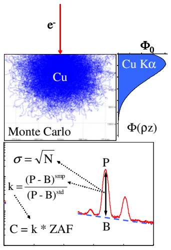
Electron-Probe Microanalysis (EPMA): Tutorial

Paul Carpenter
Earth and Planetary Sciences CB 1169
Washington University
1 Brookings Drive
St. Louis, MO 63130

paulc@levee.wustl.edu



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:
  $k = (P-B)^{smp} / (P-B)^{std}$
- Measured x-ray intensities are converted to concentration units via:
  $C_{sample} = C_{std}$ K * Z A F, $K = (P-B)^{sample} / (P-B)^{standard}$
  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.

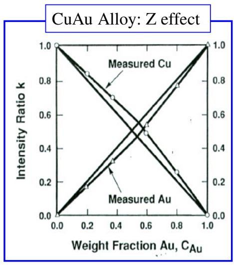
Beers Law absorption:
$$I = I_0 \, e^{(-\mu/\rho \, \rho s)}$$
I emitted X-ray intensity, I_0 generated X-ray intensity
Path length ρs and mass absorption coefficient μ/ρ

- 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

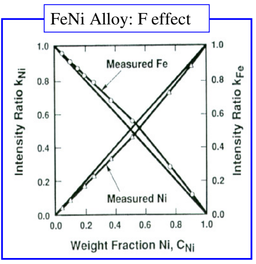
EPMA Summary: ZAF and X-ray Correction

- "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

CuAu Alloy: Z effect



FeNi Alloy: F effect



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

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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
```

Software Demo -- CalcZAF

- CalcZAF program instructive for calculating C vs. K, ZAF factors
- Expected k from known C, Calculated C from measured k
- Absorption: Mg_2SiO_4, AlCu alloys, SiC
- Atomic Number: AlCu, IrSi alloys
- Fluorescence: NiFe alloys (Ni-rich)
- $\Phi(\rho z)$ Algorithms, MAC data sets
- Alpha Factor demo: “ZAF” const., linear, polynomial term
- Demo files
- Particle analysis CaF_2 data

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.
- EDS Standardless pervasive, but accuracy not fully known. WDS Standardless elusive due to uncertainty calculating WDS efficiency.
- Automated analysis techniques: 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

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

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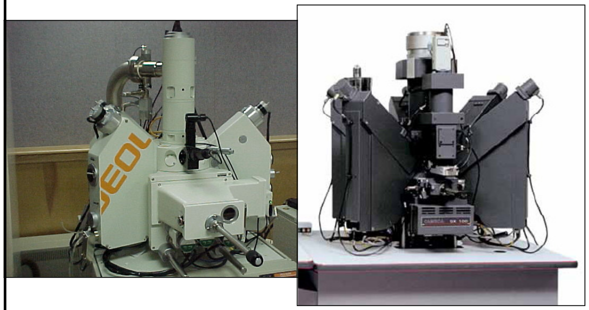
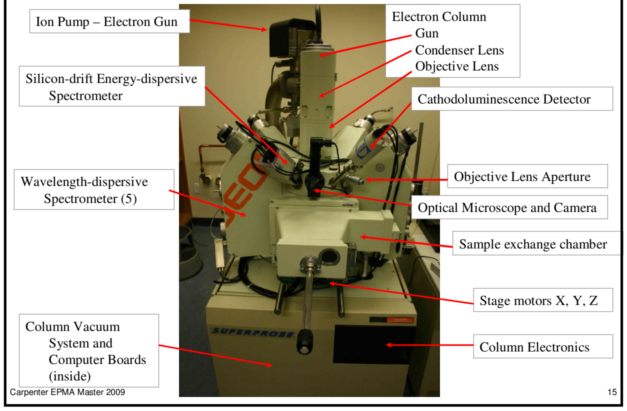
Microprobe Column with WDS, Stage Port, Optical Microscope



Electron Microprobe at Washington University STL



Ion Pump – Electron Gun

Electron Column
Gun
Condenser Lens
Objective Lens

Silicon-drift Energy-dispersive Spectrometer

Cathodoluminescence Detector

Wavelength-dispersive Spectrometer (5)

Objective Lens Aperture

Optical Microscope and Camera

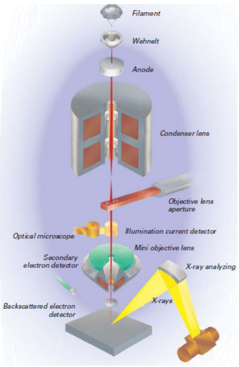
Sample exchange chamber

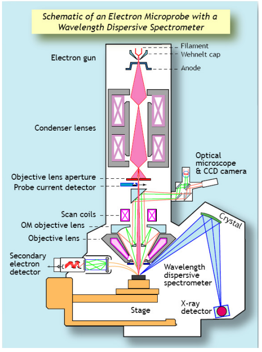
Stage motors X, Y, Z

Column Vacuum System and Computer Boards (inside)

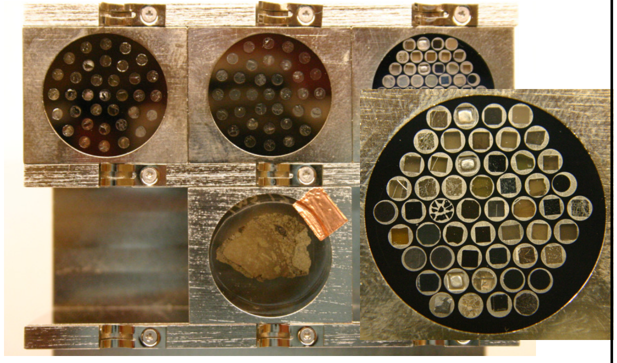
Column Electronics

Microprobe Column Cross-section





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

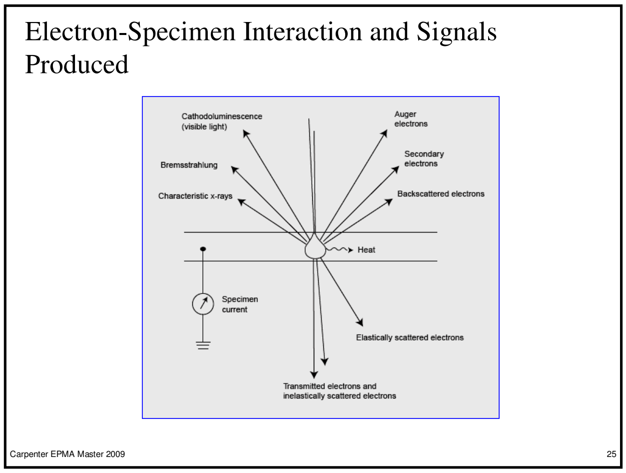
Microanalysis Software
Free or Shareware

- Winxray – Program to generate EDS spectra using Monte Carlo and $\Phi(\rho z)$ 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

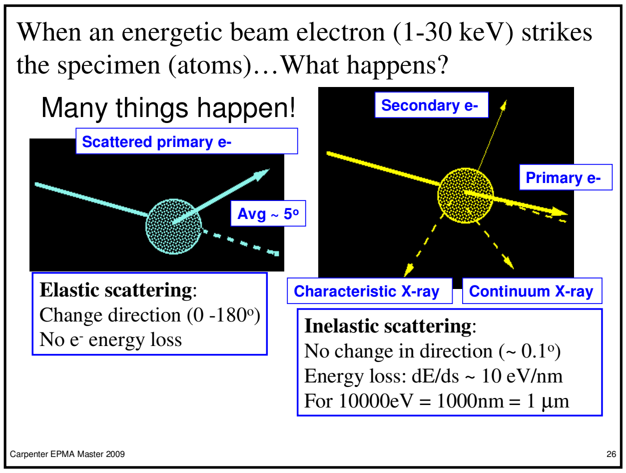
Electron-Specimen Interactions
and
X-ray Generation

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

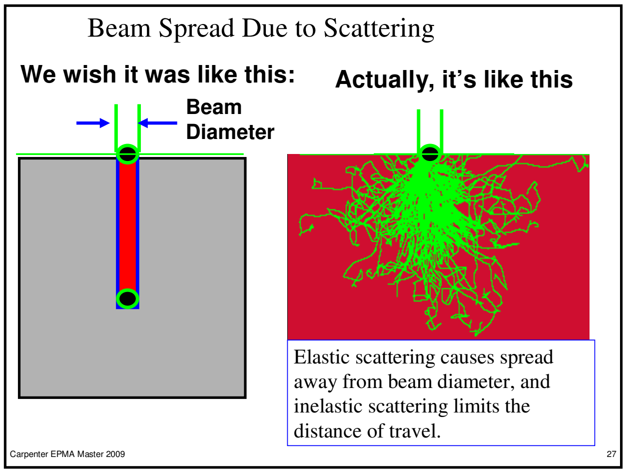


When an energetic beam electron (1-30 keV) strikes the specimen (atoms)…What happens?

Many things happen!

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

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



Beam Spread Due to Scattering

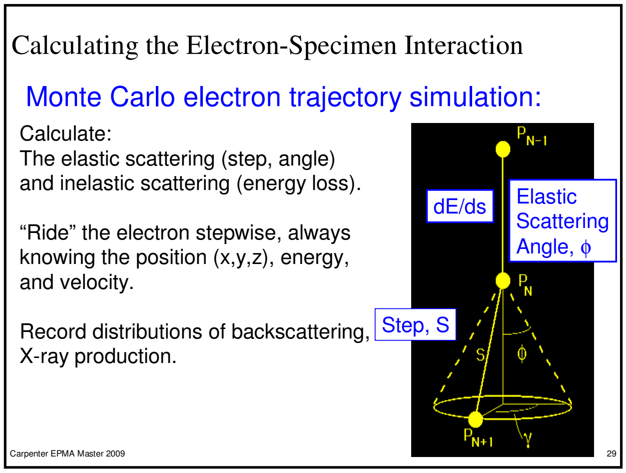
We wish it was like this:

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.



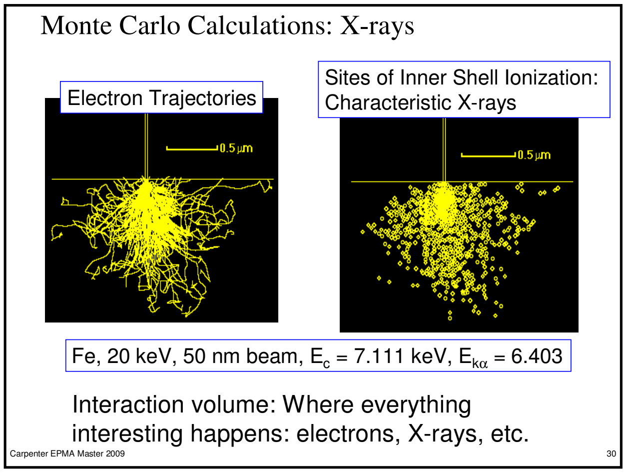
Calculating the Electron-Specimen Interaction

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.

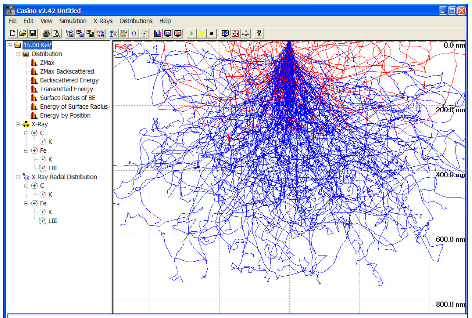


Monte Carlo Calculations: X-rays

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

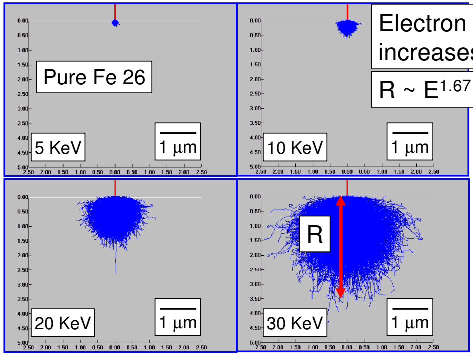


Simulation Fe_3C, 15 keV, 5000 trajectories, max depth ~750nm
Red = backscattered e-, blue e- within Fe_3C.
Scattering angle increases as e- energy decreases (curly trajectory)

Monte Carlo 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

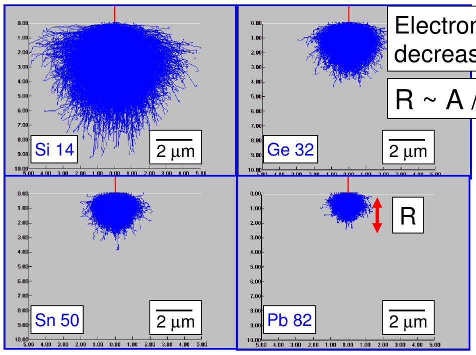
Monte Carlo Simulation
Effect of Varying Accelerating Voltage



Electron range increases with AV

$R \sim E^{1.67}$

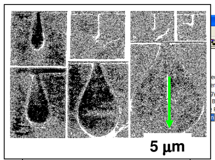
Monte Carlo Simulation
Effect of Varying Atomic Number Z @ 25 keV



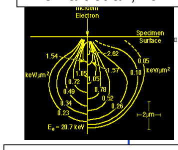
Electron range decreases with Z

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

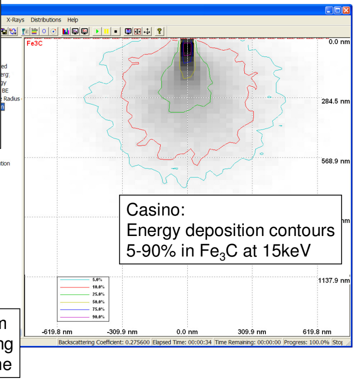
Energy Deposition: Experiment vs. Monte Carlo



Everhart et al., 1972

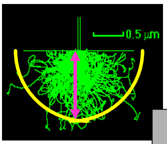


Energy deposition per mm PMMA e^- dose with etching to reveal scattering volume



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

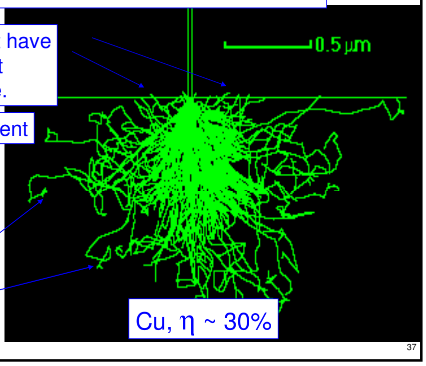
Beam electrons that have undergone sufficient scattering to escape.

Backscatter Coefficient

$\eta = n_{BSE}/n_B$

$\eta = i_{BSE}/i_B$

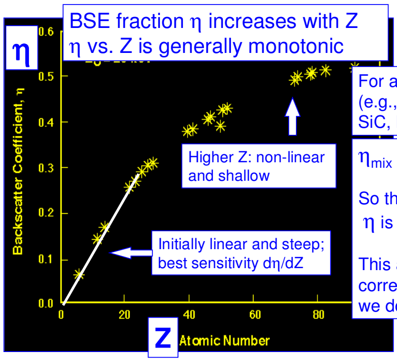
Absorbed or specimen current electrons



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 dη/dZ

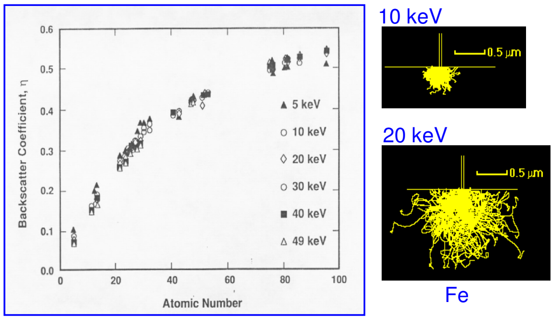
For a mixture of atoms (e.g., alloys, compounds) SiC, Mg_2SiO_4, GaAs, IrSi, etc.

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

So the weighted average η is used for correction

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

Backscattering vs. Beam Energy



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

Contrast Mechanism

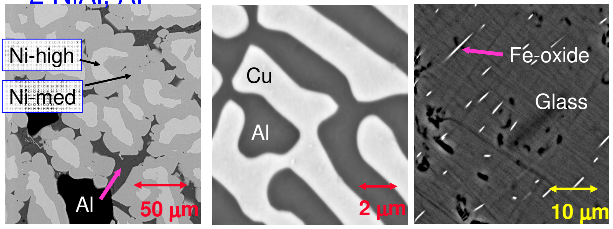
- Changes in the signal(s) ("Contrast") collected at different points in the image convey information about specimen characteristics.
- Whenever a signal changes in a predictable way as a function of specimen properties, we have the basis for a contrast mechanism.
- Example: η vs. Z is monotonic and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

Atomic Number Contrast

Raney Ni-Al
2 NiAl, Al

Al-Cu eutectic

Obsidian

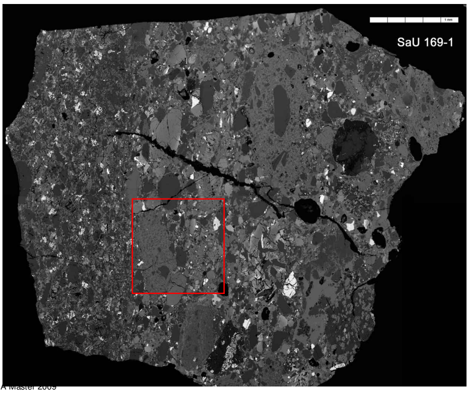


Backscattered-electrons provide a rapid and simple means to image differences in chemistry in the sample, via the dependence on average atomic number.

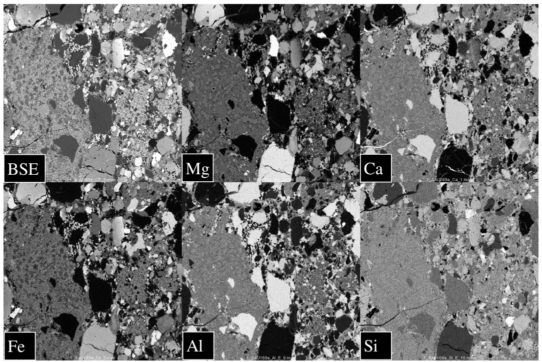
Compositional Mapping

- 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

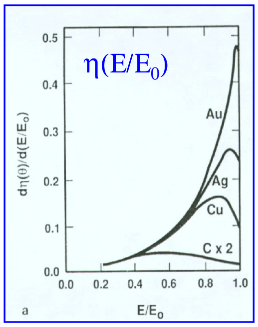
- Mean Z can be easily calculated (CalcZAF, for example)
- Typical range is ~ 10 – 20. Atomic number correction is limited if appropriate standards are used.
- Silicates
  Forsterite 10.6 Albite 10.7 Pyrope 10.7
  Fayalite 18.7 Anorthite 11.9 Almandine 15.6
- Oxides
  Periclase 10.4 Spinel 10.6 Quartz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

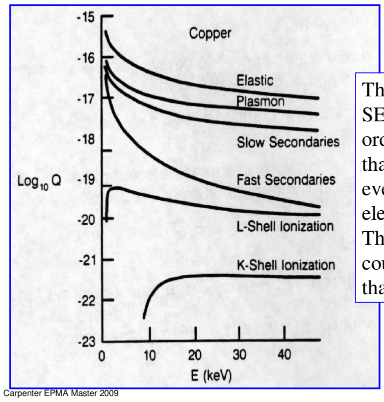
Low Z materials have few BSEs with wide range of energies and peak at low E/E_o
Carbon Z=6 for example
Not so important for BSE portion of Z correction



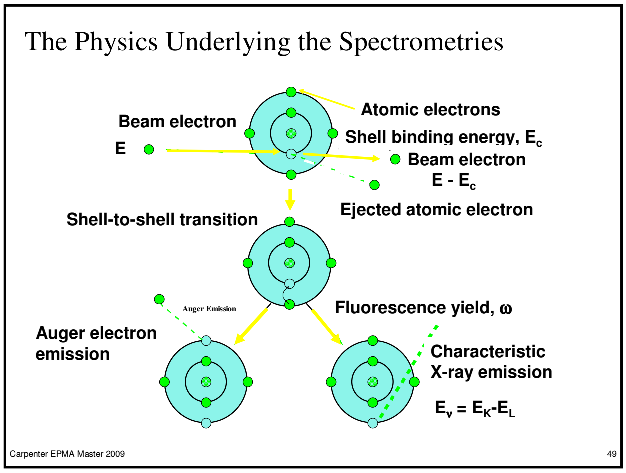
Backscattered Electrons: Summary

- 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

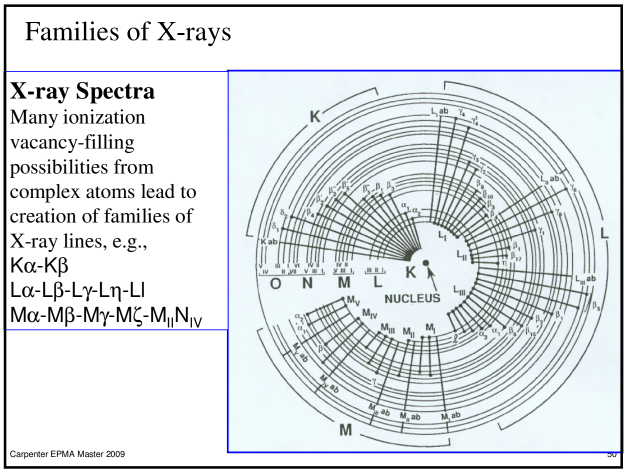
Probabilities of Scattering Events



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"

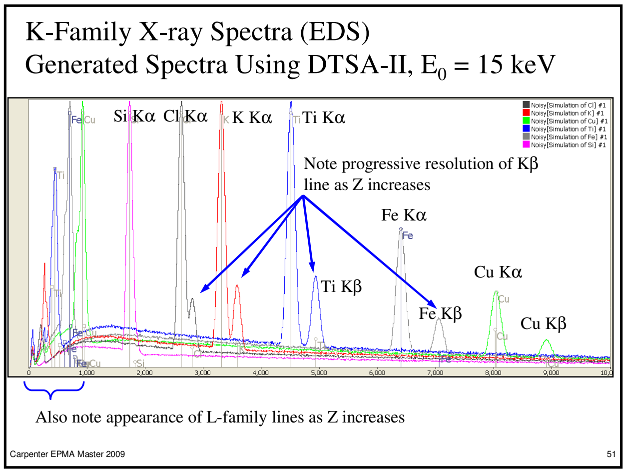


The Physics Underlying the Spectrometries



Families of X-rays

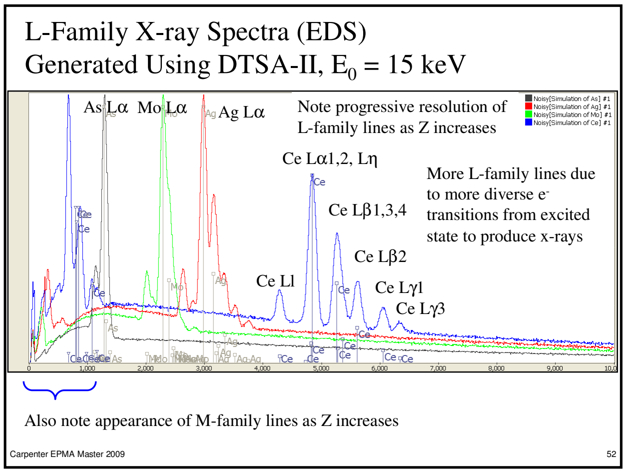
X-ray Spectra
Many ionization vacancy-filling possibilities from complex atoms lead to creation of families of X-ray lines, e.g.,
Kα-Kβ
Lα-Lβ-Lγ-Lη-Ll
Mα-Mβ-Mγ-Mζ-$M_{II}N_{IV}$



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

Note progressive resolution of Kβ line as Z increases

Also note appearance of L-family lines as Z increases

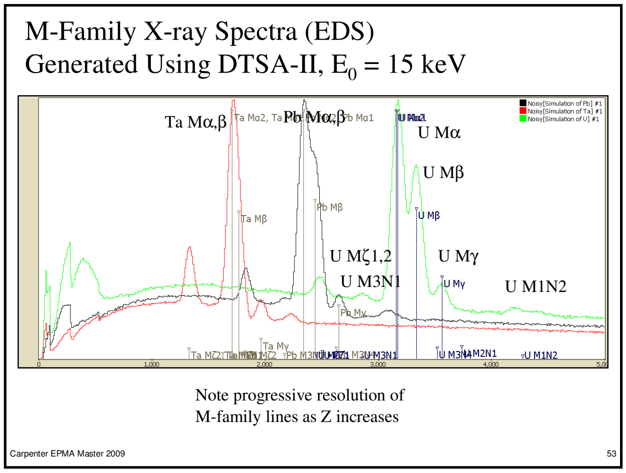


L-Family X-ray Spectra (EDS)
Generated Using DTSA-II, E_0 = 15 keV

Note progressive resolution of L-family lines as Z increases

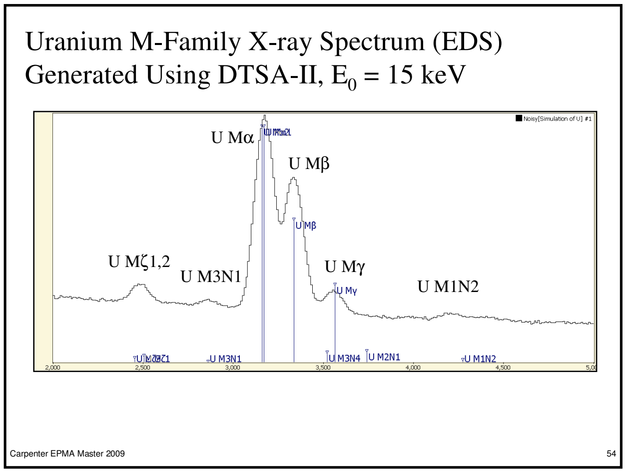
