Advanced Quantitative Electron-Probe Microanalysis

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

paulc@levee.wustl.edu

Washington University, Saint Louis
Earth and Planetary Sciences JEOL JXA-8200

The Big Picture for EPMA
Calibration, Measurement, Quantitation, Report

- Instrumental issues for EPMA:
    Column-spectrometer alignment
    Detector linearity and stability (flow, sealed)
    WDS deadtime calibration
    Spectrometer resolution, reproducibility
    New developments: SDD EDS mapping and quantitative analysis
- EPMA Standards:
    Proper selection of standards (sample vs. standard)
    Internal consistency of stds in your lab vs. international environment
- Problem Systems:
    Peak overlaps, high-order WDS interferences
    Analytical problems, high absorption correction
    Correction algorithms and mass absorption coefficient data sets
- Solutions:
    Interlaboratory collaboration, education
    Multiple KV and multiple spectrometer analysis of core std set
    Payoff – proof of internal std comps and empirical macs

Procedures for Quantitative EPMA, WDS Emphasis
Part I – Instrument Calibration and Measurement

- Electron microprobe calibration issues
    WDS and EDS spectrometer alignment, column alignment, (stage too)
    WDS deadtime characterization
    WDS pulse processing, gain/bias, PHA, P-10
- EPMA Standards characterization and accuracy of analysis
    Internal consistency of standard compositions and measurements
- WDS wavelength scans and background measurement locations
    Full peak width, scans on stds and samples
    Note: Valley between $K\alpha$-$K\beta$, $L\alpha$-$L\beta$, $M\alpha$-$M\beta$ is not true background!
- Identification of peak and background interferences
- Analytical conditions, beam sensitive materials
- New instrument, 25 year old std block with oxidized surface, why ???
- Avoid blunders
    Reliance on software defaults, automated procedures and unattended ops
    Setup without WDS scans, ignorance of pulse processing
- Precision vs. accuracy issues

Calibration Issues for Electron-Probe Microanalysis

- Microprobe performance specifications are:
    - Driven by capabilities and address problem solving for customers
    - Capabilities are funded by purchases, user/vendor development
    - Realistic specifications for WDS vs. EDS systems
- Instrument calibration during installation and testing
    - Spectrometer alignment – to electron column and mutual agreement
    - Detector linearity with count rate and deadtime issues
    - Precision = reproducibility (mechanical, electronic)
    - Accuracy = correct K-ratio measured
- Instrument calibration – short vs. long term
    - Consistent performance with time
    - Accuracy in international interlaboratory environment
- Geological EPMA
    - CMAS silicate standards used for acceptance testing (CIT, WU)

Software Tools for the Microprobe Analyst

- Interaction with experienced scientists and technicians, and thinking.
- Calczaf – correction algorithms, mac sets, parameters
    - Generated a-factors for compact correction algorithm, testing
- DTSA II, Casino, GMRfilm, (Penelope) – scattering volume, spatial sampling, simulation of x-ray spectra
- Startwin (PFE) – bias/gain scans, pha characterization, spectrometer alignment, spectrometer reproducibility, beam stability, etc.
- Probe for EPMA – all quantitative EPMA
    - Sample setups and subsets of master element list, customized
    - Formula calculation, specified elements, etc.
    - Multiple standards comparison, standards evaluation
    - Beam sensitive materials analysis via TDI
    - Multiple spectrometer measurement of (trace) elements
    - QC with record-keeping of all peaking, PHA scans
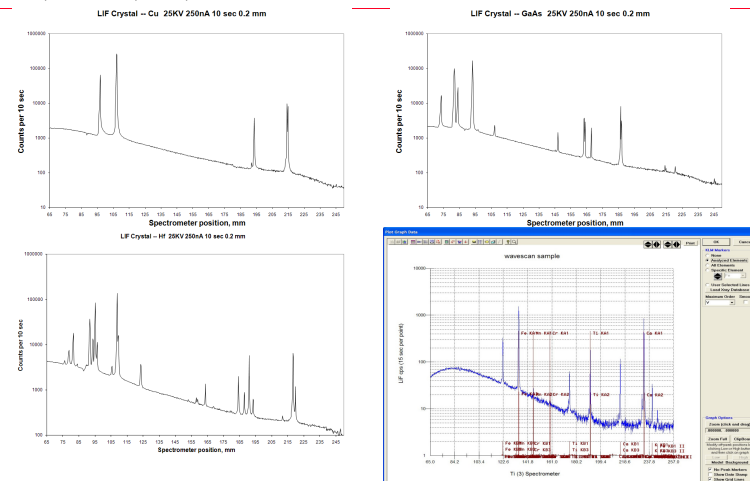- ProbeImage – x-ray and quantitative compositional mapping
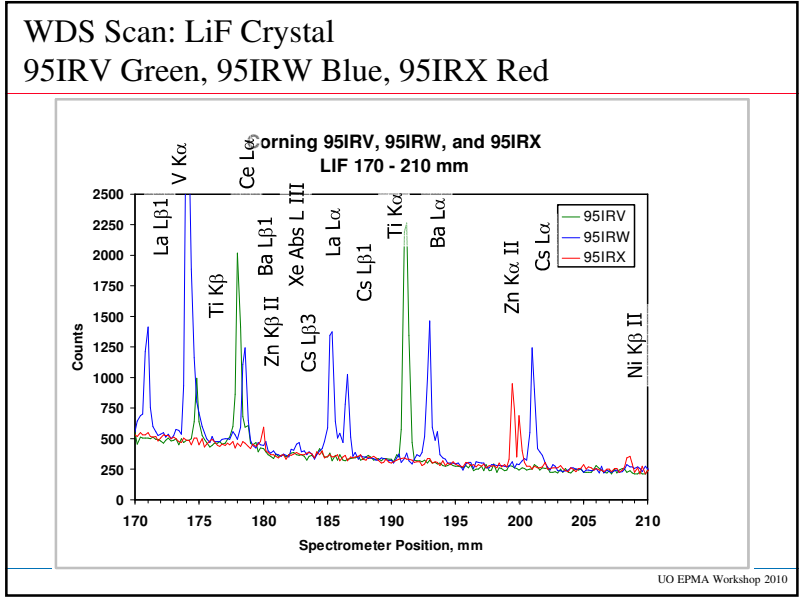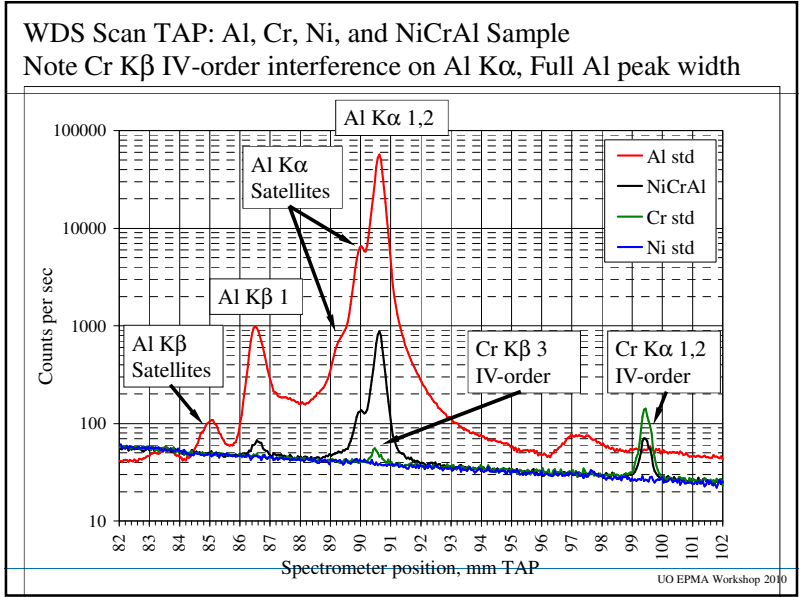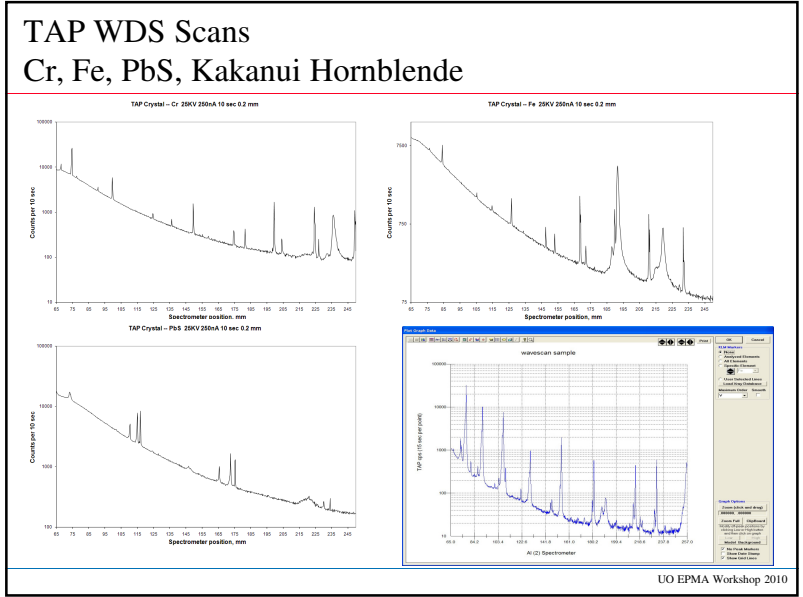
Wavelength Scans and Interferences
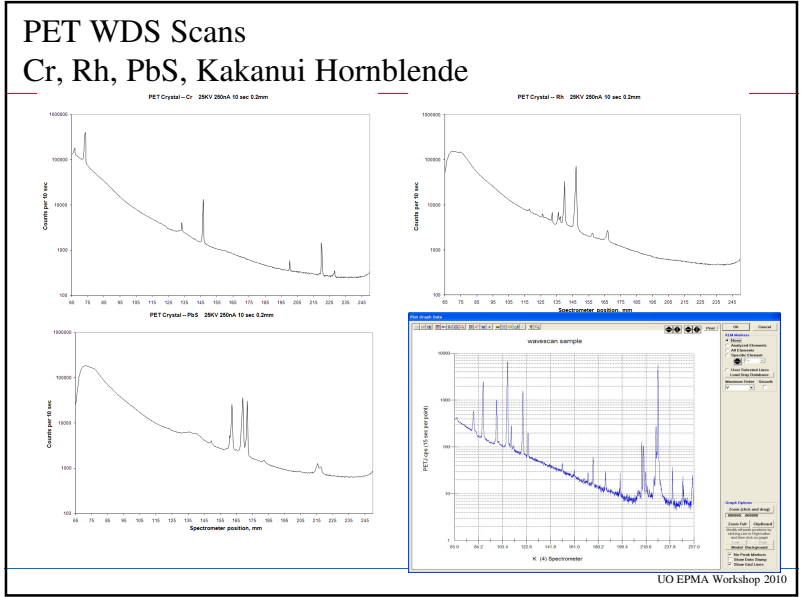
- High order interferences increase going to lower energy WDS crystals
    LiF—few, PET—more, TAP—many, LDE—up to II-order only
- Use wavescans on pure element, working standards, typical samples
    Collect scan using high kV to excite and see maximum overlaps
- Hard to visualize complex overlaps
    REE-rich phases, PGE minerals

