Electron-Probe Microanalysis (EPMA): Summary for Microprobe Lab Demo

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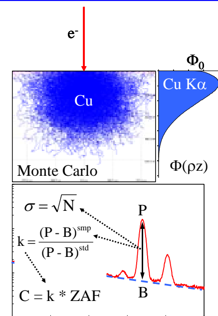


EPMA Summary Resources

Books on EPMA and Quantitative Analysis

- Scanning Electron Microscopy and X-ray Microanalysis, 3rd Ed., Goldstein et. al. 2003 Plenum. Mandatory! – Previous editions very good
- Electron Probe Quantitation, Heinrich and Newbury. 1991 Plenum. “The green book”.
- Electron Microprobe Analysis, 2nd Ed., Reed. 1997 Cambridge. Very good.
- Electron Microprobe Analysis and Scanning Electron Microscopy in Geology, 2nd Ed. Reed. 2006 Cambridge.
- X-ray Spectrometry in Electron Beam Instruments, Williams, Goldstein, and Newbury. 1995 Plenum.
- Quantitative Electron-Probe Microanalysis, Scott and Love, 2nd Ed., 1995 Prentice Hall.

Websites with EPMA Information

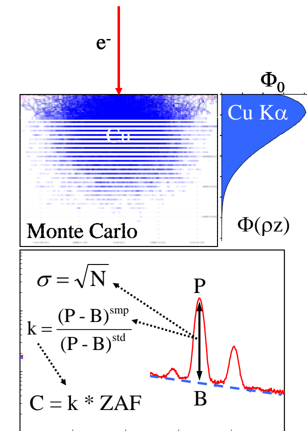
- Paul Carpenter’s lab web site http://xraysrv.wustl.edu/
- John Fournelle’s lab web site (see course materials) http://www.geology.wisc.edu/~johnf/sx51.html
- John Wittke’s lab web site http://www4.nau.edu/microanalysis/Microprobe/Probe.html

Microanalysis Software

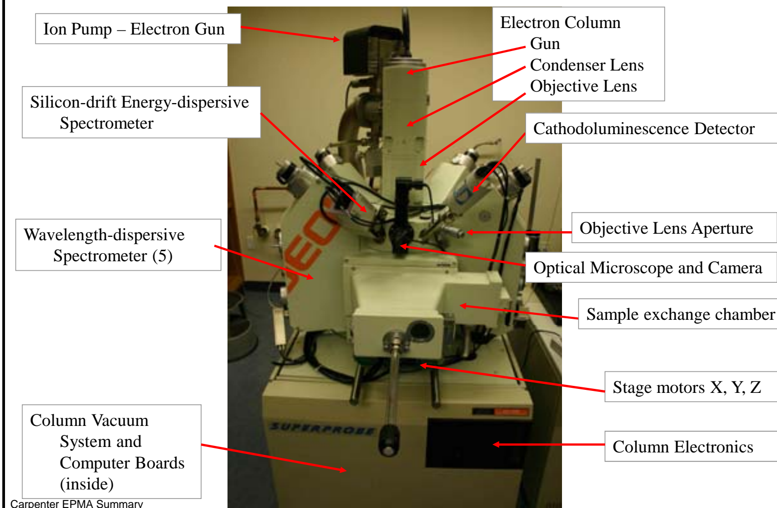
- Casino – Monte Carlo simulation program for electron scattering and x-ray Φ(ρz) distributions.
  http://www.gel.usherbrooke.ca/casino
- CalcZAF– A collection of ZAF and Φ(ρz) algorithms used to convert relative x-ray intensities to concentration. Based on CITZAF (Armstrong).
  http://epmalab.uoregon.edu/calczaf.htm
- TRYZAF – Version of CITZAF used to compare correction algorithms and data sets for given elements.
  http://www.cstl.nist.gov/div837/Division/outputs/software.htm
- GMR – Φ(ρz) thin-film correction program, includes contiuum fluorescence correction, used to calculate K or C for multilayer thin films on substrates.

EPMA Schematic Summary

- Sample: polished, conductive
- Focused electron beam ~ 5 nm
- Electron scattering (BSE)
- Characteristic x-ray excitation
  ~ 1 um analytical volume
- Generated vs. emitted x-rays
  x-ray absorption
- Comparison method
  k-ratio
- Correction for matrix effects: ZAF
  A X-ray absorption
  Z electron scattering
  F X-ray fluorescence



Electron Microprobe at Washington University



Summary of EPMA Procedure

- Sample prep and carbon coating
- Sample imaging and energy-dispersive analysis performed to generate base map and element list.
- Microprobe stabilized, software setup, elements and standards selected.
- Wavelength spectrometers peaked on standards and PHA settings confirmed.
- Standard count rates acquired on primary and secondary standards. Evaluate accuracy with secondary standards.
- Locations on samples identified using backscattered-electron imaging and energy-dispersive spectrometer, points digitized.
- X-ray measurements acquired on samples.
- ZAF (i.e., Φ(ρz)) corrections made on samples using assigned standards.
- Analyses inspected: total, stoichiometry, etc.
- Run finished, data dumped to Excel.

What Materials Are Analyzed by EPMA? Sample Requirements

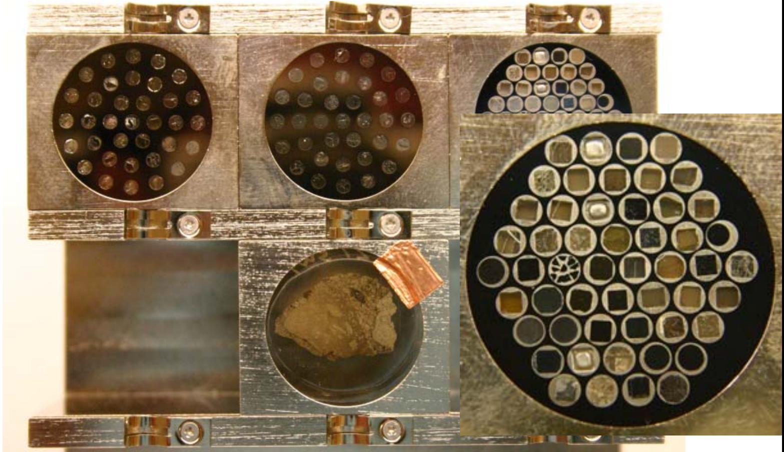
- Samples must be:
  Solid (EPMA does not include VP conditions)
  Polished flat (~0.25μm)
  Conductive or made so by evaporation of ~25 nm carbon
  Stable in vacuum and under electron beam bombardment
- Materials historically analyzed:
  Elements Be-U
  Inorganics, metals/alloys, ceramics, minerals, glasses
  Biological, pharmaceutical, organic, etc. if fixated/stabilized
- Bulk materials (homogeneous within scattering volume)
  Also particles, thin films/multilayers, rough surfaces, tilted
  All deviations from flat and normal to beam must be treated with specific modifications to correction algorithms

Sample Preparation Issues Polishing and Coating

- EPMA requires flat polished sample, usually mechanical polishing to ~0.25 um final polish.
- Biological materials other preparations methods, surface topography, results in differential x-ray absorption
- SEM imaging use Au or metal sputter coating or heavy metal fixation for high SEI emission.
  - Not preferred for microanalysis due to thickness variation
  - Vacuum ~10^{-3} Torr, thermal damage of biological matls.
- EPMA microanalysis use carbon high vacuum evaporation
  - Desire equal coat on samples and standards
  - Minimum x-ray absorption most x-rays (except Nitrogen)
  - Electron retardation affects overvoltage of energetic x-rays
  - Vacuum ~ 10^{-6} Torr, no thermal damage except radiant

High Vacuum Carbon Evaporator

Microprobe Sample Holder and Standard Mount



EPMA Summary
Matrix Effects
and
Quantitative EPMA

Summary of EPMA

- "Electron-probe microanalysis", EPMA, generically means:
  - Quantitative X-ray microanalysis using a focused electron beam
  - Wavelength-dispersive spectrometers (WDS)
  - Optical microscope for sample positioning
  - Energy-dispersive spectrometer (EDS), …*not standardless*
  - Stabilized electron column (gun shift, tilt, probe current stabilization)
- Characteristic x-rays measured on flat, polished (bulk) material at known x-ray takeoff angle to spectrometer. Elements Be-U at ~0.01-100 wt%
- Peak intensities background and deadtime corrected, precision
  σ = sqrt(N) for N number of counts.
- Comparative technique: Ratio of x-ray intensity on sample is made to same on standard ("k-ratio") using peak intensities with background subtracted:
  $k = (P\text{-}B)^{sample} / (P\text{-}B)^{standard}$
- Measured x-ray intensities are converted to concentration units via:
  $C_{sample} = C_{std}\, K * Z\, A\, F$, $K = (P\text{-}B)^{sample} / (P\text{-}B)^{standard}$
  The ZAF correction is iterative since it is a function of composition.
- Issues: sample volume, standards, background determination, secondary fluorescence, accuracy.

