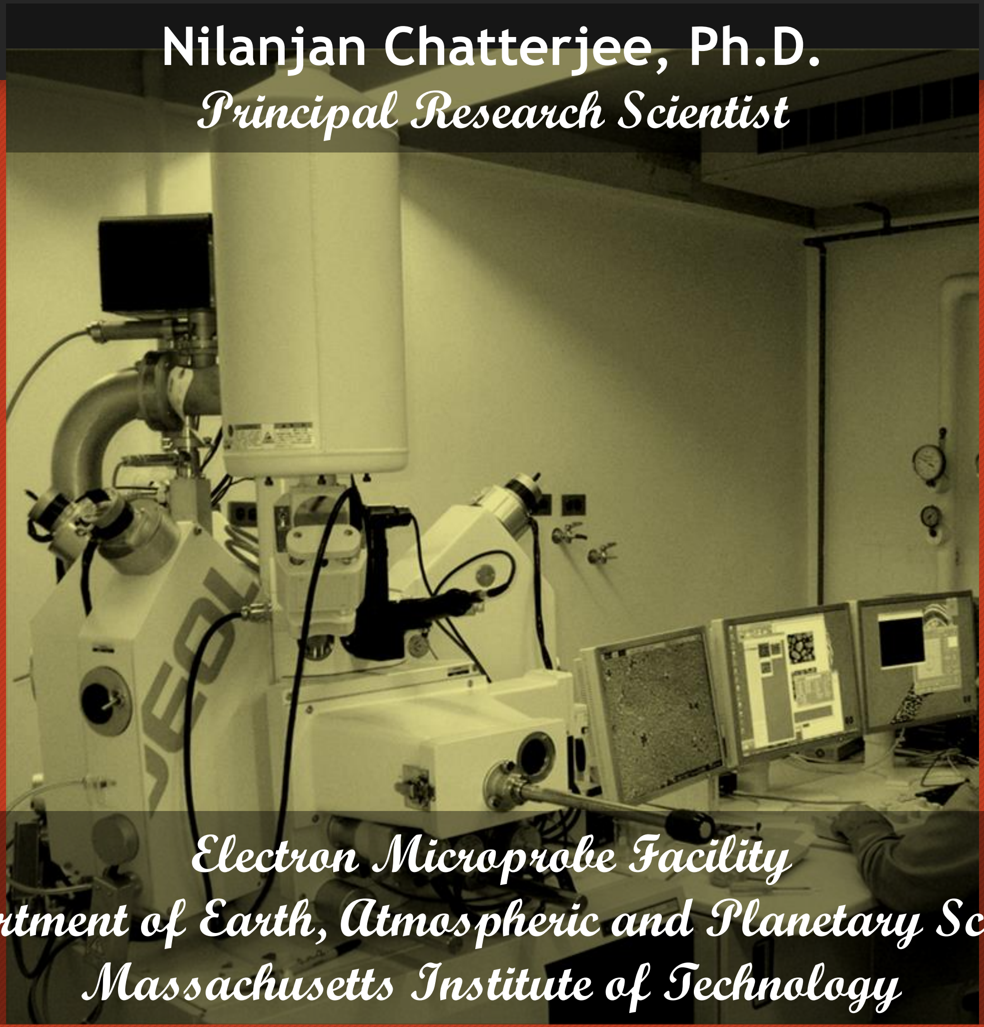
Electron Probe Micro-Analysis (EPMA)

Nilanjan Chatterjee, Ph.D.
Principal Research Scientist



Electron Microprobe Facility
Department of Earth, Atmospheric and Planetary Sciences
Massachusetts Institute of Technology

Uses of the EPMA

Complete **quantitative chemical analysis at micron-scale spatial resolution:**

- *Be to U (10-50 ppm minimum detection limit)*

High resolution imaging:

- *compositional contrast (back-scattered electron)*
- *surface relief (secondary electron)*
- *spatial distribution of elements (x-ray)*
- *trace elements, defects (light)*