LiF WDS Scans
Cu, GaAs, Hf, Kakanui Hornblende

PET WDS Scans
Cr, Rh, PbS, Kakanui Hornblende

UO EPMA Workshop 2010

TAP WDS Scans
Cr, Fe, PbS, Kakanui Hornblende

UO EPMA Workshop 2010

WDS Scan TAP: Al, Cr, Ni, and NiCrAl Sample
Note Cr Kβ IV-order interference on Al Kα, Full Al peak width

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WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red

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–3

WDS Scan: PET Crystal
95IRV Green, 95IRW Blue, 95 IRX Red

Corning 95IRV, 95IRW, and 95IRX
PET 70 - 90 mm
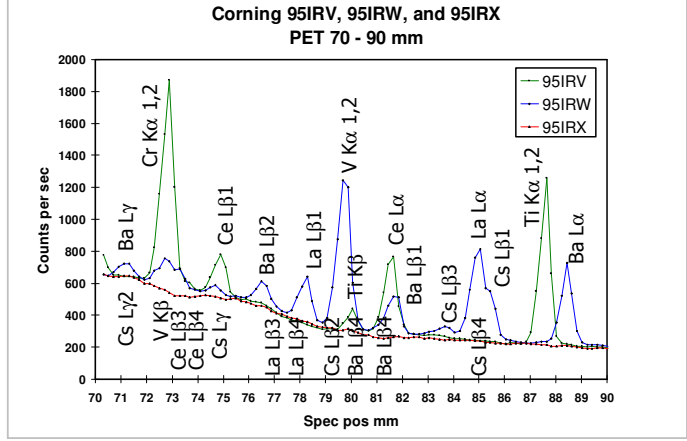
WDS Scan: PET Crystal
Th Mβ on U Mα, K Kα Peaks & Ovlp U Mβ

Corning 95IRV, 95IRW, and 95IRX
P-10 Flow counter -- PET 116-134 mm
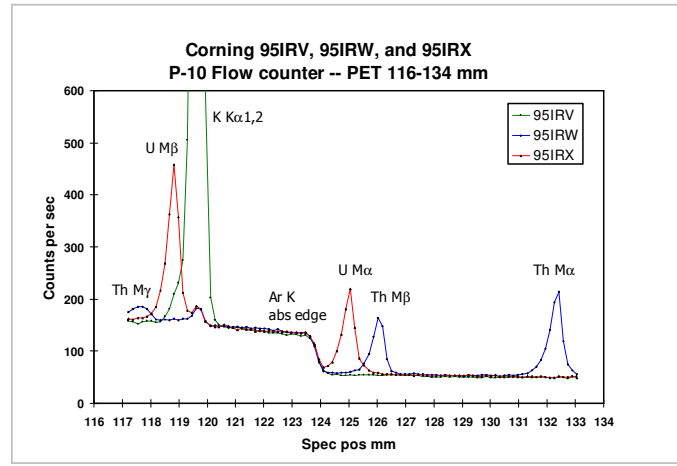
WDS Background Selection: Cd (red) Te (blue)

PET Crystal -- Cd and Te   25KV 250nA 10 sec 0.2mm
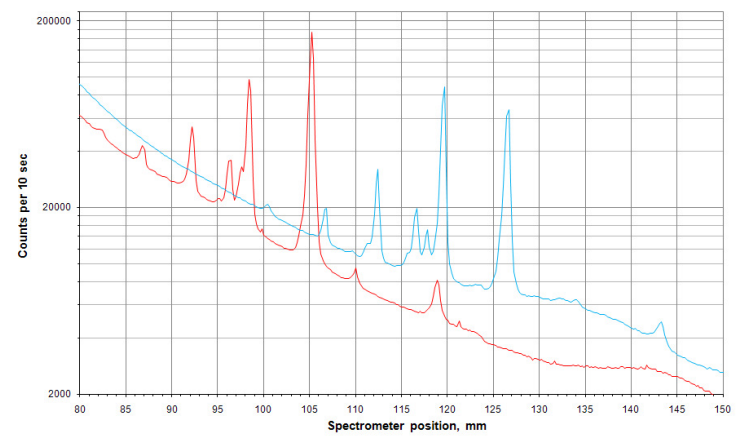
Pulse-Height Analysis
Wavelength-dispersive spectrometer