EPMA Summary: ZAF and X-ray Correction

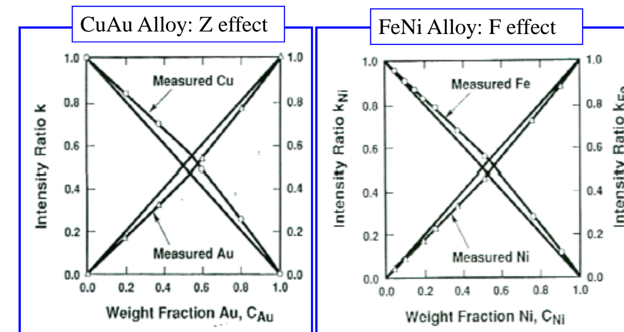
- The absorption factor A corrects for x-ray absorption.

> Beers Law absorption:
> $$\mathbf{I = I_0\, e^{(-\mu/\rho\ \rho s)}}$$
> I emitted X-ray intensity, I_0 generated X-ray intensity
> Path length ρs and mass absorption coefficient μ/ρ

- Absorption increases with MAC and path length (…TOA, keV)
  MACs Al absorber: Cu Lα 1452, Al Kα 402, Cu Kα 47
  MACs Cu absorber: Cu Lα 1590, Al Kα 4561, Cu Kα 50
- Absorption generally decreases with increasing X-ray energy, except at absorption edge of matrix element(s).
- Absorption occurs within all materials, sample and standard.
- This is the largest correction ~10% for typical materials.
  - AlCu alloy: Al Kα absorbed by Cu
  - NiFe alloy: Ni Kα absorbed by Fe
    - Fe Kα fluoresced by Ni Kα
- We measure ***Emitted*** intensity (I) but ***Generated*** (I_0) intensity is required for quantitative correction.
- Need to know generated intensity, unseen, unmeasured.
  …Fundamental reliance on algorithms and data sets

EPMA Summary: ZAF and X-ray Correction

- "Matrix effects": All elements influence electron scattering/retardation, x-ray generation, absorption, and fluorescence of the element of interest, i:
  $C_i = k_i * ZAF$ where ZAF is effect of C_j elements on C_i



EPMA Summary: ZAF and X-ray Correction

- Matrix effects arise because each element present in the analytical volume influences x-ray generation and propagation of every other element:
  - C_i is a function of all C_j elements
  - $C_i = k_i * ZAF$ where ZAF is effect of C_j elements on C_i
- Z: atomic number factor Z corrects for differences in
  - (S) stopping power, i.e., electron retardation
  - (R) electron backscattering

  …between the sample and standard.
  - Example: Al Kα in Al_3Cu_{97} with avg. Z = 28.8
  - vs. pure element standards: Al Z = 13, Cu Z = 29
  - Expect large Z correction when matls. differ in atomic number
- A: absorption factor A corrects for x-ray absorption within both the sample and standard. This is the largest correction parameter, and is critically dependent on accelerating voltage
  - Examples: Ni Kα absorbed by Fe, Al Kα abs by Cu

EPMA Summary: ZAF and X-ray Correction

- Z: atomic number factor Z corrects for differential (S) stopping power and (R) backscattering between the sample and standard.
  - Example: Al Kα in Al_3Cu_{97} with avg. Z = 28.8
  - vs. pure element standards: Al Z = 13, Cu Z = 29
  - Large Z correction when large difference in Z
- Note that R/S compensates so Z factor is not typically large
- ZAF factors typically presented as multiplicative factors

CalcZAF Results for Al_3Cu_{97} Sample (also shows large A correction for Al Kα)
calculated at 15 keV and 40 degree takeoff angle:

	A	F	Z	ZAF	S	R			
ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(x)u	Ec	Eo/Ec
Cu ka	1.0000	1.0000	1.0024	1.0024	1.0032	.9992	.9899	8.9790	1.6706
Al ka	2.5365	1.0000	.8904	2.2586	.7872	1.1311	.3498	1.5600	9.6154

ELEMENT	K-RAW	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	FORMULA	KILOVOL
Cu ka	.00000	.98471	98.704	-----	97.000	.970	15.00
Al ka	.00000	.00574	1.296	-----	3.000	.030	15.00
TOTAL:			100.000	-----	100.000	1.000	

C = k * ZAF, for Al: C = 0.00574 * 2.2586 = 0.01296 * 100% = 1.296 wt%

EPMA Summary: ZAF and X-ray Correction

- NiFe Alloy, example of (A) absorption and (F) characteristic fluorecence
  - Ni Kα absorbed by Fe, note MAC value 362
  - Fe Kα fluoresced by Ni Kα, note F value 0.78

Current Mass Absorption Coefficients From Henke (LBL, 1985) < 10KeV / CITZMU > 10KeV

Z-LINE	X-RAY	Z-ABSOR	MAC
Ni	ka	Ni	57.8
Ni	ka	Fe	362.3
Fe	ka	Ni	89.3
Fe	ka	Fe	68.3

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(x)u	Ec	Eo/Ec
Ni ka	1.0060	1.0000	.9987	1.0047	.9994	.9993	.9824	8.3330	1.8001
Fe ka	1.0039	.7768	1.0135	.7903	1.0056	1.0079	.9808	7.1120	2.1091

ELEMENT	K-RAW	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	FORMULA	KILOVOL
Ni ka	.00000	.90021	90.441	-----	90.000	.900	15.00
Fe ka	.00000	.12095	9.559	-----	10.000	.100	15.00
TOTAL:			100.000	-----	100.000	1.000	

EPMA Summary
Electron-Specimen Interactions
and
Generation and Emission of X-rays

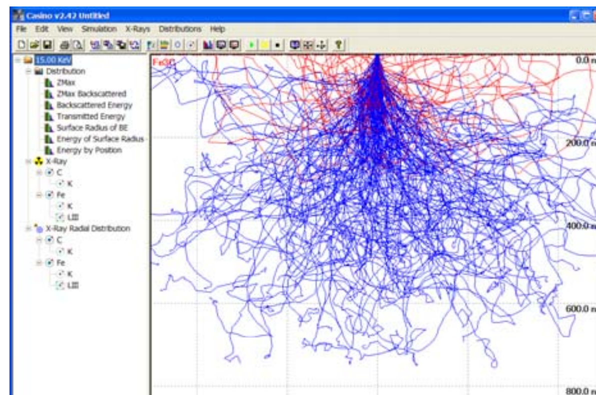
Resolution in EPMA

- There are two aspects to “resolution” in EPMA:
- Electron scattering and the emission of secondary and backscattered electrons govern the SEI and BSE image signals
- The scattering volume is a function of average atomic number Zavg
- The x-ray generation “volume” is a contoured volume depending on the excitation energy Ec for a given x-ray line
- Compare Cu Ka and Al Ka in an AlCu alloy

Monte Carlo Modeling

- Monte Carlo simulations model electron-specimen interactions and x-ray production in the specimen.
- Electron scattering, slowing down, backscattering, x-ray production, etc. are all modeled using random number generation and random electron scattering directions.
- Good agreement is observed between Monte Carlo data and experimental measurements.
- This agreement is evidence of the accuracy of quantitative analysis algorithms.

Casino Monte Carlo Program

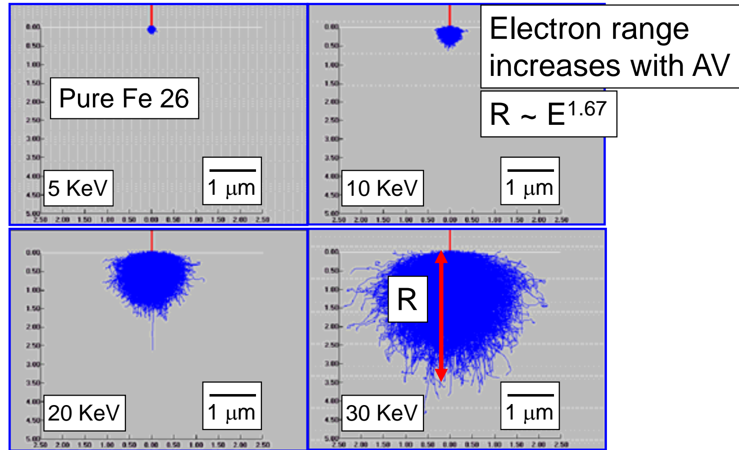


Simulation Fe_3C, 15 keV, 5000 trajectories, max depth ~750nm
Red = backscattered e-, blue e- within Fe_3C.
Scattering angle increases as e- energy decreases (curly trajectory)