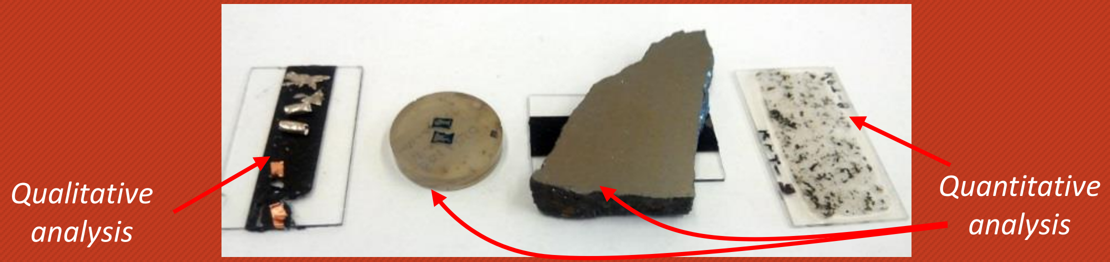
Sample preparation

- Sample cut and mounted in epoxy, if necessary

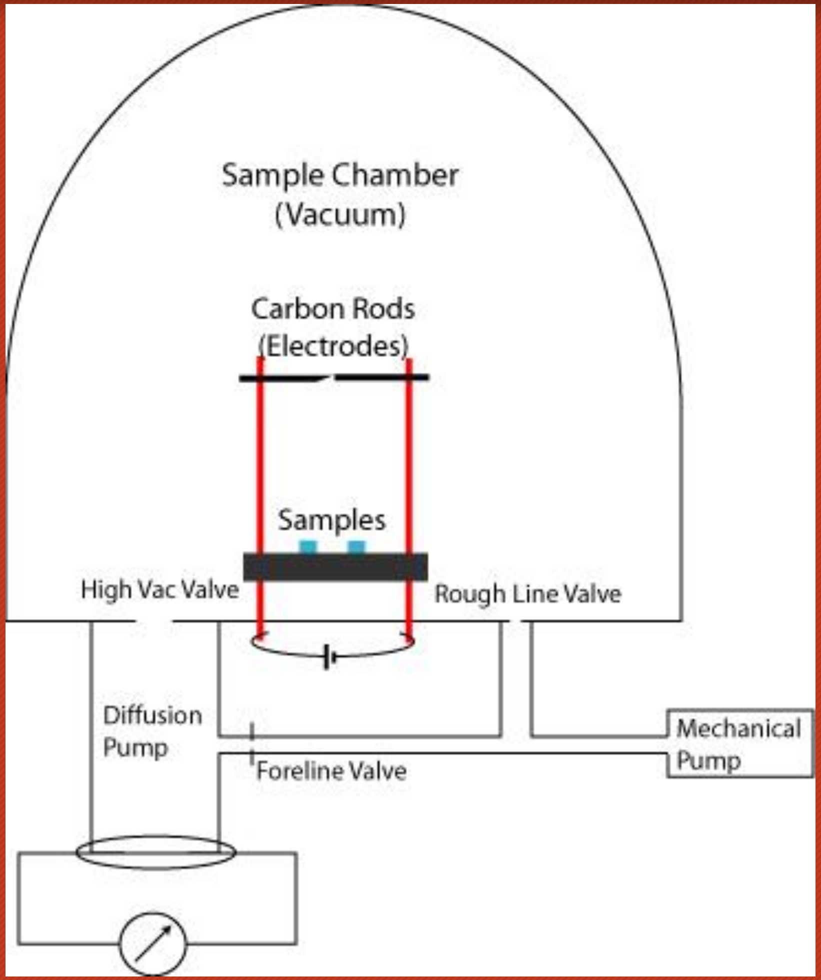
- Coarse polished with 240-600 SiC paper (53-16 μm)

- Fine polished with alumina slurry or diamond paste on cloth (grit size 1.00-0.25 μm)

- Washed with water in ultrasonic cleaner after each polishing step, dried after final step, wiped with ethanol



Carbon coating



Vacuum evaporator

25 nm

Thickness is monitored on a polished surface of brass, coated with the samples

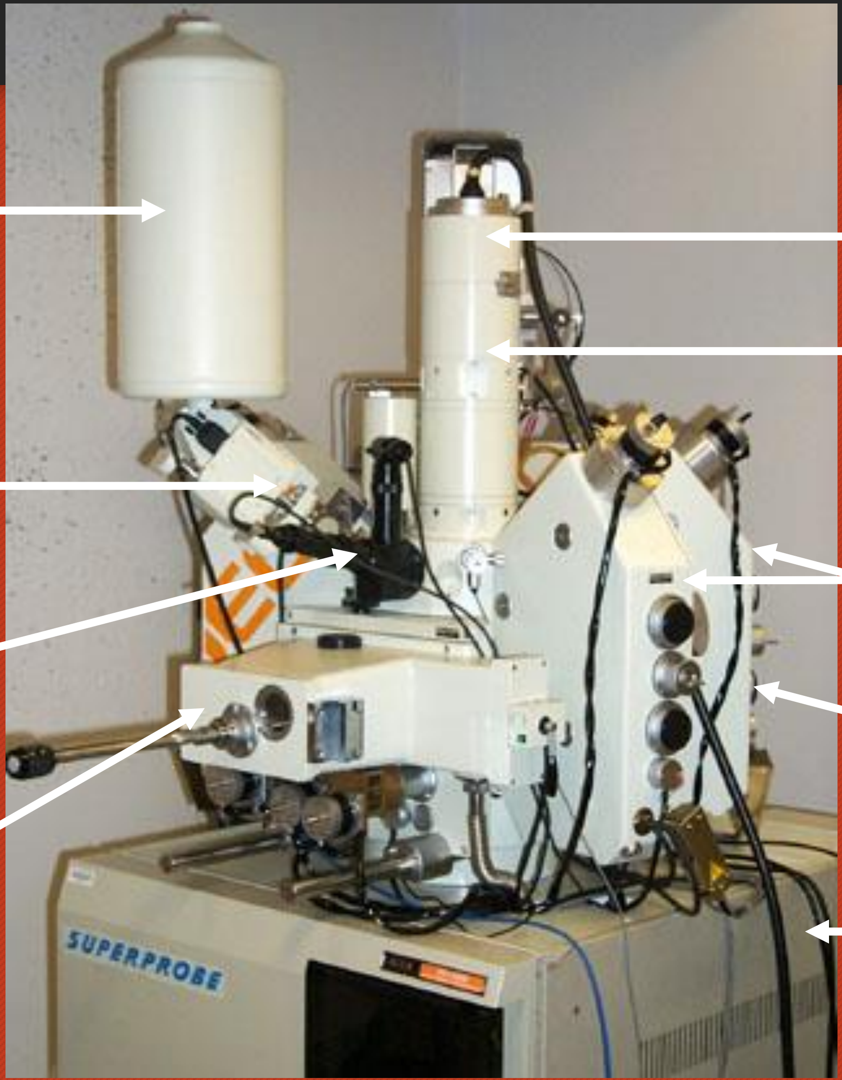
JEOL JXA-8200 Superprobe

Liquid nitrogen for EDS

Energy dispersive
X-ray spectrometer (EDS)