WDS PHA Measurement

- Low energy pulses must be discriminated from baseline noise. Need proper setting of noise threshold, baseline, and window settings of WDS pulse height analyzer.
- The pulse processing circuitry of WDS does not need to deal with pulse shaping like that of EDS, and is inherently faster.
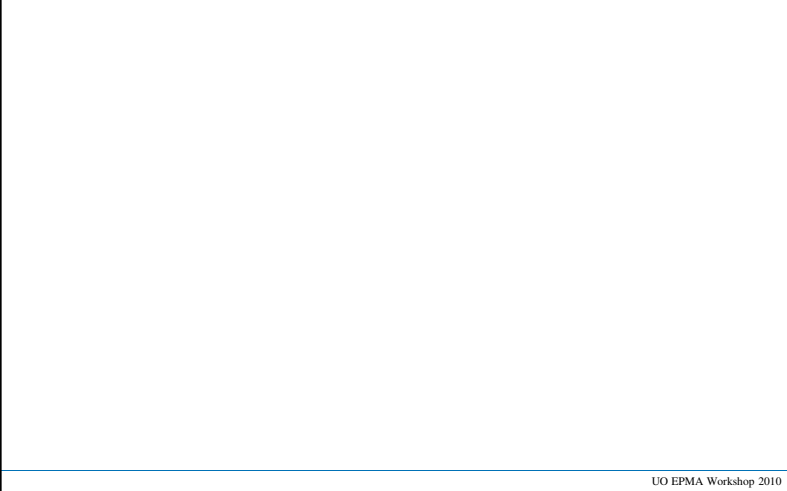- Pulse energy shift with varying count rate results in instability. At high count rates pulses are poorly discriminated from baseline noise. Use similar count rates on standard and sample.
- Avoid tight PHA window, use integral mode unless a PHA interference is observed.
- The P-10 detector gas flow rate must be stable or else gas amplification factor varies, and so does count rate.
- Temperature variation will affect gas amplification factor as well as thermal expansion of analyzer crystal.
- Low energy peaks need to be integrated due to peak centroid and peak shape/area factors. Use area-peak factor or perform integration.

Detector Bias Scan Si Kα
Vary Bias at PHA Narrow Window
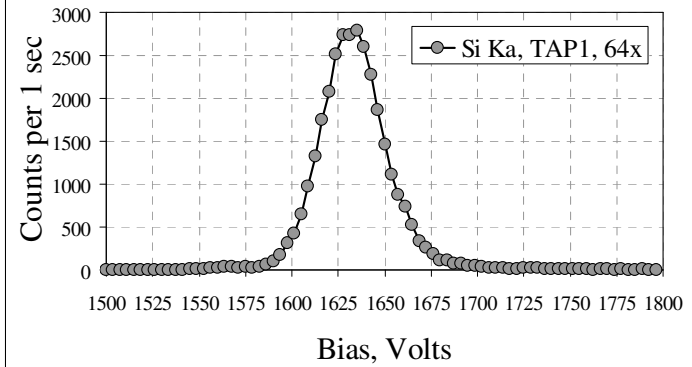
Detector bias scan using 3.9 volt baseline and 0.2 volt window on PHA.
Intended to minimize energy gain shift of PHA.
MSFC Spec 1, P-10 flow counter, TAP, 64x gain, Si Kα on SiO_2 metal @ 10k cps.

Detector PHA Scan Si Kα
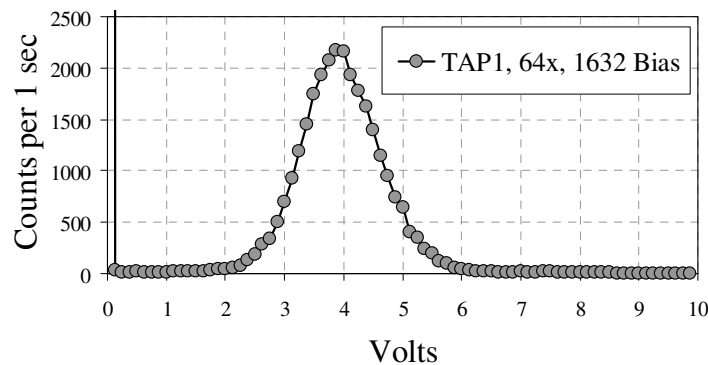
For Si Kα there is good separation between baseline and Si pulses.
Nominal baseline is 0.5 V with 9.5 V window (integral mode)
MSFC Spec 1, P-10 flow counter, TAP, 64x gain, Si Kα on SiO_2 @ 10k cps.

PHA Scans
JEOL P-10 flow detector, PET crystal

Ar escape peak observed for x-rays with E > 3.203 keV = E_c Ar K-edge
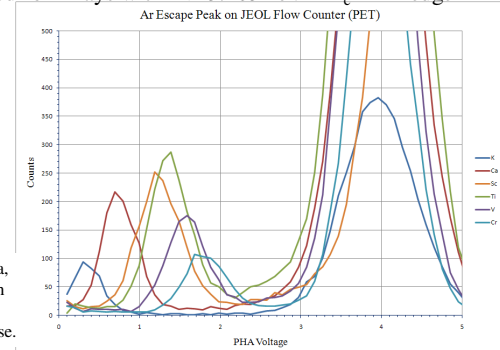
PHA scans for K-lines of K, Ca, Sc, Ti, V, and Cr, using 64x gain and detector bias necessary to produce a 4 volt PHA x-ray pulse.

Expanded scale illustrating Ar Kα escape peak position as a function of x-ray energy. As the x-ray energy increases, the Ar escape peak increases in voltage. The position of the escape peak must be treated consistently when setting the baseline of the PHA: either always include the escape peak or always exclude it, for both sample and standard measurement.

PHA Scans
JEOL sealed Xe detector, LiF crystal

Xe escape peak observed for x-rays with E > 5.452 keV = E_c Xe L-edge

PHA Scans at 64x Gain and Calibrated Bias on LiF:
K-lines of Ti, Cr, Fe, Ni, Cu and L-line of Au

PHA Scans at 64x Gain and Calibrated Bias on LiF:
K-lines of Ti, Cr, Fe, Cu and L-line of Au

PHA scans for K-lines of Ti, Cr, Fe, Ni, and Cu, and L-line of Au, using 64x gain and detector bias necessary to produce a 4 volt PHA x-ray pulse.

Expanded scale illustrating Xe Lα escape peak position as a function of x-ray energy. As the x-ray energy increases, the Xe escape peak increases in voltage. For Ti the escape peak is buried in the baseline noise, and for more energetic x-rays the positions are: Cr ~0.9V, Fe ~1.4V, Cu ~1.9V, and Au ~2.2V. The position of the escape peak must be treated consistently when setting the baseline of the PHA: either always include the escape peak or always exclude it, for both sample and standard measurement.

Calibration of PHA
Using Bias vs. ln(E) plots

- For JEOL microprobe want SCA pulse at 4 volts, Cameca at 2 volts
- Spectrometer at peak position
- Bias scan with 3.8v base, 0.2v window gives bias for 4 volt SCA
- Plot of bias vs ln of x-ray energy is linear
- Calibration performed for minimum element set which spans energy range of spectrometer for all analyzing crystals
- Detector should give same bias for Ti Kα on PET vs. LIF, others
- Calibration confirms systematic behavior of x-ray counter
- As P-10 tank empties and Ar/CH$_4$ changes, requires recalibration
- Use y = mx + b fit to bias data to provide quick calibration
- Similar plot for escape peak as function of x-ray energy

PHA Bias Plot for LIF/PET Data
Si, Ti, Ni Bias data at 8, 16, 32, 64, and 128x Gain

WU 8200 Detector Bias Spectrometer 3
Settings for 4 Volt Pulse

y = -87.037x + 1955.1

Ti, PET and LIF

Ni, LIF

y = -94.949x + 1889

y = -98.905x + 1808

y = -108.8x + 1748.9

Si, PET

y = mx + b
y = bias, x=ln(E)

