

Electron Microprobe Analysis and Scanning Electron Microscopy

Electron microprobe analysis (EMPA)

Analytical technique in which a beam of electrons is focused on a sample surface, producing X-rays from the material in the sample. Used for chemical mapping of a sample surface, and also for quantitative chemical analysis.

What is EMPA used for?

-Quantitative or qualitative chemical analysis of a very small focussed spot (<1um) on a polished sample surface. A non-destructive technique. Useful for:

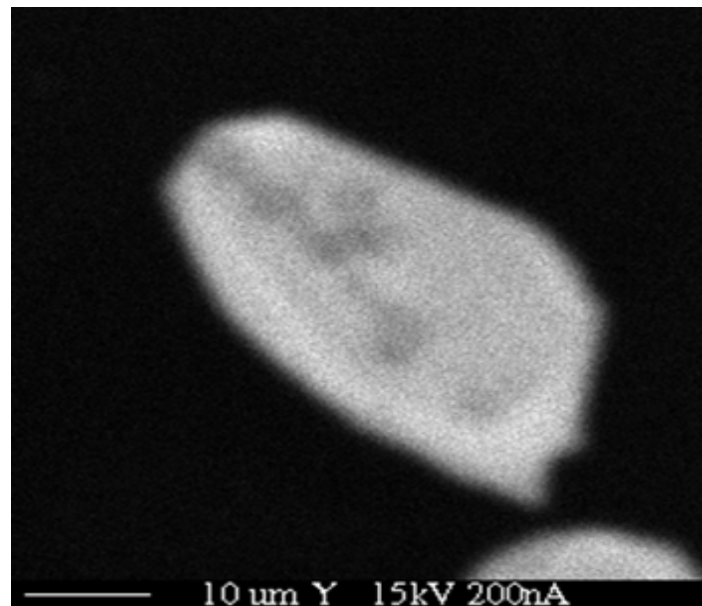
- Mineral identification
- Descriptive petrology
- Geothermometry and geobarometry
- Experimental petrology
- Cosmochemistry
- Zoning in minerals
- Diffusion studies
- Particle analysis

What is EMPA used for? (con't)

-Chemical mapping of a polished sample surface.

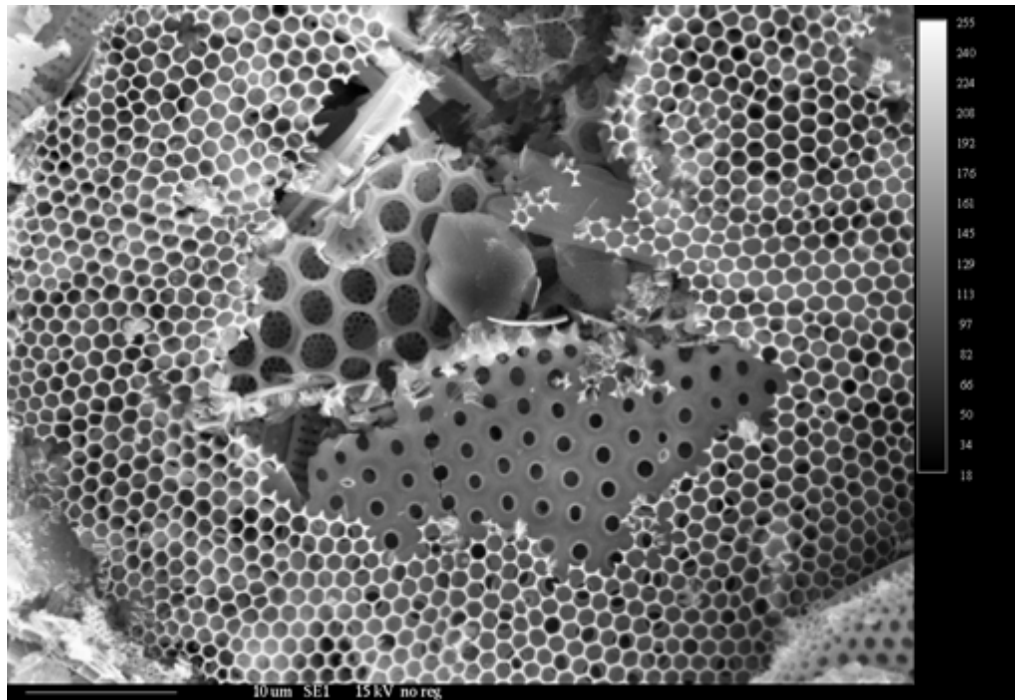
Accomplished by sweeping (rastering) the beam over the sample surface. Used for many of the same types of studies described above. Particularly useful for:

- Location and distribution of phases
- Quick location and identification of trace particles
- Subtle zoning patterns in mineral samples
- Examination of the interfaces between phases



Secondary electron imaging (SEI, also commonly SEM)

A related technique in which a very finely-focussed beam of electrons is swept across a sample surface, producing secondary electrons which are then detected by a scintillation detector. This technique is used for high-magnification and resolution imaging of a 3-D sample surface.



What is secondary electron imaging used for?

-**Morphological imaging** of a rough sample surface. Also accomplished by rastering the beam over the sample surface, but does only yields morphological, not chemical, information. Useful for:

- Determining the morphology and morphological relationship between mineral phases that can be difficult to detect with the petrographic microscope
- Determining size of very small mineral phases

The instrumentation which allows these two types of analyses is closely related, in that the electron optics system is very similar. The CAMECA SX-100 instrument is primarily an electron microprobe designed for quantitative chemical analysis, but also can also be used for secondary electron imaging.

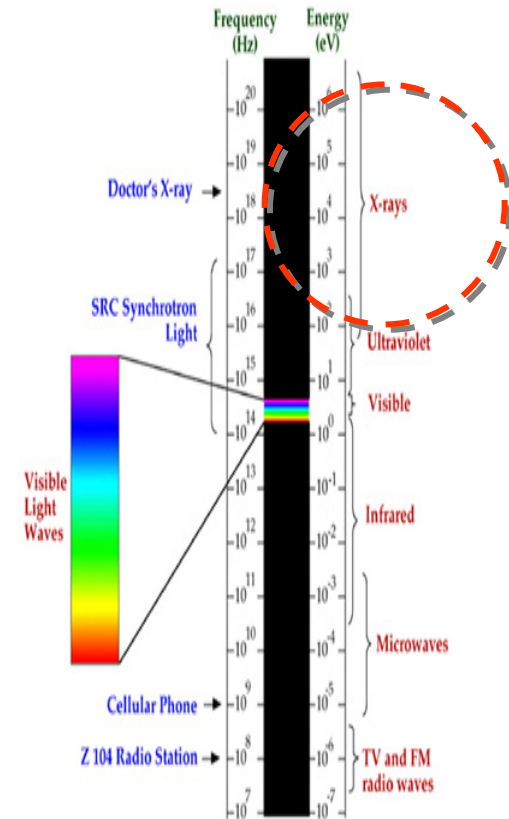


History of Electron Probe Microanalysis

X-RAYS

1895- Roentgen discovers X-rays

X-rays are high-frequency electromagnetic radiation with energy intermediate between far-UV and gamma ray regions. This leads to development in numerous fields, particularly medical.



1911- Barkla recognized characteristic radiation

This scientist recognizes that x-rays emitted from different elements produce x-rays of different energy and wavelength.

1913-1914- Moseley quantifies the relationship between atomic number and x-ray wavelength.

Moseley photographed and studied characteristic x-ray radiation. He determined that the atomic number of an atom is more important than the atomic weight in determining the characteristics of x-rays generated from that element.