Optical microscope

Sample exchanging
chamber



Electron gun

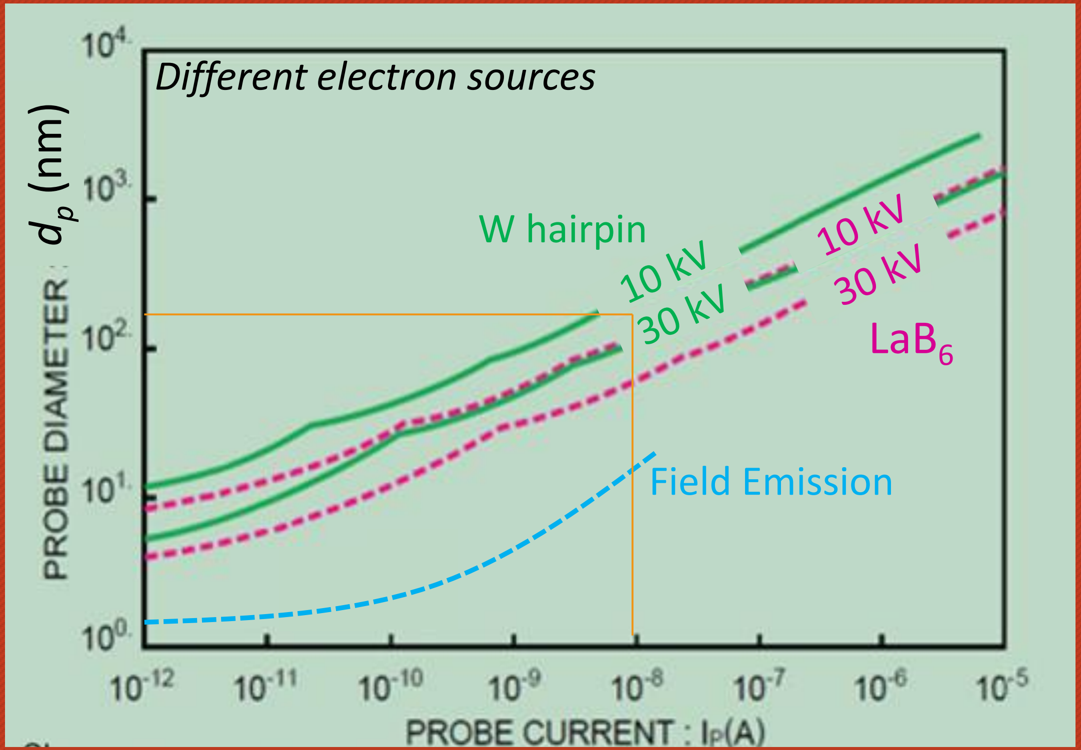
Electron beam column

Wavelength dispersive
X-ray spectrometer (WDS)

Secondary electron detector

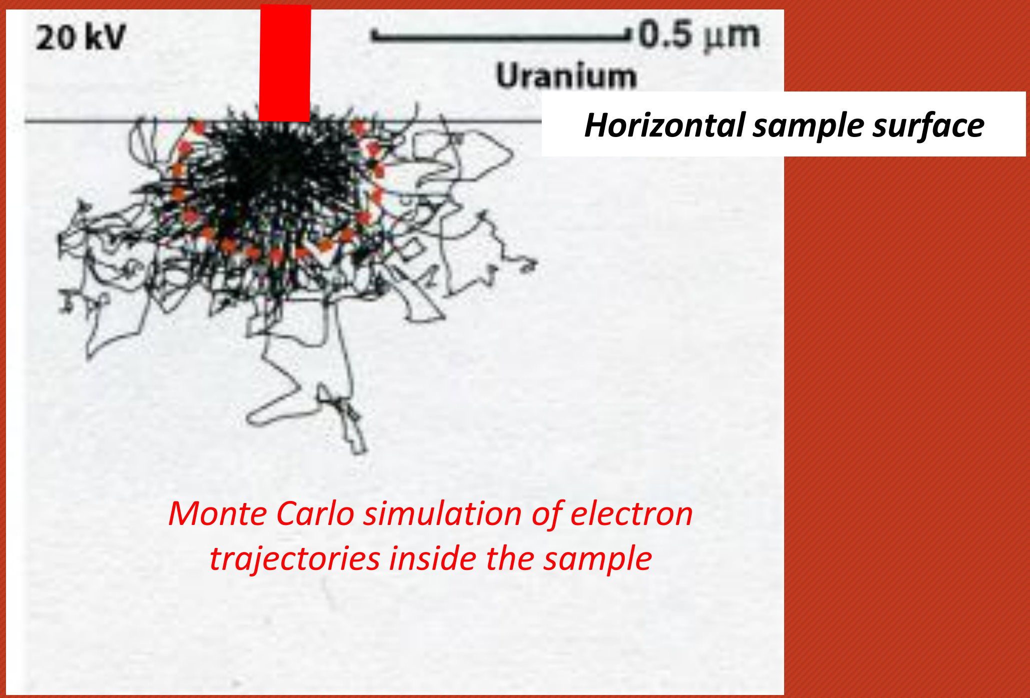
High vacuum pump
(inside)

Spatial resolution (spot size) of analysis



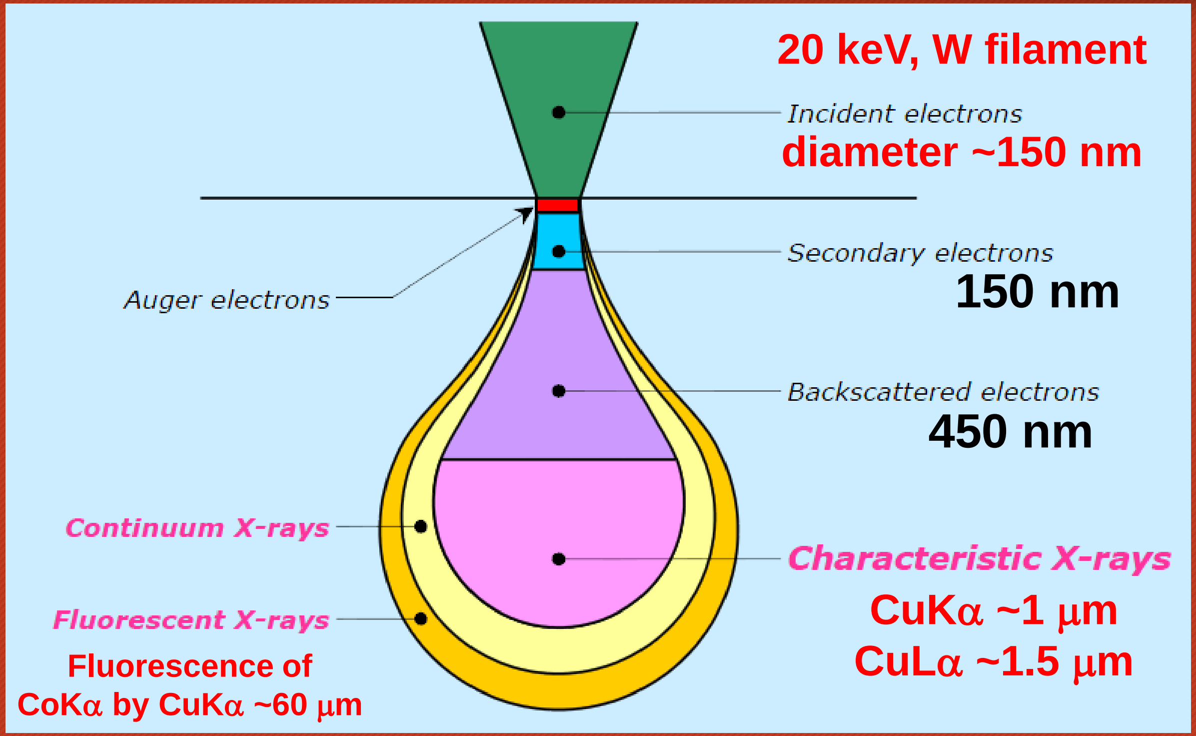
Tungsten hairpin, 15 kV, 10 nA, $d_p \approx 100$ nm

