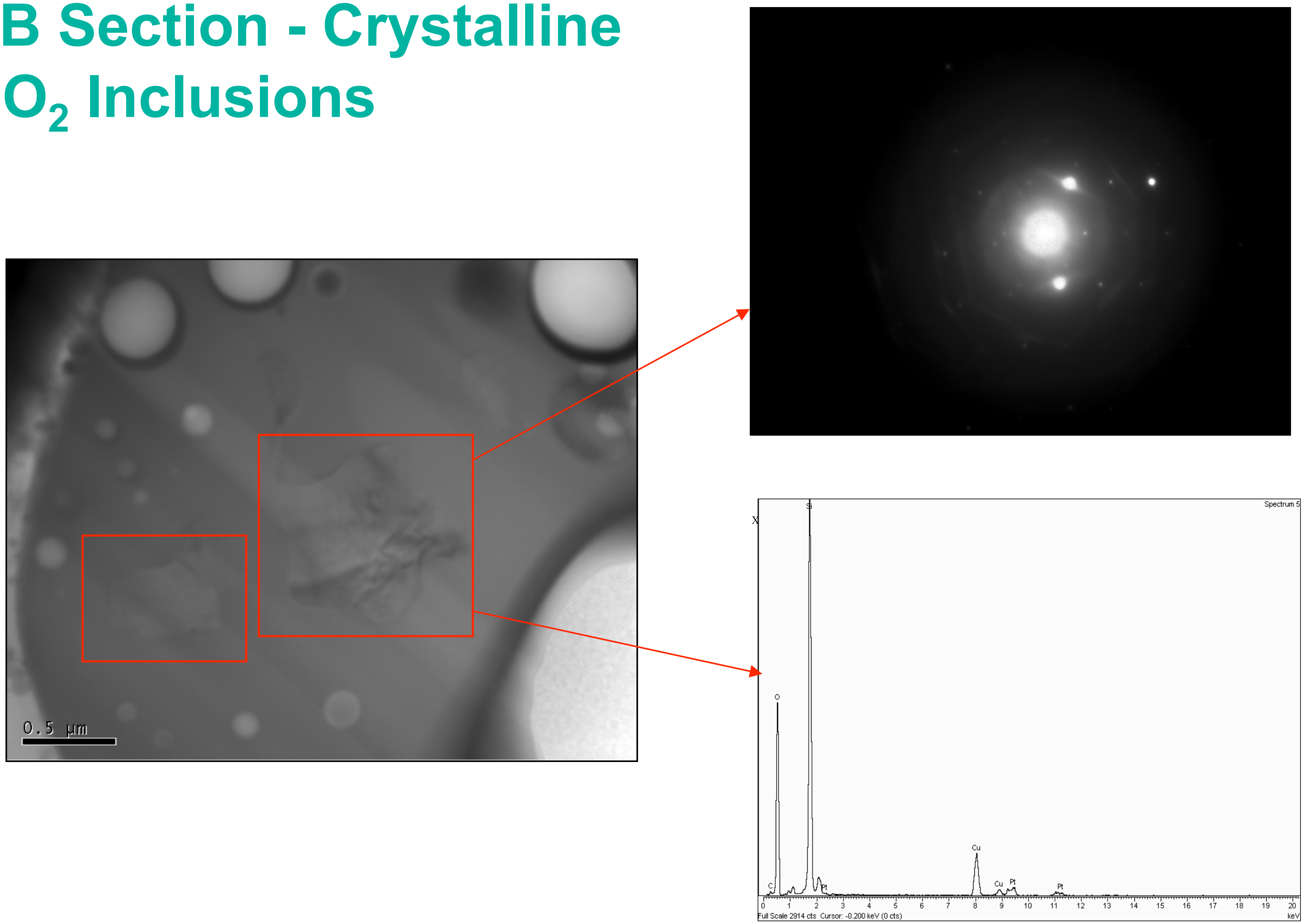


Ca Ka1

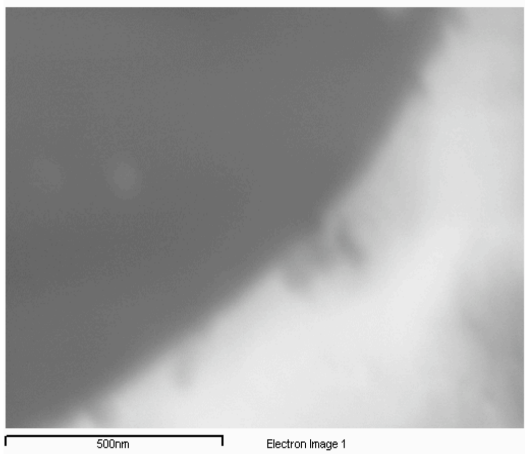


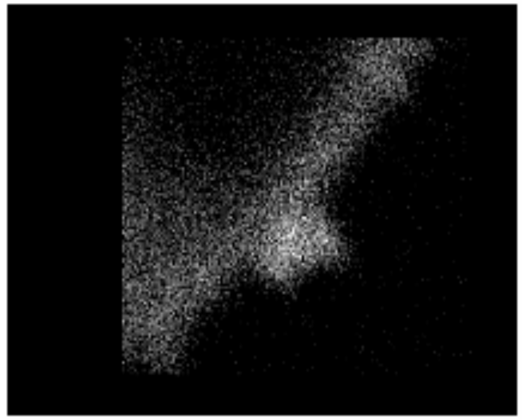
K Ka1

FIB Section - Crystalline SiO_2 Inclusions

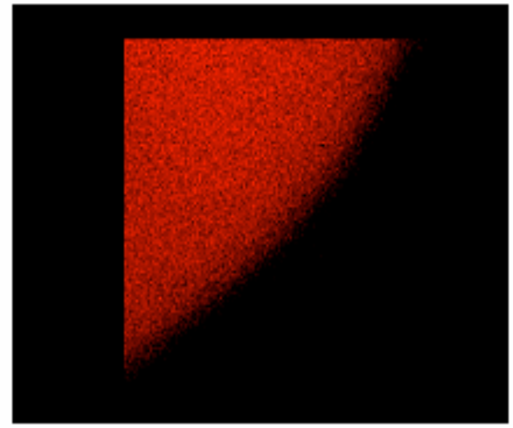


FIB Section - Al-Rich Surface Decorations

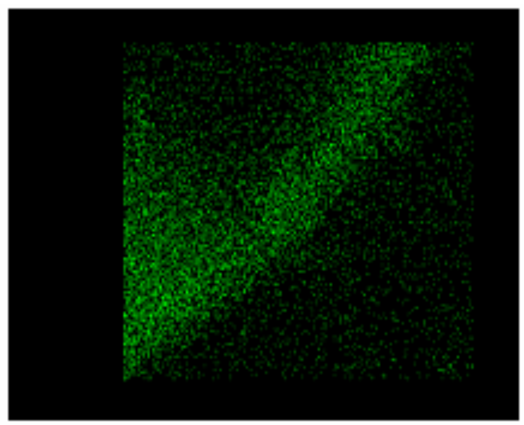




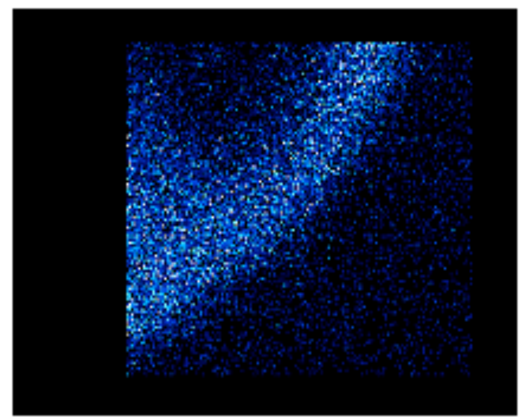
Al Ka1



Si Ka1



Ca Ka1



K Ka1

Summary of AEM Findings for FIB Section

- Particle contained spherical voids of various sizes.
- Particle was mainly amorphous silica and aluminosilicate.
- Crystalline SiO_2 regions identified by imaging, selected area electron diffraction and EDS:
  - Identified as an orthorhombic structure by PDF database search/match and diffraction pattern simulation.
  - Regions became amorphous after several minutes under the electron beam.
- Al-rich surface decorations ~60 nm or smaller in diameter were identified by EDS spot analysis and mapping.
- Uniform thickness of the sample allowed for analysis of all features of interest.

Airborne Tungsten Particles*

- Elevated levels of tungsten and cobalt have been identified in airborne dust collected in Fallon, Nevada.
- The number and size of tungsten-rich particles decreases with distance from a hard-metal industrial facility near the center of the town.
- Nevada is rich in tungsten minerals, particularly scheelite ($CaWO_4$) and huebnerite ($MnWO_4$).
- Automated electron microprobe analysis (AEMA) and TEM were used to determine whether particles collected on air filters were of natural or anthropogenic origin.

