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QS WORLD UNIVERSITY RANKINGS

QS World University Ranking 2019	Overall Rank 751-800
QS Asia University Ranking 2019	Overall Rank 137
QS World Graduate Employability Ranking 2019	Overall Rank 301-500
QS World University Ranking By Subject 2019	Overall Rank 9 Subjects
Students	47,801
International Students	529
Faculty	3,313
International Faculty	59

UiTM di hatiku

INTRODUCTION TO SEM, XRD, XRF AND EDS FOR CHARACTERIZATION ANALYSIS

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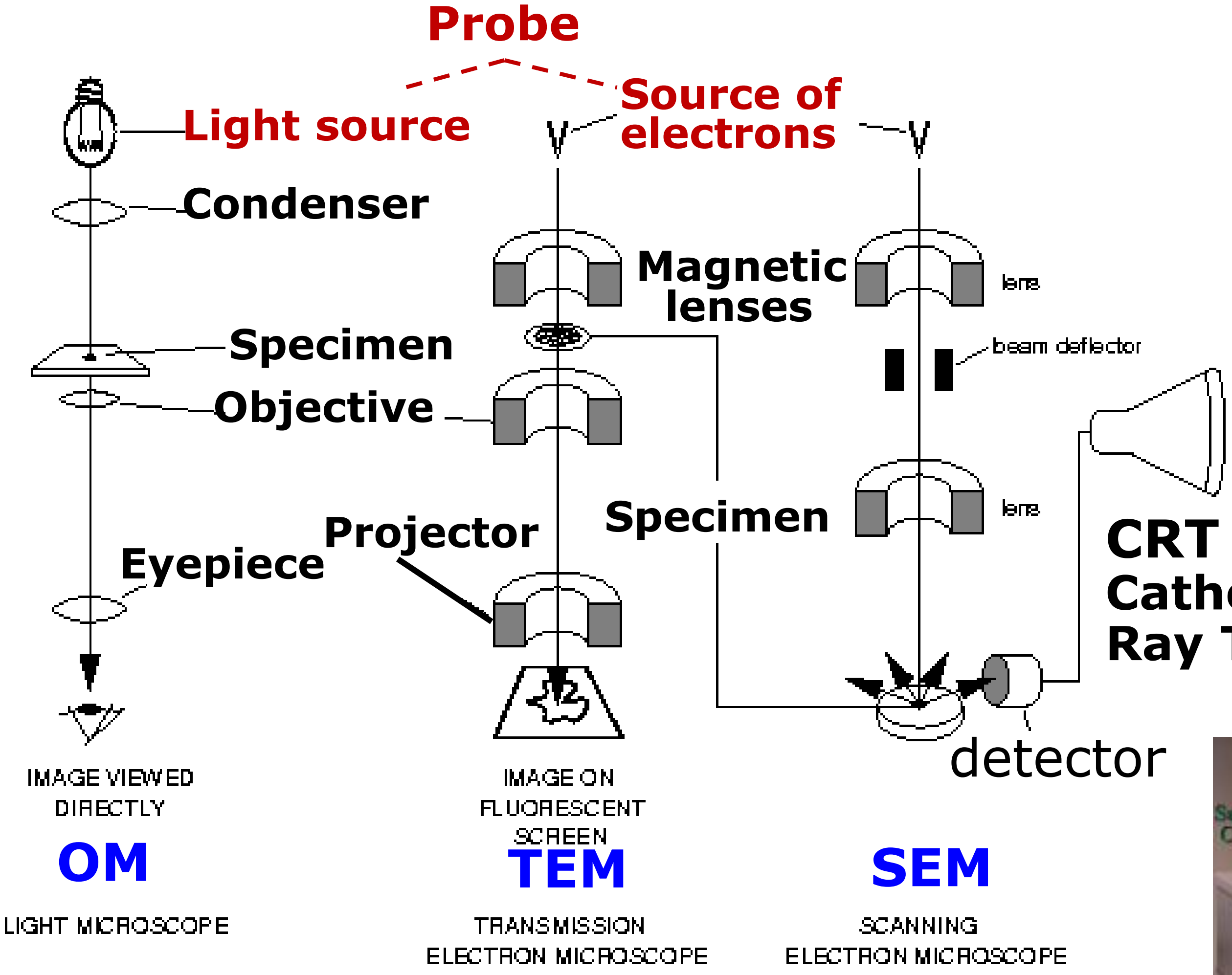
Scanning Electron Microscopy (SEM)

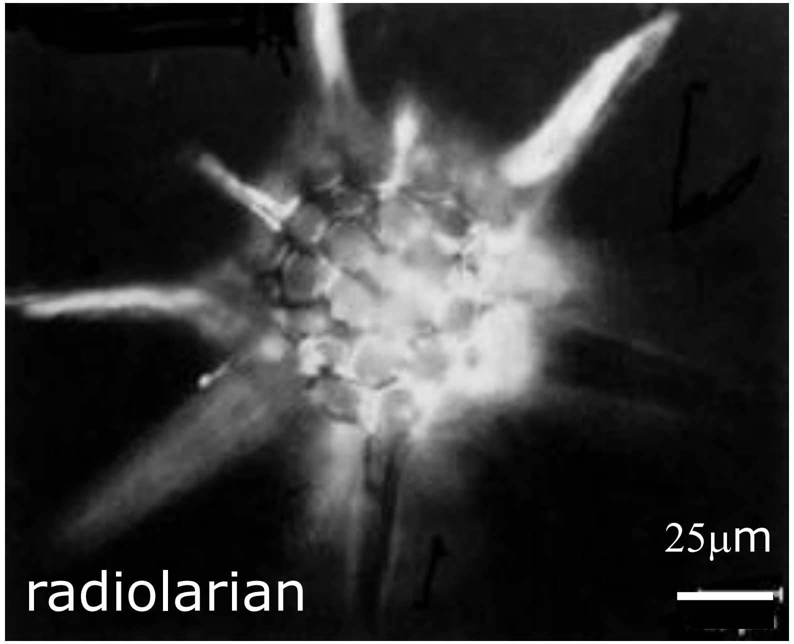
- **What is SEM?**
- **Working principles of SEM**
- **Major components and their functions**
- **Electron beam - specimen interactions**
- **Interaction volume and escape volume**
- **Magnification, resolution, depth of field and image contrast**
- Energy Dispersive X-ray Spectroscopy (EDS)
- Wavelength Dispersive X-ray Spectroscopy (WDS)
- Orientation Imaging Microscopy (OIM)
- X-ray Fluorescence (XRF)

Comparison of OM,TEM and SEM



Principal features of an optical microscope, a transmission electron microscope and a scanning electron microscope, drawn to emphasize the similarities of overall design.

Optical Microscopy (OM) vs Scanning Electron Microscopy (SEM)



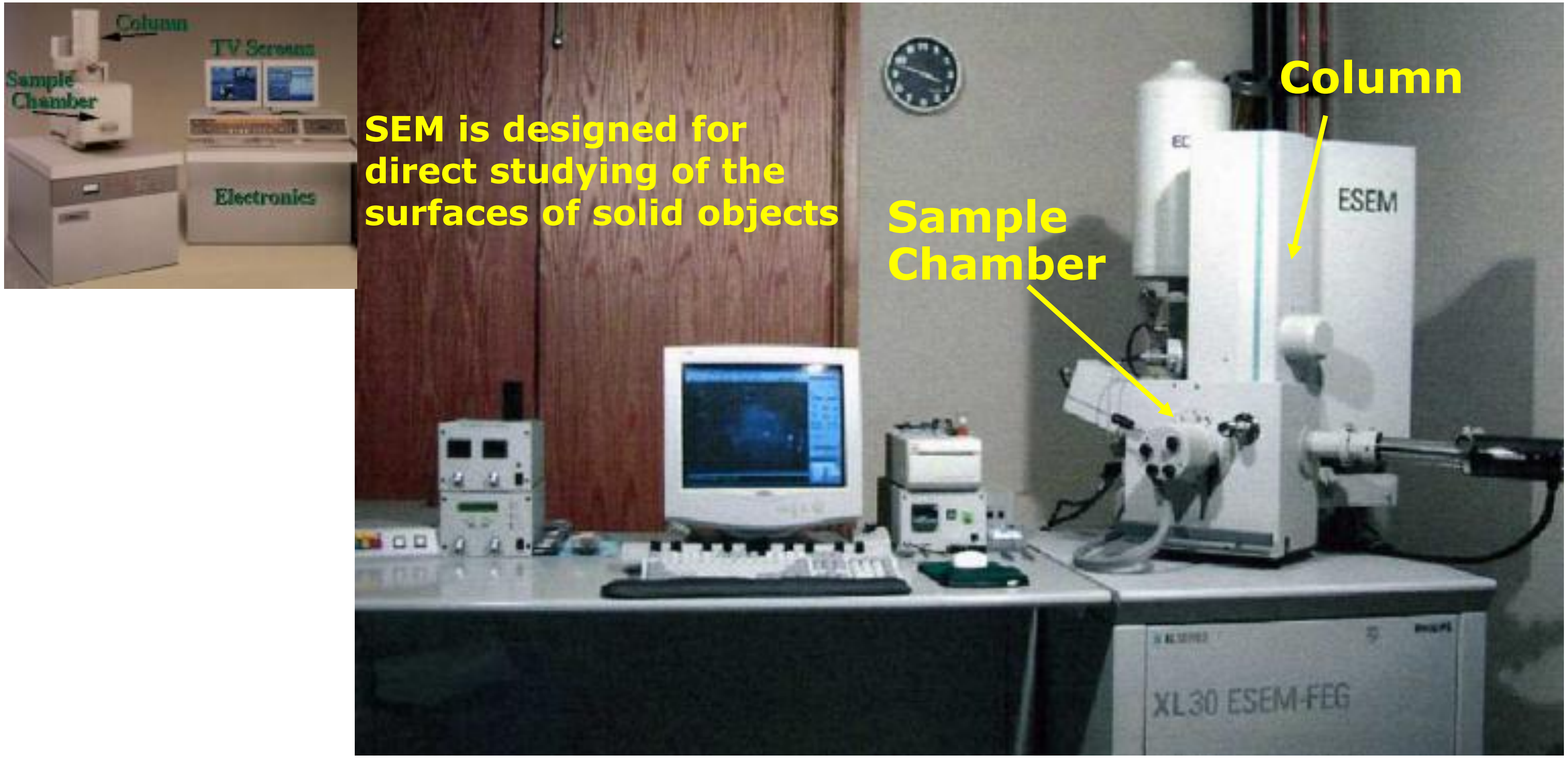
OM

SEM

Small depth of field
Low resolution

Large depth of field
High resolution

What is SEM



SEM is designed for direct studying of the surfaces of solid objects

Scanning electron microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a OM.

The most versatile instrument for a materials scientist?

What can we study in a SEM?

- Topography and morphology
- Chemistry
- Crystallography
- Orientation of grains
- In-situ experiments:
  - Reactions with atmosphere
  - Effects of temperature

“Easy” sample preparation!!

“Big” samples!

Topography and morphology

- High depth of focus

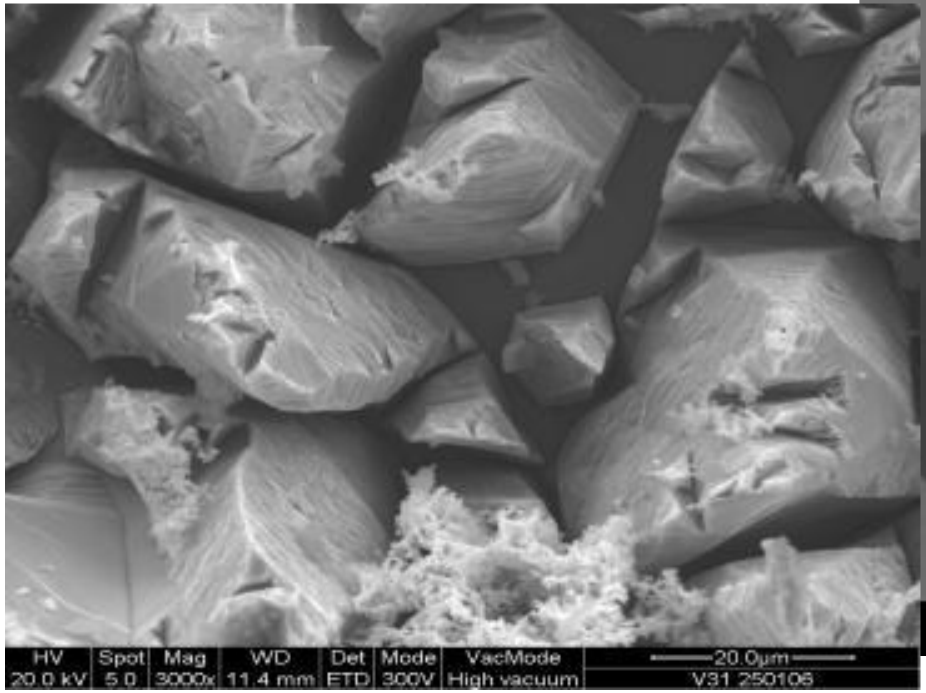


Image: Christian Kjølseth, UiO

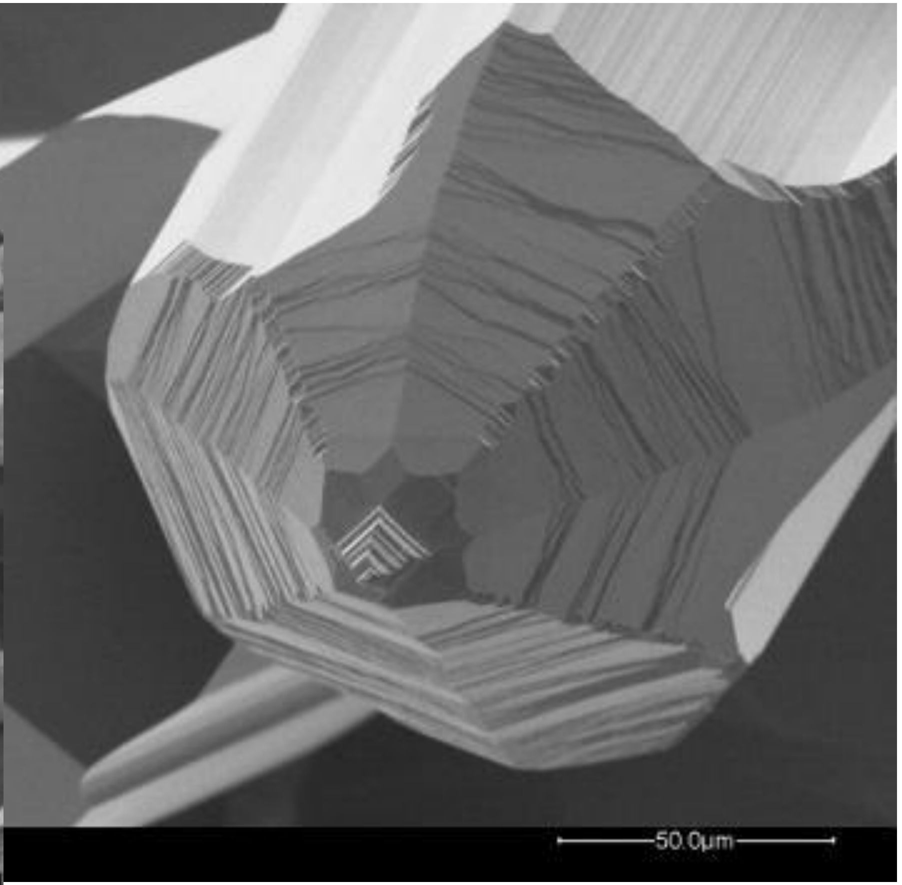


Image: Camilla Kongshaug, UiO

Depth of focus

Optical microscopy vs SEM

Screw length: ~ 0.6 cm

Images: the A to Z of Materials

- A SEM typically has orders of magnitude better depth of focus than a optical microscope making SEM suitable for studying rough surfaces
- The higher magnification, the lower depth of focus

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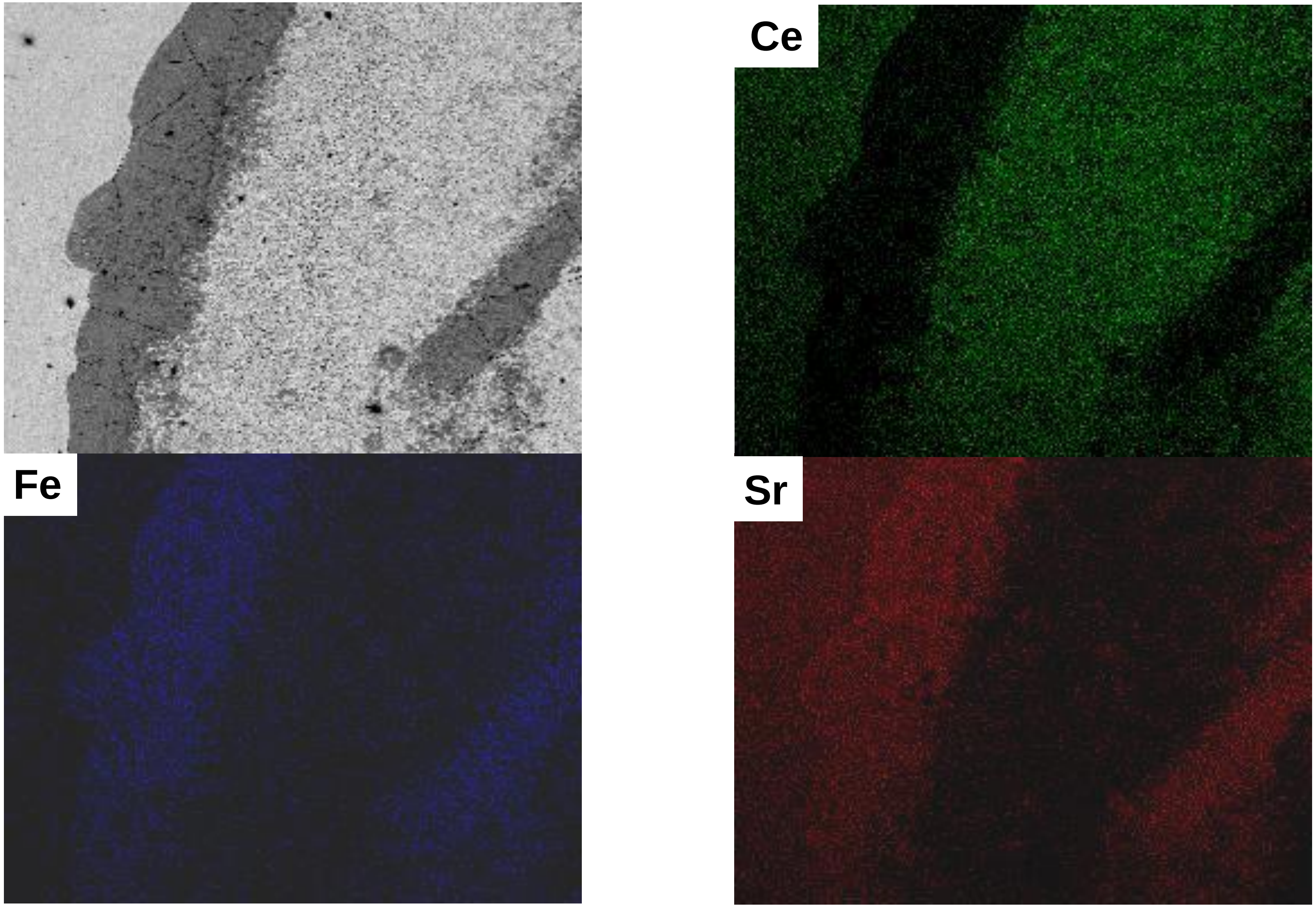
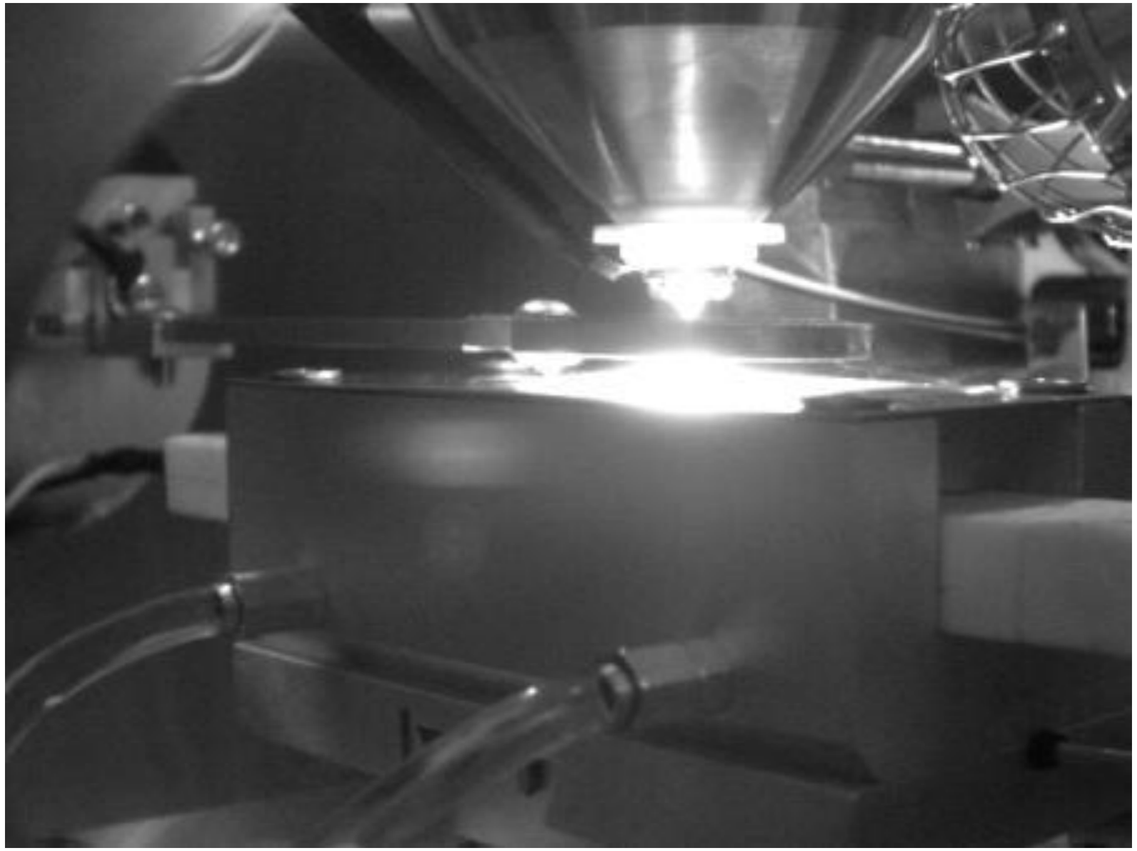
Chemistry



In-situ imaging

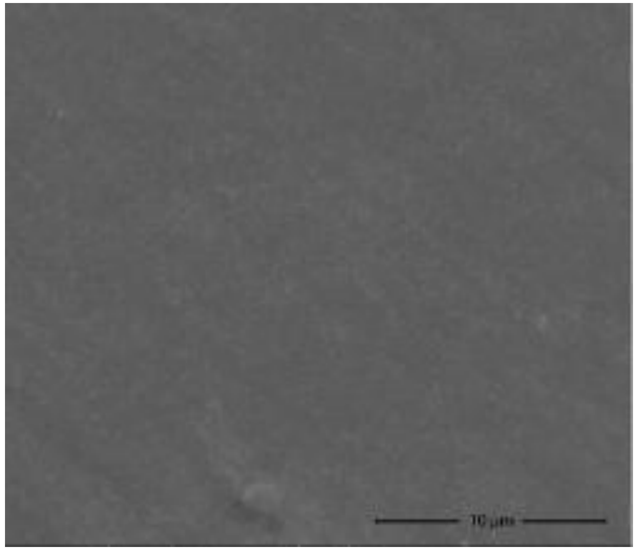
- A modern SEM can be equipped with various accessories, e.g. a hot stage



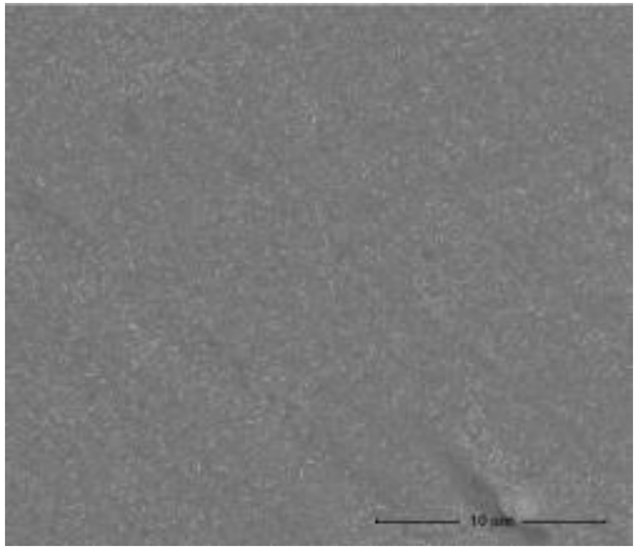
In-situ imaging: oxidation of steel at high temperatures

- 800 °C, pH_2O = 667 Pa
- Formation of Cr_2O_3

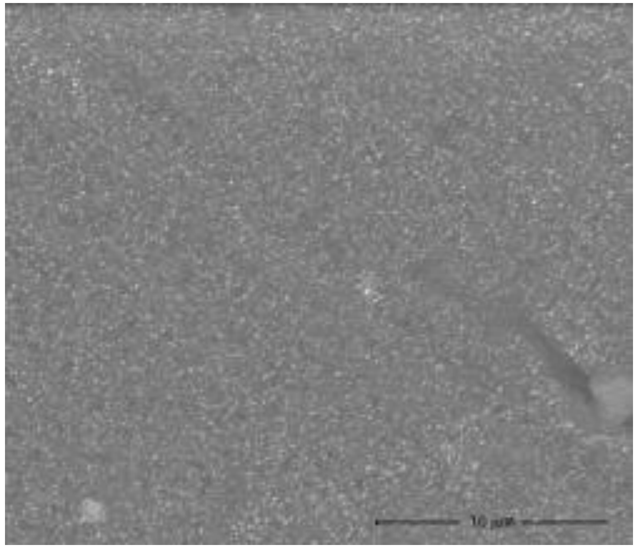
2 min



10 min



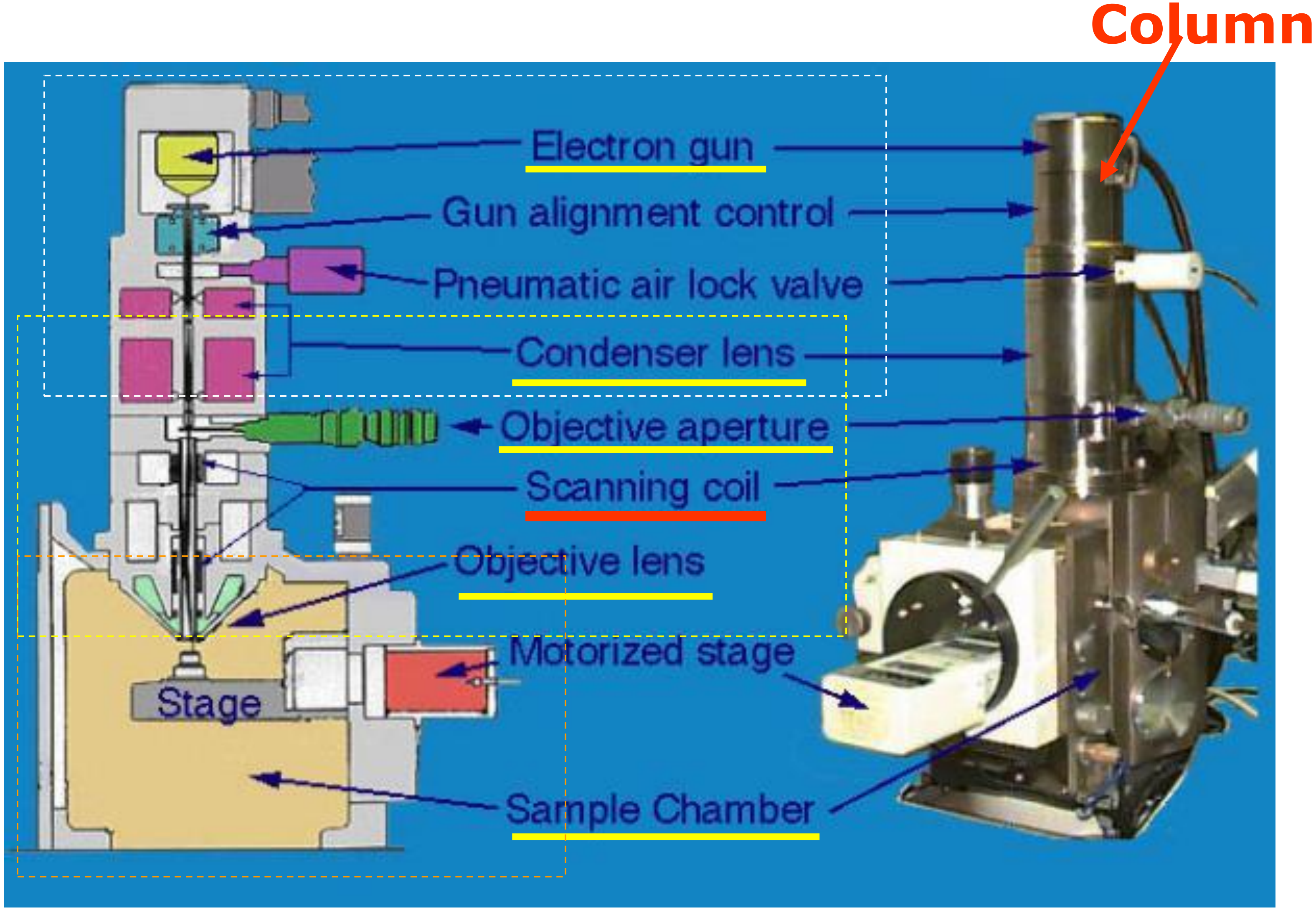
90 min



Images: Anders W. B. Skilbred

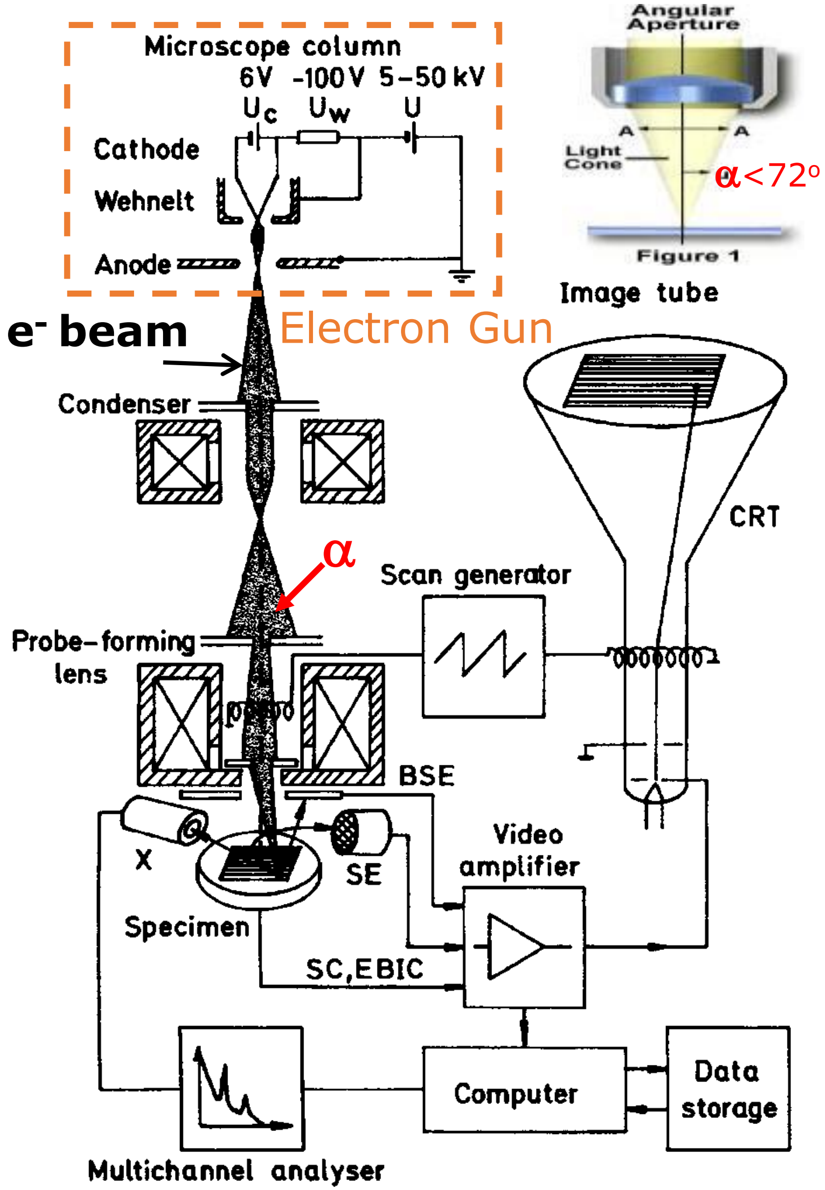
http://virtual.itg.uiuc.edu/training/EM_tutorial