Formulated Moseley's law:

$$\lambda \propto 1/Z^2$$

where λ = x-ray wavelength

Z = atomic number

1912- Von Laue. Diffraction

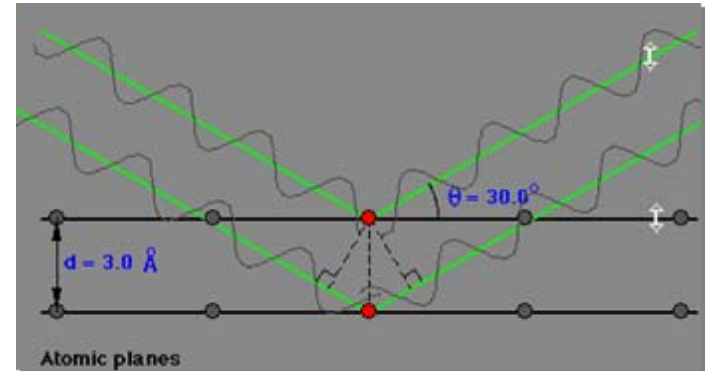
Von Laue and coworkers speculated that wavelength of x-rays and crystal lattice parameters are similar, so x-rays could be diffracted by crystals.

1914- Bragg. Developed Bragg's Law

Bragg's law defines a diffraction relationship between the wavelength of an incoming ray and the d-spacing of a diffracting crystal.

Bragg's Law:

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



where n = the order of reflection

λ = wavelength of incident ray

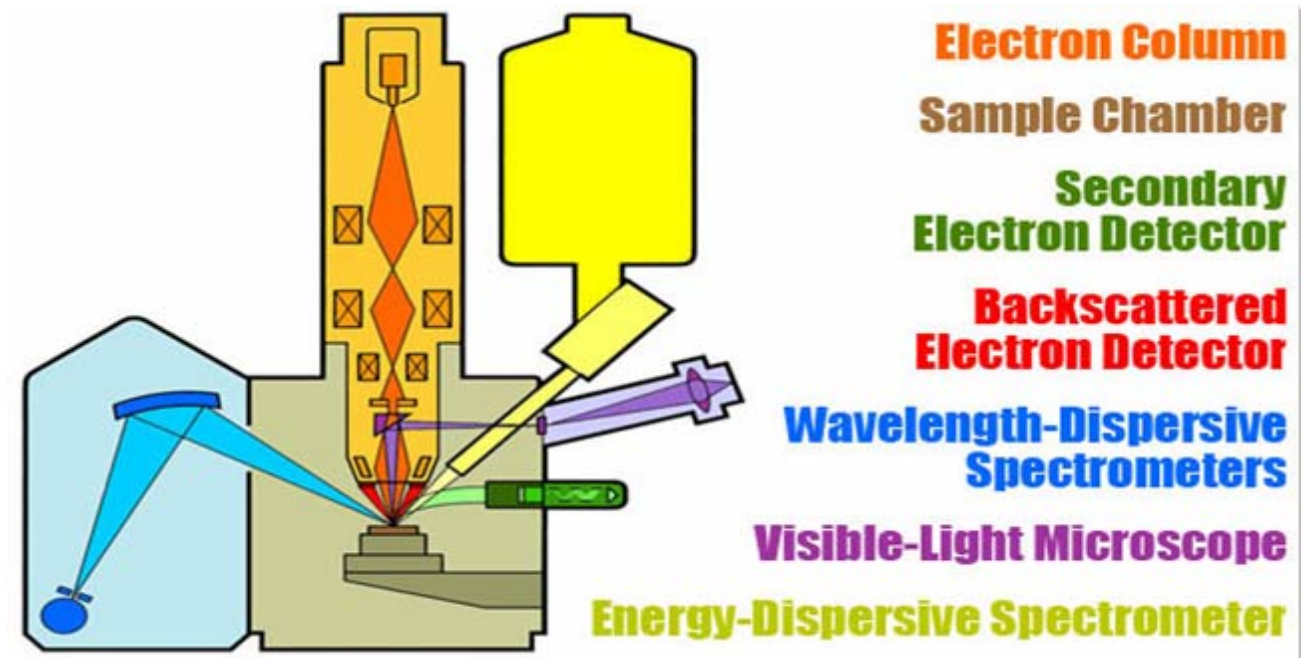
d = interplanar spacing of the crystal

θ = angle of incidence and reflection of incident ray

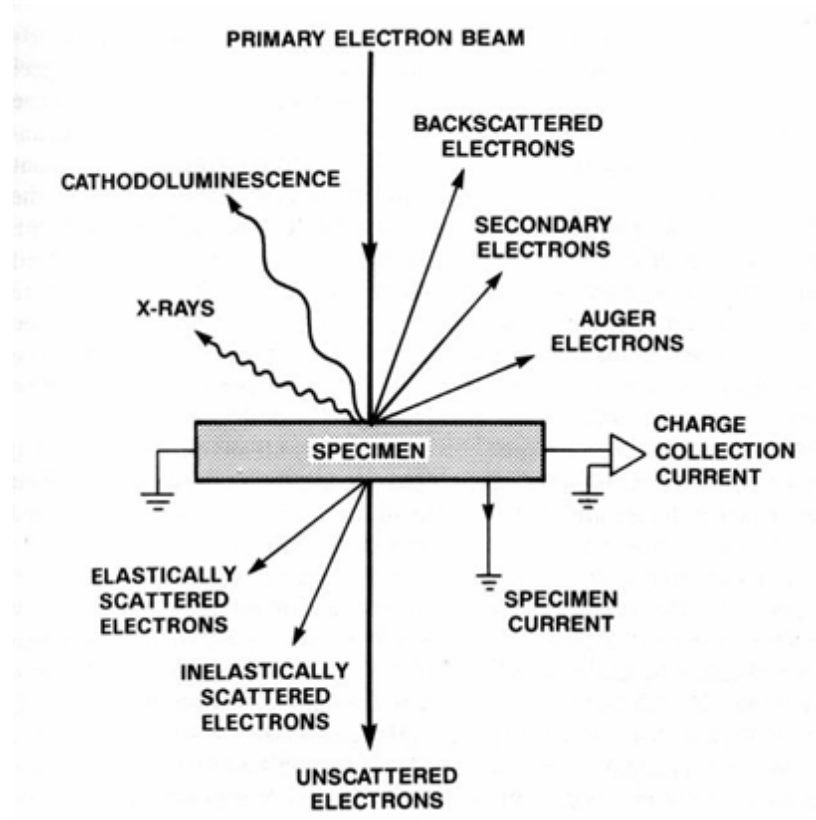
This is the principle under which the wavelength-dispersive detectors operate.

1951 R. Castaing. Developed the first electron microprobe

Castaing was a doctoral student at the University of Paris. His doctoral thesis was titled: "Application of electron beams to a method of local chemical and crystallographic analysis". He is the originator of the electron microprobe as we know it today.



Fundamental Beam Interactions



-Characteristic X-rays

Produced by electronic transitions within inner electron shells. Can be explained by examining the Rutherford-Bohr model of the atom, in which electrons orbit in a number of shells around a nucleus.

-Backscattered electrons

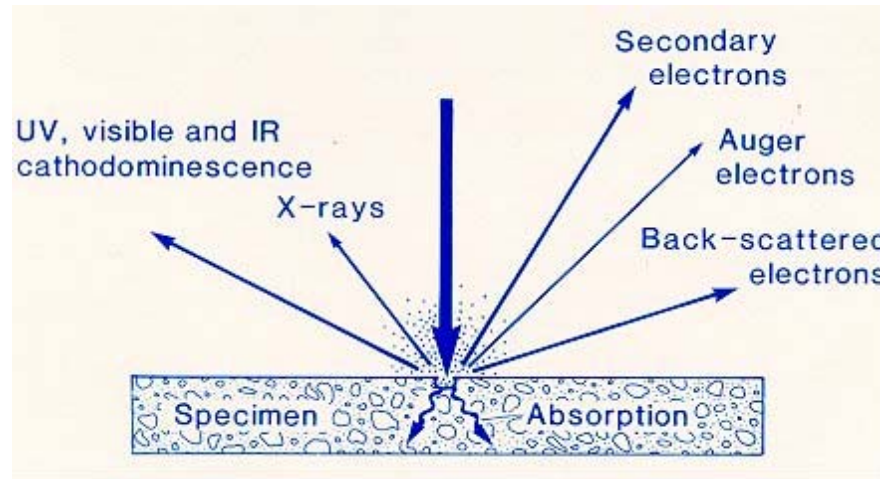
Primary electrons from the beam that undergo violent collisions with atoms in the sample and are scattered back from the sample surface. The proportion of backscattered electrons is directly proportional to the mean atomic number of the sample. Backscatter from C is 8%, from U is 50%. Modern BSE detectors can detect mean Z differences of between 0.1 and 0.3 Z .