Vertical electron beam



Width of interaction volume >> probe diameter

Spatial resolution for different signals

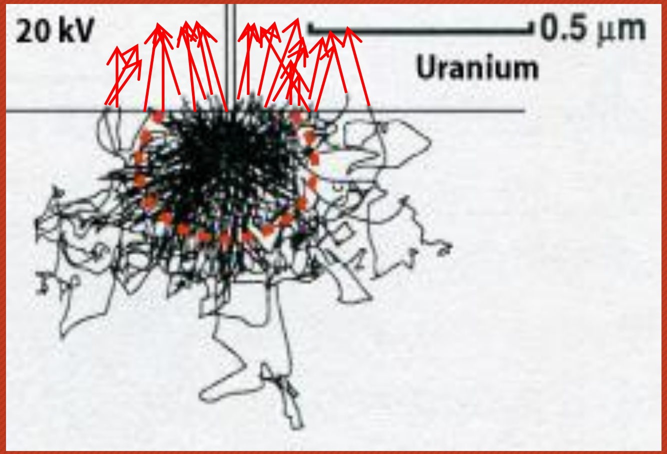


(not to scale)

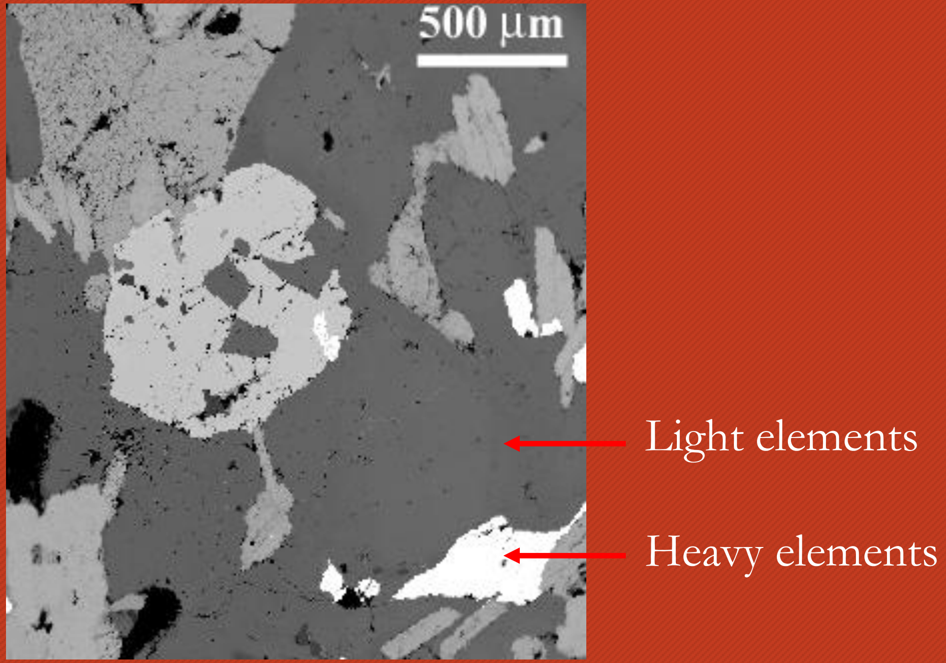
Production volume for different signals is different

The "onion shell" model:
Cu-10%Co alloy

Back-scattered electron (BSE)



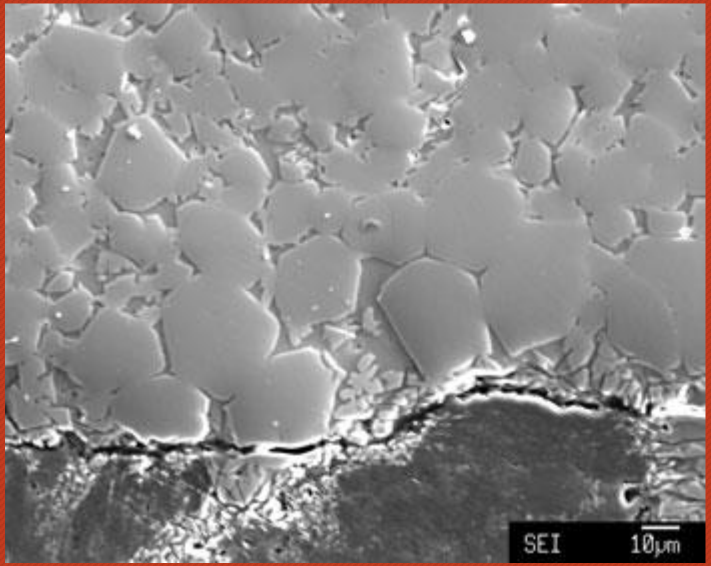
Beam electrons are scattered backward



Compositional contrast

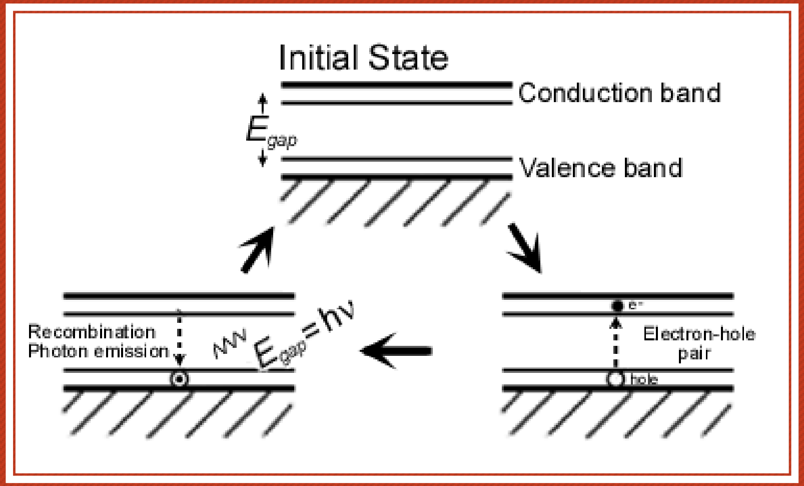
Secondary electron (SE)