A Look Inside the Column

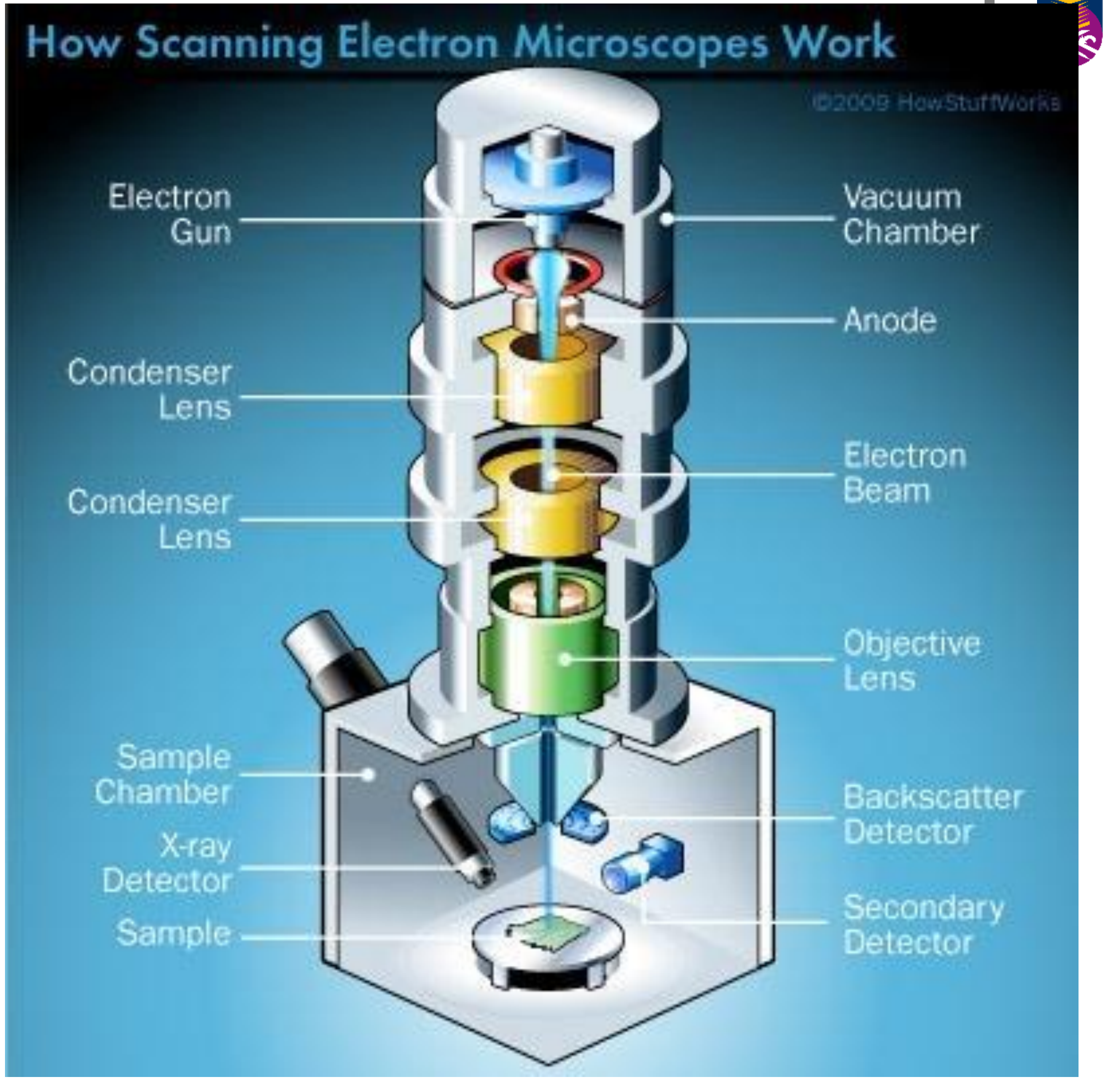


A more detailed look inside

http://www.youtube.com/watch?v=sFSFpXdAiAM

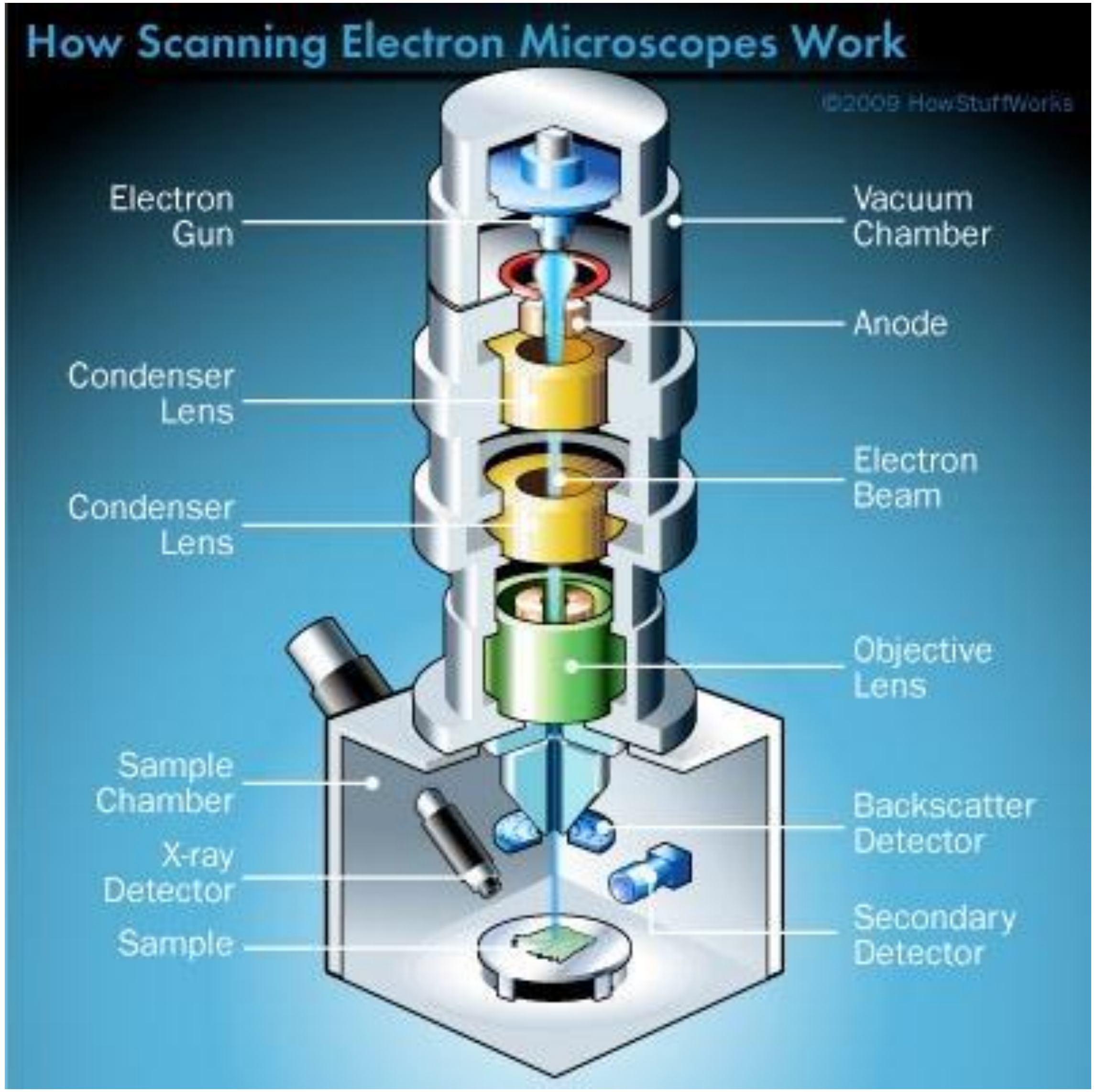


Source: L. Reimer, “Scanning Electron Microscope”, 2nd Ed., Springer-Verlag, 1998, p.2



α - beam convergence

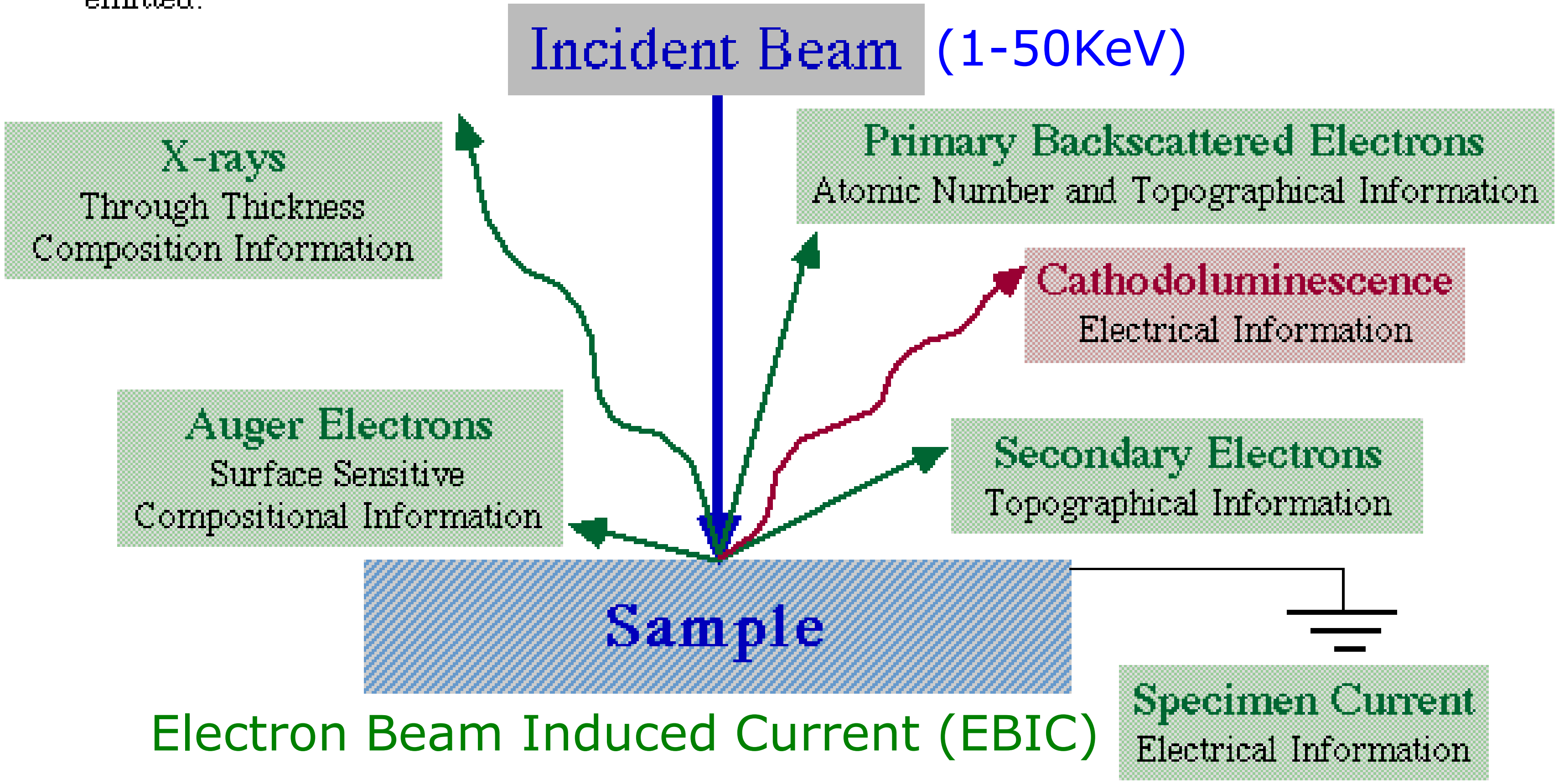
- **What is SEM?**
- **Working principles of SEM**
- **Major components and their functions**



Electron Beam and Specimen Interactions

Sources of Image Information

When the electron beam strikes the sample, both **photon** and **electron** signals are emitted.



Incident Beam (1-50KeV)

X-rays
Through Thickness
Composition Information

Primary Backscattered Electrons
Atomic Number and Topographical Information

Cathodoluminescence
Electrical Information

Auger Electrons
Surface Sensitive
Compositional Information

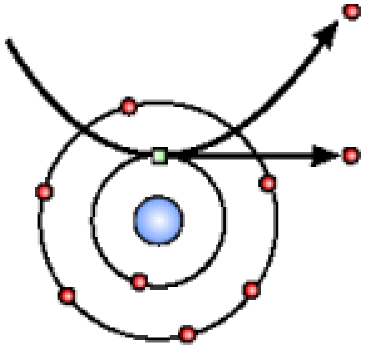
Secondary Electrons
Topographical Information

Sample

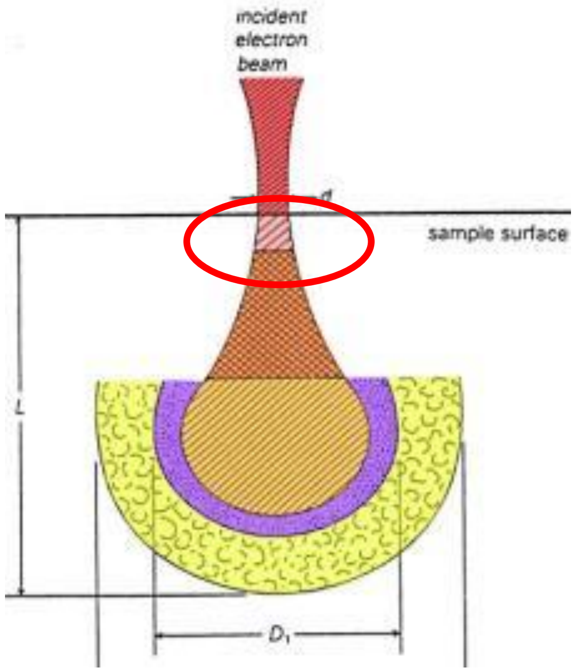
Specimen Current
Electrical Information

Electron Beam Induced Current (EBIC)

Secondary electrons (SE)

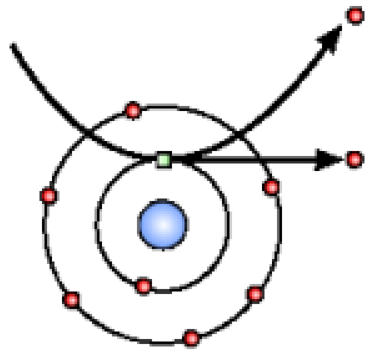


- Generated from the collision between the incoming electrons and the loosely bonded outer electrons
- Low energy electrons (~10-50 eV)
- Only SE generated close to surface escape (topographic information is obtained)
- Number of SE is greater than the number of incoming electrons
- We differentiate between SE1 and SE2



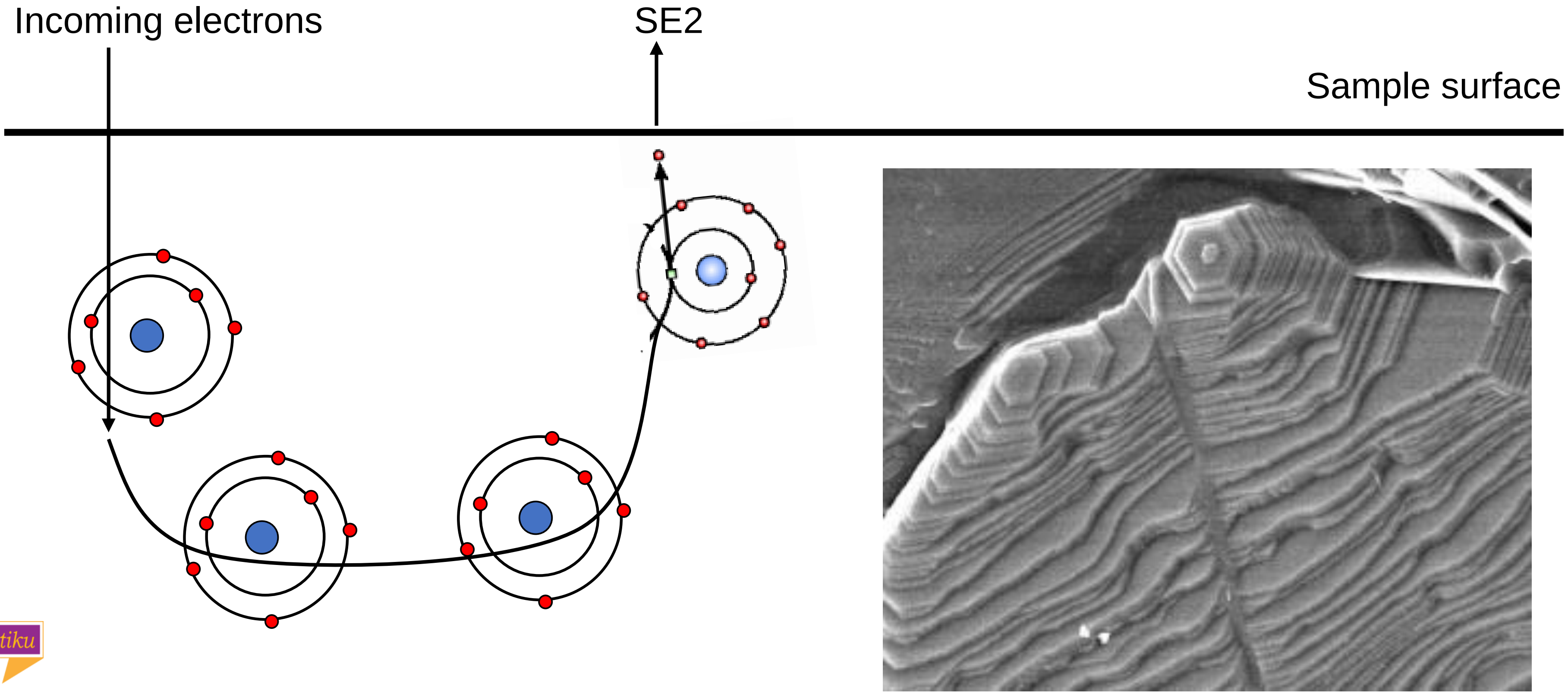
SE1

- The secondary electrons that are generated by the incoming electron beam as they enter the surface
- High resolution signal with a resolution which is only limited by the electron beam diameter



SE2

- The secondary electrons that are generated by the backscattered electrons that have returned to the surface after several inelastic scattering events
- SE2 come from a surface area that is bigger than the spot from the incoming electrons → resolution is poorer than for SE1 exclusively



Factors that affect SE emission

1. Work function of the surface
2. Beam energy (E) and beam current (i)
   - Higher E, more SE. But: Higher E, SE are created at larger depths → fewer SE can escape from the sample
   - Higher i, more SE.
   - Electron yield goes through a maximum at low acc. voltage, then decreases with increasing acc. voltage (page 283)

Factors that affect SE emission

3. Atomic number (Z)
   - More SE2 are created with increasing Z
   - The Z-dependence is more pronounced at lower beam energies

4. The local curvature of the surface (the most important factor)

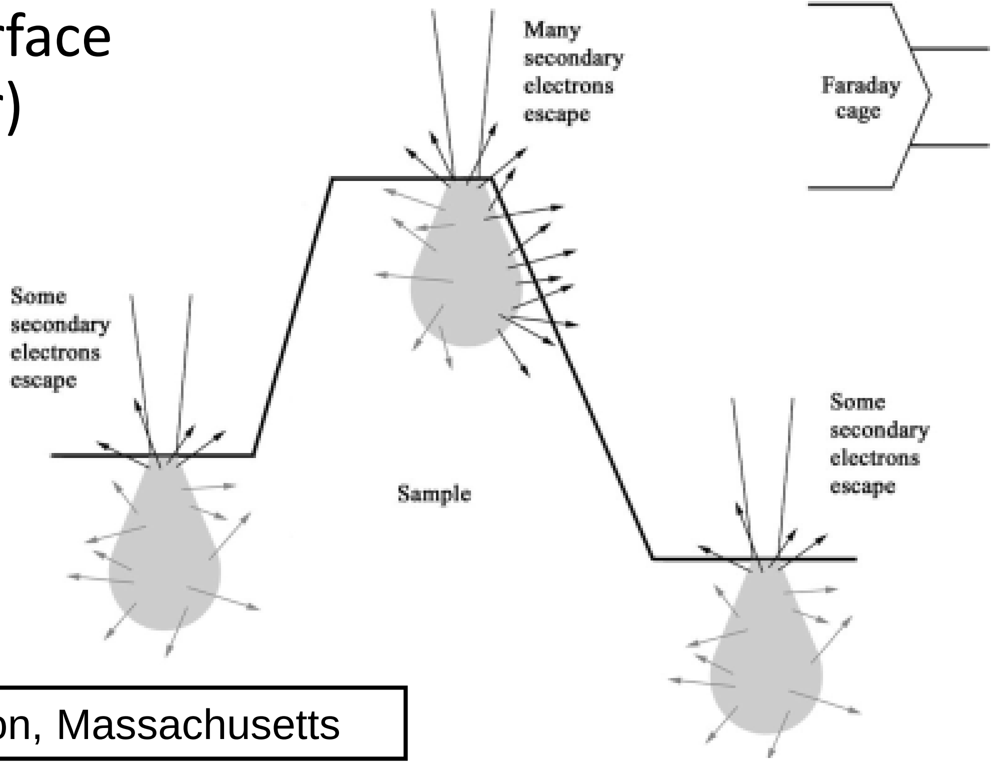
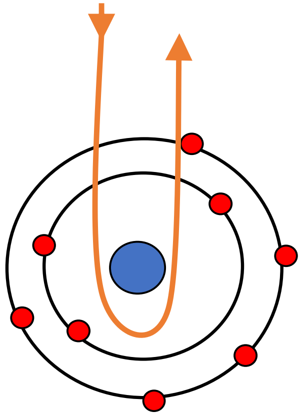


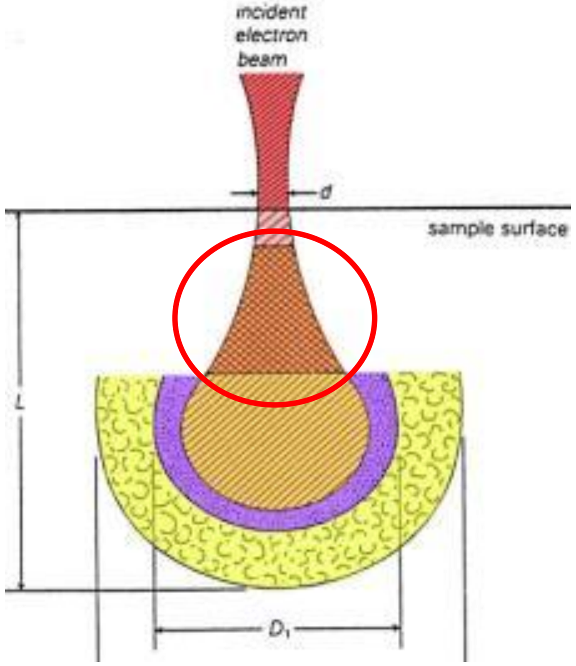
Image: Smith College Northampton, Massachusetts

Backscattered electrons (BSE)



- A fraction of the incident electrons is retarded by the electro-magnetic field of the nucleus and if the scattering angle is greater than 180 ° the electron can escape from the surface

➔ BSE

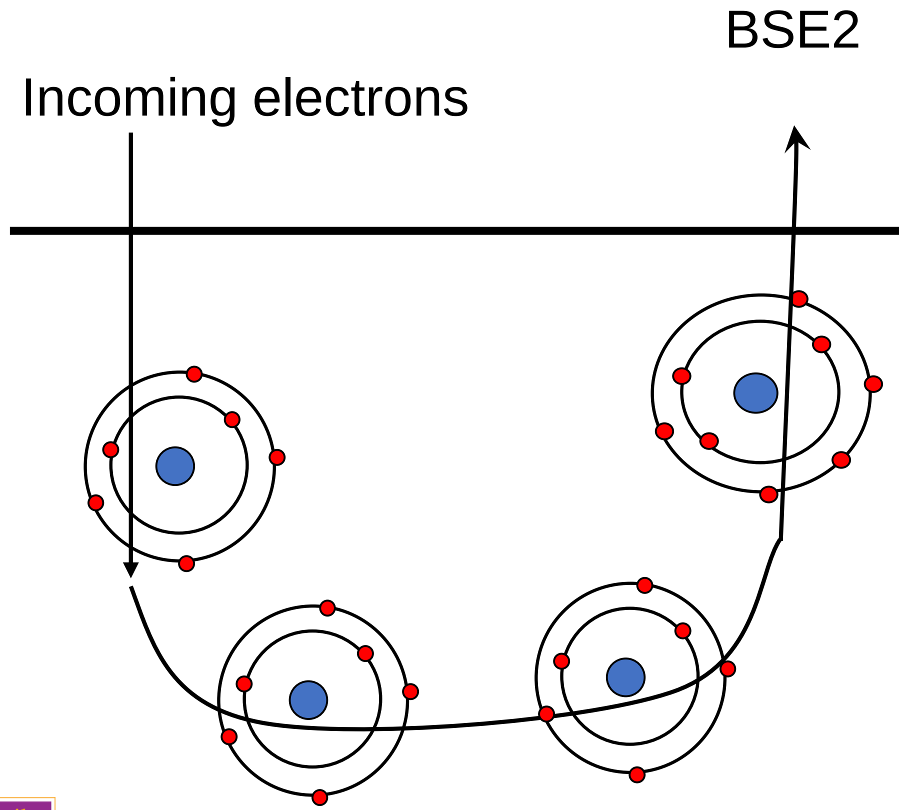


Backscattered electrons (BSE)

- High energy electrons (elastic scattering)
- Fewer BSE than SE
- We differentiate between BSE1 and BSE2

BSE2

- Most BSE are of BSE2 type



BSE as a function of atomic number

- For phases containing more than one element, it is the average atomic number that determines the backscatter coefficient η