More L-family lines due to more diverse e^- transitions from excited state to produce x-rays

Also note appearance of M-family lines as Z increases



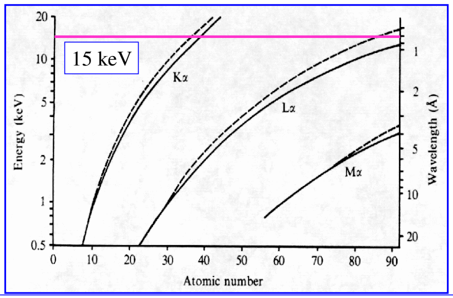
M-Family X-ray Spectra (EDS)
Generated Using DTSA-II, E_0 = 15 keV

Note progressive resolution of M-family lines as Z increases



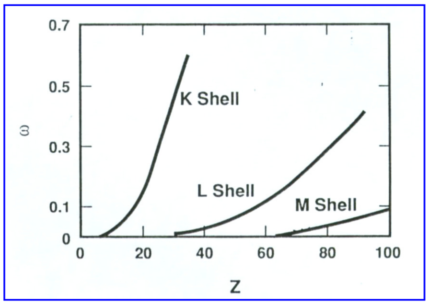
Uranium M-Family X-ray Spectrum (EDS)
Generated Using DTSA-II, E_0 = 15 keV

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

$$Q = 6.51\text{x}10^{-20}\ n_s\ b_s\ \ln(c_s\ E/E_c)\ /(E\ E_c)$$

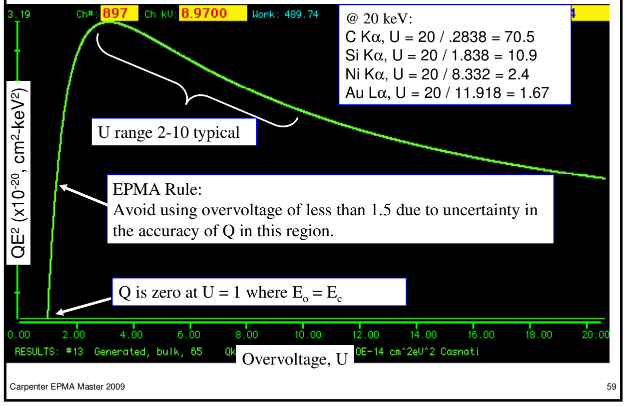
Units: ionizations / e^- / (atom/cm^2)
E beam electron energy (keV)
E_c critical excitation (binding) energy (keV)
n_s number of electrons in shell or subshell
b_s, c_s constants for the shell or subshell

$$Q = 6.51\text{x}10^{-20}\ n_s\ b_s \ln(c_s\ U)\ /\ (UE_c^2)$$

$U = E/E_c$ overvoltage

Plot QE_c^2 vs U

Plot of Ionization Cross Section QE^2 vs. Overvoltage



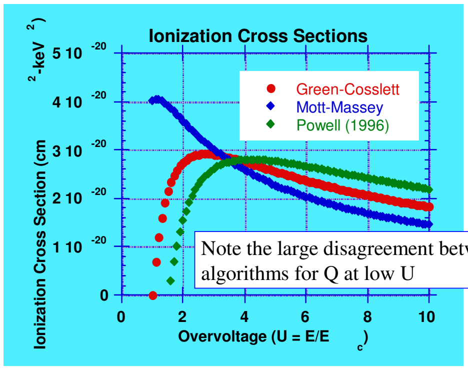
@ 20 keV:
C Kα, U = 20 / .2838 = 70.5
Si Kα, U = 20 / 1.838 = 10.9
Ni Kα, U = 20 / 8.332 = 2.4
Au Lα, U = 20 / 11.918 = 1.67

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 $E_o = E_c$

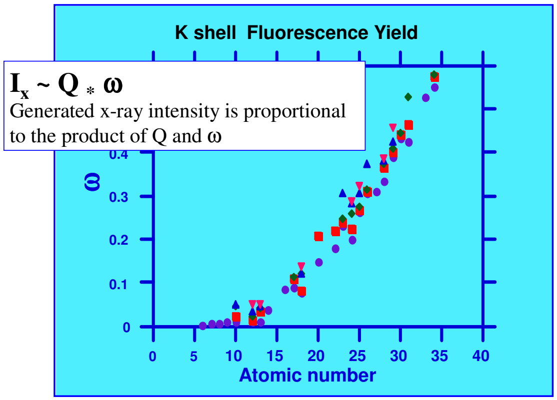
Cross Section for Inner Shell Ionization



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

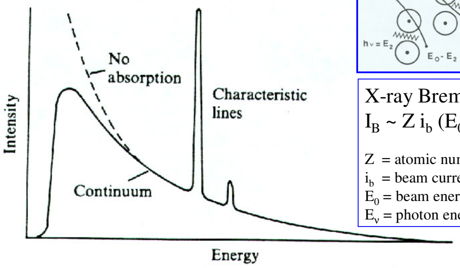
- Bremsstrahlung means “braking radiation”.
- Primary beam electrons are decelerated by the repulsive electric field of electrons surrounding an atom.
- X-rays are emitted during this deceleration. The energy of a given x-ray depends on the degree of slowing down and is continuous in this respect.
- 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”.

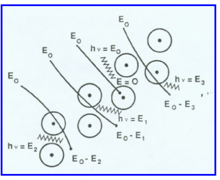
Continuum X-rays

- 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



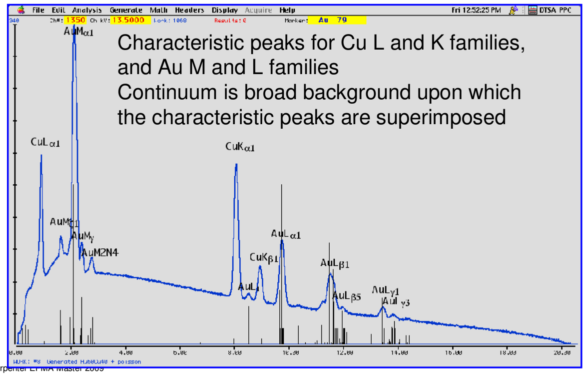


X-ray Bremsstrahlung

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

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

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



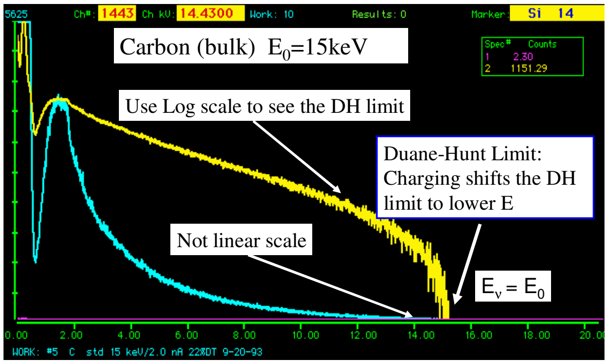
Characteristic peaks for Cu L and K families, and Au M and L families

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

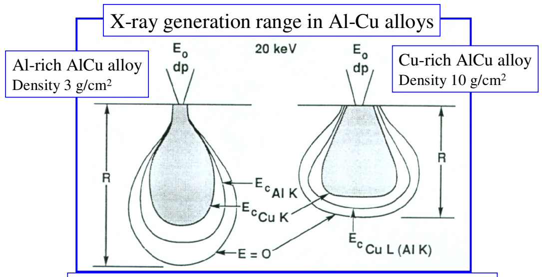
Use Log scale to see the DH limit

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

Not linear scale

$E_v = E_0$

Range of Characteristic X-ray Production



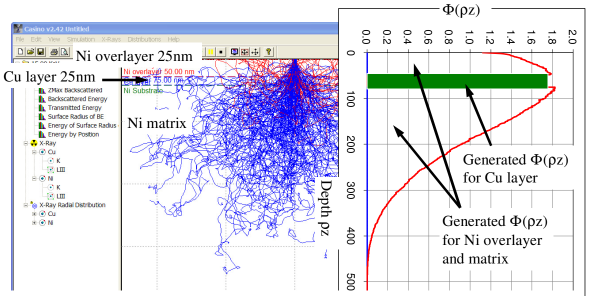
X-ray generation range in Al-Cu alloys

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

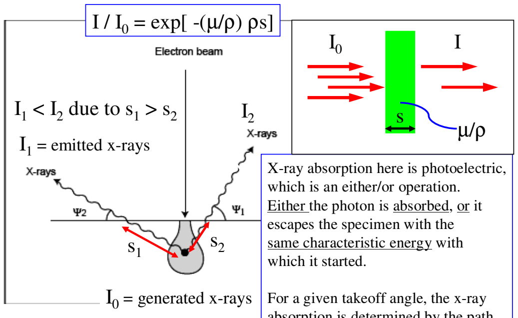
Ni matrix

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



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

$I_1 < I_2$ due to $s_1 > s_2$

I_2

I_1 = emitted x-rays

s_1

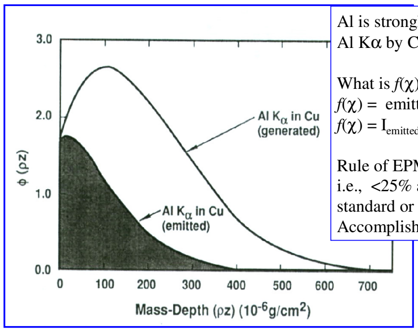
s_2

I_0 = generated x-rays

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

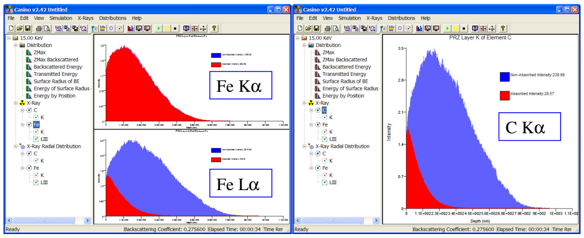


Al is strongly absorbed by Cu (μ/ρ Al Kα by Cu = 4764).

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

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

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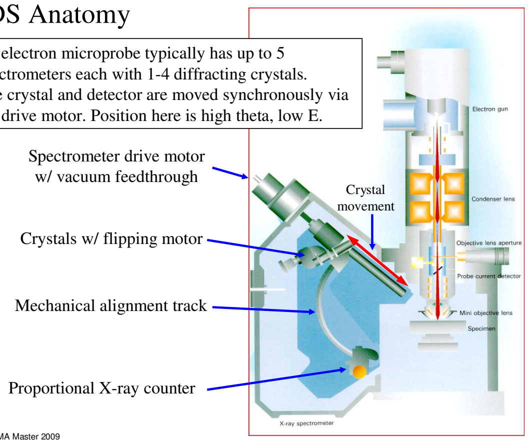
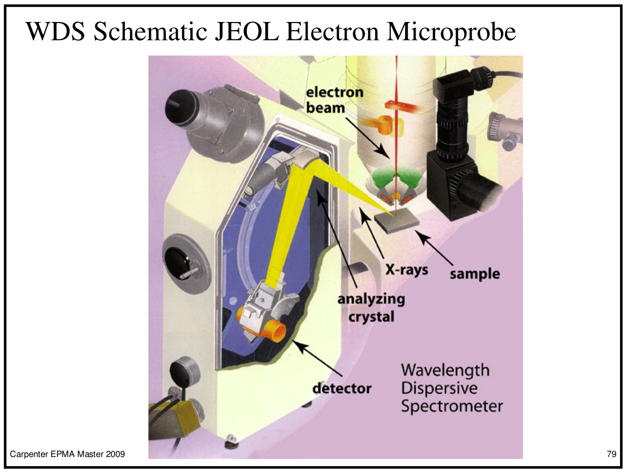
WDS Checklist for Analysts: Analysis

- 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.

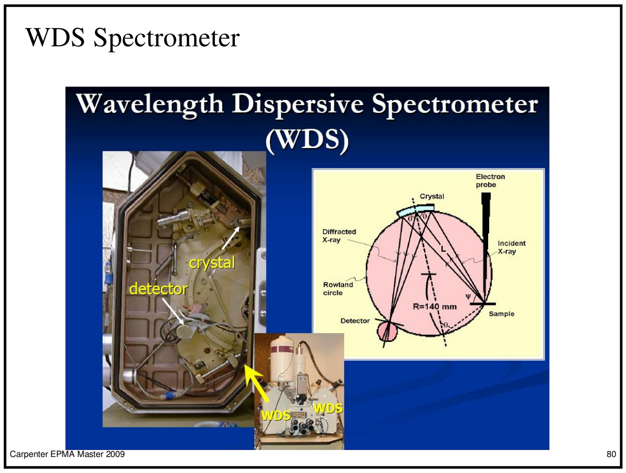
WDS Anatomy

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.



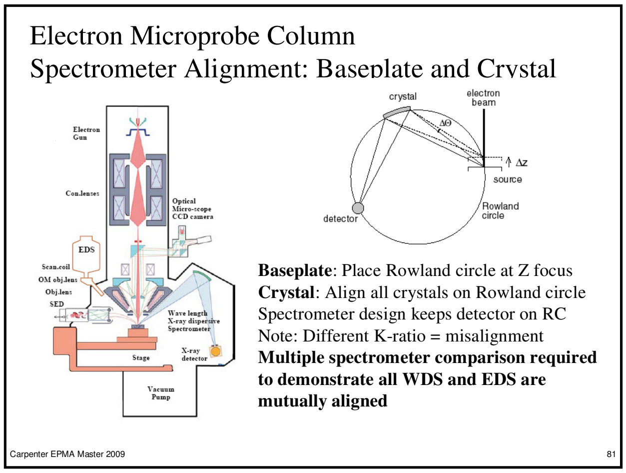


WDS Schematic JEOL Electron Microprobe



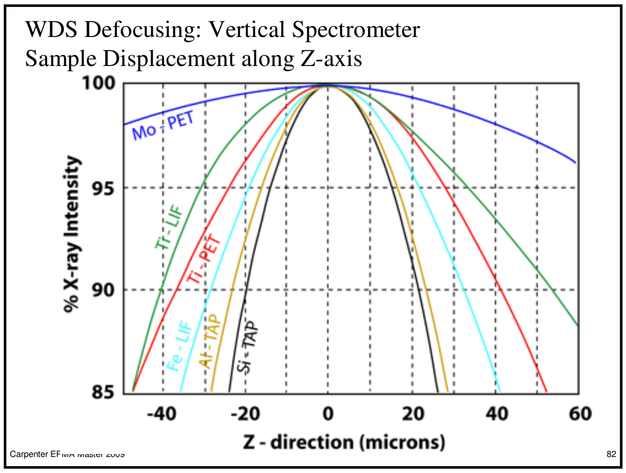
WDS Spectrometer

Wavelength Dispersive Spectrometer (WDS)

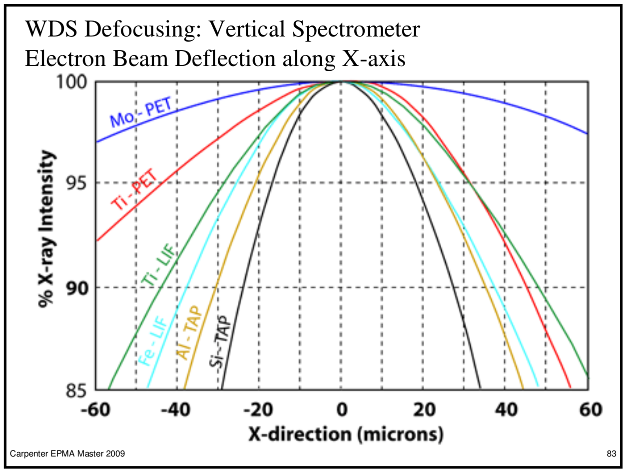


Electron Microprobe Column Spectrometer Alignment: Baseplate and Crystal

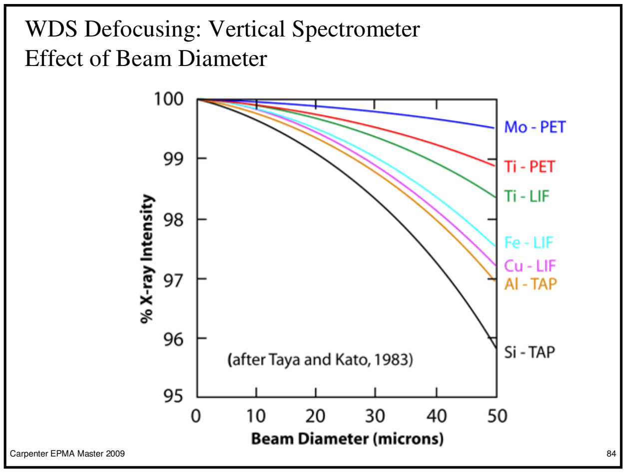
Baseplate: Place Rowland circle at Z focus
Crystal: Align all crystals on Rowland circle
Spectrometer design keeps detector on RC
Note: Different K-ratio = misalignment
Multiple spectrometer comparison required to demonstrate all WDS and EDS are mutually aligned



WDS Defocusing: Vertical Spectrometer Sample Displacement along Z-axis



WDS Defocusing: Vertical Spectrometer Electron Beam Deflection along X-axis



WDS Defocusing: Vertical Spectrometer Effect of Beam Diameter

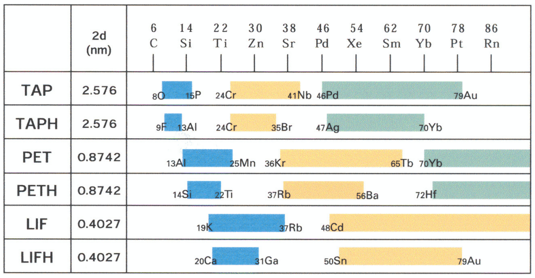
WDS Spectrometer Units

- Bragg diffraction equation including index of refraction term:
  $n\lambda = 2d \sin\theta\,(1\text{-}k/n^2)$
  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: $L = (R / d)\, n\lambda\, (1 - k / n^2)$

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

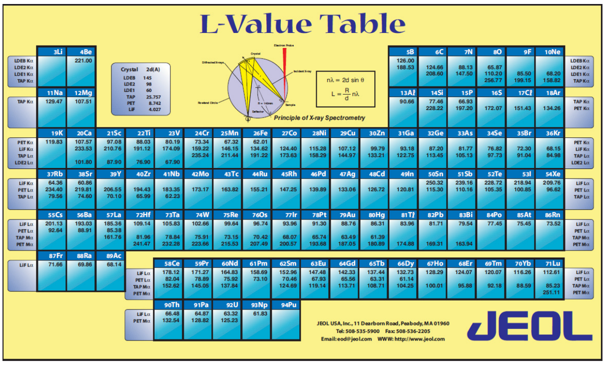
Diffracting Crystal Element Ranges



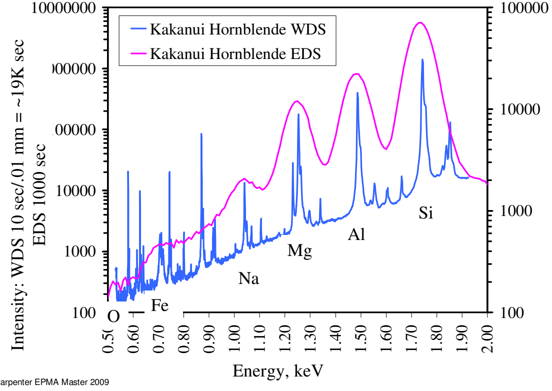
LDE Diffracting Crystal Element Ranges

	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

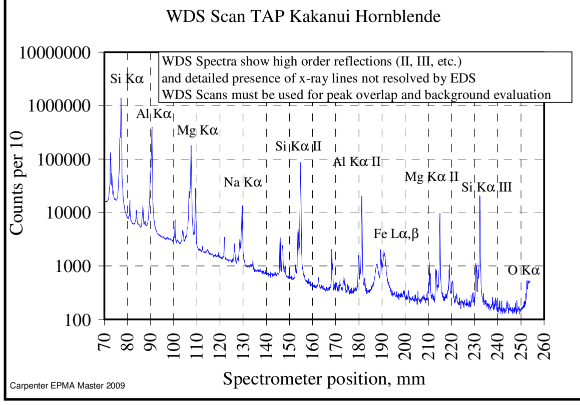


WDS and EDS Comparison: Kakanui Hornblende
WDS TAP GFC, SiLi EDS, Energy Scale



WDS Wavelength Scan

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



WDS Detector: Ar Ionization Counter

Ar ionization energy 27 eV

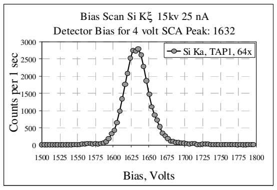
The number of ionizations is: n = Photon energy / 27 eV

Compare with Si EDS 3.8 eV detection process, factor of 7

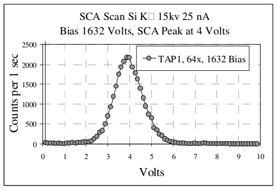
Photon	Energy eV	Ar+ per photon
Be Kα	110	4
Mg Kα	1254	46
Fe Kα	6403	237
Ge Kα	9885	366
Zr Kα	15774	584

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

Pulse-height Analysis: WDS

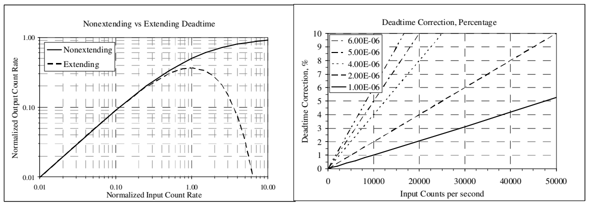


Detector bias scan for Si Ka using 3.9 volt baseline and 0.2 volt window. The bias scan is used to set the detector bias necessary to achieve a 4 volt pulse on an SCA scan (from 0-10 Volts). Bias scans are typically performed in the 1500-1800 Volt range, which is the plateau region of the x-ray detector.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

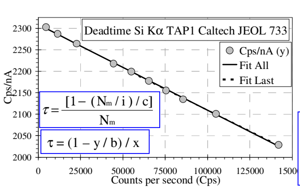
Deadtime: Time During Which System Cannot Process Additional Pulses



Left: Nonextending and Extending deadtime relations expressed for normalized count rates. For extending deadtime, each additional pulse extends the deadtime and ultimately causes paralyzable behavior similar to EDS counting systems. Non-extending deadtime exhibits a continual decrease in efficiency without paralyzable behavior.

Right: Calculated deadtime losses plotted as percent correction. Note that at 10K cps, there is a loss of 1% for each increment in deadtime constant. This means there is a 1% correction for 1 µsec constant at 10K cps (bottom line), and a 5% correction for a 5 µsec constant at the same count rate (next to top line). That is a systematic error that affects standard and sample to the extent of the count rates, and must be considered as the minimum error prior to evaluation of counting statistics and sample heterogeneity.

Measurement of WDS Deadtime Constant



$$\tau = \frac{[1-(N_m/i)/c]}{N_m}$$

$$\tau = (1 - y / b) / x$$

$$N = \frac{N_m}{(1 - N_m \tau)}$$

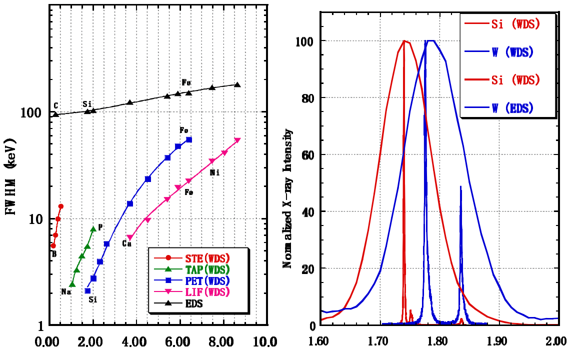
$$\frac{N_m}{i} = c(1 - N_m \tau)$$

Form y = mx + b:
$y = N_m/i$, $x = N_m$, $b = c$

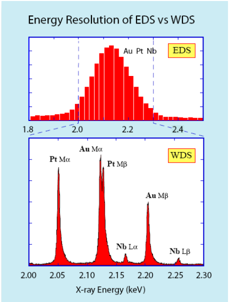
True count rate N (unknown), measured rate N_m
Assume count rate proportional to probe current i
Plot of cps vs. cps/nA used to calculate τ
Excel sheet used for discrete vs. LSQ fit for τ

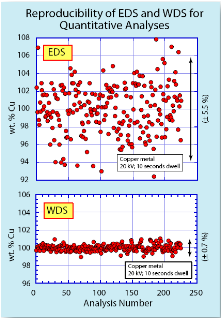
nA	Abs Cur	Abs/Probe	Time	Cps (x)	Cps/nA (y	Fit All	Fit Last	DT us All	DT Last
2.00	1.63	0.82	100	4607.9	2302.57	2299.81		0.61	
5.00	4.05	0.81	80	11436.9	2287.20	2286.17		0.83	
10.01	8.10	0.81	80	22665.3	2264.44	2263.73		0.85	
20.05	16.25	0.81	60	44469.0	2217.95	2220.18		0.89	
25.00	20.29	0.81	60	54977.1	2199.08	2199.18	2197.08	0.87	0.83
29.98	24.34	0.81	30	65298.1	2177.91	2178.56	2177.00	0.87	0.84