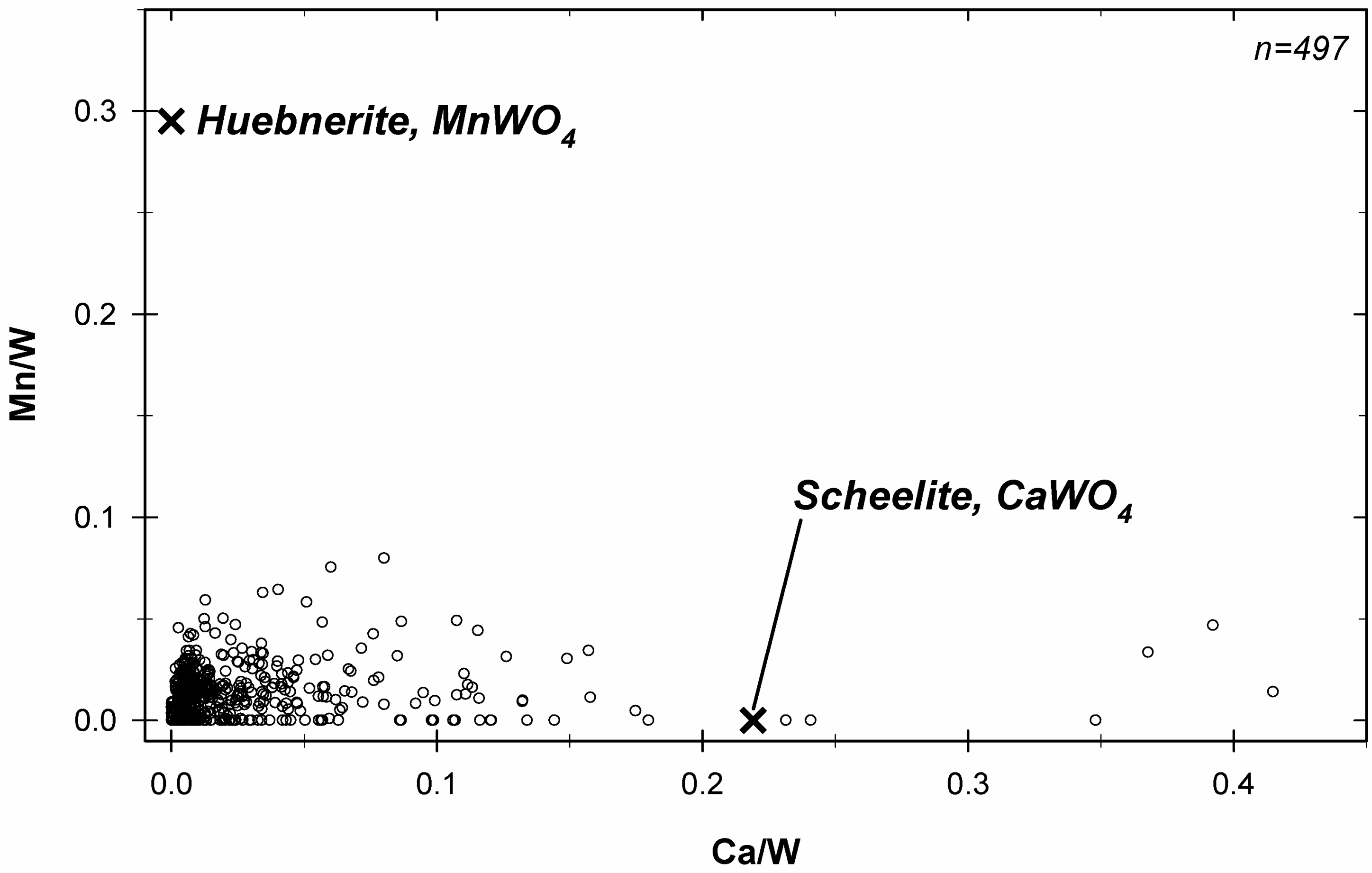
*Morphological and Chemical Characteristics of Airborne Tungsten Particles of Fallon, Nevada, P.R. Sheppard, P. Toepfer, E. Schumacher, K. Rhodes, G. Ridenour, M.L. Witten, Microscopy and Microanalysis, 13, 296-303, 2007.

Airborne Tungsten Particles – AEMA Results

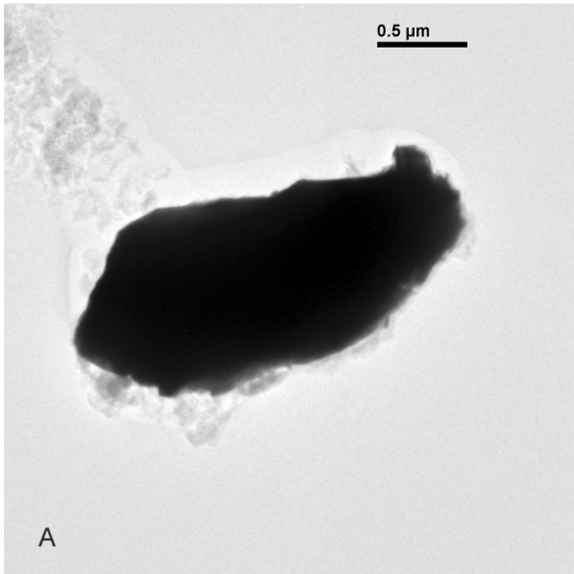
Sample Location (km from HMF[a])	No. of Particles Analyzed Using AEMA[b]	Tungsten Particle Count[c]	Maximum W particle size (µm)[d]	Tungsten Particle Types
0.50	965	337	5.9	W, W-Co, W-Co-Cr
1.31	1084	95	4.8	W, W-Co, W-Co-Cr
1.95	1000	47	2.7	W, W-Co, W-Co-Fe
3.79	1000	11	1.7	W, W-Co
6.68	1000	5	2.0	W, W-Co-Cr
13.4	1000	2	1.9	W
total	6049	497		

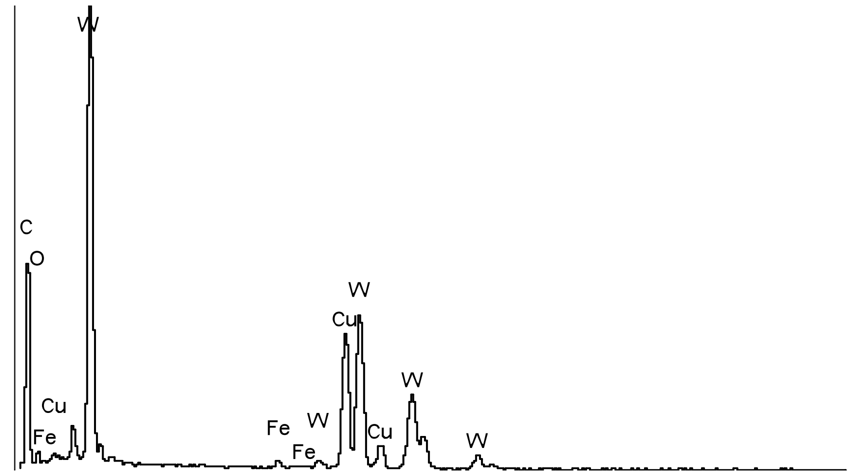
[a] Hard metal facility.
[b] For all samples, the same size of filter was analyzed, a rectangle 2.0 × 1.5 cm in dimension. Counts vary slightly due to the selection of analysis fields and times.
[c] Tungsten particles are >10% tungsten (unnormalized) and have a tungsten mass fraction ≥0.7.
[d] Area equivalent diameter.