-Secondary electrons

Secondary electrons are produced by ionization of atoms in the sample by interaction with the primary beam. Secondary electrons have low energies, and cannot escape from deep within the sample. Therefore, this electron signal produces the highest-resolution morphological images of a sample surface.

-Cathodoluminescence

Visible light emitted by minerals bombarded by electrons. Mechanism depends on the mineral in question. This property of certain minerals, particularly diamond and some types of feldspar, allow the beam to be viewed optically which is useful for focusing.

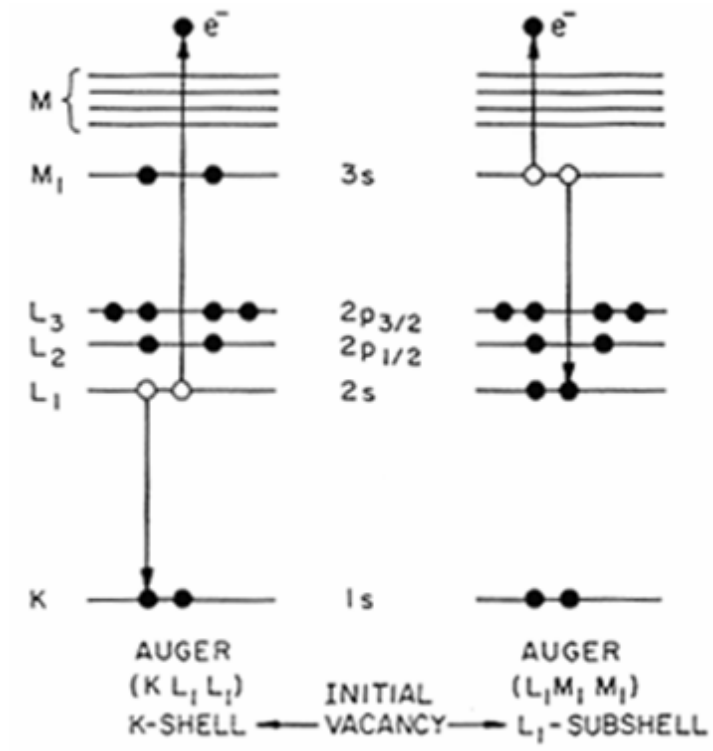


-Continuous X-rays

Most interactions between the primary beam do not produce the characteristic x-rays discussed earlier. Many electrons from the incident beam are simply decelerated by the interactions with outer orbital shell electrons from atoms within the sample. The energy released during these decelerations produces a continuous (or bremsstrahlung) x-ray spectrum. These x-rays are noise, and are undesirable, but unavoidable.

- **-Auger Electrons**

- When an atom is ionized in an inner shell, energy may be released by ejecting another bound electron, instead of producing an x-ray. These electrons can have characteristic energy. Most effective for low atomic number elements (<10).



-Characteristic X-rays

Produced by electronic transitions within inner electron shells. Can be explained by examining the Rutherford-Bohr model of the atom, in which electrons orbit in a number of shells around a nucleus.

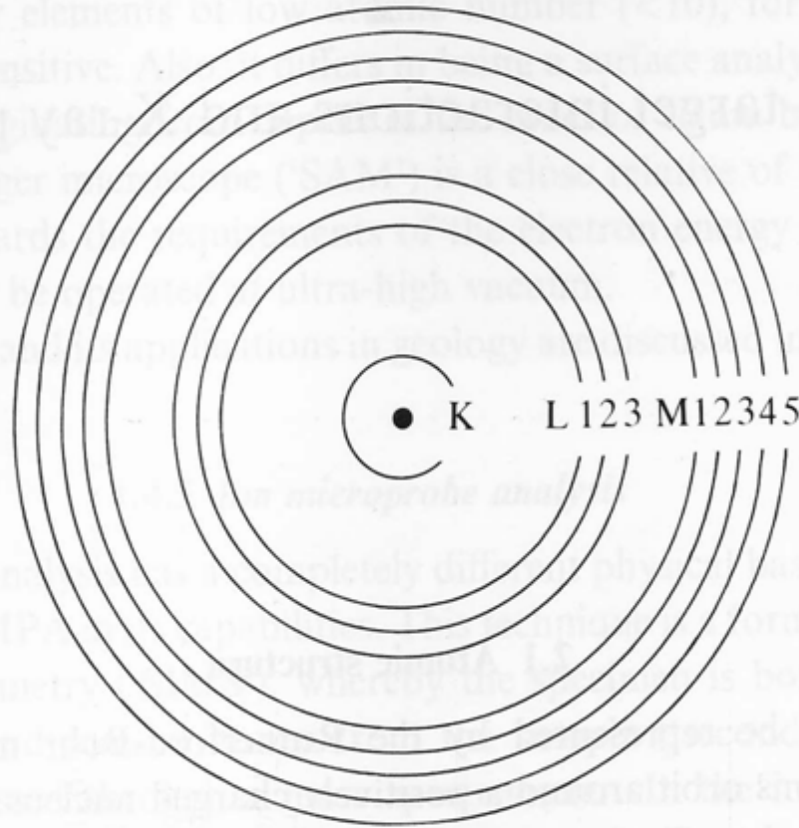
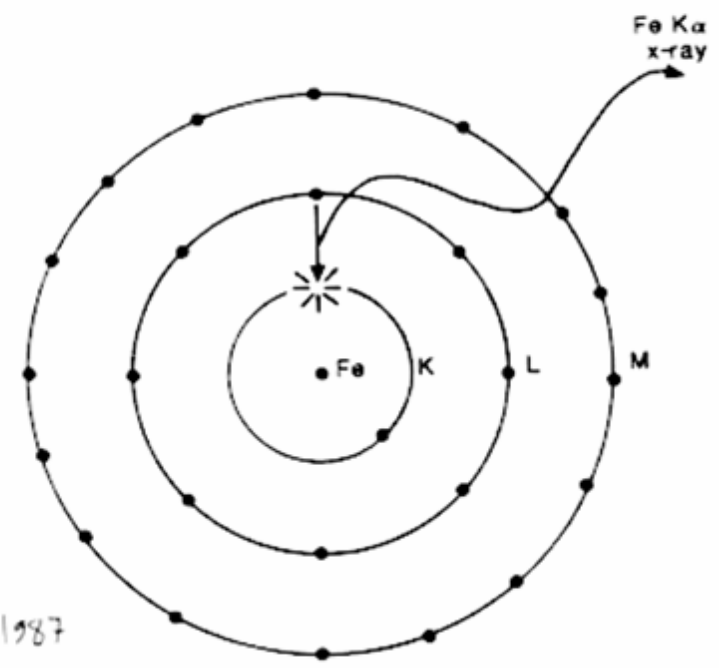
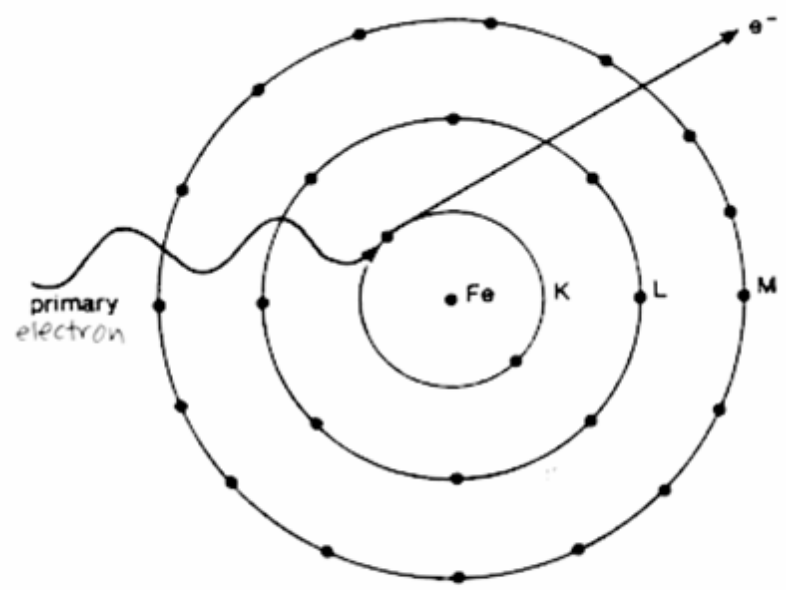