35.02	28.54	0.81	30	75474.9	2155.07	2158.23	2157.20	0.88	0.86
40.05	32.53	0.81	30	85510.0	2134.97	2138.18	2137.67	0.88	0.86
49.99	40.74	0.81	30	105026.6	2101.04	2099.19	2099.70	0.86	0.84
69.98	57.25	0.82	30	141942.7	2028.45	2025.44	2027.88	0.86	0.84
Regression Output:						Mean deadtime		0.86	0.84
All	Y intercept		2309.01	Slope	-0.0020	Sigma		0.02	0.01
High CR	Y intercept		2304.04	Slope	-0.0019	Regression DT		0.87	0.84

Energy Resolution EDS vs. WDS



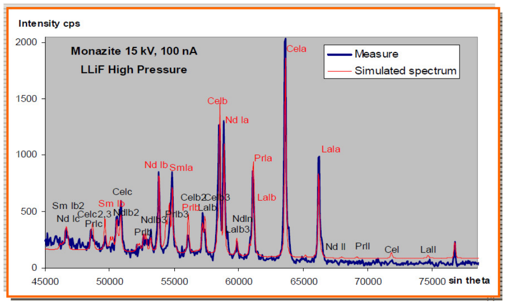
WDS Exhibits Superior Peak Resolution, P/B, Precision for Typical Systems





McSwiggen

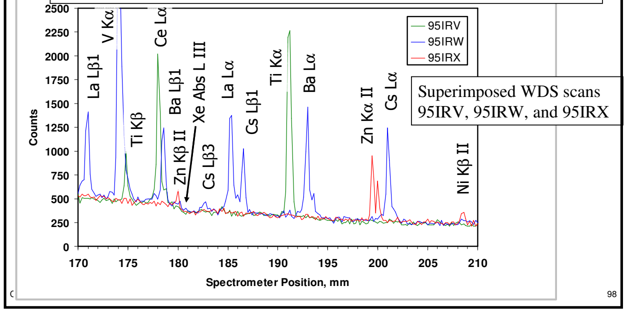
WDS Spectrum Simulation



Cameca, M&M 2001

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

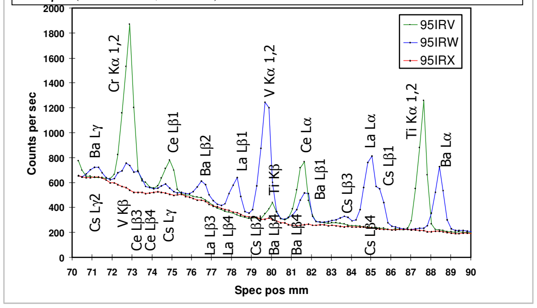
LiF crystal preferred for trace element EPMA: P/B and resolution
Note: 2nd order peaks from ~5000ppm elements, Xe edge
Interferences Ti Kβ – V Kα, Ba Lβ1 – Ce Lα, La Lα – Cs Lβ1 (unresolved, 95IRW)
Ti Kα – Ba Lα, Zn Kα II – Cs Lα



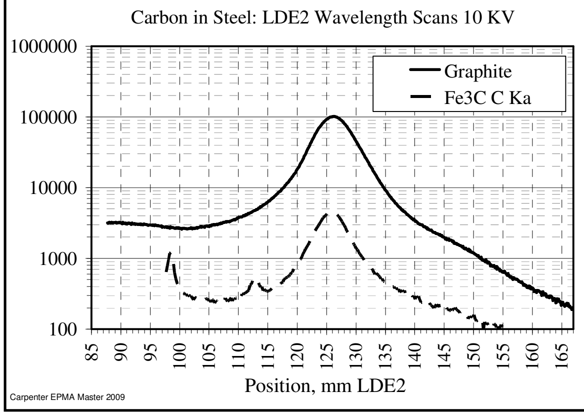
Superimposed WDS scans 95IRV, 95IRW, and 95IRX

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

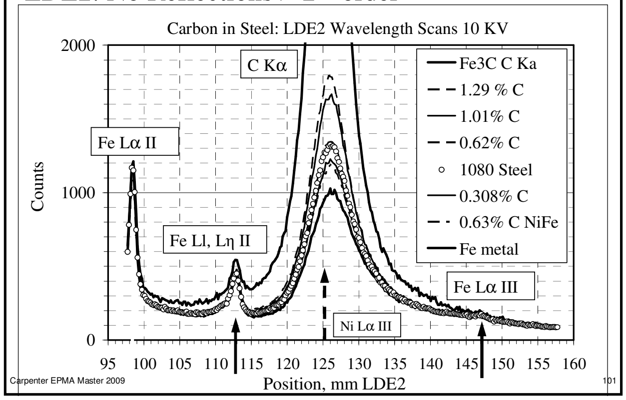
PET not preferred for trace element EPMA (if LiF applicable)
Interferences V Kβ – Cr Kα, Ti Kβ – V Kα, Ba Lβ1 – Ce Lα, La Lα – Cs Lβ1 (unresolved, 95IRW) Ti Kα – Ba Lα



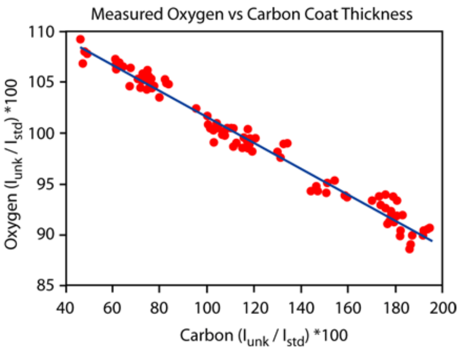
Comparison of C Kα Full Peak on Graphite w Fe_3C



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



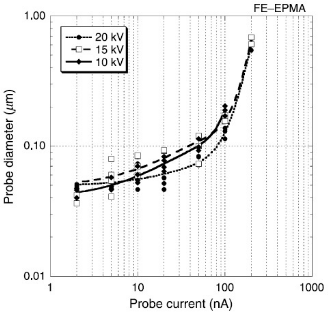
EPMA Light Element Analysis: Effect of Carbon Thickness on O Kα Emitted Intensity



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.

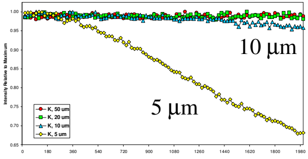
Beam Diameter vs. Probe Current: FE-EPMA
Kimura et. al., Micrchim Acta, 155, 175-178 (2006)



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

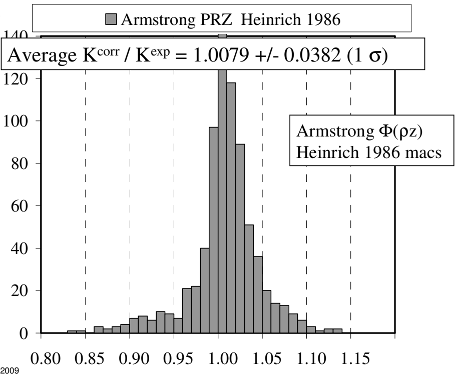
- End-member stoichiometric silicate and oxide mineral standards
- Primary standards:
  - MgO, Al_2O_3, SiO_2, $CaSiO_3$, TiO_2, and Fe_2O_3
- Analyzed suite of stoichiometric standards, natural and synthetic materials:
  - Second set of primary standards on different mounts
  - Spinel $MgAl_2O4$, Enstatite $MgSiO_3$, 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

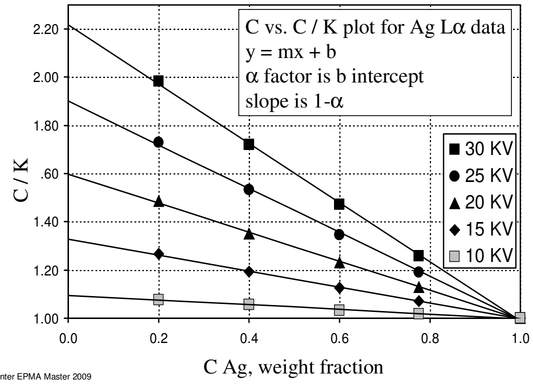
Composition in Wt% Oxide

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



Ag Lα NIST SRM 481 AgAu Alloy (ψ=40)



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

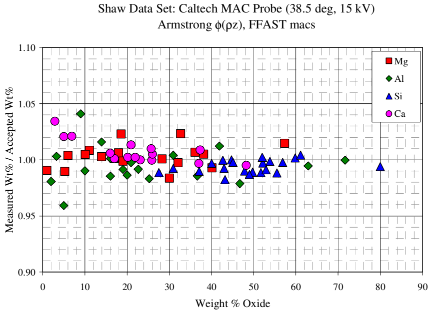
$$K_{measured} = \frac{(P-B)^{sample}}{(P-B)^{standard}}$$

$$C = K * ZAF$$

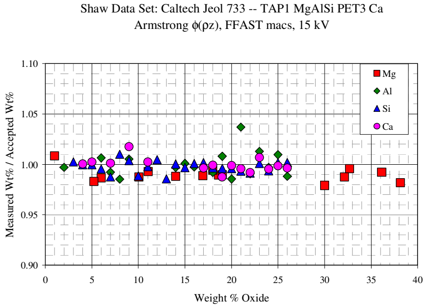
$$K_{calculated} = C / ZAF$$

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

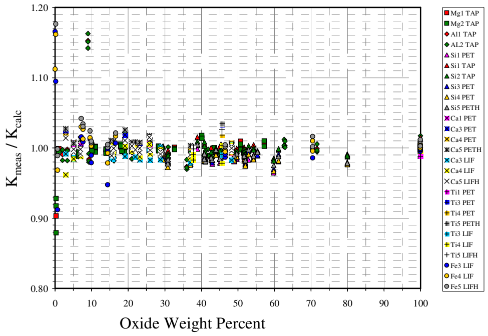
Historical CMAS Data Caltech MAC Probe, Circa 1980's



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

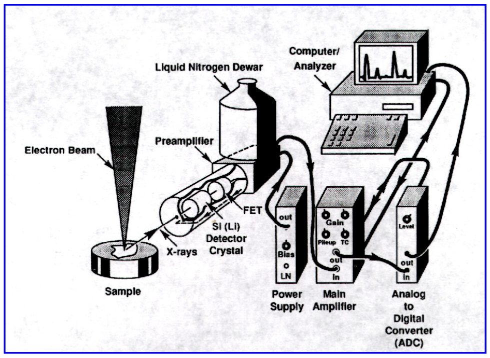


WU JXA-8200 CMASTF Data Set All WDS Data Superimposed

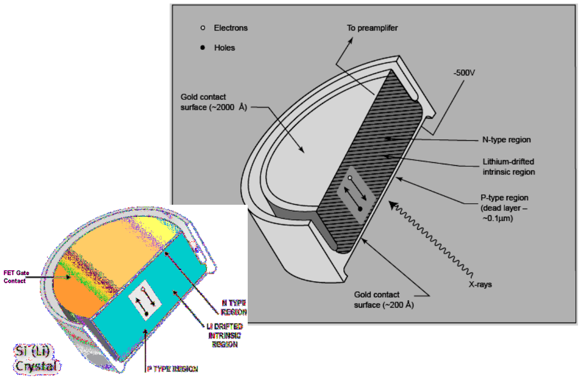


EPMA:
What's New and Important About
Energy-Dispersive Spectrometry
Silicon Drift EDS Detectors

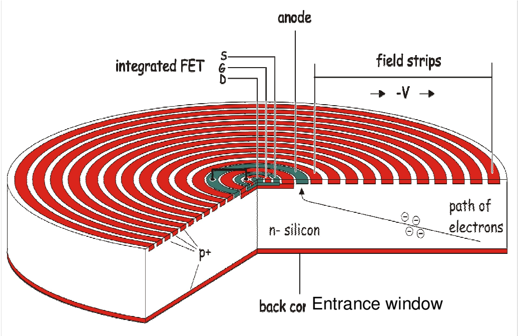
EDS Analyzer System



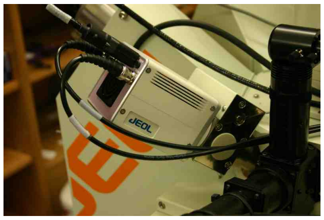
Conventional SiLi EDS Detector



Silicon Drift Detector

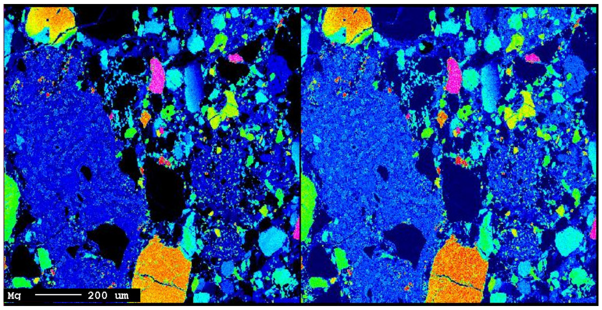


Washington University
Earth and Planetary Sciences JEOL JXA-8200



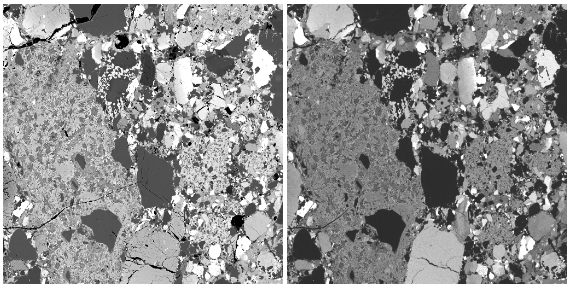
JEOL e2v Silicon Drift Detector
130 eV resolution
3 time constants T3 T2 T1
Stage and beam mapping
Quantitative EDS analysis LLSQ

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



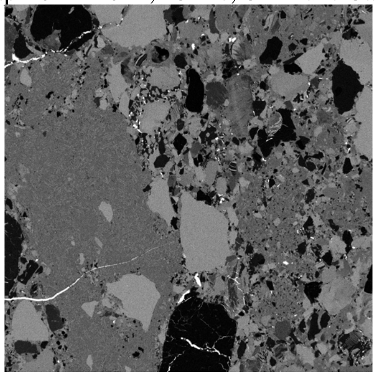
Mg WDS 1061 max counts, Mg SDD 527 max counts
1024x1024 stage map, 8 hours

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

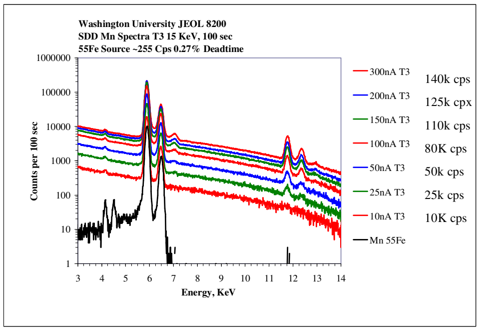


Backscattered electron vs. Fe SDD maps

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

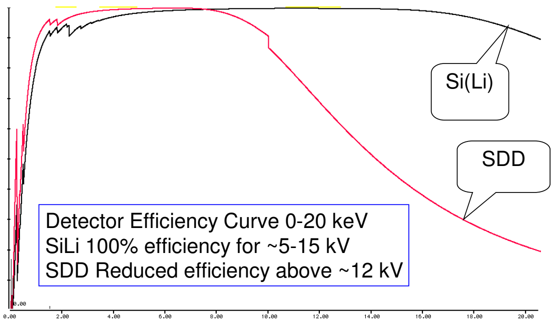


WU8200 JEOL SDD
^{55}Fe Source Mn Kα Resolution 130 eV



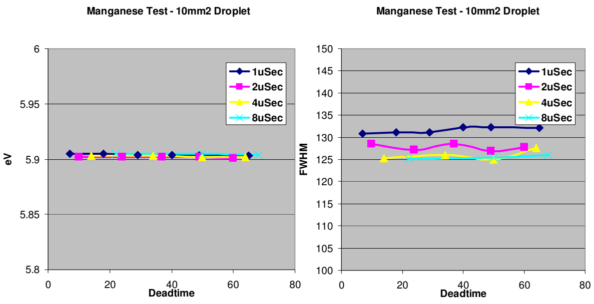
Washington University JEOL 8200
SDD Mn Spectra T3 15 KeV, 100 sec
55Fe Source ~255 Cps 0.27% Deadtime

SiLi vs. SDD Detector Efficiency

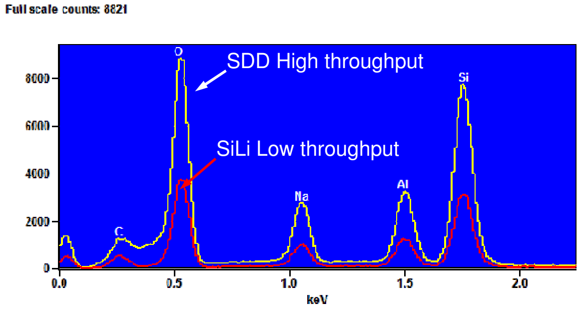


Detector Efficiency Curve 0-20 keV
SiLi 100% efficiency for ~5-15 kV
SDD Reduced efficiency above ~12 kV

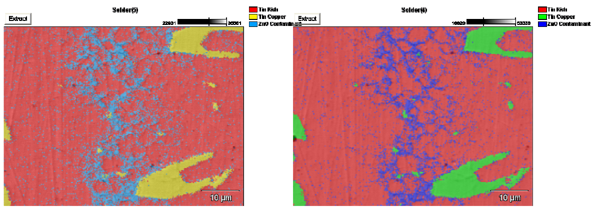
SDD Performance with increasing Count Rate



Throughput Comparison of SDD and SiLi Detectors



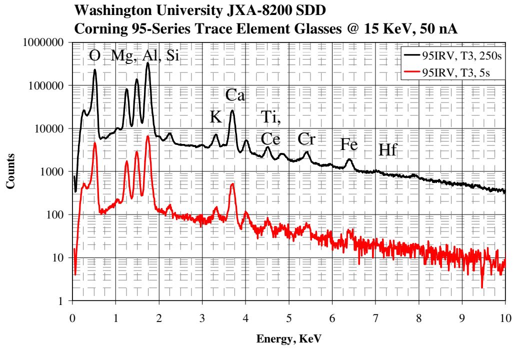
Mapping Performance SnCuZn Alloys
SiLi vs. SDD



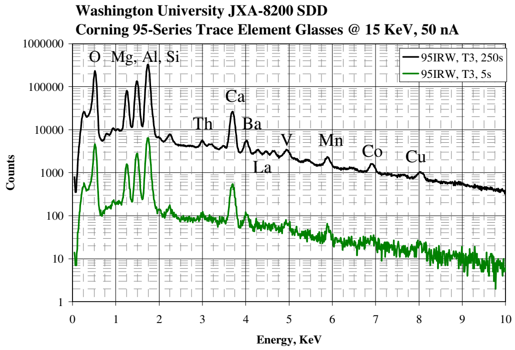
SiLi

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

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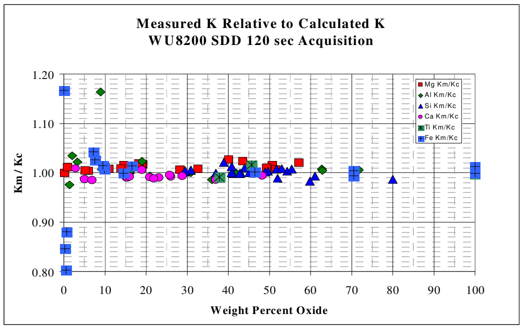
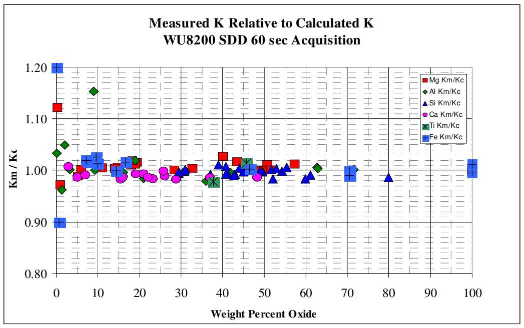
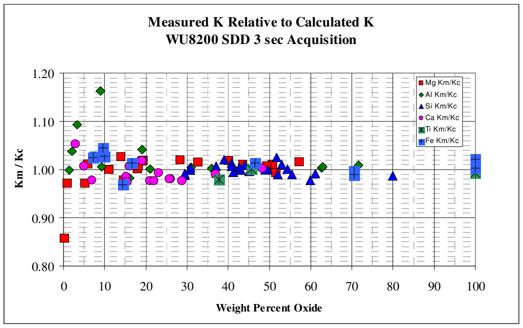
CMASTF Standard Analyses
WU8200 SDD LLSQ 120 sec. Acquisition T3



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

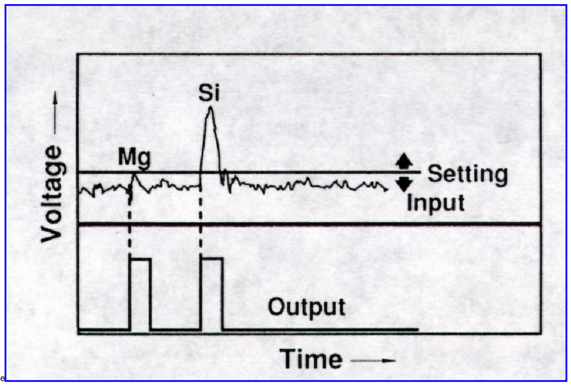
120s Data	Mg	Al	Si	Ca	Ti	Fe
Average	1.0122	1.0064	1.0017	0.9926	1.0021	1.0108
1 σ	0.0063	0.0122	0.0078	0.0066	0.0106	0.0140
Relative %	0.62	1.21	0.78	0.67	1.06	1.38
60s Data						
Average	1.0058	1.0022	0.9969	0.9895	0.9975	1.0083
1 σ	0.0118	0.0162	0.0069	0.0066	0.0150	0.0113
Relative %	1.17	1.61	0.69	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

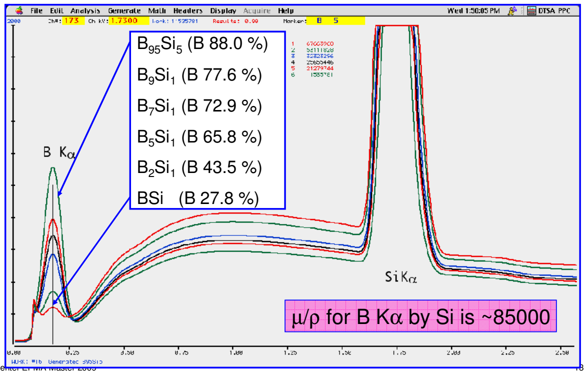
- The fast discriminator setting is used to differentiate between noise and x-ray pulses.
- A pulse having a voltage that exceeds the threshold is "detected", all others are ignored.
- The FD is good at discriminating high energy photons from noise, but is bad at discriminating low energy (i.e. light 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

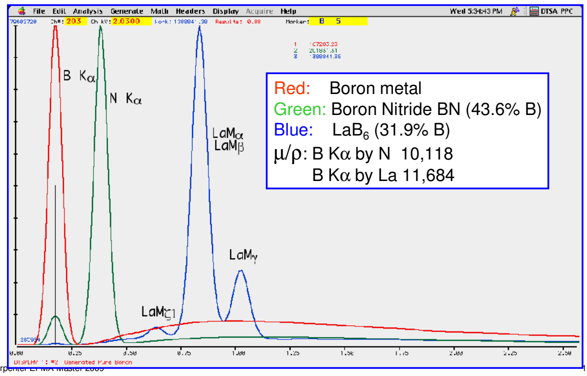


Boron Kα in Silicon – 10kV 40 degrees



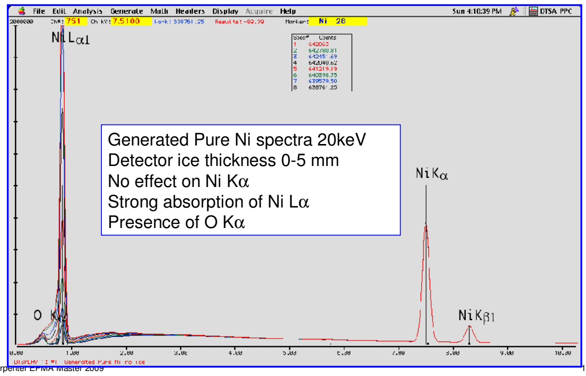
μ/ρ for B Kα by Si is ~85000

Boron EDS Spectra 10kV, 40 degrees



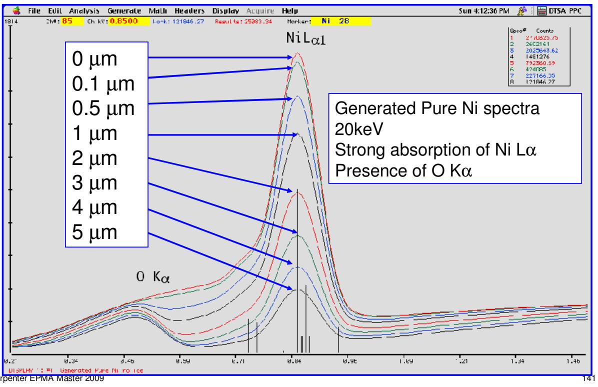
Red: Boron metal
Green: Boron Nitride BN (43.6% B)
Blue: LaB$_6$ (31.9% B)
μ/ρ: B Kα by N 10,118
B Kα by La 11,684

Ni Kα and Lα vs. Ice Thickness



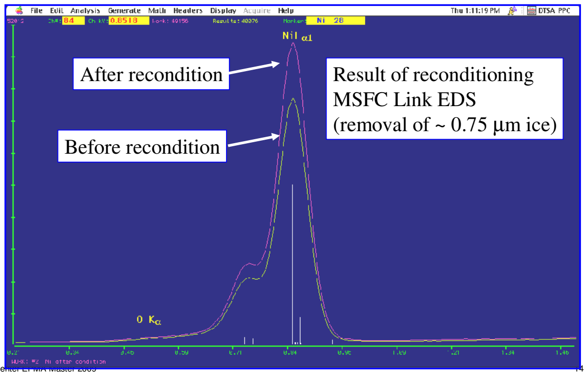
Generated Pure Ni spectra 20keV
Detector ice thickness 0-5 mm
No effect on Ni Kα
Strong absorption of Ni Lα
Presence of O Kα

Ni Lα vs. Ice Thickness



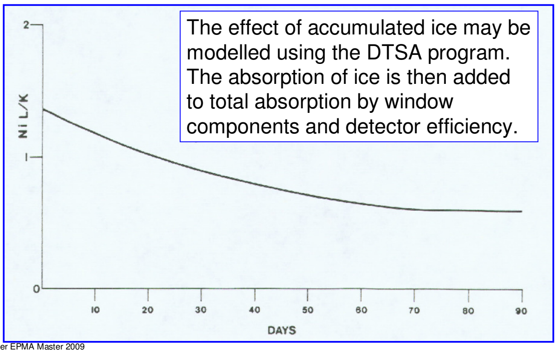
Generated Pure Ni spectra
20keV
Strong absorption of Ni Lα
Presence of O Kα

MSFC Link Recondition EDS



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

Ice Accumulation Monitor:
Ratio of Ni Lα / Ni Kα



The effect of accumulated ice may be modelled 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)

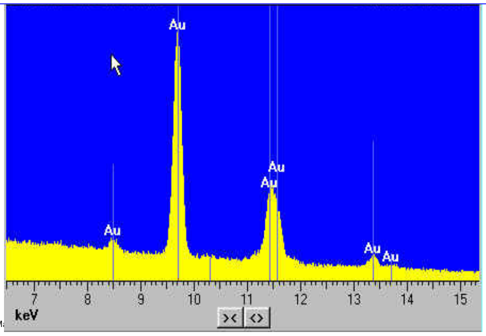
- Qualitative analysis is the identification of the elements present.
- The presence or absence of an element is established based on the presence or absence of x-ray peaks or families of peaks.
- Approximate relative concentrations may be estimated using relative peak heights, but may be subject to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

Relative X-ray Line Weights

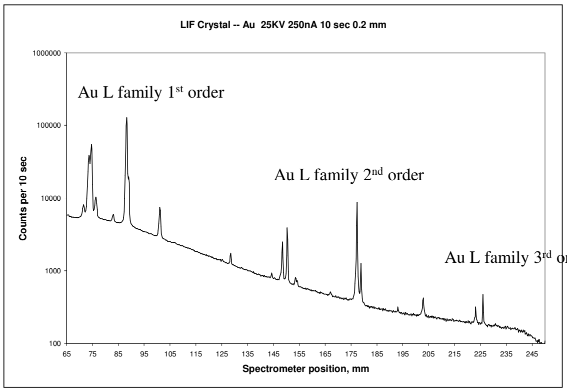
- X-ray lines intensities are referenced relative to the most intense peak, i.e., Kα, Lα, or Mα.
- These peaks are assigned a 100% relative intensity.
- All other family lines for that element are scaled relatively:
- These line weights are only approximately known and need revision
- Note: Absolute 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

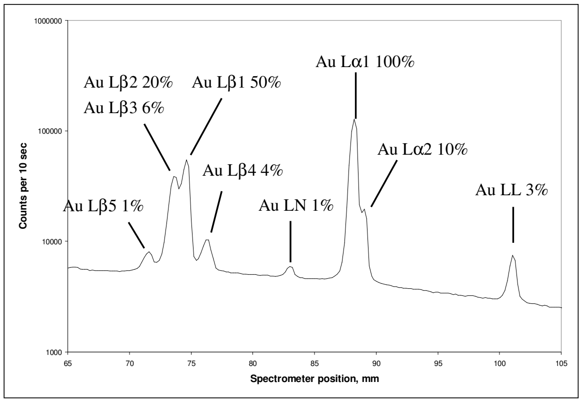
Use the position of KLM markers primarily, with relative intensity secondarily, in identification of an element



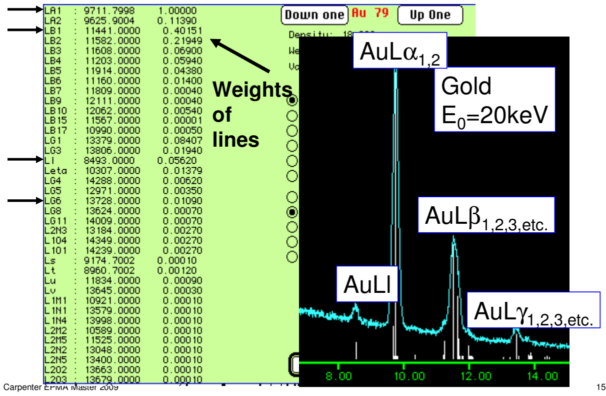
WDS Scan Au 25kV



WDS Scan Au 25kV



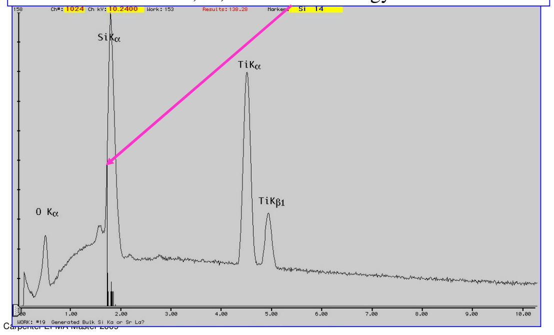
X-ray Database—Line Weights