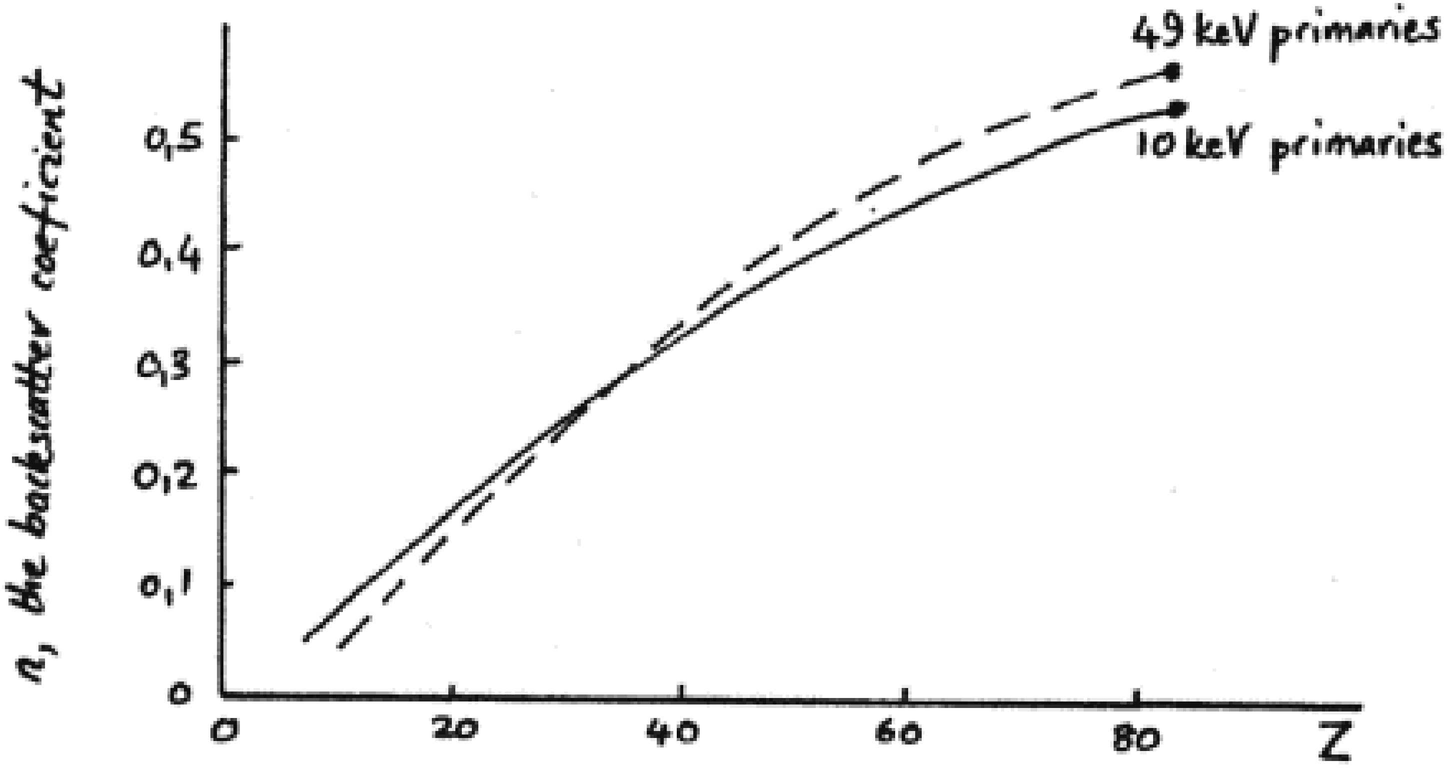


Image: University of Cape Town

Factors that affect BSE emission

- Direction of the irritated surface
  - more electrons will hit the BSE detector when the surface is aligned towards the BSE detector

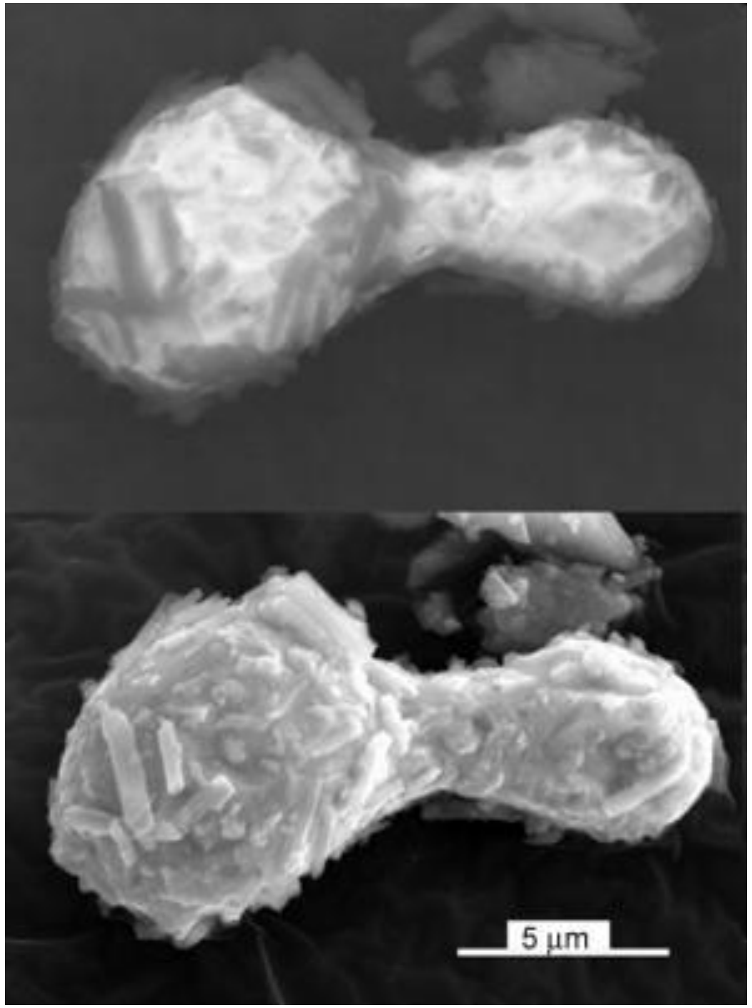
- Average atomic number

- When you want to study differences in atomic numbers the sample should be as levelled as possible (sample preparation is an issue!)

BSE

VS

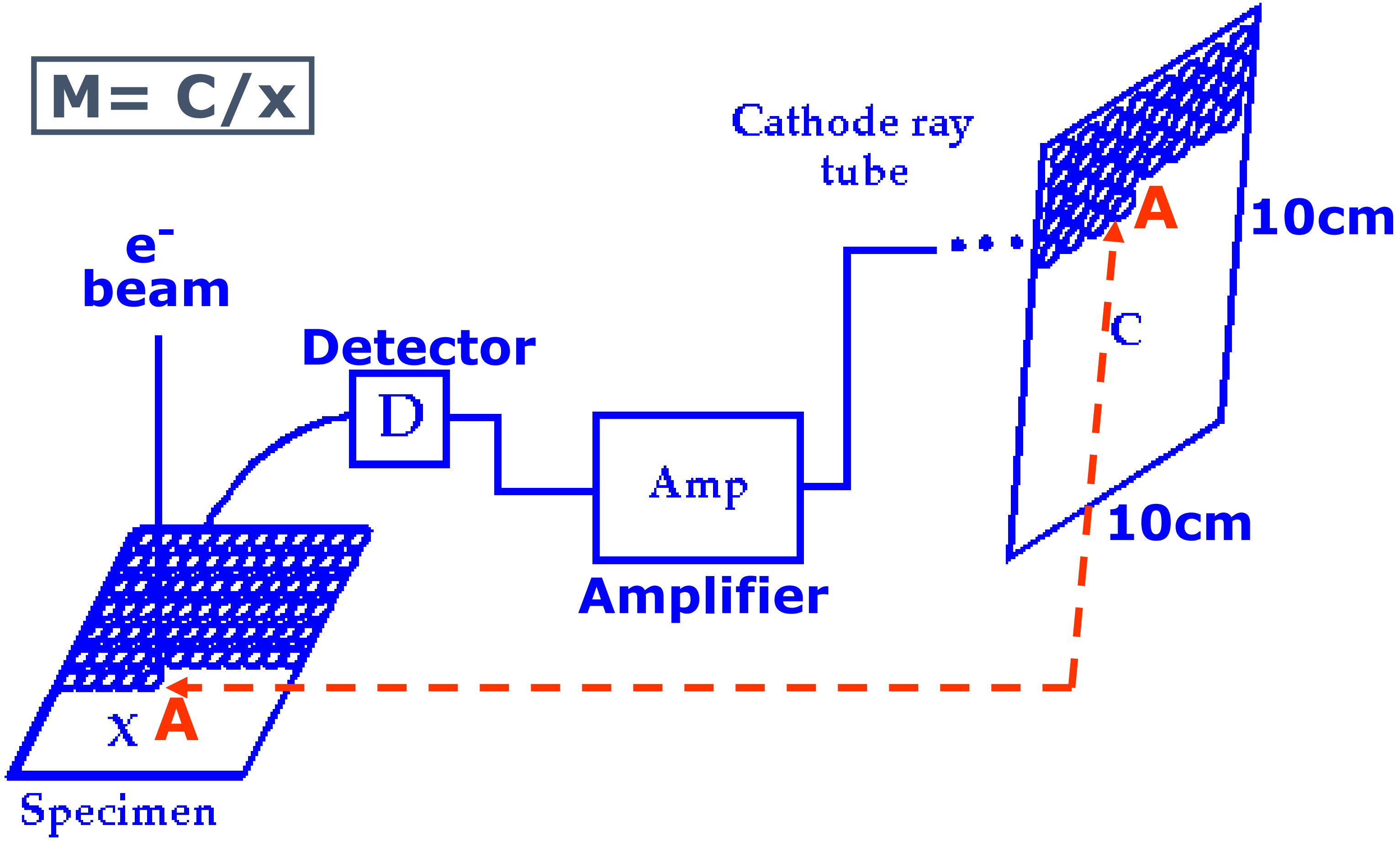
SE



Images: Greg Meeker, USGS

http://www.youtube.com/watch?v=VWxYsZPtTsI at ~4:18-4:45

Image Formation & Magnification in SEM

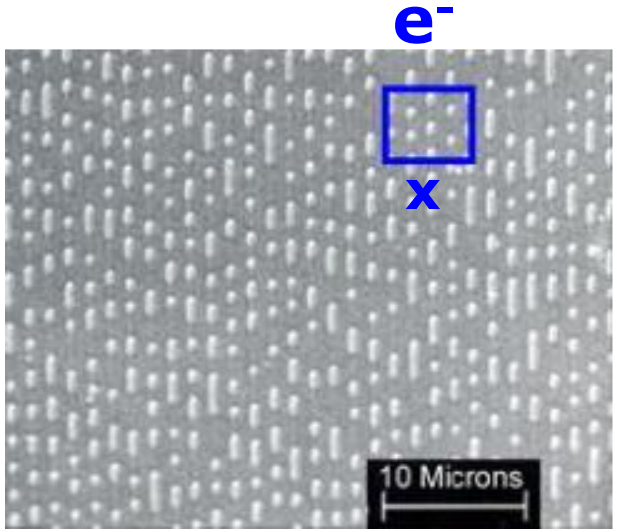


Beam is scanned over specimen in a raster pattern in synchronization with beam in CRT.

Intensity at A on CRT is proportional to signal detected from A on specimen and signal is modulated by amplifier.

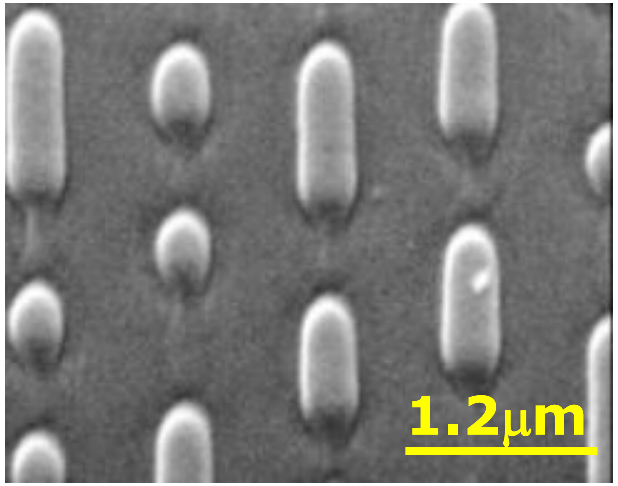
https://www.youtube.com/watch?v=Mr9-1Sz_CK0 at~11:45-11:55

Magnification



Low M
Large x
40µm

2500x



High M
small x
7µm

15000x

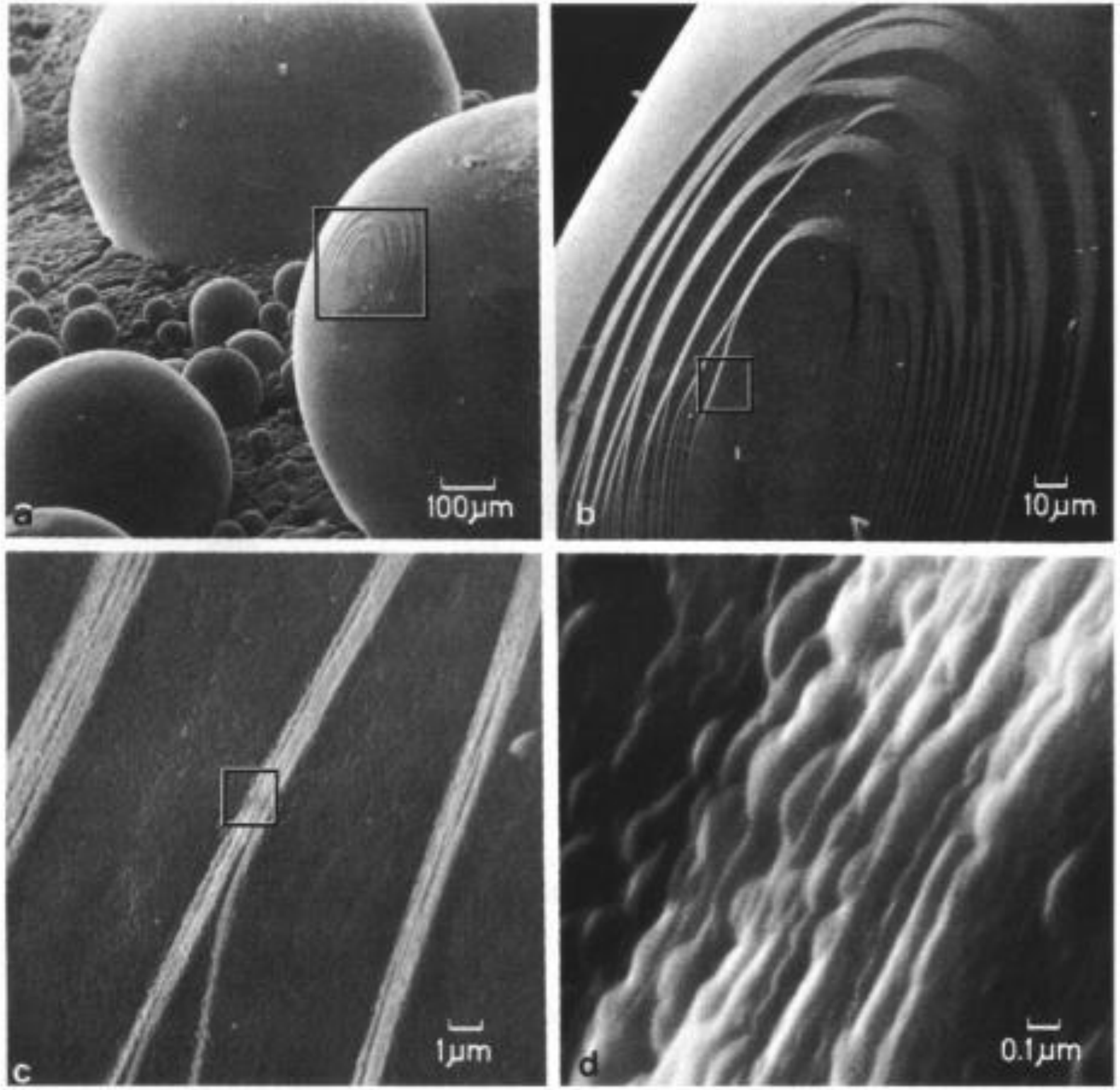
The magnification is simply the ratio of the length of the scan C on the Cathode Ray Tube (CRT) to the length of the scan x on the specimen. For a CRT screen that is 10 cm square:

$$M = C/x = 10\text{cm}/x$$

Increasing M is achieved by decreasing x.

M	x	M	x
100	1 mm	10000	10 µm
1000	100 µm	100000	1 µm

Image Magnification



Example of a series of increasing magnification (spherical lead particles imaged in SE mode)

How Fine Can We See with SEM?

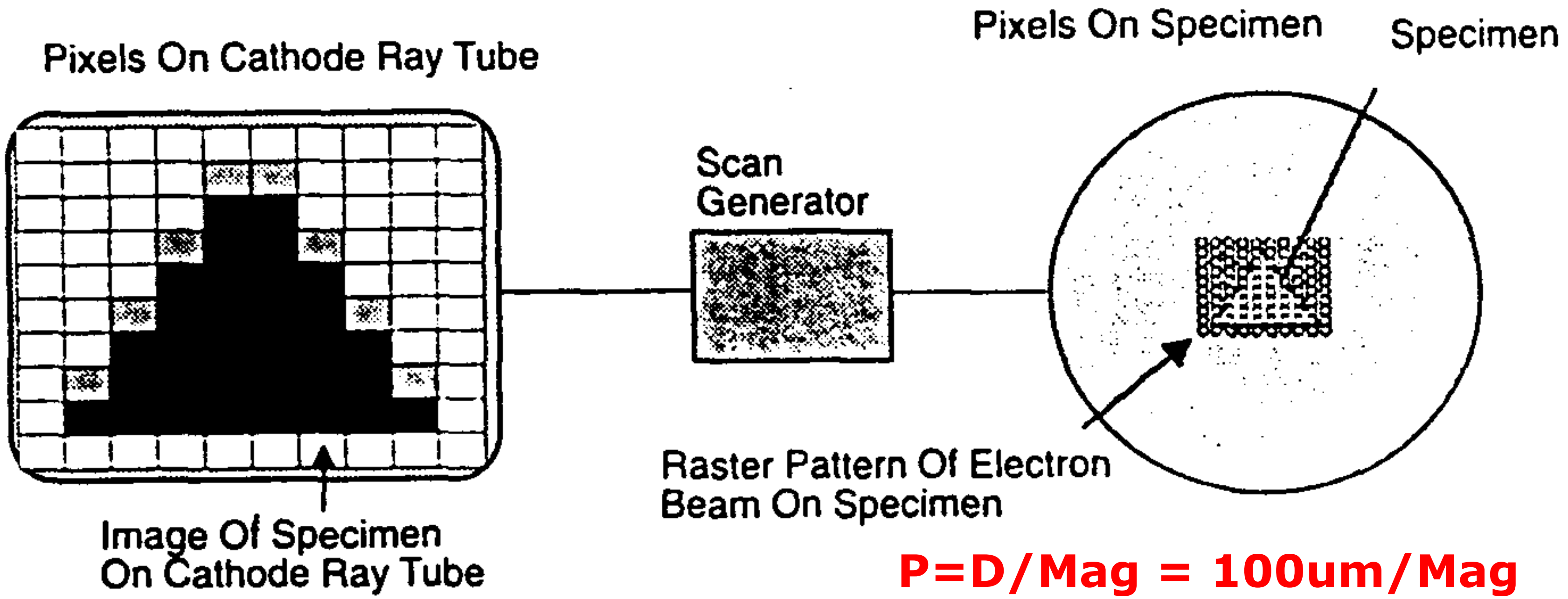
- If we can scan an area with width 10 nm (10,000,000×) we may actually see atoms!! But, can we?
- Image on the CRT consists of spots called **pixels** (e.g. your PC screen displays 1024×768 pixels of ~0.25mm pitch) which are the basic units in the image.
- **You cannot have details finer than one pixel!**

Pixel - In digital imaging, a **pixel** (**picture element**) is a physical point in a raster image, or the smallest addressable element in a display device; so it is **the smallest controllable element** of a picture represented on the screen.

http://en.wikipedia.org/wiki/Pixel

Resolution of Images: I

- Assume that there the screen can display 1000 pixels/(raster line), then you can imagine that there are 1000 pixels on each raster line on the specimen.
- The **resolution** is the **pixel diameter** on specimen surface.



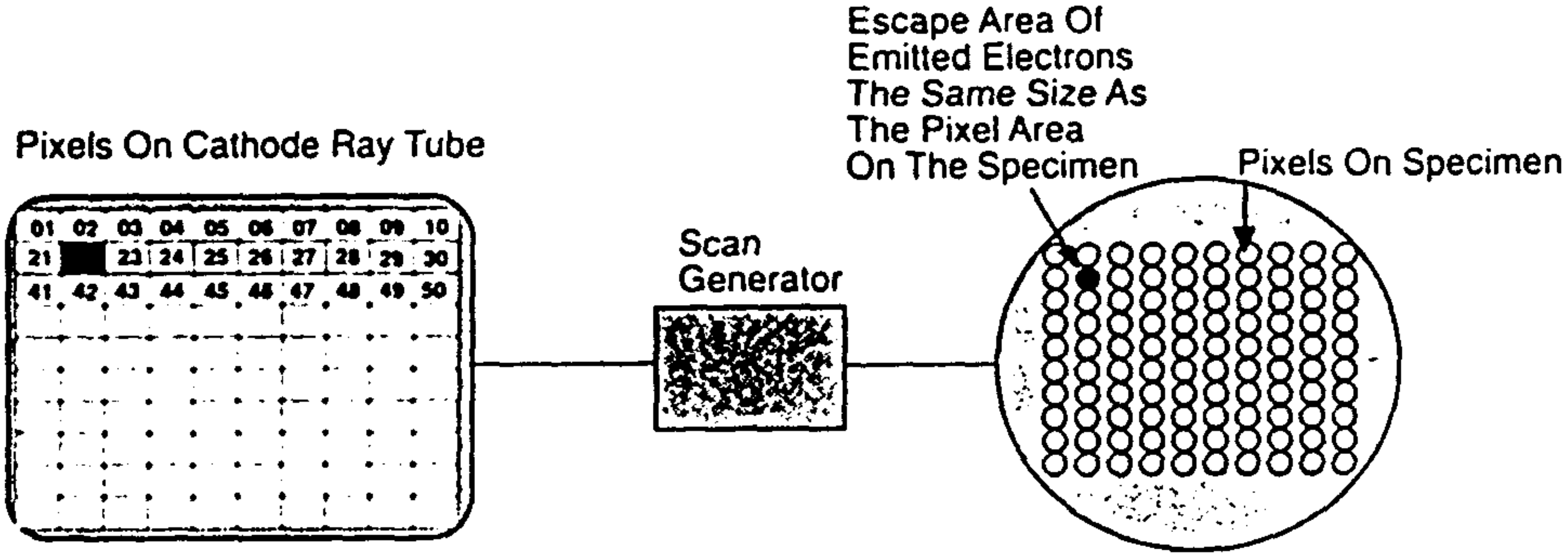
P=D/Mag = 100um/Mag

Mag	P(μm)	Mag	P(nm)
10x	10	10kx	10
1kx	0.1	100kx	1

P-pixel diameter on specimen surface
D-pixel diameter on CRT, Mag-magnification

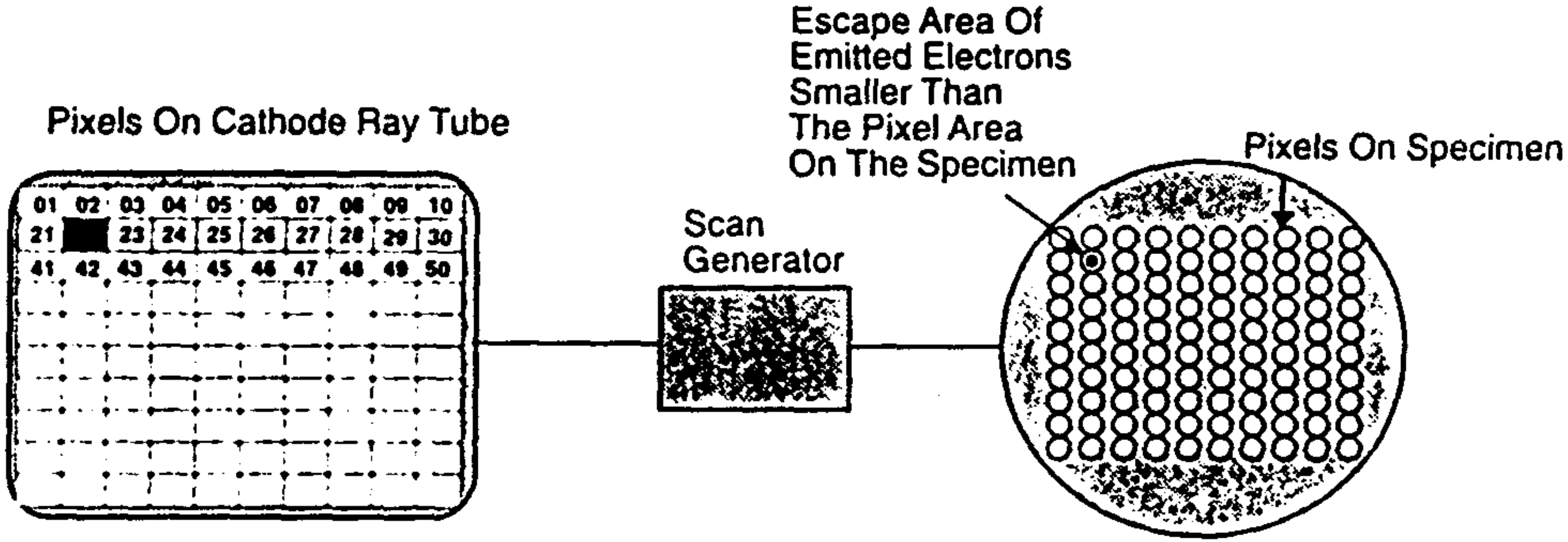
Resolution of Images: II

- The optimum condition for imaging is when the escape volume of the signal concerned equals to the pixel size.



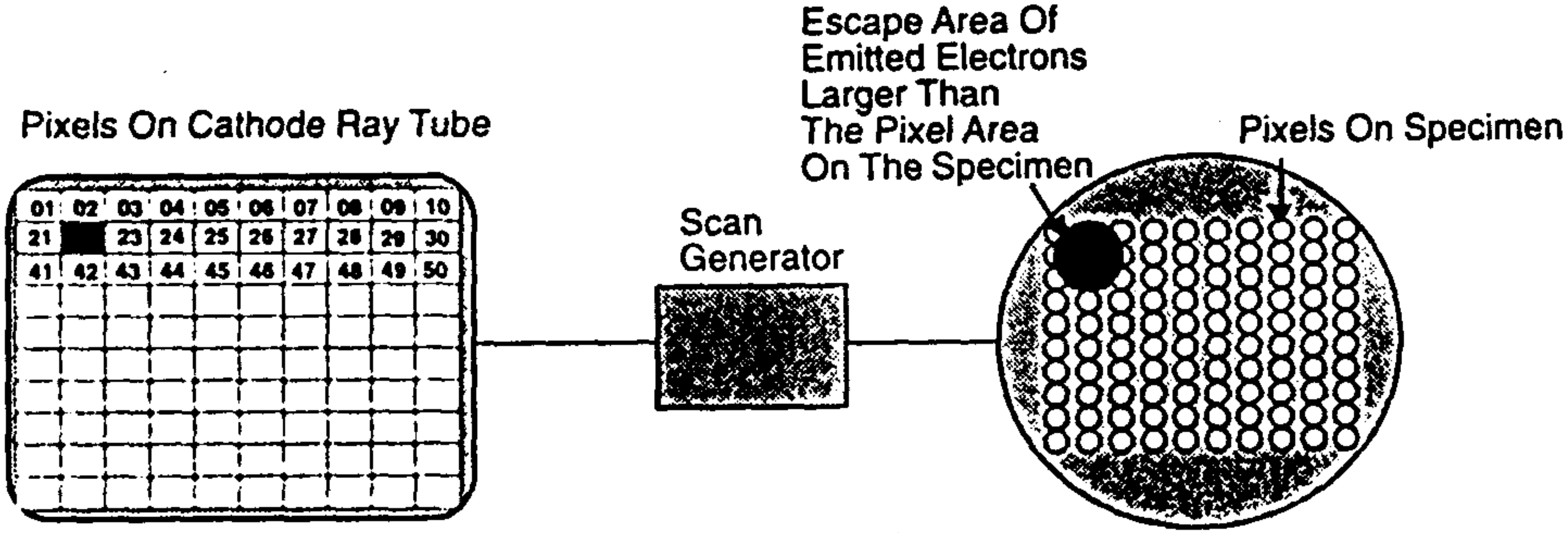
Resolution of Images: III

- Signal will be **weak** if **escape volume**, which depends on **beam size**, is **smaller** than **pixel size**, but the **resolution** is still achieved. (***Image is 'noisy'***)



Resolution of Images: IV

- Signal from different pixel will **overlap** if **escape volume** is **larger** than the **pixel size**. The image will appeared out of focus (***Resolution decreased***)



Resolution of Images: V

In extremely good SEM, **resolution** can be **a few nm**. The limit is set by the **electron probe size**, which in turn depends on the quality of the **objective lens** and **electron gun**.