Produced by ionization of the target atoms due through interaction with the electron beam

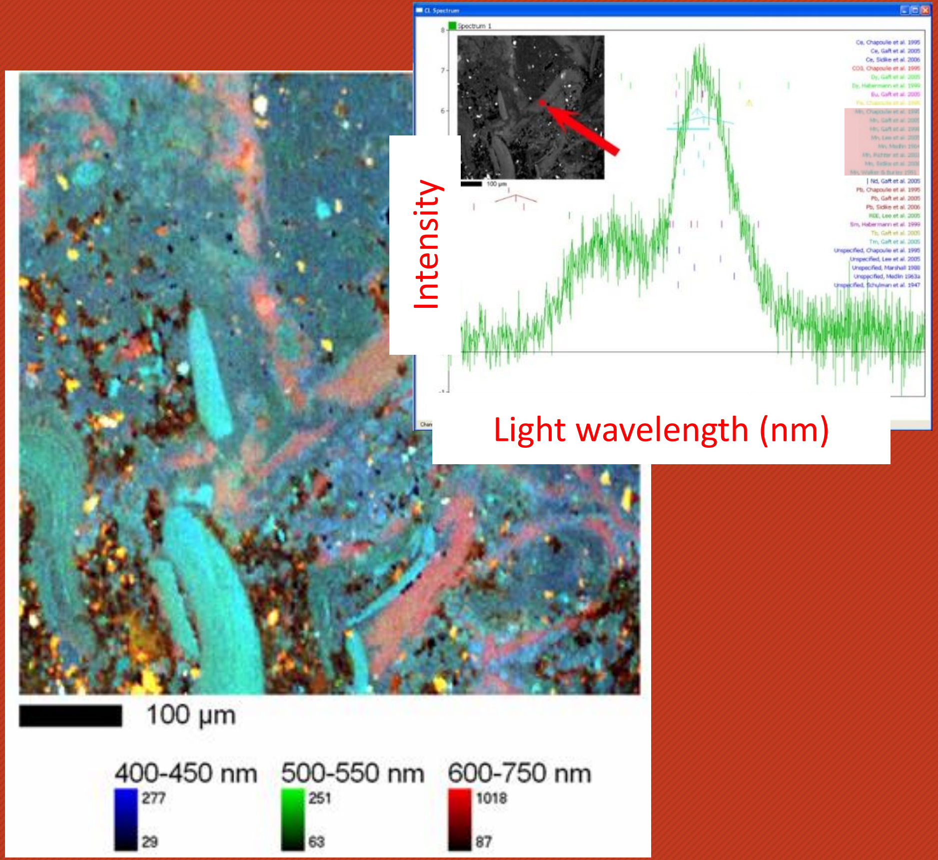


Topographic contrast

Cathodoluminescence (CL)

