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Electron Microprobe Analysis
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Uses of the EPMA

**Spot mode operation** for quantitative analysis:

- Micron-scale, complete chemical analysis
  
  *Be to U (10-50 ppm under favorable conditions)*

**Raster mode operation** for high resolution imaging:

- Back-scattered electron: *composition and topography*
- Secondary electron: *topography*
- Cathodoluminescence (light): *trace elements, defects*
- X-ray map: *spatial distribution of elements*
An example: Compositional imaging with back-scattered electrons

**Back-scattered electron**

Polished surface

Function of composition

- High-Z elements
- Low-Z elements

**Plane polarized transmitted light**

Thin section

Function of optical properties
Qualitative analysis

- Visual characterization of phases in image (shape, size, surface topography, etc.)
- Qualitative identification of elements in each phase
Semi-quantitative analysis

- Quick and approximate concentration measurement at a spot
- Elemental mapping of a surface to determine spatial distribution of elements
Quantitative analysis

- Complete chemical analysis of a micron-sized spot to determine concentration of all elements

- Concentration mapping to determine the abundance of all elements at every pixel of an image
JEOL JXA-8200 Superprobe
Electron emitting source: Tungsten hairpin

- **Cathode: Filament** at negative potential
  
  Tungsten has a high melting point and a low work-function energy barrier; heated by filament current, $i_f$, until electrons overcome the barrier

- **Wehnelt Cylinder** at a slightly higher negative potential than the filament because of the Bias Resistor
  
  Bias voltage ($V_{bias}$) automatically adjusts with changes in $i_e$ to stabilize emission; the grid cap also focuses the electron beam

- **Anode: Plate** at ground potential
  
  Potential difference (accelerating voltage, $V_0$) causes electron emission (current, $i_e$)
Electron probe parameters

Accelerating voltage, $V_0$
($V_0$ of 15 kV generates electron beam with 15 keV energy)

Final beam current, or probe current, $i_p$
Final beam diameter, or probe diameter, $d_p$
Final beam convergence angle, or probe convergence angle, $\alpha_p$
Electron probe diameter

Probe diameter decreases with:
- decrease in Probe current
- increase in Accelerating voltage
- \( W > \text{LaB}_6 > \text{Field Emission source} \)

Higher probe current improves signal but results in poorer image resolution

Tungsten hairpin, 15 kV, 10 nA, \( d_p \approx 100 \text{ nm} \)
Depth of focus

Large depth of focus

Small depth of focus
Spatial resolution: electron interaction volume

Vertical electron beam, probe diameter = 0.1 μm

Monte Carlo simulations of electron trajectories in the sample

Width of interaction volume >> probe diameter
(interaction volume can be reduced by using a lower accelerating voltage)

Low atomic number: large tear-drop shape
High atomic number: small hemisphere

Depth (μm): 0.2, 0.4, 0.6, 0.8
Electron range increases as \(E\) increases, and decreases as \(\rho\) and \(\rho Z\) increase.

E.g., at 20 kV,

\[
R = 4.29 \, \mu m \text{ in Carbon (Z = 6, A = 12.01, } \rho = 2.26 \, g/cc) \\
R = 0.93 \, \mu m \text{ in Uranium (Z = 92, A = 238.03, } \rho = 19.07 \, g/cc)
\]
Electron interaction depth (range)

Electron range increases as $E$ increases, and decreases as $\rho$ and $\rho Z$ increase.
Signal types

- Electron beam
- Cathodoluminescence
- Objective lens
- Back-scattered electron
- Secondary electron
- X-ray
- Sample
Spatial resolution for different signals

The “onion shell” model:
Cu-10%Co alloy

Production volume for different signals is different

20 keV, W filament diameter ~150 nm

Auger electrons
Secondary electrons
Backscattered electrons

150 nm

Continuum X-rays
Fluorescent X-rays
Fluorescence of CoKα by CuKα ~60 μm

450 nm

Characteristic X-rays
CuKα ~1 μm
CuLα ~1.5 μm

(not to scale)
Spatial resolution for cathodoluminescence

1 keV  5 keV  30 keV

2 μm

Gallium Nitride
Electron-specimen interactions: Elastic scattering

Back-scattered electron

\[ E_f = E_i \quad \text{large } \phi_e \]
Electron-specimen interactions: Inelastic scattering

Inner shell interactions:
- Characteristic X-rays
- Secondary electron

Outer shell interactions:
- Continuum X-rays
- Secondary electron
- Cathodoluminescence
Back-scattered electron (BSE)

- Beam electrons scattered elastically at high angles
- Commonly scattered multiple times, so energy of BSE ≤ beam energy
Electron backscatter coefficient

- Large differences between high- and low-atomic number elements
- Larger differences among low-Z elements than among high-Z elements
Back-scattered electron detector
Back-scattered electron detector

Solid-state diode
Compositional and topographic imaging with BSE

(A) A+B: Compositional mode

(B) A-B: Topographic mode
Secondary electron (SE)

- Specimen electrons mobilized by beam electrons by inelastic scattering (both outer and inner shell interactions)
- Emitted at low energies (typical: <10 eV)
  (recall BSE have high energies up to that of the electron beam)
Secondary electron detector

Located on the side wall of the sample chamber
Secondary electron detector
Imaging with the Everhart-Thornley detector

Negative Faraday cage bias
only BSE

Surfaces in direct line of sight
are illuminated

Positive Faraday cage bias
BSE + SE

All surfaces are illuminated
Cathodoluminescence (CL)

Caused by inelastic scattering of beam electrons in semiconductors

Filled valence band is separated from an empty conduction band by $E_{\text{gap}}$, characteristic of the compound

Electron beam interacts:
Valence electron is promoted to the conduction band

Trace element impurities produce additional energy levels outside the conduction band, and enable other electron transitions; emitted light has different colors with energies $E \neq E_{\text{gap}}$

Electron recombines with the valence band to generate light with energy $E_{\text{gap}}$
Cathodoluminescence spectrometer

Optical microscope camera (not used)

Optical microscope light (turned off)

Optical spectrometer (CCD array detector)
Cathodoluminescence spectrum

Dolomite with trace of Mn
A continuous ($\lambda = 200$ to 950 nm) light spectrum is collected at each point of the image area.

Intensity range of 203-949 nm light: 722-2090 counts (red shades)

Intensity of 400-450 nm light: 29-277 counts (blue shades)

Intensity of 500-550 nm light: 63-251 counts (green shades)

Intensity of 600-750 nm light: 87-1018 counts (red shades)
Hyperspectral CL imaging

Intensity range of light (all wavelengths) in grey scale:
Black: no light
White: maximum intensity

Intensity range of 361-668 nm light in multicolor scale:
Blue (≤ 0 counts): no light
Red (9884 counts): maximum intensity
The X-ray spectrum

- Characteristic X-rays
- Continuum X-rays
Energy Dispersive Spectrometer (EDS)

- EDS detector: solid-state semiconductor, window and aperture
- Multichannel analyzer (MCA) processes the X-ray signal
Energy Dispersive Spectrometer (EDS)

- A single crystal of silicon
- Pure Si is a semiconductor. But impurity of boron, a p-type dopant, makes it a conductor
- Lithium, an n-type dopant, counteracts the effect of boron and produces an intrinsic semiconductor
Qualitative analysis with BSE and EDS

Mean Atomic Number

ilmenite

hornblende

plagioclase