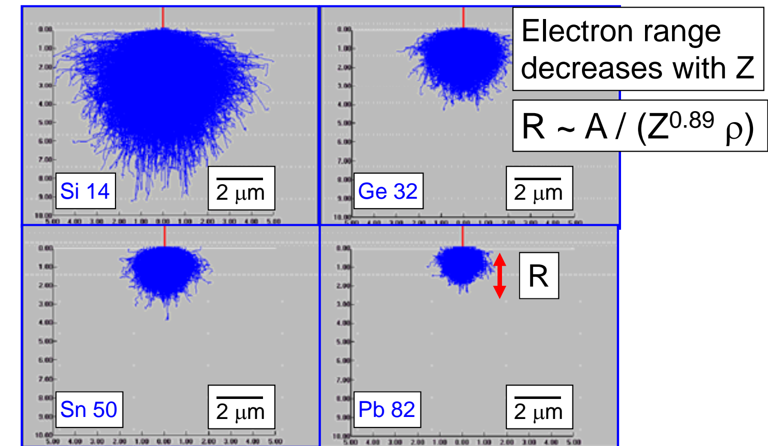
Monte Carlo Software – Casino, DTSA II

- Casino:
  Scattering volume
  $\Phi(\rho z)$ curves for generated vs. emitted X-rays (K vs. L-lines)
  Electron data, e.g. BSE energy distribution for Al vs. Au targets
  Bulk vs. Layer geometry or grain boundary
- DTSA-II
  EDS spectrum simulation: Experimental vs. Calc Spectra
  Monte Carlo vs. Algorithmic X-ray simulation
  Powerful scripting capabilities: Comp, Geometry, Structure

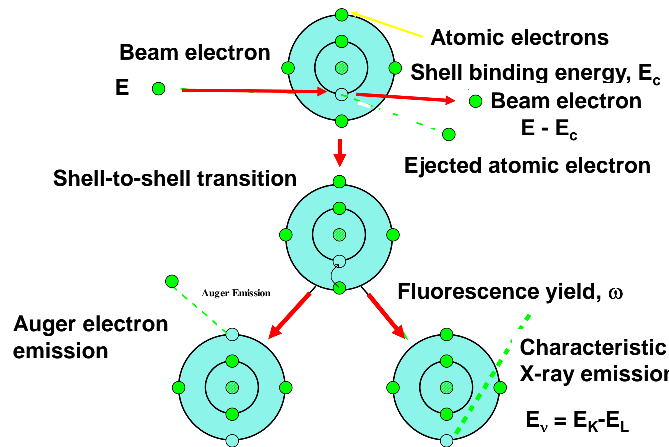
Monte Carlo Simulation
Effect of Varying Accelerating Voltage



Monte Carlo Simulation
Effect of Varying Atomic Number Z @ 25 keV



The Physics Underlying the Spectrometries



Families of X-rays

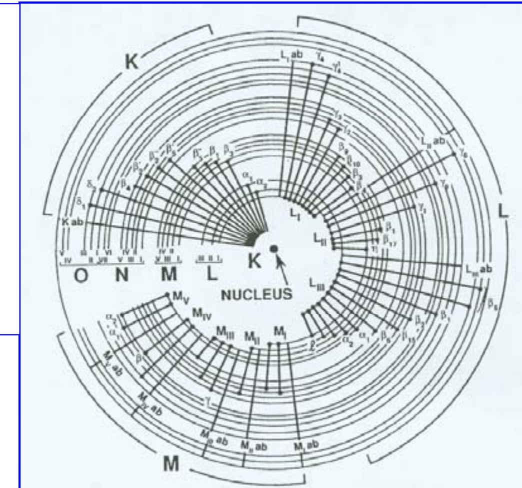
X-ray Spectra

Many ionization vacancy-filling possibilities from complex atoms lead to creation of families of X-ray lines, e.g.,

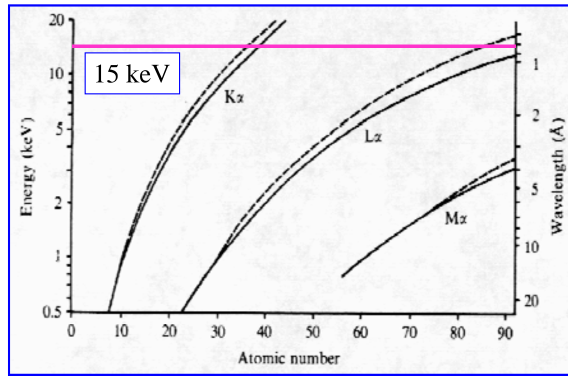
Kα-Kβ

Lα-Lβ-Lγ-Lη-Ll

Mα-Mβ-Mγ-Mζ-$M_{II}N_{IV}$

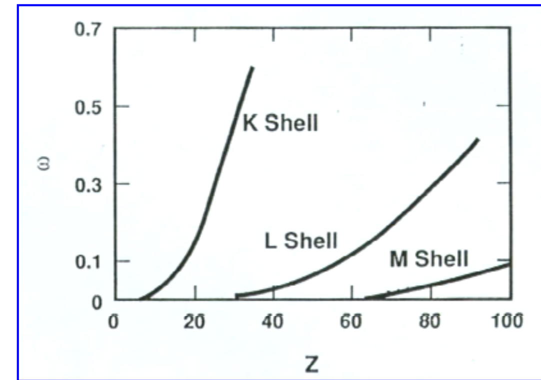


Characteristic X-ray Energy vs. Z



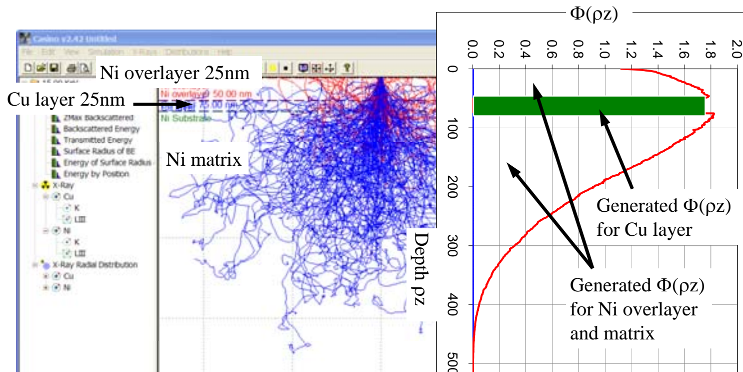
X-ray peak energy solid lines
Excitation energy dashed lines
At 15 keV at least one line can be excited for all Z

Fluorescence Yield ω vs. Z



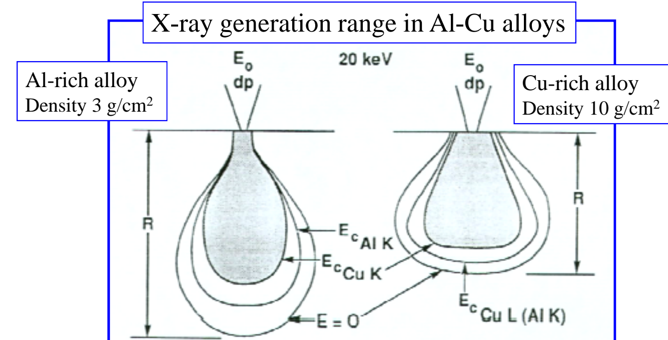
ω = fraction of ionizations resulting in characteristic x-ray emission relative to total number of ionizations, and 1-ω is the fraction of auger electrons.

Casino MC Simulation of Φ(ρz) Experiment



The Φ(ρz) distribution for Cu Kα is obtained from the emitted intensity of a layer of Cu sandwiched in a matrix with similar Z (Ni) so that scattering properties are similar. Measurements are made for progressively buried layers.
This intensity is scaled relative to that from an isolated Cu foil to yield the Φ(ρz) curve.
The curves are then generalized to model x-ray behavior for elements in general.

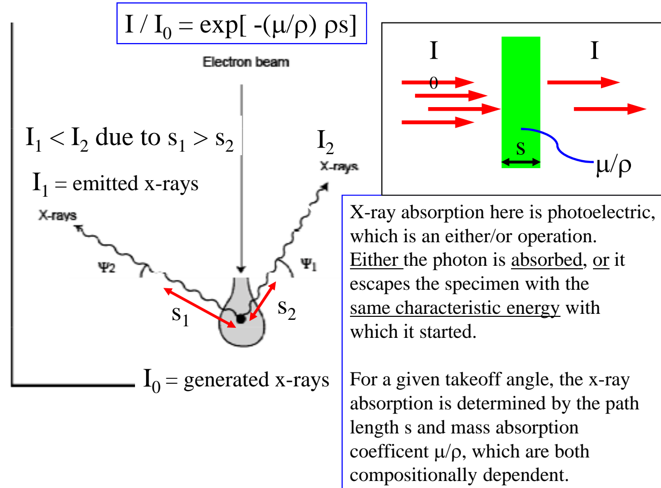
Range of Characteristic X-ray Production



The depth distribution of primary x-ray generation depends on Z_{avg} and the relative excitation energies E_c of the elements in the sample:
Al Kα E_c = 1.559 keV generated in larger volume E > 1.559 keV
Cu Kα E_c = 8.98 keV, generated in small volume E > 8.98 keV

X-ray absorption depends on path length and μ/ρ

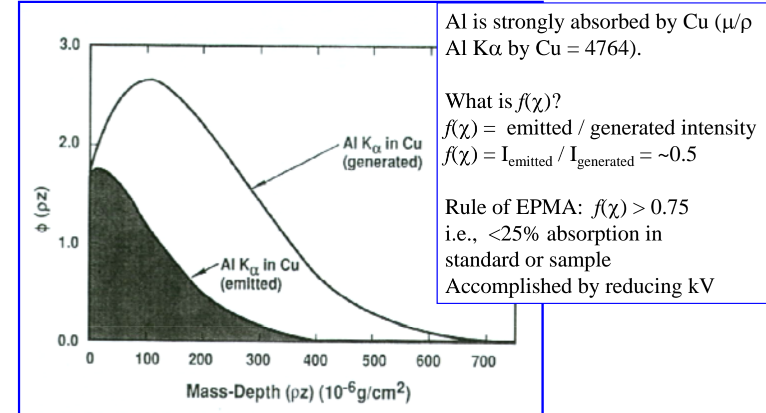
$I / I_0 = \exp[-(\mu/\rho)\rho s]$



X-ray absorption here is photoelectric, which is an either/or operation. Either the photon is absorbed, or it escapes the specimen with the same characteristic energy with which it started.