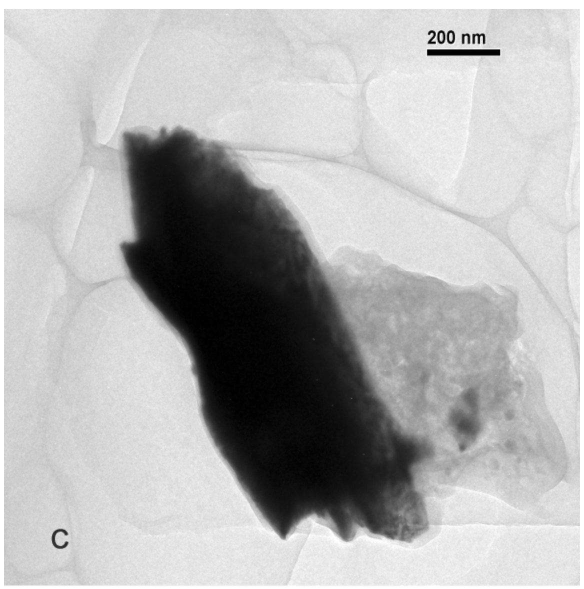
Airborne Tungsten Particles – AEMA Results

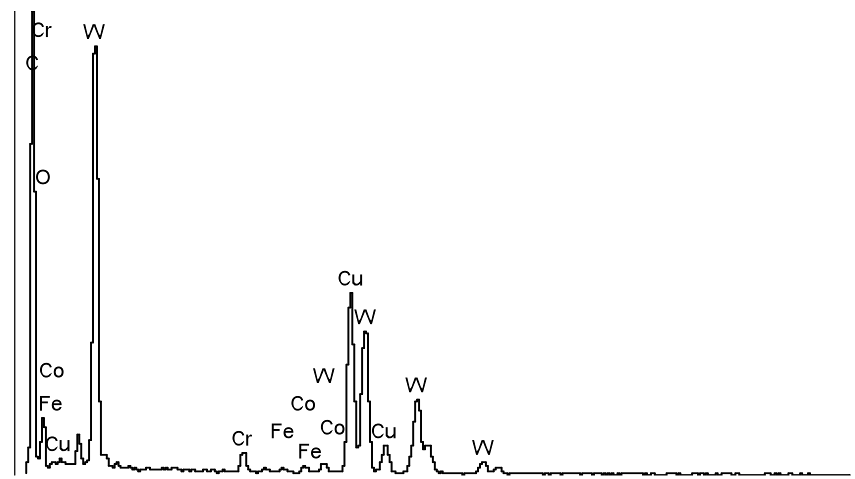


Airborne Tungsten Particles – TEM Results









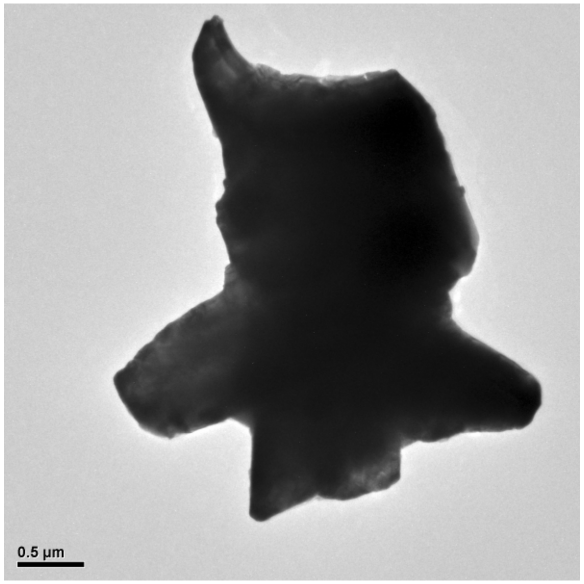
Airborne Tungsten Particles – TEM SAED

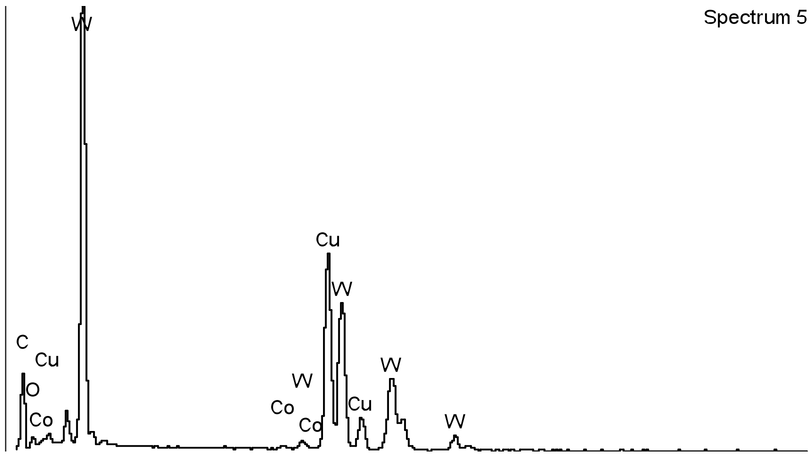
Particle measured d-spacings (Å)			ICDD database spacing table for WC (PDF No. 04-002-2679)	
A	B	C	d-Spacing (Å)	Intensity
			2.8365	36
2.51	2.52	2.47	2.5167	89
1.90		1.88	1.8825	100
		1.79[a]		
1.46	1.45	1.45	1.4530	25
			1.4183	8
1.29		1.28	1.2932	28
1.25	1.26		1.2583	14
	1.25	1.25	1.2356	25
1.14		1.14	1.1502	22
	0.95	0.95	0.9512	12