Bias, Volts

Ln Energy

- LIF 8x
- LIF 16x
- LIF 32x
- LIF 64x
- LIF 128x
- PET 32x
- PET 64x
- PET 128x
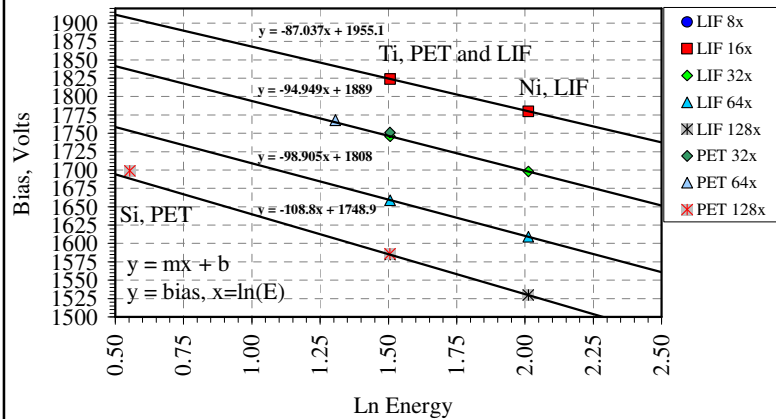
Gain Shift Due to Count Rate
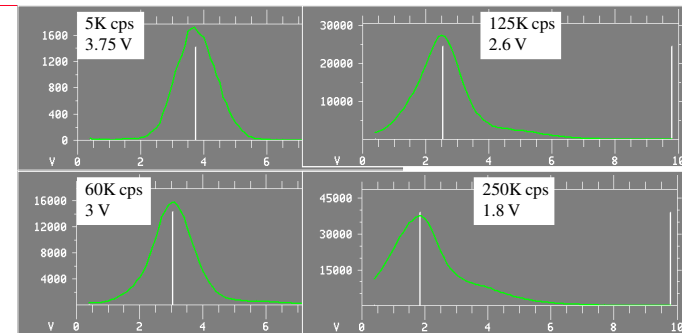
Gain shift due to count rate, detector bias arbitrarily set to 1700 volts.
Observed shift is ~ 0.008 volts per 1 K cps (1.95 volt shift over 245 K cps range).
At ~125k cps baseline noise discrimination deteriorates.
Older PCS electronics exhibit complete shift into baseline noise.
MSFC Spec 1, P-10 flow counter, TAP, 32x gain, Si Kα on Si metal.

PHA Scan Ti Lα 20K CPS

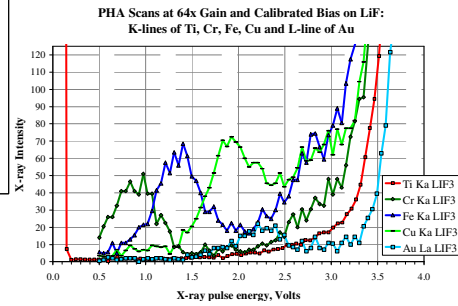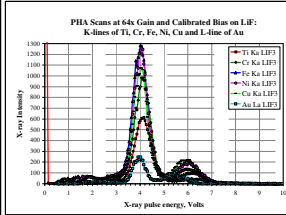Light element / low energy x-rays are poorly resolved from baseline noise.
Gain shifts with count rate – PHA peak shifts toward baseline with increasing count rate. Use integral mode unless PHA energy discrimination required – counts extend to upper limit of PHA scan.
MSFC Spec 1 with P-10 flow counter, LDE2, 128x gain, Ti Lα on Ti metal @ 20k cps.

Carbon Kα PHA Scans Graphite, Fe3C

Scaled PHA Scans C Kα LDE2 10 KeV

Legend:
— Graphite 100 nA > 65 kcps
— Graphite 25 nA ~ 23 kcps
— Fe3C 100 nA ~ 2 kcps

Scaled PHA scans demonstrate consistent PHA behavior
No baseline – noise is present
LDE2, 128x gain, 1750V

Baseline 0.5V, 9.5V Window

Relative Intensity (y-axis), Baseline, Volts (x-axis)
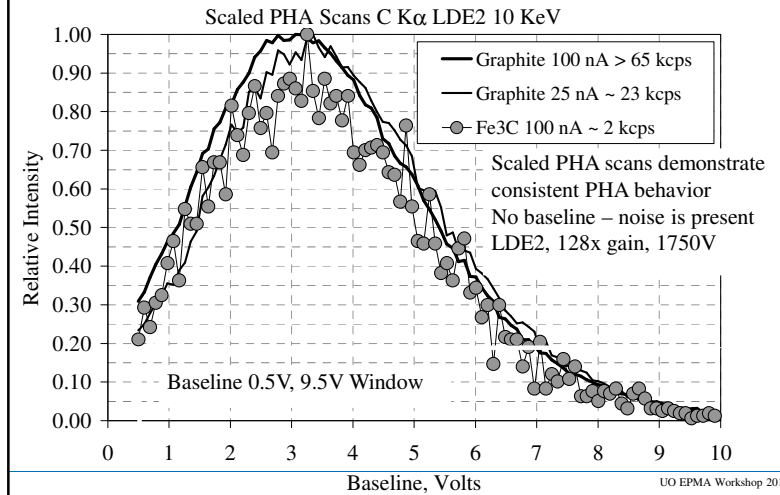
Deadtime Measurement on the Wavelength-Dispersive Spectrometer

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WDS Deadtime Issues in EPMA

- Deadtime – time interval during which counting electronics are unable to process subsequent incoming pulses
- Deadtime error is non-negligible, systematic, affects all measurements
- General problem:
- Counting behavior of WDS systems is undocumented and poorly known
- End-users make measurements with assumed WDS deadtime behavior
- User knowledge of deadtime issues needs improvement
- Specific problem areas:
    - No software to conveniently evaluate deadtime on turnkey systems
    - No agreed method for setting bias, gain, and sca on systems
    - SCA pulse shift behavior with count rate undocumented
    - Deadtime dependence on X-ray energy undocumented and unknown
    - Low vs. high count rate behavior and deadtimes inconsistent

Deadtime Behavior:
Extending vs. Nonextending

Nonextending: $N = N_m (1 - N\tau)$, $N_{max} = 1/\tau$
Extending: $N = N_m e^{-Nm\tau}$, $N_{max} = 1/e\tau$

Legend:
— Nonextending
-- Extending
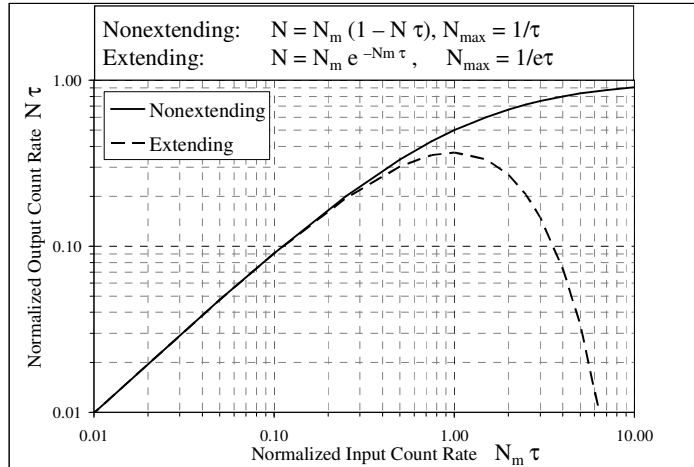
Y-axis: Normalized Output Count Rate $N\tau$ (1.00, 0.10, 0.01)
X-axis: Normalized Input Count Rate $N_m\tau$ (0.01, 0.10, 1.00, 10.00)

Deadtime Losses
Input – Output Curves for μsec Deadtime Constants

WDS Deadtime Losses

Legend:
— 1.00E-06
-- 2.00E-06
···· 4.00E-06
—· 5.00E-06
—·· 6.00E-06
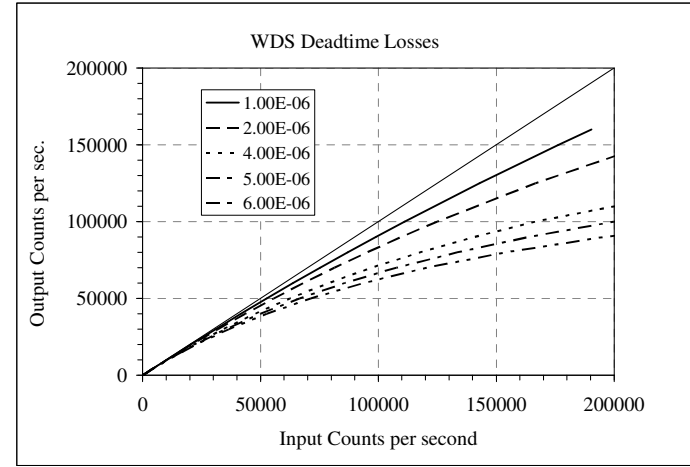
Y-axis: Output Counts per sec. (0, 50000, 100000, 150000, 200000)
X-axis: Input Counts per second (0, 50000, 100000, 150000, 200000)

Percentage Deadtime Losses
Percent Level Corrections Apply to All Measurements

At 1 μsec, 1% correction at 10Kcps, 5% at 50Kcps
At 2 μsec, 2% correction at 10Kcps, 10% at 50Kcps