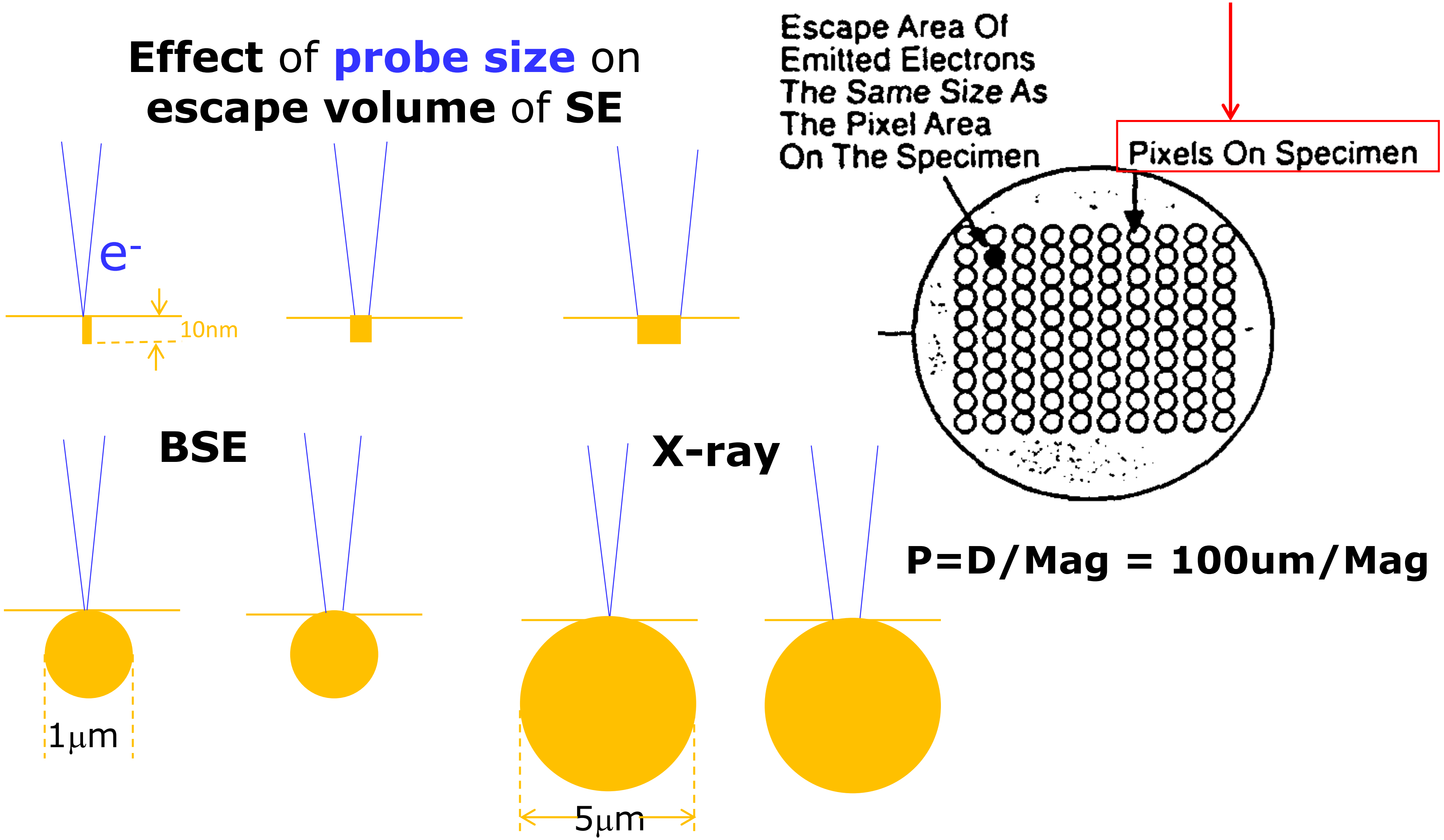
Magnification	Pixel diameter on Specimen	
	µm	nm
10	10	10000
100	1	1000
1000	0.1	100
10000	0.01	10
100000	0.001	1

Resolution of Images

The **resolution** is the **pixel diameter** on **specimen surface**.

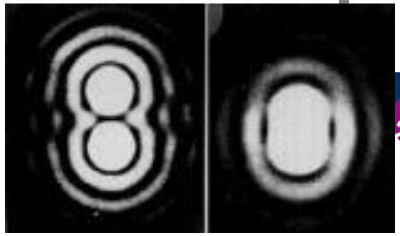
The optimum condition for imaging is when the escape volume of the signal concerned equals to the pixel size.

Effect of **probe size** on **escape volume** of **SE**



P=D/Mag = 100um/Mag

Depth of Field



Depth of Field

$$D = \frac{4\times10^{5}W}{AM}\ (\mu m)$$

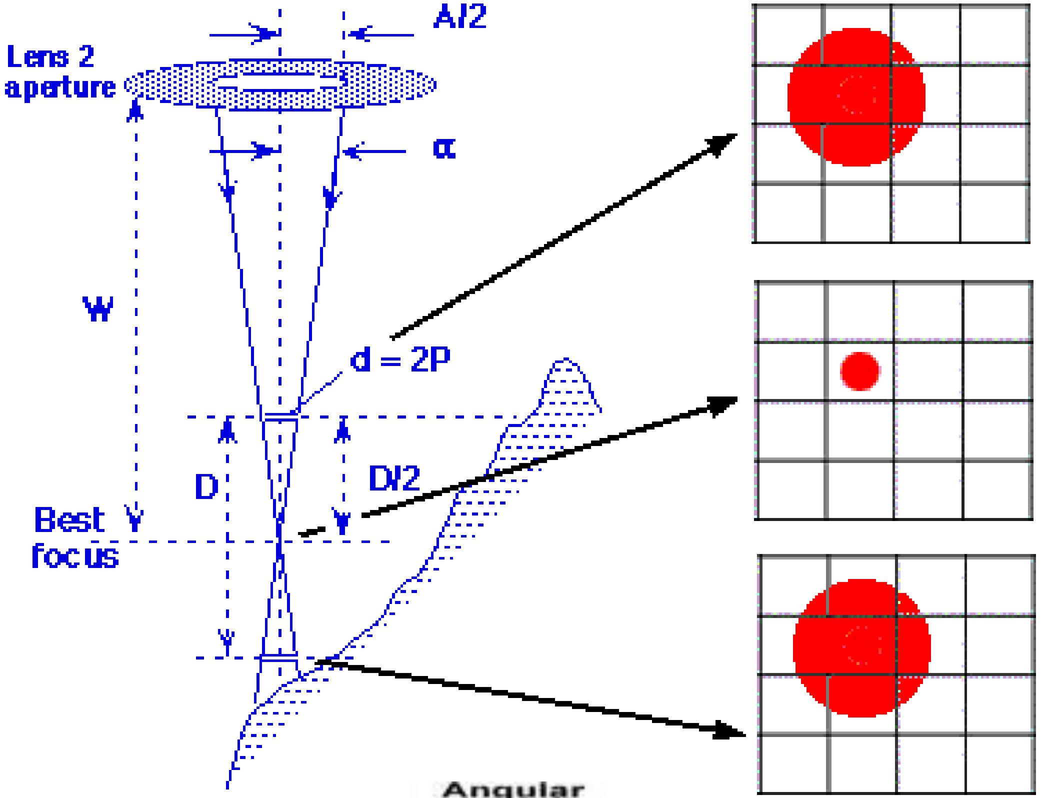
$A/2 = \alpha$

To increase **D**

Decrease aperture size, A

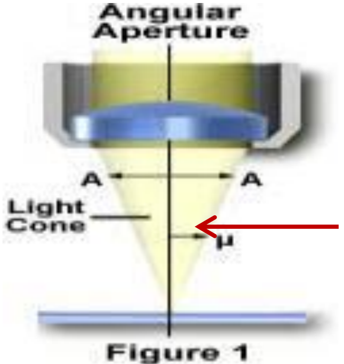
Decrease magnification, M

Increase working distance, W (mm)



$\alpha = 5\times10^{-3} = 0.005$

$(1^{o} = 0.0175)$

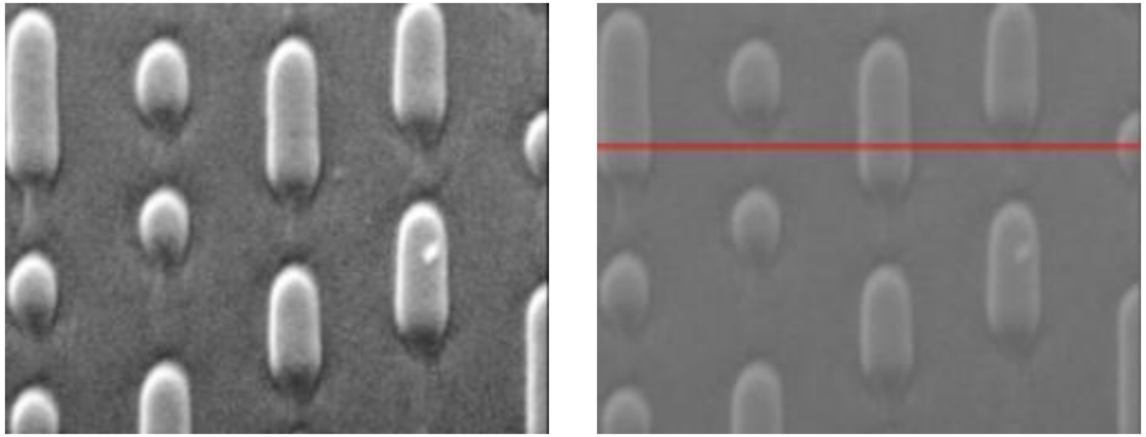


OM

$\alpha \leq 72^{o} = 1.26$

Image Contrast

SE Images



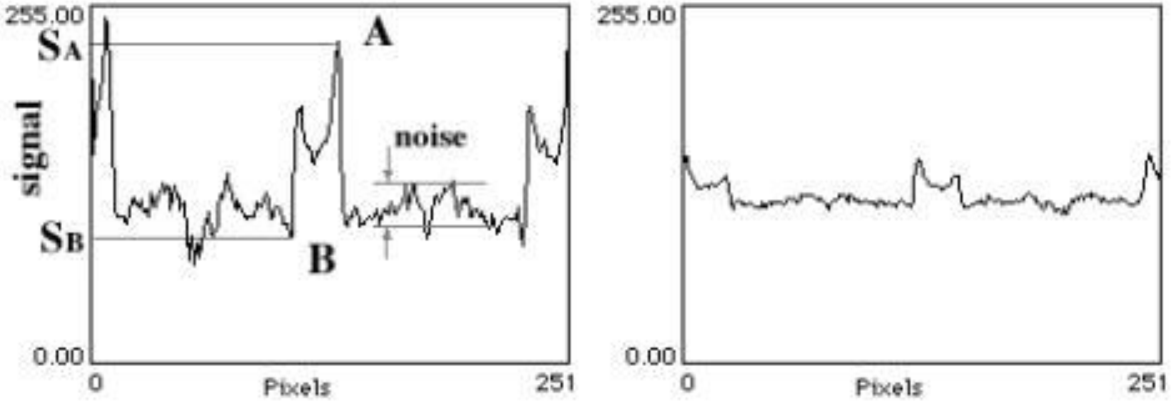


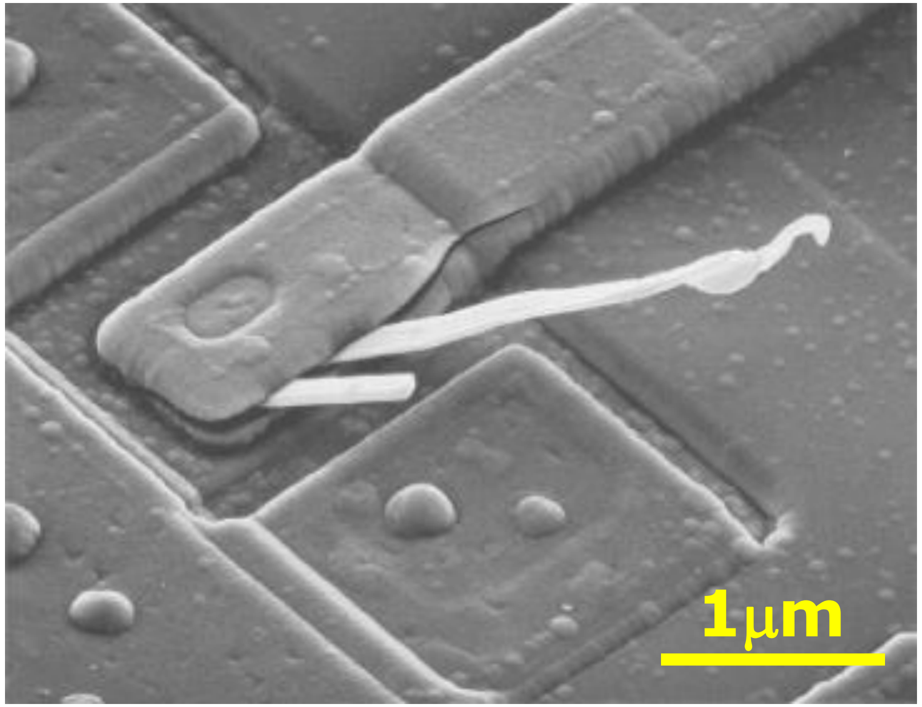
Image contrast, C is defined by

$$C = \frac{S_A - S_B}{S_A} = \frac{\Delta S}{S_A}$$

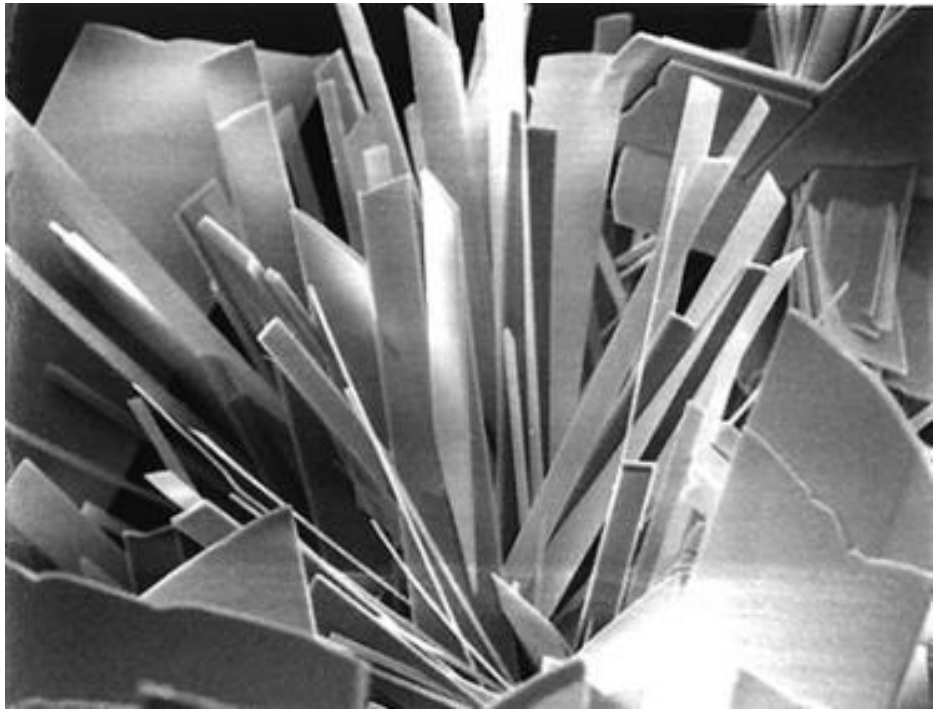
S_A, S_B Represent signals generated from two points, e.g., A and B, in the scanned area.

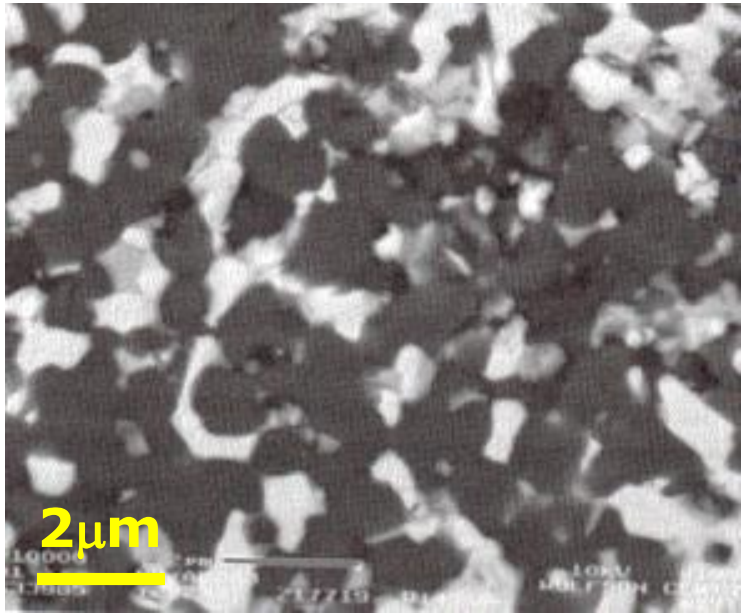
In order to detect objects of small size and low contrast in an SEM it is necessary to use a high beam current and a slow scan speed (i.e., improve signal to noise ratio).

SE-topographic and BSE-atomic number contrast



Defect in a semiconductor device

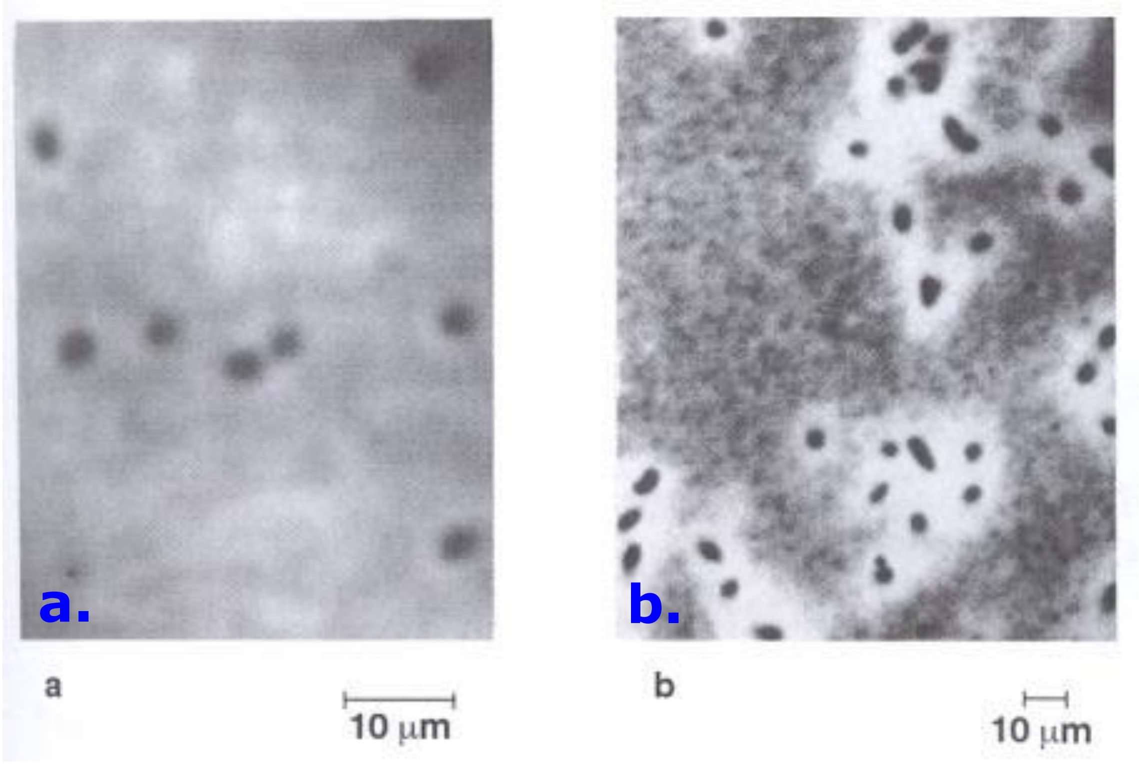




Z (Nb) = 41, Z (Al) = 13 and Z(O) = 8

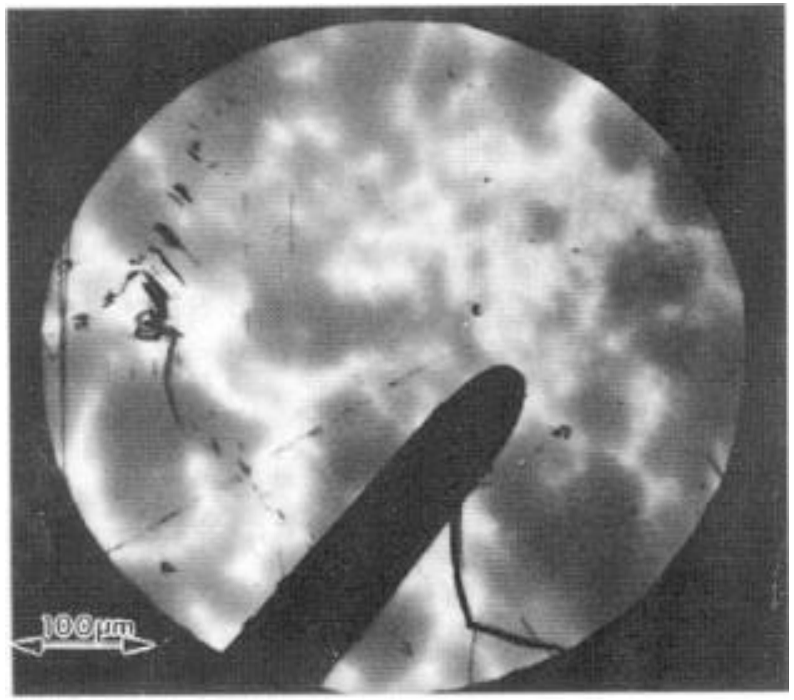
Alumina-Al_2O_3

CL micrographs of Te-doped GaAs



a. Te=10^{17}cm^{-3}, dark-dot dislocation contrast
b. Te=10^{18}cm^{-3}, dot-and-halo dislocation contrast which shows variations in the doping concentration around dislocations

EBIC Image of Doping Variations in GaAs Wafer



The variations in brightness across the material are due to **impurities** in the wafer. The extreme sensitivity (10^{16}cm^{-3}, i.e., 1 part in 10^7) and speed of this technique makes it ideal fro the characterization of as-grown semiconductor crystals.

What’s the point?

We utilize the **x-rays** produced by the **electron microprobe** for many research applications.

There are other techniques, similar in some ways, that are worth discussing, that utilize x-rays for secondary x-ray fluorescence. Two in particular are:

- XRF (X-Ray Fluorescence), where x-rays from a sealed tube are used to produce x-rays by secondary fluorescence in samples of interest (traditionally a macro-technique)
- Synchrotron Radiation, where electrons are accelerated in ~10s-100s meters diameter rings, and then made to produce highly focused beams of extremely intense x-rays or light, which are then fed into many different types of experiments.

The benefits of secondary x-ray fluorescence include very low detection limits (10s of ppm easy in 10 seconds, no backgrounds)

XRF Basics

The basics of XRF are very similar to those of EPMA—we are dealing with characteristic x-rays and continuum x-rays— with the exception that we are doing secondary fluorescence : x-ray spectroscopy of our samples using x-rays coming out of a sealed tube to excite the atoms in our specimen.

The big difference is that

- there is NO continuum generated in the sample (x-rays can’t generate the Bremsstrahlung), and

- we are using BOTH characteristic x-rays of the sealed tube target (e.g., Cr, Cu, Mo, Rh) AND continuum x-rays to generate the characteristic x-rays of the atoms in the sample.

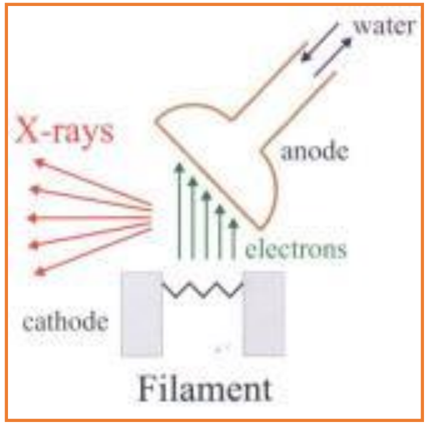
XRF has been a bulk analytical tool (grind up 50-100 grams of your rock or sample to analyze), though recently people are developing “micro XRF” to focus the beam on a ~100 µm spot.

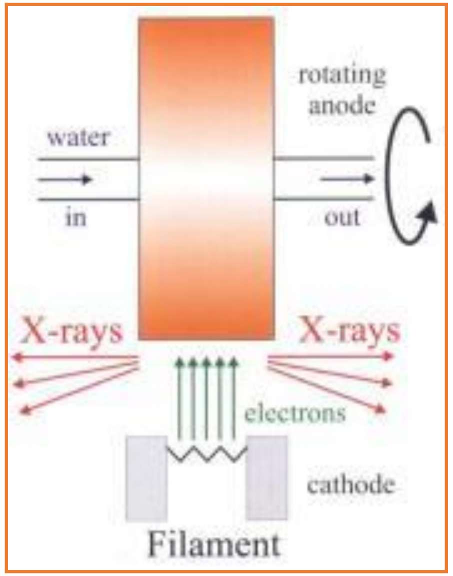
X-ray Sources

The standard X-ray tube (top right) was developed by Coolidge (at GE) around 1912.

It is desirable to produce the maximum intensity of x-rays; a Cu target tube might be able to deliver 2 kW. The limiting factor is the heat that the target (anode) can handle; cold water is used to remove heat.

Higher power can be delivered by dissipating the heat over a larger volume, with a rotating anode (bottom right). However, this is not normally used for XRF.

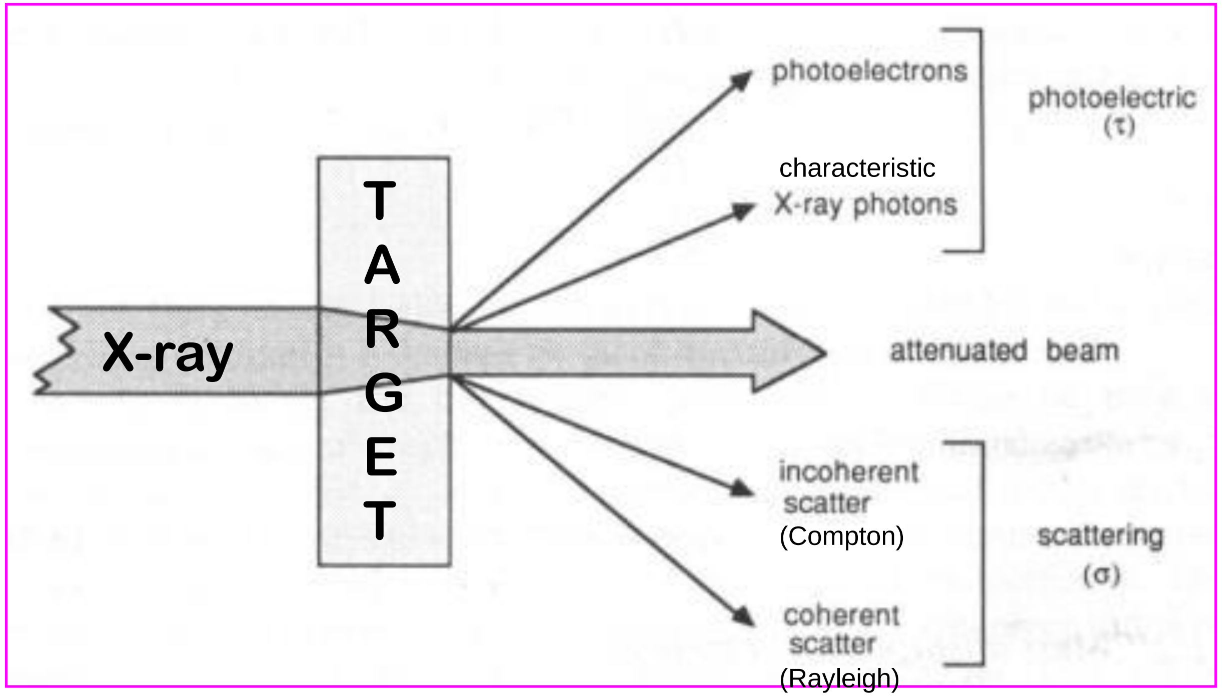




* Power in watts = current [amps] x voltage [volts]

From Als-Nielsen and McMorrow, p. 31

X-ray Attentuation



This figure shows the attenuation of the X-rays in the target (sample).

In addition to photoelectric absorption (producing characteristic X-rays and photoelectrons [includes Auger electrons]), the original X-rays may be scattered.

There are two kinds of scattering: coherent (Rayleigh) and incoherent (Compton).

X-ray Scattering

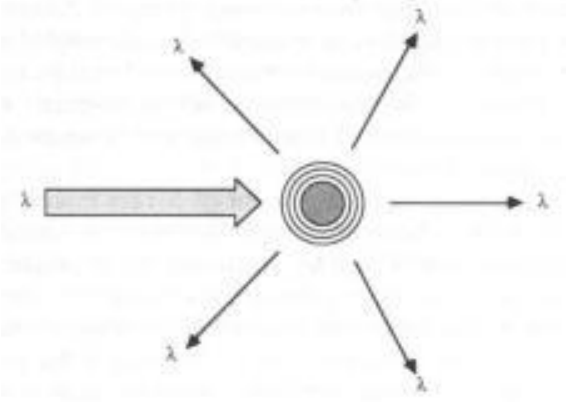
<u>Coherent (Rayleigh) scattering</u> happens when the X-ray collides with an atom and deviates without a loss in energy. An electron in an alternating electromagnetic field (e.g. X-ray photon), will oscillate at the same frequency (in all directions).

It essentially becomes a small radiating dipole, scattering the incident energy in all directions at the same frequency of the X-ray.

This is useful for understanding X-ray diffraction (in depth).

This is elastic scattering – no loss of in energy.

One impact in XRF is that the X-ray line of the X-ray source may be "backscattered" off of the sample onto the detector and show up as something present in the sample.



Coherent

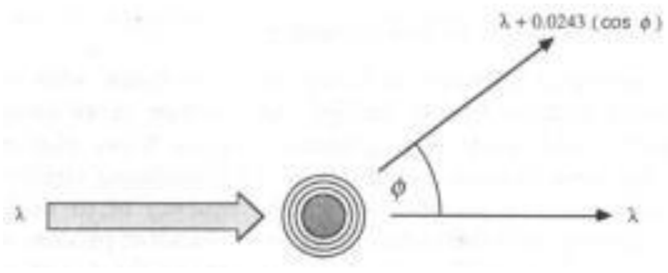
(Rayleigh scattering also explains why the sky is blue. Rayleigh scattering has a strong inverse dependence on the wavelength of the radiation. So the shorter wavelength blue light is scattering more than other colors.)