For a given takeoff angle, the x-ray absorption is determined by the path length s and mass absorption coefficent μ/ρ, which are both compositionally dependent.

Effect of X-ray Absorption: Trace Al in Cu @ 20 keV



Al is strongly absorbed by Cu (μ/ρ Al Kα by Cu = 4764).

What is $f(\chi)$?
$f(\chi)$ = emitted / generated intensity
$f(\chi) = I_{emitted} / I_{generated}$ = ~0.5

Rule of EPMA: $f(\chi) > 0.75$
i.e., <25% absorption in standard or sample
Accomplished by reducing kV

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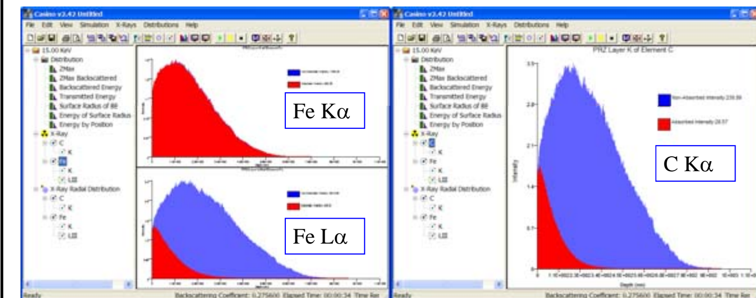
Casino $\Phi(\rho z)$ Curves Calculated for Fe_3C



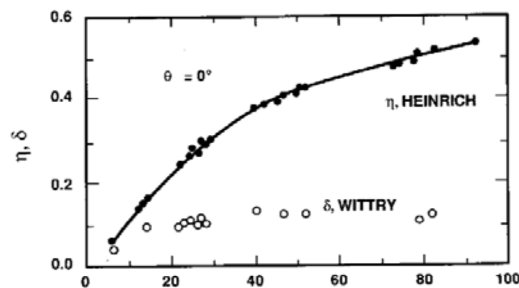
Casino Monte Carlo calculated $\Phi(\rho z)$ curves
Generated x-ray distribution in blue, Emitted x-ray distribution in red
These intensities can be used to calculate k-ratios and compared with k-ratios from experimental and $\Phi(\rho z)$ algorithms

Backscattered Electron Imaging
and
X-ray Mapping

Contrast Mechanism

- Changes in the signal(s) ("Contrast") collected at different points in the image convey information about specimen characteristics.
- Whenever a signal changes in a predictable way as a function of specimen properties, we have the basis for a contrast mechanism.
- Example: η vs. Z is monotonic and predictable. This forms the basis for atomic number (compositional) contrast.

Backscattered Electron Dependence on Z Atomic Number



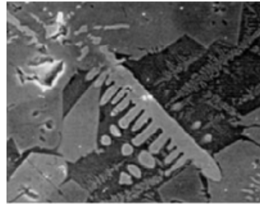
Backscattered electrons: primary beam electrons scattered at high angles by the nucleus of atoms in the sample. The fraction of BSE is eta and is a function of atomic number Z for pure elements and average Z for compounds. The BSE signal is used for mineral ID.

Secondary electrons are emitted from the valence shell of atoms and are not sensitive to the Z of the material, so are not useful for identifying phases

Mean Atomic Number of Minerals

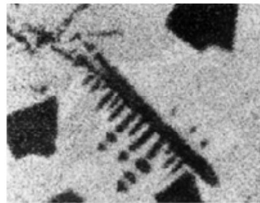
- Mean Z can be easily calculated (CalcZAF, for example)
- Typical range is ~ 10 – 20. Atomic number correction is limited if appropriate standards are used.
- Silicates
  Forsterite 10.6 Albite 10.7 Pyrope 10.7
  Fayalite 18.7 Anorthite 11.9 Almandine 15.6
- Oxides
  Periclase 10.4 Spinel 10.6 Quartz 10.8
  Ilmenite 19.0 Ulvospinel 20.0 Magnetite 21.0
- Sulfides
  Pyrite 20.7 Chalcocite 26.4 Galena 73.2
- Carbonates
  Dolomite 8.9 Calcite 12.4 Siderite 16.5 Cerussite 65.3
- Misc
  Apatite 14.1 Allanite 22.0 Zircon 24.8 Monazite 38.7
- See SJB Reed Electron Microprobe Analysis and Scanning Electron Microscopy in Geology ISBN 0521483506 (paperback)

Image Signals from Metallographic Sample



Secondary electron

Backscattered electron



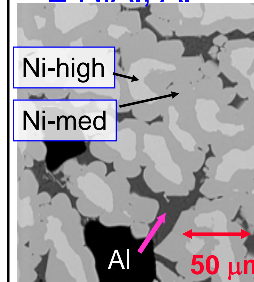
Silicon x-ray

Aluminum x-ray

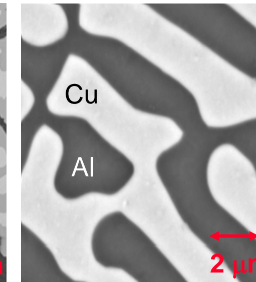
20 kV 1100x, JEOL

Atomic Number Contrast

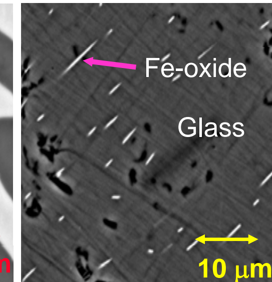
Raney Ni-Al
2 NiAl, Al



Al-Cu eutectic



Obsidian

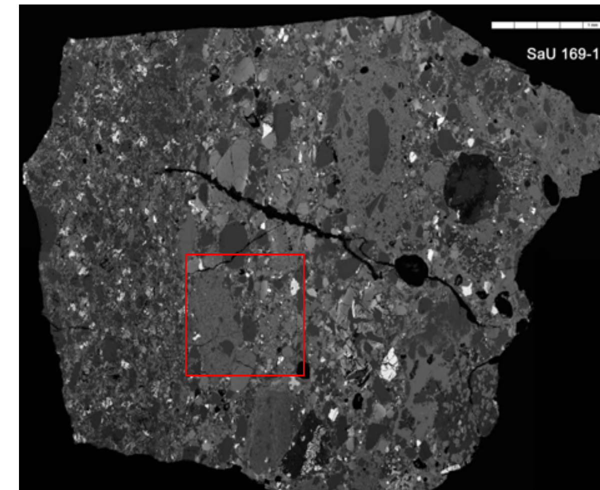


Backscattered-electrons provide a rapid and simple means to image differences in chemistry in the sample, via the dependence on average atomic number.

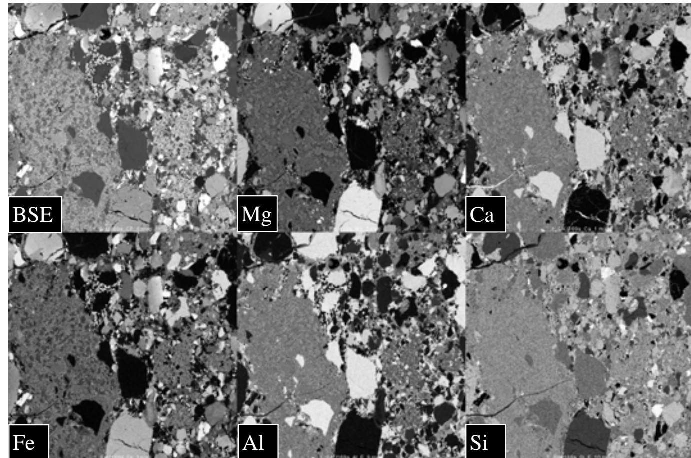
Compositional Mapping

- Normal x-ray mapping is performed by setting up an energy region of interest (ROI) in the EDS spectrum. All x-rays falling in that ROI are assigned to the digital map for that element.
- Drawback is each map has only information for that element and can not be used to perform quantitative analysis. X-rays from other elements also may be counted in the ROI – peak overlaps, continuum x-rays, etc.
- Sophisticated mathematical approaches have been used in recent years to process x-ray map data. These involve correlation between elements, but also correlation between groups of elements.
- Examples of these approaches are Concentration Histogram Imaging and Principle Component Analysis.
- Spectrum Imaging is a mapping technique where the entire EDS spectrum is saved at each pixel location and is available for processing after the run.