```
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
L1O4  : 14349.0000   0.00270
L1O1  : 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
L2O2  : 13663.0000   0.00010
L2O3  : 13679.0000   0.00010
```

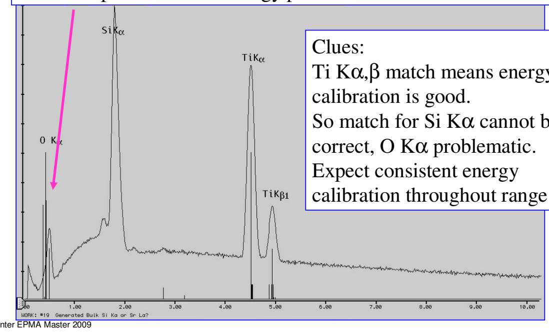
Peak Identification – Is it Si Kα or ?
Spectrum Displayed/Acquired at 0-10 keV

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



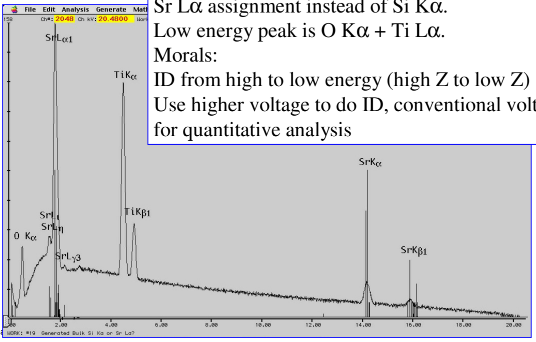
Is it O Kα or Ti Lα ?
Spectrum Acquired at 0-10 keV

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



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

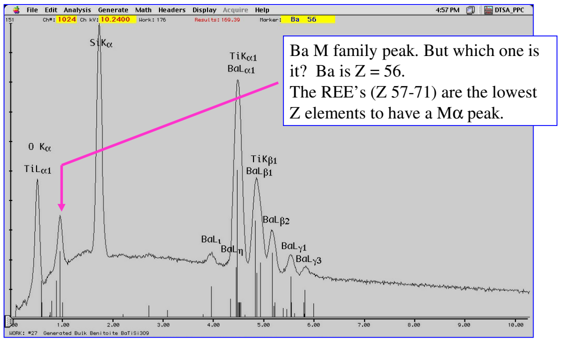
SrTiO$_3$ Confirmed by 20 keV Acquisition



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

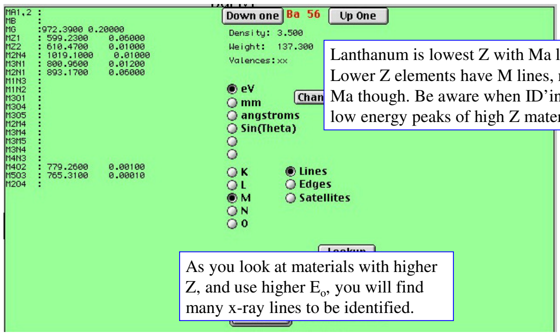
---

Benitoite BaTiSi$_3$O$_9$



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
```