X-ray Scattering

Incoherent (Compton) scattering is where the incident X-ray loses some of its energy to the scattering electron. It is **inelastic** scatter. As total momentum is preserved, the wavelength of the scattered photon increases by the equation

$$\Delta\lambda = 0.0243(1-\cos\phi) \qquad \text{(in Å)}$$

where ϕ is the scatter angle. Since ϕ is near 90° , there will be an addition peak from the main tube characteristic peak at about 0.024Å higher wavelength

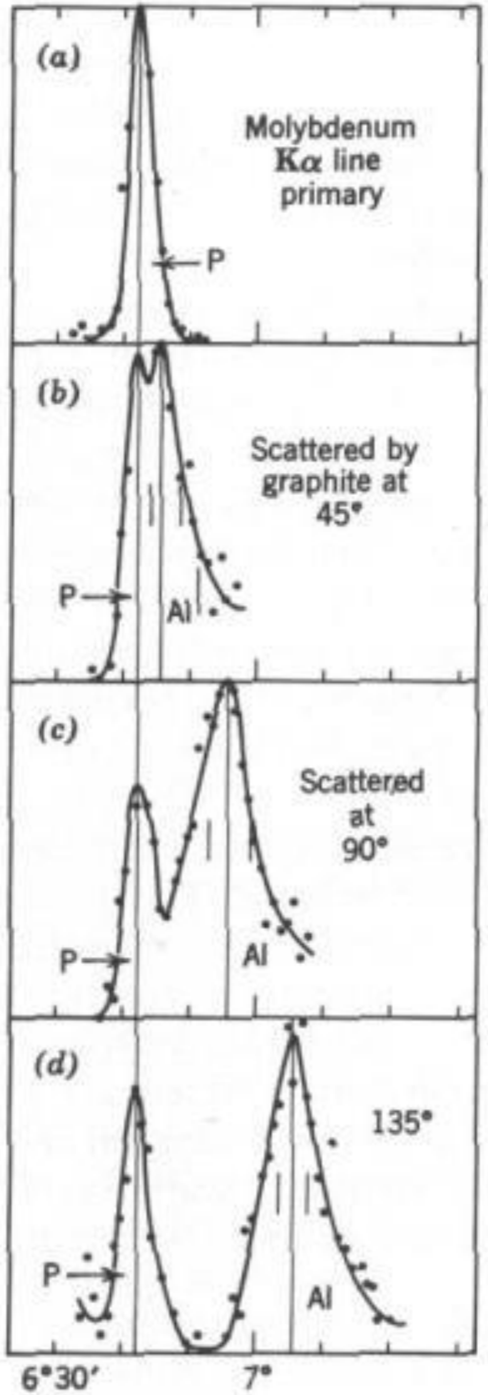


Incoherent

Compton Scattering Peaks

The top figure shows a wavelength spectrum of the Mo Ka peak from the x-ray tube (P=primary, Mo Ka).

The other 3 figures show the splitting of the primary Mo Ka peak into a Compton Scattering Peak due to the incoherent scattering in an Al target, and the effect of changing the scattering angle.



From Liebhafsky et al, 1972

Continuum of X-ray Tube in XRF

Secondary fluorescence by x-rays in the sample does not produce continuum x-rays there. However, the continuum is produced within the selected x-ray tube which is the "gun" in XRF.

This continuum is of interest here as it is useful for excitation source in XRF.

Kramers (1923) deduced the relationship between continuum intensity, wavelength and atomic number of the x-ray source ("target"):

$$I(\lambda)\cdot d\lambda = KiZ\{(\lambda/\lambda_{\min}) - 1\}\{1/\lambda^2\}\cdot d\lambda$$

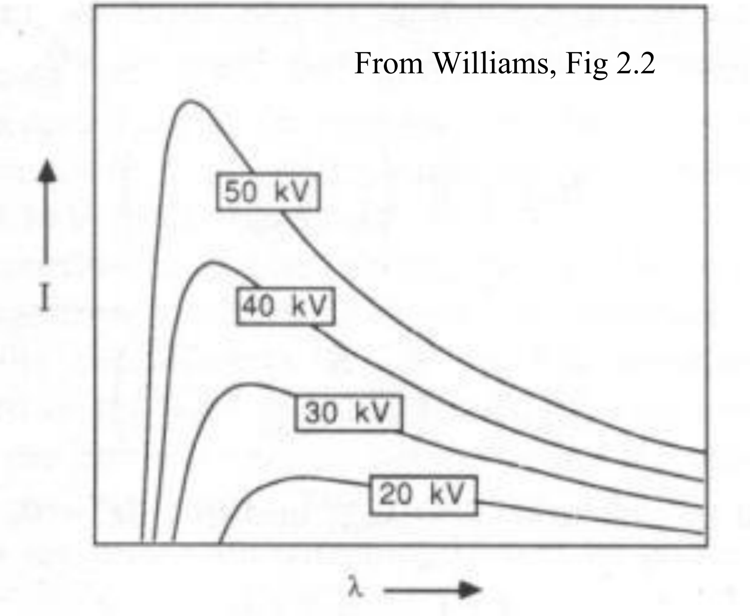
where the x-ray intensity I is a function of x-ray tube current i, Z is the mean Z of the target and $\lambda_{\min}$ is the E0 equivalent.

Kramers Law and Continuum Intensity

$$I(\lambda)\cdot d\lambda = KiZ\{(\lambda/\lambda_{min}) - 1\}\{1/\lambda^2\}\cdot d\lambda$$

Some comments:

- for maximum XRF counts, you want to maximize your current (I) and minimize your λ_{min} which is to say 12.4/E0 …or… run at the highest accelerating voltage your x-ray tube can handle (40-50 keV)

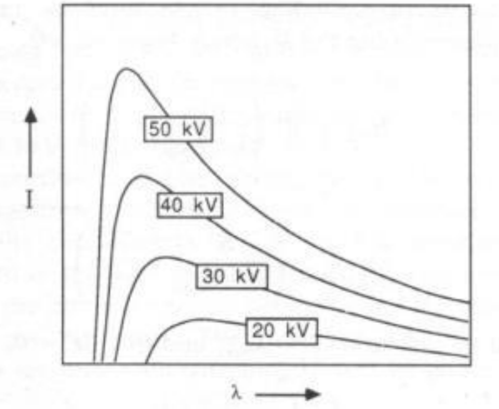

From Williams, Fig 2.2

- obviously, the higher the Z of the target in the tube, the higher the counts

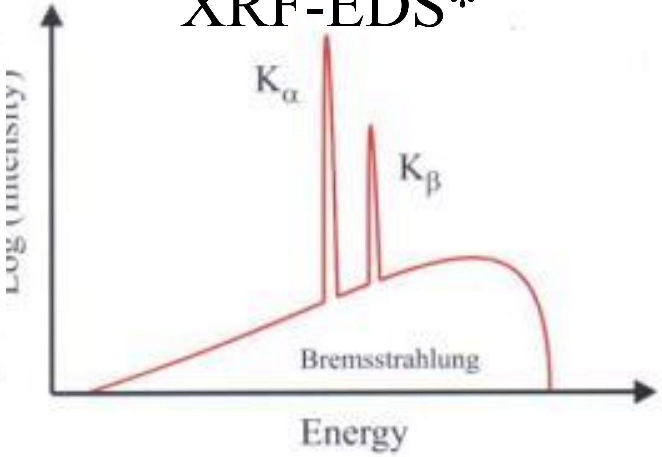
- finally, Kramers Law is sometimes used in EPMA for theoretically modelling the Bremsstrahlung there

An EDS spectral comparison: XRF vs SEM

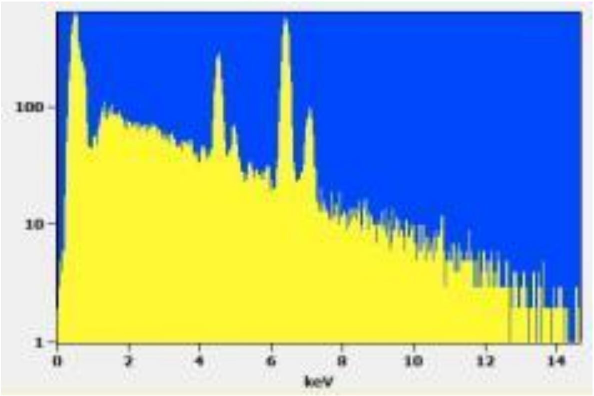
XRF



XRF-EDS*



SEM-EDS



Why do these look so different from our “normal” EDS view of a spectrum?

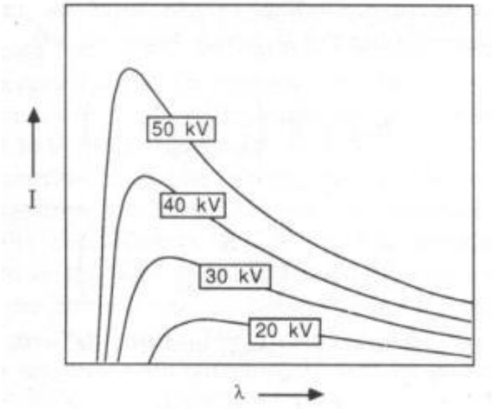
Why is there a ‘whale-like’ hump at the high energy end?

And not on the EDS spectrum?

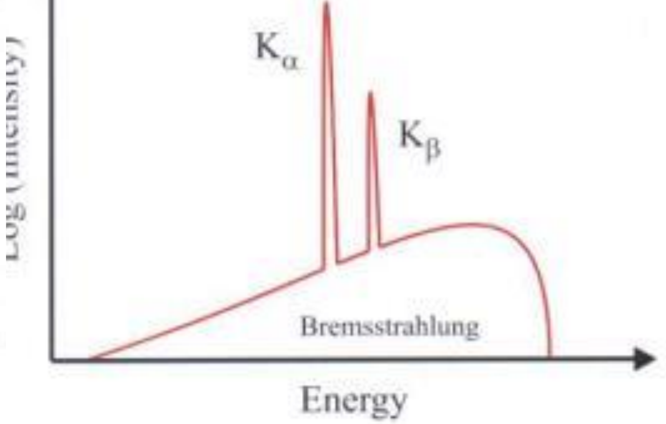
* Highly simplified

Explanation: XRF vs SEM EDS – part 1

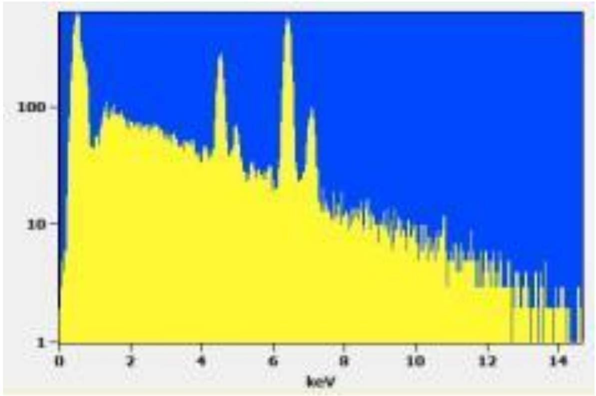
XRF



XRF-EDS*



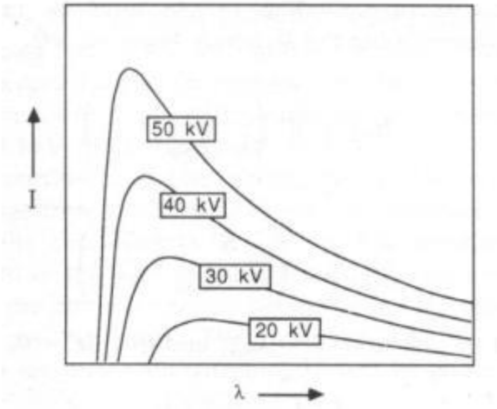
SEM-EDS



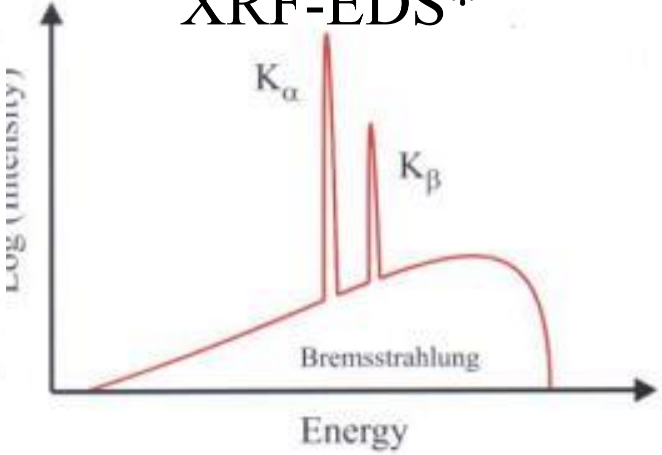
This question has stumped me for years. In the past 6 months, I’ve had 2 people who saw this slide on the web, ask me to explain it. Here’s the best explanation I can come up with: it stems from the fundamental differences between processes. EDS in SEM is a 2 step process (electrons from W-filament hit unknown sample, whose x-rays are generated) vs a 3 step process in XRF (electrons from W-filament hit a [say Mo] metal target [anode], then all those x-rays (continuum plus Mo characteristic) hit the unknown sample, whose x-rays [=Secondary Fluorescence] are generated including Compton-scattering peaks from the (say) Mo anode.

Explanation: XRF vs SEM EDS – part 2

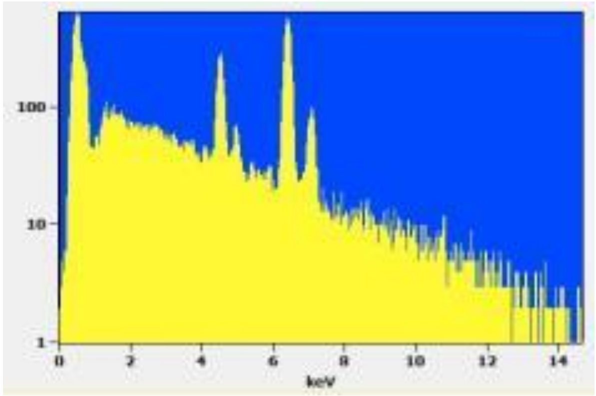
XRF



XRF-EDS*

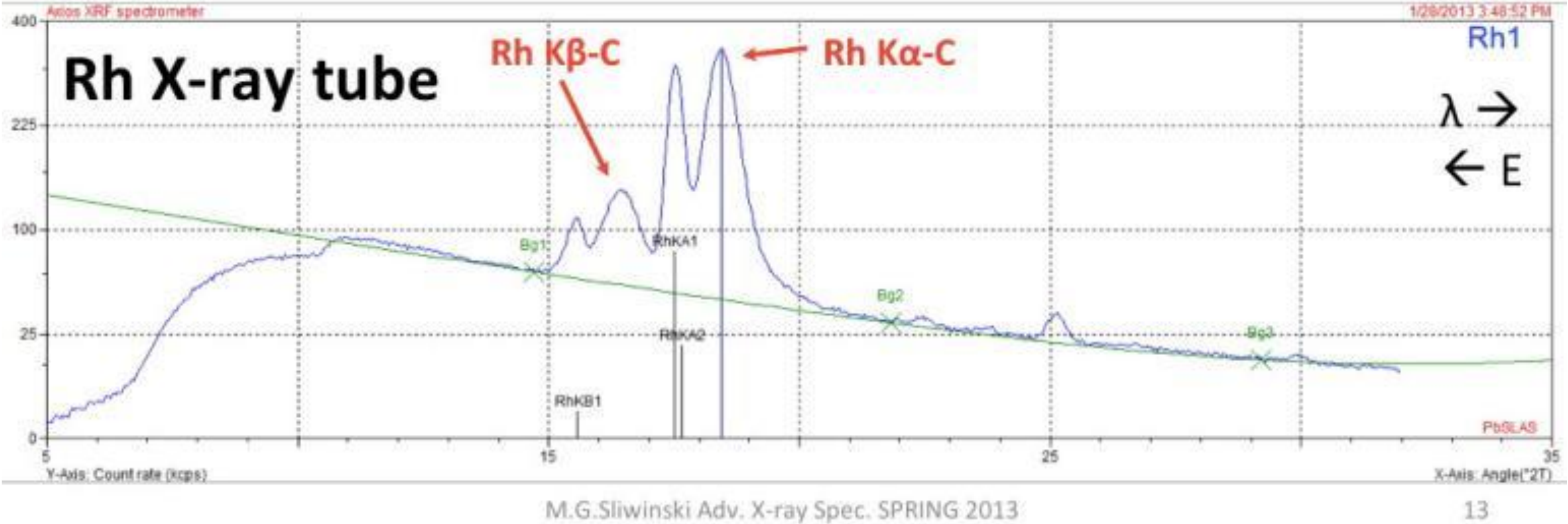


SEM-EDS



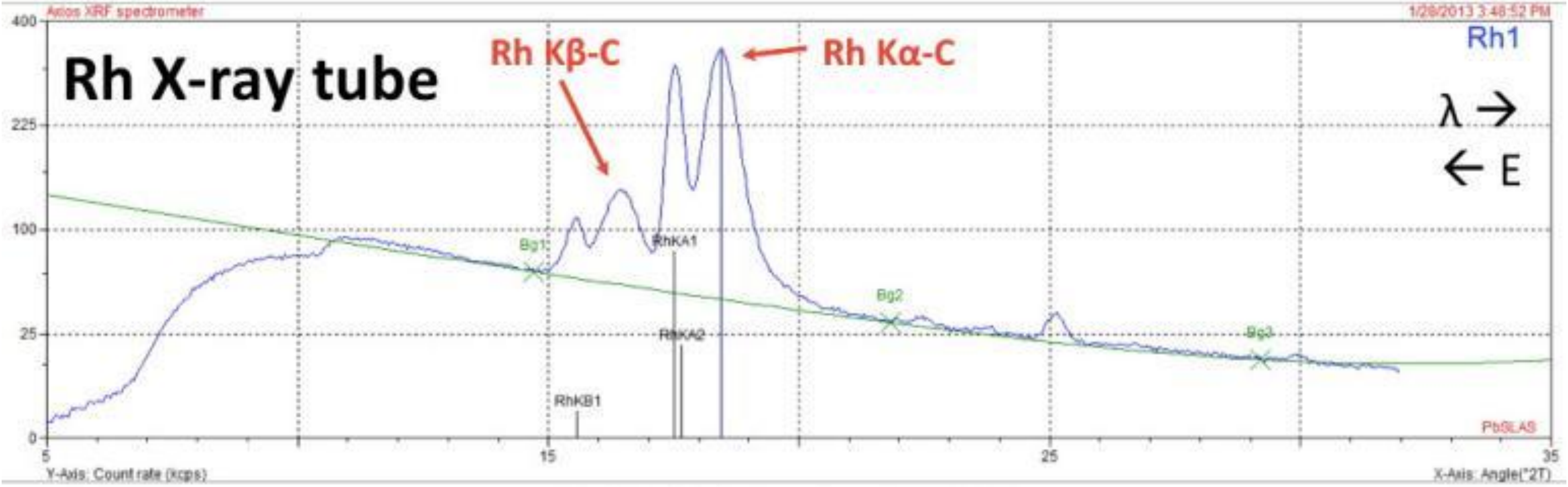
The middle figure is hokey in that it doesn't show the characteristic peaks of the sample (e.g. like the O, Ti and Fe peaks of the ilmenite in the SEM-EDS), only the anode's peaks (much less the Compton peaks that would be there). Whatever. The W-filament in say a Rh-anode X-ray tube might be run at 66 keV, which means there will be the characteristic plus Compton Rh Ka-Kb peaks around 22 keV as well as continuum x-rays out of the x-ray tube up to 66 keV, able to excite the unknown specimen. Let's look at a REAL XRF spectrum (OK, it's WDS, but it's real and we'll flip it around in our heads into EDS space.)

Explanation: XRF vs SEM EDS – part 3



Here is the high energy end of an actual XRF spectrum; most of the elements being analyzed are off the screen to the right, and we see here the Rh K lines plus their associated Compton peaks (“C”). To the left is a drop in the background (absorption edge of ?) and then there is a more gradual drop off of the background, not the dramatic one I copied out of textbooks. So I am thinking that there are significant x-rays generated at energies higher than Rh Kb (22.7 keV) because the original continuum coming off the Rh anode is interacting with the specimen, but presumably the probability of X-rays is less and less.

Explanation: XRF vs SEM EDS – part



M.G.Sliwinski Adv. X-ray Spec. SPRING 2013 13

Actually, at the very far left lower part of the spectrum are some little bumps…these are REE Ka and Kb peaks, but with extremely low P/B, so unusable. So the spectrum doesn't actually drop off a cliff at the high energy end.

(Thanks to Maciej Sliwinski for assistance with is tough problem.)

OK, what do Compton scattering peaks look like? this is using a Rh target….using a SiLi detector, so there is a Si-escape peak too), energy increases to the right.

(Shackley, 2011)

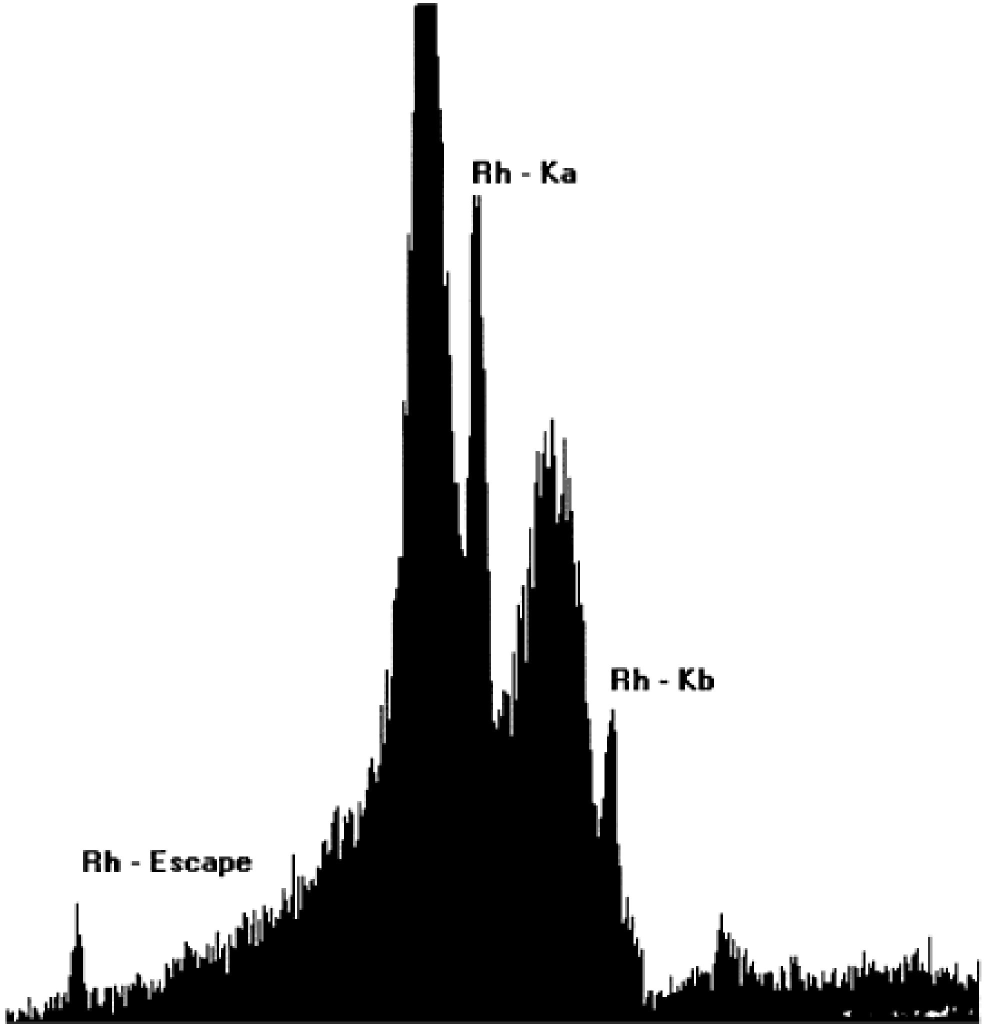


Fig. 2.4 A Compton scatter showing the Rh escape peak at 1.74 keV

OK, what does an XRF spectrum REALLY look like… note, this is using a Rh target)

(Shackley, 2011)

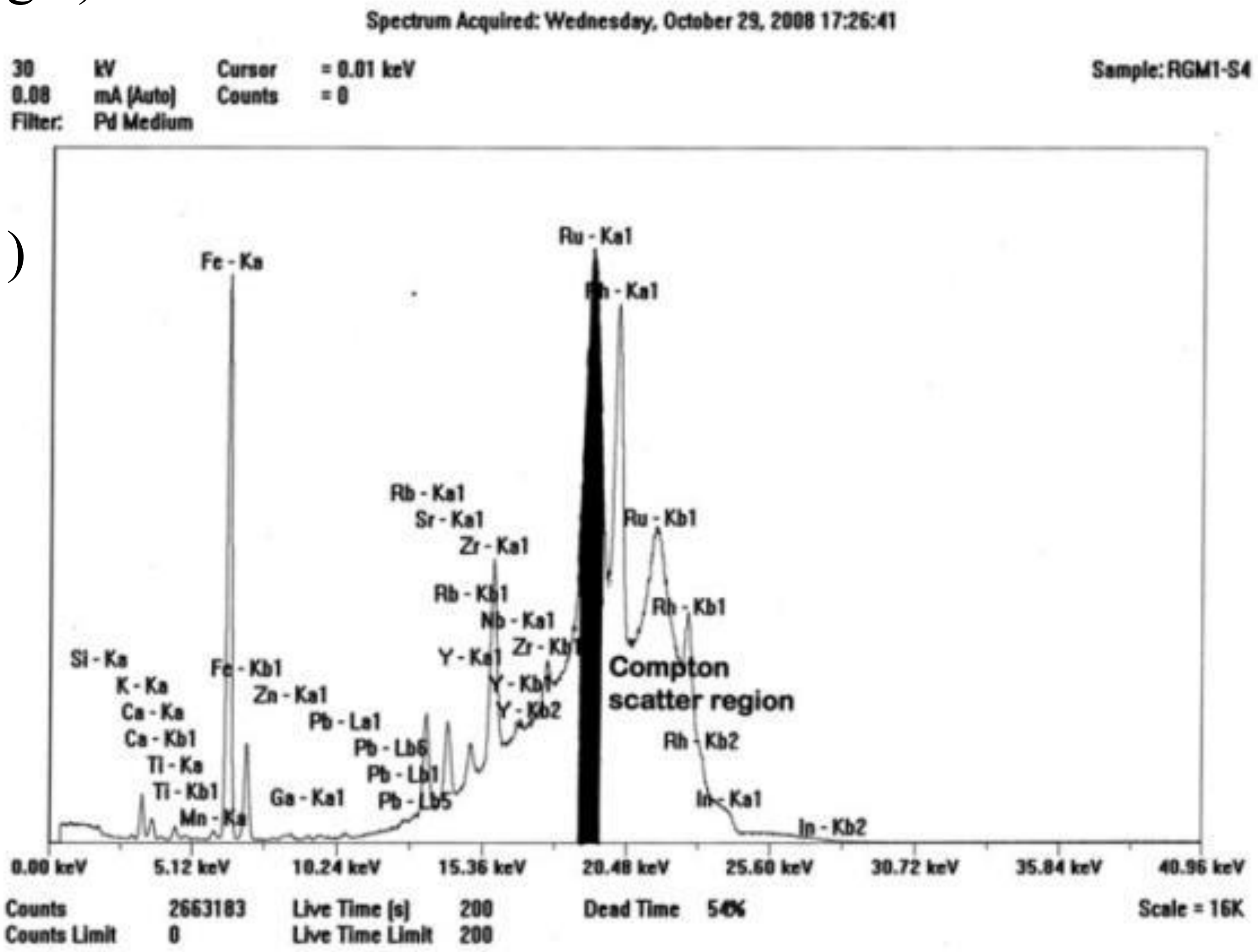


Fig. 2.2 Spectrum of the ThermoScientific Quant'X mid-Zb analysis of USGS RGM-1, showing the Compton scattered "hump" and that portion of the region under the Ru peak (*blackened*) used for peak ratioing

…and an expert refers to "Bremsstrahlung scattering does appear at the heavy end of the spectrum" particularly useful for Ba in volcanic rocks.