[a]Matched by WO_3, PDF No. 01-089-1287.

Tungsten Carbide Reclaim Particles – TEM Results

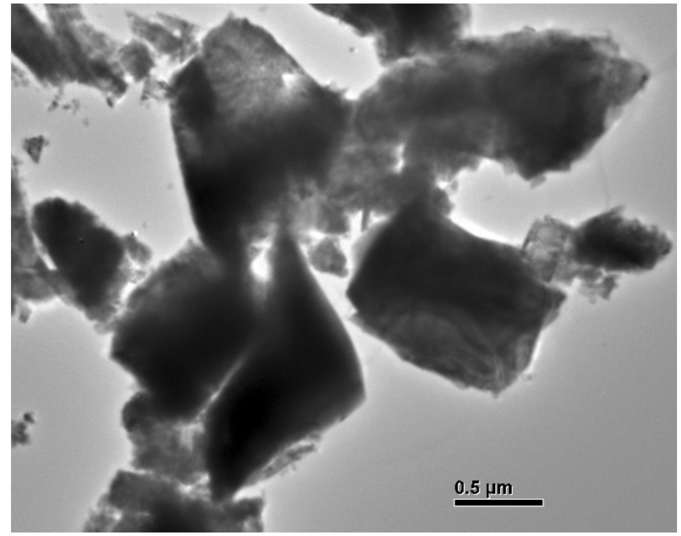
Particle measured d-spacings (Å)	ICDD database spacing table for WC (PDF No. 04-002-2679)	
A	d-Spacing (Å)	Intensity
2.82	2.8365	36
2.75		
2.50	2.5167	89
1.89	1.8825	100
	1.4530	25
1.43	1.4183	8
	1.2932	28
	1.2583	14
1.23	1.2356	25
1.15	1.1502	22
0.94	0.9512	12

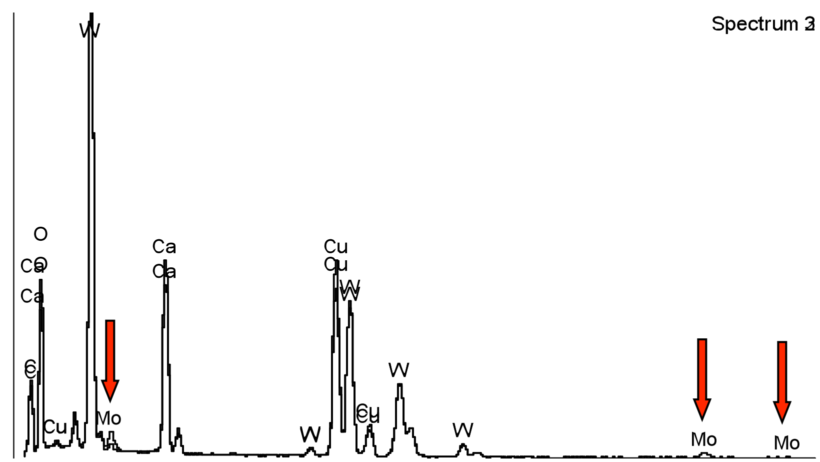




Scheelite ($CaWO_4$) Particles – TEM Results

Particle measured d-spacings (Å)		ICDD database spacing table for $CaWO_4$ (PDF No. 00-041-1431)	
A	B	d-Spacing (Å)	Intensity
4.76	4.74	4.7646	84
3.10	3.12	3.1049	100
3.08		3.0715	30
2.84	2.85	2.8427	39
2.60	2.61	2.6213	19
		2.3803	1
		2.2963	18
2.26		2.2563	3
		2.0866	6
	1.99	1.9943	10
1.93		1.9277	36
	1.85	1.8563	15
1.59	1.59	1.5922	23