● eV
○ mm
○ angstroms
○ Sin(Theta)

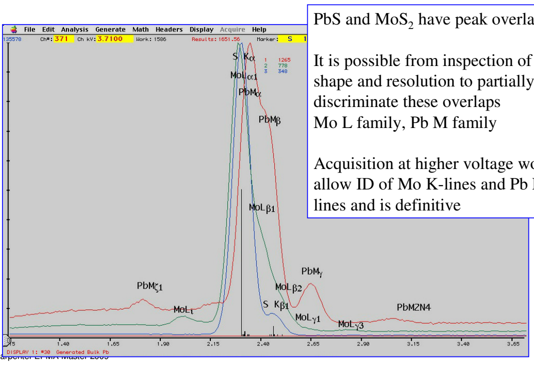
○ K
○ L
● M
○ N
○ O

● Lines
○ Edges
○ Satellites

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

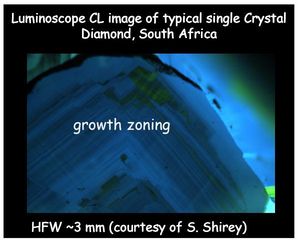


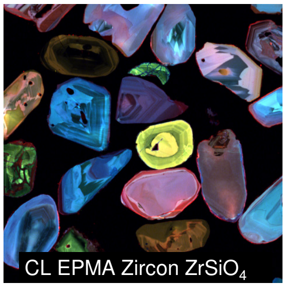
PbS and MoS$_2$ have peak overlaps

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

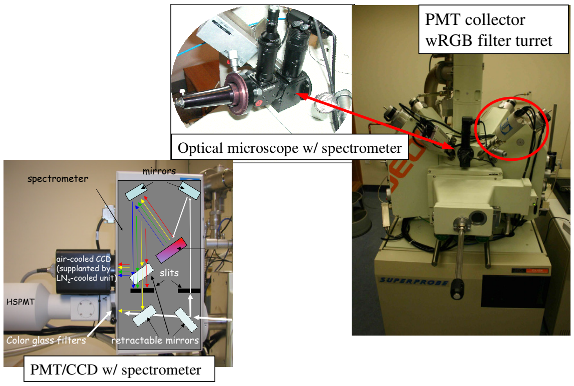




Cathodoluminescence

- 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

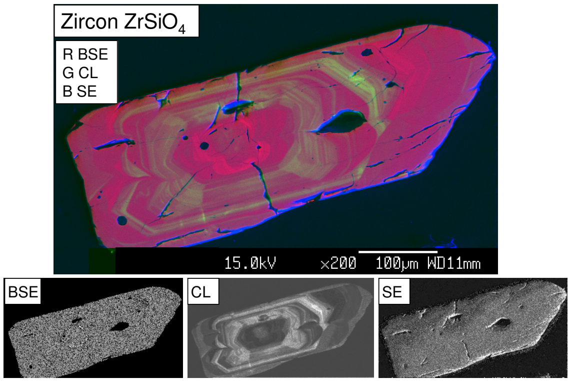


PMT collector wRGB filter turret

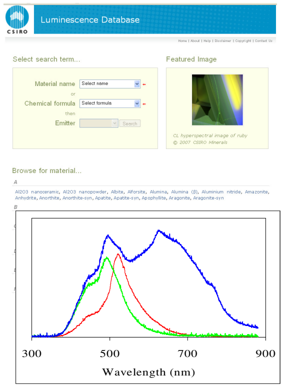
Optical microscope w/ spectrometer

PMT/CCD w/ spectrometer

Combined CL, BSE, SE Images in Zircon



Luminescence database



CL hyperspectral image of ruby © 2007 CSIRO Minerals

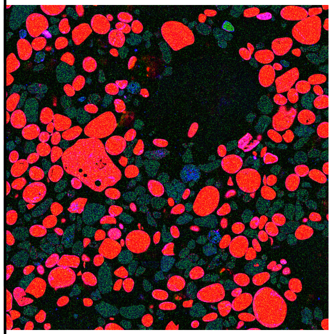
Al2O3 nanoceramic, Al2O3 nanopowder, Albite, Alforsite, Alumina, Alumina (β), Aluminium nitride, Amazonite, Anhydrite, Anorthite, Anorthite-syn, Apatite, Apatite-syn, Apophyllite, Aragonite, Aragonite-syn