Lunar Meteorite SaU 169 BSE Mosaic



Lunar Meteorite SaU 169 SDD X-ray Maps



EPMA Summary
Wavelength-Dispersive Spectrometery

Carpenter EPMA Summary

WDS Anatomy

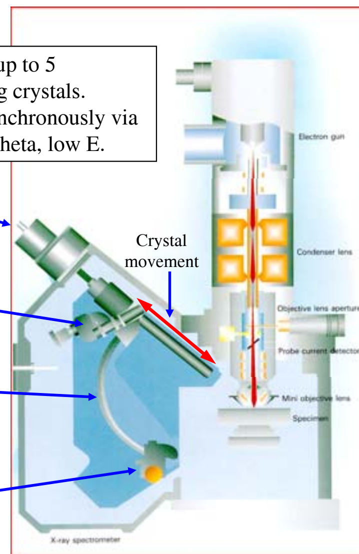
An electron microprobe typically has up to 5 spectrometers each with 1-4 diffracting crystals. The crystal and detector are moved synchronously via the drive motor. Position here is high theta, low E.

Spectrometer drive motor w/ vacuum feedthrough

Crystals w/ flipping motor

Mechanical alignment track

Proportional X-ray counter



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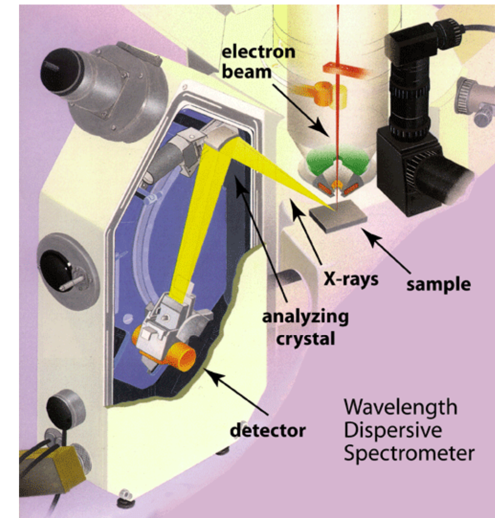
WDS Schematic JEOL Electron Microprobe



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WDS Spectrometer Units

- Bragg diffraction equation
  including index of refraction term:
  $n\lambda = 2d \sin\theta\,(1 - k/n^2)$
  - n = diffraction order, λ = wavelength
  - d = d-spacing of analyzing crystal
  - θ = diffraction angle, k = refraction factor
- Cameca: $\sin\theta = n\lambda\,(1 - k/n^2)\ /\ 2d$
- For JEOL instruments:
  $n\lambda/2d = \sin\theta = L/2R$ where R is rowland radius
  $L = (R/d)\, n\lambda$, L value in mm

JEOL: $L = (R/d)\, n\lambda\,(1 - k/n^2)$

$$E = \frac{12.3985}{\lambda(Angstroms)}(\text{keV})$$

L-Value X-ray Peak Positions for JEOL Microprobe

L-Value Table

Principle of X-ray Spectrometry

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

$L = \frac{R}{d} n\lambda$

JEOL

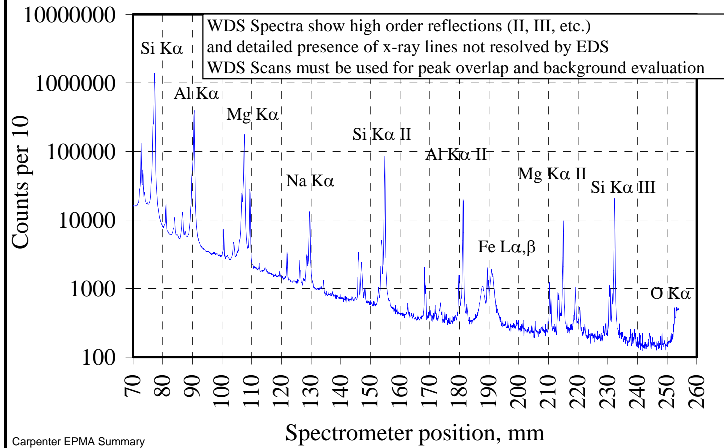
Diffracting Crystal Element Ranges

	2d (nm)	6 C · 14 Si · 22 Ti · 30 Zn · 38 Sr · 46 Pd · 54 Xe · 62 Sm · 70 Yb · 78 Pt · 86 Rn
TAP	2.576	8O – 15P; 24Cr – 41Nb; 46Pd – 79Au
TAPH	2.576	9F – 13Al; 24Cr – 35Br; 47Ag – 70Yb
PET	0.8742	13Al – 25Mn; 36Kr – 65Tb; 70Yb –
PETH	0.8742	14Si – 22Ti; 37Rb – 56Ba; 72Hf –
LIF	0.4027	19K – 37Rb; 48Cd –
LIFH	0.4027	20Ca – 31Ga; 50Sn – 79Au

Mg Kα peak using TAP crystal on Kakanui Hornblende

WDS Wavelength Scan

TAP Spec 2 25 KV 300 nA 70 - 266 mm 10 sec per point 0.1 / .09 mm step



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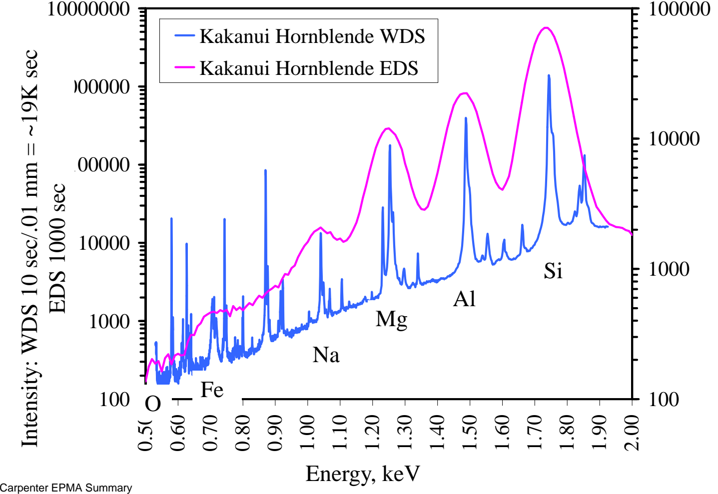
WDS and EDS Comparison: Kakanui Hornblende WDS TAP GFC, SiLi EDS, Energy Scale



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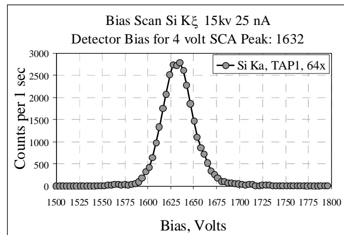
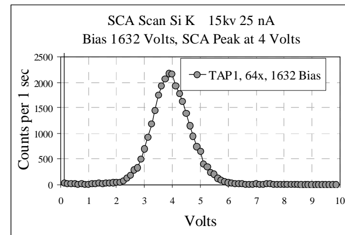
Pulse-height Analysis: WDS





Detector bias scan for Si Ka using 3.9 volt baseline and 0.2 volt window. The bias scan is used to set the detector bias necessary to achieve a 4 volt pulse on an SCA scan (from 0-10 Volts). Bias scans are typically performed in the 1500-1800 Volt range, which is the plateau region of the x-ray detector. This is for uniform application of detector gain and consistent detector deadtime behavior.

SCA (single channel analyzer) scan over detector voltages produced by entry of Si Ka photons into the gas-flow counter when the WDS is set to the Si Ka peak position. The detector bias is set to the value determined in the bias scan, which ensures that the SCA pulse is at the nominal value (here 4 Volts). An SCA scan is typically performed over the range 0-10 Volts. This uniform application of detector gain enables the use of uniform baseline and window values, and also minimizes the effect of gain variations on deadtime. Note the baseline noise below 0.25 Volts. At high count rates the pulse will shift to lower values and will eventually merge into the baseline due to inability of the counting electronics to resolve the pulse energy. For this reason it is important to monitor the bias and SCA voltage values used for an element.