Fig. 2.1. Schematic diagram of inner atomic electron shells; characteristic X-rays are produced by transitions between these shells. From Reed, 1996

From Reed, 1996



After
Potts, 1987

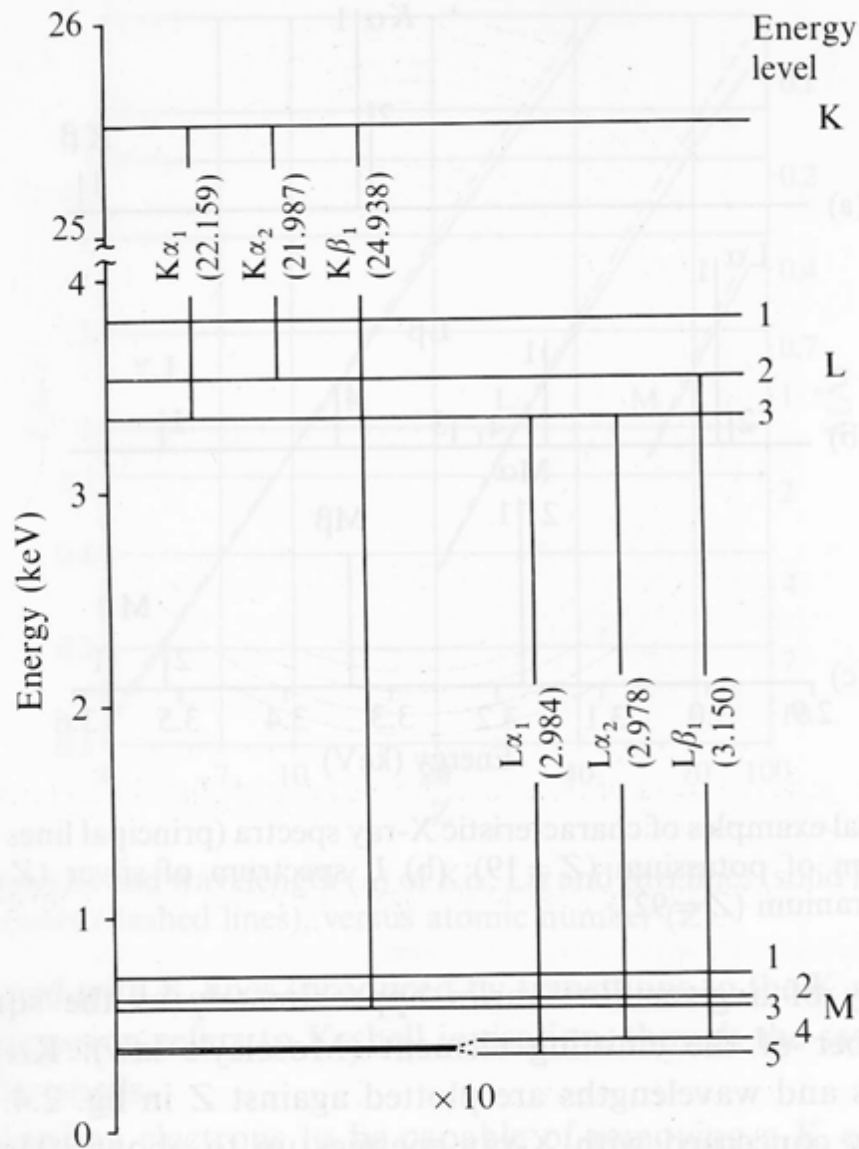


Fig. 2.2. Energy level diagram for silver ($Z = 47$); characteristic X-ray energy (given in kiloelectronvolts) is equal to the difference in energy between the levels involved in the transition.

From Reed, 1996

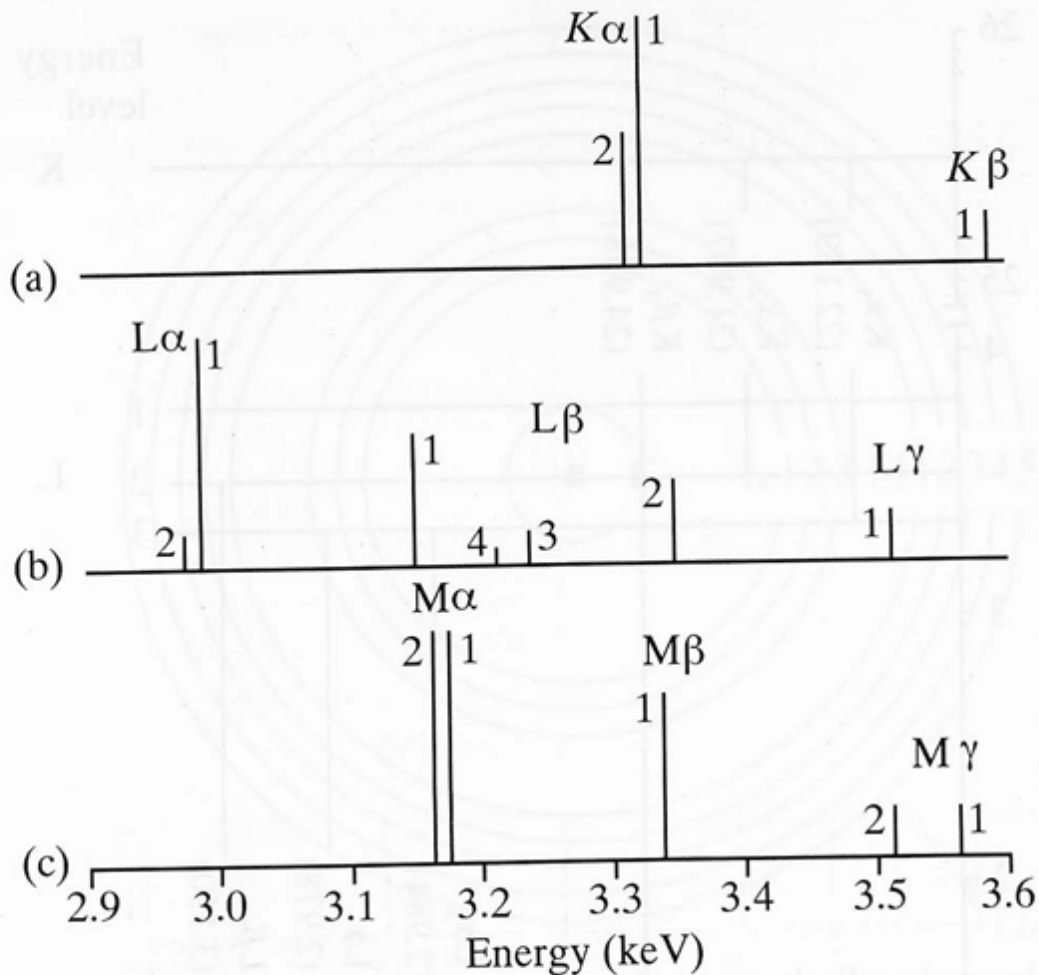
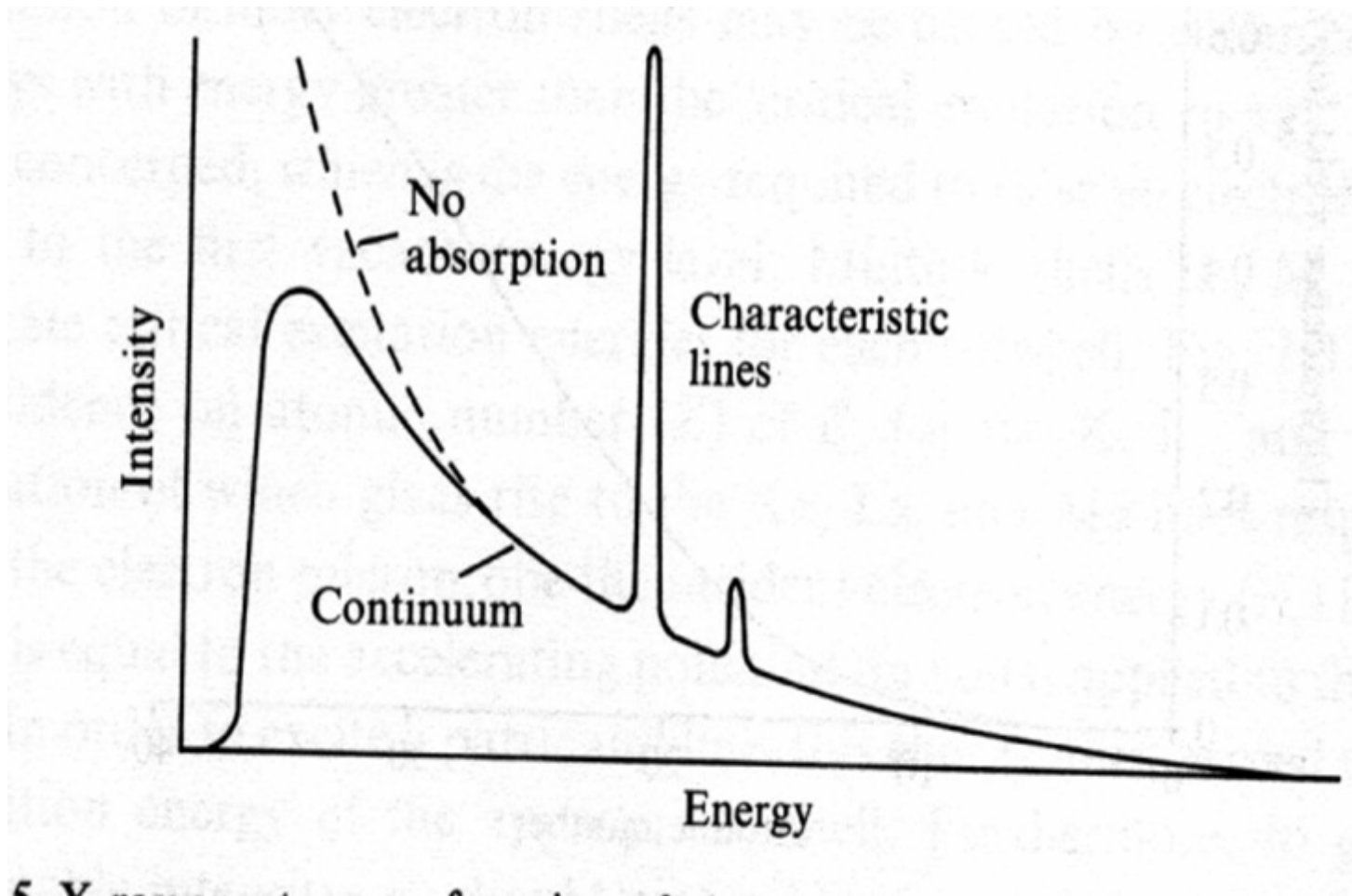


