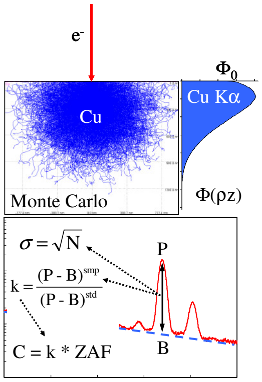
Everything You Always Wanted to Know About Electron-Probe Microanalysis (EPMA):

An Overview

Paul Carpenter
Earth and Planetary Sciences
CB1169
Washington University
1 Brookings Drive
St. Louis, MO 63130

paulc@levee.wustl.edu



Summary of EPMA

- Characteristic x-rays measured by WDS 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"):
  $k = (P\text{-}B)^{smp} / (P\text{-}B)^{std}$
- Iterative correction for atomic number (Z), x-ray absorption (A), and x-ray fluorescence (F) due to other elements on element of interest. Correction is function composition:
  C = k * ZAF, accuracy typically ≥ 2% relative
- Issues: sample volume, standards, background determination, secondary fluorescence, accuracy

EPMA Summary: ZAF and X-ray Correction

- Measured x-ray intensities are converted to concentration units via:
  $C_{sample} = C_{std}\, K * Z\, A\, F$, $K = (P\text{-}B)^{sample} / (P\text{-}B)^{standard}$
- Matrix effects arise because each element present in the analytical volume influences x-ray generation and propagation of every other element.
- The atomic number factor Z corrects for differences in the stopping power (S) and backscattering (R) between the sample and standard.
  Example: Al Kα in Al_3Cu_{97} vs. Al metal
- The 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
  Example: Ni Kα absorbed by Fe
- The fluorescence factor F corrects for characteristic x-ray fluorescence within the sample and standard.
  Example: Fe Kα fluoresced by Ni Kα

Summary of EPMA, cont.

- Analytical volume determined by e^- scattering, ~1µm, differs for x-rays of dissimilar energy.
- Best standards similar to sample to minimize ZAF correction. Lack of multielement standards a problem.
- Standardless elusive due to uncertainty calculating WDS efficiency.
- Automated analysis: spot, line, grid, map.
- Z-axis positioning of sample critical for WDS focus, use of optical microscope for positioning.
- EDS essential for ID of materials, mapping, quant.
- Technique provides complete analysis, limited by continuum background for trace elements.

Electron Microprobe Essential Characteristics

- Dedicated wavelength-dispersive spectrometers (WDS)
- Optical microscope coaxial with electron column, autofocus
- Stabilization of e- gun shift and tilt, feedback circuit
- Energy-dispersive spectrometer (EDS)
- Stage: multisample, non-tilting, large xy range
- Automation of vacuum, electron optic, stage, spectrometer
- Software system for imaging, quantitative analysis
- Electron gun: W, LaB6/CeB6, field emission
- Backscattered and secondary e- detectors
- Cathodoluminescence detector / spectrometer

Advances in EPMA

- Improvements in vacuum systems, computer automation/operating systems, electronic stability
- Improved imaging resolution using field-emission gun and CeB6 sources
- Specialized WDS analyzing crystals and high intensity spectrometer configurations
- SDD revolution transitioning to microprobe systems
- Cathodoluminescence spectrometers and detectors
- Research on standards and correction algorithms
- More and improved software tools to aid the analyst
- X-ray mapping via stage and beam scanning

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 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
- Particles, thin films/multilayers, rough surfaces, tilted
  All deviations from flat and normal to beam must be treated with specific modifications to correction algorithms

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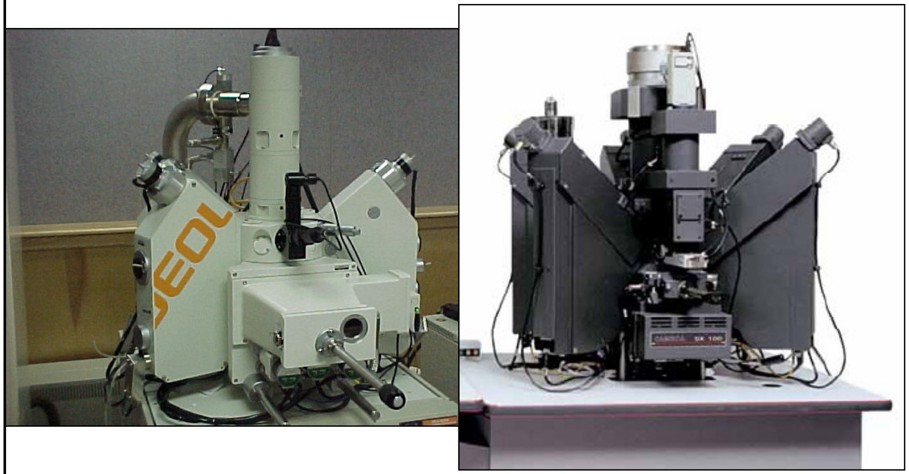
Commercial Electron Microprobe Instruments
JEOL JXA-8200/8500F, Cameca SX-100

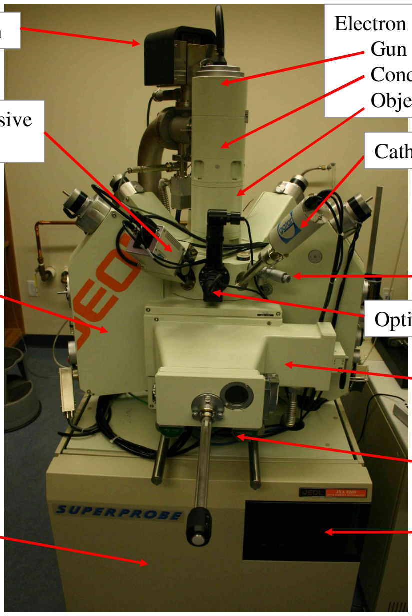
Continued integration of computer control and improvements in imaging and analytical capabilities.

Additional options from Probe Software, Advanced Microbeam, and Shimadzu for software and/or hardware systems and upgrades

Microprobe Column with WDS, Stage Port, Optical Microscope



Electron Microprobe at Washington University STL



Ion Pump – Electron Gun

Electron Column
- Gun
- Condenser Lens
- Objective Lens

Silicon-drift Energy-dispersive Spectrometer

Cathodoluminescence Detector

Objective Lens Aperture

Wavelength-dispersive Spectrometer (5)

Optical Microscope and Camera

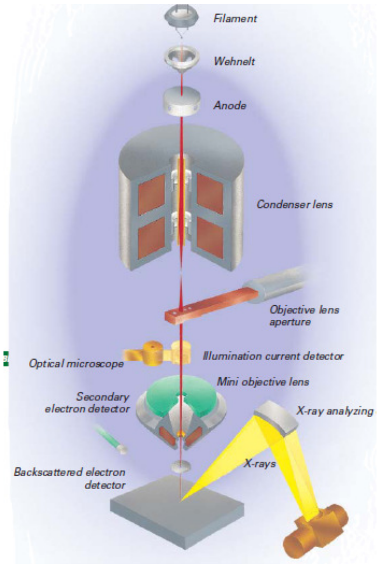
Sample exchange chamber

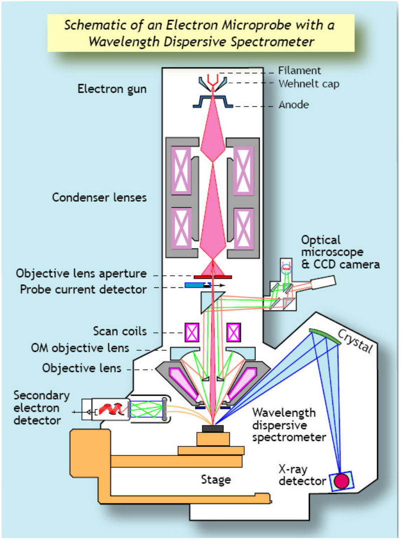
Stage motors X, Y, Z

Column Vacuum System and Computer Boards (inside)

Column Electronics

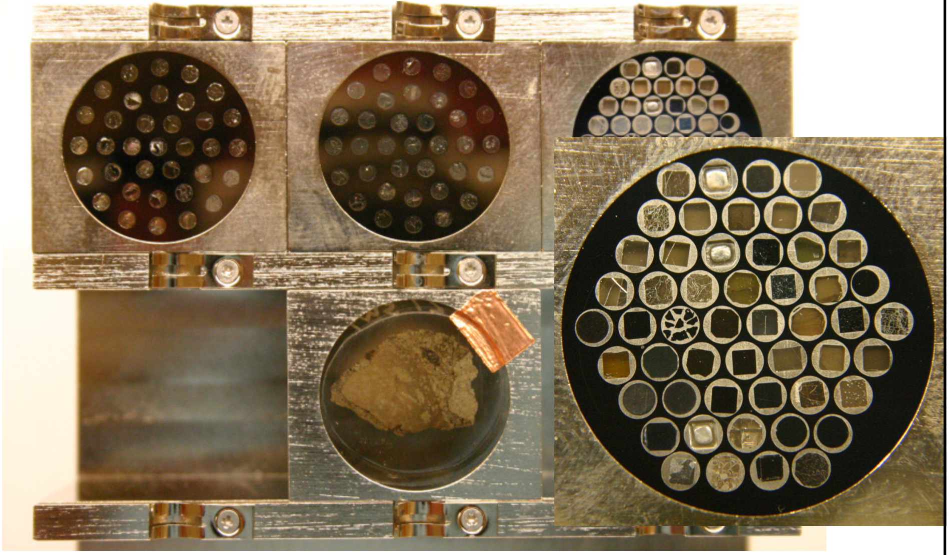
Microprobe Column Cross-section





Schematic of an Electron Microprobe with a Wavelength Dispersive Spectrometer

Microprobe Sample Holder and Standard Mount



Introduction
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.

Journals on X-ray Spectrometry, Microscopy, and Quantitative Analysis

- Microscopy and Microanalysis. MSA, MAS official journal. Also proceedings of M&M meetings since 1995. Cambridge.
- X-ray Spectrometry. Elsevier.
- Scanning.
- Microbeam Analysis. Proceedings of Microbeam Analysis Society (up to 1995).

Microanalysis Software
Free or Shareware

- CalcZAF– A collection of ZAF and $\Phi(\rho z)$ 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 – $\Phi(\rho z)$ thin-film correction program, includes contiuum fluorescence correction, used to calculate K or C for multilayer thin films on substrates.
- Casino – Monte Carlo simulation program for electron scattering and x-ray $\Phi(\rho z)$ distributions. http://www.gel.usherbrooke.ca/casino

Microanalysis Software
Free or Shareware

- Winxray – Program to generate EDS spectra using Monte Carlo and Φ(ρz) algorithms.
  http://montecarlomodeling.mcgill.ca
- NIST Software Products – DTSA-II (Desktop Spectrum Analyzer).
  http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/
- Lispix – Image processing program by Dave Bright at NIST, very powerful features for x-ray maps.
  http://www.cstl.nist.gov/div837/Division/outputs/software.htm
- Penelope – Advanced Monte Carlo program
  ftp://giga.sct.ub.es/serveis/msonda

Microanalysis Resources
EPMA Course Notes on the WWW

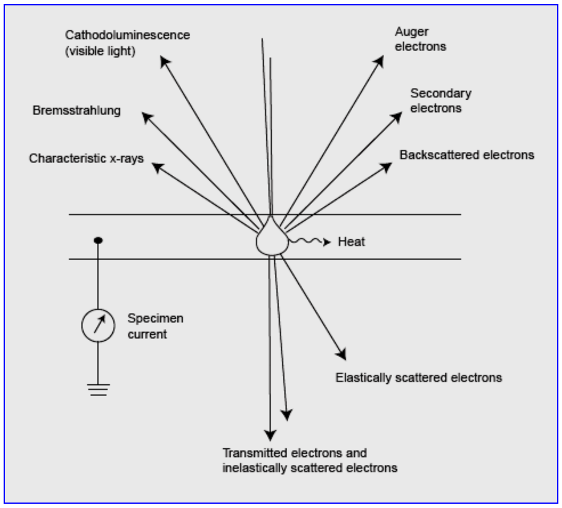
- James Wittke, Univ. Northern Arizona, Geology 510 (new):
  http://www4.nau.edu/microanalysis/Microprobe/Probe.html
- John Donovan, University of Oregon, Geol 619:
  http://epmalab.uoregon.edu/geol619.htm
- John Fournelle, University of Wisconsin, Geol 777:
  http://www.geology.wisc.edu/~johnf/sx51.html
- Paul Carpenter, Washington University:
  http://xraysrv.wustl.edu/
- Lehigh Microscopy School Short Courses:
  http://www.lehigh.edu/microscopy/

Electron-Specimen Interactions
and
X-ray Generation

Electron – Specimen Interactions

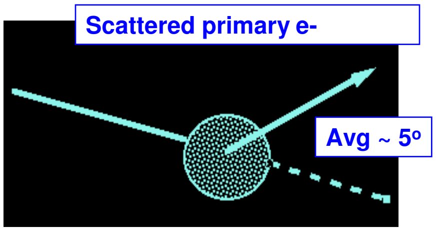
- Electrons from the beam are involved in elastic and inelastic scattering events in the sample.
- Elastic scattering is responsible for backscattered-electrons and is a valuable compositional imaging tool, due to Z contrast.
- Inelastic scattering is responsible for characteristic and continuum x-ray production, secondary and Auger electrons, electron-hole pairs in Si(Li) and SDD detectors, cathodoluminescence (long λ radiation in vis, UV, and IR), lattice vibrations (phonons), and electron oscillations (plasmons).
- The probability of an elastic or inelastic scattering event taking place is described by Q, the scattering cross-section, (units cm^2), so as Q increases, the "area" increases as does the probability of an event.

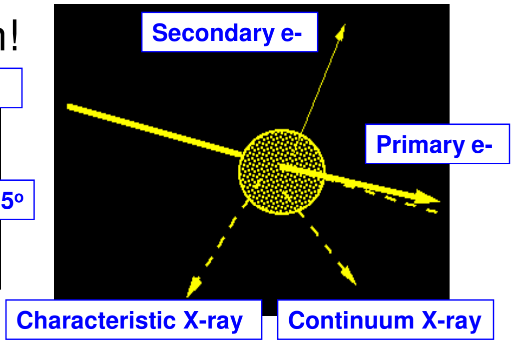
Electron-Specimen Interaction and Signals Produced



When an energetic beam electron (1-30 keV) strikes the specimen (atoms)…What happens?

Many things happen!



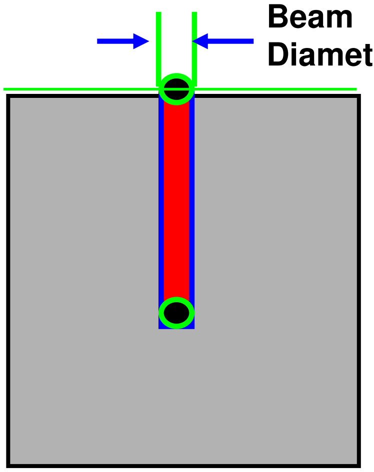


Elastic scattering:
Change direction (0 -180º)
No e^- energy loss

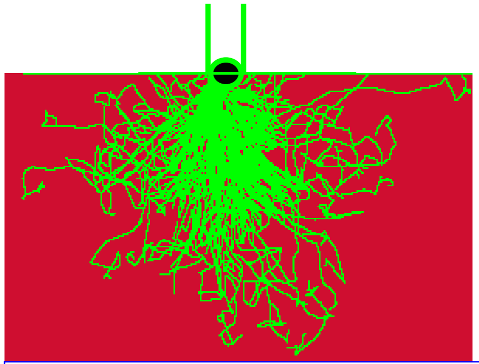
Inelastic scattering:
No change in direction (~ 0.1º)
Energy loss: dE/ds ~ 10 eV/nm
For 10000eV = 1000nm = 1 µm

Beam Spread Due to Scattering

We wish it was like this:



Actually, it’s like this



Elastic scattering causes spread away from beam diameter, and inelastic scattering limits the distance of travel.

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.

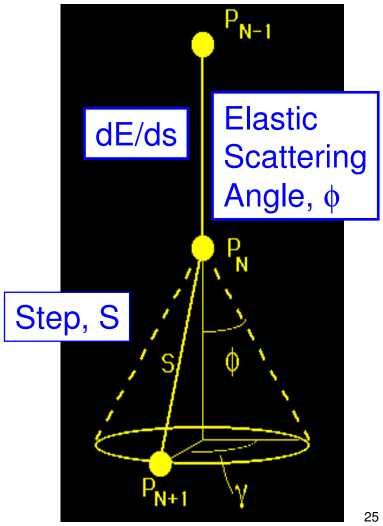
Calculating the Electron-Specimen Interaction

Monte Carlo electron trajectory simulation:

Calculate:
The elastic scattering (step, angle) and inelastic scattering (energy loss).

“Ride” the electron stepwise, always knowing the position (x,y,z), energy, and velocity.

Record distributions of backscattering, X-ray production.



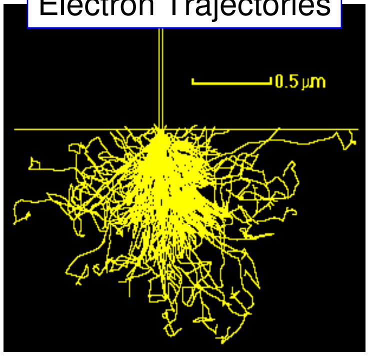
dE/ds

Elastic Scattering Angle, ϕ

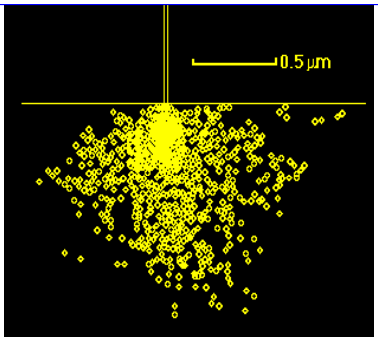
Step, S

Monte Carlo Calculations: X-rays

Electron Trajectories



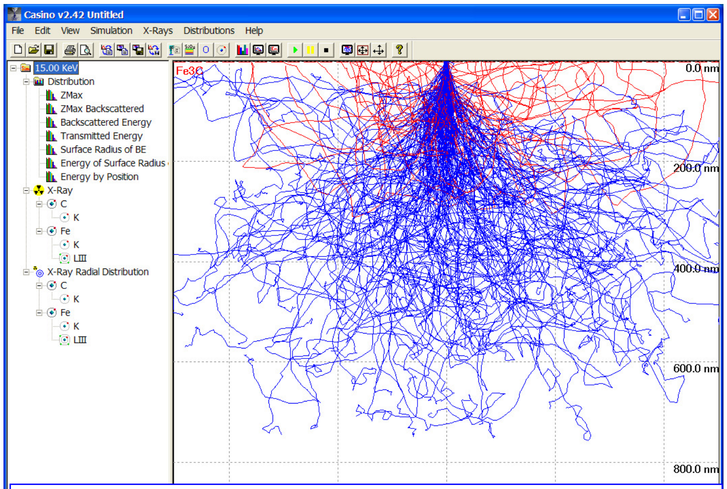
Sites of Inner Shell Ionization: Characteristic X-rays



Fe, 20 keV, 50 nm beam, E_c = 7.111 keV, $E_{k\alpha}$ = 6.403

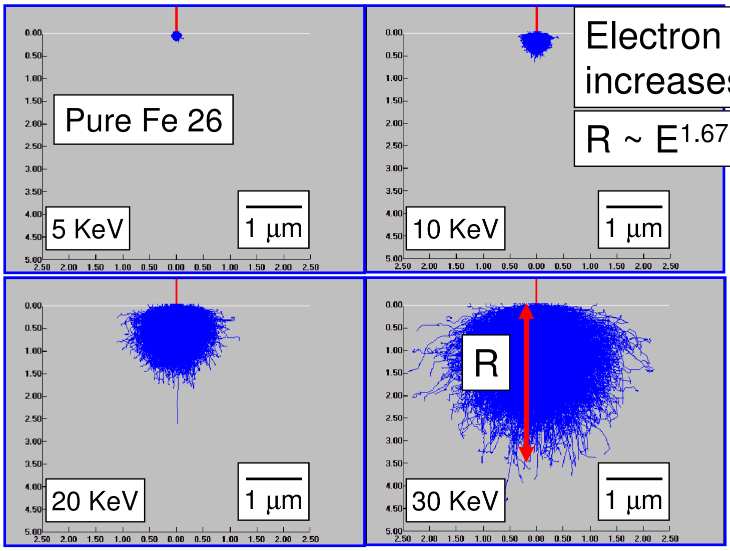
Interaction volume: Where everything interesting happens: electrons, X-rays, etc.

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)

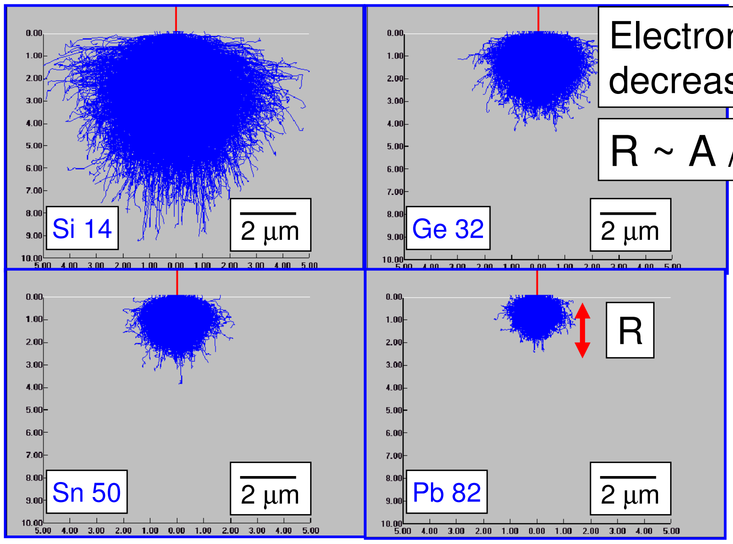
Monte Carlo Simulation
Effect of Varying Accelerating Voltage



Electron range increases with AV

$R \sim E^{1.67}$

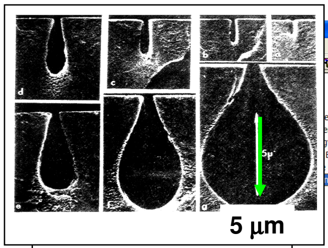
Monte Carlo Simulation
Effect of Varying Atomic Number Z @ 25 keV



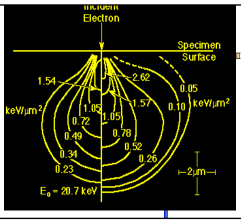
Electron range decreases with Z

$R \sim A / (Z^{0.89} \rho)$

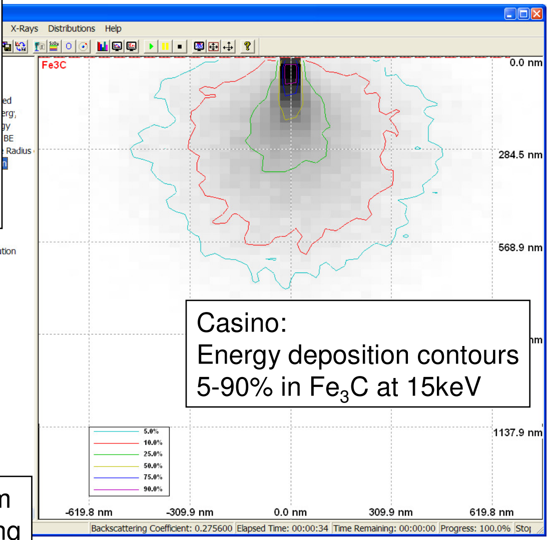
Energy Deposition: Experiment vs. Monte Carlo



Everhart et al., 1972



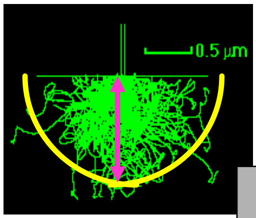
Energy deposition per mm PMMA e$^-$ dose with etching to reveal scattering volume



Backscattering Coefficient: 0.275600 | Elapsed Time: 00:00:34 | Time Remaining: 00:00:00 | Progress: 100.0%

Casino:
Energy deposition contours 5-90% in Fe_3C at 15keV

Electron Range (Kanaya & Okayama)

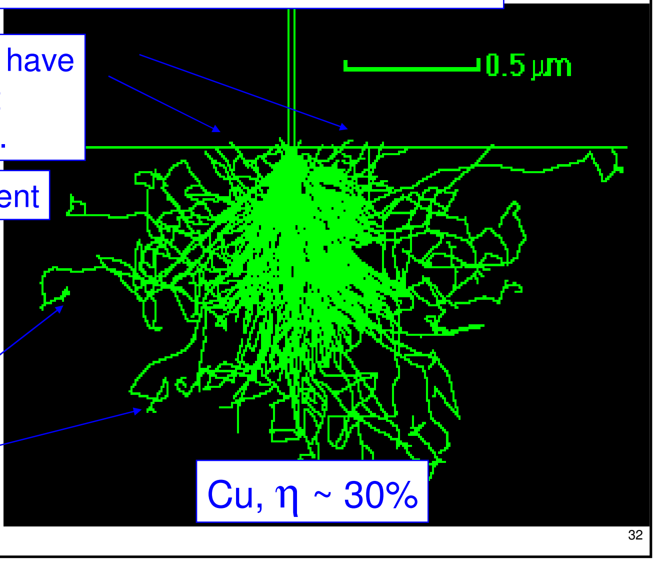


$$R_{K\text{-}O}(\mu m) = 0.0276\ (A/Z^{0.89}\ \rho)\ E_0^{1.67}$$

Electron Range increases w E_o, decreases with Z

Element	5 keV	10 keV	20 keV	30 keV
C	450 nm	1.4 µm	4.5 µm	8.9 µm
Al	413 nm	1.3 um	4.2 µm	8.2 µm
Fe	159 nm	505 nm	1.6 µm	3.2 µm
Ag	135 nm	431 nm	1.4 µm	2.7 µm
Au	85 nm	270 nm	860 nm	1.7 µm

What Signals Come from the Specimen?