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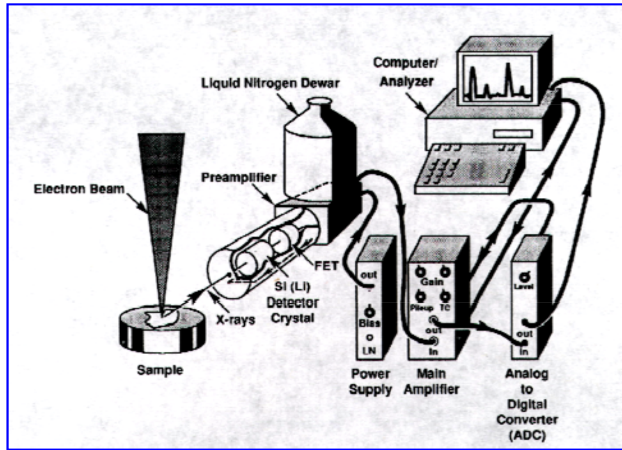
EPMA Summary
Energy-Dispersive Spectrometry
Silicon Drift EDS Detectors
Cathodoluminescence

EDS Analyzer System



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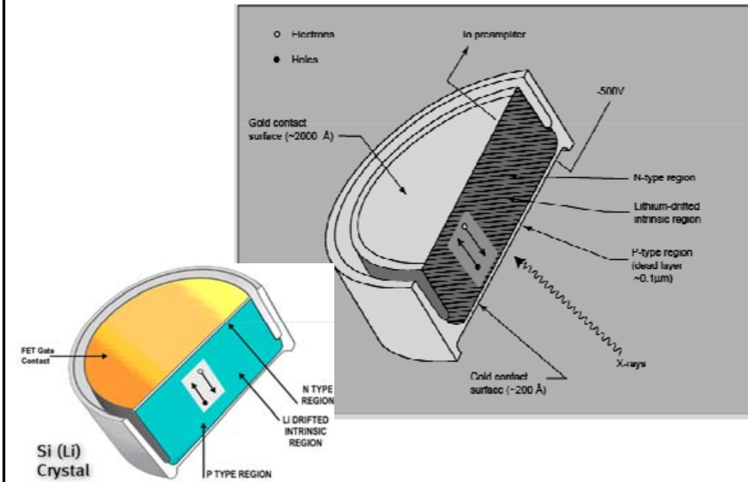
Conventional SiLi EDS Detector



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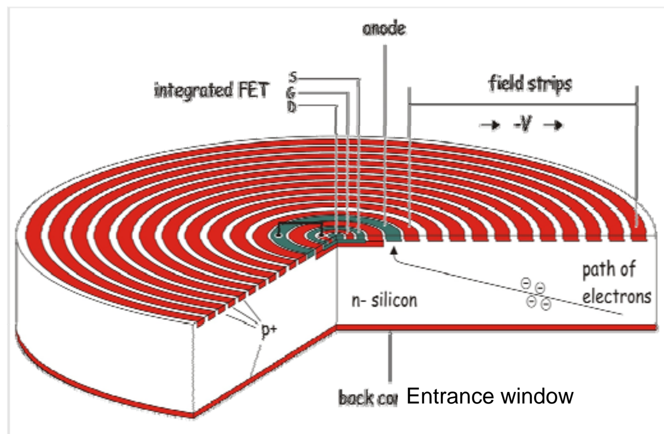
Silicon Drift Detector



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Washington University
Earth and Planetary Sciences JEOL JXA-8200

JEOL e2v Silicon Drift Detector
130 eV resolution
3 time constants T3 T2 T1
Stage and beam mapping
Quantitative EDS analysis LLSQ

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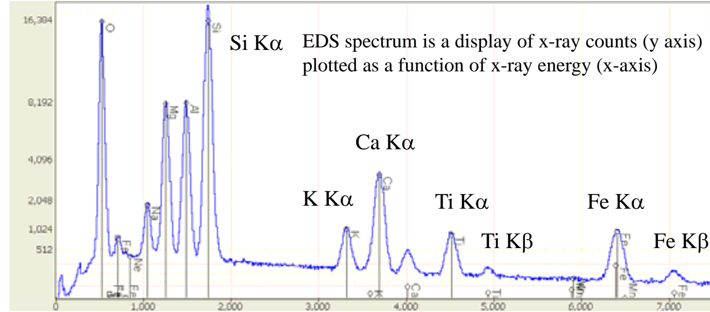
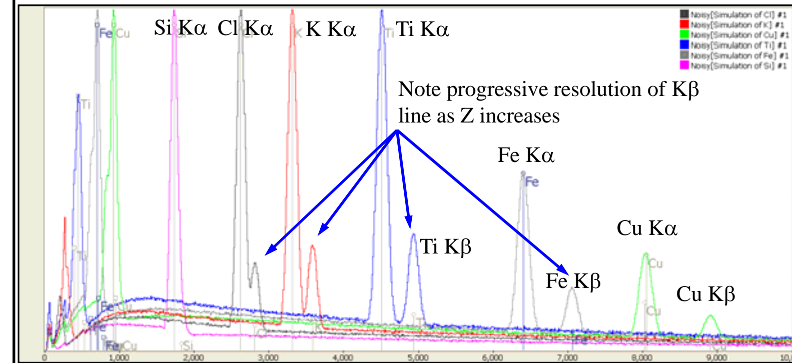
Kakanui Hornblende EDS X-ray Spectrum Generated Using DTSA-II



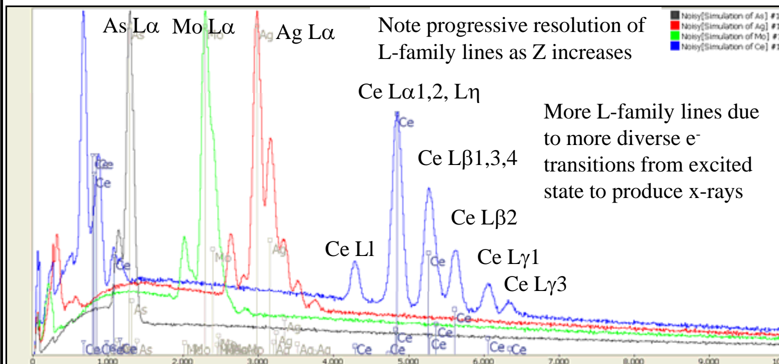
The EDS spectrum has **characteristic** x-ray peaks produced by specific transitions from the atom's excited state that are specific to each element. These characteristic peaks are superimposed on **continuum** ("Bremsstralung") produced by decelerating electrons.
The EDS spectrum is used for routine identification of phases and for analysis.
Note increasing energy resolution with increasing x-ray energy (Si vs. Fe)
Peak overlaps (Na-Si Ka peaks, and n-1 element Kβ peak on n element Kα (K, Ca)

K-Family X-ray Spectra (EDS) Generated Spectra Using DTSA-II, E_0 = 15 keV



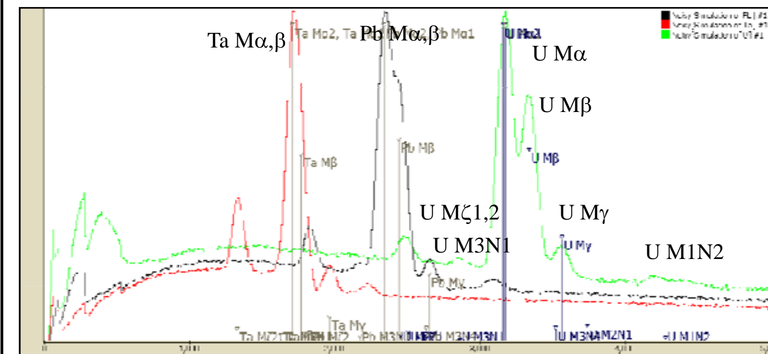
Also note appearance of L-family lines as Z increases

L-Family X-ray Spectra (EDS) Generated Using DTSA-II, E_0 = 15 keV



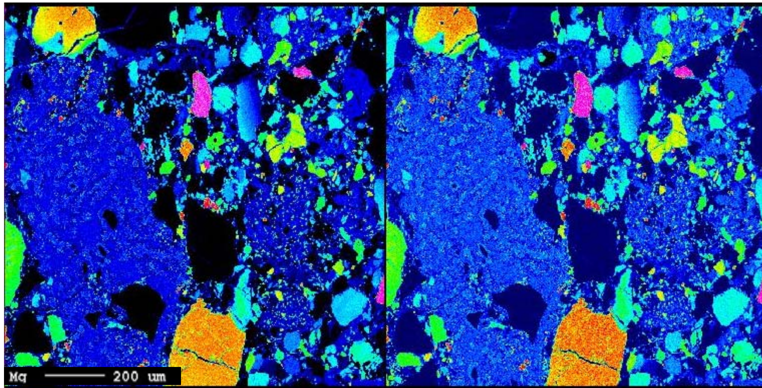
Also note appearance of M-family lines as Z increases

M-Family X-ray Spectra (EDS) Generated Using DTSA-II, E_0 = 15 keV



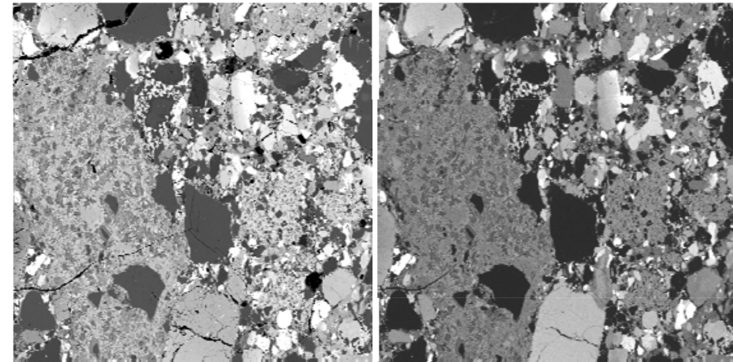
Note progressive resolution of M-family lines as Z increases