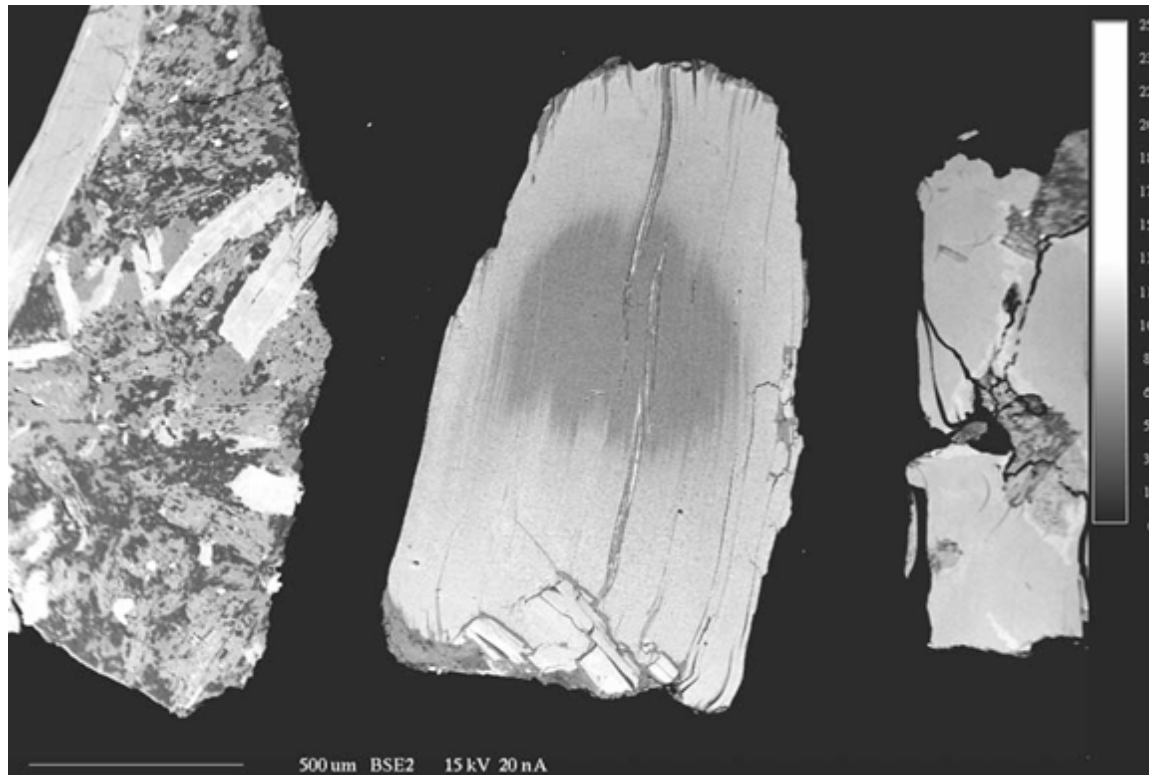
Fig. 2.3. Typical examples of characteristic X-ray spectra (principal lines only shown): (a) K spectrum of potassium ($Z = 19$); (b) L spectrum of silver ($Z = 47$); (c) M spectrum of uranium ($Z = 92$).