(Shackley, 2011)

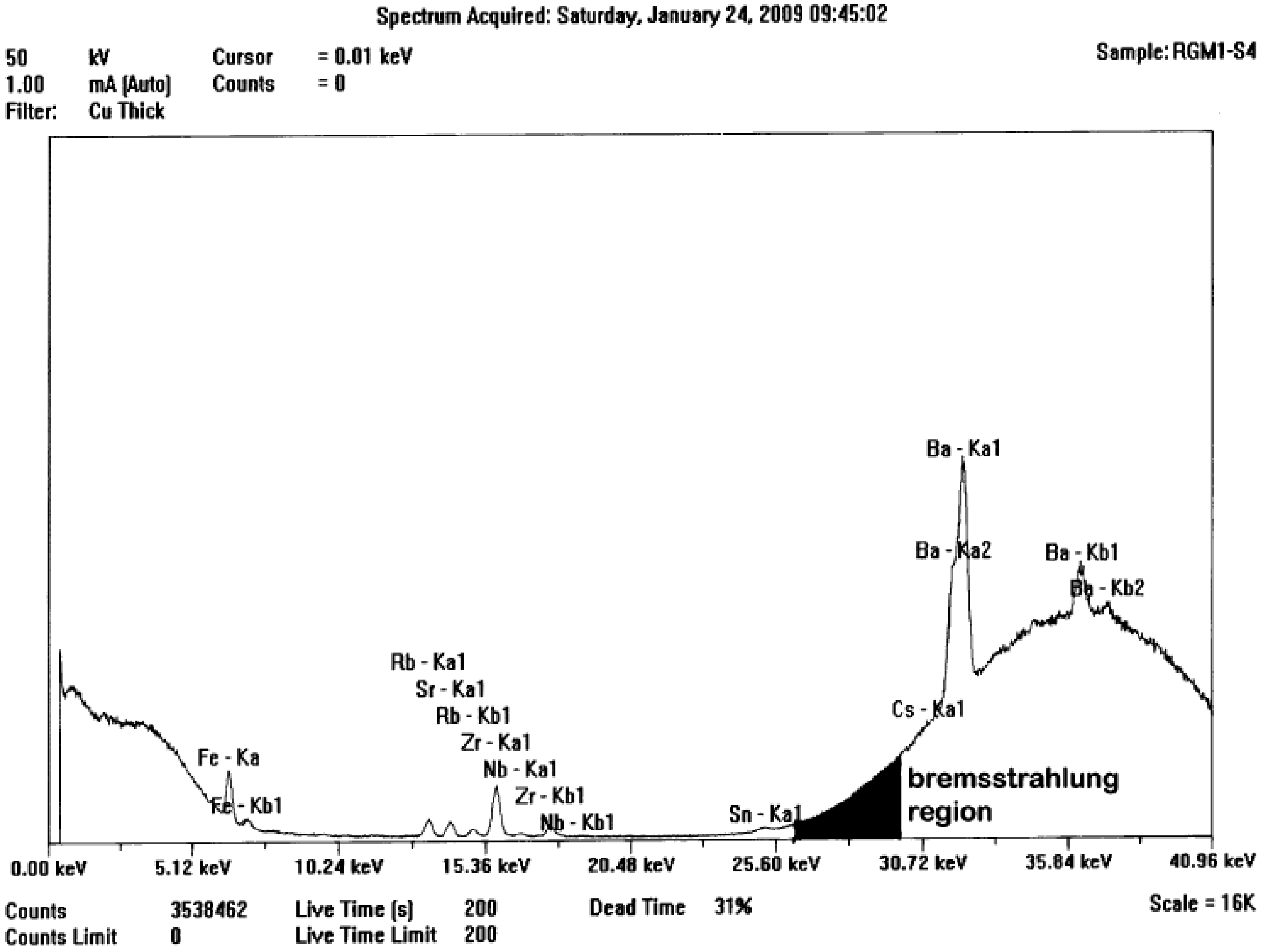
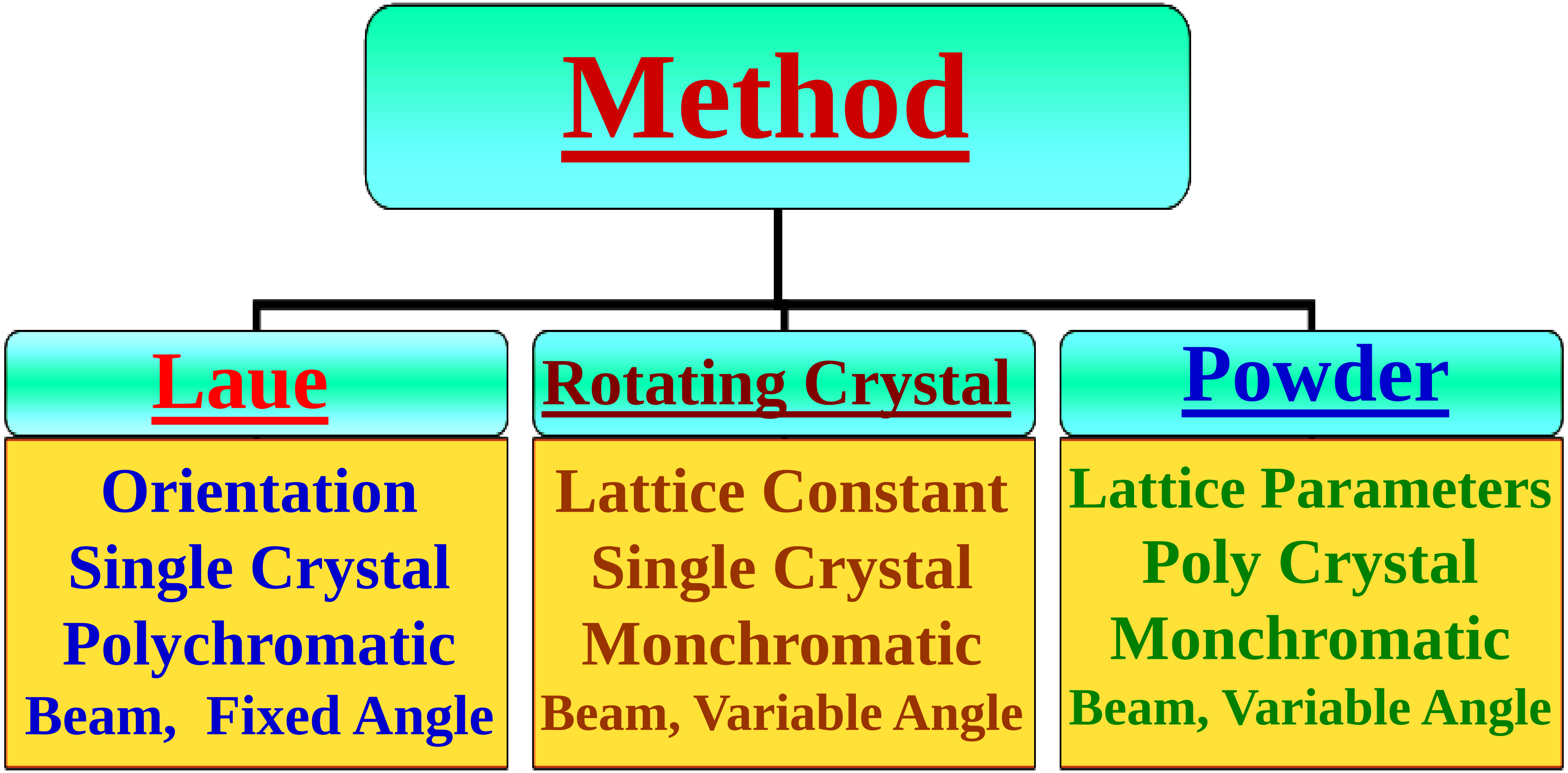


Fig. 2.3 Spectrum of the ThermoScientific Quant'X high-Za analysis of USGS RGM-1, showing the bremsstrahlung region and that portion of the region (*blackened*) used for peak ratioing

X-Ray Diffraction Methods



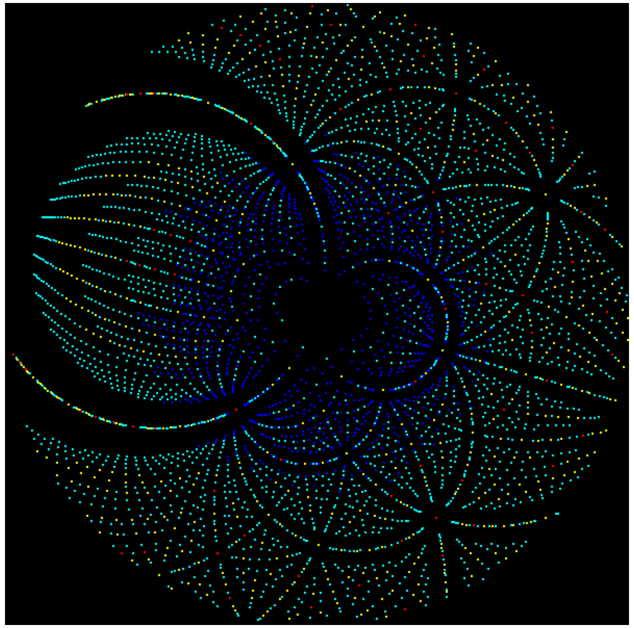
Method

Laue	**Rotating Crystal**	**Powder**
Orientation Single Crystal Polychromatic Beam, Fixed Angle	Lattice Constant Single Crystal Monchromatic Beam, Variable Angle	Lattice Parameters Poly Crystal Monchromatic Beam, Variable Angle

Laue Method

- The Laue method is mainly used **to determine the orientation of large single crystals** while radiation is reflected from, or transmitted through a **fixed crystal**.

- The diffracted beams form arrays of spots, that lie on curves on the film.



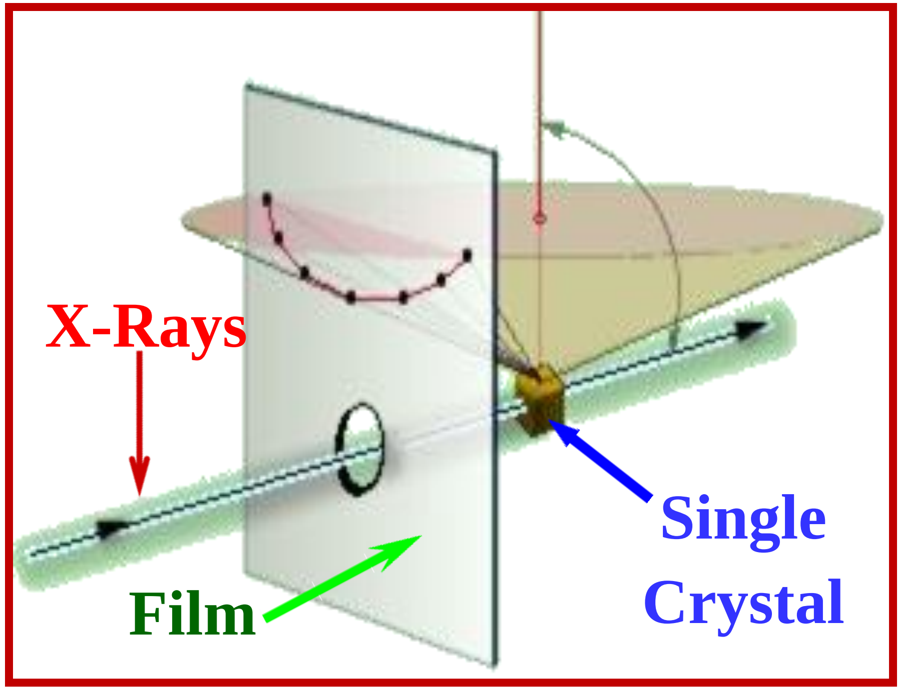
The Bragg angle is fixed

- for every set of planes in the crystal. Each set of planes picks out & diffracts the particular wavelength from the white radiation that ***satisfies the Bragg law for the values of d & θ*** involved.

Back-Reflection Laue Method

- In the back-reflection method, the film is placed ***between*** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

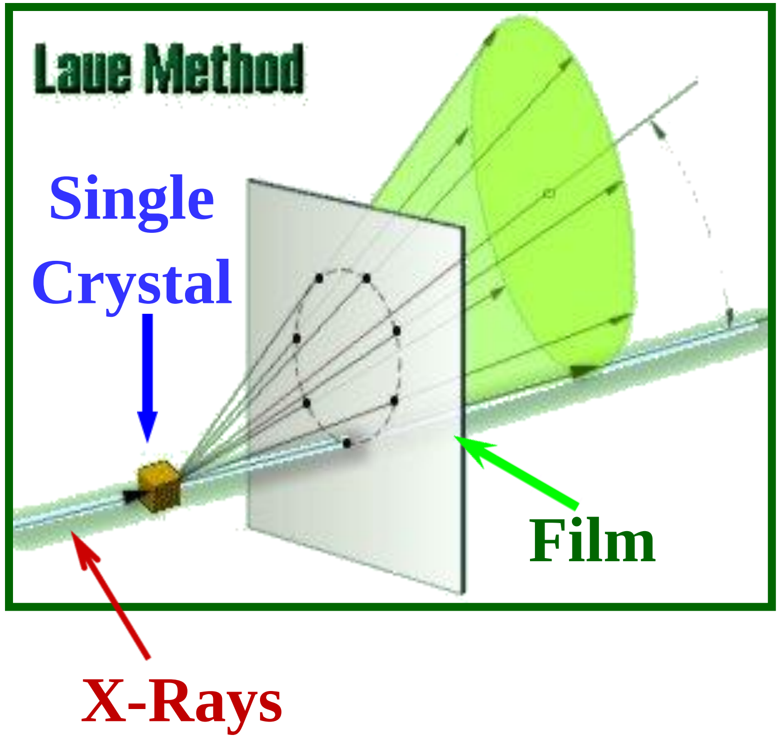
- One side of the cone of Laue reflections is defined by the transmitted beam.
- The film intersects the cone, with the diffraction spots generally lying on a hyperbola.



Transmission Laue Method

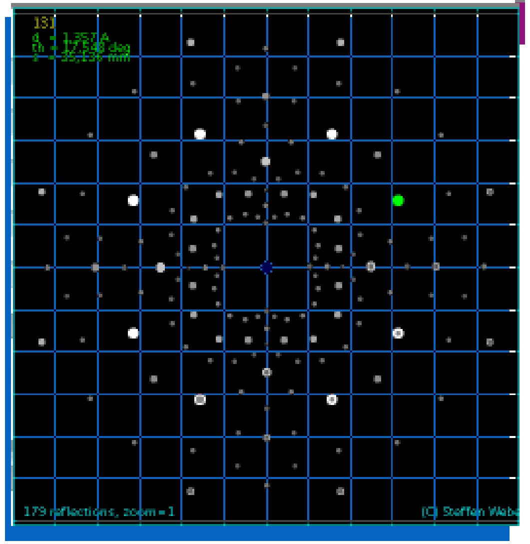
- In the transmission Laue method, ***the film is placed behind the crystal to record beams*** which are transmitted through the crystal.

- In the transmission Laue method, ***the film is placed behind the crystal to record beams*** which are transmitted through the crystal.
- One side of the cone of Laue reflections is defined by the transmitted beam.
- The film intersects the cone, with the diffraction spots generally lying on an ellipse.



Laue Patterns

- The symmetry of the Laue spot pattern reflects ***the symmetry of the crystal when viewed along the direction of the incident beam.***



- The Laue method is often used to determine the orientation of single crystals by illuminating the crystal with a continous spectrum of X-Rays.

Single Crystals

Continous Spectrum of X-Rays

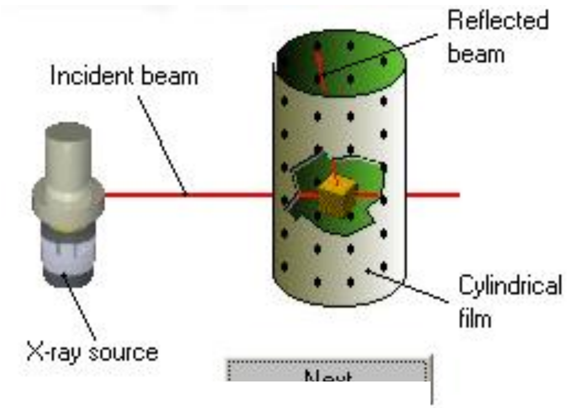
Symmetry & Orientation of Crystals

Crystal Structure Determination by the Laue Method

- The Laue method is mainly used to determine the **crystal orientation.**
- Although the Laue method can also be used to determine the crystal structure, **several wavelengths can reflect in different orders from the same set of planes,** with the different order reflections superimposed on the same spot in the film. This makes crystal structure determination by spot intensity ***diffucult.***
- The rotating crystal method overcomes this problem.

Rotating Crystal Method

- In the rotating crystal method, **a single crystal** is mounted with an axis normal to a **monochromatic x-ray beam.** A cylindrical film is placed around it & the **crystal is rotated about the chosen axis.**



- As the crystal rotates,

Sets of lattice planes will at some point make the correct Bragg angle

for the monochromatic incident beam, & at that point a diffracted beam will be formed.

Rotatıng Crystal Method

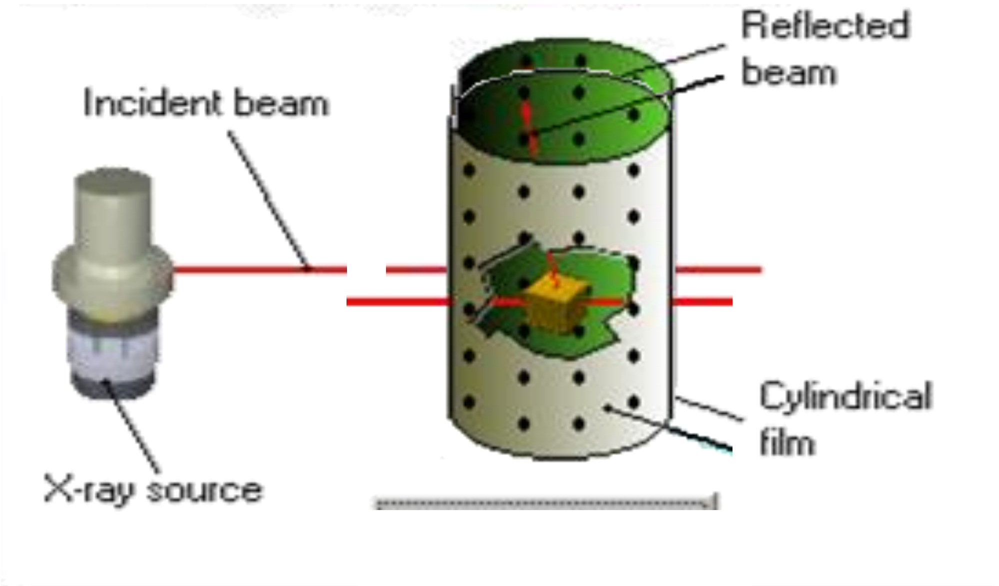
The Lattice constant of the crystal can be determined with this method. For a given wavelength **λ** if the angle **θ** at which a reflection occurs is known, **d** can be determined by using ***Bragg's Law***.

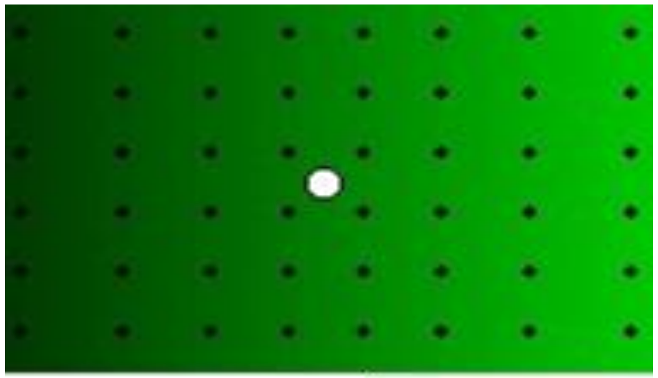
$$\boxed{d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}}$$

$$\boxed{2d \sin\theta = n\lambda}$$

Rotating Crystal Method

The reflected beams are located on the surfaces of imaginary cones. By recording the diffraction patterns (both angles & intensities) for various crystal orientations, one can determine the **shape & size of unit cell** as well as the **arrangement of atoms** inside the cell.





Film

The Powder Method

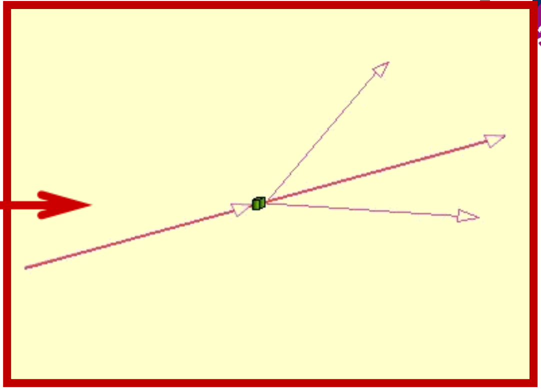
- If **a powdered crystal** is used **instead of a single crystal**, then there is ***no need to rotate*** it, because there will always be some small crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.
- Useful for samples that are difficult to obtain in single crystal form.
- The powder method is used to determine the **lattice parameters** accurately. Lattice parameters are the magnitudes of the primitive vectors **a, b and c** which define the unit cell for the crystal.

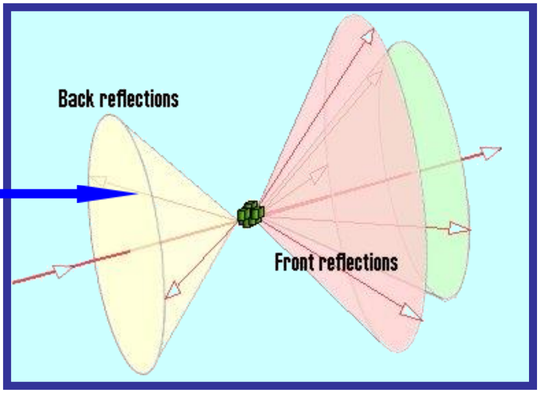
The Powder Method

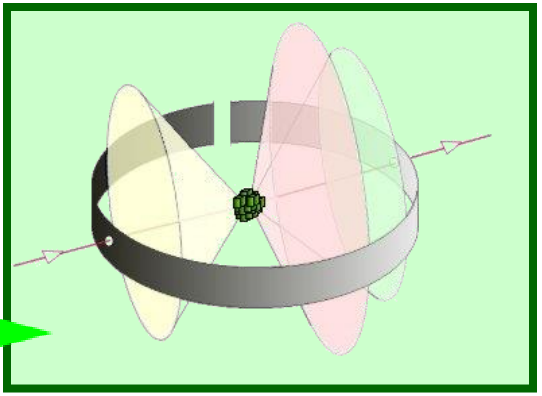
- For every set of crystal planes, by chance, ***one or more crystals*** will be in the ***correct orientation*** to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction.
- Each diffraction line is made up of a large number of small spots, each from a separate crystal. Each spot is so small as to give the appearance of a continuous line.

The Powder Method

- If a monochromatic X-ray beam is directed at a single crystal, then only one or two diffracted beams may result. **See figure**
- For a sample of several randomly orientated single crystals, the diffracted beams will lie on the surface of several cones. The cones may emerge in all directions, forwards and backwards. **See figure**
- For a sample of hundreds of crystals (powdered sample), the diffracted beams form continuous cones. A circle of film is used to record the diffraction pattern as shown. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film. **See figure**



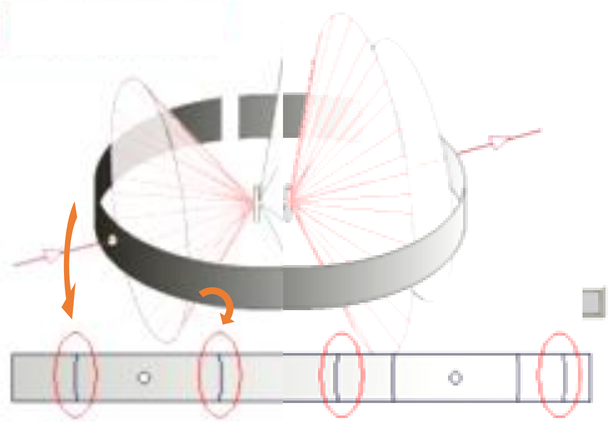




Debye Scherrer Camera

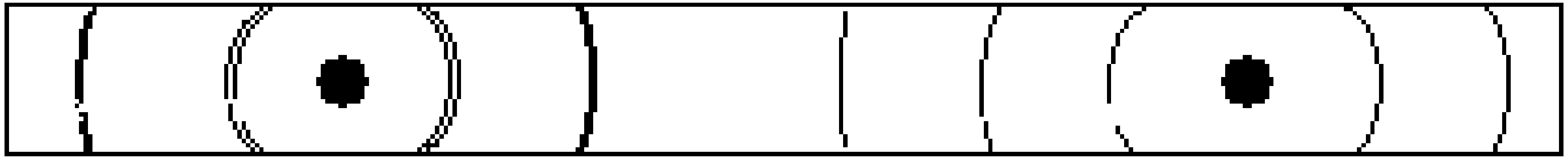
- A small amount of powdered material is sealed into a fine capillary tube made from glass that does not diffract **X-Rays**.
- The sample is placed in the **Debye Scherrer** camera and is accurately aligned to be in the center of the camera. **X-Rays** enter the camera through a collimator.

- The powder diffracts the **X-Rays** in accordance with Braggs Law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.



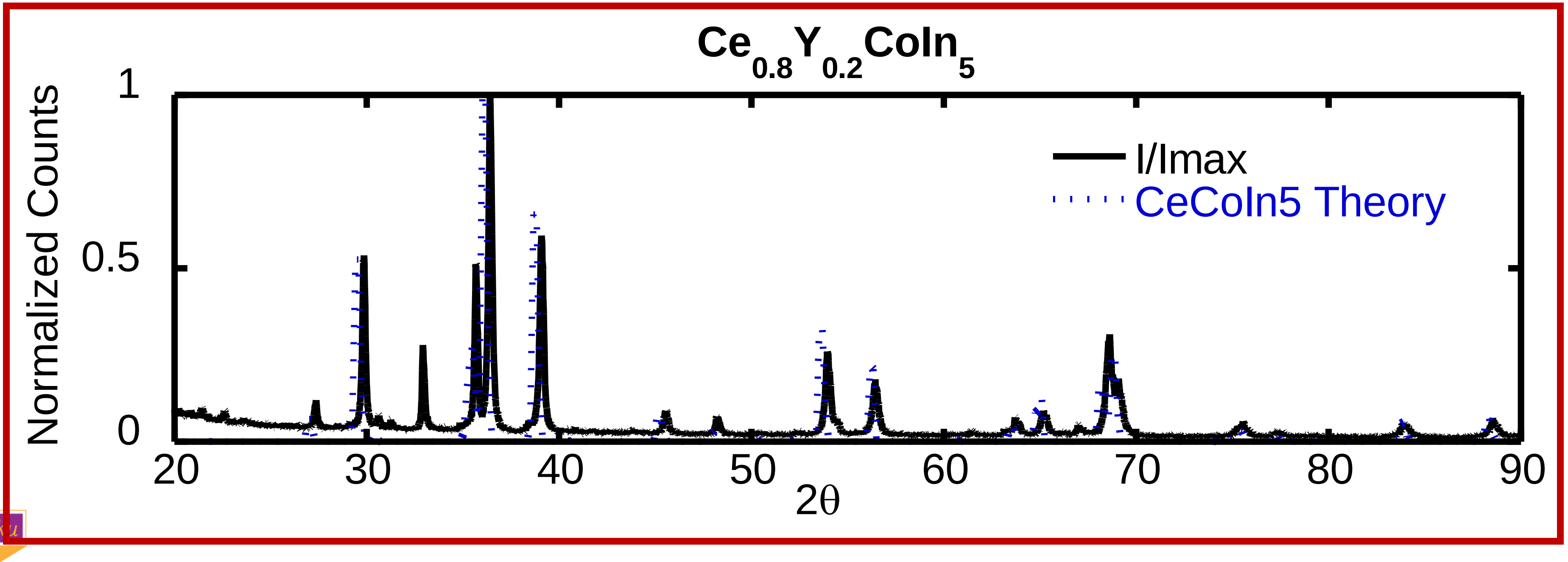
Powder Diffraction Film

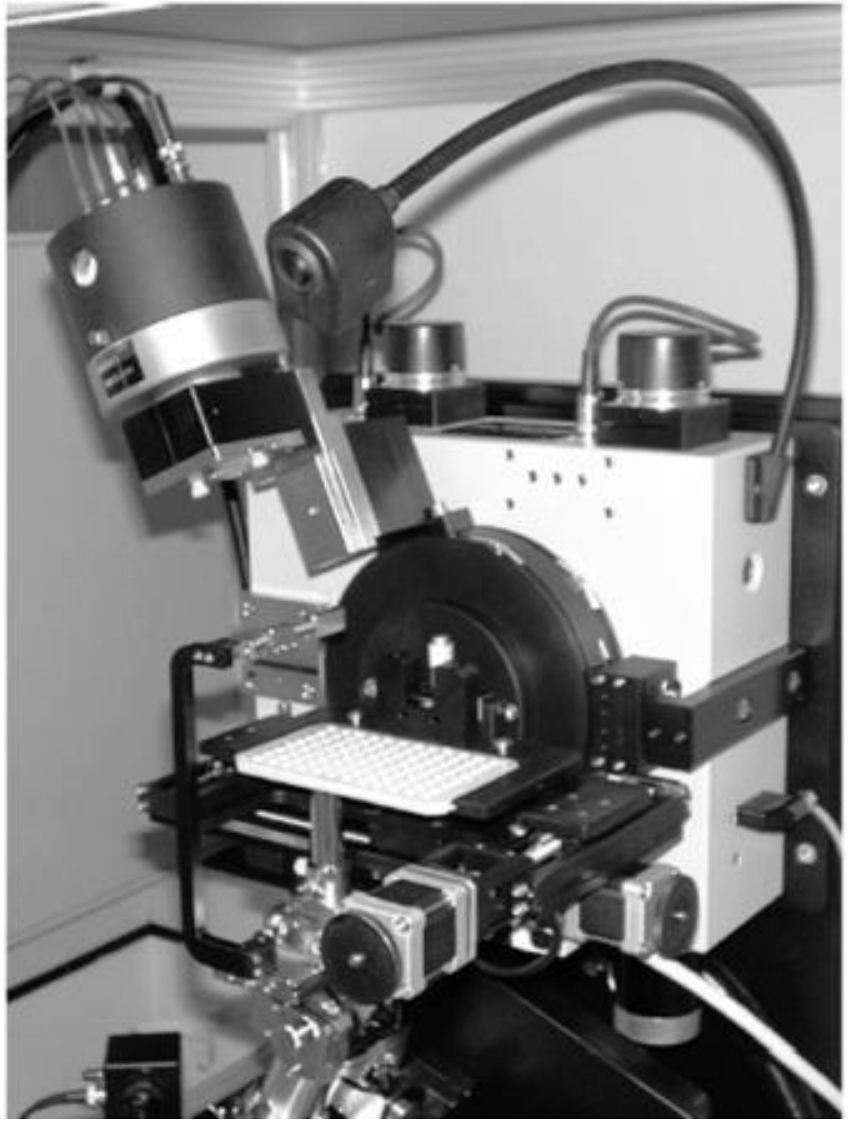
- When the film is removed from the camera, flattened & processed, it shows the diffraction lines & the holes for the incident & transmitted beams.