JEOL 8200 Stage Maps: Lunar Meteorite SAU169 WDS vs. SDD Mg @ 15KV, 120nA, 25ms dwell



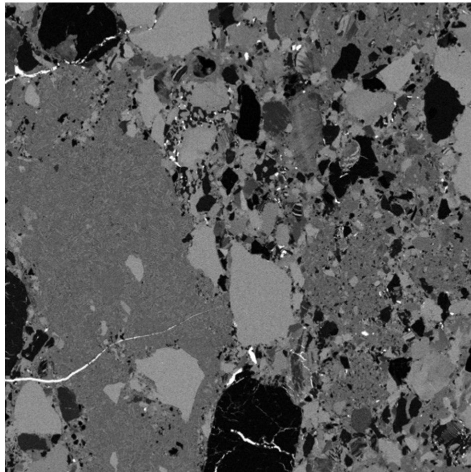
Mg WDS 1061 max counts, Mg SDD 527 max counts
1024x1024 stage map, 8 hours

Lunar Meteorite SAU169 Stage map 1024x1024, 25 ms, 8 hr run



Backscattered electron vs. Fe SDD maps

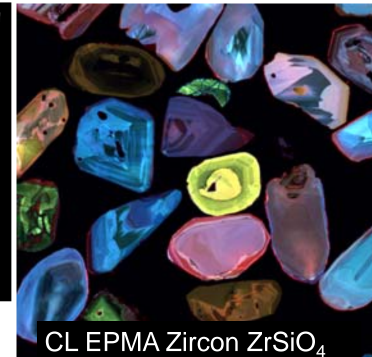
Lunar Meteorite SAU169 Stage map 1024x1024, 25 ms, 8 hr run: Ca Kα SDD



Cathodoluminescence Advances

Luminoscope CL image of typical single Crystal Diamond, South Africa

HFW ~3 mm (courtesy of S. Shirey)

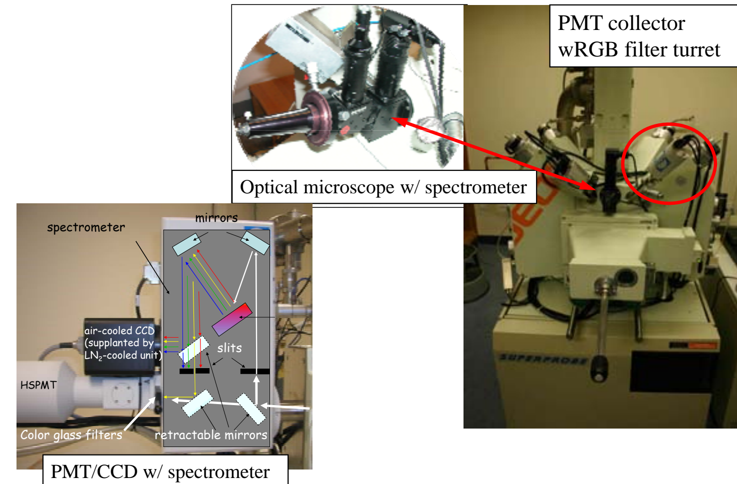


CL EPMA Zircon $ZrSiO_4$

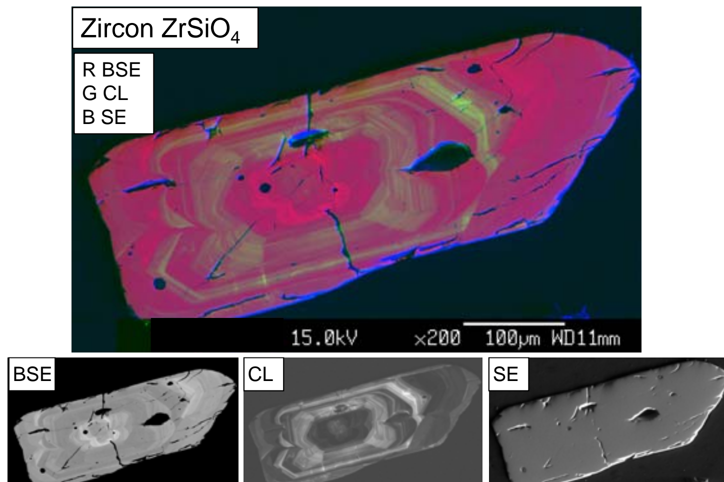
Cathodoluminescence

- CL is the emission of photons in the visible light region resulting from electron bombardment; EPMA with focused beam is excellent for CL
- The spectroscopy and interpretation of CL are complex
- CL is produced by defects (semiconductors) and/or trace elements (minerals)
- Activation can be produced by trace elements at ppb-ppm concentrations, well below nominal EPMA sensitivity (bse, x-ray)
- Minerals: activation by Mn, REE, etc., quenched at high concentration and by Fe
- CL collected by photomultiplier, parabolic mirror, fiber optic/grating systems
- Total CL signal vs. spectral and hyperspectral data collection
- Quantification requires spectrum peak deconvolution

Types of EPMA CL systems



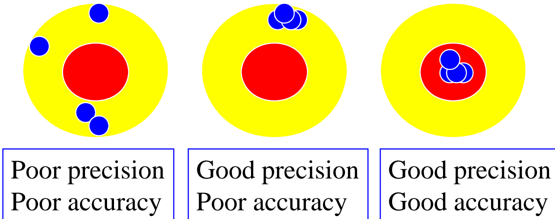
Combined CL, BSE, SE Images in Zircon



EPMA Summary
Precision and Accuracy
in
Microanalysis

Precision vs. Accuracy

- Precision is the reproducibility of replicate measurements. High precision means reproducible. Target practice: grouping of impact points.
- Accuracy is the correctness of the measurement. Target practice: proximity to bullseye.

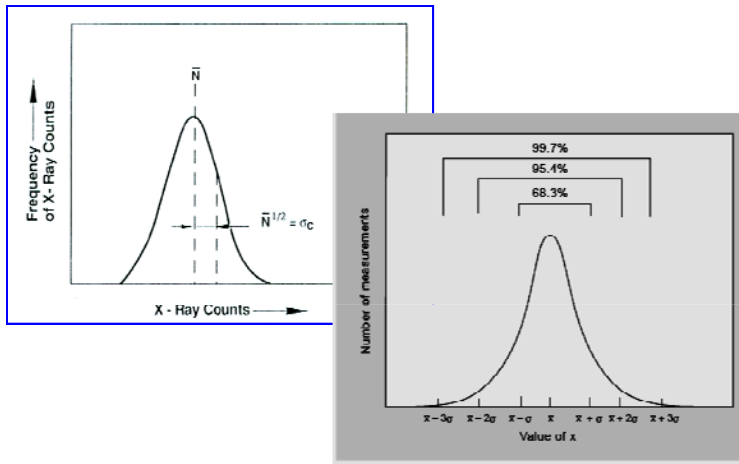


What is the Precision of Analysis?

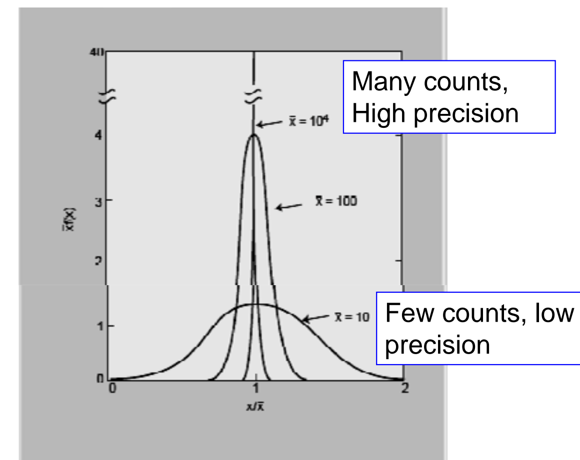
- Precision is the reproducibility of a measurement, which accuracy is the degree of correctness of a measurement.
- X-ray production is statistical, and counting experiments yield a gaussian distribution of counts for which the standard deviation σ_c is the square root of the mean of the counts N_m:

  $\sigma_c = (N_m)^{1/2}$
- σ_c is 1-sigma (67% confidence level), multiply by 2 for 2-sigma (97%), by 3 for 3-sigma (99%).
- Without drift or other instrumental instabilities, the precision of the measurement is determined by the number of x-rays counted.
- In the case of EDS, the relatively poor P/B makes it unclear as to what is the “peak” and what is the “background”. Counts are obtained from the fitting procedure. Peak channel has highest P/B and is not the whole story.