Legend:
—·· 6.00E-06
—· 5.00E-06
···· 4.00E-06
-- 2.00E-06
— 1.00E-06

~1.25 μsec
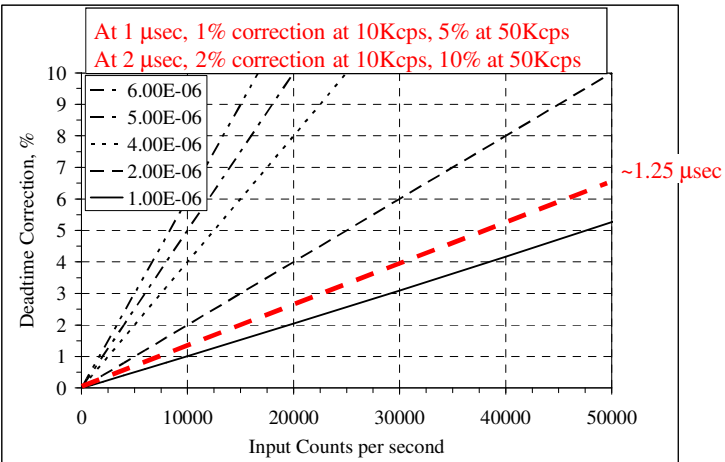
Y-axis: Deadtime Correction, % (0–10)
X-axis: Input Counts per second (0, 10000, 20000, 30000, 40000, 50000)

Deadtime Relations
Calculation of Deadtime Constant

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

• N = true count rate, N_m = measured count rate with deadtime losses ($N_m < N$), and τ is the deadtime constant, which ranges from 1 to several μsec for WDS counting systems. It is necessary to know N_m and N to calculate τ. We assume the proportionality of N to the probe current i is constant. This may not be true at low count rates.

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

• N_m / i = measured count rate in counts per second per nA, and c is the constant N / i
Form: y = mx + b
(N_m / i) is y, x is N_m, y-intercept b is constant c (= N / i).

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

• Equivalent to $\tau = (1 - y/b)/x$
Measure x-ray intensity at increasing probe current
Use count rate N_m and N_m / i to evaluate the deadtime constant τ over a range of intensity values

—8

Deadtime Evaluation Plot
N_m vs. N_m / i to determine LS Fit to τ

Deadtime Si Kα TAP1 Caltech JEOL 733

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

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

Verification of Probe Current vs. Absorbed Current Linearity and/or Detection of Sample Charging
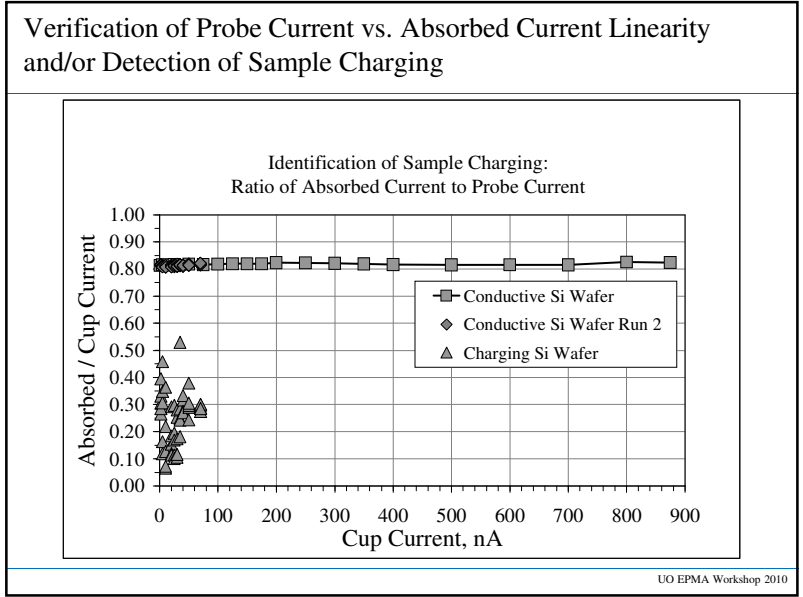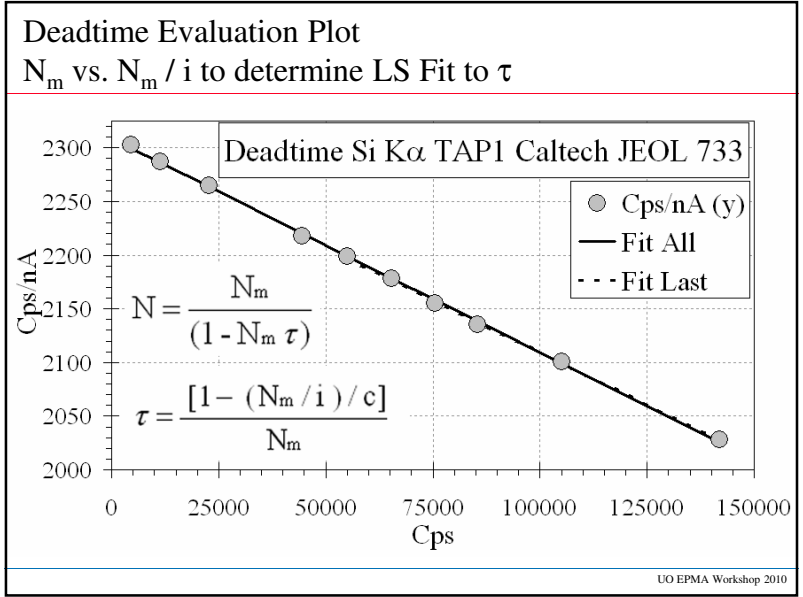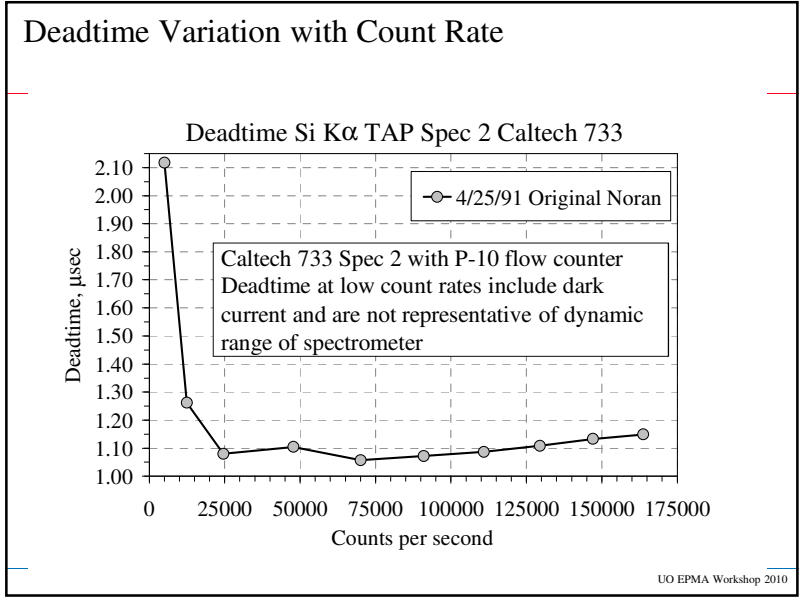

Identification of Sample Charging:
Ratio of Absorbed Current to Probe Current

Deadtime Calculation from Excel Spreadsheet

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

Excel Sheet: X is N_m and Y is N_m/i. Deadtime evaluated from each intensity (DT) and from least squares fit to data (Fit) using Excel *linest* function. All data and high intensity only data are compared with average values (Mean deadtime) and standard deviation. Ratio of absorbed/probe current checks conductivity. If linear all data agree.