Backscattered electrons

Beam electrons that have undergone sufficient scattering to escape.

Backscatter Coefficient

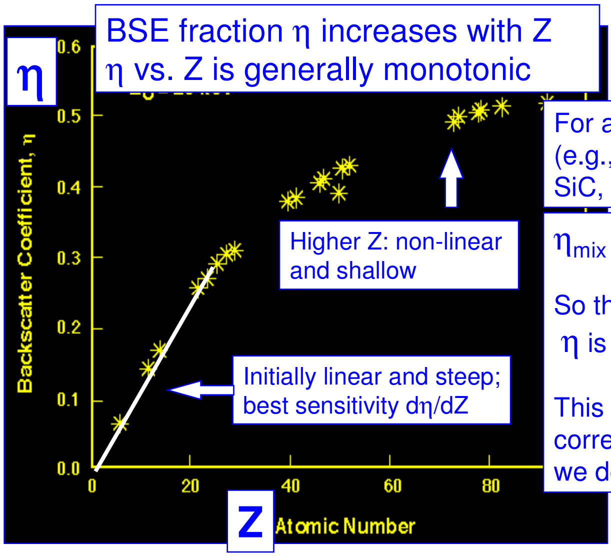
$\eta = n_{BSE}/n_B$

$\eta = i_{BSE}/i_B$

Absorbed or specimen current electrons

Cu, η ~ 30%

Characteristics of Backscattered Electrons: Effect of Specimen Composition, η vs. Z



BSE fraction η increases with Z
η vs. Z is generally monotonic

Higher Z: non-linear and shallow

Initially linear and steep; best sensitivity $d\eta/dZ$

For a mixture of atoms (e.g., alloys, compounds) SiC, Mg_2SiO_4, GaAs, IrSi, etc.

$$\eta_{mix} = \eta_A C_A + \eta_B C_B + \ldots$$

So the weighted average η is used for correction

This approach is used for correction parameters when we don't have specific data

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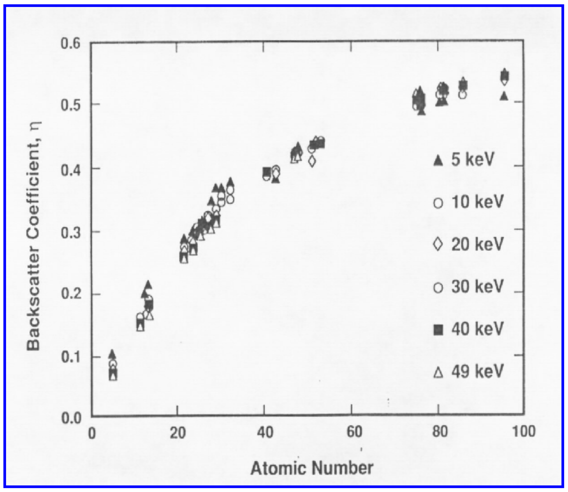
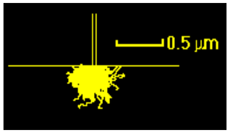
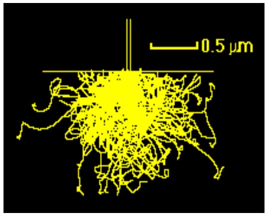
Backscattering vs. Beam Energy



10 keV



20 keV



Fe

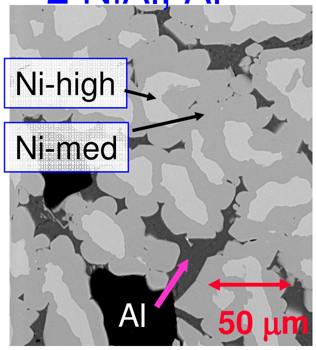
As accelerating voltage is increased, penetration depth and scattering volume both increase, but bse fraction is weak function of voltage

Contrast Mechanism

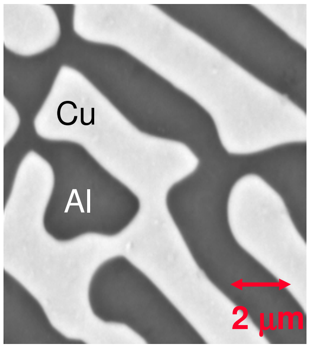
- Changes in the signal(s) (“Contrast”) collected at different points in the image convey information about specimen characteristics.
- Whenever a signal changes in a <u>predictable</u> way as a function of specimen properties, we have the basis for a contrast mechanism.
- Example: η vs. Z is monotonic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

Atomic Number Contrast

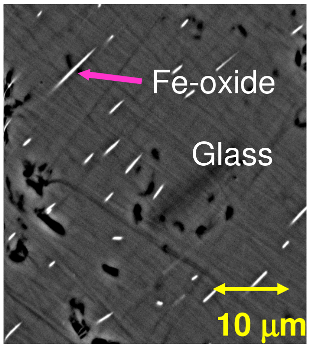
Raney Ni-Al
2 NiAl, Al



Al-Cu eutectic



Obsidian

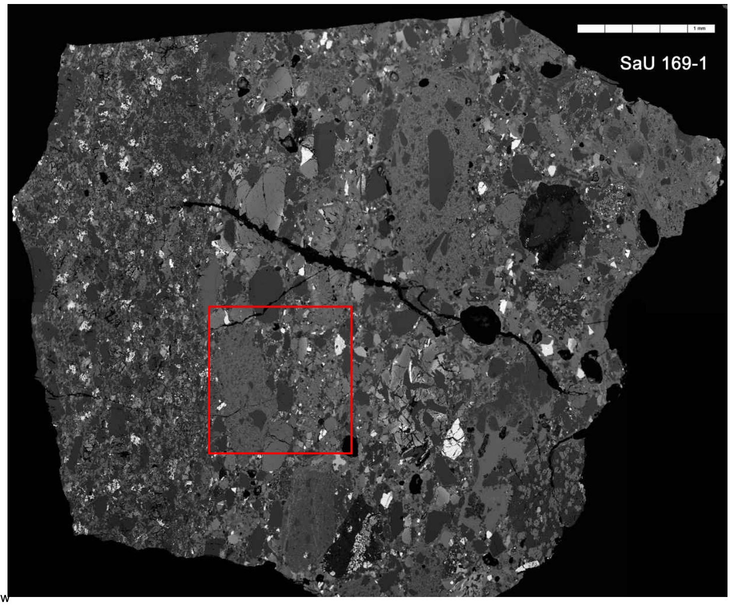


Backscattered-electrons provide a rapid and simple means to image differences in chemistry in the sample, via the dependence on average atomic number.

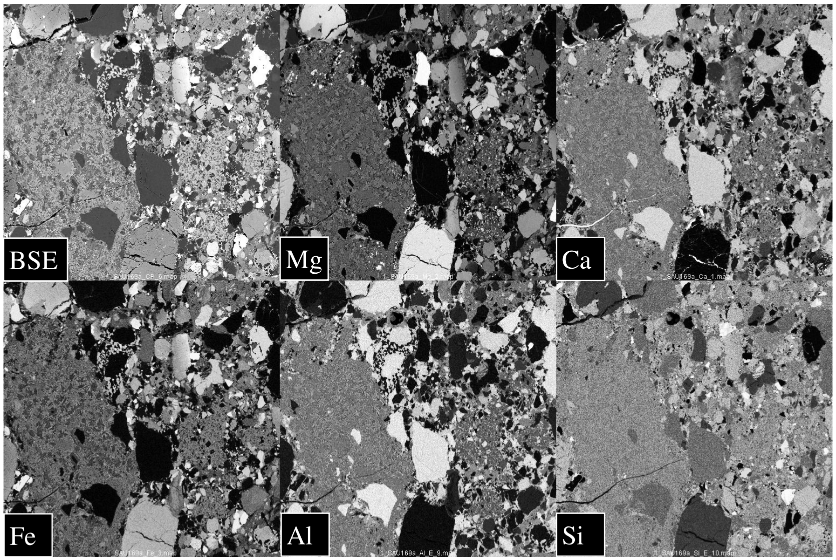
Compositional Mapping

- 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



Mean Atomic Number of Minerals

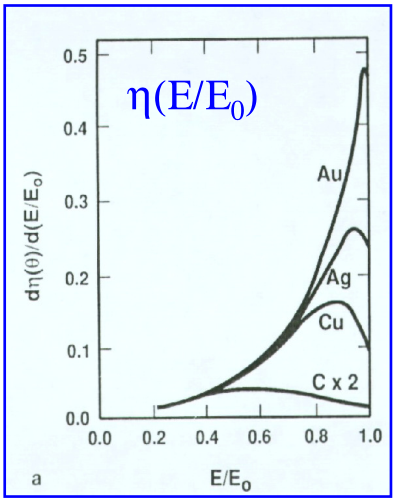
- Mean Z can be easily calculated (CalcZAF, for example)
- Typical range is ~ 10 – 20. Atomic number correction is limited if appropriate standards are used.
- Silicates
  Forsterite 10.6 Albite 10.7 Pyrope 10.7
  Fayalite 18.7 Anorthite 11.9 Almandine 15.6
- Oxides
  Periclase 10.4 Spinel 10.6 Quartz 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)

Backscattered Electrons: Energy Distribution

Number of BSEs as a function of energy relative to accelerating potential E_o
Total number of BSEs is integral

High Z materials have many BSEs with narrower range of energies and peak at high E/E_o
Gold Z=79 for example
Important for Z correction as BSEs add to x-ray generation

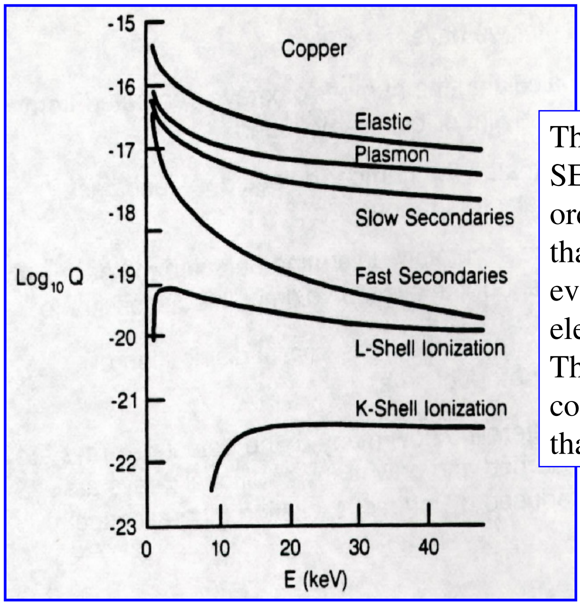
Low Z materials have few BSEs with wide range of energies and peak at low E/E_o
Carbon Z=6 for example
Not so important for BSE portion of Z correction



Backscattered Electrons: Summary

- Origin: Beam electrons elastically scattered many times
- Abundance: large, 5%(C) - 50%(Au) of beam current
- Information carried: number sensitive to composition; number and trajectories sensitive to topography
- Information Depth: 0.15 (Au) to 0.3 (C) D/R_{K-O} for 90% BSE
- Lateral resolution: 0.2 (Au) to 0.5 (C) R/R_{K-O} for 90% BSE
- Energy: variable, 0 to beam energy; for Z > 20, more than 50% of BSEs escape with more than half of beam energy; high Z elements scatter more high energy BSEs
- BSEs have sufficient energy to directly excite SEM detectors

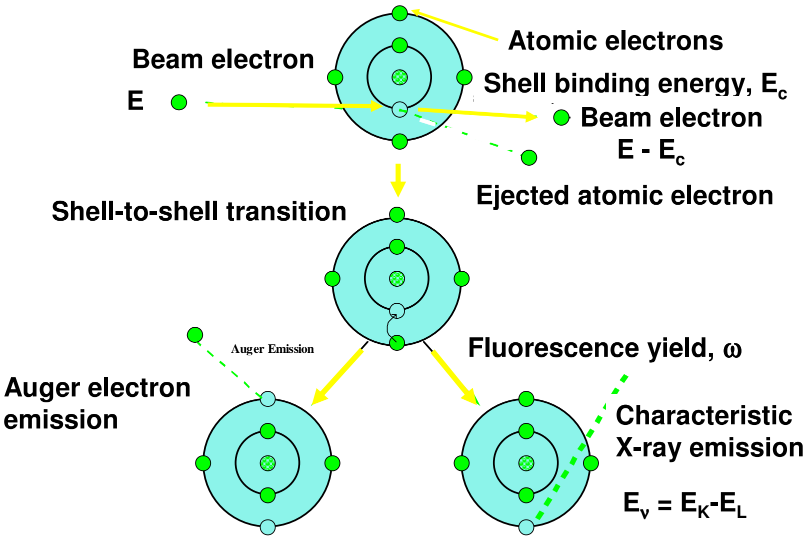
Probabilities of Scattering Events



The probability of a BSE or SE scattering event is 5-6 orders of magnitude greater than for an x-ray scattering event, i.e. 1 x-ray per 10^6 electrons!

This is the reason that x-ray count rates are so much lower than electron "count rates"

The Physics Underlying the Spectrometries



Beam electron

E

Atomic electrons

Shell binding energy, E_c

Beam electron

$E - E_c$

Ejected atomic electron

Shell-to-shell transition

Auger Emission

Auger electron emission

Fluorescence yield, ω

Characteristic X-ray emission

$E_\nu = E_K - E_L$

Families of X-rays

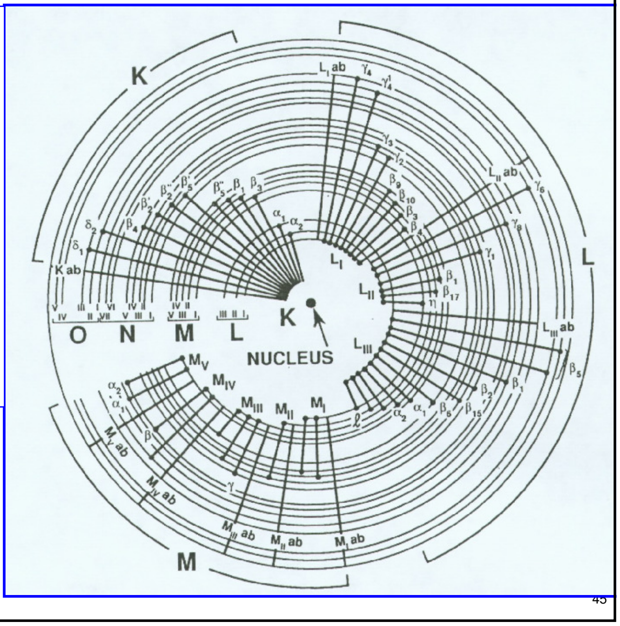
X-ray Spectra

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

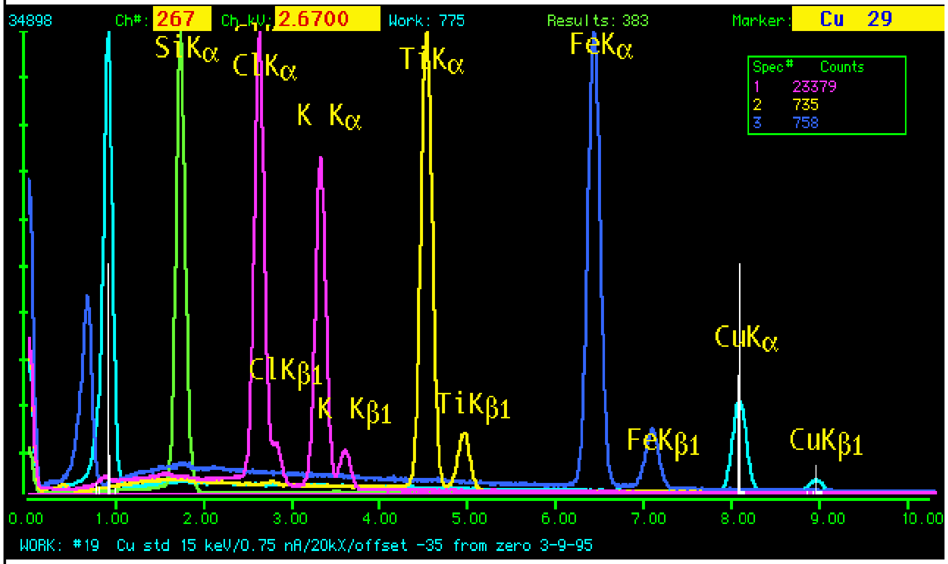
Kα-Kβ

Lα-Lβ-Lγ-Lη-Ll

Mα-Mβ-Mγ-Mζ-$M_{II}N_{IV}$



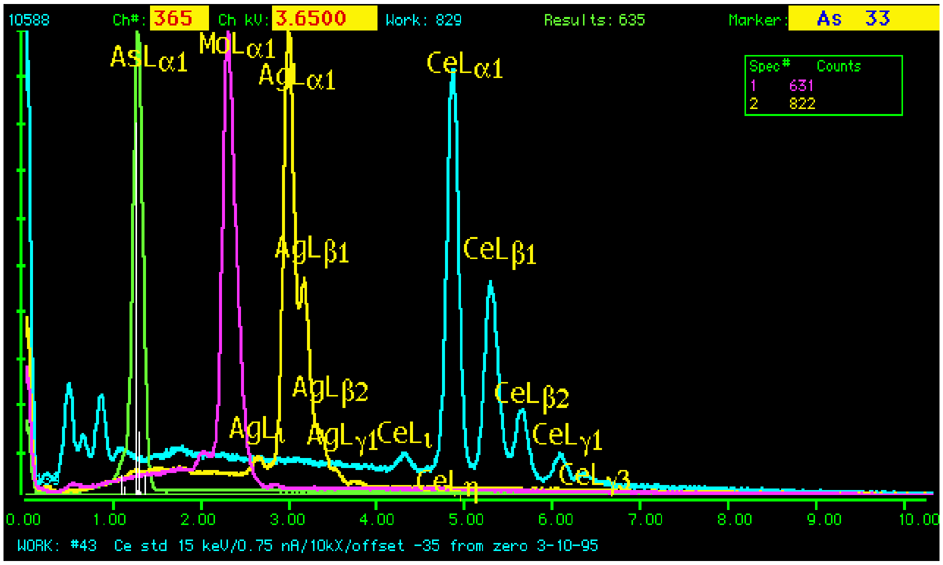
K-Family X-ray Spectra (EDS)



```
34898    Ch#: 267    Ch_kV: 2.6700    Work: 775    Results: 383    Marker: Cu  29
Spec#   Counts
1       23379
2       735
3       758
WORK: #19  Cu std 15 keV/0.75 nA/20kX/offset -35 from zero 3-9-95
```

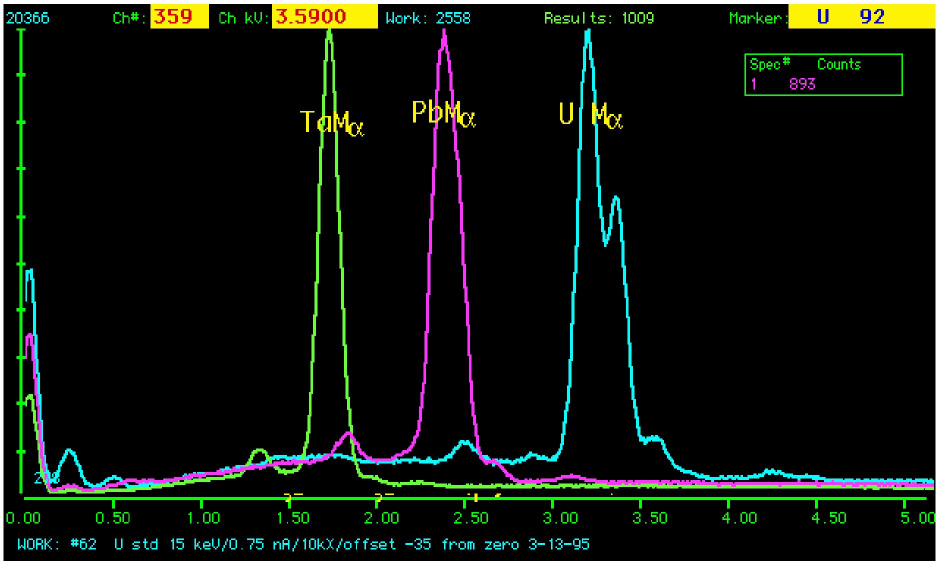
E_0 = 15 keV

L-Family X-ray Spectra (EDS)



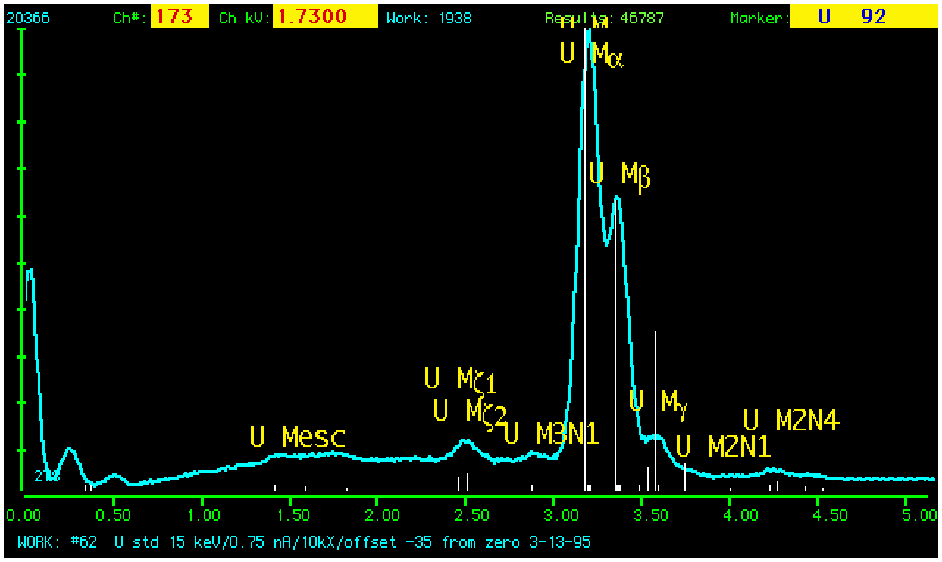
E_0 = 15 keV

M-Family X-ray Spectra (EDS)



E_0 = 15 keV

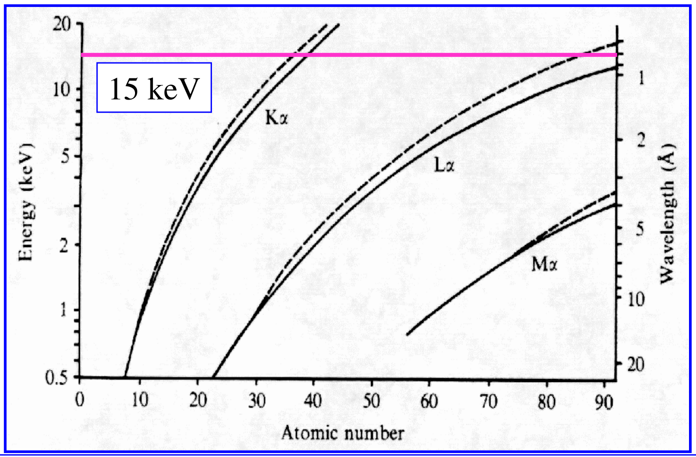
Uranium M-Family X-ray Spectrum (EDS)



WORK: #62 U std 15 keV/0.75 nA/10kX/offset -35 from zero 3-13-95

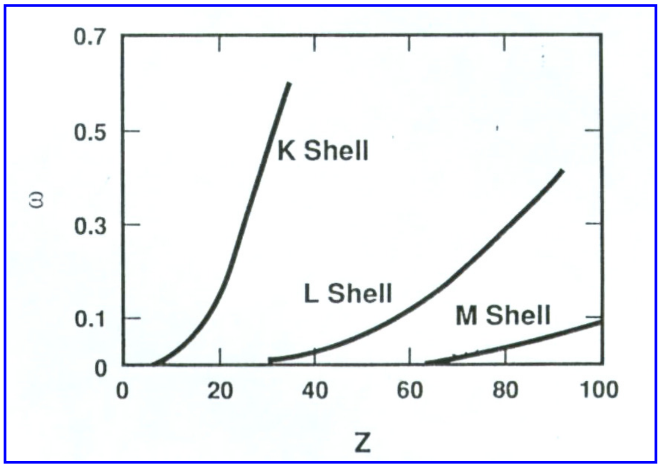
E_0 = 15 keV

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.