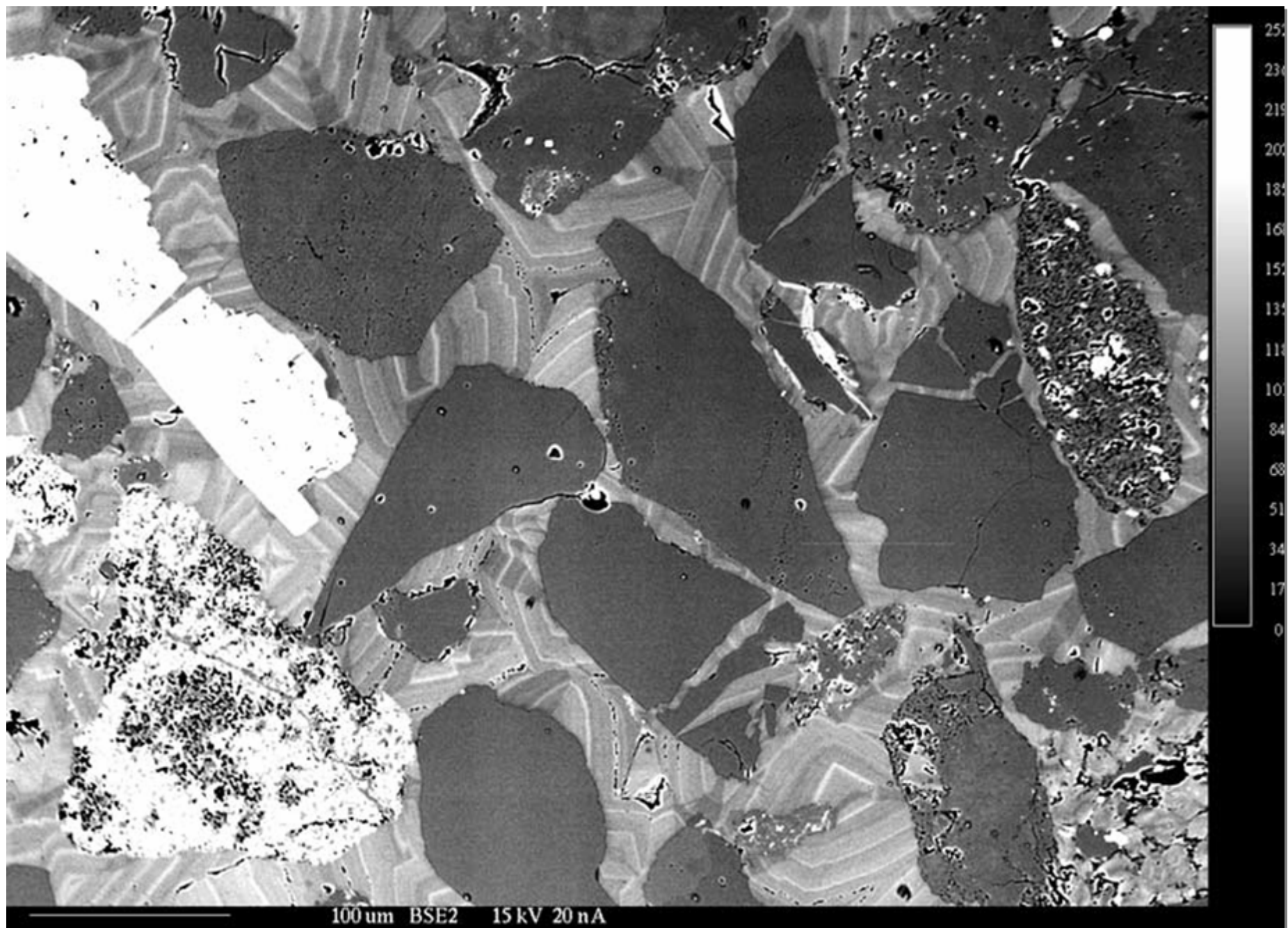


From Reed, 1996

-Backscattered electrons

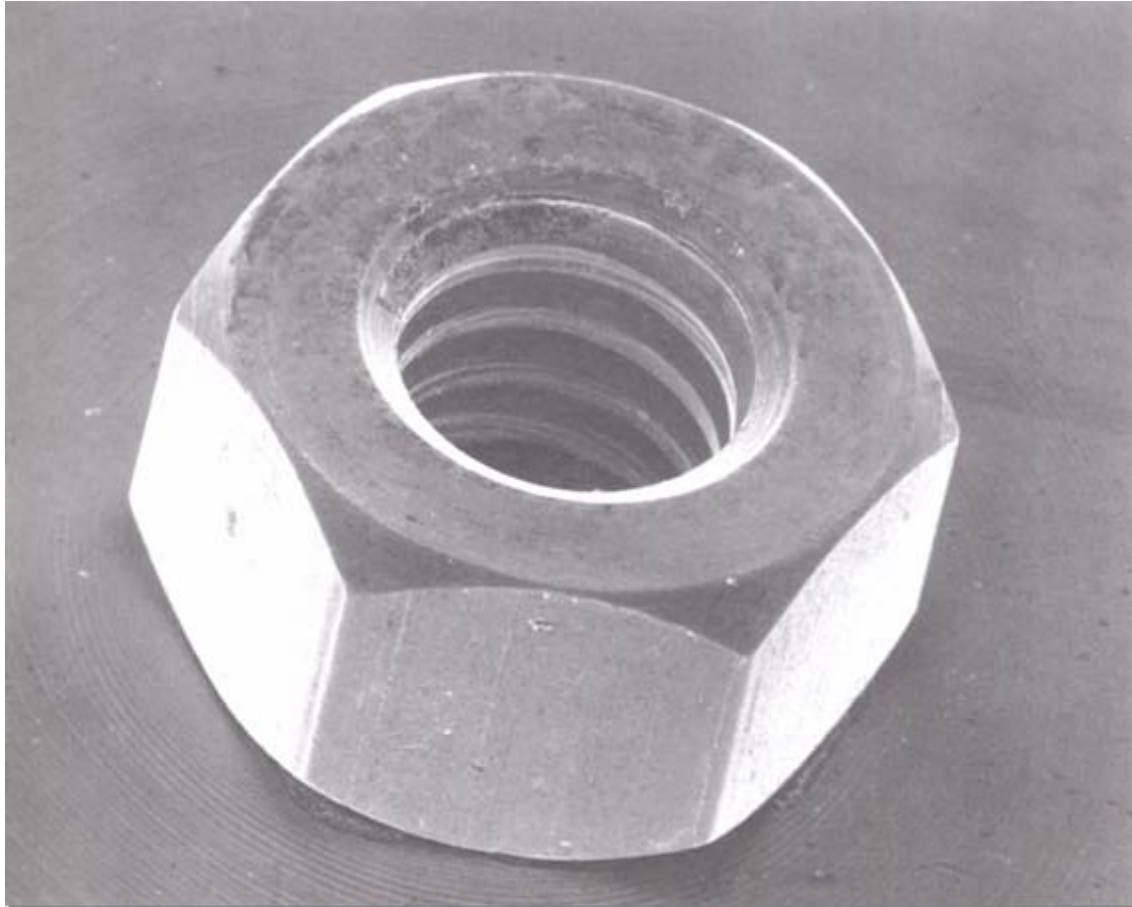
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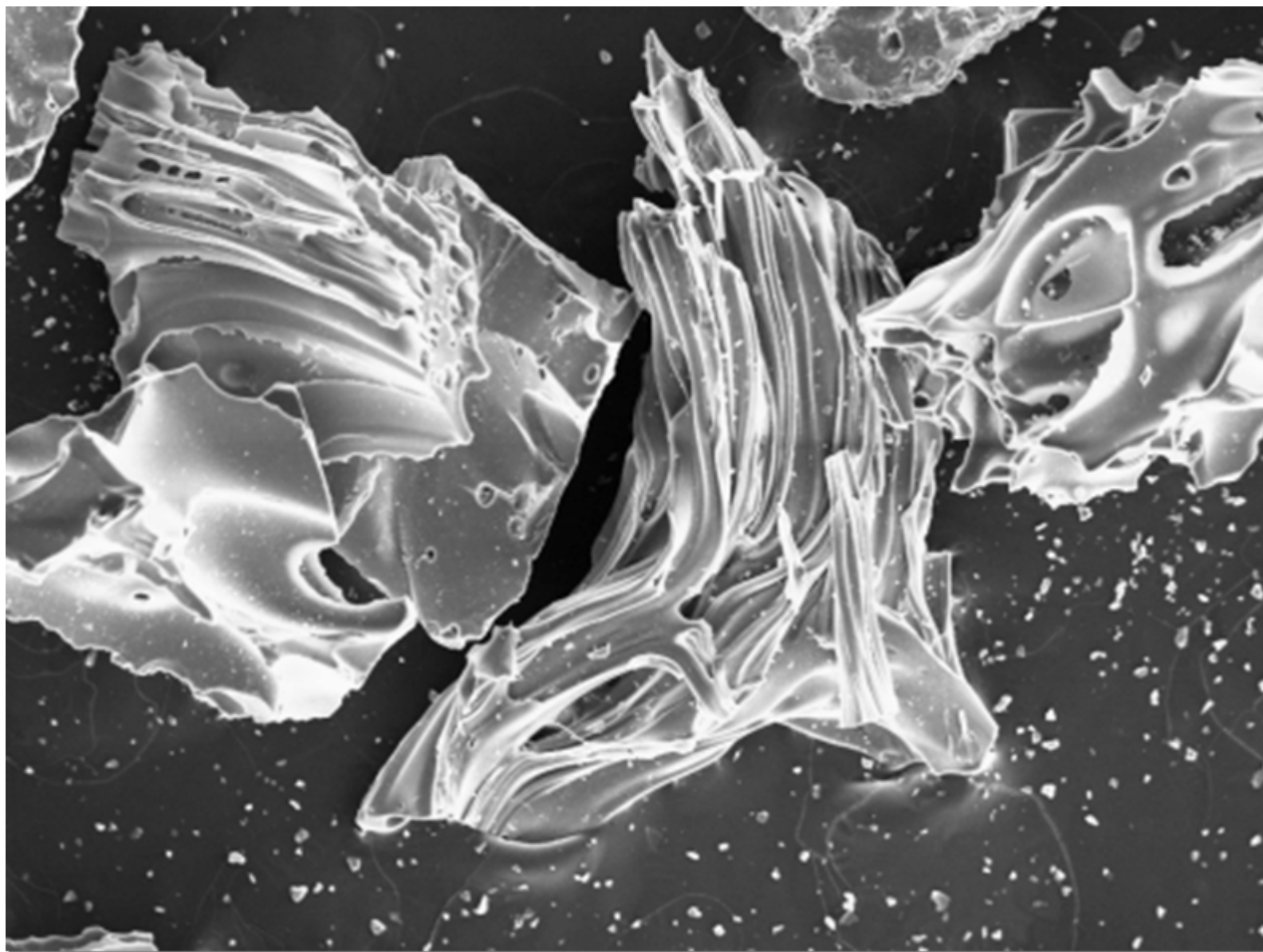