Deadtime Variation with Count Rate

Deadtime Si Kα TAP Spec 2 Caltech 733

Caltech 733 Spec 2 with P-10 flow counter Deadtime at low count rates include dark current and are not representative of dynamic range of spectrometer

–9

Deadtime Variation With Time and P-10 Gas Chemistry
Comparison of Original and New Tracor PCS Electronics

Deadtime Si Kα TAP2 Caltech JEOL 733

Date	Deadtime	Sigma
04/25/91	1.12	0.06
06/14/91	1.17	0.05
06/17/91	1.21	0.04
11/05/91	1.24	0.06
11/11/91	0.98	0.02
12/03/91	1.02	0.04
12/04/91	0.97	0.04

Legend:
- 4/25/91 Old
- 11/5/91 Old
- 11/11/91 New
- 12/4/91 New

X-axis: Counts per second
Y-axis: Deadtime, μsec
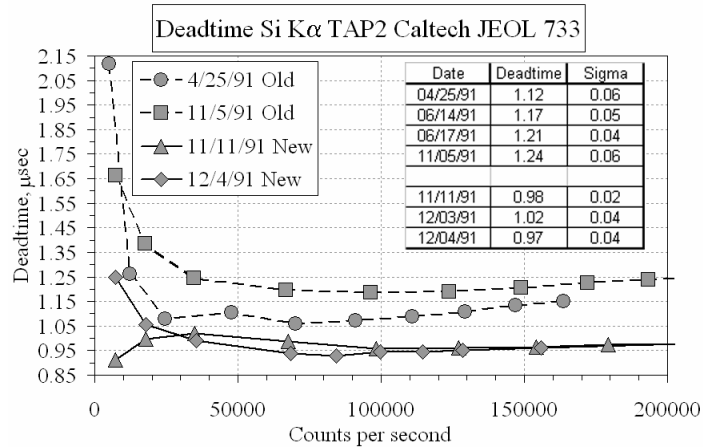
## Establishing Calibration of an Electron Microprobe

- Wavelength spectrometer aligned vertically (baseplate) to coincide with optical microscope focal point in z-space
- Diffracting crystal aligned to be on Roland circle
- All WDS should focus on same z-axis and coincident xy area ~ 50 um in diameter
- Characteristics of correct alignment
  - All WDS & EDS have identical X-ray takeoff angle
  - Maximum X-ray intensity at z focus position, but also require:
  - Measure identical k-ratio within counting statistics
- Simultaneous k-ratio measurement is ultimate test of alignment
- Initial CMAS standard set used on Caltech MAC and JEOL JXA-733
- Expanded CMASTF standard set used for Wash U JXA-8200

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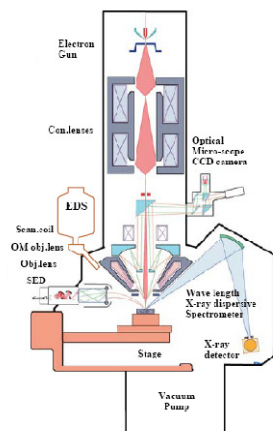
Baseplate: Place Rowland circle at Z focus
Crystal: Align all crystals on Rowland circle
Spectrometer design keeps detector on RC
Note: Different K-ratio = misalignment
Multiple spectrometer comparison required to demonstrate all WDS and EDS are mutually aligned

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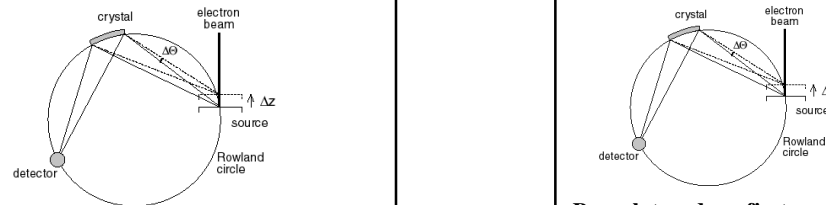
WDS Spectrometer Alignment--Baseplate and Crystal
(JEOL, vertical spectrometers)

Crystal alignment PET Si Kα

Baseplate alignment PET Cr Kα
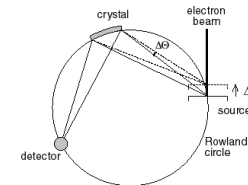
Baseplate – done first
Place Rowland circle at Z focus
Use PET Cr Kα, other low peak
Crystal – done for each crystal
Align all crystals on Rowland circle
Use PET Si Kα, others

Here baseplate is set using Cr
Crystal Spec 5 PET set, 3&4 need further adjustment
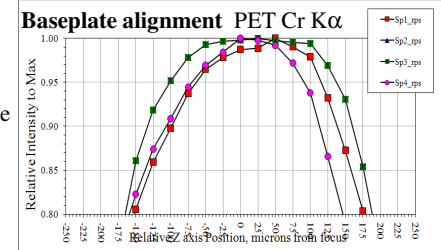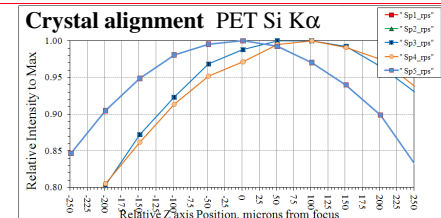
CMASTF Silicate Standards
Geological materials are multicomponent

- End-member stoichiometric silicate and oxide mineral standards
- Primary standards:
  MgO, Al_2O_3, SiO_2, $CaSiO_3$ (CaO 48.27, SiO₂ 51.73), 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 Standard Inventory: Natural & Synthetic
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

Armstrong PRZ Heinrich 1986

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

Armstrong $\Phi(\rho z)$ Heinrich 1986 macs
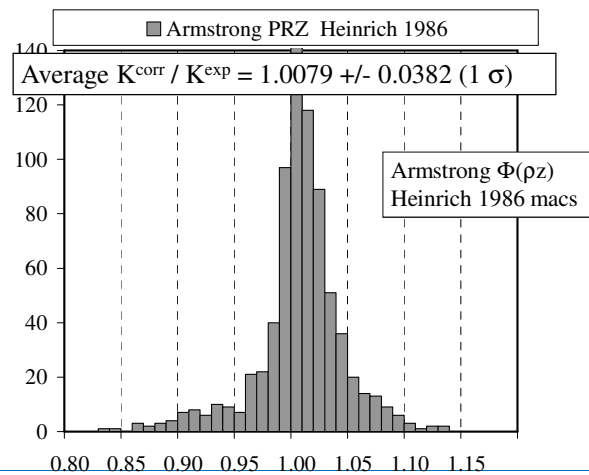
Ag Lα NIST SRM 481 AgAu Alloy (ψ=40)

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

- 30 KV
- 25 KV
- 20 KV
- 15 KV
- 10 KV

C / K

C Ag, weight fraction

–11
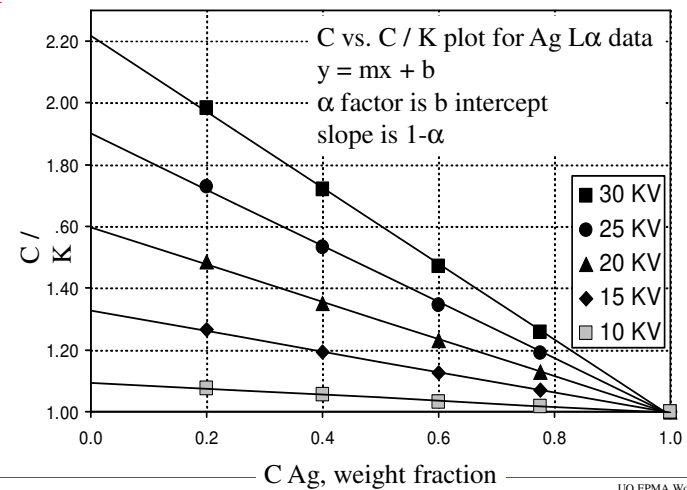
Accuracy Study for EPMA
Comparison of Measured to Calculated K-ratio

- $K_{measured}$ 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

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

$$C = K * ZAF$$

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

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

Historical CMAS Data
Caltech MAC Probe, Circa 1980's

Shaw Data Set: Caltech MAC Probe (38.5 deg, 15 kV)
Armstrong φ(ρz), FFAST macs

Legend: Mg, Al, Si, Ca
X-axis: Weight % Oxide
Y-axis: Measured Wt% / Accepted Wt%
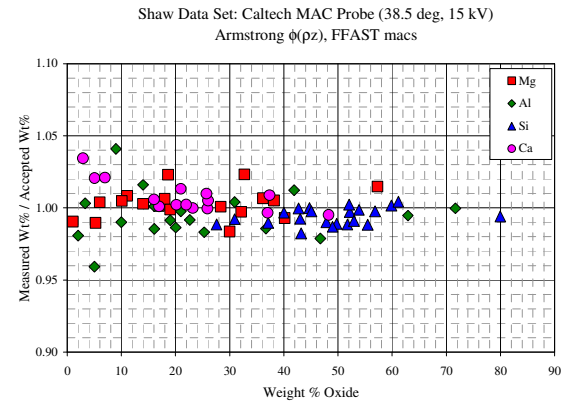
Caltech JEOL 733 1990's
Spectrometer 124 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP:1Mg 2Al 4Si
Armstrong φ(ρz), FFAST macs, 15 kV