Some Typical Measurement Results

- **Laue** - “white” **X-rays**
  - Yields stereoscopic projection of reciprocal lattice
- **Rotating-Crystal method**: monochromatic **X-rays**
  - Fix source & rotate crystal to reveal reciprocal lattice
- **Powder diffraction** - monochromatic **X-rays**
  - Powder sample to reveal “all” directions of RL

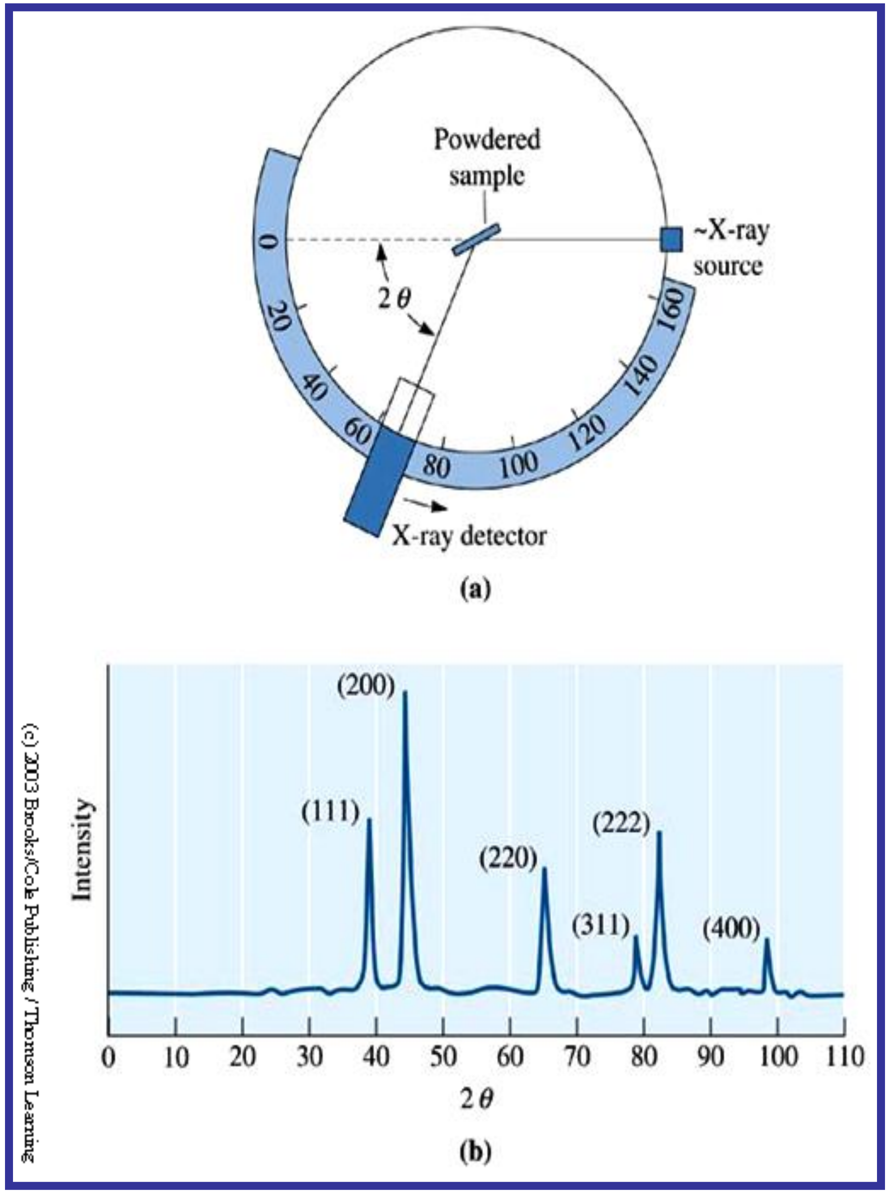




Photograph of a

XRD Diffractometer

(*Courtesy H&M Services.*)

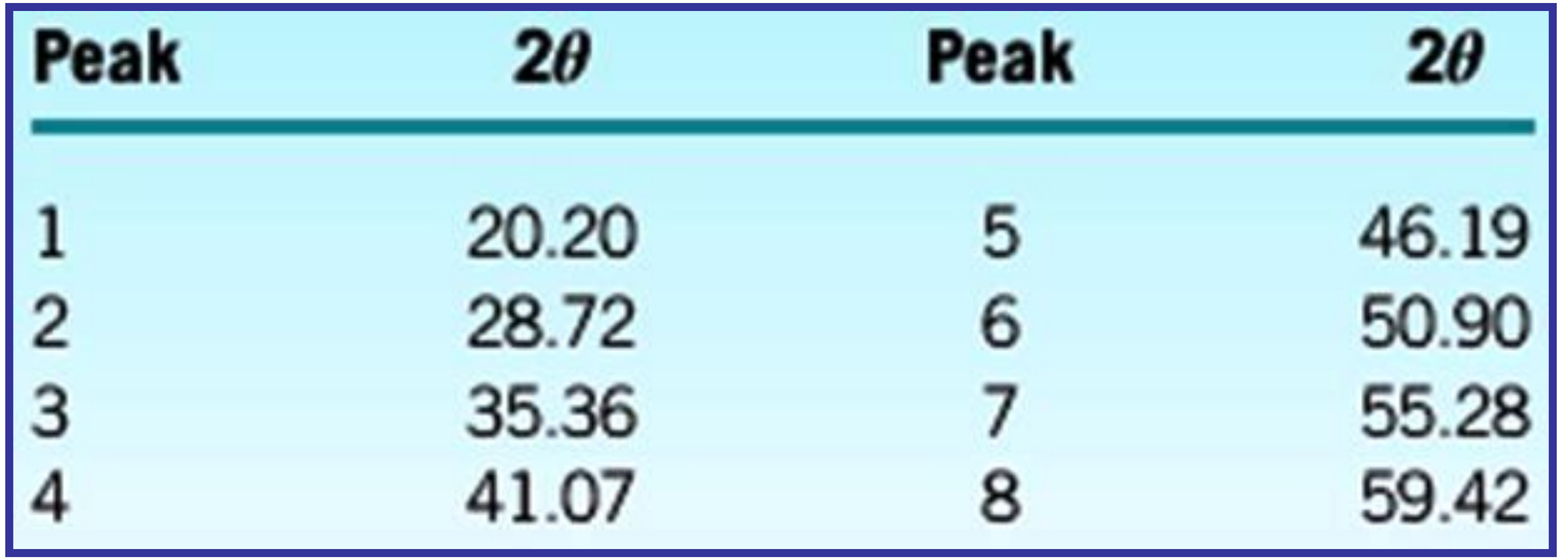


(a) Diagram of a ***diffractometer*** showing a powdered sample, incident & diffracted beams.

(b) Diffraction Pattern from a sample of gold powder.

Example (From the Internet)

The results of a diffraction experiment using **X-Rays** with **λ = 0.7107 Å** (radiation obtained from a molybdenum, Mo, target) show that diffracted peaks occur at the following **2θ** angles:

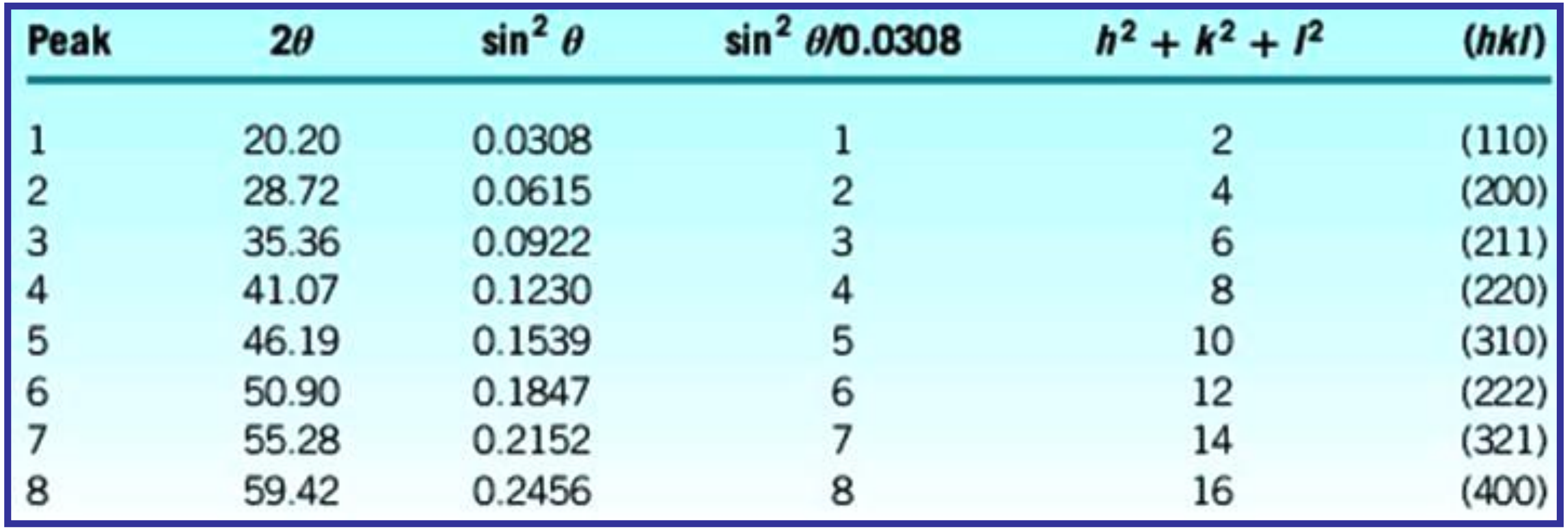


Peak	2θ	Peak	2θ
1	20.20	5	46.19
2	28.72	6	50.90
3	35.36	7	55.28
4	41.07	8	59.42

Find: The crystal structure, the indices of the plane producing each peak, & the lattice parameter of the material.

Example (Solution)

First calculate the **$\sin^2\theta$** value for each peak, then divide through by the lowest denominator, **0.0308.**



Peak	2θ	$\sin^2\theta$	$\sin^2\theta/0.0308$	$h^2+k^2+l^2$	(hkl)
1	20.20	0.0308	1	2	(110)
2	28.72	0.0615	2	4	(200)
3	35.36	0.0922	3	6	(211)
4	41.07	0.1230	4	8	(220)
5	46.19	0.1539	5	10	(310)
6	50.90	0.1847	6	12	(222)
7	55.28	0.2152	7	14	(321)
8	59.42	0.2456	8	16	(400)

Example (Solution Continued)

Then use the **2θ** values for any of the peaks to calculate the interplanar spacing & thus the lattice parameter.

Picking Peak 8: 2θ = 59.42° or θ = 29.71°

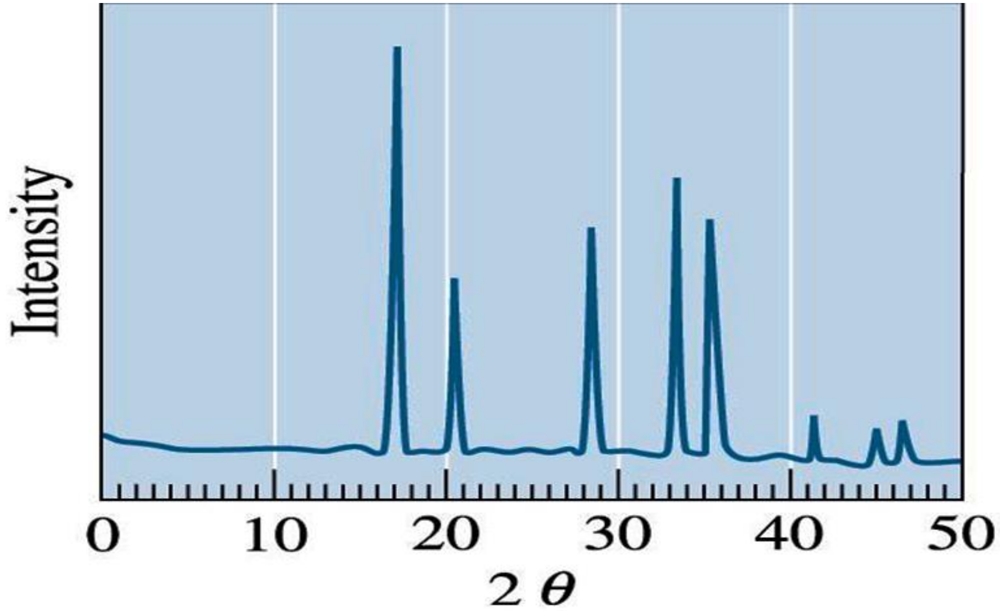
So, for example:

$$d_{400} = \frac{\lambda}{2\sin\theta} = \frac{0.7107}{2\sin(29.71)} = 0.71699 \text{ Å}$$

$$a_0 = d_{400}\sqrt{h^2 + k^2 + l^2} = (0.71699)(4) = 2.868 \text{ Å}$$

This is the lattice parameter for body-centered cubic iron.

Measurement Results



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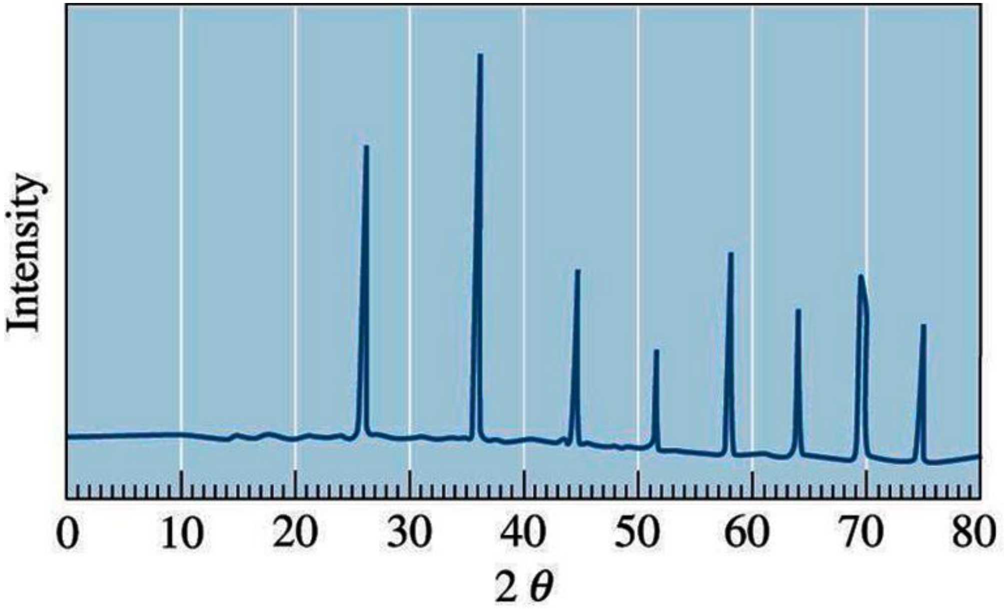
XRD Pattern

for **NaCl**

XRD Pattern

for **KCl**



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Applications of XRD

Note: XRD is a nondestructive technique!

Some uses of XRD include:

1. **Distinguishing** between crystalline & amorphous materials.
2. **Determination** of the structure of crystalline materials.
3. **Determination** of electron distribution within the atoms, & throughout the unit cell.
4. ***Determination*** of the orientation of single crystals.
5. **Determination** of the texture of polygrained materials.
6. **Measurement** of strain and small grain size…..etc.

Advantages & Disadvantages of XRD Compared to Other Methods

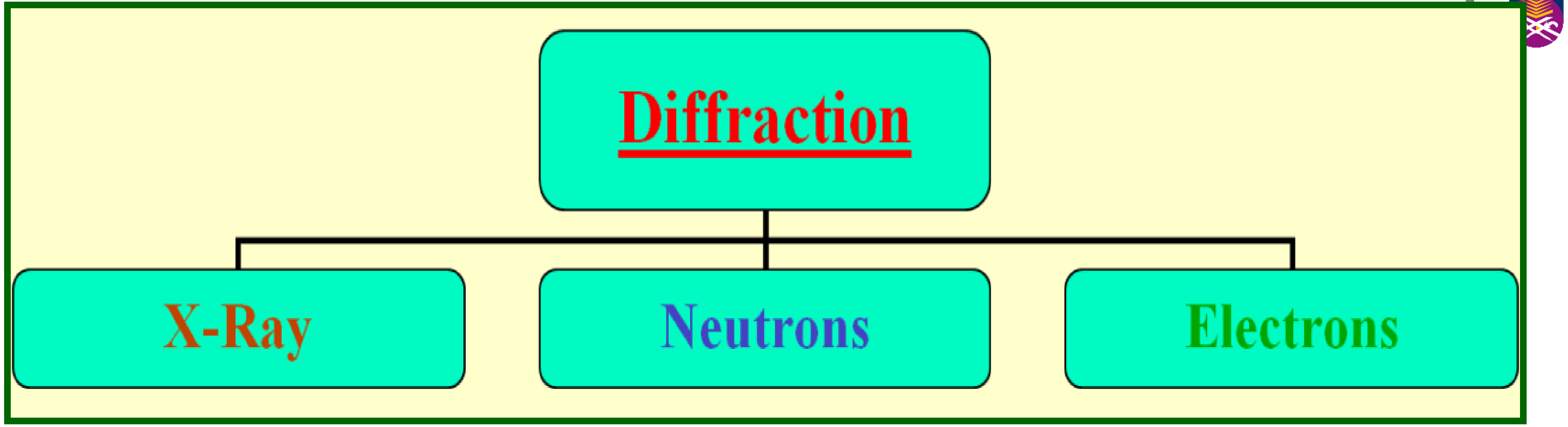
Advantages

- **X-Rays** are the least expensive, the most convenient & the most widely used method to determine crystal structures.
- **X-Rays** are not absorbed very much by air, so the sample need not be in an evacuated chamber.

Disadvantages

- **X-Rays** do not interact very strongly with lighter elements.

Diffraction Methods



Diffraction

X-Ray

Neutrons

Electrons

- Other radiation sources than **X-Rays,** such as **neutrons** or **electrons** can also be used in crystal diffraction experiments.
- The physical basis for the diffraction of **electrons** or **neutrons** is the same as that for the diffraction of **X Rays.** The only difference is in the mechanism of scattering.

Neutron Diffraction

- Neutrons were discovered in 1932 & their (de-Broglie) wave properties were proven in 1936.

Energy: $E = (p^2)/(2m_n)$

Momentum: $p = (h/\lambda)$

λ = Wavelength,

m_n = Mass = 1.67×10^{-27} kg

- Wavelengths needed for crystal diffraction are of the order of

$\lambda \sim 1$Ǻ

- So this gives needed neutron energies of

$E \sim 0.08$ eV

This is of the same order of magnitude as the thermal energy at room temperature, **$kT \sim 0.025$ eV**. For this reason, these are called thermal neutrons.

Neutron Diffraction

has several advantages over

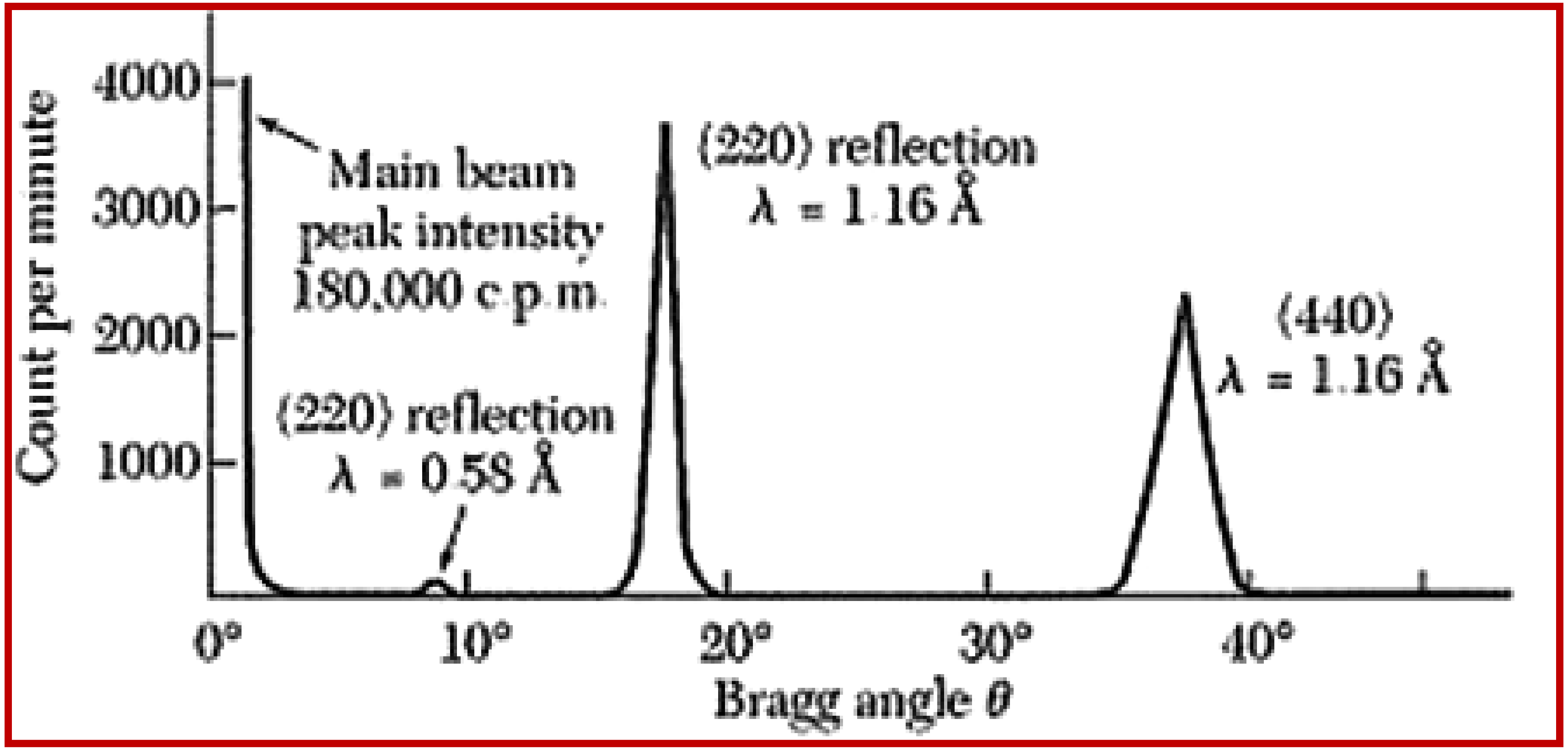
X-Ray Diffraction.

- It is an important tool in the investigation of the magnetic ordering that occurs in some materials.
- Light atoms such as **H** are better resolved in a neutron pattern because, having only a few electrons to scatter the **X-Rays**, they do not contribute significantly to an **X-Ray** diffraction pattern.

- Because **they are neutral,** ***neutrons do not interact with electrons in the crystal***. So, unlike X-Rays, which are scattered entirely by electrons, neutrons are scattered entirely by nuclei.
- Although uncharged, neutrons have **an intrinsic magnetic moment**, ***so they will interact strongly with atoms & ions in the crystal which also have a magnetic moment*****.**
- Neutrons are more useful than X-rays for determining the crystal structures of solids containing light elements.
- Neutron sources in the world are limited so neutron diffraction is a very special tool & is very expensive.

Typical Neutron Diffraction Data

1.16 Ǻ Neutrons on CaF_2



- **Electron Diffraction** has also been used in the analysis of crystal structure. The electron, like the neutron, possesses **wave-like properties:**

For $\lambda \approx 2A^0$

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e \lambda^2} = 40eV$$

- Of course, electrons are ***charged*** & so interact strongly with all atoms. So electrons with an energy of a few eV are completely ***absorbed by the crystal***.

Electron Diffraction

- Electrons with an energy of a few eV are completely ***absorbed by the crystal***.

For $\lambda \approx 2A^0$

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{h^2}{2m_e\lambda^2} = 40eV$$

- In order to enable an electron beam to penetrate into a crystal, it must have a very high energy (50 keV to 1MeV). In addition, the crystal must be thin (100-1000 nm).
- If low electron energies are used, the penetration depth will be very small (only about 50 Å), & the beam will be reflected from the surface. Consequently, electron diffraction is a useful technique for surface structure studies.
- Electrons are scattered strongly in air, so diffraction experiments must be carried out high vacuum. This brings complication and it is expensive as well.

Diffraction Methods

Neutrons	**Electrons**
λ ~ 1 Å E ~ 0.08 eV interact with nuclei, highly penetrating	λ ~ 1 Å E ~ 150 eV interact with electrons, less penetrating

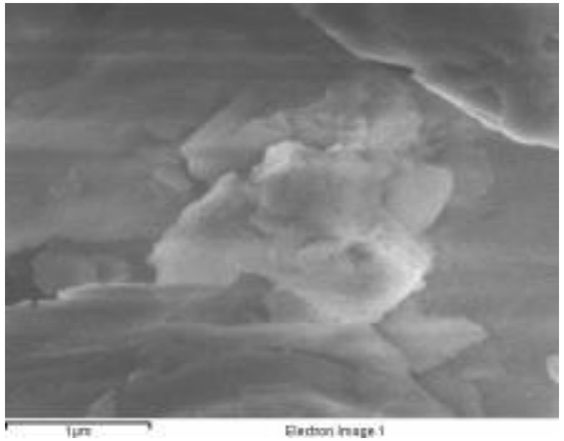
electrons,
penetrating

Charging

When a poorly conducting specimen is imaged in a conventional SEM, the surface rapidly accumulates charge. This can result in a severely distorted image, as the incident electrons are repelled by the charged areas of the surface. A typical feature of charging is that some regions appear extremely bright, as can be seen here.

In order to avoid this problem, specimens can be covered with a conducting coating of gold or carbon. Coating with a heavy metal such as gold also has the beneficial effect of increasing the yield of secondary electrons from the specimen.

An alternative to coating is to use a “low vacuum” SEM. This kind of microscope operates with a small pressure of water vapour in the chamber. The water molecules become positively charged and neutralize the negatively charged regions on the surface.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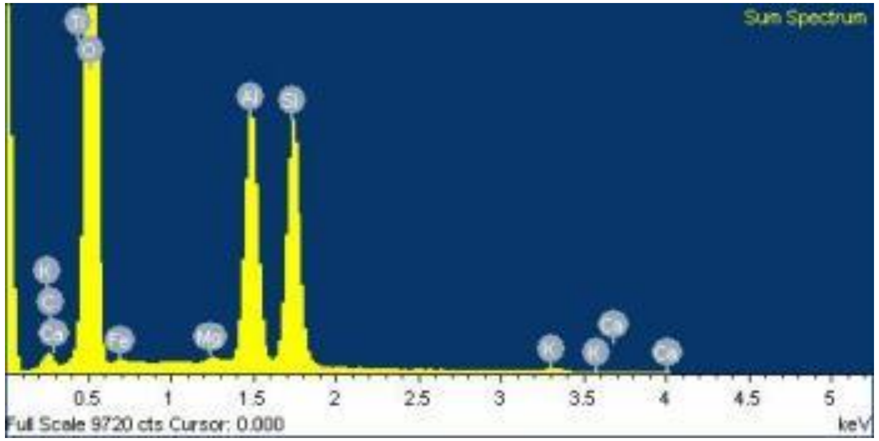
Electron Image 1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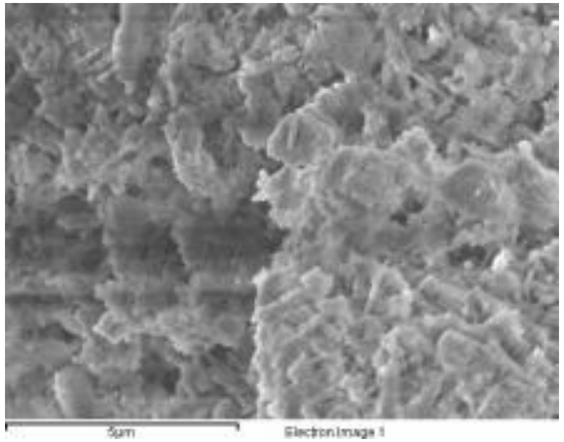
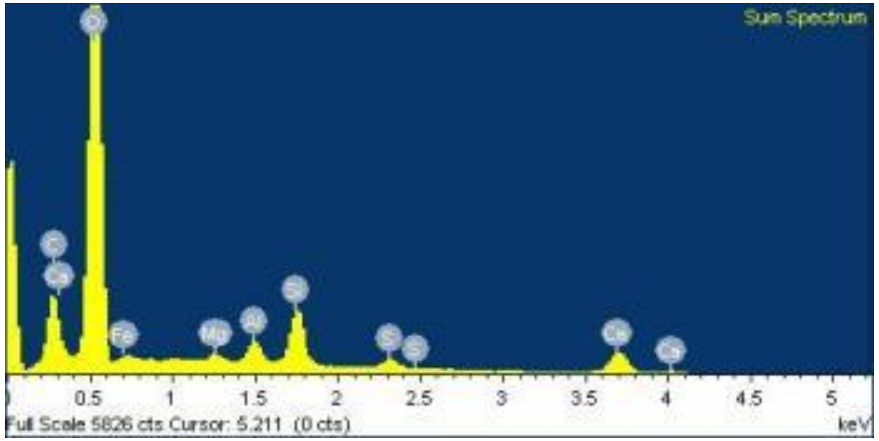
O
Al
Si
K
C
Ca
Fe
Mg
K
Ca
K
Ca
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
keV
Full Scale 9720 cts Cursor: 0.000