X-ray Ionization Cross Section Q

- The ionization cross-section Q is the probability of generating an x-ray of a specific energy for a specific atom, e.g., Cu Kα from a Cu atom.
- Q has units of area, larger Q is a larger area presented to an electron (or fluorescing x-ray).
- Q is a function of overvoltage, $U = E_o / E_c$ for an x-ray line.
- At 20 keV, typical values of U:
  C Kα, U = 20 / .2838 = 70.5
  Si Kα, U = 20 / 1.838 = 10.88
  Ni Kα, U = 20 / 8.332 = 2.4
  Au Lα, U = 20 / 11.918 = 1.67
- From U considerations alone one would use the highest possible U to generate x-rays for measurement.
  But x-ray absorption increases with U and limits emission.
- We measure the emitted x-rays, not the generated x-rays

Ionization Cross Section: Bethe Form

$$Q = 6.51\times10^{-20}\, n_s\, b_s\, \ln(c_s\, E/E_c)\,/(E\, E_c)$$

Units: ionizations / e^- / (atom/cm^2)

E beam electron energy (keV)

E_c critical excitation (binding) energy (keV)

n_s number of electrons in shell or subshell

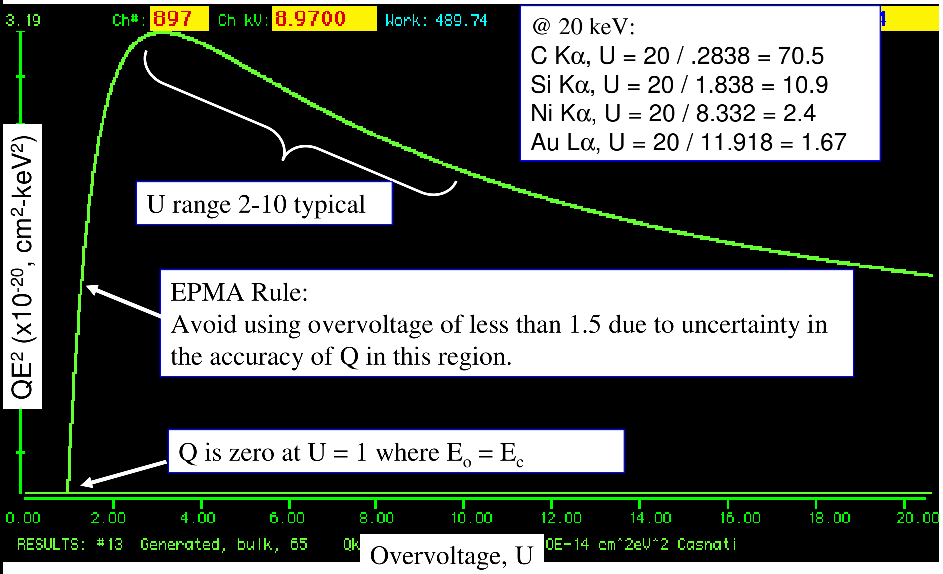
b_s, c_s constants for the shell or subshell

$$Q = 6.51\times10^{-20}\, n_s\, b_s \ln(c_s\, U) / (UE_c^2)$$

$U = E/E_c$ overvoltage

Plot QE_c^2 vs U

Plot of Ionization Cross Section QE^2 vs. Overvoltage



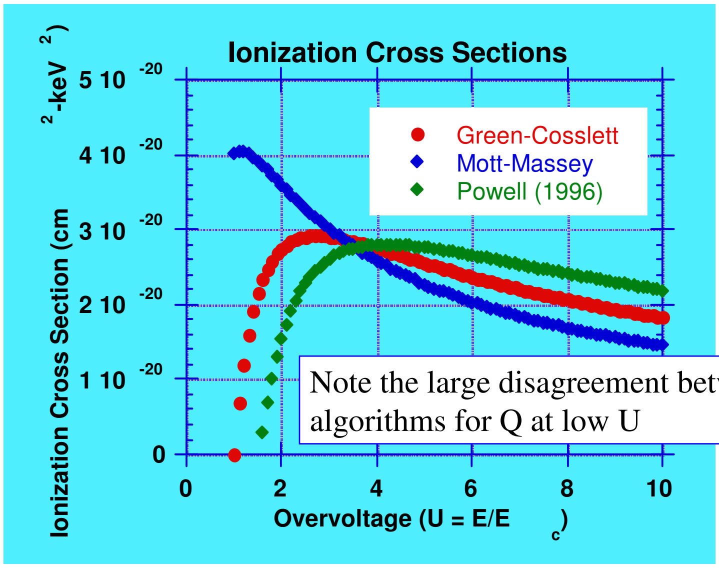
@ 20 keV:
C Kα, U = 20 / .2838 = 70.5
Si Kα, U = 20 / 1.838 = 10.9
Ni Kα, U = 20 / 8.332 = 2.4
Au Lα, U = 20 / 11.918 = 1.67

U range 2-10 typical

EPMA Rule:
Avoid using overvoltage of less than 1.5 due to uncertainty in the accuracy of Q in this region.

Q is zero at U = 1 where $E_o = E_c$

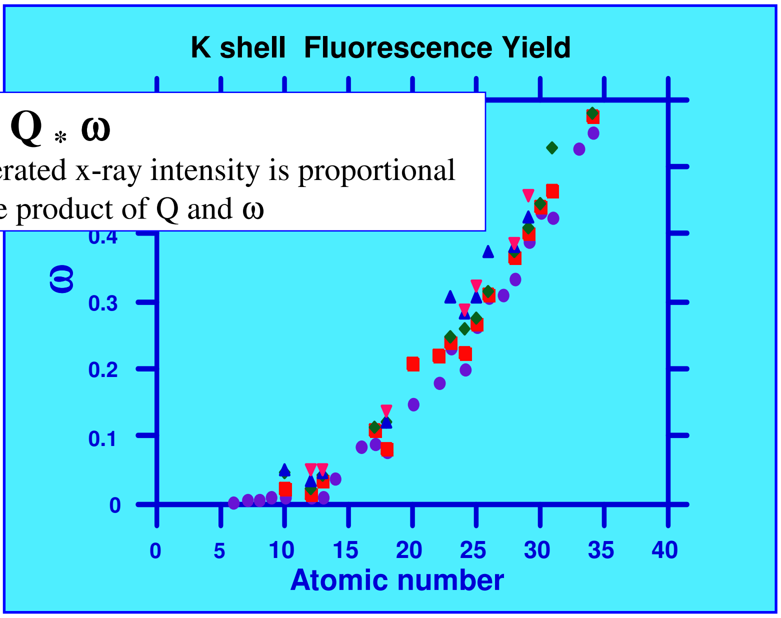
Cross Section for Inner Shell Ionization



Note the large disagreement between algorithms for Q at low U

Powell, C.J., Rev. Mod. Phys. 48 (1976) 33; (1996)

K Shell Fluorescence Yield



$I_x \sim Q * \omega$

Generated x-ray intensity is proportional to the product of Q and ω

Continuum (Bremsstrahlung) X-rays

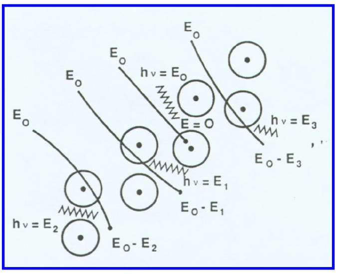
- Bremsstrahlung means "braking radiation".
- Primary beam electrons are decelerated by the repulsive electric field of electrons surrounding an atom.
- X-rays are emitted during this deceleration. The energy of a given x-ray depends on the degree of slowing down and is continuous in this respect.
- Continuum x-rays can be produced by any atom and are therefore not uniquely produced by a given element in the way that characteristic x-rays are.
- Continuum x-rays range in energy from essentially zero up to the nominal beam energy.
- The high energy cutoff of the EDS spectrum is known as the "Duane-Hunt Limit".

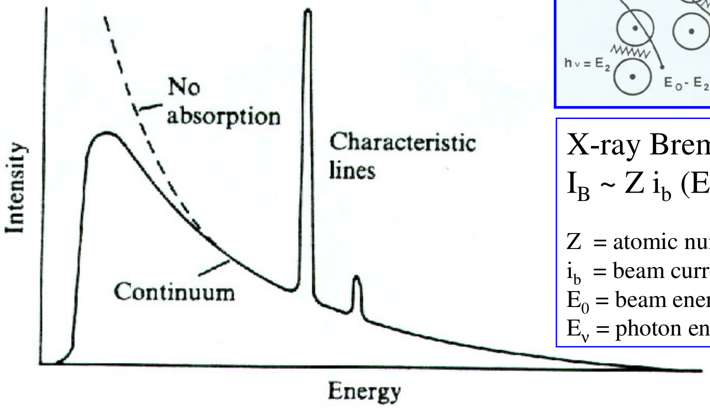
Continuum X-rays

- Many different electron-specimen interactions can result in continuum x-ray emission. A 15 KeV beam electron could:
  (1) Slow down to zero velocity and energy — in one step and emit a 15 keV continuum x-ray.
  (2) Generate a Cu Kα x-ray and a 6.02 keV continuum x-ray:
  (E = 15 keV – 8.98 keV = 6.02 keV). And so on...
- Since any material can generate the full range of continuum x-ray energies, they are not diagnostic like characteristic x-rays.
- Higher background from high Z materials (Au vs. Si).
- The background or continuum must be subtracted from the peak intensity to perform quantitative analysis.
- In EDS spectra there may be a significant contribution of continuum beneath a peak.

Schematic Energy-Dispersive Spectrum

Continuum intensity increases at lower energies, but due to absorption we do not see these x-rays emitted



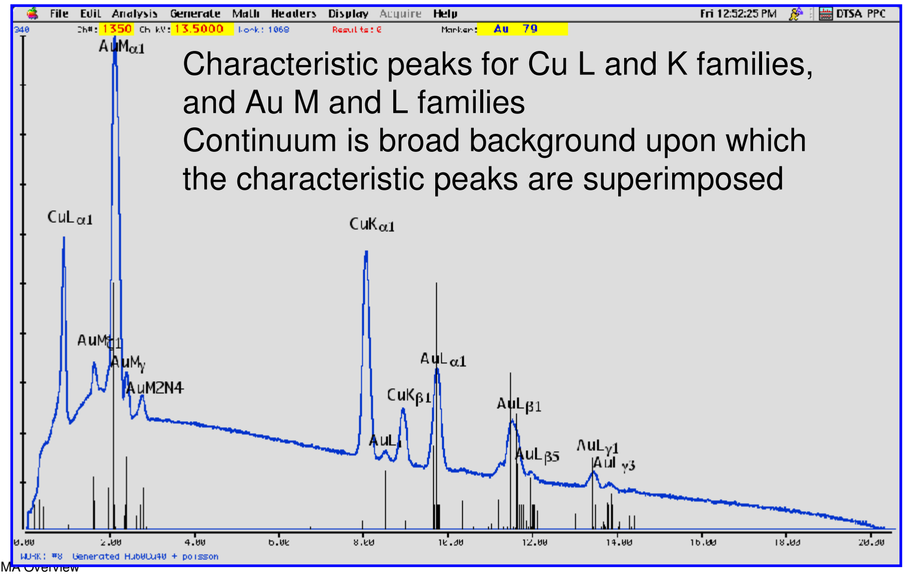


X-ray Bremsstrahlung

$I_B \sim Z\, i_b\, (E_0 - E_\nu)/E_\nu$

Z = atomic number
i_b = beam current
E_0 = beam energy
E_ν = photon energy

NIST SRM 482 $Cu_{40}Au_{60}$ Alloy

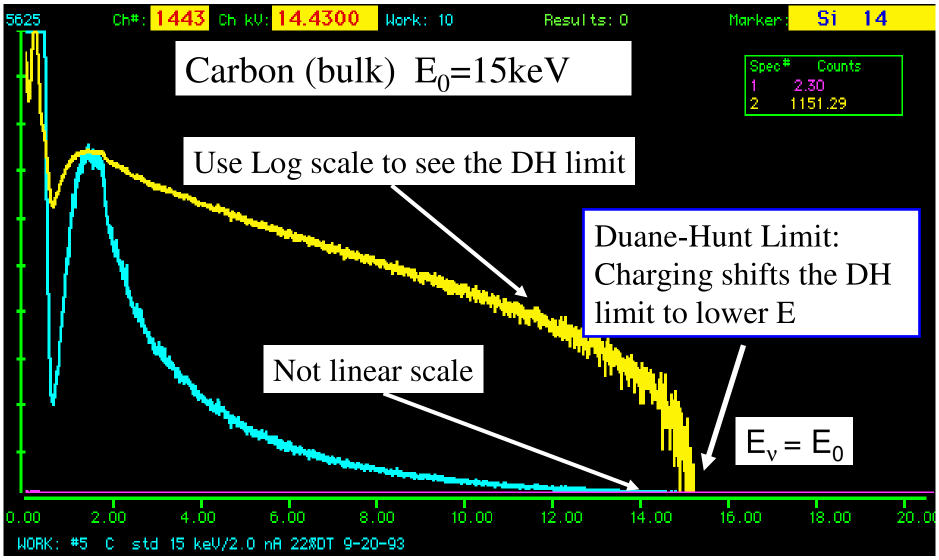


Characteristic peaks for Cu L and K families, and Au M and L families
Continuum is broad background upon which the characteristic peaks are superimposed

Duane – Hunt Limit:
Detction of Charging and E_o Measurement

- The DH limit is conveniently measured by EDS if the acquired upper energy limit exceeds the accelerating potential (as it should, i.e., use 0-20keV range for 15 keV accelerating potential).
- The DH limit is sensitive to sample charging and is an indicator of problems with sample conductivity.
- Sample charge buildup decelerates incoming electrons, so a continuum x-ray produced will register with $E < E_o$. Typically charging reduces the DH limit by several 10s-100s eV.
- The DH limit is the observed E_o for a sample and is therefore a variable if charging exists.
- Pulse pileup causes x-rays to be recorded at an energy higher than actual, so be careful in interpreting the DH limit.
- For SDD EDS systems being run at high throughput in mapping mode, there can be significant pulse pileup at E_o.

DH Limit of X-ray Bremsstrahlung (Continuum)



Carbon (bulk) E_0=15keV

Use Log scale to see the DH limit

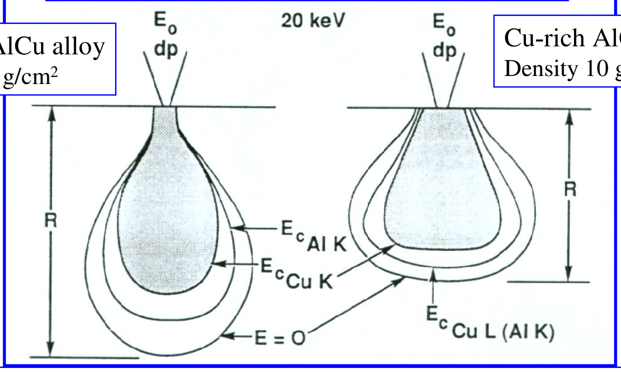
Duane-Hunt Limit: Charging shifts the DH limit to lower E

Not linear scale

$E_v = E_0$

Range of Characteristic X-ray Production

X-ray generation range in Al-Cu alloys

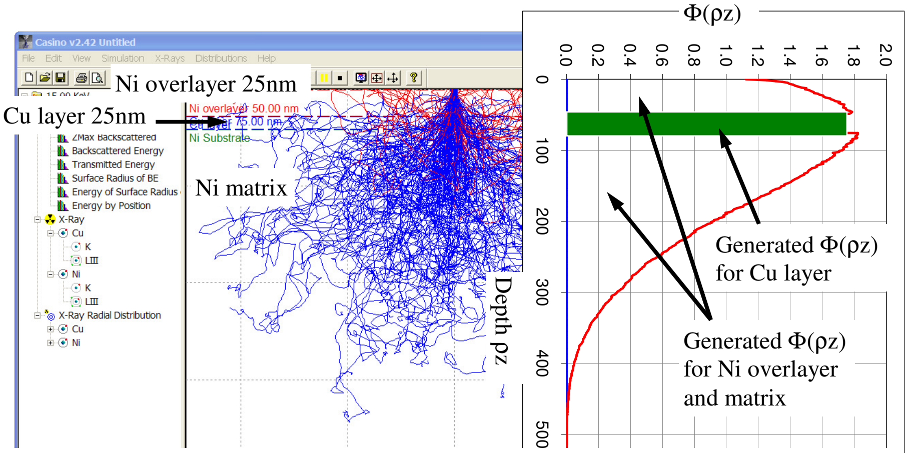


Al-rich AlCu alloy
Density 3 g/cm^2

Cu-rich AlCu alloy
Density 10 g/cm^2

The depth distribution of primary x-ray generation is dependent on the sample composition!

Casino MC Simulation of Φ(ρz) Experiment



Ni overlayer 25nm

Cu layer 25nm

Ni matrix

Depth ρz

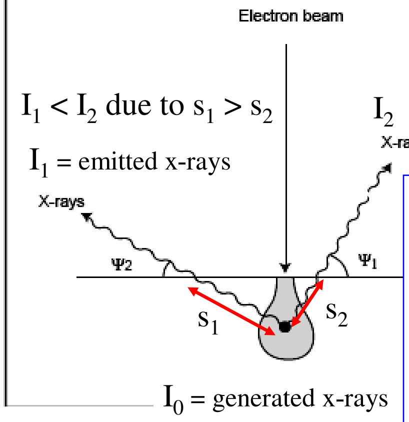
Generated Φ(ρz) for Cu layer

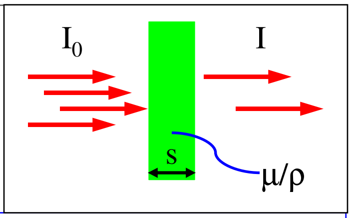
Generated Φ(ρz) for Ni overlayer and matrix

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.

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

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

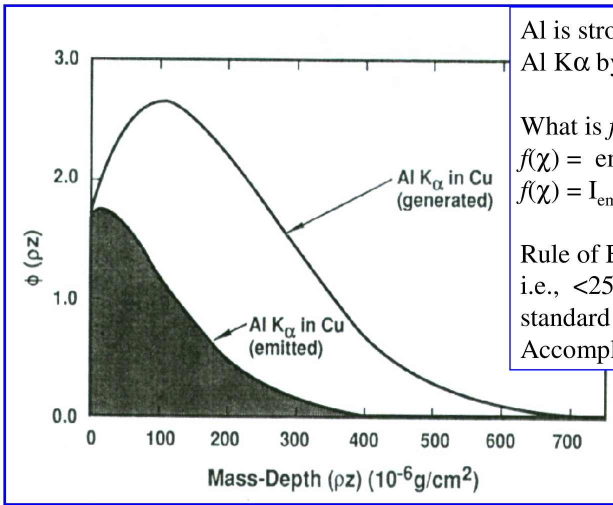




X-ray absorption here is photoelectric, which is an either/or operation. Either the photon is absorbed, or it escapes the specimen with the same characteristic energy with which it started.

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

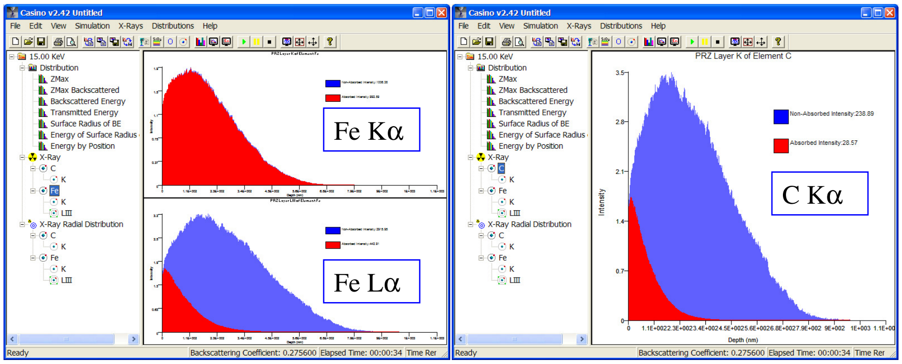


Al is strongly absorbed by Cu (μ/ρ Al Kα by Cu = 4764).

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

Casino Φ(ρz) Curves Calculated for Fe_3C



Casino Monte Carlo calculated Φ(ρz) 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 Φ(ρz) algorithms

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Wavelength-Dispersive Spectrometry

Wavelength-Dispersive Spectrometry (WDS) Summary

- X-ray measurement by Bragg diffraction using crystals of known d-spacing, counted by gas ionization in x-ray detector
- Superior resolution (~10eV) and P/B (~1000) result in excellent ability to resolve interferences, make precise measurements at concentrations down to 100-1000 ppm*
- Peak shape and shift observed for low energy x-rays
- Serial acquisition mode, complemented by EDS+SDD
- Mechanical alignment and reproducibility issues, temperature dependence of d-spacing (PET)

WDS Spectrometry: Advances

- Spectrometer mechanisms established for decades, counting electronics simple compared to EDS/SDD
- Reliance on sealed and flow proportional counters Exciting possibilities with SDD detector element for high throughput pulse processing
- Layered dispersive crystals enhance light element capabilities for Be, B, C, N, O, F
- Specialized H-type and large crystal spectrometers for high sensitivity
- Software: peak overlap correction, multiple spectrometer measurement (trace elements), multiple standards, multiple kV/probe current configurations
- CL systems
- Compositional mapping via beam, stage, mosaic imaging

WDS Checklist for Analysts: Measurement

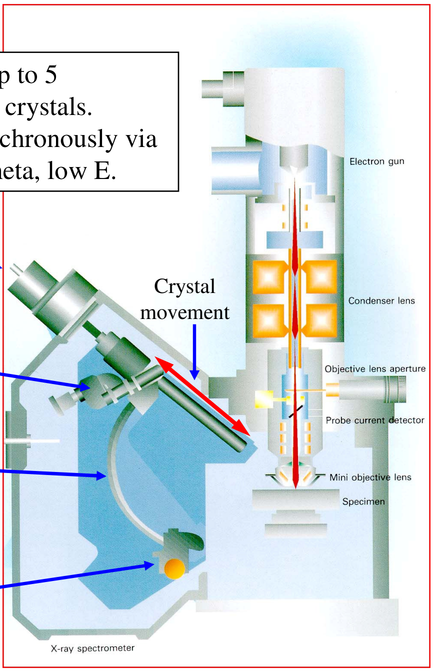
- Microprobe stabilized? Vacuum, column alignment, gun/beam, sample, etc.
- Spectrometers aligned, deadtime calibrated, PHA set for elements to be analyzed, esp. for light elements
- Wavelength scans on standards and unknowns including high and low concentrations, interfering elements
- Background selection: Use full width from high conc. standard, otherwise overestimating background
- Avoid large differences in count rate and reliance on deadtime correction
- Peak shape and shift, standard vs. samples, use correct position for measurements if different on std vs. sample
- Beam sensitive materials: defocus, correct for time-dependent behavior of standard and sample

WDS Checklist for Analysts: Analysis

- Intelligently choose primary and secondary standards:
    - Spectrometer setup vs. perform accurate microanalysis
- Consult μ/ρ data and be wary of high absorption correction
    - Adjust kV accordingly, use alternate analytical line
    - High absorption dictates standard selection, esp. light elements
- Use highest practical energy x-ray line:
  Fewer peak interferences and absorption correction is smaller
    - K in preference to L (use K up to ~Se)
    - L in preference to M (use L up to ~Bi)
- EPMA is surface analysis, emphasis on cleanliness and C-coat thickness
- Correction algorithms:
    - $\Phi(\rho z)$ superior to ZAF
    - Assess accuracy by reference to different algorithms and μ/ρ sets
    - Always using one $\Phi(\rho z)$ and μ/ρ set will someday result in mistake
- Employ software tools to understand analytical problem:
    - Monte Carlo/simulation: Scattering volume, spatial constraints
    - CalcZAF: Correction algorithms, nature of analytical constraints
- Is the sample presented consistent with what you observe?
    - Multilayer, particles, misidentified materials, etc.

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.