Legend: Mg, Al, Si, Ca
X-axis: Weight % Element
Y-axis: Measured Wt% / Accepted Wt%
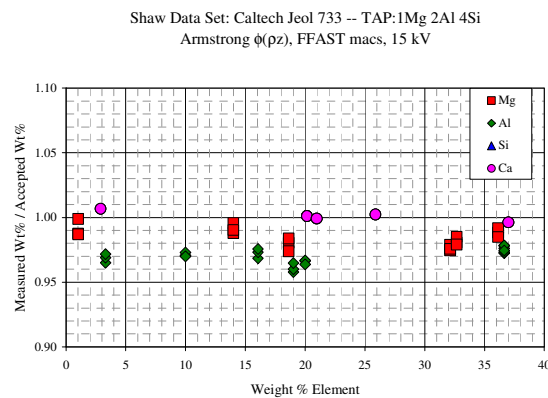
Caltech JEOL 733 1990's
Spectrometer 1 TAP for Mg Al Si (Ca PET)
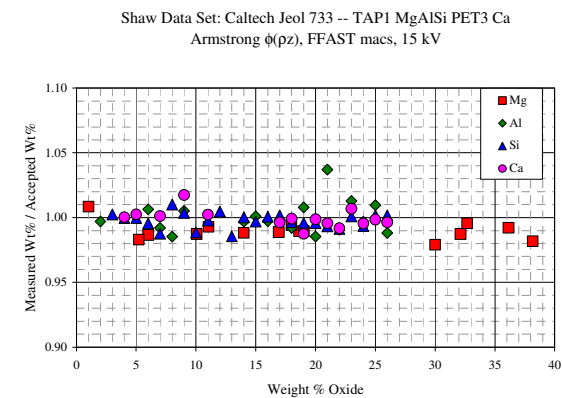
Shaw Data Set: Caltech Jeol 733 -- TAP1 MgAlSi PET3 Ca
Armstrong φ(ρz), FFAST macs, 15 kV

Legend: Mg, Al, Si, Ca
X-axis: Weight % Oxide
Y-axis: Measured Wt% / Accepted Wt%

WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed
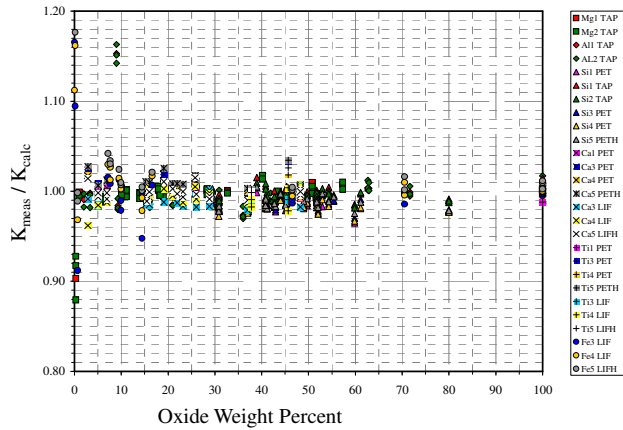
Average K_{meas} / K_{calc} for CMASTF Standards
Washington University JEOL 8200

WDS	Spec 1	Spec 2	Spec 3	Spec 4	Spec 5
Mg TAP	0.9997	0.9971			
Al TAP	0.9950	0.9946			
Si TAP	0.9981	0.9955			
Si PET	0.9855		0.9865	0.9837	0.9880
Ca PET	1.0013		1.0064	1.0035	1.0101
Ca LIF			0.9908	0.9948	0.9989
Ti PET	1.0000		1.0059	1.0044	1.0115
Ti LIF			0.9919	0.9949	1.0084
Fe LIF			0.9962	1.0051	1.0131

Accuracy, 1σ % Error in K_{meas} / K_{calc} CMASTF
Standards Washington University JEOL 8200

WDS	Spec 1	Spec 2	Spec 3	Spec 4	Spec 5
Mg TAP	0.65	1.30			
Al TAP	1.06	1.22			
Si TAP	0.74	0.64			
Si PET	0.71		0.71	0.75	0.70
Ca PET	0.79		0.73	0.70	0.74
Ca LIF			0.74	0.92	0.69
Ti PET	2.27		1.44	0.98	1.54
Ti LIF			0.61	1.15	1.14
Fe LIF			1.75	1.27	1.26

WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed Expanded Scale

–13
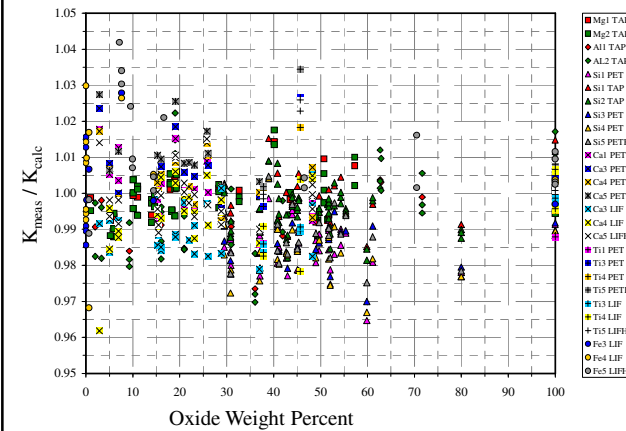
Washington University JEOL JXA-8200
SDD Quantitative Analysis Data

- SDD great for mapping, what about quantitative analysis?
- SDD EDS data acquired at 120s, 60s, and 3s acquisitions at T3
- Standards used: MgO, Al_2O_3, SiO_2, $CaSiO_3$ (CaO 48.27, SiO_2 51.73), TiO_2, and Fe_2O_3
- Linear least-squares peak deconvolution (JEOL software)
- Extracted raw K-ratios processed using Armstrong $\Phi(\rho z)$ and FFAST macs for comparison with WDS data

CMASTF Standard Analyses
WU8200 SDD LLSQ 120 sec. Acquisition T3

Measured K Relative to Calculated K
WU8200 SDD 120 sec Acquisition
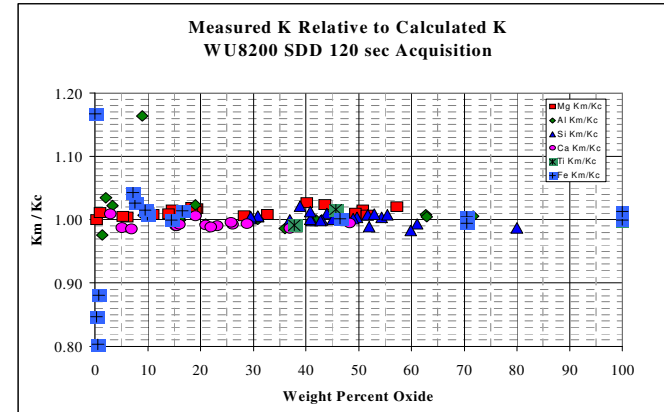
CMASTF Standard Analyses
WU8200 SDD LLSQ 60 sec. Acquisition T3

Measured K Relative to Calculated K
WU8200 SDD 60 sec Acquisition
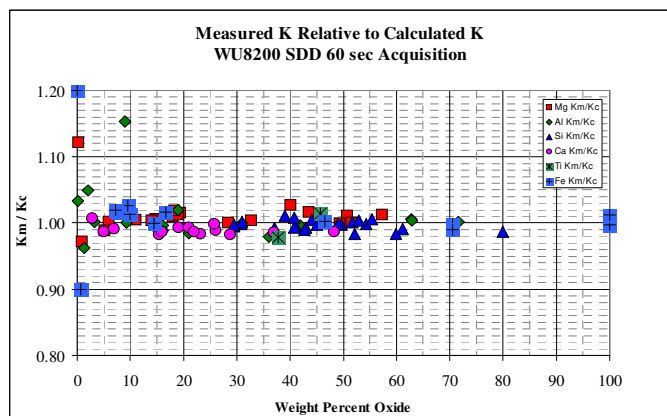
CMASTF Standard Analyses
WU8200 SDD LLSQ 3 sec. Acquisition T3