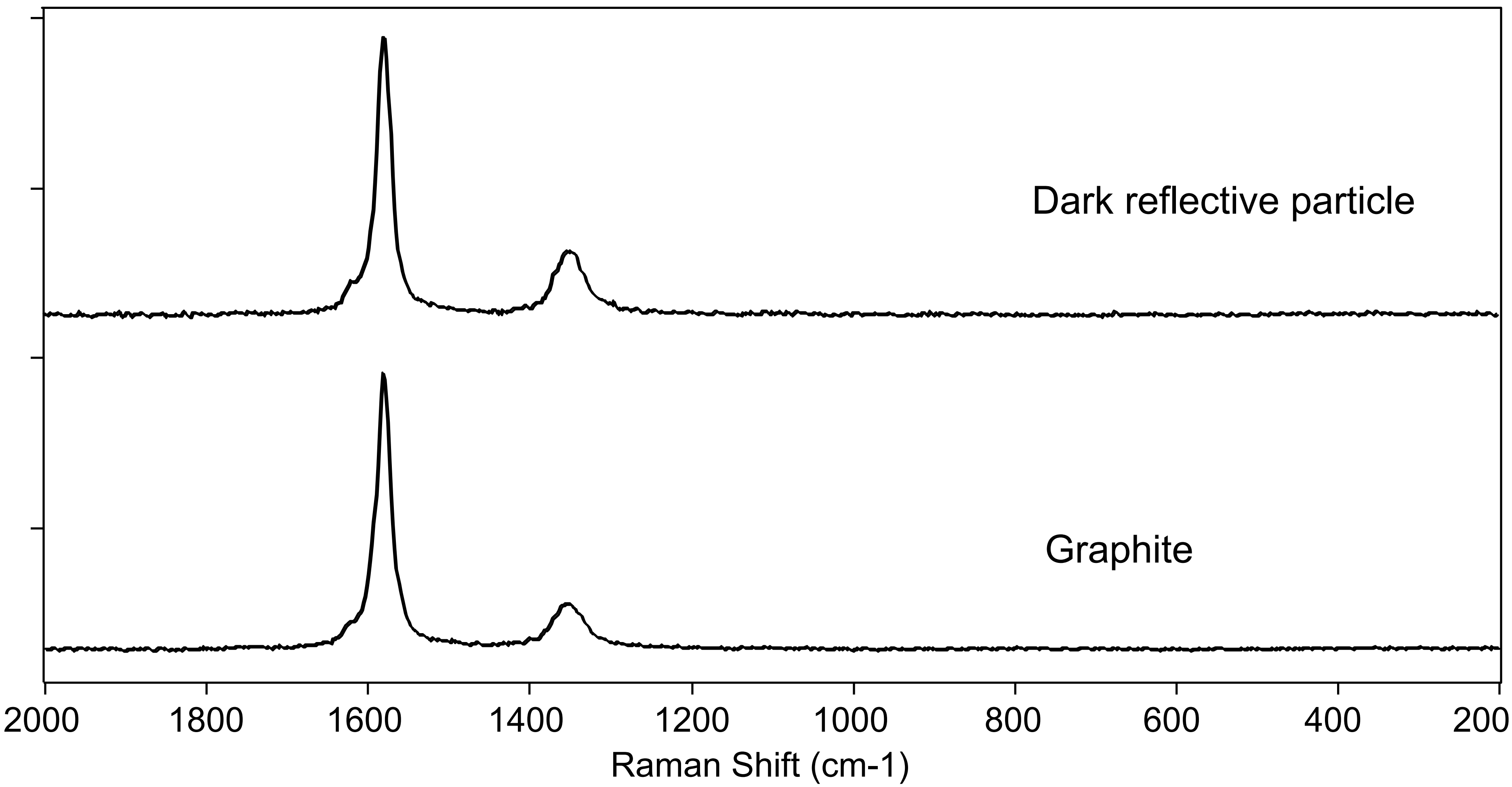
Airborne Tungsten Particles – Conclusions

- W-rich particles were consistently small; morphology was angular and irregular.
- EDS indicated presence of metals: Fe, Cr, Co and Cu.
- No particles relocated and manually analyzed by EDS were confirmed as natural tungsten minerals.
- TEM selected area electron diffraction results were consistent with identification as tungsten carbide, a product of hard metal metallurgy.
- Results indicate that the particles are of anthropogenic origin.

Identification of Graphite Particles

- Carbonaceous materials are common contaminants. Characterization of morphology, crystallinity and trace elements may point to a source.
- Raman spectroscopy can be used to identify a material as carbonaceous, and to indicate the degree of graphitization.
- Graphite was identified in contaminant sample using Raman, but client wanted confirmation.