Crystal movement

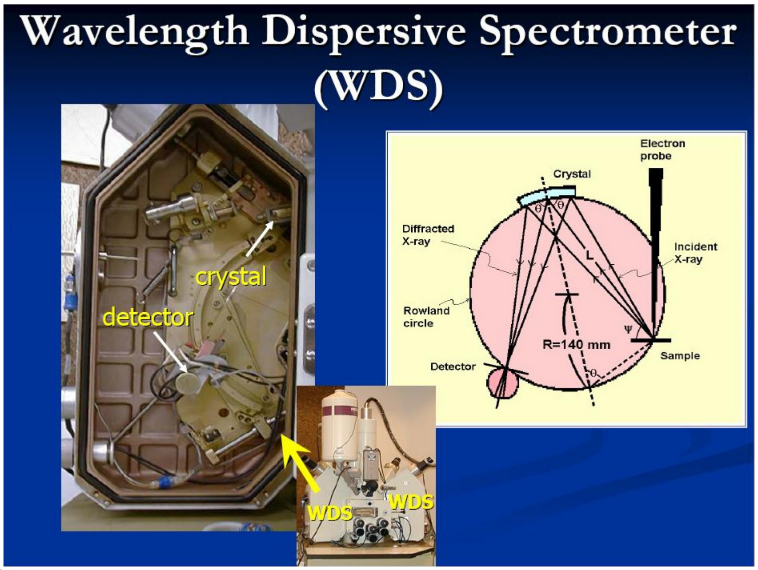
Spectrometer drive motor w/ vacuum feedthrough

Crystals w/ flipping motor

Mechanical alignment track

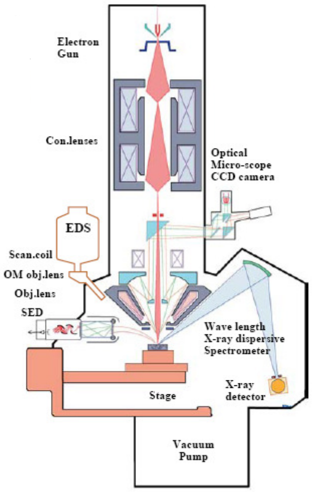
Proportional X-ray counter

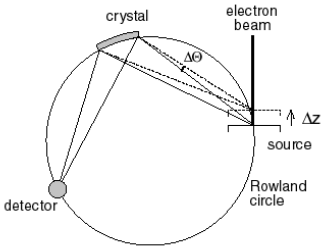
WDS Spectrometer



Wavelength Dispersive Spectrometer (WDS)

Electron Microprobe Column
Spectrometer Alignment: Baseplate and Crystal





Baseplate: Place Rowland circle at Z focus
Crystal: Align all crystals on Rowland circle
Spectrometer design keeps detector on RC
Note: Different K-ratio = misalignment
Multiple spectrometer comparison required to demonstrate all WDS and EDS are mutually aligned

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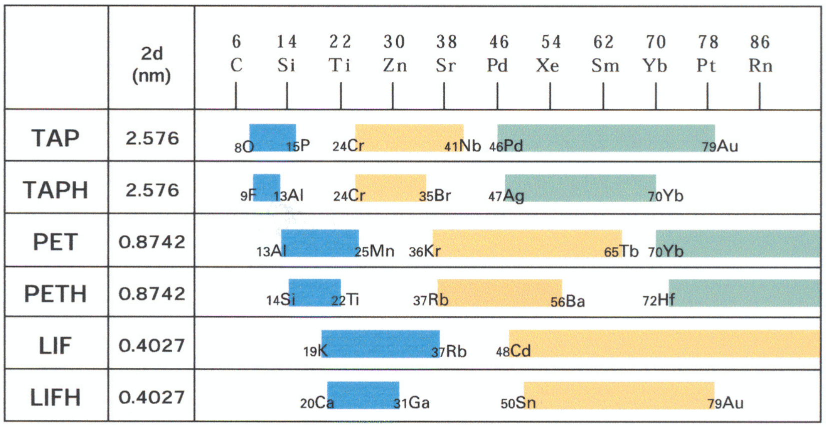
WDS Spectrometer Units

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

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

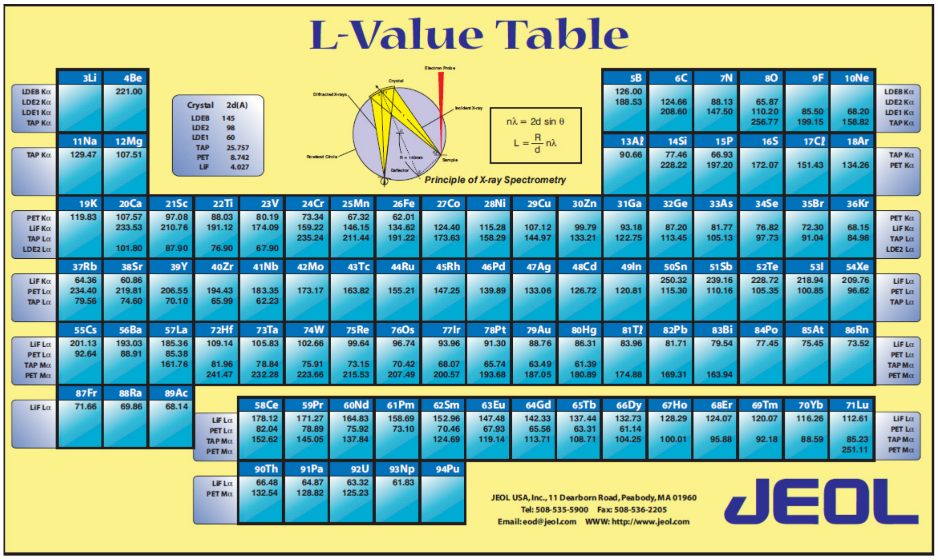
Diffracting Crystal Element Ranges



LDE Diffracting Crystal Element Ranges

	2d (nm)	Be	B	C	N	O	F
NSTE	約10		○	○	○	○	
LDE1	約6			△	◎	◎	◎
LDE2	約10		◎	◎	◎	○	
LDEB	約14.5	◎	○				
LDE1H	約6			△	⊚	⊚	
LDE2H	約10		⊚	⊚			
LDENH	約8			○	⊚		
LDE3H	約20	⊚	○				
LDE5H	約8			◎	⊚		
LDEBH	約14.5	◎	◎				

L-Value X-ray Peak Positions for JEOL Microprobe



L-Value Table

Crystal	2d(A)
LDEB	145
LDE2	98
LDE1	60
TAP	25.757
PET	8.742
LiF	4.027

Principle of X-ray Spectrometry

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

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

	3Li	4Be	5B	6C	7N	8O	9F	10Ne	
LDEB Kα		221.00	126.00						LDEB Kα
LDE2 Kα			188.53	124.66	88.13	65.87			LDE2 Kα
LDE1 Kα				208.60	147.50	110.20	85.50	68.20	LDE1 Kα
TAP Kα						256.77	199.15	158.82	TAP Kα

	11Na	12Mg	13Aℓ	14Si	15P	16S	17Cℓ	18Ar	
TAP Kα	129.47	107.51	90.66	77.46	66.93				TAP Kα
				228.22	197.20	172.07	151.43	134.26	PET Kα

	19K	20Ca	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn	31Ga	32Ge	33As	34Se	35Br	36Kr	
PET Kα	119.83	107.57	97.08	88.03	80.19	73.34	67.32	62.01											PET Kα
LiF Kα		233.53	210.76	191.12	174.09	159.22	146.15	134.62	124.40	115.28	107.12	99.79	93.18	87.20	81.77	76.82	72.30	68.15	LiF Kα
TAP Lα						235.24	211.44	191.22	173.63	158.29	144.97	133.21	122.75	113.45	105.13	97.73	91.04	84.98	TAP Lα
LDE2 Lα		101.80	87.90	76.90	67.90														LDE2 Lα

	37Rb	38Sr	39Y	40Zr	41Nb	42Mo	43Tc	44Ru	45Rh	46Pd	47Ag	48Cd	49In	50Sn	51Sb	52Te	53I	54Xe	
LiF Kα	64.36	60.86												250.32	239.16	228.72	218.94	209.76	LiF Lα
PET Lα	234.40	219.81	206.55	194.43	183.35	173.17	163.82	155.21	147.25	139.89	133.06	126.72	120.81	115.30	110.16	105.35	100.85	96.62	PET Lα
TAP Lα	79.56	74.60	70.10	65.99	62.23														TAP Lα

	55Cs	56Ba	57La	72Hf	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg	81Tℓ	82Pb	83Bi	84Po	85At	86Rn	
LiF Lα	201.13	193.03	185.36	109.14	105.83	102.66	99.64	96.74	93.96	91.30	88.76	86.31	83.96	81.71	79.54	77.45	75.45	73.52	LiF Lα
PET Lα	92.64	88.91	85.38																PET Lα
TAP Mα			161.76	81.96	78.84	75.91	73.15	70.42	68.07	65.74	63.49	61.39							TAP Mα
PET Mα				241.47	232.28	223.66	215.53	207.49	200.57	193.68	187.05	180.89	174.88	169.31	163.94				PET Mα

	87Fr	88Ra	89Ac
LiF Lα	71.66	69.86	68.14

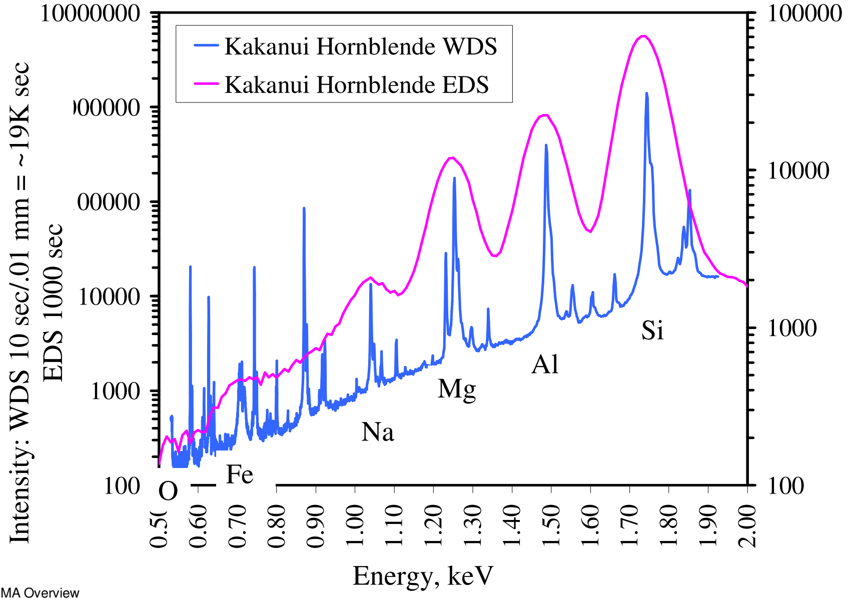
	58Ce	59Pr	60Nd	61Pm	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb	71Lu	
LiF Lα	178.12	171.27	164.83	158.69	152.96	147.48	142.33	137.44	132.73	128.29	124.07	120.07	116.26	112.61	LiF Lα
PET Lα	82.04	78.89	75.92	73.10	70.46	67.93	65.56	63.31	61.14						PET Lα
TAP Mα	152.62	145.05	137.84		124.69	119.14	113.71	108.71	104.25	100.01	95.88	92.18	88.59	85.23	TAP Mα
PET Mα														251.11	PET Mα

	90Th	91Pa	92U	93Np	94Pu
LiF Lα	66.48	64.87	63.32	61.83	
PET Mα	132.54	128.82	125.23		

JEOL USA, Inc., 11 Dearborn Road, Peabody, MA 01960
Tel: 508-535-5900 Fax: 508-536-2205
Email: eod@jeol.com WWW: http://www.jeol.com

JEOL

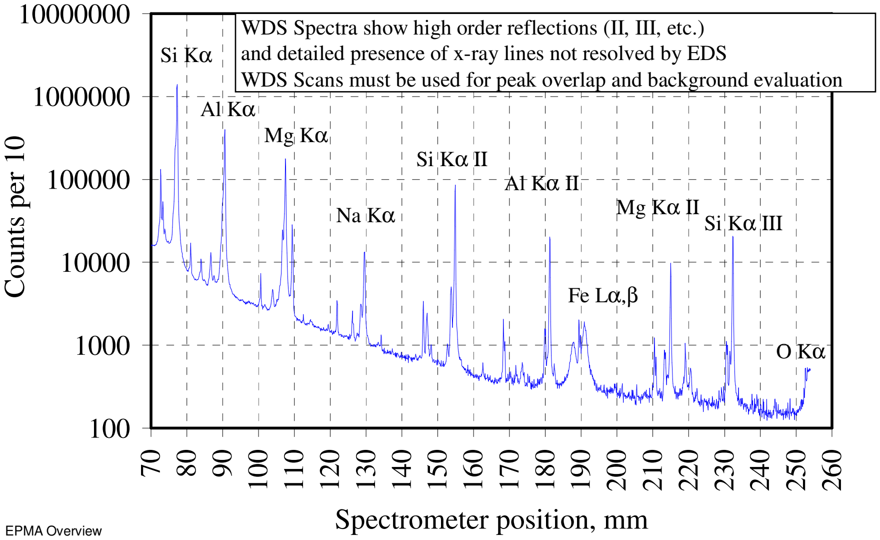
WDS and EDS Comparison: Kakanui Hornblende WDS TAP GFC, SiLi EDS, Energy Scale



WDS Wavelength Scan

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

WDS Scan TAP Kakanui Hornblende



WDS Spectra show high order reflections (II, III, etc.)
and detailed presence of x-ray lines not resolved by EDS
WDS Scans must be used for peak overlap and background evaluation

---

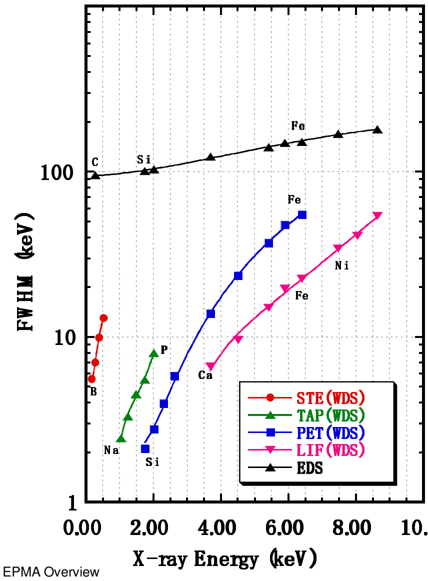
WDS Detector: Ar Ionization Counter

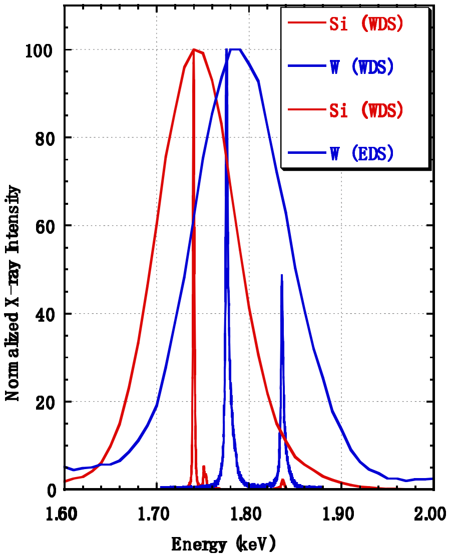
Ar ionization energy 27 eV
The number of ionizations is: n = Photon energy / 27 eV
Compare with Si EDS 3.8 eV detection process, factor of 7

Photon	Energy eV	Ar+ per photon
Be Kα	110	4
Mg Kα	1254	46
Fe Kα	6403	237
Ge Kα	9885	366
Zr Kα	15774	584

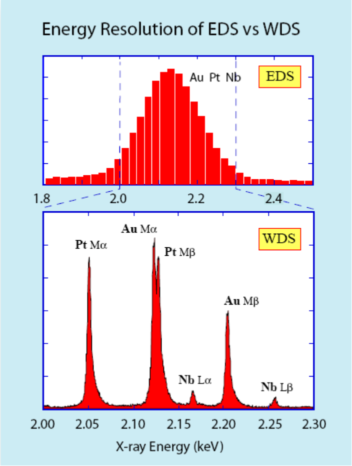
These low signals are then amplified by the counter which is operated in the proportional mode, with $10^2 – 10^5$ amplification

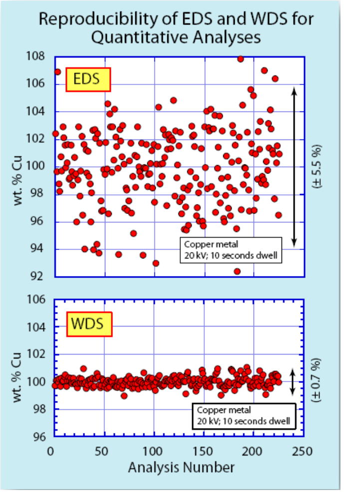
Energy Resolution EDS vs. WDS





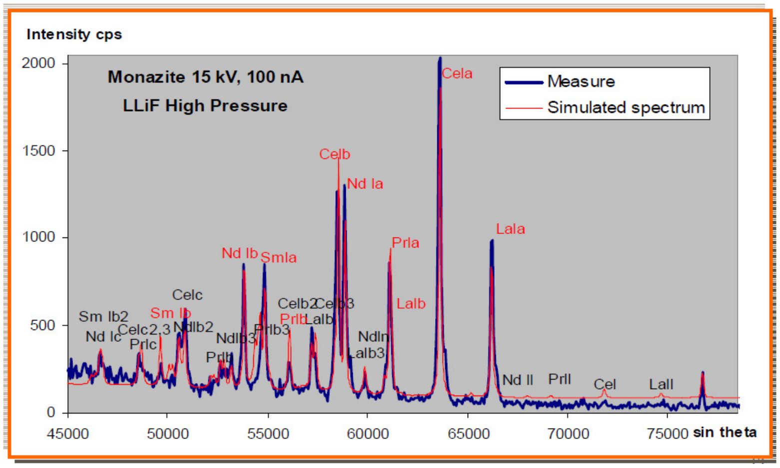
WDS Exhibits Superior Peak Resolution, P/B, Precision for Typical Systems


Energy Resolution of EDS vs WDS


Reproducibility of EDS and WDS for Quantitative Analyses

McSwiggen

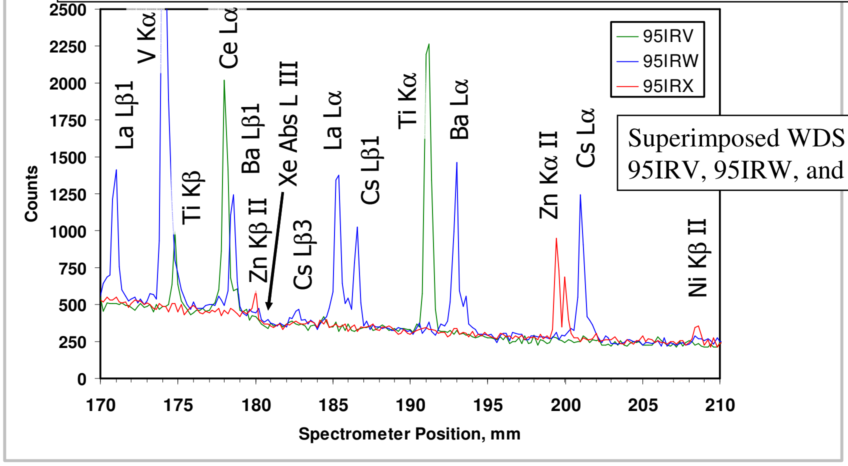
WDS Spectrum Simulation



Cameca, M&M 2001

WDS Scan: LiF on JEOL 733 w/ sealed Xe counter
Corning 95IR trace element glasses (~0.79 wt% oxide)

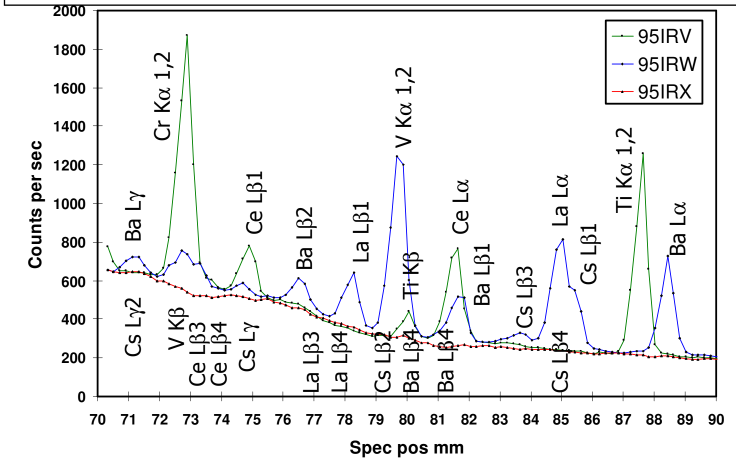
LiF crystal preferred for trace element EPMA: P/B and resolution
Note: 2nd order peaks from ~5000ppm elements, Xe edge
Interferences Ti Kβ – V Kα, Ba Lβ1 – Ce Lα, La Lα – Cs Lβ1 (unresolved, 95IRW)
Ti Kα – Ba Lα, Zn Kα II – Cs Lα



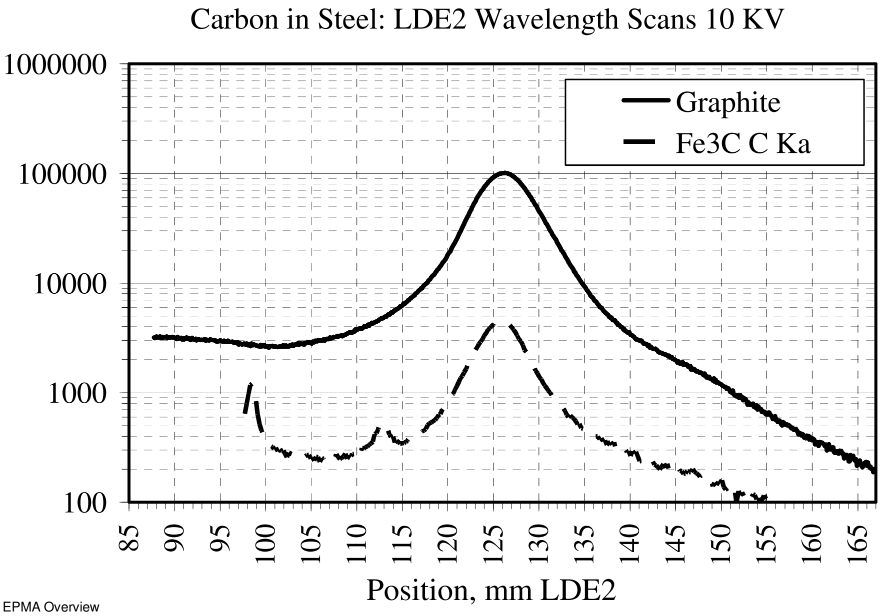
Superimposed WDS scans 95IRV, 95IRW, and 95IRX

WDS Scan: PET on JEOL 733
Corning 95IR trace element glasses (~0.79 wt% oxide)

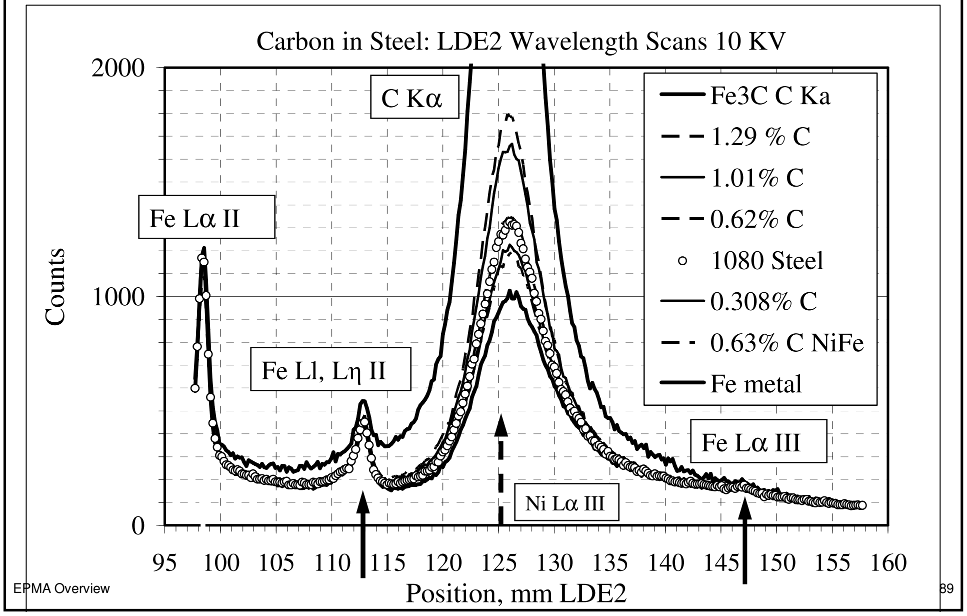
PET not preferred for trace element EPMA (if LiF applicable)
Interferences V Kβ – Cr Kα, Ti Kβ – V Kα, Ba Lβ1 – Ce Lα, La Lα – Cs Lβ1 (unresolved, 95IRW) Ti Kα – Ba Lα



Comparison of C Kα Full Peak on Graphite w Fe_3C



Experimental WDS Scans Carbon in Steel LDE2: No Reflections > 2nd order



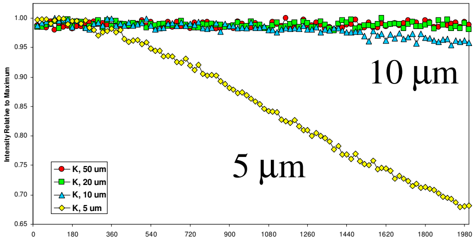
Beam Sensitive Materials

- Is the sample or standard stable under the electron beam? At the probe current proposed for measurement?
- Reduce the probe current, at constant beam diameter, to reduce beam damage. Voltage is not an issue for SEM/EPMA.
- Defocusing the beam reduces the electron dose per unit area, and is the most effective means of reducing damage.
- Determine stability by performing “time scan”, measuring the count rate as a function of time; the count rate should not go up or down. Recheck sample charging.
- Alternatively, perform replicate analyses on the same spot. If subsequent analyses duplicate the first, either no damage has occurred or it all occurred in the first analysis.
- After completion of the analysis, inspect the analysis point using secondary and backscattered-electron imaging. There should be no detectable damage or burn mark.