- **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:**

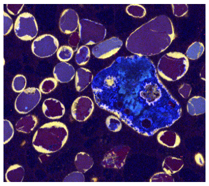
www.csiro.au/luminescence

McRae, CSIRO

Quartz grains with overgrowth



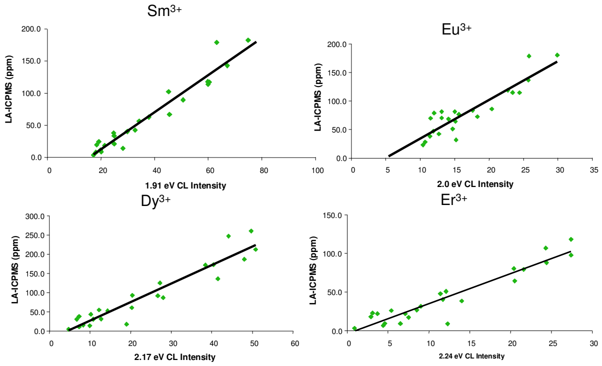
X-ray map
🟦 Al
🟩 Fe
🟥 Si



Cathodoluminescence

McRae, CSIRO

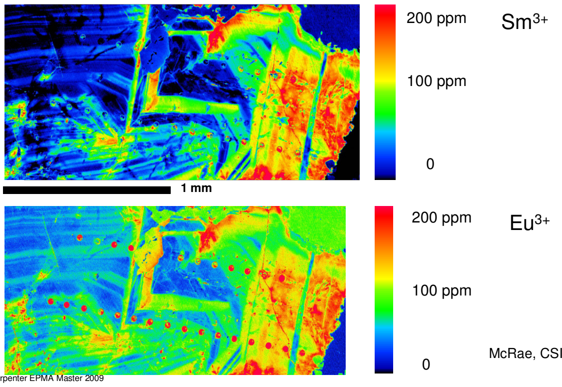
Comparison between LA-ICP-MS and CL region



McRae, CSIRO

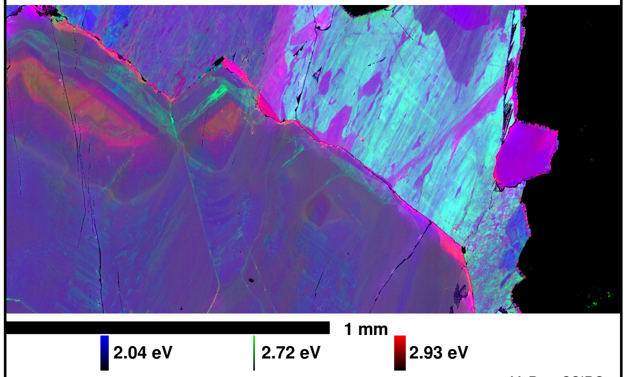
Calibrated CL maps

Spectral collection using microprobe optical microscope



McRae, CSIRO

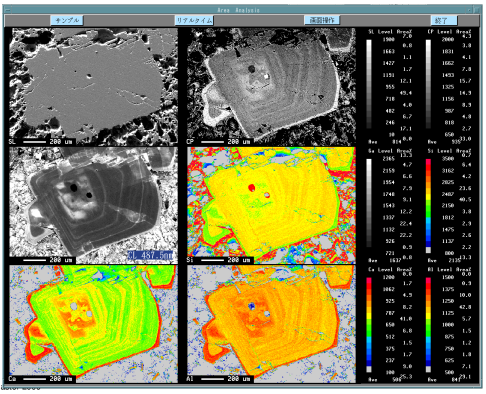
Pink Spodumene – Kunzite ($LiAlSi_2O_6$)



CL activation by trace Mn (?)

McRae, CSIRO

Combined CL, BSE, X-ray Mapping



Quantitative Analysis
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?

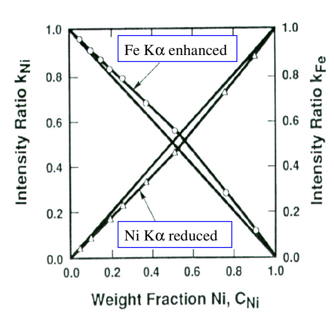
- WDS: excellent resolution -- measurements are made on top of the peak and two adjacent backgrounds, then background under the peak is determined from y=mx+b fit to the two backgrounds, then background is subtracted from the peak intensity.
- EDS spectra have much poorer resolution, and it is not clear 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):
  $C = C_{std}\ k\ Z\ A\ F$

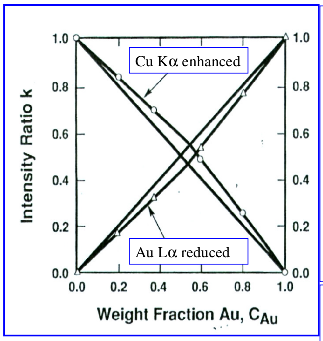
Matrix Effects—Fe Ni Alloy
Similar Z, Absorption and Fluorescence



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

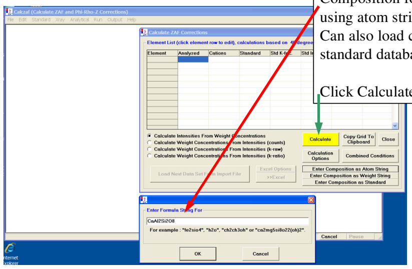
Summary: CuAu system
Absorption, not fluorescence
Different Z – requires atomic number correction (diff. scattering)

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



Element List (click element row to edit), calculations based on 40 degree

● Calculate Intensities From Weight Concentrations
○ Calculate Weight Concentrations From Intensities (counts)
○ Calculate Weight Concentrations From Intensities (k-raw)
○ Calculate Weight Concentrations From Intensities (k-ratio)

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.

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) detector, 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 likliehood of an event.

Stopping Power S

- Electrons lose energy during inelastic scattering events.
- This energy loss, dE/ds is ~ 10 eV/nm.
- The energy loss increases with increasing beam energy, and with increasing atomic number. These parameters are built-in to the stopping power formula.
- The “continuous slowing down” approximation is used in development of the stopping power relation. That is, the electron is considered to slow down in equal steps for simplification.
- Stopping power $S = - (1/\rho)\ dE/ds$. Units are mass distance (g/cm^2), rather than linear distance. The stopping power decreases with increasing Z, contrary to intuition.
- Stopping power is actually greater for low Z targets than high Z. At 20 keV, the stopping power for Al is 50% greater than for Au.

Backscatter Correction R

- Electrons are elastically backscattered out of the sample. Electrons enter the sample, producing x-rays, and scatter back out, also producing x-rays, but leaving the sample before expending all energy. This is accounted for by the backscatter correction.
- The backscatter fraction η is i_{bse} / i_b, the fraction of total beam electrons (i.e. probe current) that backscatter. η increases with atomic number Z, and forms the basis for atomic number contrast in backscattered electron imaging.
- Backscattered electrons have an energy distribution that is a function of Z. As Z increases, η, the fraction of bse’s increases, and also the energy distribution becomes more peaked and increases relative to the excitation energy of the beam electrons.

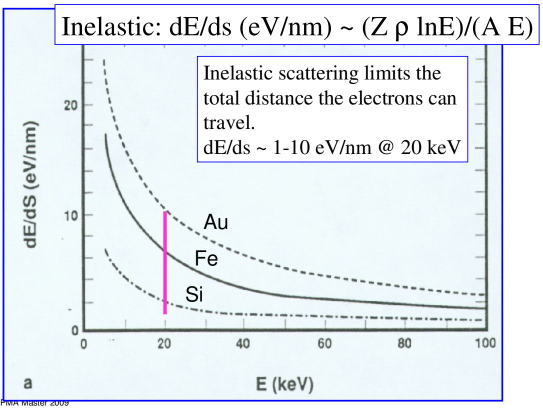
Backscatter Correction R

- As Z increases, more bse’s are produced, having an energy that increases towards E_o.
- R, the backscatter correction factor, is the ratio of the total number of x-rays produced in the sample, compared to the amount that would have been produced had there been no backscattering.
- R is typically 0.5-1, and approaches 1 for low Z materials. That is, it is important for high Z materials, and for large differences between Z of the sample and standard.
- R is a function of Z and of overvoltage $U = E/E_c$. As either Z or U increases, R decreases.

Atomic Number Correction Z

- The atomic number correction is formed by combining the stopping power correction S, with the backscatter correction R. This is applied as a ratio comparing the magnitude of the corrections for the sample and standard:
  $Z = (R_{sample} / R_{standard}) * (S_{standard} / S_{sample})$
- The effects of R and S tend to counter one another, and the magnitude of the correction is usually not large, compared to the absorption correction.
- The atomic number correction is large when there is a large difference in average atomic number between the sample and standard. Example: Al_3Cu_{97} alloy, using pure Al and Cu as standards; reduced reliance on atomic number correction would be to use a known AlCu alloy as a standard.

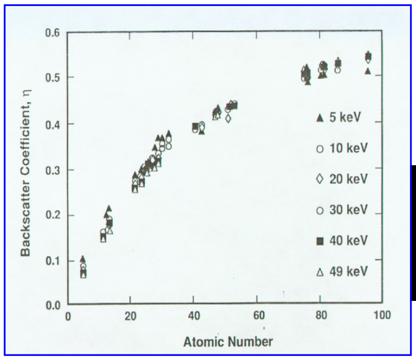
Energy Loss of Electrons



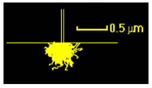
Inelastic: $dE/ds\ (eV/nm) \sim (Z\ \rho\ \ln E)/(A\ E)$

Inelastic scattering limits the total distance the electrons can travel.
dE/ds ~ 1-10 eV/nm @ 20 keV

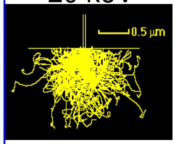
Backscattering vs. Beam Energy



10 keV



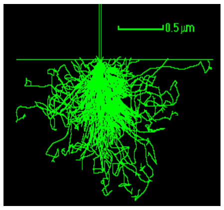
20 keV



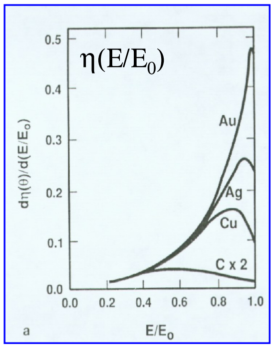
Fe

Backscattered Electrons: Energy Distribution

As beam electrons travel in the specimen, they lose energy (dE/ds, ~ 1 - 10 eV/nm) prior to backscattering.

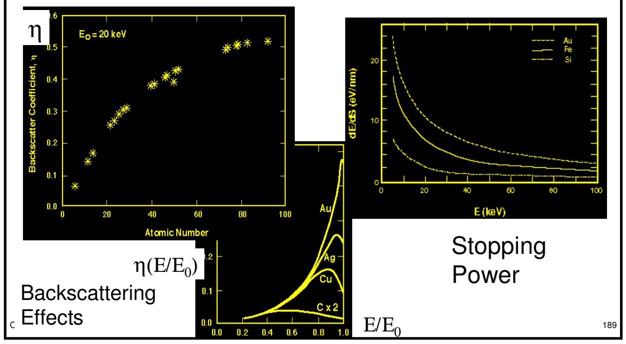


High Z produces more high energy BSEs



Matrix Corrections: Atomic Number

Atomic Number Correction (Z): arises because of backscattering (η and η(E)) and stopping power (dE/ds)



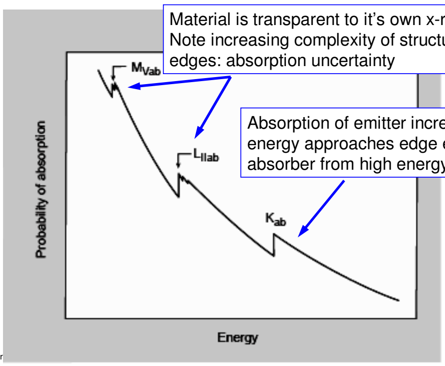
Backscattering Effects

Stopping Power

Absorption Correction A

- X-rays of a given element that are generated in the excitation volume of the sample are absorbed by all elements present in the sample on the way out to the detector. The emitted x-ray intensity is the generated intensity minus the absorbed intensity.
- The amount of absorption depends on the mass absorption coefficient (mac), μ/ρ, for the emitted x-ray by the absorber element, and the path length of absorption. The units are cm^2/g.
- Examples: small mac of 11.2 for Cu Kα by O (hard x-ray through "air"), intermediate mac of 4764 for Al Kα by Cu, and large mac of 23,600 for N Kα by C.
- The path length over which absorption occurs is z csc ψ, where csc ψ is the cosecant of the x-ray takeoff angle.

X-ray absorption discontinuities -- Edges



Material is transparent to it's own x-rays
Note increasing complexity of structure for L and M edges: absorption uncertainty

Absorption of emitter increases as x-ray energy approaches edge energy of absorber from high energy side

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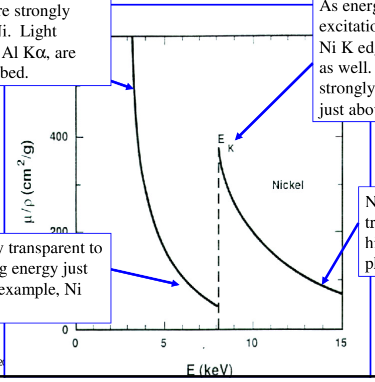
Mass Absorption Coefficients for Ni Absorber



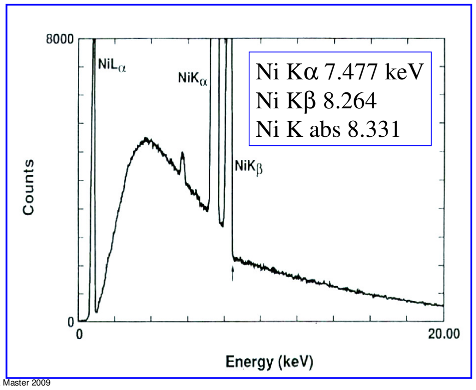
As photon energy decreases, x-rays are more strongly absorbed by Ni. Light elements, i.e., Al Kα, are strongly absorbed.

As energy decreases to the excitation energy for the Ni K edge, μ/ρ increases as well. X-rays most strongly absorbed are those just above E_k. Like Cu Kβ

Ni is relatively transparent to higher energy photons

Ni is relatively transparent to photons having energy just below E_k, for example, Ni Kα.

Ni Absorption edge in Ni EDS Spectrum



Ni Kα 7.477 keV
Ni Kβ 8.264
Ni K abs 8.331

Absorption Correction A

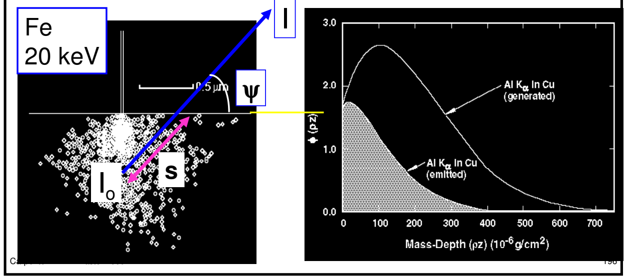
- The quantity "μ/ρ csc ψ" is abbreviated as χ, and is used to describe the absorption correction.
- The term f(χ) is called "f of χ" and is the ratio of the emitted x-ray intensity to the generated intensity:
  f(χ) = emitted intensity / generated intensity
- The absorption correction A is the ratio of f(χ) for the standard and the sample:
  $A = f(\chi)_{standard} / f(\chi)_{sample}$

Absorption Correction A

- Three variables affect f(χ), the mac for the measured element, the accelerating potential, and the takeoff angle.
- If possible, f(χ) should be > 0.7. This is accomplished by reducing the accelerating voltage, as this reduces the absorption path length.
- The analysis of light elements, low-energy x-rays, or an element in a strongly absorbing matrix are critically dependent on the accuracy of the absorption correction.

Matrix Corrections: X-ray Absorption

- Absorption Correction (A): arises because of X-ray generation distribution and photoelectric absorption during propagation to reach surface:
  $I / I_0 = \exp[-(\mu/\rho) \rho s]$

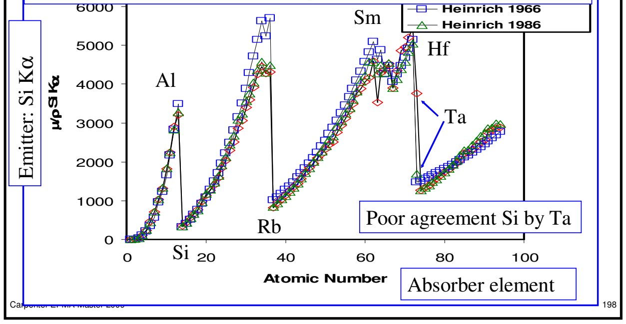


Mass Absorption Coefficient Plots

- mac of an emitter (Si Kα) is plotted for all absorber elements (Be through U)
- Discontinuities occur at K, L, and M edges of absorber element
- These discontinuities are a significant change in mac for the emitter element

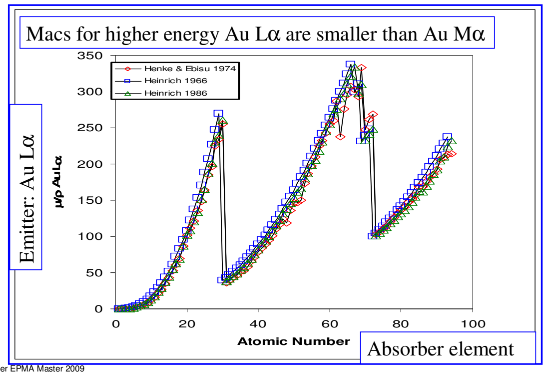
Mass Absorption Coefficients: Si Kα

Si Kα absorbed by Al (K edge), Kr (L edge) and Hf,Ta (M edge)
Minimal absorption of Si Ka by Si, Rb, W etc.
These plots give immediate absorption info for emitter element



Poor agreement Si by Ta

Mass Absorption Coefficients: Au Lα

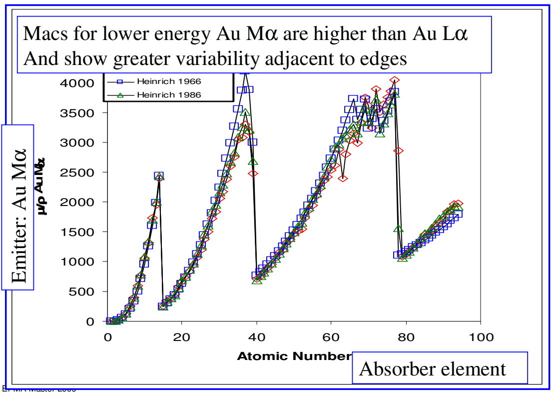


Macs for higher energy Au Lα are smaller than Au Mα

Emitter: Au Lα

Absorber element

Mass Absorption Coefficients: Au Mα



Macs for lower energy Au Mα are higher than Au Lα
And show greater variability adjacent to edges

Emitter: Au Mα

Absorber element

Characteristic Fluorescence Correction F

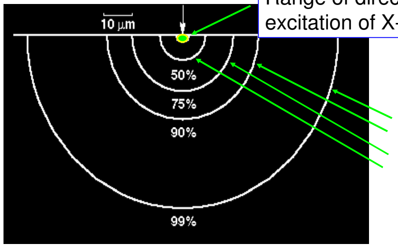
- If the energy of a characteristic x-ray of a given element is higher than the excitation energy of another element in the sample, it may be fluoresced. Example: Fe Kα by Ni Kα.
- The intensity of the fluoresced element is greater, and of the fluorescing element is lower, than the generated intensities.
- Fluorescence is most efficient when the fluorescing energy is within 5 keV of the fluoresced element. It is most important for K by K, less so for other combinations.
- The fluorescence correction also includes correction for the absorption of the fluorescing radiation.
- The fluorescence correction F is:
  $F = 1 / (1 + \Sigma\, If / Ip)$
  which calculates the total fluorescent radiation divided by the primary radiation and adds the sum to 1.
- The magnitude of the F correction is usually small, but is most important for transition element K-lines (Cr, Fe, Ni, etc.)