Identification of Graphite Particles



Identification of Graphite Particles

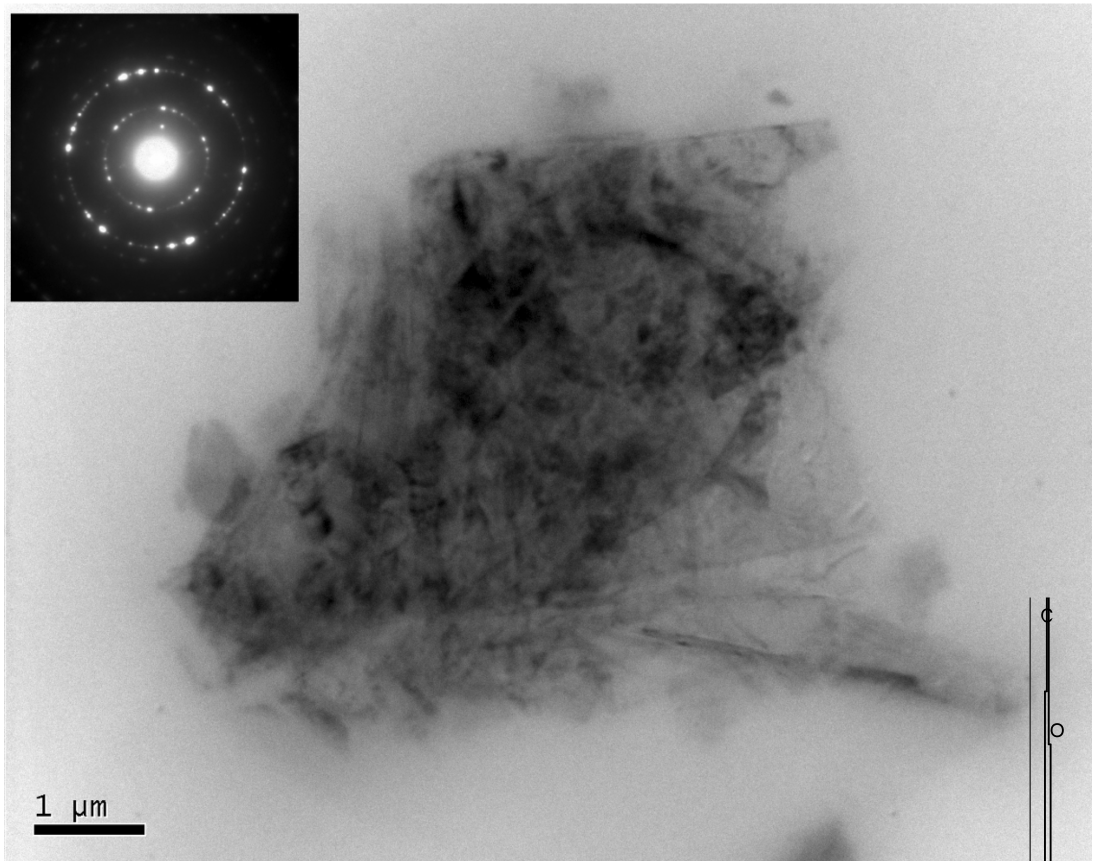
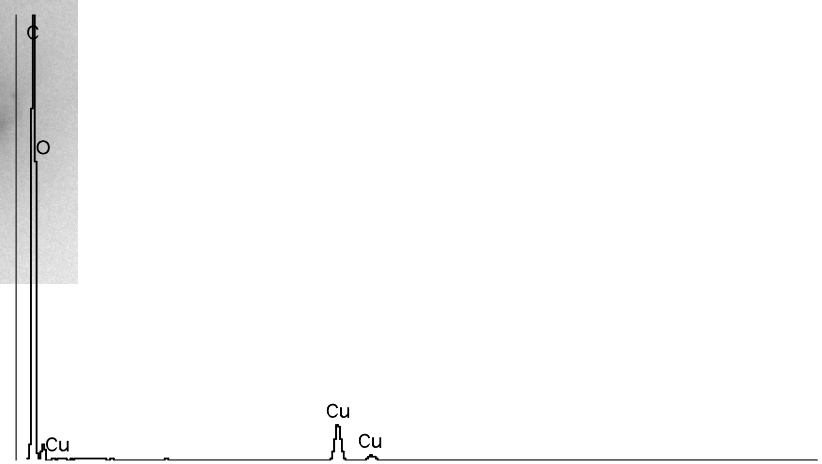
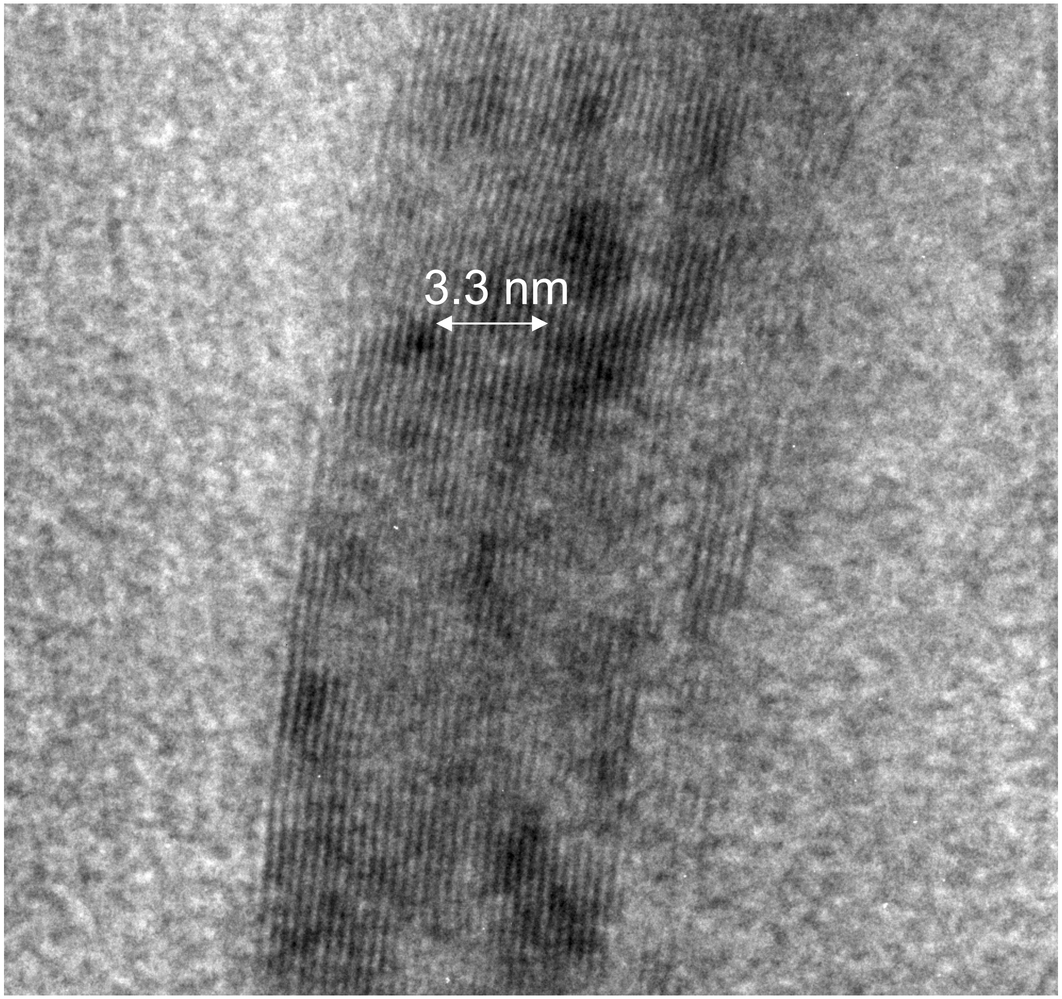