Beam-sensitive Materials:
Time-dependent X-ray Count Rate

Normalized X-ray Intensity vs. Time (2000 sec FS)

95IRV: K



Time, seconds (2000 sec FS)

Calculated ΔT for i, d

	Diameter, µm				
	1	5	10	20	100
100 nA	96 K	19	10	5	1
250 nA	240	48	24	12	2.4

ΔT (degrees K) from Castaing equation:

$$\Delta T = 4.8\ E_o\ i / \lambda\ d$$

E_o beam voltage keV
i probe current uA
λ thermal conductivity W/cm deg K
d beam diameter in µm

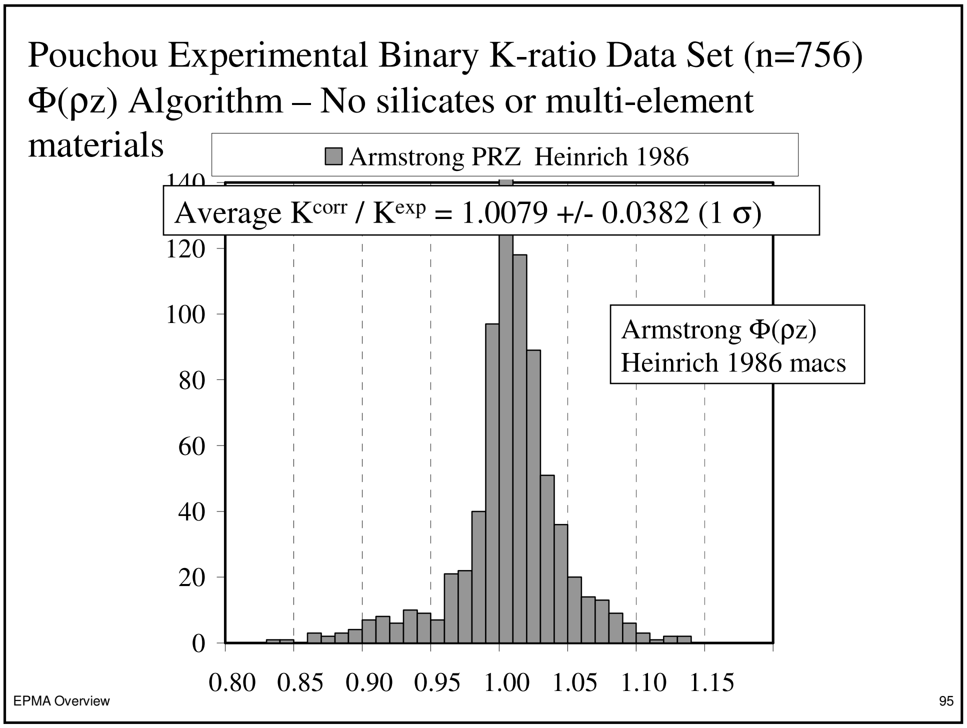
Accuracy, WDS vs. EDS
WDS Alignment Verification

CMASTF Silicate Standards
Geological materials are multicomponent

- End-member stoichiometric silicate and oxide mineral standards
- Primary standards:
  - MgO, Al_2O_3, SiO_2, $CaSiO_3$, TiO_2, and Fe_2O_3
- Analyzed suite of stoichiometric standards, natural and synthetic materials:
  - Second set of primary standards on different mounts
  - Spinel $MgAl_2O4$, Enstatite $MgSiO_3$, Forsterite Mg_2SiO_4
  - Kyanite Al_2SiO_5
  - Fayalite Fe_2SiO_4
- Well characterized natural mineral standards and glasses:
  - Olivines $(Mg,Fe)_2SiO_4$
  - Diopside $CaMgSi_2O_6$, Anorthite $CaAl_2Si_2O_8$, Sphene $CaTiSiO_5$
  - Ilmenite $FeTiO_3$
  - Synthetic glasses in CMAS and CMASF system:
    - Weill CMAS glasses, NBS K411, K412

CMASTF Stds: Natural & Synthetic Minerals
Composition in Wt% Oxide

Standard	MgO	Al2O3	SiO2	CaO	TiO2	FeO* or Fe2O3
Alaska Anorthite		36.03	44.00	19.09		0.62
Boyd Olivine	51.63		40.85			7.17
Ilmen Mtns Ilmenite	0.31				45.70	46.54
K411 Glass	14.67	0.10	54.30	15.47		14.42
K412 Glass	19.33	9.27	45.35	15.25		9.96
Kyanite P236		62.91	37.09			
Natural Bridge Diopside	18.31	0.06	55.40	25.78	0.01	0.26
ORNL, RDS Fayalite			29.49			70.51
San Carlos Olivine	49.42		40.81			9.55
Shankland Forsterite	57.30		42.70			
Springwater Olivine	43.58		38.95			16.62
Taylor Kyanite	0.00	62.70	37.00			0.16
Taylor Olivine	50.78		41.15			7.62
Taylor Sphene		1.36	30.83	28.82	37.80	0.66
Taylor Spinel	28.34	71.66				
Weill A	11.05	16.07	49.72	23.15		
Weill B	13.99	16.05	48.99	20.97		
Weill D	17.97	20.96	45.07	16.00		
Weill E*	6.00	8.99	79.97	5.04		
Weill Enstatite Glass	40.15	0.00	59.85			
Weill F	10.07	30.93	52.06	6.94		
Weill G	32.69	3.31	61.12	2.89		
Weill H	5.22	41.90	30.91	21.97		
Weill I	19.03	2.01	52.95	26.01		
Weill J	1.01	19.02	42.98	36.99		

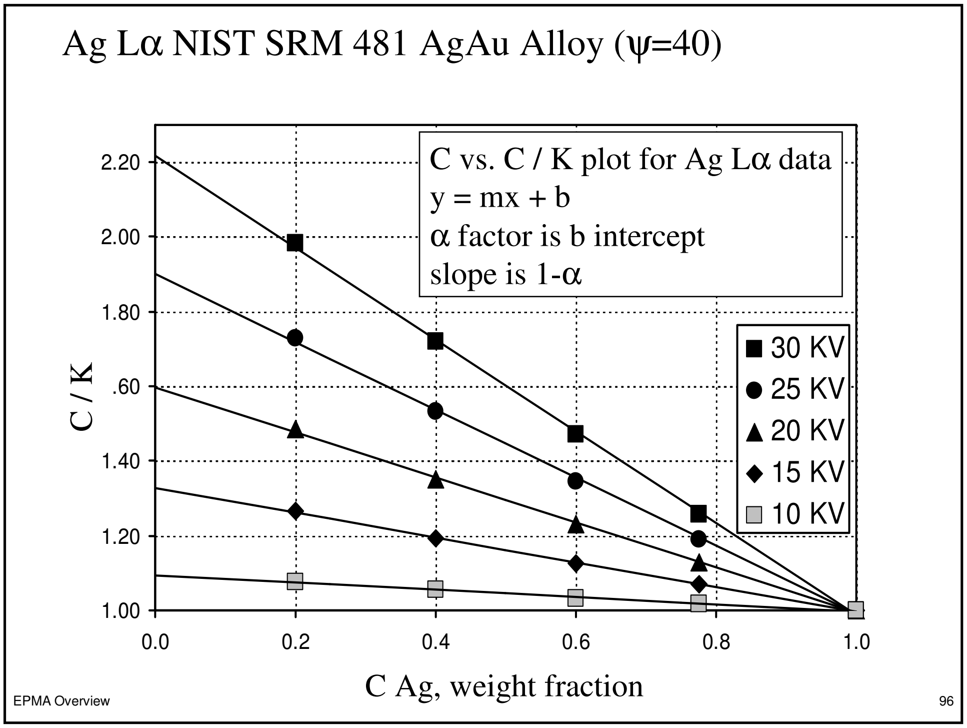


Pouchou Experimental Binary K-ratio Data Set (n=756) $\Phi(\rho z)$ Algorithm – No silicates or multi-element materials

Average K^{corr} / K^{exp} = 1.0079 +/- 0.0382 (1 σ)

Armstrong $\Phi(\rho z)$
Heinrich 1986 macs

EPMA Overview



Ag Lα NIST SRM 481 AgAu Alloy (ψ=40)

C vs. C / K plot for Ag Lα data
y = mx + b
α factor is b intercept
slope is 1-α

EPMA Overview

Accuracy Study for EPMA
Comparison of Measured to Calculated K-ratio

- $K_{measured}$ dependent on:
  - Accelerating Potential
  - Probe current
  - Detector (gas, sealed)
  - Pulse processing
  - PHA calibration
  - Deadtime
  - Spectrometer alignment
  - Sample homogeneity
  - P-B determination, stripping, counting statistics
  - Other sampling/drift factors
- $K_{calculated}$ dependent on:
  - Correct composition of standard
  - Correction algorithms
  - Data sets, mass absorption coefficients
  - Other algorithmic factors

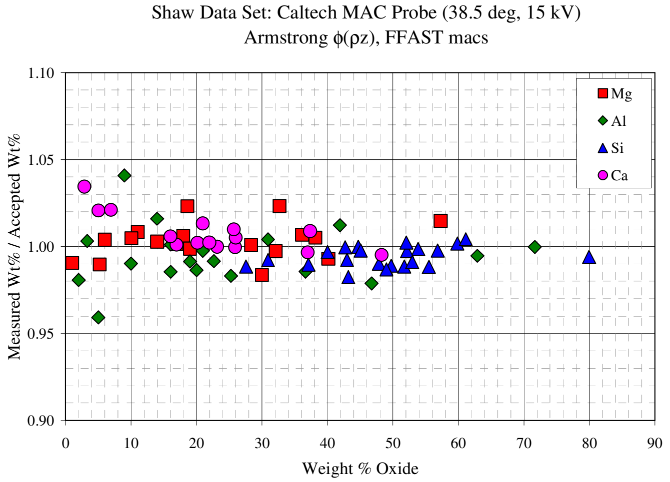
$$K_{measured} = \frac{(P-B)^{sample}}{(P-B)^{standard}}$$

$$C = K * ZAF$$

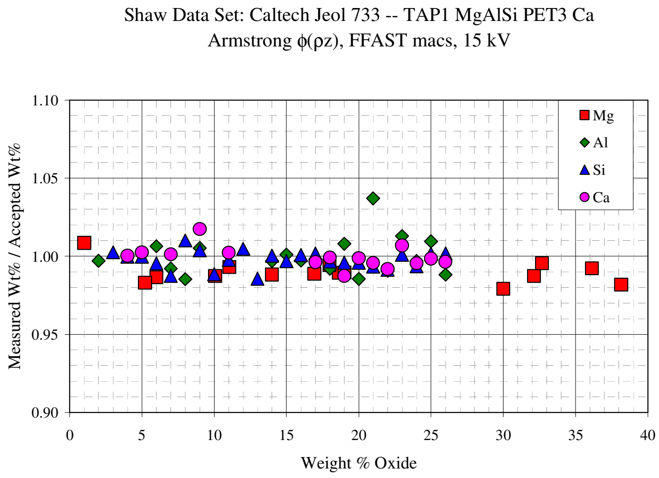
$$K_{calculated} = C / ZAF$$

$$\text{Evaluate}: \frac{K_{measured}}{K_{calculated}}$$

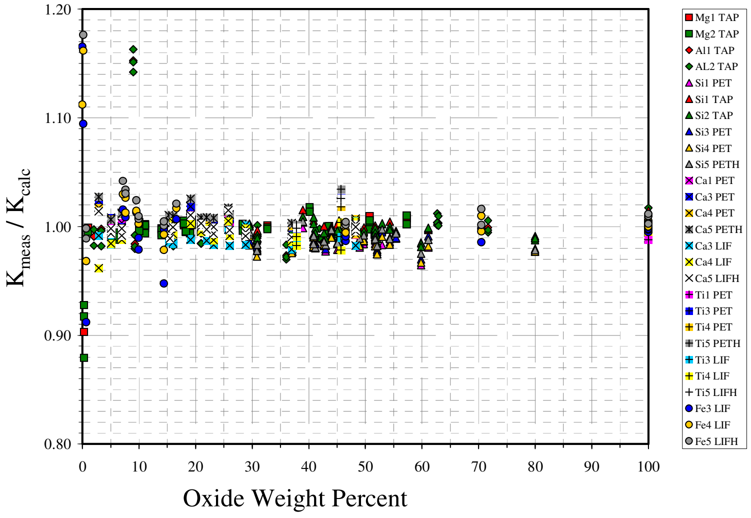
Historical CMAS Data
Caltech MAC Probe, Circa 1980’s



Caltech JEOL 733 1990's
Spectrometer 1 TAP for Mg Al Si (Ca PET)

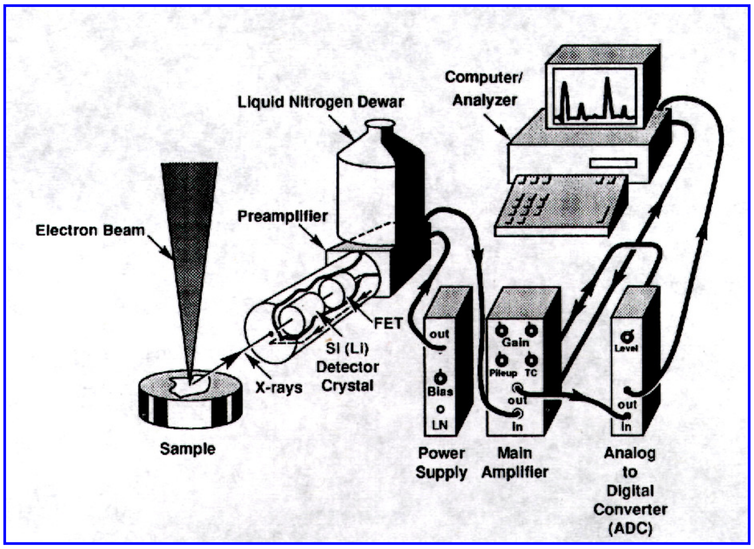


WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed

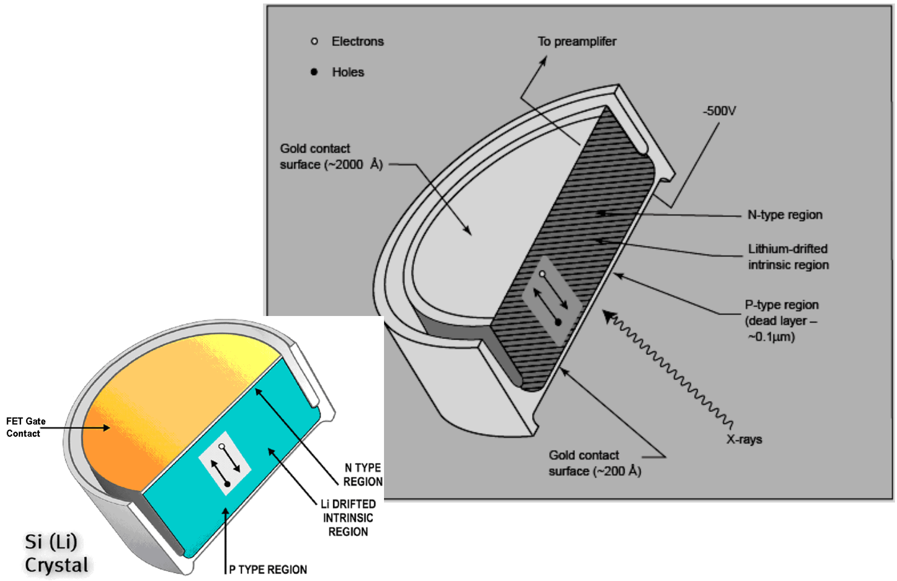


EPMA:
What’s New and Important About
Energy-Dispersive Spectrometry
Silicon Drift EDS Detectors

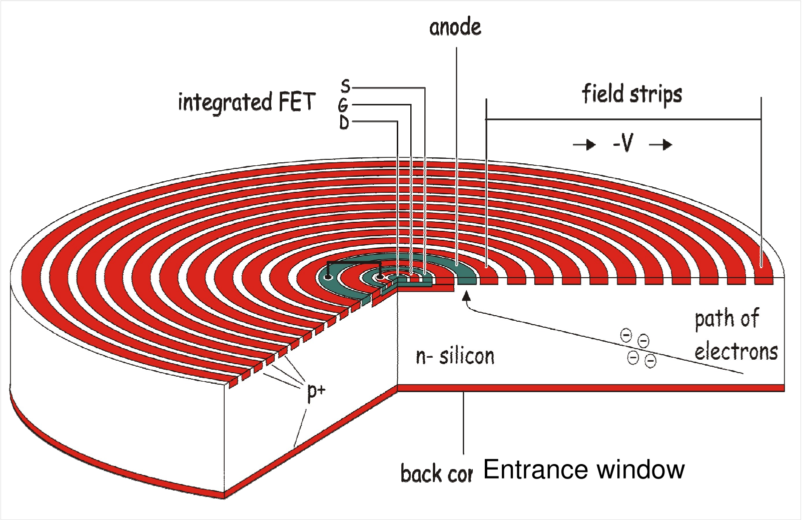
EDS Analyzer System



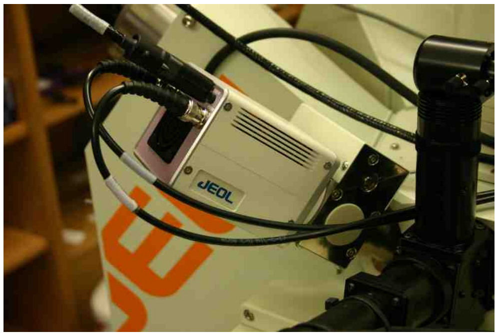
Conventional SiLi EDS Detector



Silicon Drift Detector

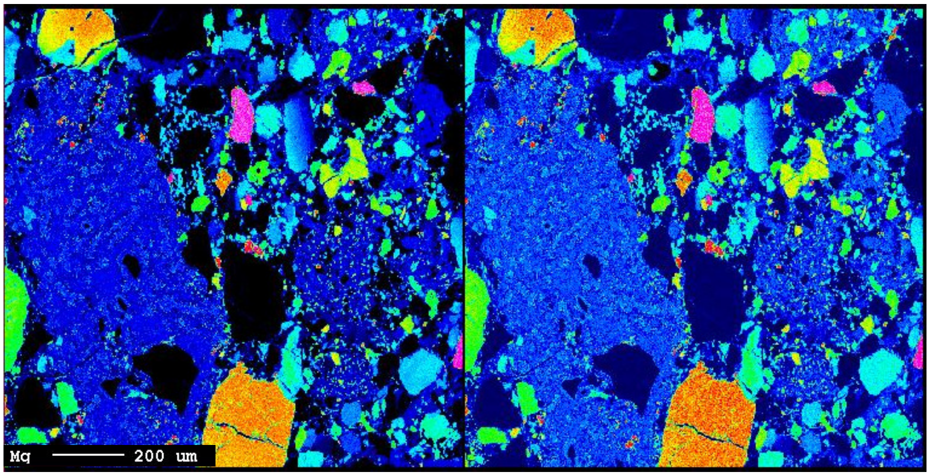


Washington University
Earth and Planetary Sciences JEOL JXA-8200
S



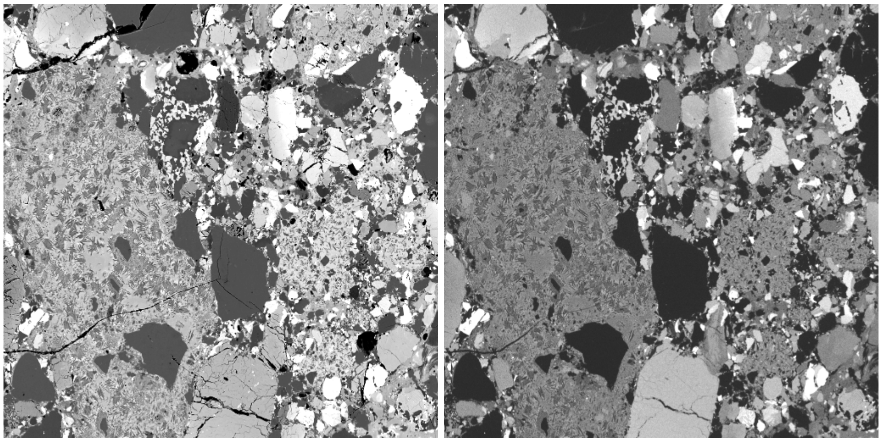
JEOL e2v Silicon Drift Detector
130 eV resolution
3 time constants T3 T2 T1
Stage and beam mapping
Quantitative EDS analysis LLSQ

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



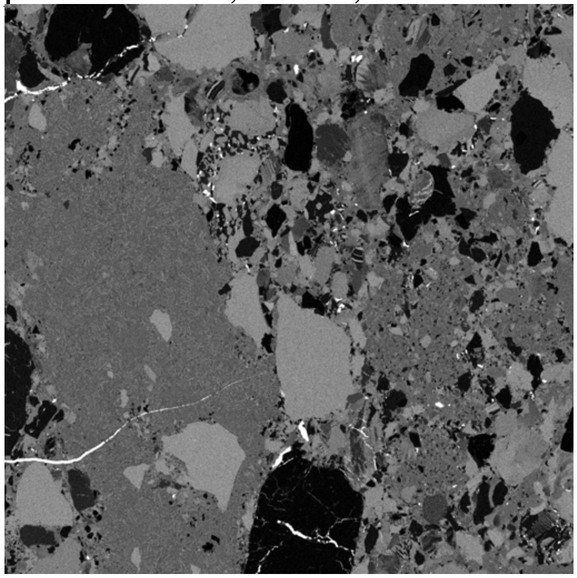
Mg WDS 1061 max counts, Mg SDD 527 max counts
1024x1024 stage map, 8 hours

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

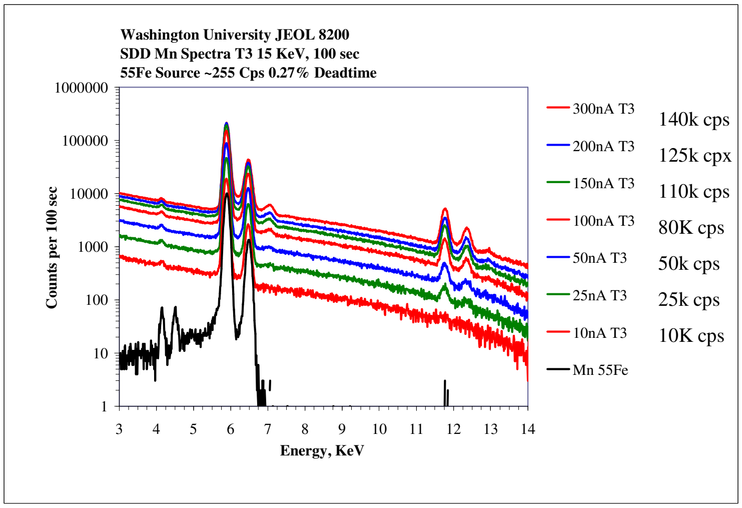


Backscattered electron vs. Fe SDD maps

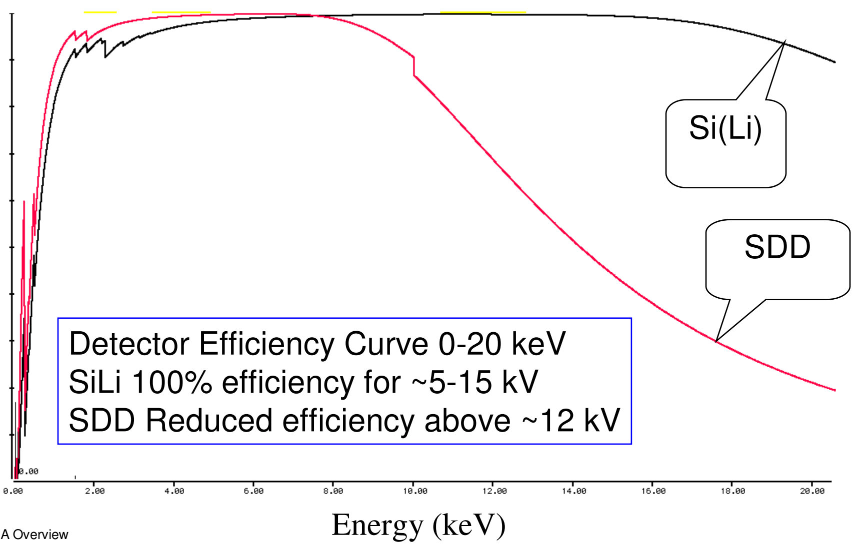
Lunar Meteorite SAU169
Stage map 1024x1024, 25 ms, 8 hr run: Ca Kα SDD



WU8200 JEOL SDD
^{55}Fe Source Mn Kα Resolution 130 eV

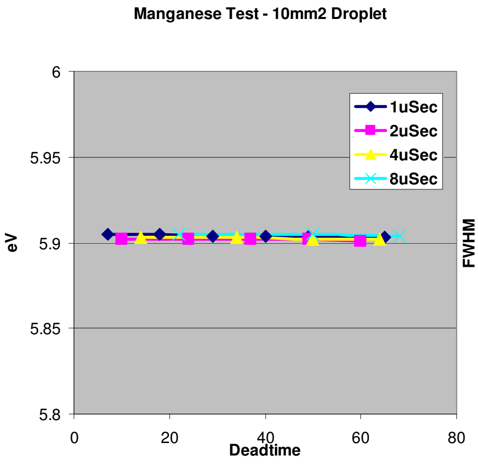


SiLi vs. SDD Detector Efficiency

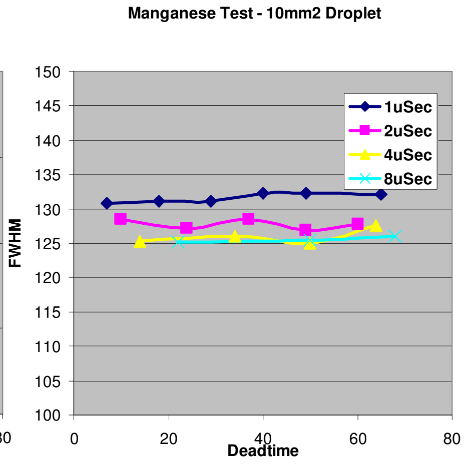


Detector Efficiency Curve 0-20 keV
SiLi 100% efficiency for ~5-15 kV
SDD Reduced efficiency above ~12 kV