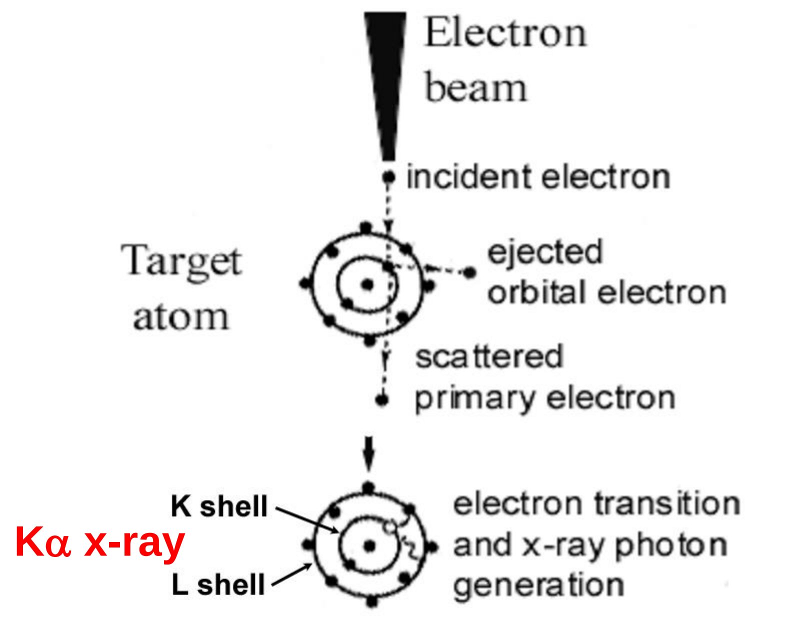


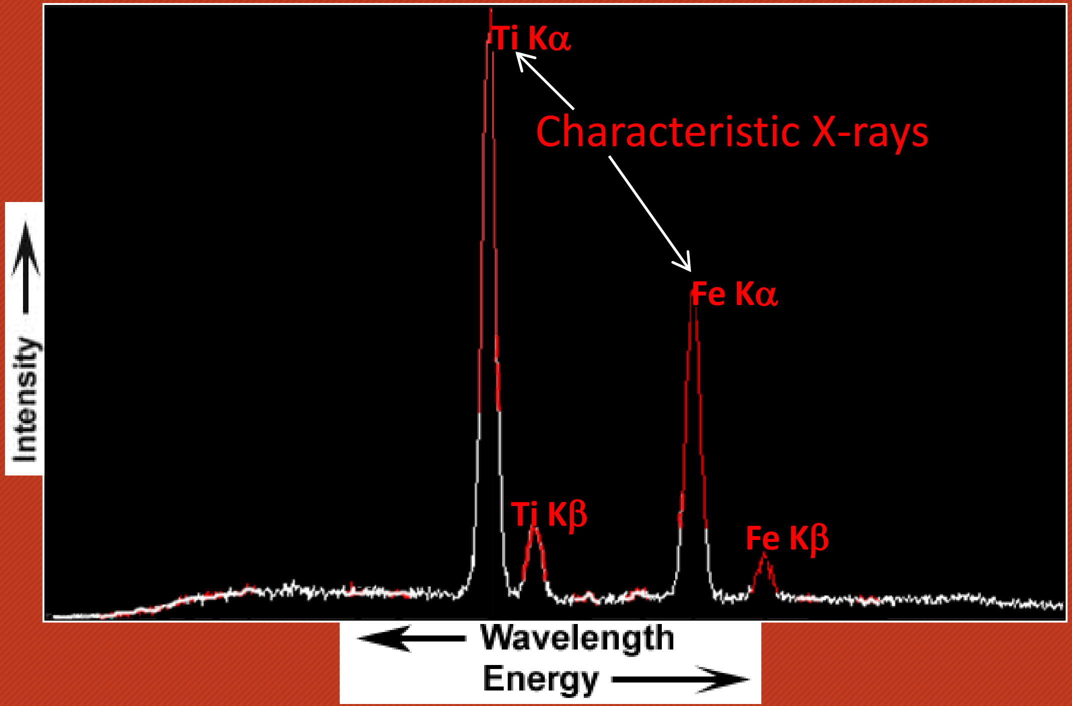
Light generation in semiconductors



Trace impurities generate different light

Characteristic X-ray generation





Inner-shell ionization

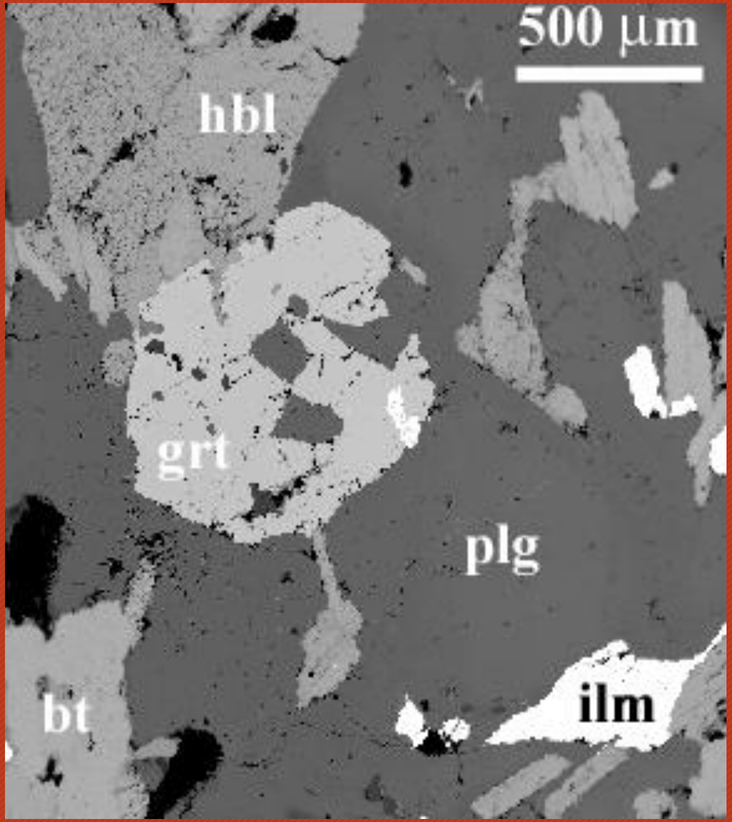
Overvoltage, $U = E/E_c > 1$

E : electron beam energy

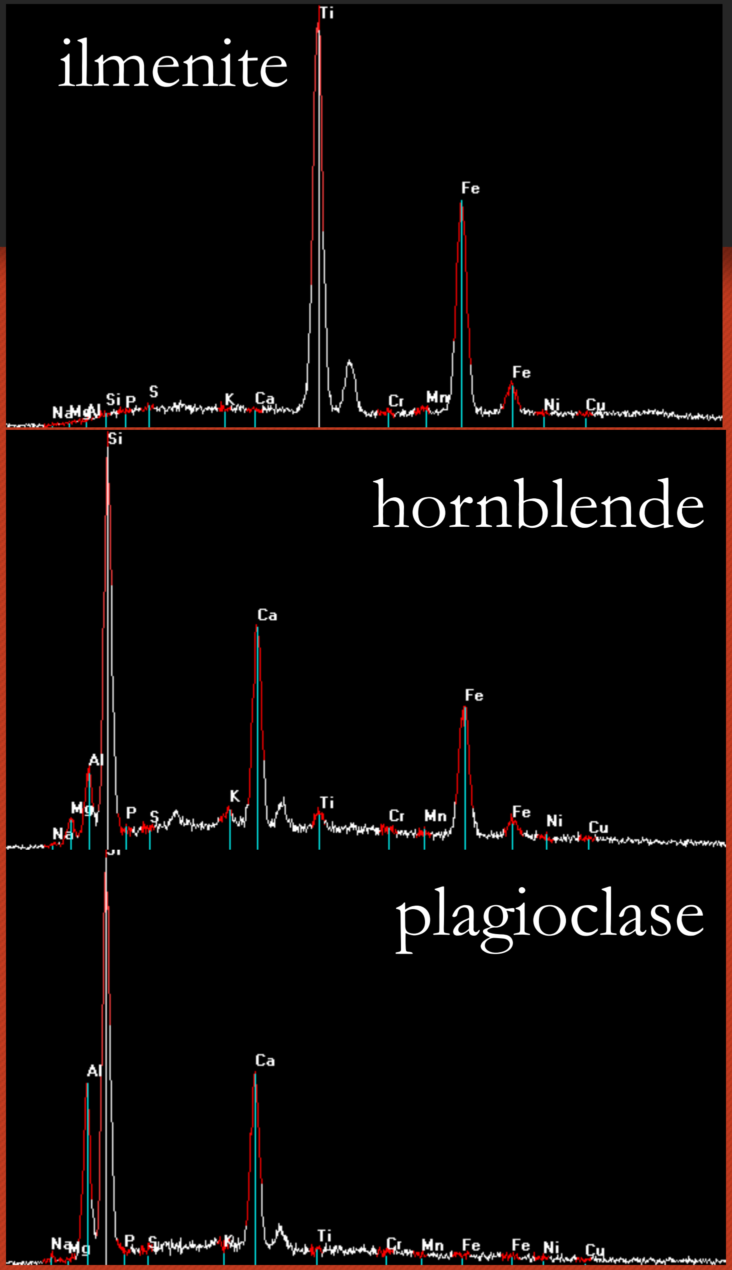
E_c : critical excitation energy