Plate-like, crystalline carbon particles found in heterogeneous particle mixture

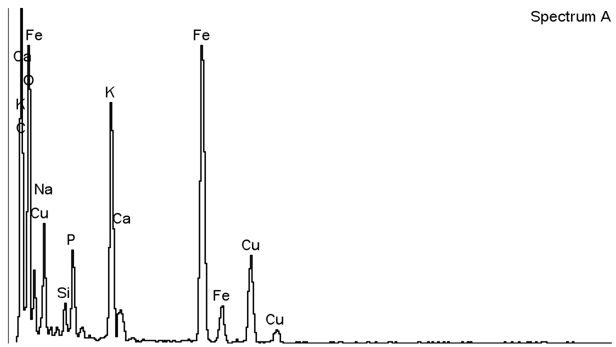


Identification of Graphite Particles

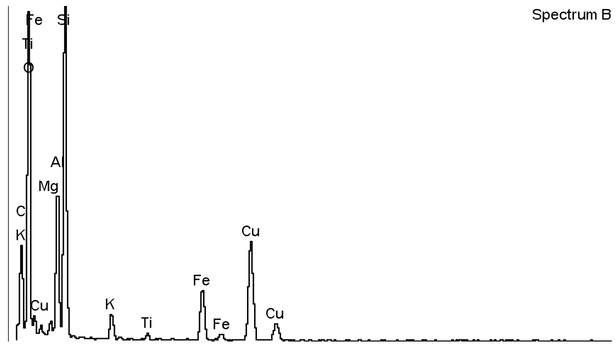


A distance of 3.3 nm measured across ten lattice fringes gives a lattice spacing of 0.33 nm, consistent with the basal plane spacing of graphite.

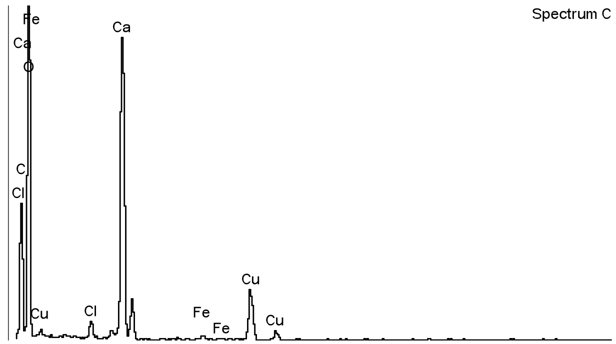
TEM EDS of Iron Tannate Ink



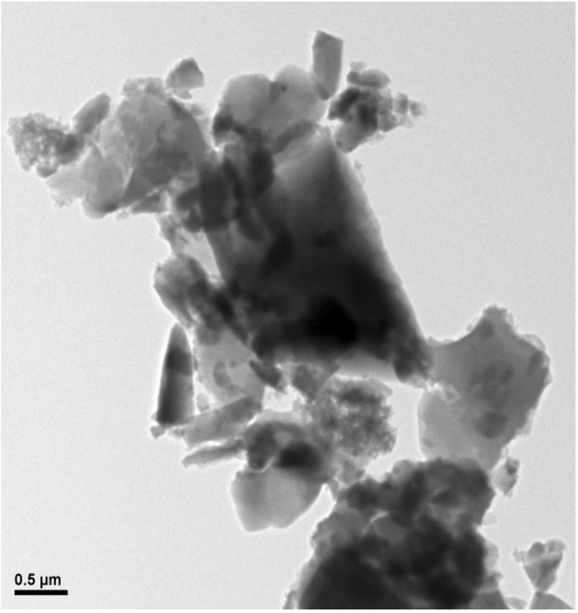
Fe/K/P ink



Aluminosilicate,
plate-like, crystalline,
probable clay



Ca oxide or oxalate,
possibly from plants



TEM image of aggregate of typical iron-rich particles. High spatial resolution EDS spectra clarified association of elements identified in SEM.

Conclusions

- Microanalysis of particles is vital to efforts such as environmental monitoring, design of new materials, product manufacturing and process control.
- Among techniques for microanalysis, the TEM is unique in its ability to probe morphology, elemental composition, crystal structure and electronic state, all with extremely high spatial resolution, and often on less than ideal samples.
- The TEM is particularly useful when the sample amount is limited or the features of interest are extremely small.
- TEM may be the best option for a given sample, but there is always value in using a multi-technique approach.

Thank you.
Questions?

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