SDD Performance with increasing Count Rate

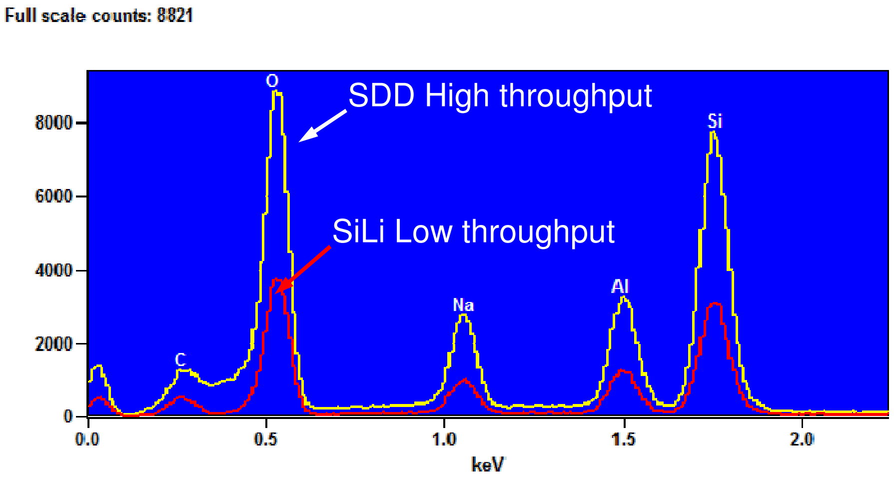


Manganese Test - 10mm2 Droplet

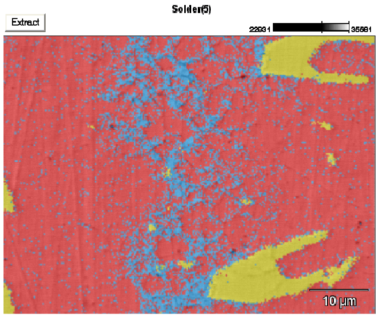


Manganese Test - 10mm2 Droplet

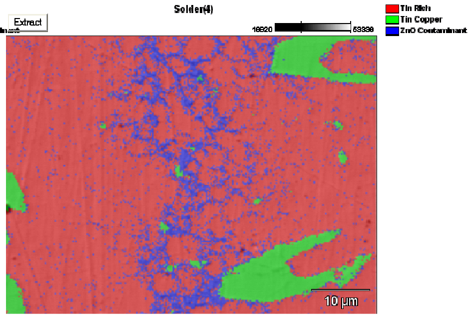
Throughput Comparison of SDD and SiLi Detectors



Mapping Performance SnCuZn Alloys
SiLi vs. SDD

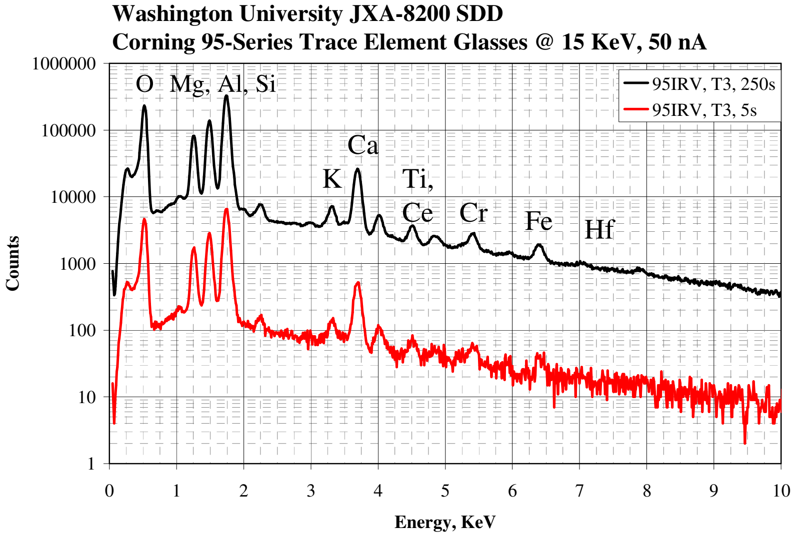


SiLi

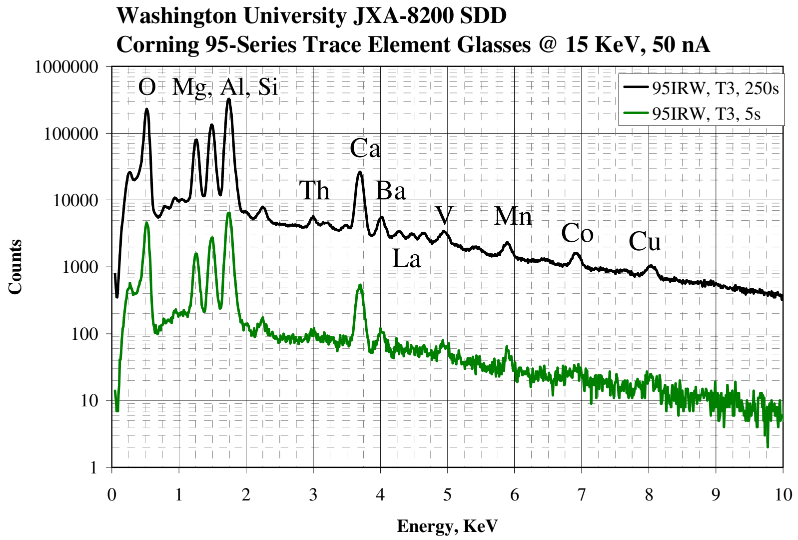


SDD

Washington University JXA-8200 SDD
Corning 95IRV: K, Ti, Cr, Fe, Ce, Hf



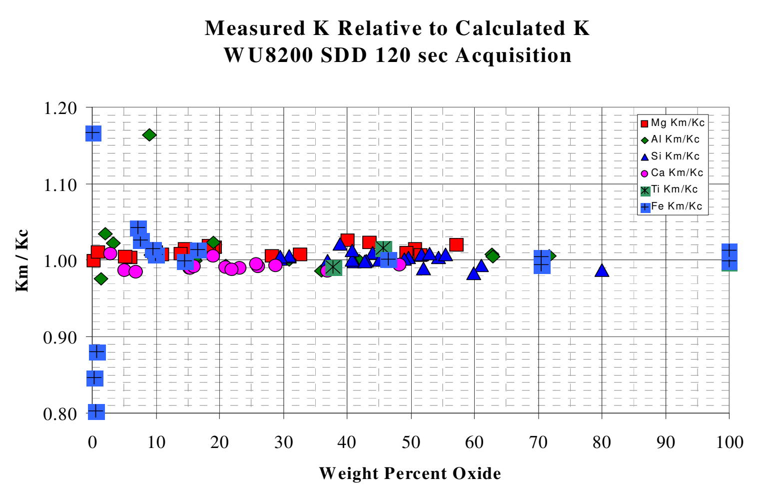
Washington University JXA-8200 SDD Corning 95IRW: V, Mn, Co, Cu, Cs, Ba, La, Th



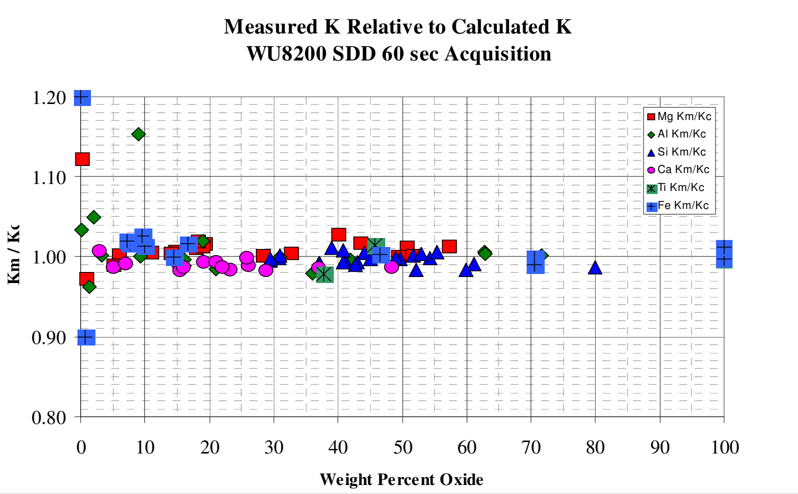
Washington University JEOL JXA-8200 SDD Quantitative Analysis Data

- SDD great for mapping, what about quantitative analysis?
- SDD EDS data acquired at 120s, 60s, and 3s acquisitions at T3 time constant
- Standards used: MgO, Al_2O_3, SiO_2, $CaSiO_3$, TiO_2, and Fe_2O_3
- Linear least-squares peak deconvolution (JEOL software)
- Extracted raw K-ratios processed using Armstrong $\Phi(\rho z)$ and FFAST macs for comparison with WDS data

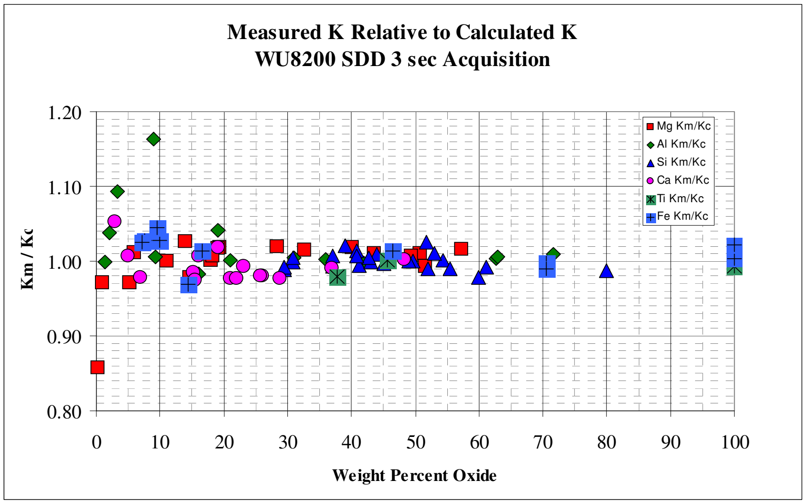
CMASTF Standard Analyses
WU8200 SDD LLSQ 120 sec. Acquisition T3



CMASTF Standard Analyses
WU8200 SDD LLSQ 60 sec. Acquisition T3



CMASTF Standard Analyses
WU8200 SDD LLSQ 3 sec. Acquisition T3



Average Kmeas / Kcalc for CMASTF Standards
WU8200 SDD Data @ 120, 60, 3 s acquisition T3

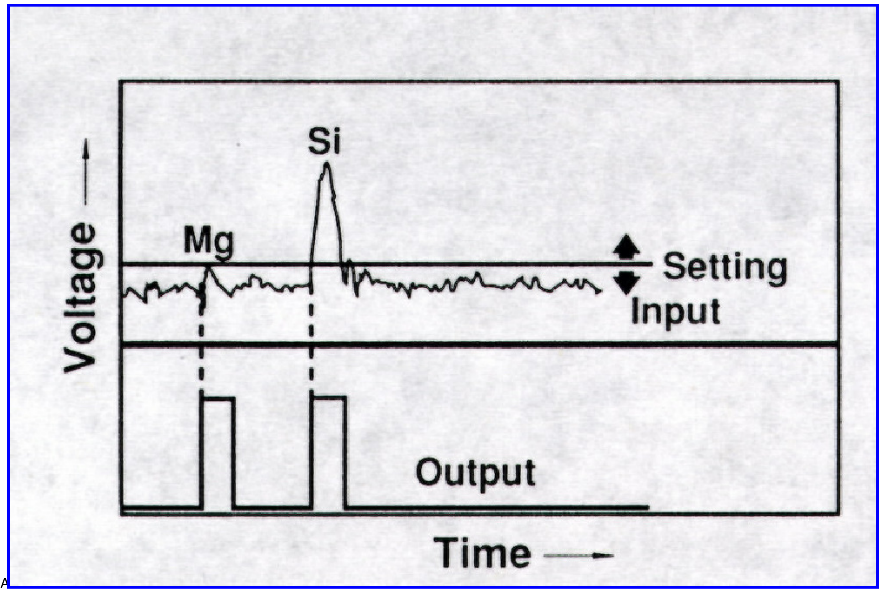
120s Data	**Mg**	**Al**	**Si**	**Ca**	**Ti**	**Fe**
Average	1.0122	1.0064	1.0017	0.9926	1.0021	1.0108
1 σ	0.0063	0.0122	0.0078	0.0066	0.0106	0.0140
Relative %	0.62	1.21	0.78	0.67	1.06	1.38
60s Data						
Average	1.0058	1.0022	0.9969	0.9895	0.9975	1.0083
1 σ	0.0118	0.0162	0.0069	0.0066	0.0150	0.0113
Relative %	1.17	1.61	0.69	0.67	1.51	1.12
3s Data						
Average	1.0061	1.0135	1.0001	0.9933	0.9947	1.0123
1 σ	0.0162	0.0263	0.0104	0.0213	0.0118	0.0211
Relative %	1.61	2.59	1.04	2.14	1.19	2.09

Fast Discriminator

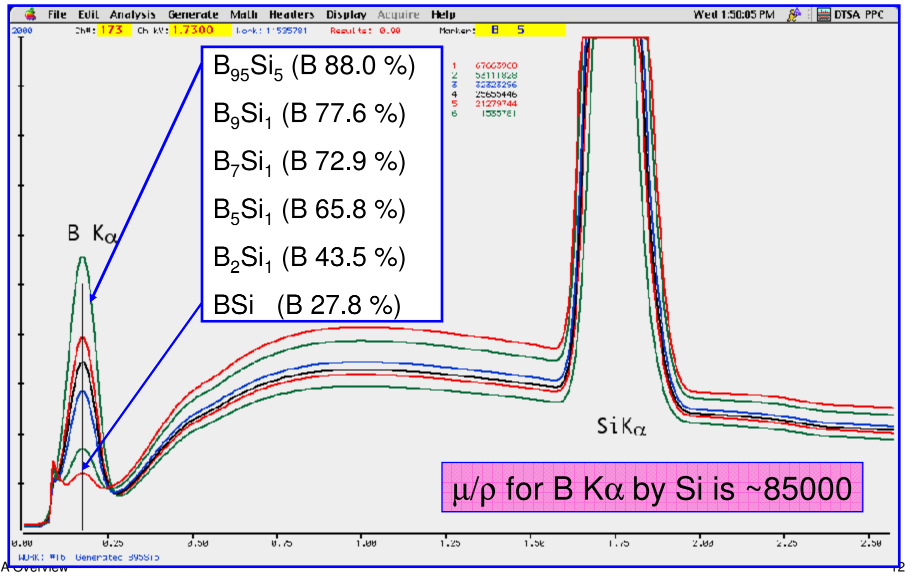
- The fast discriminator setting is used to differentiate between noise and x-ray pulses.
- A pulse having a voltage that exceeds the threshold is “detected”, all others are ignored.
- The FD is good at discriminating high energy photons from noise, but is bad at discriminating low energy (i.e. light element) photons.
- If the FD is set too high, low energy photons are ignored. If the FD is set too low, noise is processed and competes with real x-rays for processing time.
- Slow drift in the detector electronics requires periodic inspection of the FD setting. It is critical to set the FD properly for light element analysis.

Light Element EDS Analysis
and
Detector Performance

Fast Discriminator Setting



Boron Kα in Silicon – 10kV 40 degrees



$B_{95}Si_5$ (B 88.0 %)

B_9Si_1 (B 77.6 %)

B_7Si_1 (B 72.9 %)

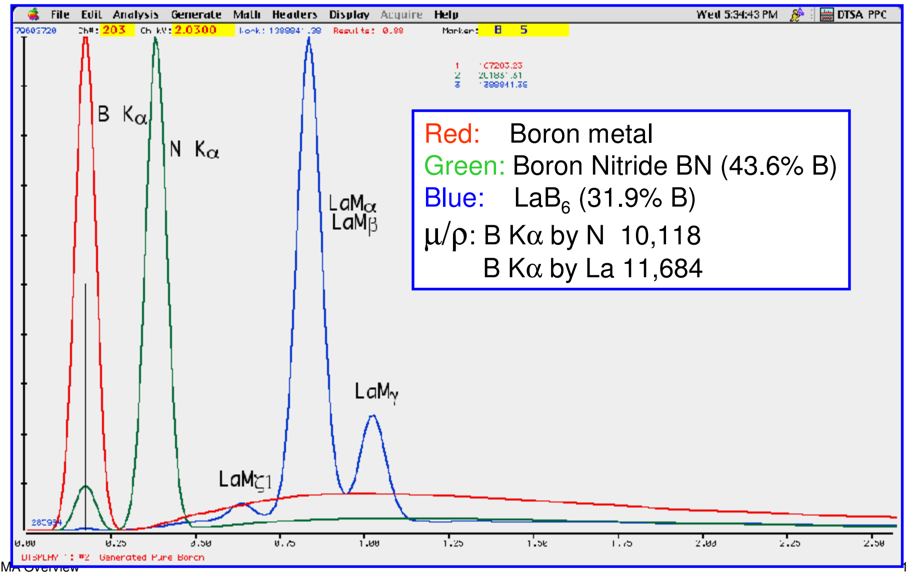
B_5Si_1 (B 65.8 %)

B_2Si_1 (B 43.5 %)

BSi (B 27.8 %)

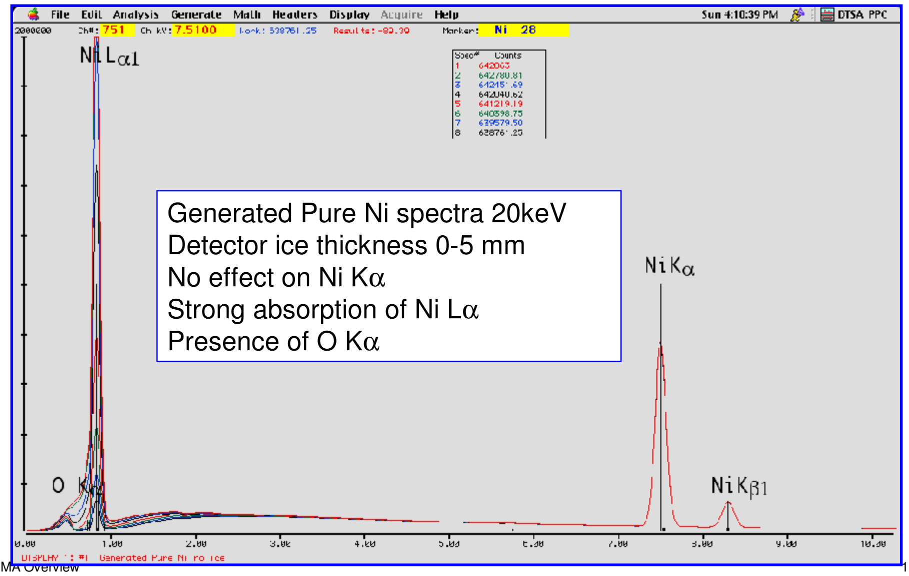
μ/ρ for B Kα by Si is ~85000

Boron EDS Spectra 10kV, 40 degrees



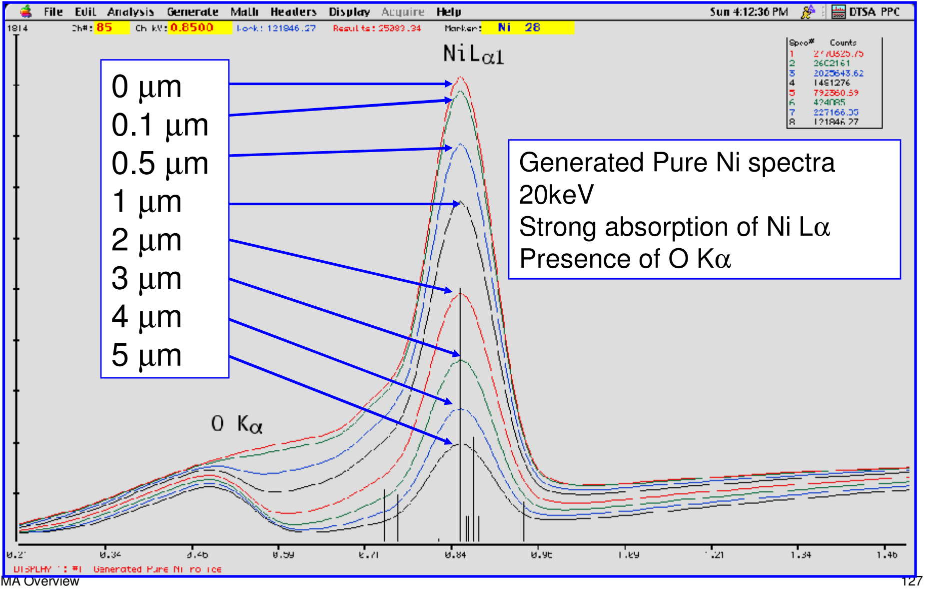
Red: Boron metal
Green: Boron Nitride BN (43.6% B)
Blue: LaB_6 (31.9% B)
μ/ρ: B Kα by N 10,118
B Kα by La 11,684

Ni Kα and Lα vs. Ice Thickness
Applicable to SiLi LN-cooled EDS systems only!



Generated Pure Ni spectra 20keV
Detector ice thickness 0-5 mm
No effect on Ni Kα
Strong absorption of Ni Lα
Presence of O Kα

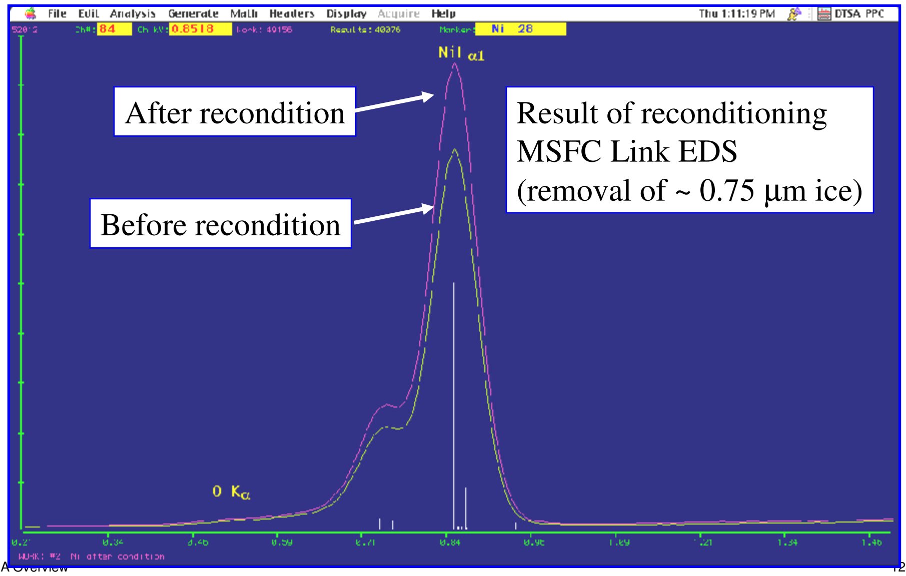
Ni Lα vs. Ice Thickness
Applicable to SiLi LN-cooled EDS systems only!



Spec#	Counts
1	2770625.75
2	2602161
3	2025643.62
4	1481276
5	792360.59
6	424085
7	227166.35
8	121846.27

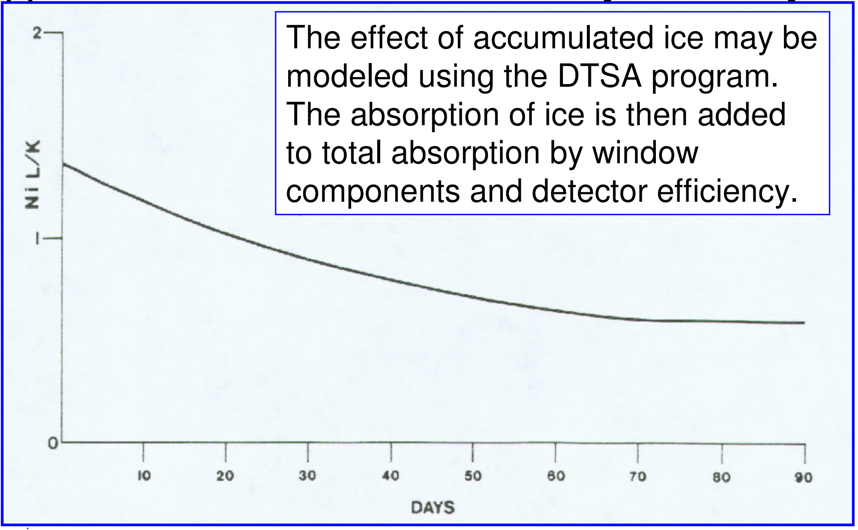
Generated Pure Ni spectra
20keV
Strong absorption of Ni Lα
Presence of O Kα

MSFC Link Recondition EDS
Applicable to SiLi LN-cooled EDS systems only!



Result of reconditioning
MSFC Link EDS
(removal of ~ 0.75 µm ice)

Ice Accumulation Monitor:
Ratio of Ni Lα / Ni Kα
Applicable to SiLi LN-cooled EDS systems only!



The effect of accumulated ice may be modeled using the DTSA program. The absorption of ice is then added to total absorption by window components and detector efficiency.

Qualitative Analysis
Reliance on EDS for ID of Elements

Qualitative Analysis (EDS)

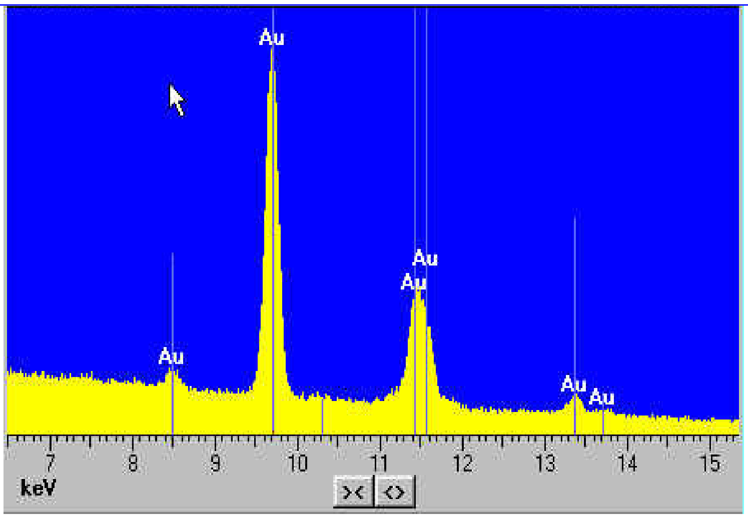
- Qualitative analysis is the identification of the elements present.
- The presence or absence of an element is established based on the presence or absence of x-ray peaks or families of peaks.
- Approximate relative concentrations may be estimated using relative peak heights, but may be subject to large uncertainty.
- X-ray database – list of x-ray peaks and heights.
- Energy calibration of EDS spectrum.