Secondary Fluorescence Due to Characteristic X-rays

- X-rays generated in the primary excitation volume can travel a great distance, because materials are more transparent to x-rays than electrons.
- Example: A Ni Kα x-ray is generated in the analysis volume, then travels 100 μm to fluoresce a Fe Kα x-ray in a completely different phase.
- An x-ray may be detected at several μm to hundreds of μm from the analysis point!
- The EDS detector, with fairly large solid angle collection, may detect these x-rays, quite efficiently.

Matrix Corrections: X-ray Fluorescence

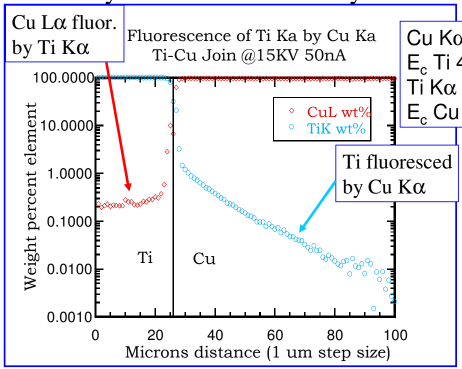
- Fluorescence Correction (F): arises because X-ray photoelectric absorption ionizes the absorbing atom, which subsequently emits its own X-ray(s). F is generally a second order effect compared to Z and A.



Range of direct electron excitation of X-rays

Contours give range for X-ray-induced fluorescence

Secondary Fluorescence:
Ti Kα by Cu Kα and Cu Lα by Ti Kα



Cu Lα fluor. by Ti Kα

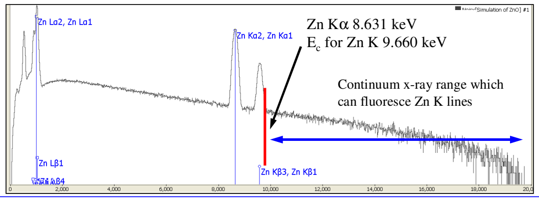
Ti fluoresced by Cu Kα

Cu Kα 8.047 keV
E_c Ti 4.964
Ti Kα 4.510 keV
E_c Cu Lα 0.933

Fluorescence by the Continuum

- Any electron or x-ray having energy greater than the excitation energy of an element, may generate an x-ray. Continuum x-rays, like characteristic x-rays, can cause fluorescence.
- Continuum fluorescence is important for high Z elements having high energy x-rays, analyzed in a low Z matrix. It is also important in thin film analysis.
- Examples: Cu Kα in biological tissue, Ge Kα in Si (not Ge Lα), Pt Lα in thin film on Ni substrate.
- The correction reduces the intensity due to continuum fluorescence. If ignored, the high Z line will be over-estimated.
- Most correction programs do not include continuum fluorescence routines. COR and GMR Film do.

Continuum Fluorescence



Zn Kα 8.631 keV
E_c for Zn K 9.660 keV

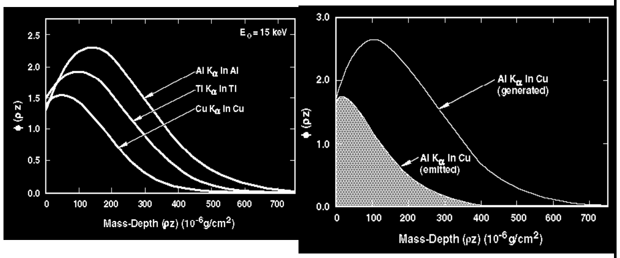
Continuum x-ray range which can fluoresce Zn K lines

Simulated EDS spectrum of ZnO using DTSA-II (20keV)
CF important for element with energetic line (Zn Kα) of heavy element (produces higher continuum) in light matrix (oxygen).
Any continuum x-ray with $E > E_c$ for Zn K can cause fluorescence.
CF is additive, here intensity of Zn Kα enhanced by CF, so Zn wt% higher.

Problem: CF present in experimental data used to develop ZAF/Φ(ρz) equations, so an explicit CF correction duplicates “built-in” treatment of CF.

What is the Φ(ρz) method?

Φ(ρz) curves are experimentally measured X-ray depth distribution functions. To generalize, they are parameterized as a function of Z, E_0, E_c



How Do the Φ(ρz) and ZAF Methods Differ?

- Important point: The Φ(ρz) and ZAF “methods” are really sets of computational algorithms. One really should specifically state which set of algorithms are being used. Example: PAPS Φ(ρz), Philibert-Duncumb-Reed ZAF. All ZAF/ Φ(ρz) are not equal!
- The Φ(ρz) curve describes the generated x-ray intensity. It has the effect of stopping power and electron backscattering “built-in”. Correction for x-ray absorption and fluorescence are made just like the ZAF approach.
- In the ZAF approach, corrections for atomic number, absorption, and fluorescence are made via multiplicative factors applied to the measured k-ratio.
- Both methods make use of iteration. Each successive calculated C is used to further refine the correction.

Iteration Procedure for Correction

- The k-ratio is measured, and converted to concentration by C = k * ZAF. But each ZAF factor is a function of composition. An iterative procedure is used.
- The measured k-ratios are normalized (total = 1). This is a first guess at the composition, just to start.
- ZAF factors are calculated from this first guess.
- The 2nd guess at concentration is C = k * ZAF.
- ZAF factors are calculated using this 2nd guess.
- ...and so on ($C_n = k * ZAF_{n-1}$), until the difference in subsequent guesses of concentration is less than a specified amount (~.01 wt%). Go to printout.

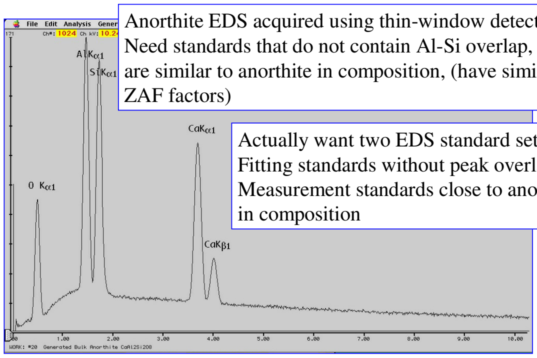
ZAF Example — EDS Anorthite $CaAl_2Si_2O_8$

- Most materials require a correction for x-ray absorption. Minerals, ceramics, oxides, and glasses are typical in that the predominant correction is for absorption, with Z and F effects secondary.
- For EDS analysis, Al_2O_3, SiO_2, and $CaSiO_3$ were used as primary standards (no peak overlap) for Al Kα, Si Kα, and Ca Kα. Analysis performed at 30 degree takeoff, 15 keV, 100 sec counts, and 400 pA on Fe_2SiO_4 absorbed current reference.
- A sample of anorthite was analyzed as an unknown, using the MLLSQ peak fitting technique.
- The standard intensities were: Al Kα 2556 counts, Si Kα 2934 counts, and Ca Kα 1760 counts.

ZAF Example — EDS Anorthite $CaAl_2Si_2O_8$

- K-ratios calculated relative to the standards used (Al_2O_3, SiO_2, and $CaSiO_3$): K-std = $(P - B)^{sample} / (P - B)^{standard}$
- CITZAF Armstrong Φ(ρz) algorithm used for correction.
- The φ(ρz) routine first calculates the K-ratio relative to a pure element (K-purel), not the oxide, using K = C / ZAF. This underscores the relation between K and C.
- This K-ratio relative to a pure element standard is the starting point for iterative correction.
- When finished, the program prints the Z, A, and F factors, and the calculated concentrations of Al, Si, and Ca, with O calculated by stoichiometry.

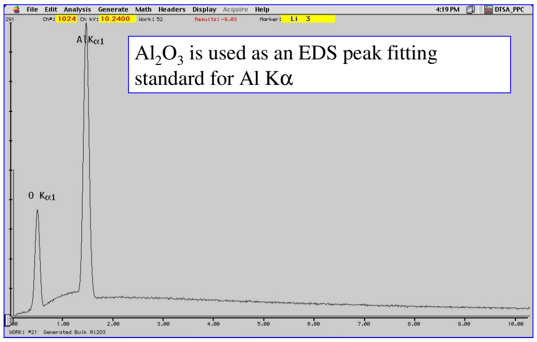
ZAF Example — EDS Anorthite $CaAl_2Si_2O_8$



Anorthite EDS acquired using thin-window detector. Need standards that do not contain Al-Si overlap, and are similar to anorthite in composition, (have similar ZAF factors)

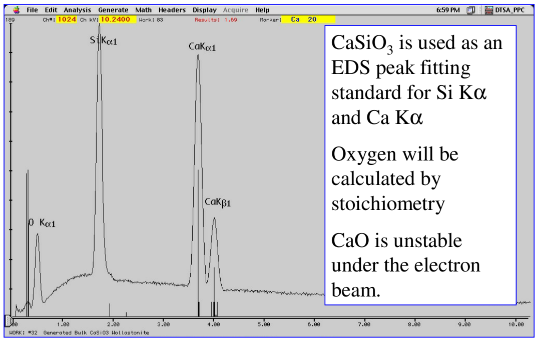
Actually want two EDS standard sets:
Fitting standards without peak overlaps
Measurement standards close to anorthite in composition

Al_2O_3 Standard for Al Kα



Al_2O_3 is used as an EDS peak fitting standard for Al Kα

$CaSiO_3$ Standard for Si Kα and Ca Kα

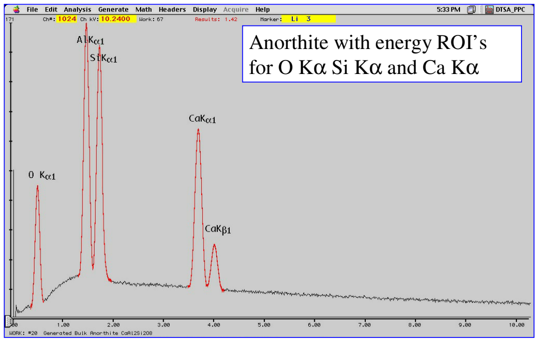


$CaSiO_3$ is used as an EDS peak fitting standard for Si Kα and Ca Kα

Oxygen will be calculated by stoichiometry

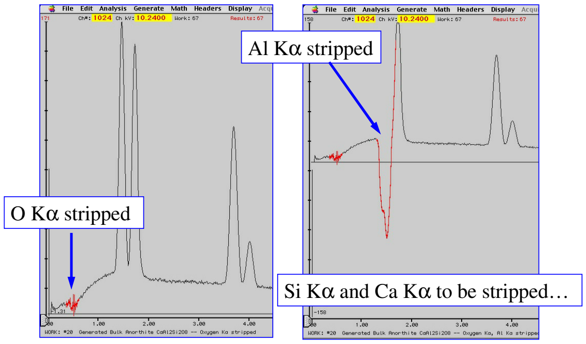
CaO is unstable under the electron beam.

Anorthite Spectrum with ROI's



Anorthite with energy ROI's for O Kα Si Kα and Ca Kα

Anorthite Spectrum w. Oxygen (L) and Al (R) Peaks Stripped



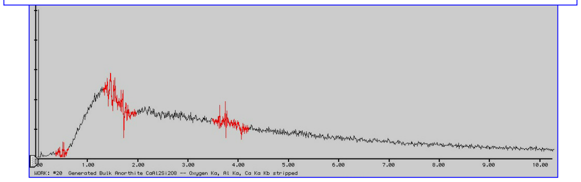
Al Kα stripped

O Kα stripped

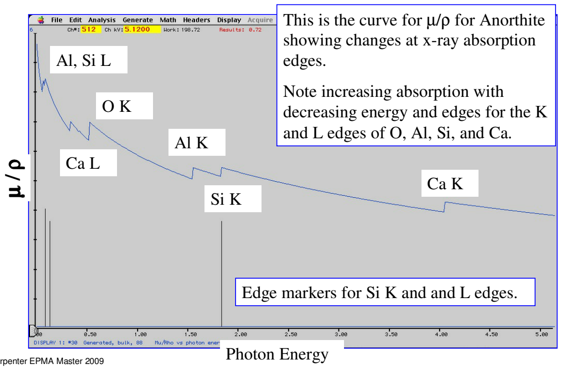
Si Kα and Ca Kα to be stripped…

Anorthite Residual Spectrum

Anorthite residual spectrum after O Kα Si Kα and Ca Kα peaks all stripped. Only continuum should remain.
Any missed elements are evident after stripping. Also, a calibration error will be apparent with S-shaped residuals.
The χ^2 value is mathematical representation of this fit. If fitted peaks adequately represent the spectrum structure, then χ^2 is minimized.



Anorthite μ/ρ vs. Energy

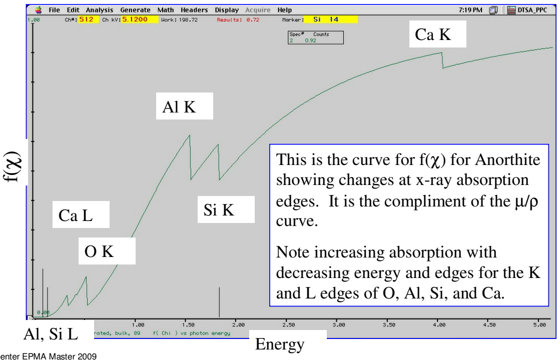


This is the curve for μ/ρ for Anorthite showing changes at x-ray absorption edges.

Note increasing absorption with decreasing energy and edges for the K and L edges of O, Al, Si, and Ca.

Edge markers for Si K and and L edges.

Anorthite f(χ) vs. Energy
f(χ) = emitted / generated intensity



This is the curve for f(χ) for Anorthite showing changes at x-ray absorption edges. It is the compliment of the μ/ρ curve.

Note increasing absorption with decreasing energy and edges for the K and L edges of O, Al, Si, and Ca.

ZAF Example—Standards

El	K-purel	Z	A	F	ZAF	C wt%
Al	0.4187	1.041	1.214	1.000	1.264	52.93
O						47.07

Al_2O_3 Standard
K-purel is obtained from K = C / ZAF

El	K-purel	Z	A	F	ZAF	C wt%
Si	0.3994	1.031	1.136	1.000	1.171	46.74
O						53.26

SiO_2 Standard

El	K-purel	Z	A	F	ZAF	C wt%
Si	0.1982	1.012	1.211	0.996	1.220	24.18
Ca	0.3189	1.050	1.030	1.000	1.082	34.50
O						41.32

$CaSiO_3$ Standard

ZAF factors calculated using CITZAF:
Armstrong Φ(ρz), Heinrich 1986 macs, 15keV, 40deg

ZAF Example—Anorthite $CaAl_2Si_2O_8$

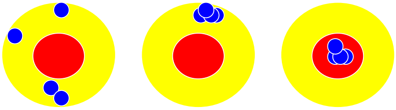
El	P-B smp	P-B std	K-std	K-purel	Z	A	F	ZAF	C wt%
Al	881	2556	0.3447	0.1460	1.044	1.277	0.992	1.322	19.29
Si	1042	2934	0.3552	0.1430	1.016	1.399	0.997	1.417	20.26
Ca	720	1760	0.4089	0.1307	1.056	1.043	1.000	1.101	14.38
O									46.36

K-purel for sample is obtained from K = K-std * K-purel for that standard.
Z correction: 6% for Ca, 4% for Al, 2% for Si, S>R, stopping power dominates the atomic number correction.
A correction: (all absorbed) 40% for Si, 28% for Al, 4% for Ca
F correction: 0.8% for Al (by Si and Ca), 0.3% for Si (by Ca) 0% for Ca
Concentration calculated from C = K-purel * ZAF

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.

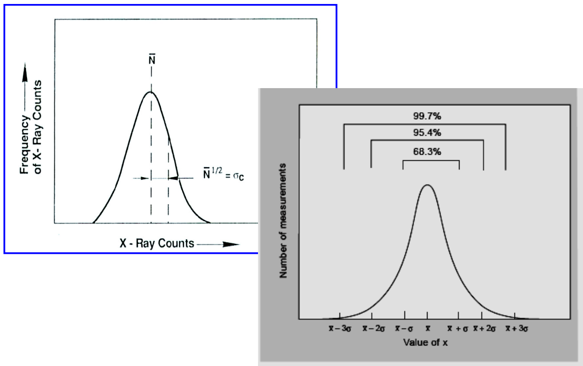


Poor precision Poor accuracy	Good precision Poor accuracy	Good precision Good accuracy

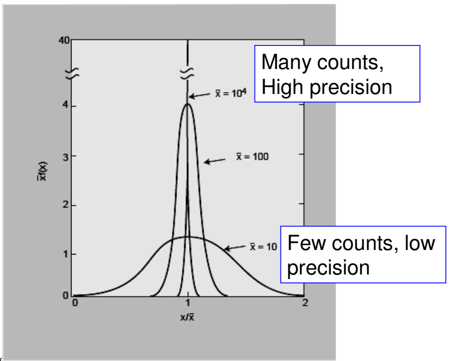
What is the Precision of Analysis?