Counting Statistics—Gaussian Distribution



Relative Precision as a Function of Number of X-rays Counted



Precision of X-ray Counting

Counts N_m	σ_c	$\sigma_c / N_m * 100$ (relative percent)
100	10	10 %
1000	31.62	3.16 %
10,000	100	1.0 %
100,000	316.2	0.316 %
1,000,000	1000	0.1 %

Actual Standard Deviation

- The actual standard deviation of a set of measurements is the sum of the standard deviation due to counting statistics alone, plus the actual variation of an element in a sample, plus any other factors that cause variation (drift, for example):

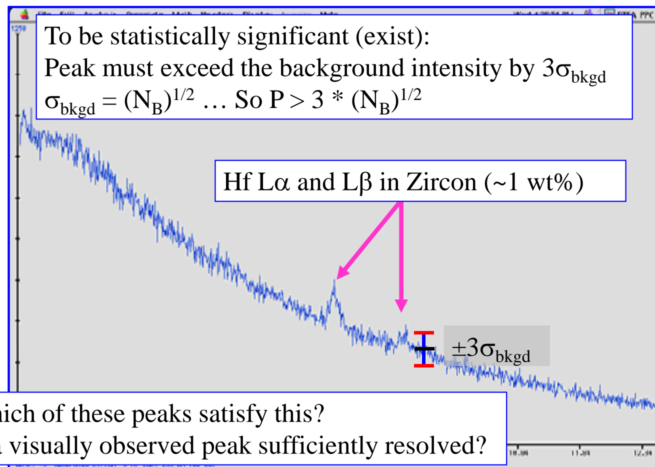
  $\sigma_{Total} = \sigma_{\text{count stats}} + \sigma_{actual} + \sigma_{drift} + \ldots$

- The actual standard deviation is:

$$S_c = \left[\sum_{i=1}^{n} \frac{(N_i - \overline{N}_i)^2}{(n-1)} \right]^{1/2}$$

  where n is the number of measurements and N bar is the mean.

Are These Peaks Real?



Detection Limit

- An element is present when the peak exceeds 3 times the standard deviation of the background intensity measured at the peak position. This is a statistical approach, 3 σ is 99% of the background variation and any counts outside of that range must be a "peak".

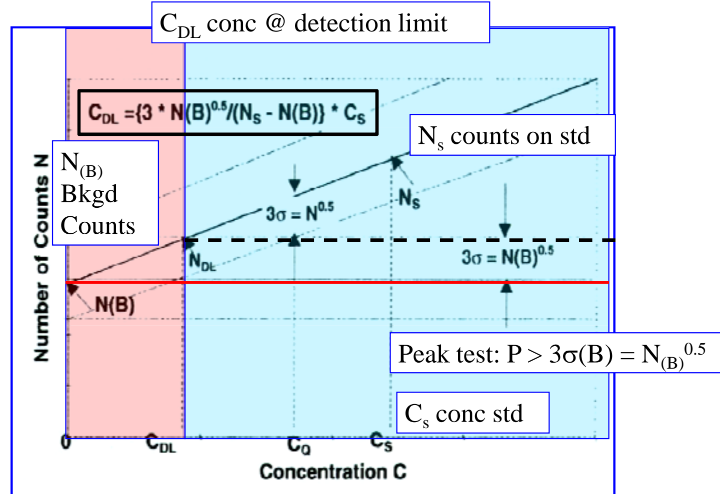
  $N_p > 3(N_b)^{1/2}$, Np is peak, Nb is background

- A convenient formula for calculation of detection limit is that of Ziebold (1967):

$$C_{DL} \geq \frac{3.29a}{(ntP \cdot P/B)^{1/2}}$$

  where t is the time of measurement, n is # of repetitions, P is count rate on pure element, P/B is peak-to-background of pure element, and a is the c/k factor (i.e. ZAF). P^2/B is the figure of merit.

Detection Limit



Detection Limit EDS vs. WDS

Table 9.17. Comparison of the Minimum Detectability Limit of Various Elements Using an EDS and WDS Detection System on the Basis of Optimized Operating Conditions[a]

Analysis	Element	P (cps)	B (cps)	P/B	Wet chem. (wt %)	C_{DL} (wt %)
EDS	Na *Kα*	32.2	11.5	2.8	3.97	0.195
	Mg *Kα*	111.6	17.3	6.4	7.30	0.102
	Al *Kα*	103.9	18.2	5.7	4.67	0.069
	Si *Kα*	623.5	27.3	22.8	26.69	0.072
	Ca *Kα*	169.5	19.9	8.5	12.03	0.085
WDS	Na *Kα*	549	6.6	83	3.97	0.021
	Mg *Kα*	2183	8.9	135	7.30	0.012
	Al *Kα*	2063	16.1	128	4.67	0.008
	Si *Kα*	13390	37.0	362	26.69	0.009
	Ca *Kα*	2415	8.2	295	12.03	0.009

[a] Geller (1977). Analysis of D1-JD-35: EDS data collected at 2000 cps for 180 s, dead-time corrected (25%) (1.75 nA probe current at 15 keV); WDS data collected for 30 s for each element; 180 s total analysis time (30 nA probe current at 15 keV).

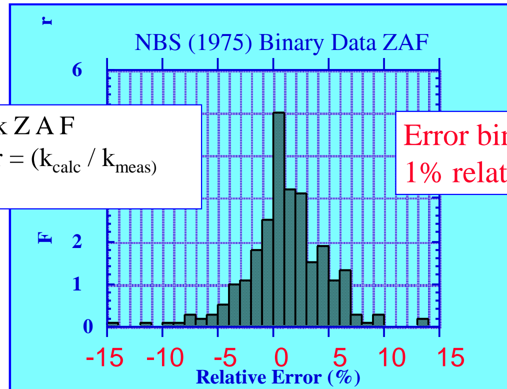
What is the Accuracy of Microanalysis?

- Precision is determined by the total number of x-rays counted for a given element. In general, measurements are made to better precision than accuracy warrants.
- Do not confuse precision with accuracy: replication of measurements does not tell you anything about the accuracy.
- Accuracy is dependent on all aspects of measurement:
  Standards—how well characterized are the compositions?
  Measurement process—systematic errors (takeoff angle?) instrument stable? Same conditions for std and smp?
  Peak fitting procedure—calibration differences sample vs. standard, other artifacts of peak stripping?
  X-ray correction algorithms and data sets—how accurate are the calculated results given “perfect” measurements?
- There is no global “accuracy” for EPMA measurements!

How Can Accuracy Be Determined?

- Analysis of a secondary standard as an unknown, under the same conditions as sample measurement, allows determination of accuracy.
- Accuracy should be calculated from:
  %Rel Acc = 100 * (Meas – Accepted) / (Accepted)
  The sign is important + is high, - is low.
- Evaluation of experimental binary alloy data sets using different x-ray correction algorithms yields k_{corr} / k_{exp} histograms. But what if these data sets were used to develop the correction procedure? Is this a test?
- Critical evaluation of experimental data sets suggests that for the best measurements the accuracy is ~1-2%, and is probably limited by precision.
- For “problem” elements the accuracy may be much worse, perhaps 5-10-20-50-100% !! Depends on concentration too.

Error Distribution for Matrix Corrections with ZAF/Standards (Pure Elements,Binary Compounds)

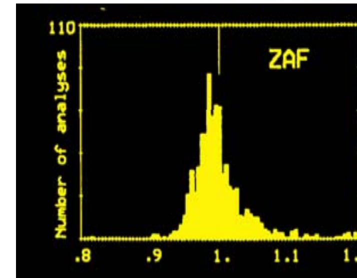


$C = C_{std}$ k Z A F
Rel Error = (k_{calc} / k_{meas}) *100

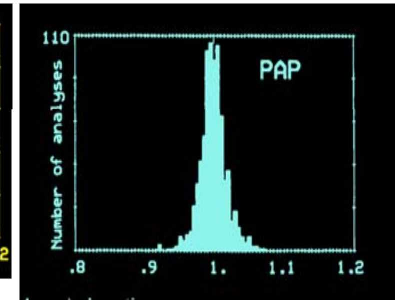
Error bins are 1% relative wide

This distribution has σ = 2.5%. 95% of analyses are expected to lie within ±5% relative of the correct value.

What If the Φ(ρZ)/standards Method Is Used Instead of ZAF/standards?



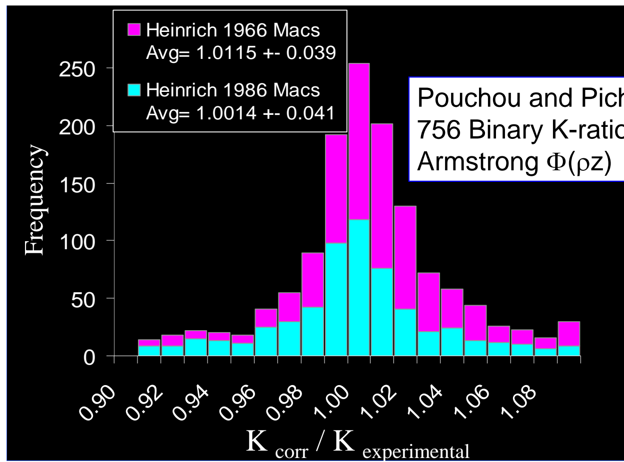
Conventional ZAF



Pouchou & Pichoir Φ(ρz)

The relative error distribution may be narrower yet!
The improvement depends on the particular elements.
Light element quantitation is particularly improved.

Heinrich 1966 vs. 1986 Mass Absorption Coefficients



Pouchou and Pichoir
756 Binary K-ratio
Armstrong Φ(ρz)