Relative X-ray Line Weights

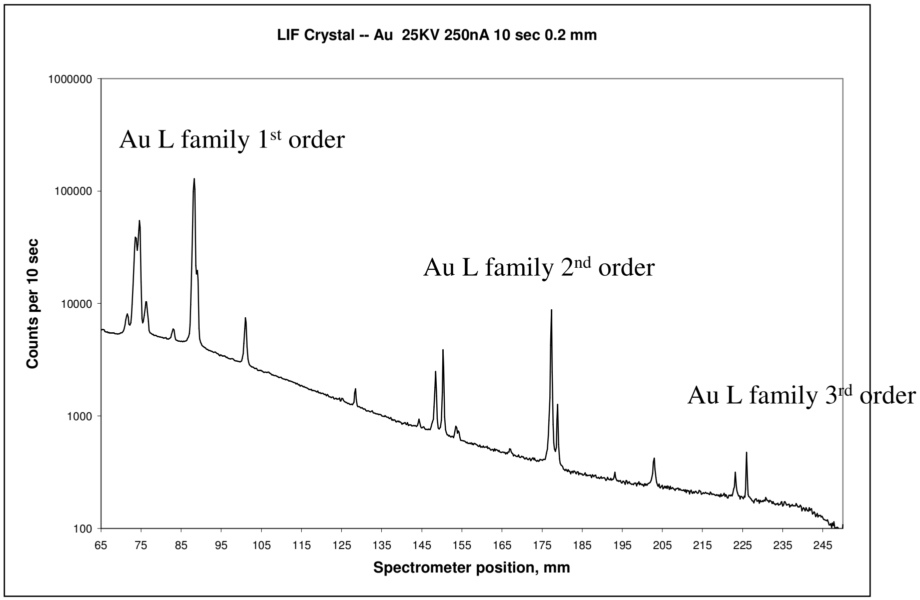
- X-ray lines intensities are referenced relative to the most intense peak, i.e., Kα, Lα, or Mα.
- These peaks are assigned a 100% relative intensity.
- All other family lines for that element are scaled relatively:
- These line weights are only approximately known and need revision
- Note: Absolute x-ray intensity depends on: keV, U, E_c, μ/ρ, detector efficiency, etc.
  So intensity of Al Kα is not equal to Cu Kα, etc.
- The relative intensity values are at best consistent only for a given family of an element.

Au L Family from Pure Au

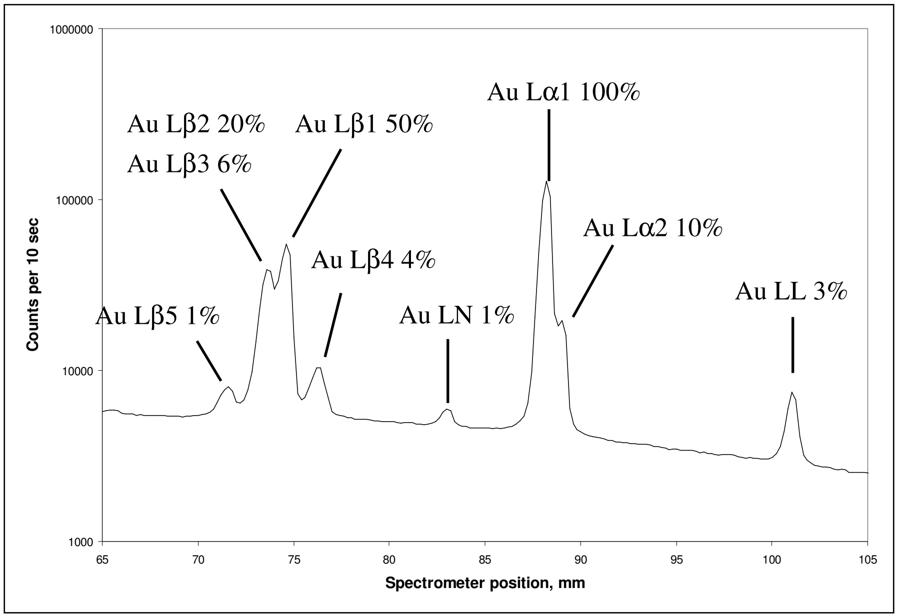
Use the position of KLM markers primarily, with relative intensity secondarily, in identification of an element



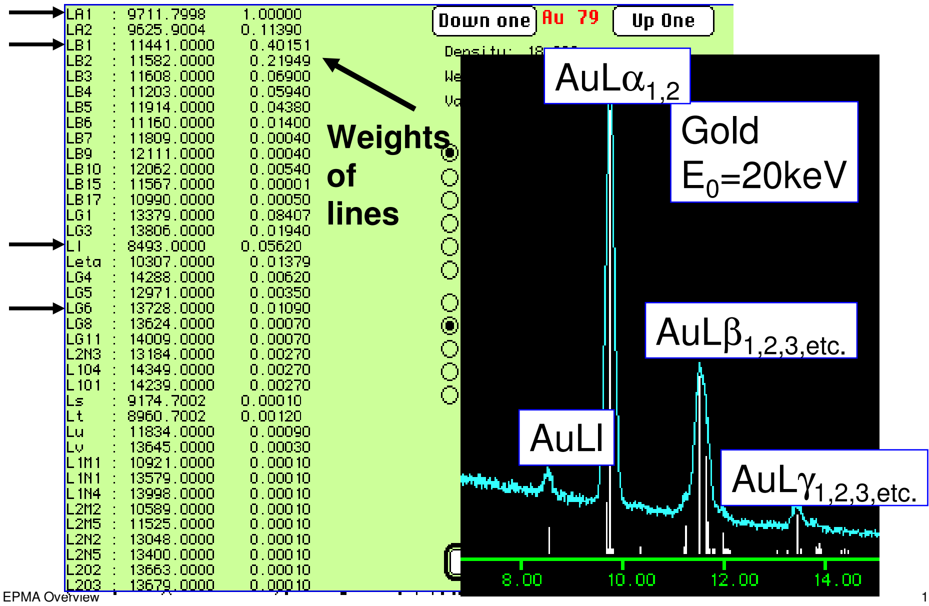
WDS Scan Au 25kV



WDS Scan Au 25kV



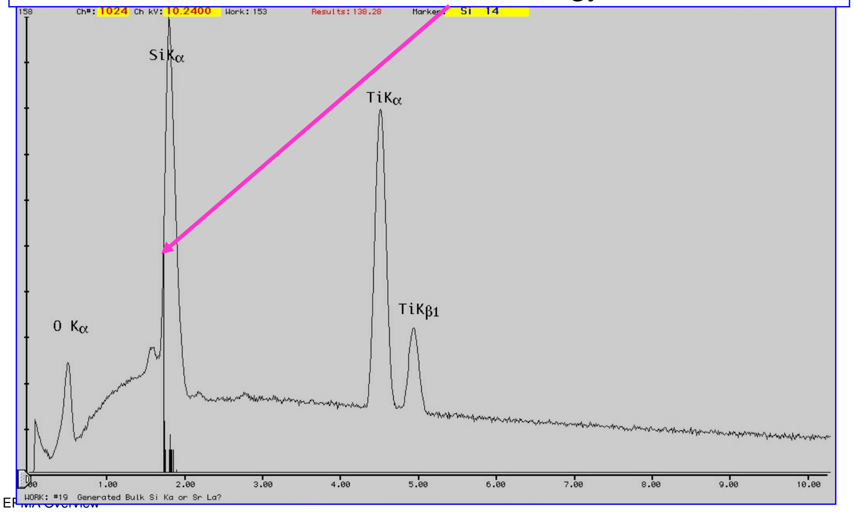
X-ray Database—Line Weights



```
LA1  :  9711.7998   1.00000
LA2  :  9625.9004   0.11390
LB1  :  11441.0000   0.40151
LB2  :  11582.0000   0.21949
LB3  :  11608.0000   0.06900
LB4  :  11203.0000   0.05940
LB5  :  11914.0000   0.04380
LB6  :  11160.0000   0.01400
LB7  :  11809.0000   0.00040
LB9  :  12111.0000   0.00040
LB10 :  12062.0000   0.00540
LB15 :  11567.0000   0.00001
LB17 :  10990.0000   0.00050
LG1  :  13379.0000   0.08407
LG3  :  13806.0000   0.01940
Ll   :  8493.0000   0.05620
Leta :  10307.0000   0.01379
LG4  :  14288.0000   0.00620
LG5  :  12971.0000   0.00350
LG6  :  13728.0000   0.01090
LG8  :  13624.0000   0.00070
LG11 :  14009.0000   0.00070
L2N3 :  13184.0000   0.00270
L104 :  14349.0000   0.00270
L101 :  14239.0000   0.00270
Ls   :  9174.7002   0.00010
Lt   :  8960.7002   0.00120
Lu   :  11834.0000   0.00090
Lv   :  13645.0000   0.00030
L1M1 :  10921.0000   0.00010
L1N1 :  13579.0000   0.00010
L1N4 :  13998.0000   0.00010
L2M2 :  10589.0000   0.00010
L2M5 :  11525.0000   0.00010
L2N2 :  13048.0000   0.00010
L2N5 :  13400.0000   0.00010
L202 :  13663.0000   0.00010
L203 :  13679.0000   0.00010
```

Peak Identification – Is it Si Kα or ?
Spectrum Displayed/Acquired at 0-10 keV

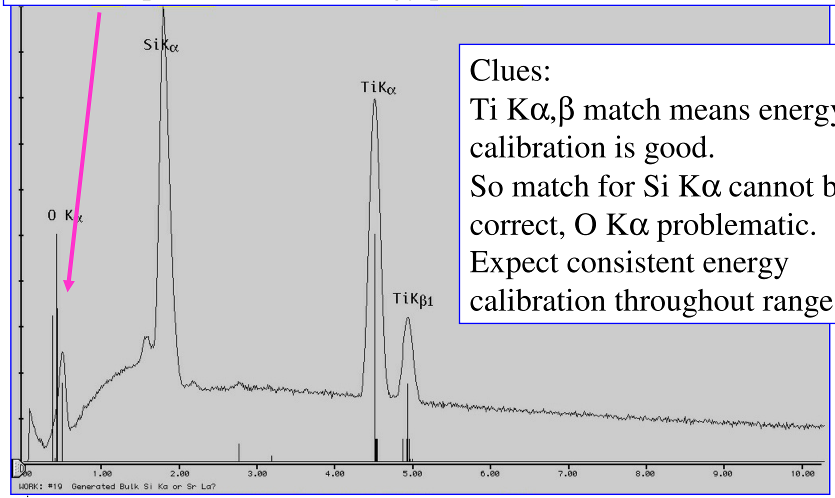
Initial ID indicates Ti, Si, and O. Poor energy match for Si Kα


158 Ch#: 1024 Ch kV: 10.2400 Work: 153 Results: 138.28 Marker: Si 14

WORK: #19 Generated Bulk Si Ka or Sr La?

Is it O Kα or Ti Lα ?
Spectrum Acquired at 0-10 keV

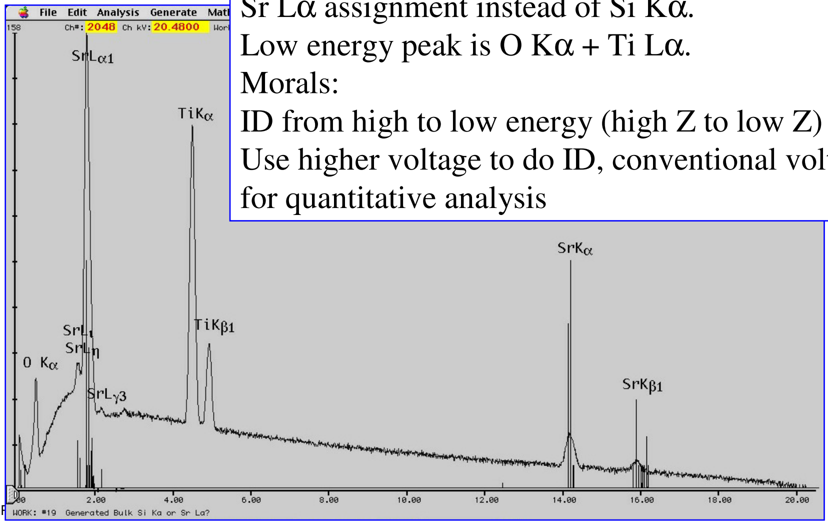
Closer inspection of low energy peak. Is it O Kα or Ti Lα ?


WORK: #19 Generated Bulk Si Ka or Sr La?

Clues:
Ti Kα,β match means energy calibration is good.
So match for Si Kα cannot be correct, O Kα problematic.
Expect consistent energy calibration throughout range

$SrTiO_3$ Confirmed by 20 keV Acquisition

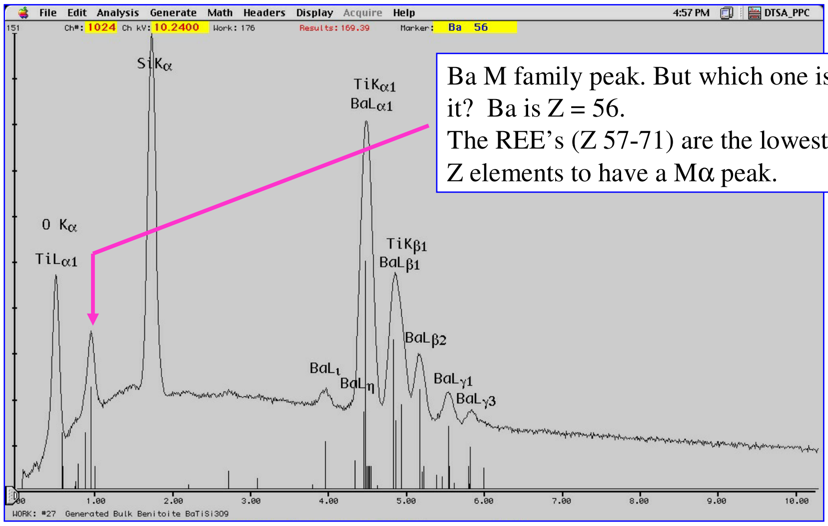
ID of Sr Kα,Kβ peaks at higher energy
Sr Lα assignment instead of Si Kα.
Low energy peak is O Kα + Ti Lα.
Morals:
ID from high to low energy (high Z to low Z)
Use higher voltage to do ID, conventional voltage for quantitative analysis



Ch#: 2048 Ch kV: 20.4800

WORK: #19 Generated Bulk Si Ka or Sr La?

Benitoite $BaTiSi_3O_9$

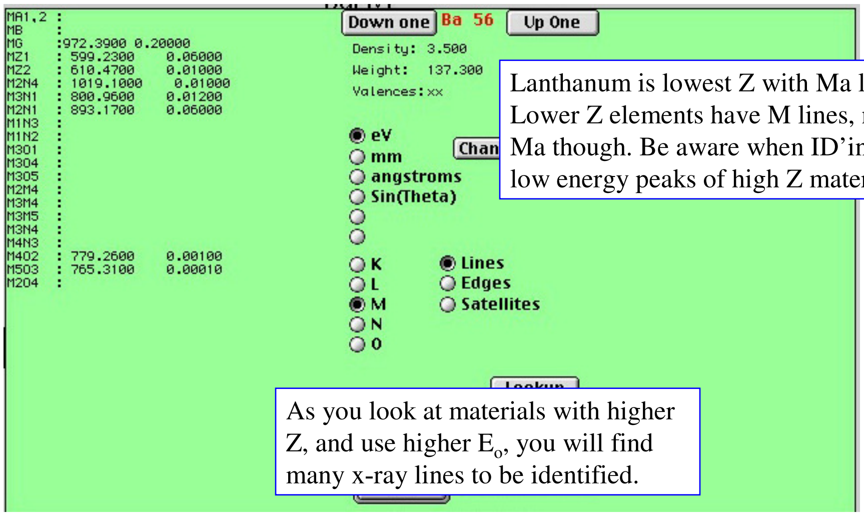


Ch#: 1024 Ch kV: 10.2400 Work: 176 Results: 169.39 Marker: Ba 56

WORK: #27 Generated Bulk Benitoite BaTiSi309

Ba M family peak. But which one is it? Ba is Z = 56.
The REE's (Z 57-71) are the lowest Z elements to have a Mα peak.

Ba has no Mα line, only Mγ, Mz1, Mz2, etc.



```
MA1,2 :
MB    :
MG    :972.3900 0.20000
MZ1   : 599.2300    0.06000
MZ2   : 610.4700    0.01000
M2N4  : 1019.1000    0.01000
M3N1  : 800.9600    0.01200
M2N1  : 893.1700    0.06000
M1N3  :
M1N2  :
M301  :
M304  :
M305  :
M2M4  :
M3M4  :
M3M5  :
M3N4  :
M4N3  :
M402  : 779.2600    0.00100
M503  : 765.3100    0.00010
M204  :
```

Density: 3.500

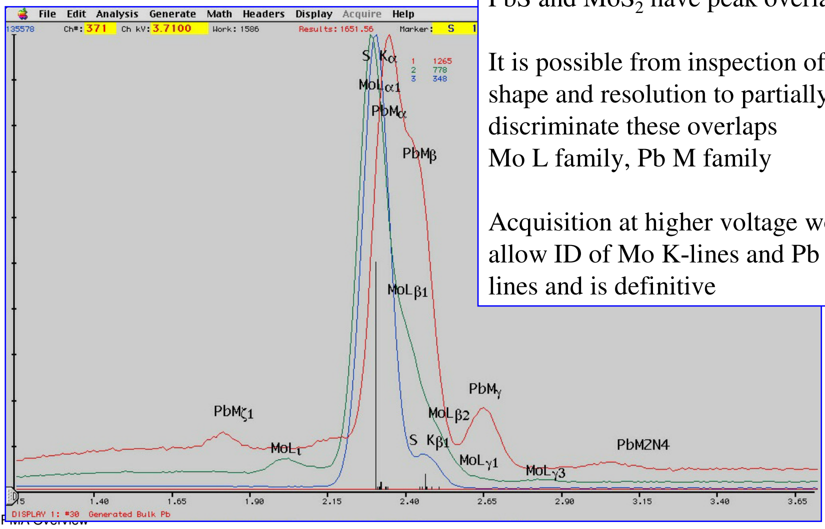
Weight: 137.300

Valences: xx

Lanthanum is lowest Z with Ma line
Lower Z elements have M lines, not Ma though. Be aware when ID'ing low energy peaks of high Z materials

As you look at materials with higher Z, and use higher E_o, you will find many x-ray lines to be identified.

Classic Overlap: S Kα, Mo Lα, and Pb Mα



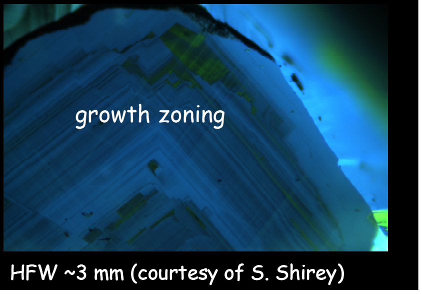
PbS and MoS_2 have peak overlaps

It is possible from inspection of peak shape and resolution to partially discriminate these overlaps
Mo L family, Pb M family

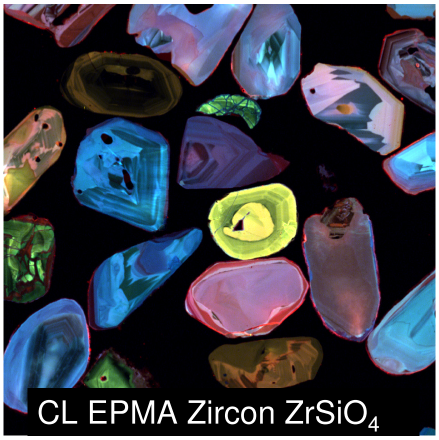
Acquisition at higher voltage would allow ID of Mo K-lines and Pb L-lines and is definitive

Cathodoluminescence Advances

Luminoscope CL image of typical single Crystal Diamond, South Africa



HFW ~3 mm (courtesy of S. Shirey)

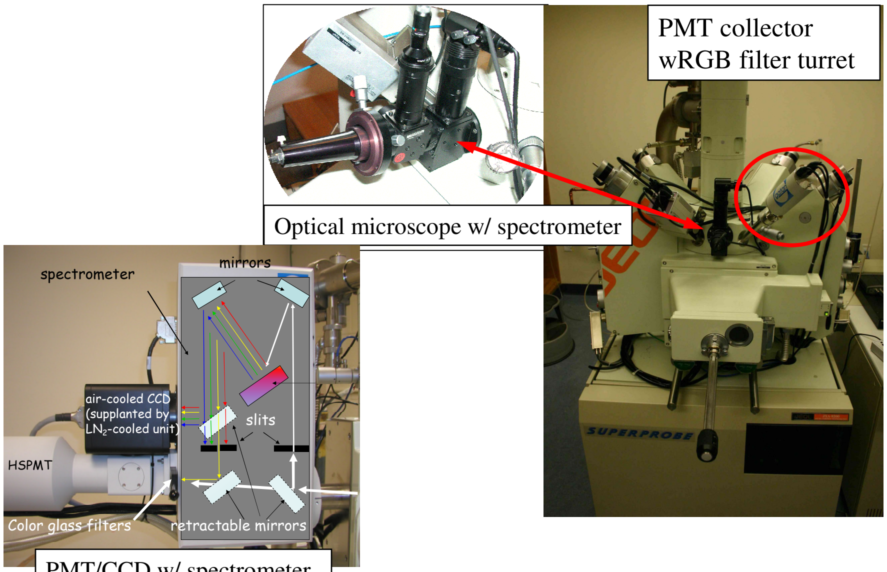


CL EPMA Zircon $ZrSiO_4$

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



PMT collector wRGB filter turret

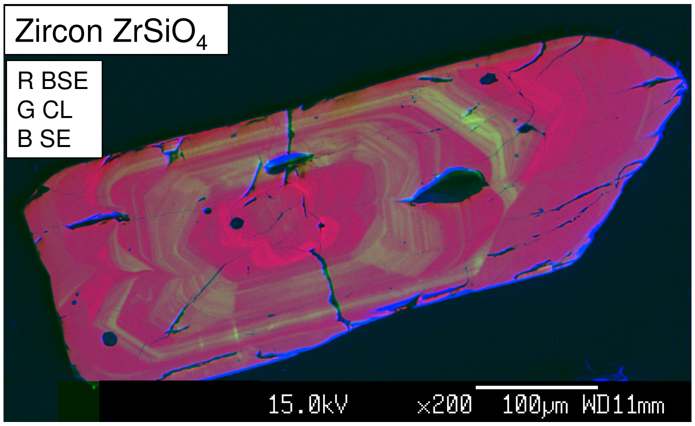
Optical microscope w/ spectrometer

PMT/CCD w/ spectrometer

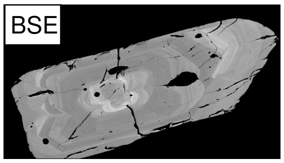
Combined CL, BSE, SE Images in Zircon

Zircon $ZrSiO_4$

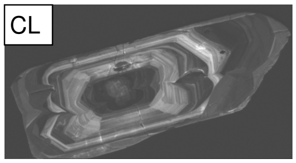
R BSE
G CL
B SE



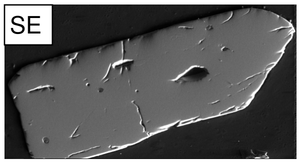
BSE



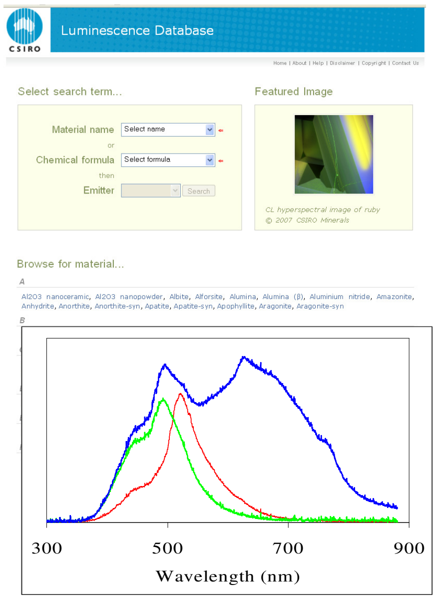
CL



SE



Luminescence database



CL hyperspectral image of ruby
© 2007 CSIRO Minerals

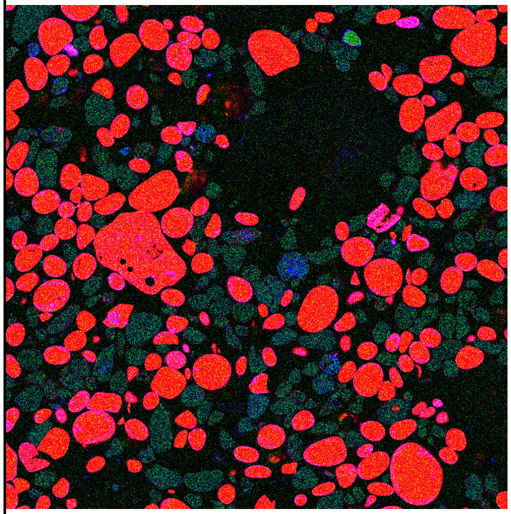
Al2O3 nanoceramic, Al2O3 nanopowder, Albite, Alforsite, Alumina, Alumina (β), Aluminium nitride, Amazonite, Anhydrite, Anorthite, Anorthite-syn, Apatite, Apatite-syn, Apophyllite, Aragonite, Aragonite-syn