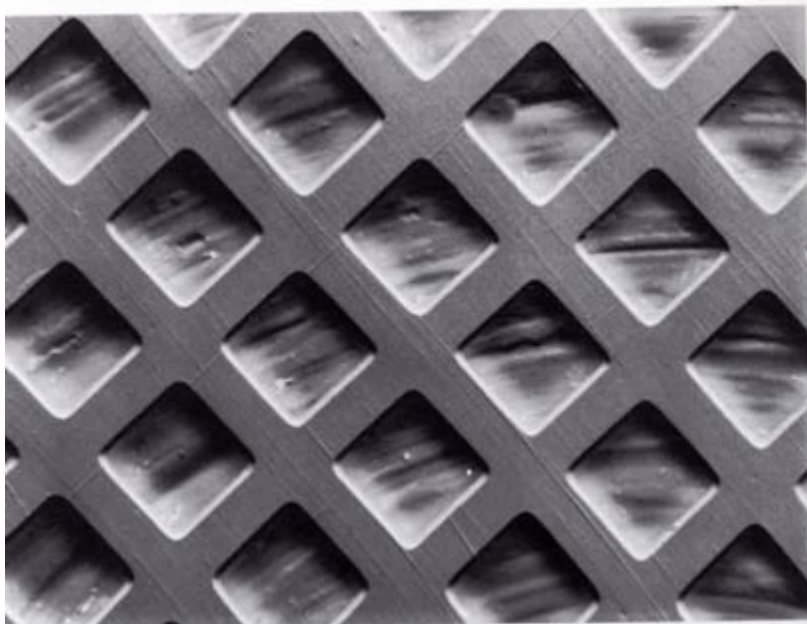
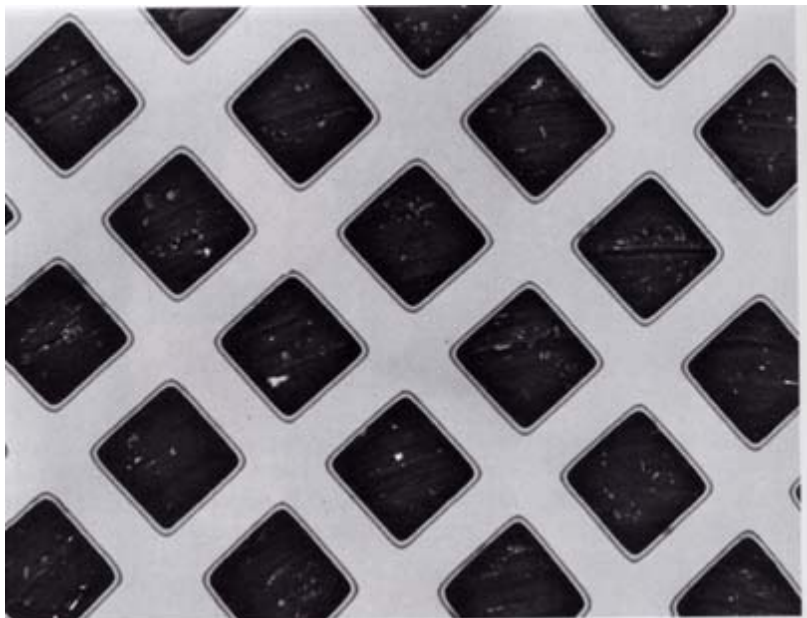


-Secondary electrons

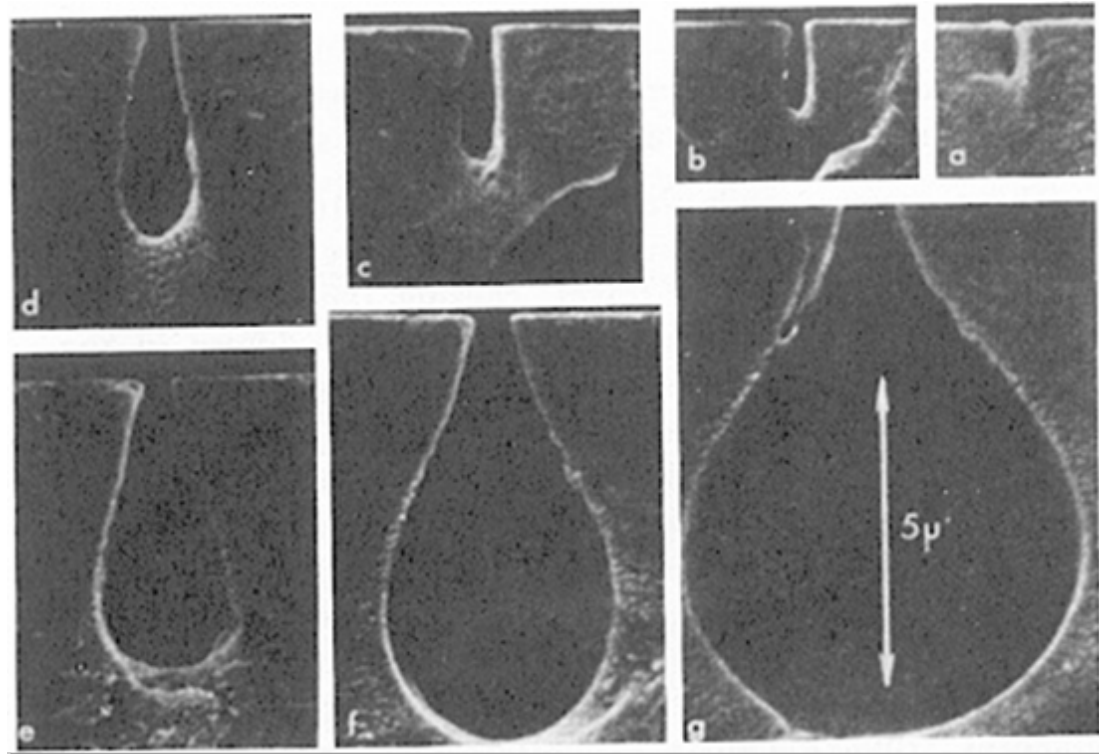
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Electron interaction volumes



Effect of beam interaction (damage) in plastic (polymethylmethacrylate), from Everhart et al., 1972. All specimens received same beam dosage, but were etched for progressively longer times, showing in (a) strongest electron energies, to (g) the region of least energetic electrons. Note teardrop shape in (g)

Major components of an electron microprobe

1. Electron optic system.

- Electron gun
- focussing lenses and apertures
- associated electronics

2. Optical microscope and sample stage

- optical/video apparatus for viewing sample
- high-precision stage that holds samples and standards

3. X-ray optic system

- spectrometers
- secondary electron detector
- backscatter electron detector
- flow-proportional gas counters

Major components of an electron microprobe (cont')