5µm
Electron Image 1


Sum Spectrum
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C
Ca
Fe
Mg
Al
Si
S
S
Ca
Ca
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1
1.5
2
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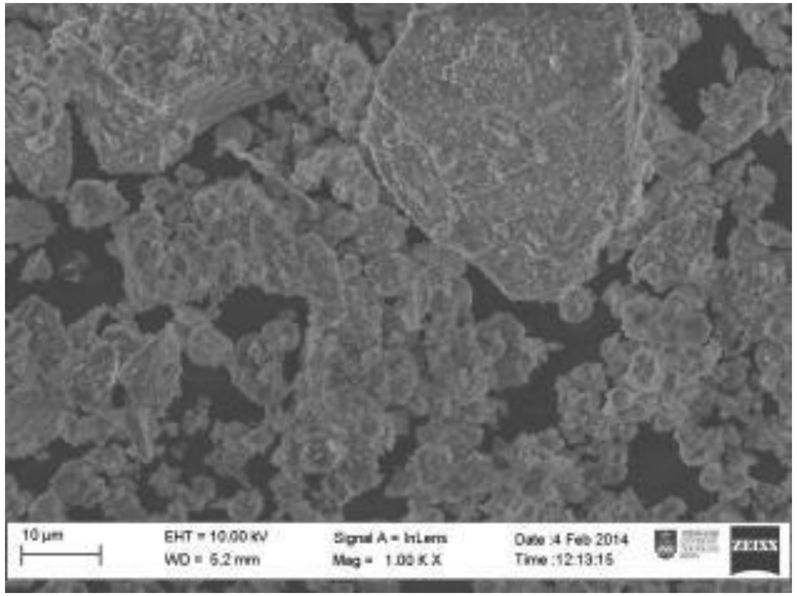
3
3.5
4
4.5
5
keV
Full Scale 5826 cts Cursor: 5.211 (0 cts)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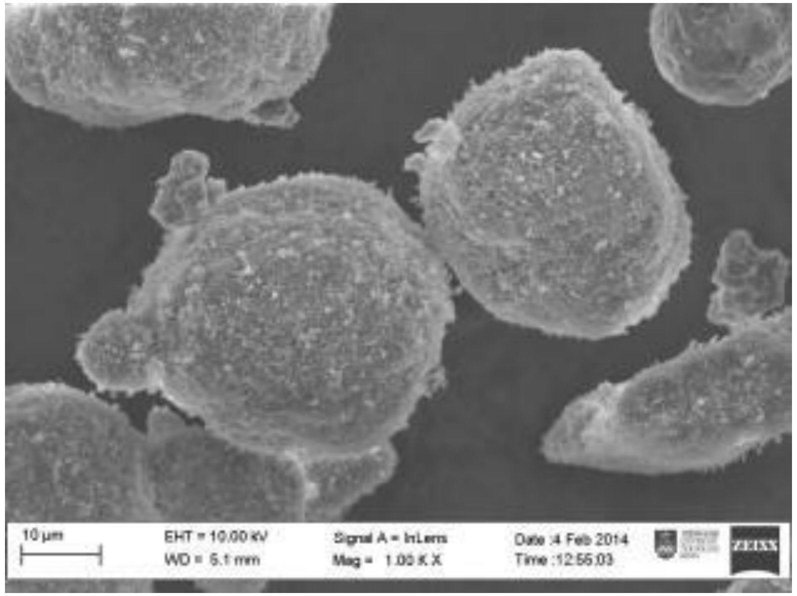
ZEISS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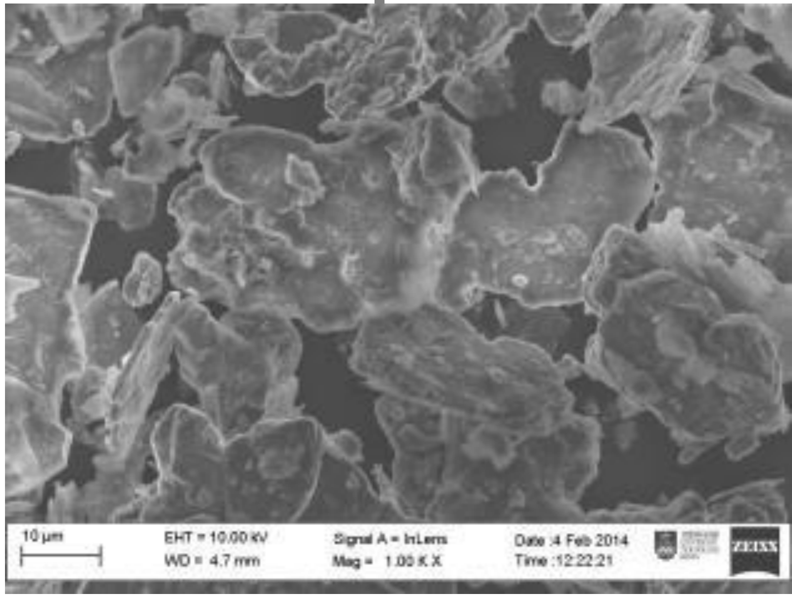
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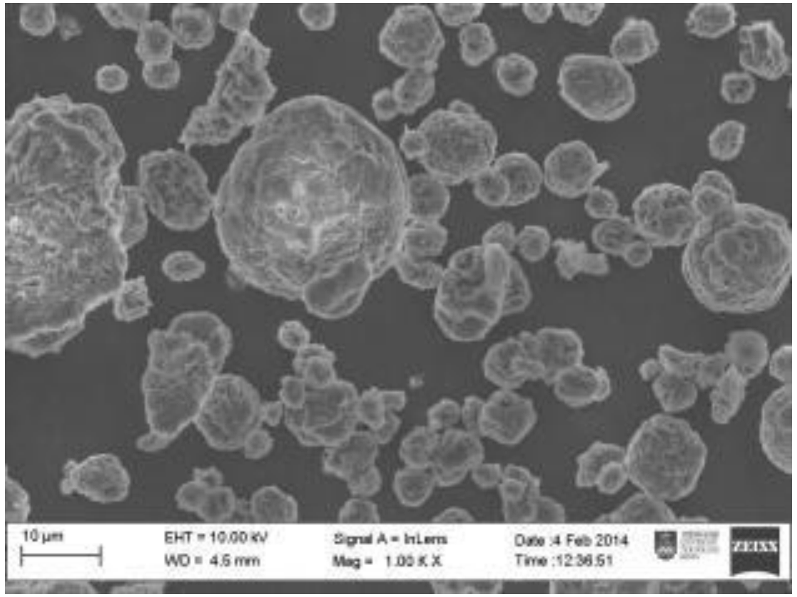
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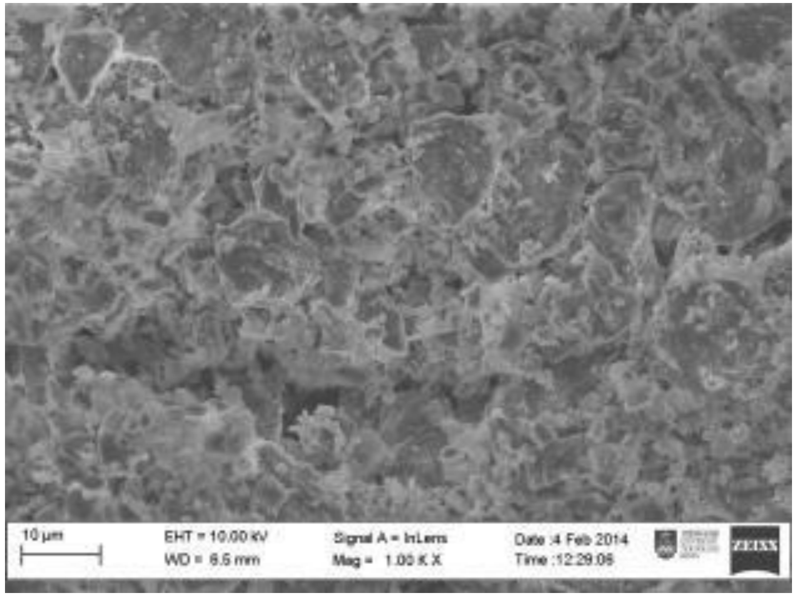
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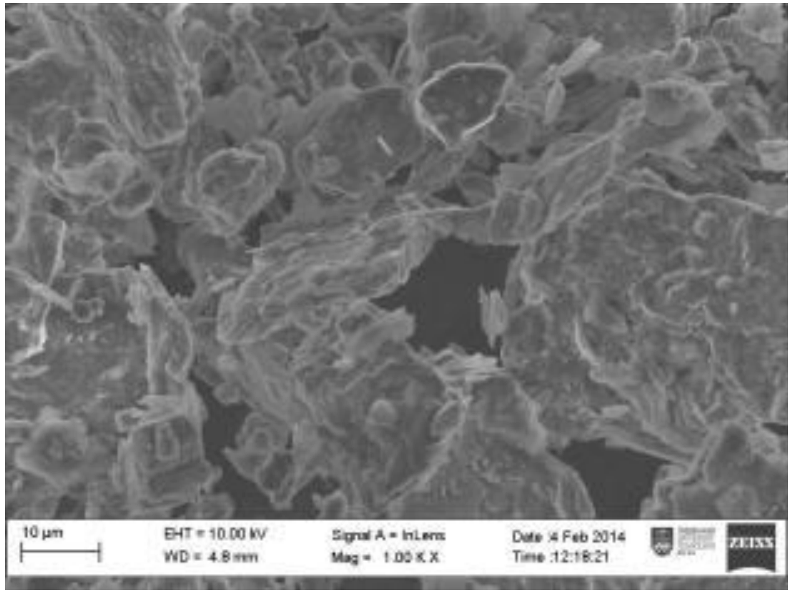
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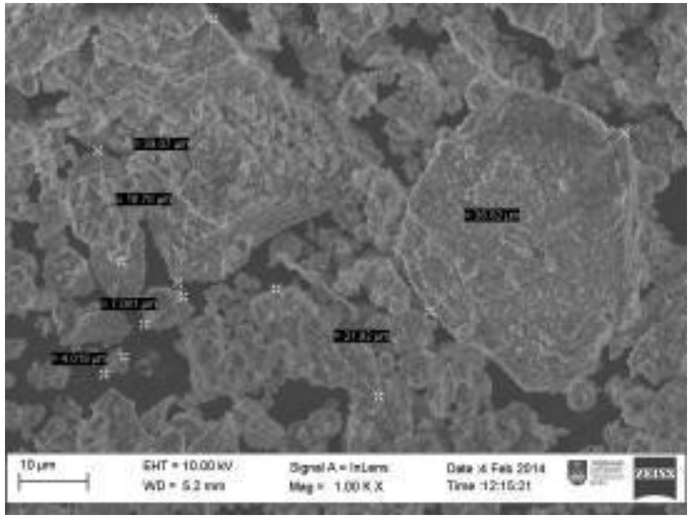

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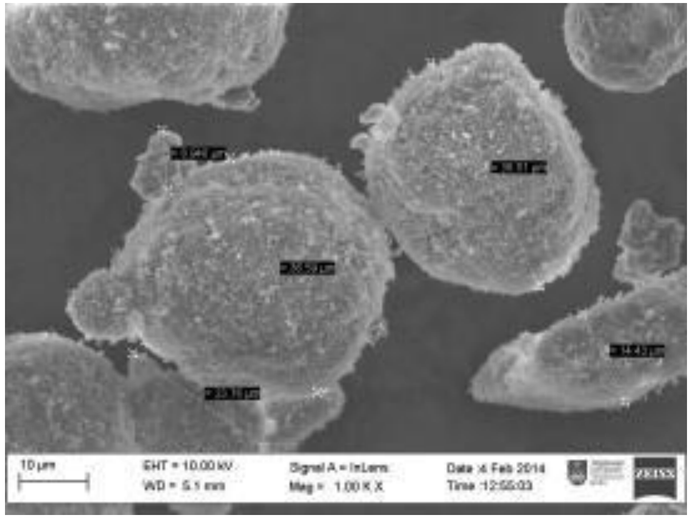

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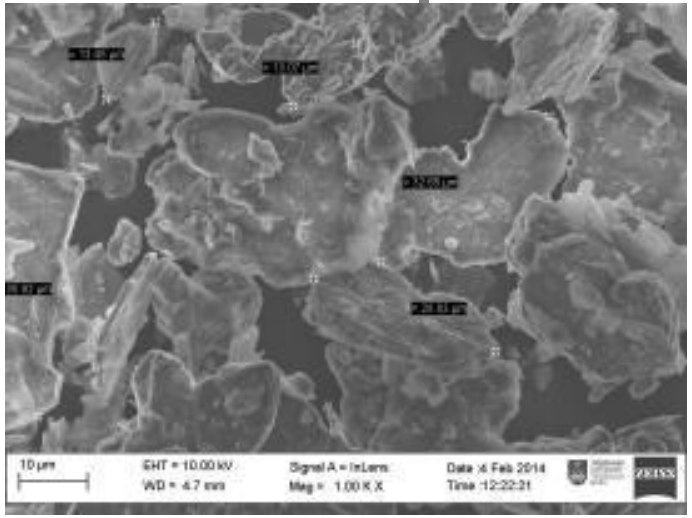

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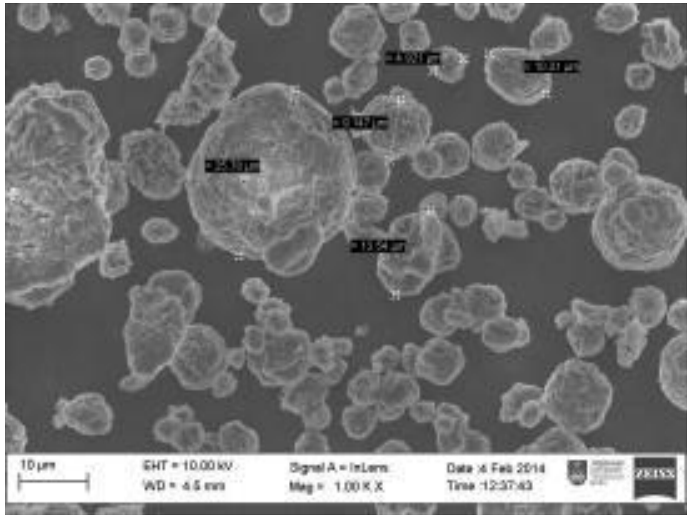

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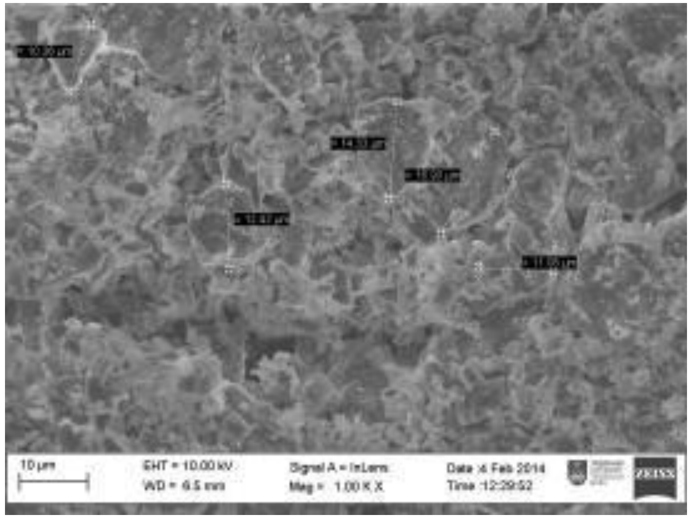

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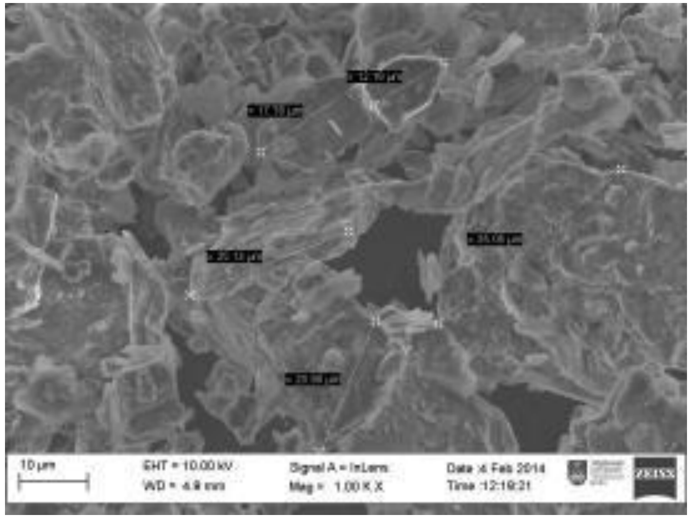

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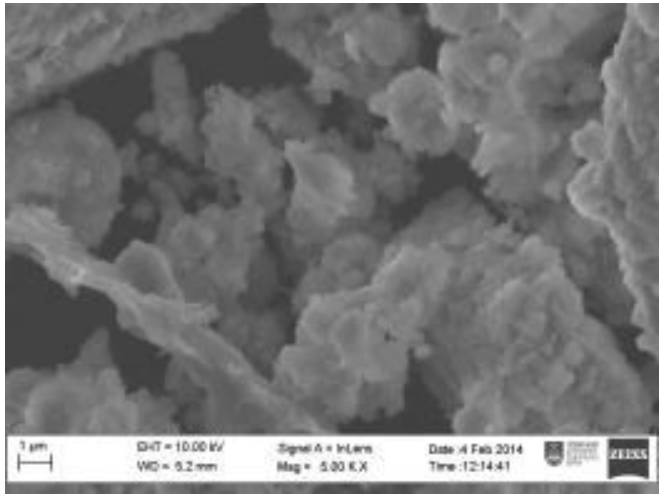
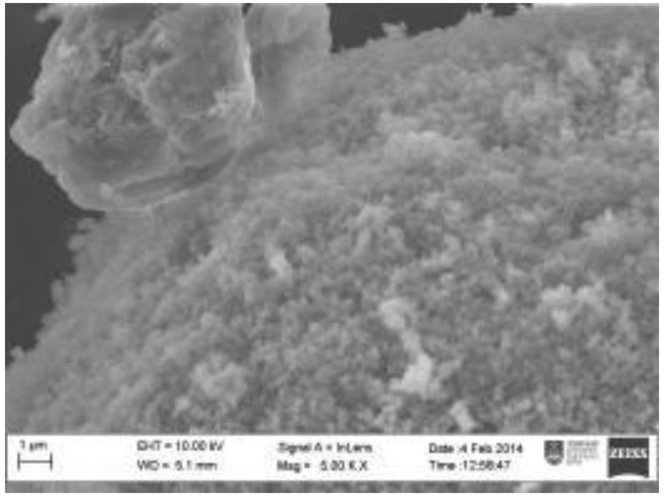
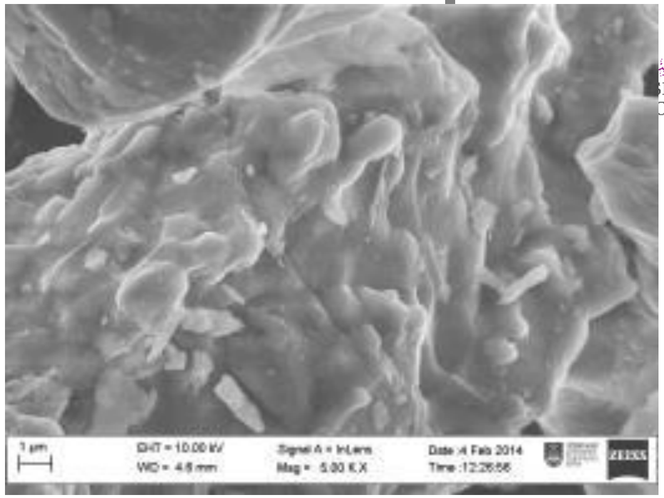
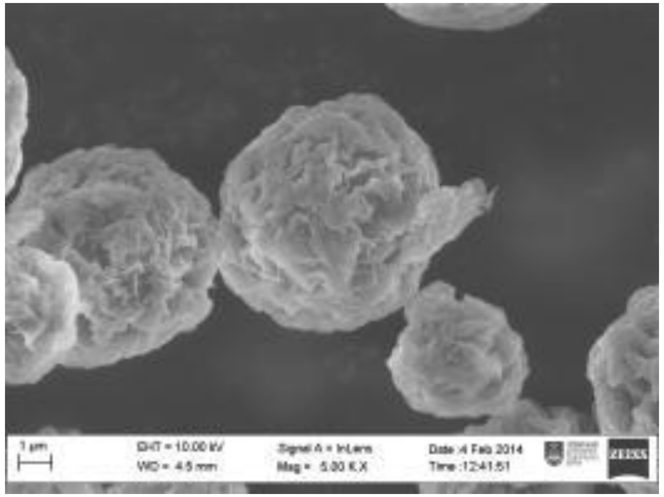
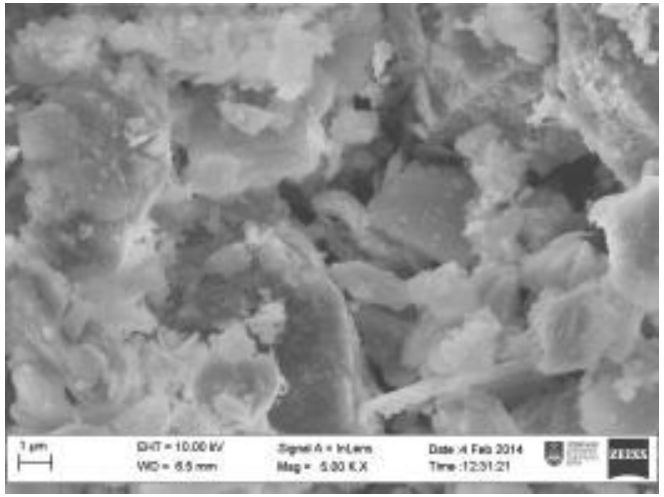
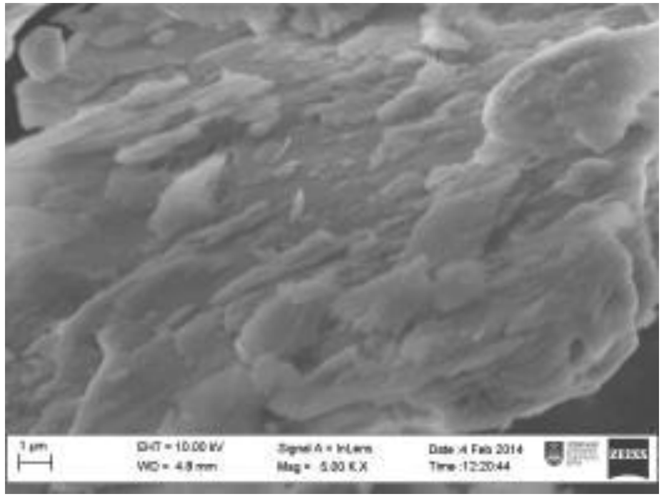




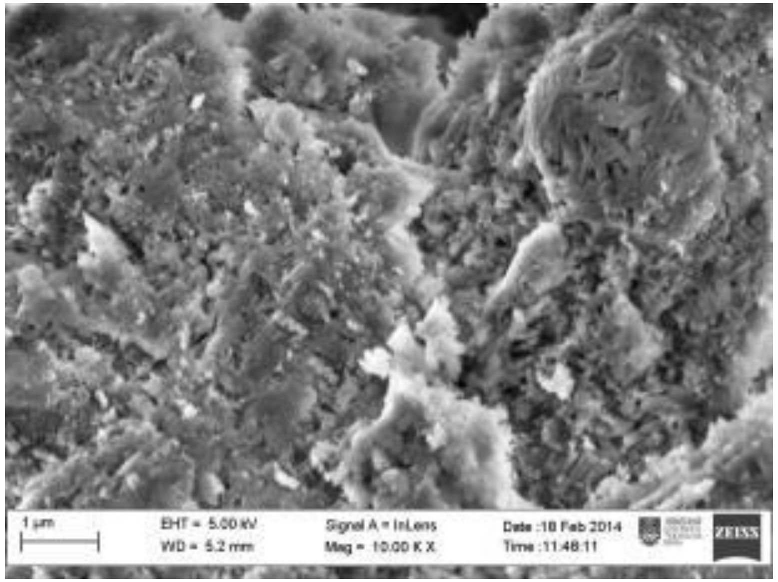








UiTM di hatiku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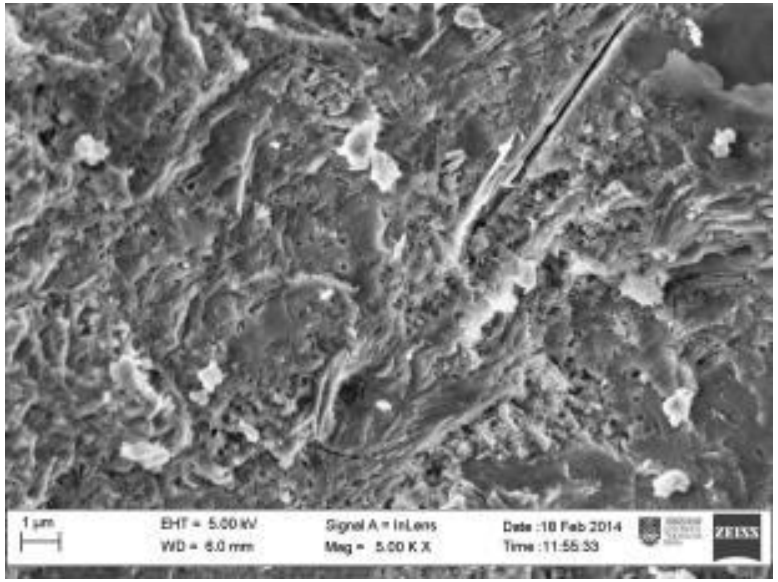
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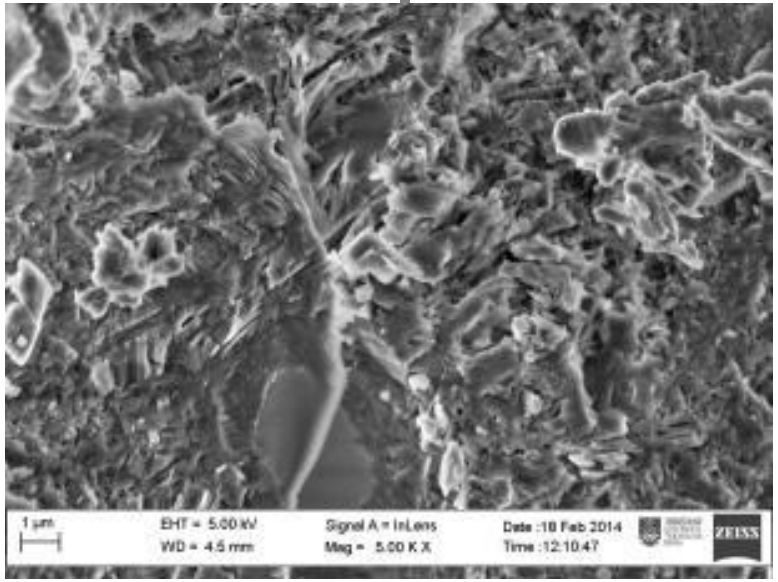
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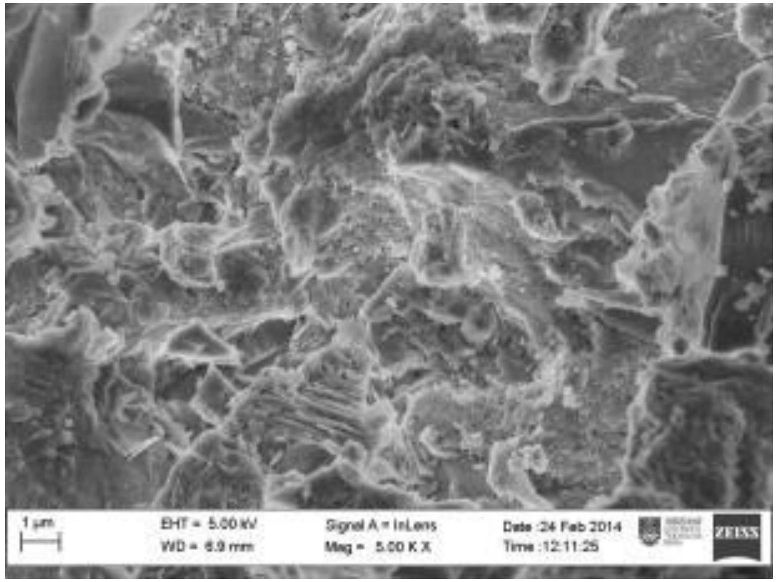
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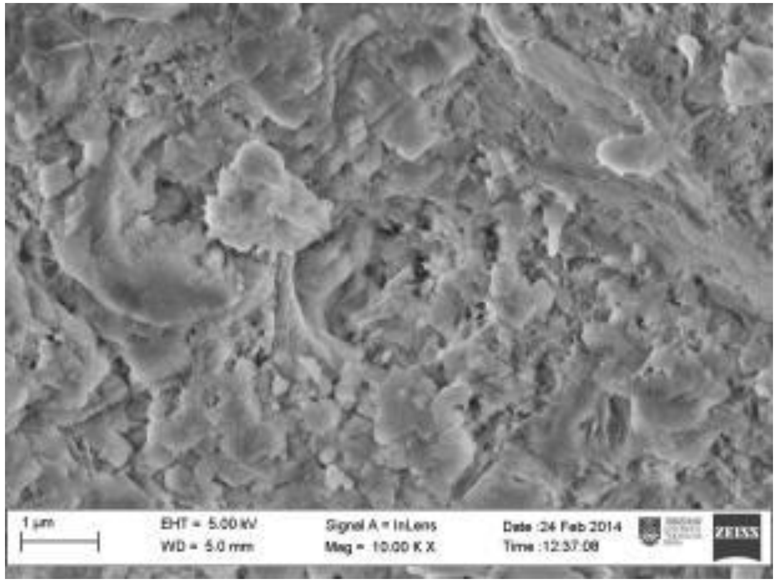
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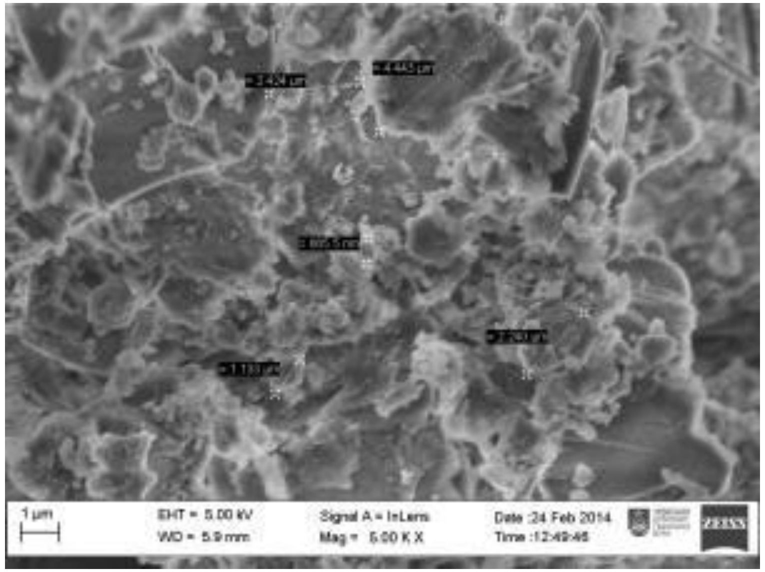
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ZEISS

Further information

- **The recommended book for this course is "Electron microscopy and analysis", by Goodhew, Humphreys and Beanland.**
- **Need advice regarding material properties, morphology, petrography, structure integrity, FESEM, XRF and XRD.. Feel free to contact me**

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PRINCIPAL RESEARCHER / SENIOR LECTURER

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UiTM Shah Alam, Selangor, Malaysia

0135121286 / muhdnorhasri@uitm.edu.my / norhasri@gmail.com

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