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Electron Microprobe Analysis

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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)
An example: Compositional imaging with back-scattered electrons

- **Back-scattered electron**
- **Plane polarized transmitted light**

**Polished surface**

- **Function of composition**

- **Thin section**

- **Function of optical properties**

- **High-Z elements**

- **Low-Z elements**
Types of analysis

Qualitative analysis
- Visual characterization (shape, size, surface relief, etc.)
- Identification of elements in each phase

Semi-quantitative analysis
- Quick and approximate concentration measurement of a spot
- Elemental mapping (spatial distribution of elements)

Quantitative analysis
- Complete chemical analysis of a micron-sized spot
- Concentration mapping of all elements
JEOL JXA-8200 Superprobe

Electron gun

Condenser lens

Optical Microscope

LN₂

Objective lens

SE

BSE

WDS

Stage

High vacuum

Electron Column

High brightness electron gun

Wehnelt cap with pre-centered filaments

6 l tilt alignment coil

6 l shift alignment coil

Dual zoom condenser lens

Oil Aperture

Upper scan coils

Lower scan coils

Stigmator coils

Objective lens

SE detector

BE detector

Specimen
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, $i_e$)
Lens modes

Normal: Large depth of focus for rough surfaces
Depth of focus

Large depth of focus

Small depth of focus
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, $\alpha_p$
At 10 nA and 15 kV, a Tungsten hairpin filament produces a beam with $d_p \approx 100$ nm.
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

Spatial resolution can be improved by using a lower accelerating voltage that reduces the interaction volume.
Electron interaction depth (range)

\[ R = 0.0276 \ E^{1.67} \ \frac{A}{\rho Z^{0.889}} \]

- \( R \) : Kanaya-Okayama electron range
- \( E \) : beam energy
- \( A \) : atomic weight
- \( \rho \) : density
- \( Z \) : atomic number

Electron range increases with increasing \( E \), and decreasing \( \rho \) and \( \rho Z \)

E.g., at 20 kV,

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

Electron range increases with increasing $E$, and decreasing $\rho$ and $\rho Z$. 
Other signals include phonon excitation (manifested by heating), plasmon excitation (generated by moving electrons in metals), and auger electron (ejected from atom by internally absorbed x-ray)
Spatial resolution for different signals (production volume)

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

Production volume is different for each signal

20 keV, W filament

Diameter ~150 nm

150 nm

450 nm

Production volume is different for each signal

The “onion shell” model: Cu-10%Co alloy
Production volume for cathodoluminescence

Gallium Nitride

1 keV  5 keV  30 keV

2 µm
Electron-specimen interactions: Elastic scattering

Back-scattered electron (BSE)
Electron-specimen interactions: Inelastic scattering

Inner shell interactions:
- Characteristic X-rays
- Secondary electron (SE)

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

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

Fraction of beam electrons scattered backward

- 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+B: Compositional mode

A-B: Topographic mode
Secondary electron (SE)

- Specimen electrons mobilized by beam electrons through inelastic scattering (causing outer and inner shell ionizations)

- Emitted at low energies (mostly $\leq 10$ eV for slow secondaries, less commonly $\leq 50$ eV for fast secondaries)

(recall BSE have high energies up to that of the electron beam)
Secondary electron detector

Located on the side wall of the sample chamber
When Faraday cage is positively biased, secondary electrons are pulled into the 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

Electron beam interacts:
- Valence electron moves to the conduction band

Filled valence band is separated from an empty conduction band by $E_{\text{gap}}$.

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

Trace element impurities expand the conduction band and enable additional electron transitions.

Emitted light has additional energy components $E \neq E_{\text{gap}}$.
Cathodoluminescence spectrometer

- Optical microscope camera (not used)
- Optical microscope light (turned off)
- Optical spectrometer (CCD array detector)
Cathodoluminescence spectrum

Light wavelength (nm)

(Ca,Mg)CO$_3$ (dolomite) with Mn

Mn
Hyperspectral CL imaging

A continuous spectrum covering all light wavelengths is collected at each point of the image area.

Total intensities of 200-950 nm light at each pixel (red shades represent 722-2090 counts)

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

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

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

Total intensities of light of all wavelengths at each pixel in grey scale:

Black: no light
White: maximum intensity

Total intensities of 361-668 nm light at each pixel 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, coated with lithium on one side
- Pure silicon 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

ilmenite
hornblende
plagioclase

Mean Atomic Number