4. Vacuum system

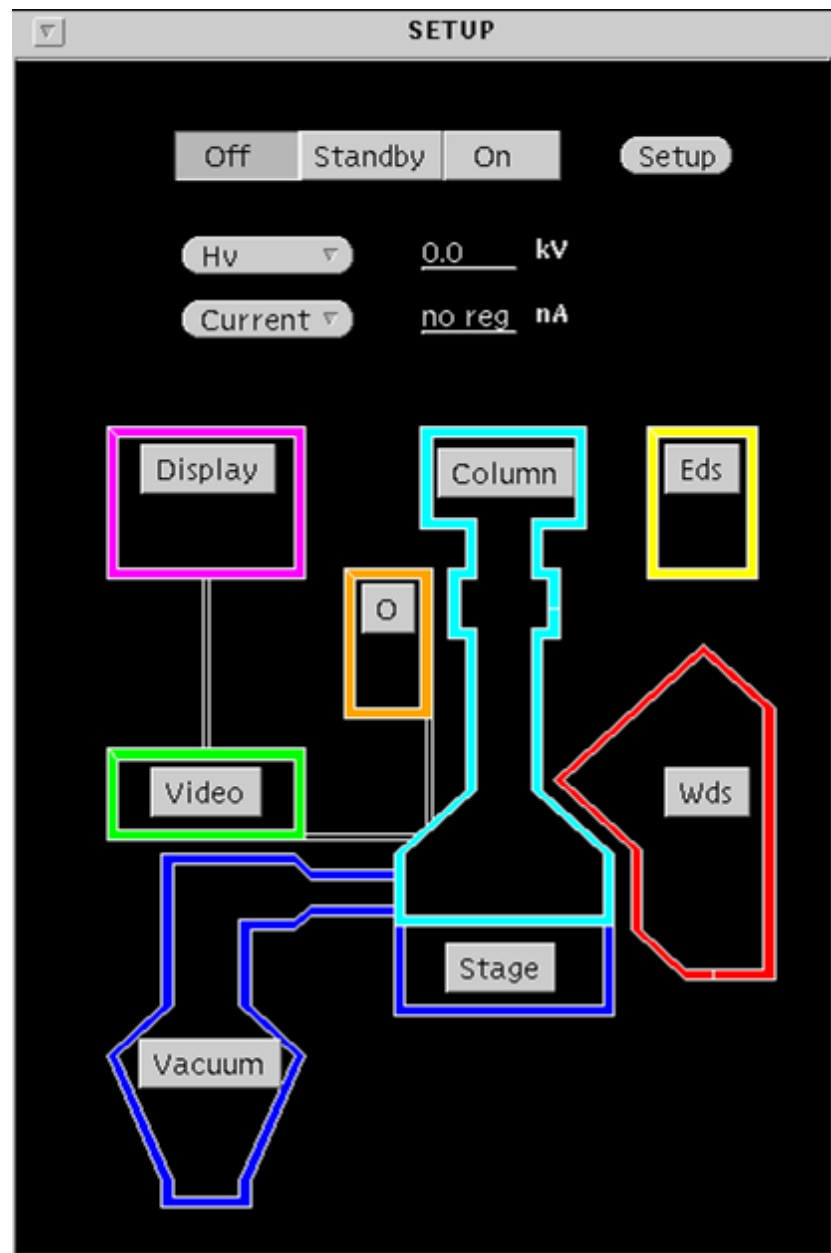
- roughing pumps
- diffusion pump
- ion pump

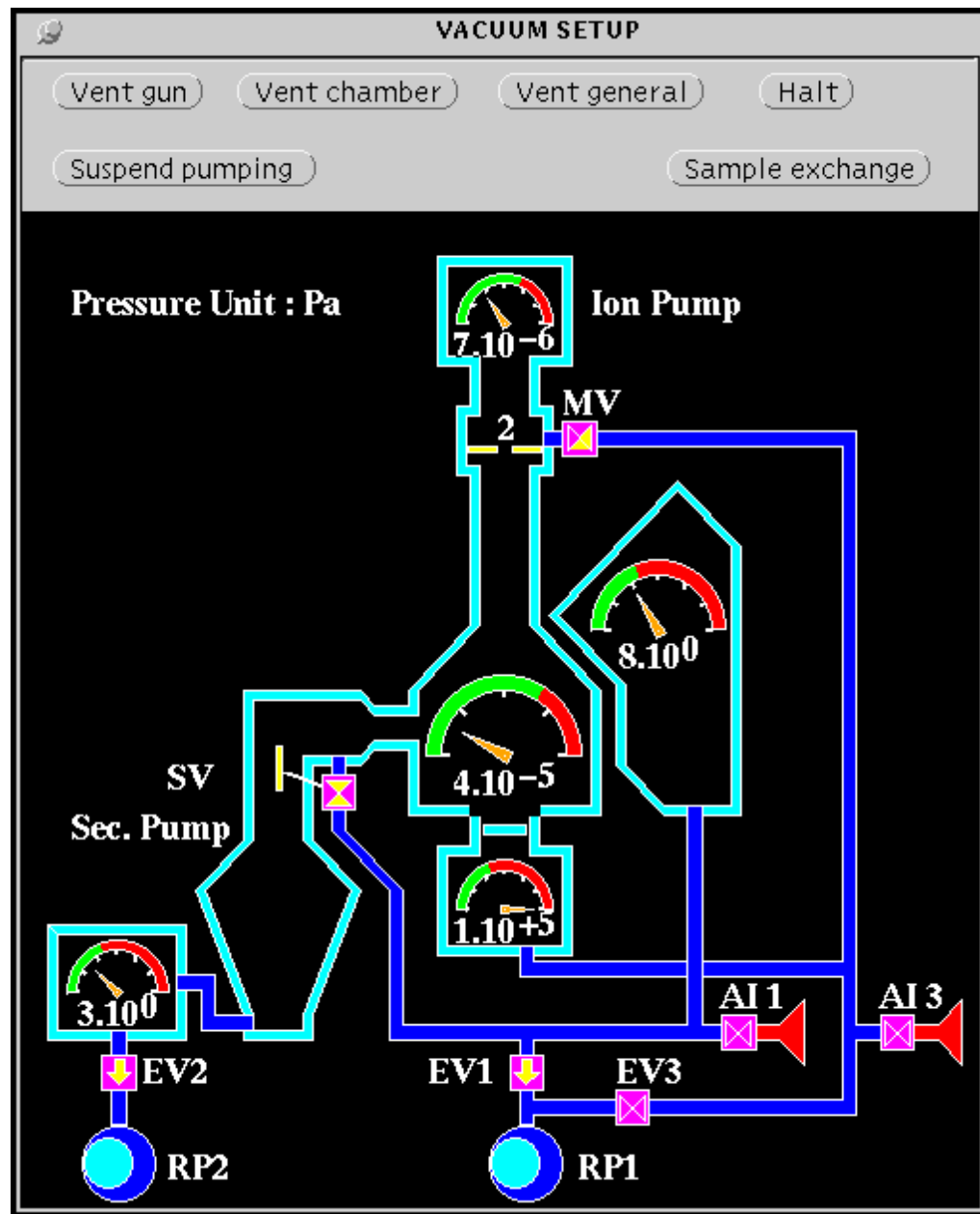
5. Amplification/electronics

- amplification of signals

6. Computer Controller

- interface between instrument and operator
- image collection and processing systems
- quantitative data reduction programs





BEAM SETUP

SOURCE

Off

Standby

On

Measure

Heat

214

Hv

15.0

kV

I emission

60

uA

ALIGNMENT

Auto alignment

Xhigh

-723

Yhigh

115

Xlow

161

Ylow

64

CURRENT

C1

1255

C2

1255

Beam current

2.0

nA

Reg.

Off

On

Aper.

150

uM

FOCUS

Auto focus

Focus

3316

Wobble

Off

On

Beam size

15

um

STIGMATOR

Ampl.

464

Angle

241

Stigmatism aid

Off

On

Hysteresis

Gun

Gun Alignment

C1

C2

Aper. Fara Cup

Foc.

Sample



WDS SYNOPTIC

Wds 3
LLIF
68111