of shell in target atom

Qualitative analysis with BSE and EDS



Mean Atomic Number



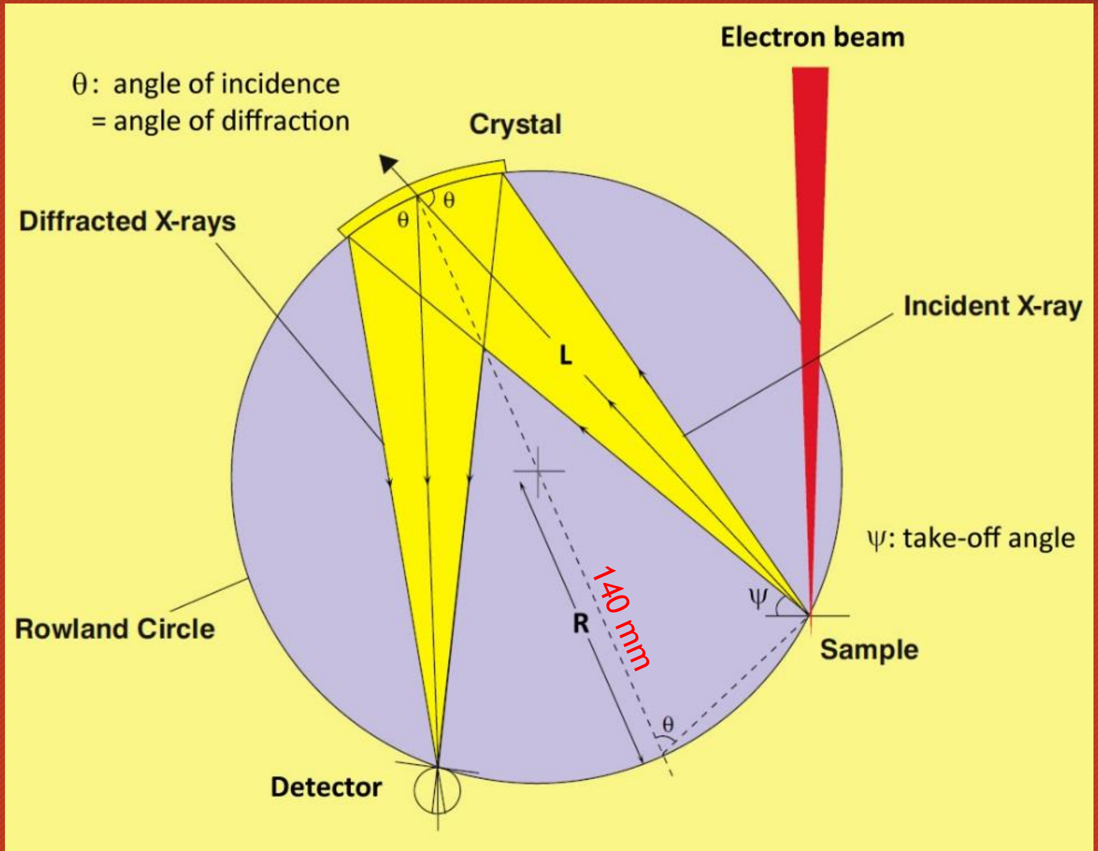
Wavelength Dispersive Spectrometer (WDS)

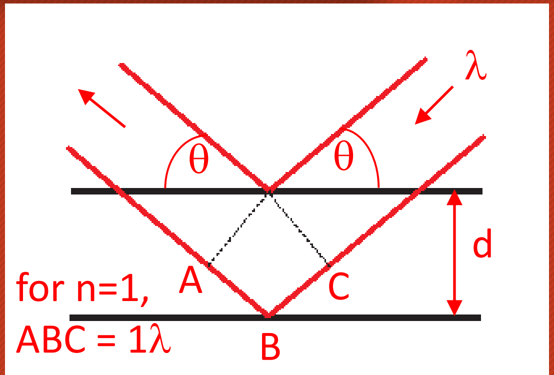
$$\sin\theta = \frac{L}{2R}$$

θ: angle of incidence or diffraction

L: distance between sample and crystal $= n\lambda\,(R/d)$

R: radius of focusing (Rowland) circle





Bragg's Law:

$$n\lambda = 2d\sin\theta$$

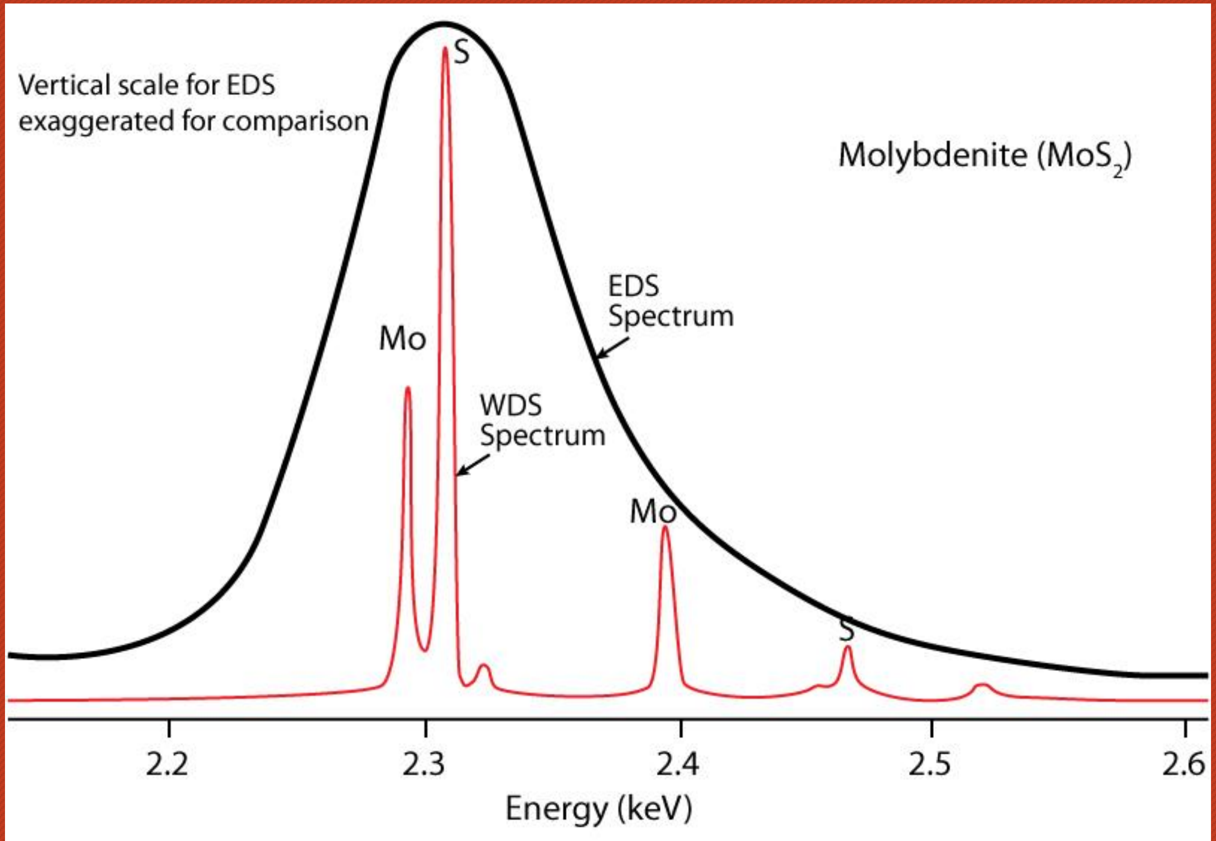
n: order of diffraction

λ: wavelength of X-ray

d: lattice spacing in diffracting crystal

θ: angle of incidence or diffraction

WDS vs. EDS spectral resolution



Peak resolution

*with WDS (FWHM ~**10 eV**)*

*with EDS (FWHM ~**150 eV**)*

EPMA Quantitative analysis

X-ray intensity is proportional to the concentration, $C \propto I$

$$\frac{C_i}{C_{(i)}} \propto \frac{I_i}{I_{(i)}}$$

C_i , I_i : concentration and intensity in sample

$C_{(i)}$, $I_{(i)}$: concentration and intensity in standard

$$\frac{I_i}{I_{(i)}} = k_i \ \textbf{(k - ratio)}$$

$$\frac{C_i}{C_{(i)}} = k_i \cdot [\mathbf{ZAF}]_i$$

ZAF Matrix corrections:

Z: Atomic Number correction

A: Absorption correction

F: Fluorescence correction

EPMA Analytical procedure

- Sample preparation (mounting, polishing, carbon coating)

Carbon coating non-conducting material

- Setting up the Electron Microprobe

Accelerating voltage, beam current, probe diameter, WDS crystal/proportional counters, counting time for each element

- Qualitative analysis with EDS

If nothing is known about the chemical composition

- Measurement of X-ray intensities in standards (calibration) by WDS

- Measurement of X-ray intensities in the specimen by WDS and data reduction

Matrix corrections

Typical quantitative analysis output

Element		k-Ratio	El-Wt%	MDLel%	Ox-Wt%	MDLox%	At-Prop	Error%
		k-ratio	Element Wt%		Oxide Wt%		Atomic proportion	
SiO2	Ka	0.9119	17.30	0.03	37.01	0.05	2.960	0.68%
TiO2	Ka	0.0021	0.13	0.05	0.22	0.09	0.013	20.28%
Al2O3	Ka	0.5200	11.46	0.03	21.66	0.05	2.042	0.86%
Cr2O3	Ka	0.0000	0.00	0.06	0.00	0.08	0.000	99.00%
FeO	Ka	1.0431	21.43	0.07	27.57	0.09	1.844	1.58%
MnO	Ka	0.0809	2.89	0.08	3.73	0.11	0.253	4.29%
MgO	Ka	0.0781	1.36	0.02	2.26	0.04	0.269	2.93%
CaO	Ka	0.3565	5.20	0.04	7.28	0.05	0.624	1.82%
Na2O	Ka	0.0011	0.01	0.04	0.02	0.05	0.003	99.00%
O			39.95				12.000	
Total:			99.75		99.75	Cation:	8.007	

Minimum detection limit (El-Wt%)

Minimum detection limit (Ox-Wt%)

Cation Sum based on a certain #O

Uncertainty

Types of errors and counting statistics

Systematic Error

Fixed (but unknown) offsets in all measurements

Low systematic error: high accuracy

Random Error

Fluctuations in each measurement

Low random error: high precision

For N counts, $N \pm \sqrt{N}$

i.e., the uncertainty is $\frac{\sqrt{N}}{N}$ X 100, or $\frac{1}{\sqrt{N}}$ X 100 %

The percent uncertainty decreases as N increases (more precise)

E.g., uncertainty for 25 counts is 20%

for 100 counts is 10%

for 10,000 counts is 1%

Imaging and mapping modes

- *Screen capture of beam rastered BSE and SE images:*
  - *fast, high resolution and high quality*

- *Simultaneous mapping with BSE (or SE), CL, and elemental x-rays:*
  - *Beam-raster mode (may have defocusing issues)*
  - *Stage mode: stage moves under electron beam (preferred for large areas)*

Map (image) quality and acquisition times

- Image resolution:
  number of points measured within the imaged area
- X-ray Signal:
  beam current and counting (dwell) time per point

Acquisition time:

- *Screen capture: 1-2 minutes*
- *Simultaneous mapping: Dwell time x Number of pixels + Stage movement time*

E.g., Time required to map 1 cm x 1 cm area at 10 micron resolution (1000 x 1000 pixels) using a 25 millisec dwell time

= 25 x 1000,000 millisec + time for stage movement

= ~7 hours + 1 hour (approximately *8 hours*, or *0.03 sec/pixel*)

Combined BSE, CL and X-ray mapping