- 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



Many counts, High precision

Few counts, low precision

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 %

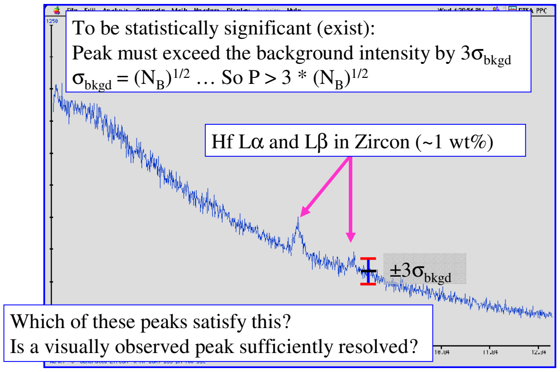
Actual Standard Deviation

- 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?



To be statistically significant (exist):
Peak must exceed the background intensity by $3\sigma_{bkgd}$
$\sigma_{bkgd} = (N_B)^{1/2}$ … So $P > 3 * (N_B)^{1/2}$

Hf Lα and Lβ in Zircon (~1 wt%)

Which of these peaks satisfy this?
Is a visually observed peak sufficiently resolved?

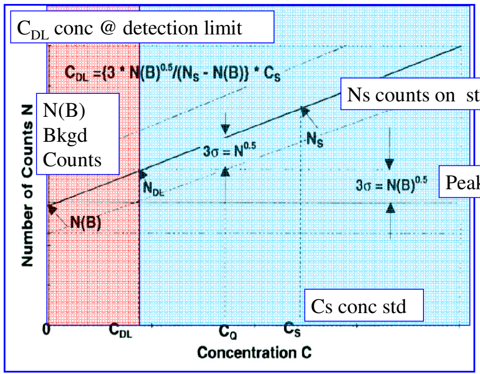
Detection Limit

- 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



C_{DL} conc @ detection limit

N(B) Bkgd Counts

Ns counts on std

Peak test

Cs conc std

Detection Limit EDS vs. WDS

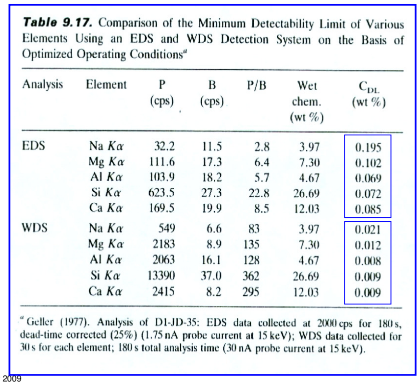


Table 9.17. Comparison of the Minimum Detectability Limit of Various Elements Using an EDS and WDS Detection System on the Basis of Optimized Operating Conditions[a]

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 DI-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).

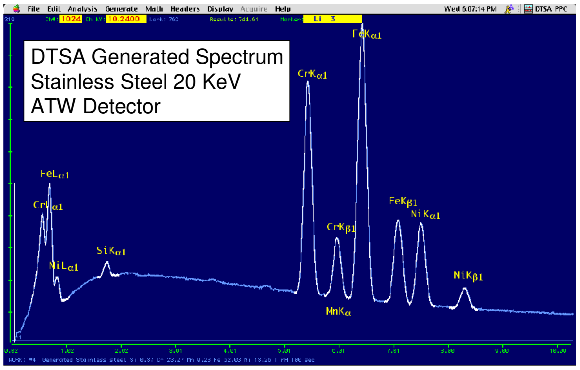
DTSA Stainless Steel Example

- Stainless steel sample is submitted for microanalysis.
- What is the expected uncertainty in the measurement of major vs. trace elements?
- Problem: Mn Kα peak of low intensity and strongly overlapped by Cr.
- DTSA allows simulation of counting experiments.
- Determine P/B, Error in Concentration, etc. using generated EDS spectra.

- Composition of Stainless Steel, in wt. %:

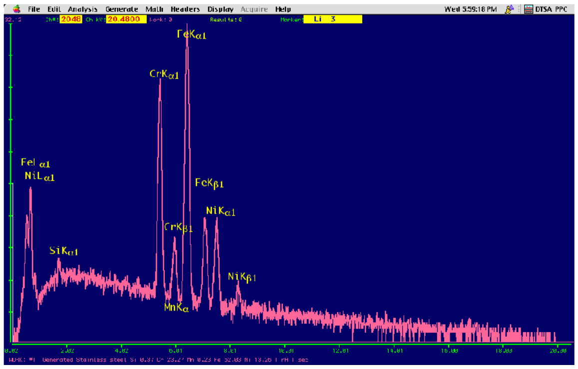
```
Si   0.37
Cr  23.72
Mn   0.23
Fe  62.03
Ni  13.26
---------
    99.61
```

Generated Spectrum

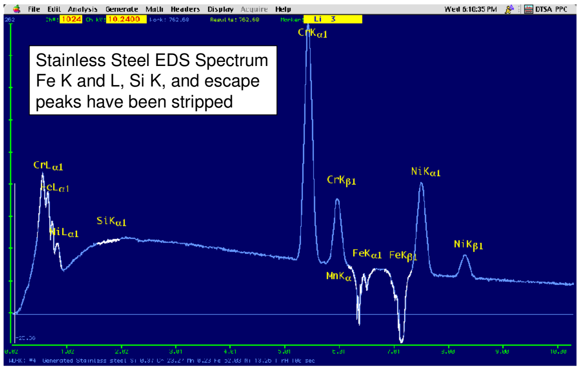


DTSA Generated Spectrum
Stainless Steel 20 KeV
ATW Detector

Generated Spectrum with Poisson Noise

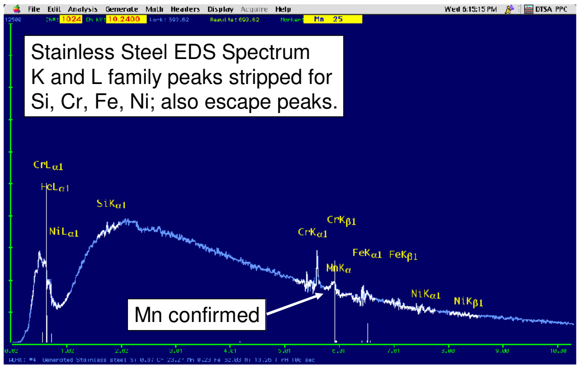


Simplex Peak Stripping -- Intermediate



Stainless Steel EDS Spectrum
Fe K and L, Si K, and escape peaks have been stripped

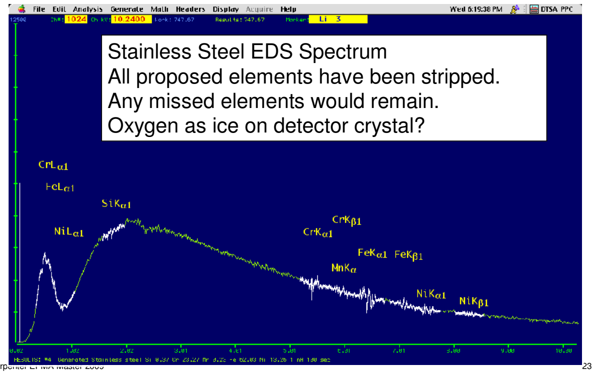
Simplex Strip – All Except Mn



Stainless Steel EDS Spectrum
K and L family peaks stripped for Si, Cr, Fe, Ni; also escape peaks.

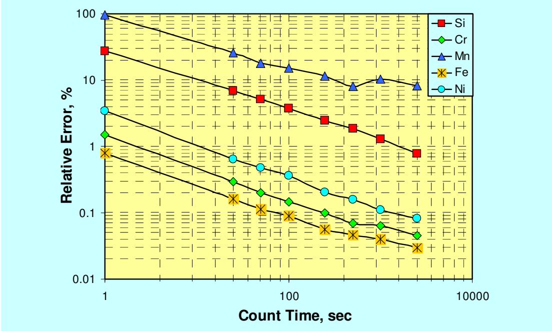
Mn confirmed

Simplex Stripping Complete



Stainless Steel EDS Spectrum
All proposed elements have been stripped.
Any missed elements would remain.
Oxygen as ice on detector crystal?

Stainless Steel
Time Required for Desired Precision



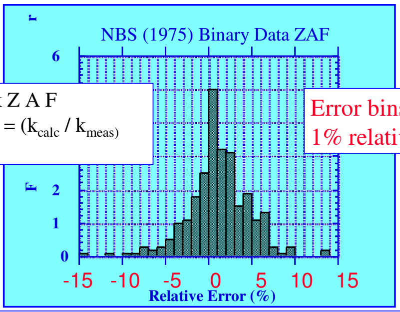
What is the Accuracy of Microanalysis?

- 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.

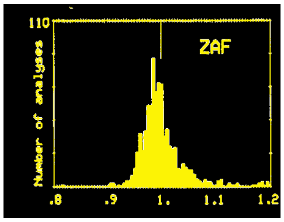
What Does This Error Distribution Mean?

Oddsmaker's Guide to Quantitative X-ray Microanalysis

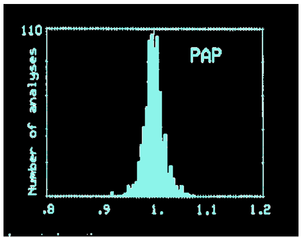
Relative Accuracy Needed	Analyst's Odds
± 1 %	2:1 against
± 2.5 %	1:1 (even money)
± 5 %	8:1 for
± 10 %	75:1 for

Conditions: flat, polished samples
EDS: Concentrations > 5% WDS: Concentrations > 1%
Source: Harvey "The Fixer" Yakowitz

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



Conventional ZAF

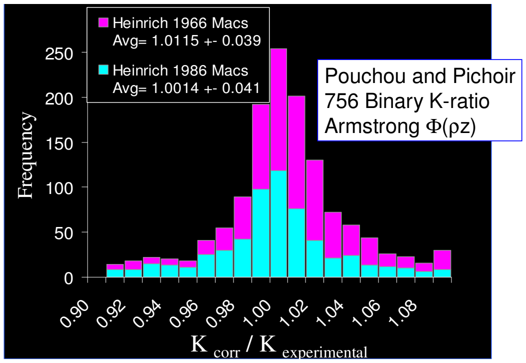


Pouchou & Pichoir Φ(ρz)

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)

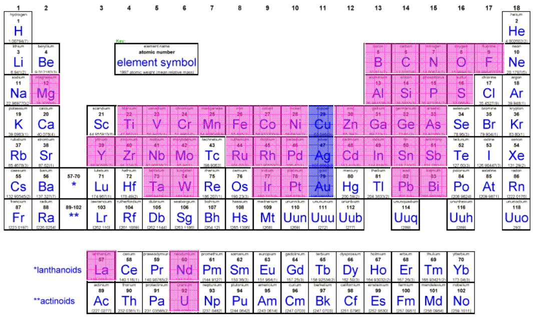
How to Evaluate Accuracy?

- Experimental measurements in binary systems yield K-ratios, which have been used to develop and adjust correction algorithms. How do we apply these data to multicomponent samples?
- Accuracy determined by analyzing secondary standards of known composition and performing error analysis, all relative to primary standards.
- What does the analysis of one secondary standard indicate about systematic errors as a function of composition? Cu-Au binary.
- Need standards that are similar in composition to sample under consideration. Typically do not exist.
- Standards may be readily synthesized for stoichiometric compounds or glasses, but systems exhibiting extensive solid solution are a problem.

Experimental Binary Data

WebElements: the periodic table on the world-wide web

http://www.webelements.com/



Quantitative Electron Probe Microanalysis by Energy Dispersive X-ray Spectrometry

NIST SRM 482 Au-Cu Microprobe Standards

Cu, wt%	Certified	Rel Err %	Au, wt%	Certified	Rel Err %
20.0	19.83	+0.9	80.0	80.15	-0.2
39.8	39.64	+0.4	60.2	60.36	-0.3
60.9	59.92	+1.6	39.1	40.10	-2.5
80.6	79.85	+0.9	19.4	20.12	-3.6

Beam energy 20 keV, Standards: Pure Au and Cu
Relative error = 100 * (measured – true) / true
(EDS data normalized to analytical total)

Alpha Factors

- Alpha factor analysis relates measured K-ratio to known C in binary systems (Ag-Au).
- Alpha factors obtained from known C are used to correct for analysis in ternary and higher systems.
- Can be used to identify erroneous analyses in data set, and precision.
- Samples can be used to derive alpha factors where ZAF and/or mac errors cannot be tolerated.
- Alpha factors can be defined for very specific binary compositional systems (HgTe – CdTe).
- Linear and polynomial formulations have been used.
- Originally used due to computer limitations.
- Can be used to correct pixel by pixel in digital images.

Alpha Factors in Binary Systems

$$\frac{C^A_{AB}}{K^A_{AB}} = \alpha^A_{AB} + \left(1 - \alpha^A_{AB}\right)C^A_{AB}$$

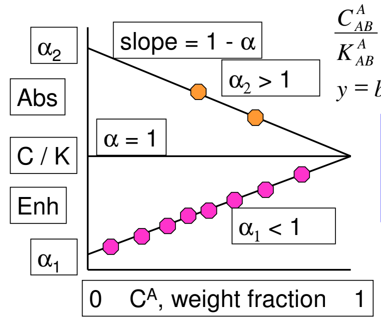
$$y = b + mx$$

C^A_{AB} Concentration of element A in AB binary relative to pure A, as weight fraction

K^A_{AB} Intensity of the x-ray of element A in AB binary relative to pure A

α^A_{AB} Alpha factor for x-ray element A in AB binary relative to pure A. Determined from b intercept or slope of data on C/K vs. C plot (if linear).

Extraction of α-factors from Experimental Measurements



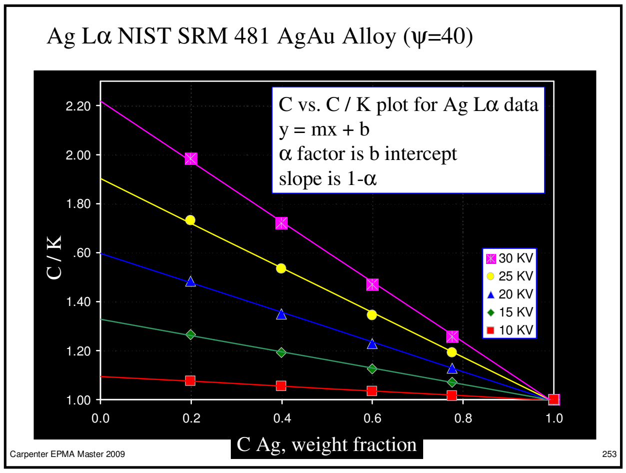
$$\frac{C^A_{AB}}{K^A_{AB}} = \alpha^A_{AB} + \left(1 - \alpha^A_{AB}\right)C^A_{AB}$$

$$y = b + mx$$

$$\boxed{\alpha^A_{AB} = \frac{\left[\dfrac{C^A_{AB}}{K^A_{AB}} - C^A_{AB}\right]}{1 - C^A_{AB}}}$$

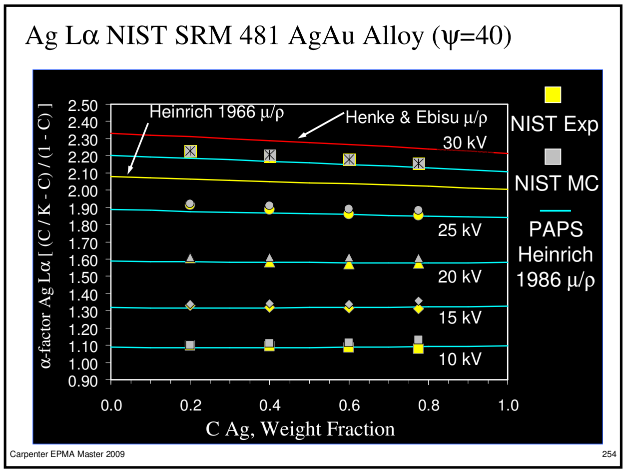
Compositional End Members in Binary Systems

- End members may be any components for the purposes of α-factor calculation. CaO, O_2, etc.
- Composition and k-ratio are expressed relative to the chosen end members.
- Improved accuracy and convenience of standards.
- Extension to ternary and higher systems via β–factors (i.e. [β = Σ Cα / Σ C] and C = β K).
- Pure elements Mg – Fe
- Pure oxides MgO – FeO
- Olivine binary Mg_2SiO_4 – Fe_2SiO_4 $(Mg,Fe)_1Si_{1/2}O_2$
- $Hg_{1-x}Cd_xTe$ HgTe – CdTe

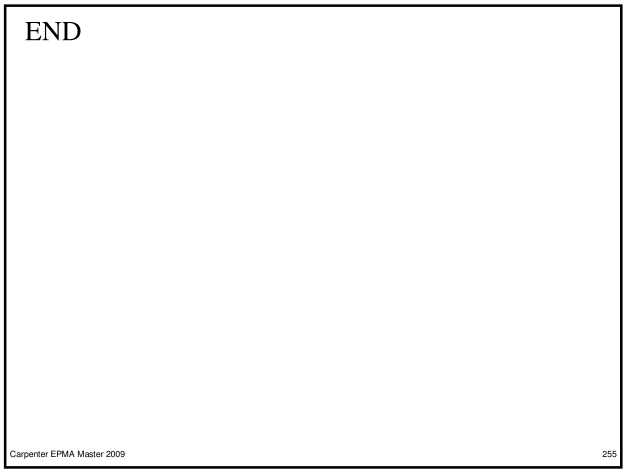


Ag Lα NIST SRM 481 AgAu Alloy (ψ=40)

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



Ag Lα NIST SRM 481 AgAu Alloy (ψ=40)



END