- **Database covers luminescence generated by**
  - Cathodoluminescence
  - Photoluminescence
  - Ionoluminescence
  - X-ray induced luminescence
- **Database contains**
  - Minerals (92) and Compounds (64)
  - List of emitters both Intrinsic and Extrinsic
  - Major and minor classification
  - Peak with FWHM or Band
  - Spectra available as an image & text
- **Search by Mineral or Compound name or formula**
- **Details on references for further information:**

www.csiro.au/luminescence

McRae, CSIRO

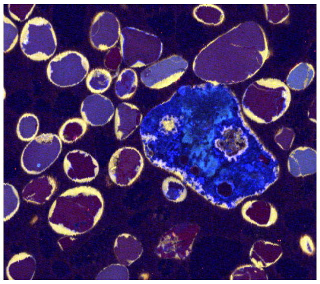
Quartz grains with overgrowth



0 3000µm

X-ray map

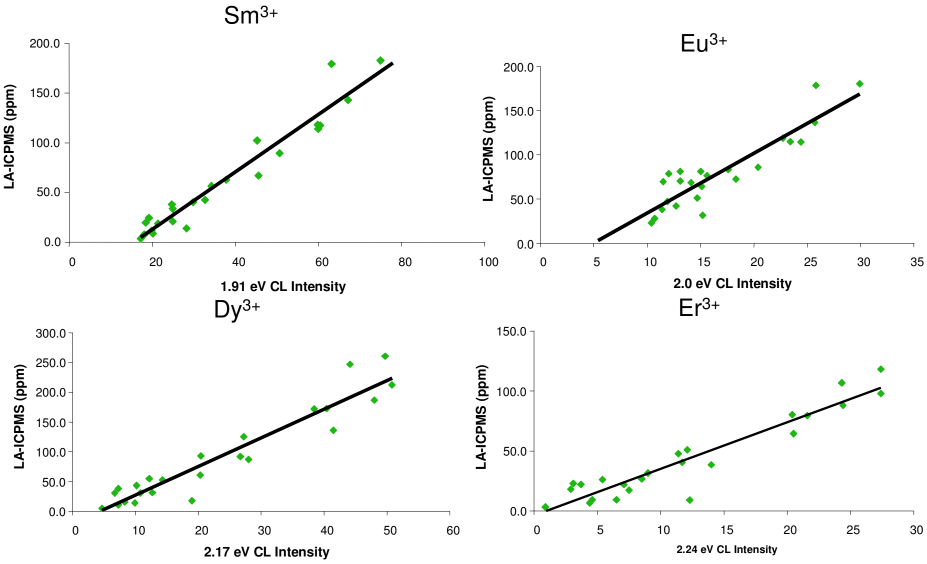
- 🟦 Al
- 🟩 Fe
- 🟥 Si



Cathodoluminescence

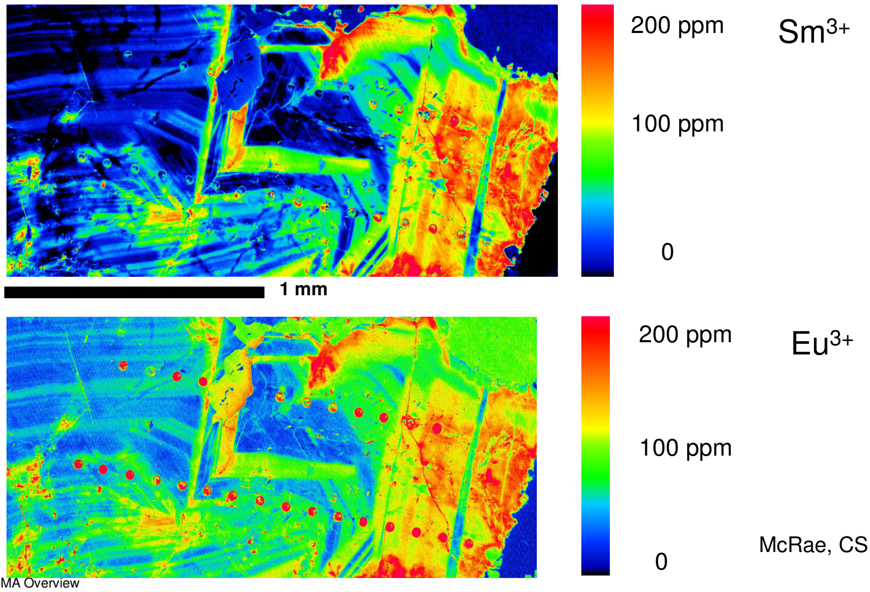
McRae, CSIRO

Comparison between LA-ICP-MS and CL region



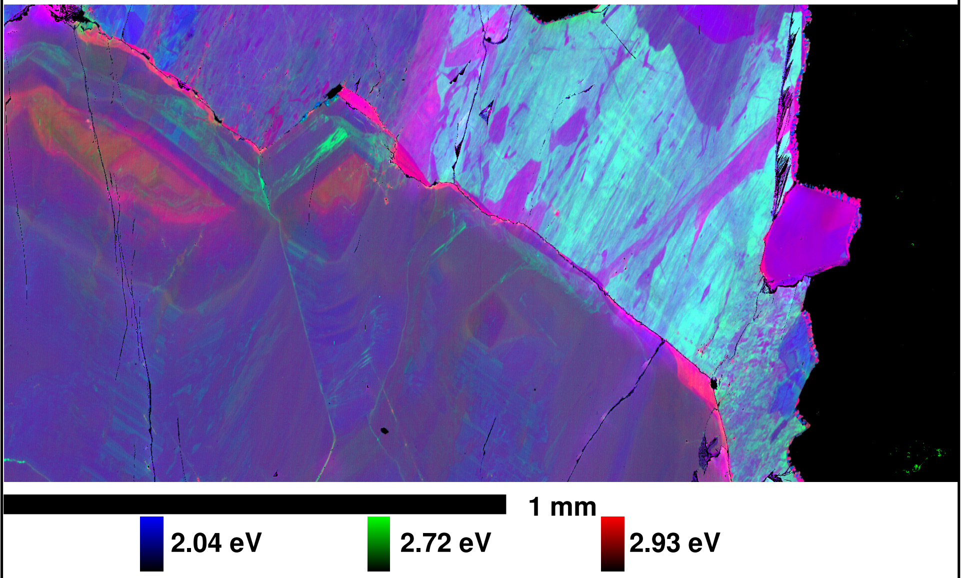
McRae, CSIRO

Calibrated CL maps
Spectral collection using microprobe optical microscope



McRae, CSIRO

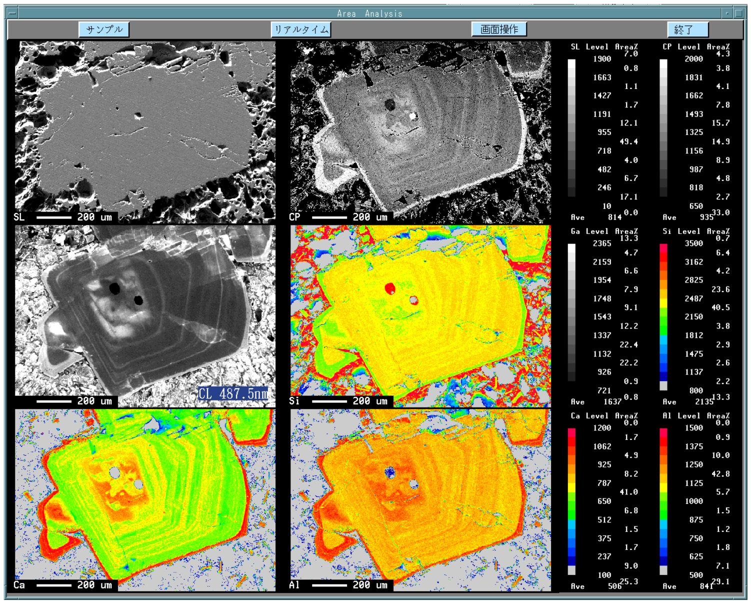
Pink Spodumene – Kunzite ($LiAlSi_2O_6$)



CL activation by trace Mn (?)

McRae, CSIRO

Combined CL, BSE, X-ray Mapping



Quantitative Analysis
Part 1

Quantitative Analysis
Peak Intensity Measurement
Precision and Accuracy
Matrix Effects -- ZAF Correction
Case Studies

Quantitative Analysis Summary

- Quantitative analysis is the measurement of the amount or concentration of each element present. Results are presented in weight or atomic percent (or fraction).
- X-ray intensity is measured on both sample and standard, using exactly the same analysis conditions. Comparative technique.
- Corrections are made for the effects of atomic number, fluorescence, and absorption for all elements in both the sample and the standard.
- Errors are dependent on instrumental setup, x-ray intensities, degree of certaintly of standard composition, and correction algorithms used.

Intensity Measurement: K-ratio

- The fundamental measurement is the characteristic background-subtracted peak intensity (x-ray counts) of the chosen element. This intensity is measured on the sample and divided by the same on the standard. This is the k-ratio:

  $K = (P - B)^{sample} / (P - B)^{standard}$
- By definition, K=1 if the standard is analyzed as an "unknown", and K=0 at zero concentration (below the detection limit).
- Further corrections may need to be made for any difference in count time t, deadtime, and probe current i, that were used when acquiring the sample and standard. In the case of EDS, elements are counted for live time, so the deadtime correction has already been performed.

  K is multiplied by: $(i_{sample} / i_{std}) * (t_{sample} / t_{std})$

Peak Intensity Measurement

How to Extract Peak from Background?

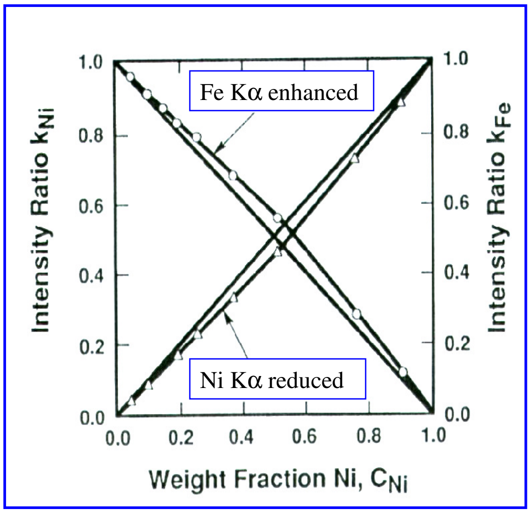
- WDS: excellent resolution -- measurements are made on top of the peak and two adjacent backgrounds, then background under the peak is determined from y=mx+b fit to the two backgrounds, then background is subtracted from the peak intensity.
- EDS spectra have much poorer resolution, and it is not clear which counts belong to the peak and which belong to the background.
- Additional problems: absorption edges due to elements in the sample result in a discontinuity in the background (absorption edges are produced by the detector as well). Incomplete charge collection results in counts well away from the peak.

Matrix Effects
and
X-ray Correction

Matrix Effects and X-ray Correction

- If we take the measured x-ray intensity k, and attempt to equate that to concentration:
  $\mathbf{i_{A,unk}/i_{A,std} = k_A = C_A / C_{std}}$, i.e., k ~ C
  we find very large errors result.
  We need to correct for matrix effects.
- Matrix effects arise because the element is influenced by other elements in the analytical volume.
- The k-value we measure for element "A" is influenced by the presence of elements "B", "C" ,etc. that are present in the excitation volume of the sample.
- The physical origins of matrix effects occur because of the processes of electron backscattering and stopping power (Z), x-ray absorption (A), and x-ray fluorescence (F):
  $C = C_{std}\ k\ Z\ A\ F$

Matrix Effects—Fe Ni Alloy
Similar Z, Absorption and Fluorescence

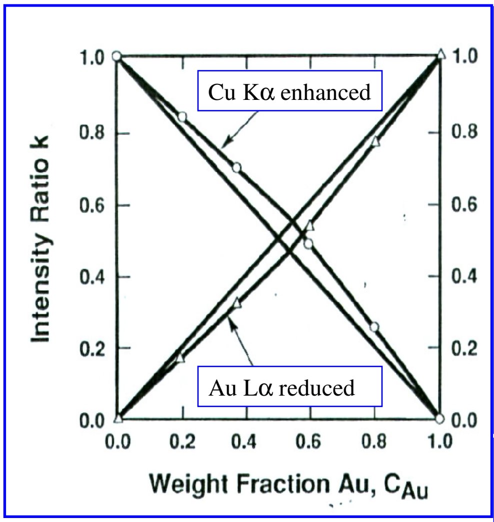


Measured K and known C show systematic differences. Why? The Fe Kα intensity is enhanced, due to fluorescence by Ni Kα, and Ni Kα intensity is reduced, due to absorption by Fe atoms. Because Z for Fe and Ni are similar (26 vs. 28), the matrix corrections are for x-ray fluorescence and x-ray absorption.

Fe Kα 6.403 keV, E_c 7.111 keV
Ni Kα 7.477 keV, E_c 8.331 keV

Summary: FeNi system
Absorption and fluorescence
Similar Z – no atomic number correction (similar scattering)

Matrix Effects—Cu-Au Alloy
Different Z, Stopping Power & Backscattering



Measured K and known C show systematic differences.
The Cu Kα intensity is enhanced, and Au Lα intensity is reduced.
Absorption and fluorescence are small (1% and 2%). Because Z for Cu and Au are different (29 vs. 79), the matrix corrections are for stopping power S and backscattering R.
Cu: S>R, Z<1.0 Au: S<R, Z>1.0
Cu Kα 8.047 keV, E_c 8.980 keV
Au Lα 9.711 keV, E_c 11.919 keV

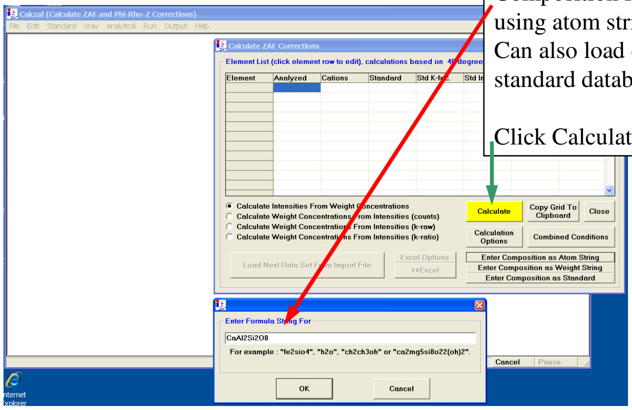
Summary: CuAu system
Absorption, not fluorescence
Different Z – requires atomic number correction (diff. scattering)

CalcZAF Example of Absorption Case (predominant)
Anorthite CaAl2Si2O8

Launch CalcZAF, set analytical conditions

Composition for anorthite entered using atom string “CaAl2si2O8”
Can also load compositions from standard database

Click Calculate button



Enter Formula String For: CaAl2Si2O8

For example : "fe2sio4", "h2o", "ch2ch3oh" or "ca2mg5si8o22(oh)2".

CalcZAF Output for Anorthite: Absorption Example 15kV, 40 deg Armstrong Φ(ρz), FFAST macs

```
Ca-Al2-Si2-O8 = Ca1Si2Al2O8 =  278.216g/mol, Ca 14.41%  Si 20.19%  Al 19.4%  O 46.01%
Ca 14.4061 Si 20.1901 Al 19.3964 O  46.0074


Sample 1

Current Mass Absorption Coefficients From:
FFAST    Chantler (NIST v 2.1, 2005)

  Z-LINE   X-RAY Z-ABSOR     MAC
      Ca      ka      Ca  1.4160e+02
      Ca      ka      Si  5.5490e+02
      Ca      ka      Al  4.3680e+02
      Ca      ka      O   1.1130e+02
      Si      ka      Ca  1.0871e+03
      Si      ka      Si  3.2500e+02
      Si      ka      Al  3.3036e+03
      Si      ka      O   9.7140e+02
      Al      ka      Ca  1.6558e+03
      Al      ka      Si  4.9540e+02
      Al      ka      Al  3.7410e+02
      Al      ka      O   1.4974e+03
      O       ka      Ca  2.1866e+04
      O       ka      Si  7.5458e+03
      O       ka      Al  5.6796e+03
      O       ka      O   1.1220e+03

 ELEMENT  ABSFAC  ZEDFAC  FINFAC STP-POW BKS-COR   F(x)e
   Ca ka  1.0364  3.9856  4.1306   .2259   .9002   .9649
   Si ka  1.0965  3.9489  4.3299   .2309   .9119   .9120
   Al ka  1.1178  4.0854  4.5667   .2246   .9175   .8946
   O  ka  1.3968  3.9154  5.4691   .2438   .9546   .7159
```

Output shows parsed anorthite composition

Lists mass absorption coefficients for all elements in anorthite

Next are ZAF factors for pure elements which are ultimate reference for any material

ABSFAC = absorption correction
STP-POW = stopping power pure el
BKS-COR = backscatter corr. pure el
F(x)e = f(chi) pure el (emit/gen)

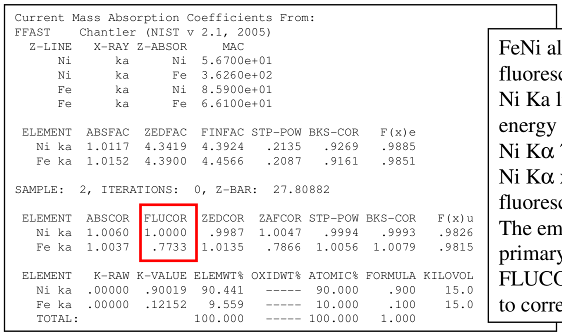
CalcZAF Output for Anorthite: Absorption Example 15kV, 40 deg Armstrong Φ(ρz), FFAST macs

```
SAMPLE:  1, ITERATIONS:  0, Z-BAR:  11.90996

 ELEMENT  ABSCOR  FLUCOR  ZEDCOR  ZAFCOR STP-POW BKS-COR   F(x)u
   Ca ka  1.0337  1.0000  1.0562  1.0918  1.1115   .9502   .9335
   Si ka  1.2992   .9984  1.0164  1.3184  1.0343   .9827   .7020
   Al ka  1.2146   .9870  1.0441  1.2517  1.0546   .9901   .7365
   O  ka  2.8721   .9995   .9550  2.7415   .9324  1.0242   .2493

 ELEMENT   K-RAW K-VALUE ELEMWT% OXIDWT% ATOMIC% FORMULA KILOVOL
   Ca ka  .00000  .13195  14.406   -----   7.692   1.000    15.0
   Si ka  .00000  .15314  20.190   -----  15.385   2.000    15.0
   Al ka  .00000  .15495  19.396   -----  15.385   2.000    15.0
   O  ka  .00000  .16782  46.007   -----  61.538   8.000    15.0
   TOTAL:                100.000   ----- 100.000  13.000
```

Next are ZAF factors for anorthite sample, followed by analysis.
This is running ZAF in reverse:
Input C to calculate k
For analysis we measure k to calculate C

ABSCOR = absorption correction, A
FLUCOR = characteristic fluorescence correction, F
ZEDCOR = atomic number correction, Z
ZAFCOR = total multiplicative ZAF factor
STP-POW = stopping power portion of Z
BKS-COR = backscatter portion of Z
F(x)u = f(chi) this material (emitted intensity/generated intensity)
K-value = k-ratio relative to pure element calculated by this ZAF algorithm and mac
Note that C/K is > 1 which indicates reduction in x-ray intensity (primarily due to absorption)
For most materials the absorption correction ABSCOR dominates

CalcZAF Output for $Fe_{10}Ni_{90}$: Fluorescence Example 15kV, 40 deg Armstrong Φ(ρz), FFAST macs



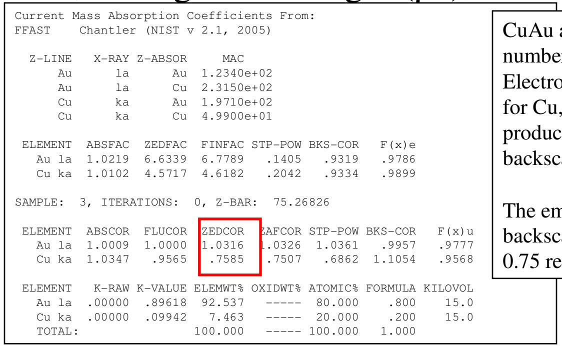
```
Current Mass Absorption Coefficients From:
FFAST    Chantler (NIST v 2.1, 2005)
  Z-LINE   X-RAY Z-ABSOR     MAC
      Ni      ka      Ni  5.6700e+01
      Ni      ka      Fe  3.6260e+02
      Fe      ka      Ni  8.5900e+01
      Fe      ka      Fe  6.6100e+01

 ELEMENT  ABSFAC  ZEDFAC  FINFAC STP-POW BKS-COR   F(x)e
   Ni ka  1.0117  4.3419  4.3924   .2135   .9269   .9885
   Fe ka  1.0152  4.3900  4.4566   .2087   .9161   .9851

SAMPLE:  2, ITERATIONS:  0, Z-BAR:  27.80882

 ELEMENT  ABSCOR  FLUCOR  ZEDCOR  ZAFCOR STP-POW BKS-COR   F(x)u
   Ni ka  1.0060  1.0000   .9987  1.0047   .9994   .9993   .9826
   Fe ka  1.0037   .7733  1.0135   .7866  1.0056  1.0079   .9815

 ELEMENT   K-RAW K-VALUE ELEMWT% OXIDWT% ATOMIC% FORMULA KILOVOL
   Ni ka  .00000  .90019  90.441   -----  90.000    .900    15.0
   Fe ka  .00000  .12152   9.559   -----  10.000    .100    15.0
   TOTAL:                100.000   ----- 100.000   1.000
```

FeNi alloy is a good example of x-ray fluorescence and absorption.
Ni Ka line energy is just above the edge energy for Fe K:
Ni Kα 7.477 keV, Fe K Ec 7.111 keV
Ni Kα x-rays are absorbed by Fe atoms and fluoresce Fe Ka x-rays in the process.
The emitted Fe Kα intensity consists of both primary and fluoresced x-rays and the FLUCOR value of 0.77 reduces the Fe k-ratio to correct for fluorescence by Ni.

ABSCOR = absorption correction, A
FLUCOR = characteristic fluorescence correction, F
ZEDCOR = atomic number correction, Z
ZAFCOR = total multiplicative ZAF factor
STP-POW = stopping power portion of Z
BKS-COR = backscatter portion of Z
F(x)u = f(chi) this material (emitted intensity/generated intensity)
K-value = k-ratio relative to pure element calculated by this ZAF algorithm and mac

Note for Fe C/K is < 1 which indicates enhancement in x-ray intensity due to fluorescence
Fluorescence is important when the line energy is higher and close to the edge energy of other matrix elements. It is most important for K by K, less so for fluorescence by L and M lines.

CalcZAF Output for $Cu_{20}Au_{80}$: Atomic Number Example 15kV, 40 deg Armstrong Φ(ρz), FFAST macs



```
Current Mass Absorption Coefficients From:
FFAST    Chantler (NIST v 2.1, 2005)

  Z-LINE   X-RAY Z-ABSOR     MAC
      Au      la      Au  1.2340e+02
      Au      la      Cu  2.3150e+02
      Cu      ka      Au  1.9710e+02
      Cu      ka      Cu  4.9900e+01

 ELEMENT  ABSFAC  ZEDFAC  FINFAC STP-POW BKS-COR   F(x)e
   Au la  1.0219  6.6339  6.7789   .1405   .9319   .9786
   Cu ka  1.0102  4.5717  4.6182   .2042   .9334   .9899

SAMPLE:  3, ITERATIONS:  0, Z-BAR:  75.26826

 ELEMENT  ABSCOR  FLUCOR  ZEDCOR  ZAFCOR STP-POW BKS-COR   F(x)u
   Au la  1.0009  1.0000  1.0316  1.0326  1.0361   .9957   .9777
   Cu ka  1.0347   .9565   .7585   .7507   .6862  1.1054   .9568

 ELEMENT   K-RAW K-VALUE ELEMWT% OXIDWT% ATOMIC% FORMULA KILOVOL
   Au la  .00000  .89618  92.537   -----  80.000    .800    15.0
   Cu ka  .00000  .09942   7.463   -----  20.000    .200    15.0
   TOTAL:                100.000   ----- 100.000   1.000
```

CuAu alloy is a good example of atomic number effects.
Electron backscattering by Au is greater than for Cu, so Cu atoms have enhanced x-ray production due to both primary and backscattered electron bombardment.

The emitted Cu Kα intensity is higher due to backscattering and the ZEDCOR value of 0.75 reduces the Cu k-ratio to correct for this.

ABSCOR = absorption correction, A
FLUCOR = characteristic fluorescence correction, F
ZEDCOR = atomic number correction, Z
ZAFCOR = total multiplicative ZAF factor
STP-POW = stopping power portion of Z
BKS-COR = backscatter portion of Z
F(x)u = f(chi) this material (emitted intensity/generated intensity)
K-value = k-ratio relative to pure element calculated by this ZAF algorithm and mac

Note for Cu C/K is < 1 which indicates enhancement in x-ray intensity due to backscattering by Au
Backscattering is important when there is a large difference in atomic number of elements in the material.

End
More to come…