Measured K Relative to Calculated K
WU8200 SDD 3 sec Acquisition
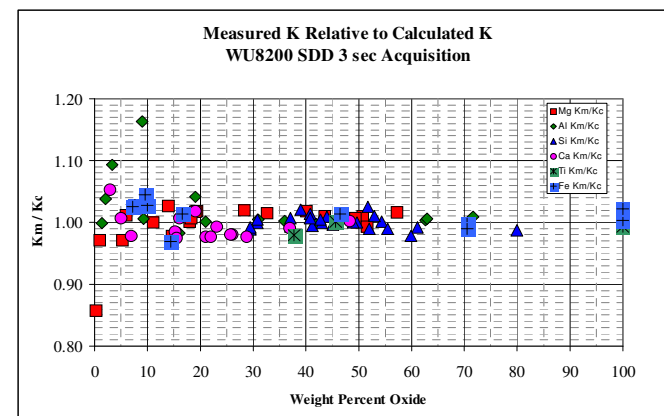
Average Kmeas / Kcalc for CMASTF Standards
WU8200 SDD Data @ 120, 60, 3 sec acquisition T3

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

Procedures for Quantitative EPMA, WDS Emphasis
Part II – Quantitation, X-ray Physics

- Evaluate and understand analysis for chosen system
  ZAF factors for standards and samples
  Identification of high x-ray absorption (kV), dissimilar std vs. sample
  Attention to mass absorption coefficients
- Classify relative to representative systems, i.e.,
  Absorption – Al in Mg silicates, light elements, abs edge proximity
  Fluorescence, characteristic – FeNi system, secondary fluorescence
    Continuum – hard line generated in light matrix, Ge Ka in GeO2
  Atomic number – dissimilar Z, CuAu, SiIr, etc.

EPMA of San Carlos Olivine
Correction Method and macs @ 20 KV, 40 TOA

Oxide	Wet Chem	PDR Ox / H66	PAPF-1 Ox / H86	Arm-1 Ox / H86	PAPF-2 Ol / H86	Arm-2 Ol / H86	PAPF-3 Ol / FF	Arm-3 Ol / FF
MgO	49.42	50.10	50.04	49.82	49.44	49.44	48.98	49.00
SiO_2	40.81	40.74	40.66	40.07	40.56	40.58	40.34	40.69
FeO*	9.55	10.13	10.08	9.89	9.89	9.89	9.89	9.74
Total	100.29	101.66	101.47	100.47	100.60	100.60	99.90	100.12
ΣM^{2+}	2.005	2.025	2.025	2.034	2.016	2.016	2.014	2.003
Si	0.997	0.986	0.986	0.982	0.991	0.991	0.992	0.997
Mg/(Mg+Fe)	0.902	0.898	0.899	0.900	0.899	0.901	0.898	0.900

PDR: Philibert-Duncumb-Reed ZAF, oxide standards, Heinrich 1966 macs
PAPF-1 and Arm-1: Φ(ρz) algorithms, oxide standards, Heinrich 1986 macs
PAPF-2 and Arm-2: synthetic olivine standards, Heinrich 1986 macs
PAPF-3 and Arm-3: synthetic olivine standards, FFAST macs
Same k-ratios, n=4, CaO 0.09, Cr_2O_3 0.06, MnO 0.14, NiO 0.37 (wt %)
Olivine Formula: $M^{2+}_2SiO_4$

Mass Absorption Coefficients
Example TaSi alloy

–15

Mass Absorption Coefficients for Si Kα
By Absorber Z, All MAC Data Sets Compared

MAC for Si Ka by Z Absorber Elements

Silicon Kα MAC at L-edge of Absorber

MAC for Si Ka by Z Absorber Elements
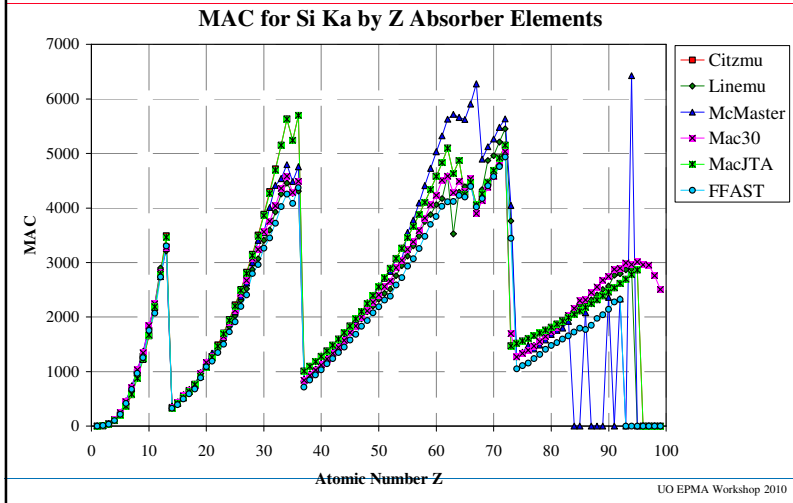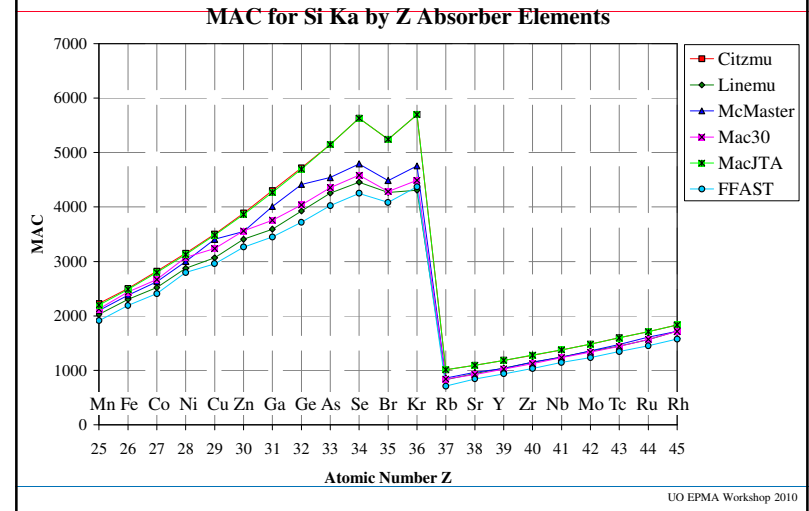
Silicon Kα MAC at M-edge of Absorber
Si Ka close to the Ta M5 absorption edge

MAC for Si Ka by Z Absorber Elements

Si Kα line energy 1.73984 keV, M5 edges: Hf 1.662, Ta 1.735, W 1.810 keV

Comparison of Si Kα MACS
Relative percent σ

MAC for Si Ka by Z Absorber Elements

UO EPMA Workshop 2010

–16

Elevated and Uncertain MAC Values for K, L, M Lines: Proximity to Absorption Edge of Matrix Element

K-Lines and absorber for K, L, M edge

L-Lines and absorber for K, L, M edge

M-Lines and absorber for K, L, M edge

Error Analysis Ta Lα in TaSi$_2$
All algorithms and MAC sets (PAPF-FFAST = 1.0)

Error Histogram Ta Lα in TaSi2
Relative to PAP-FFAST Nominal K-ratios

Φ(ρz) Models

PAPF-FFAST = 1.0

Philibert-Duncumb-Reed ZAF

Frequency

Kcorr / Kexp

Error Analysis Si Kα in TaSi$_2$
All algorithms and MAC sets (PAPF-FFAST=1.0)

Dramatic demonstration of choice of MAC data set:
Variation of Φ(ρz) models and 4 mac data sets

Φ(ρz) Models

Φ(ρz) Models

McMaster

Linemu

PAPF-FFAST = 1.0

Philibert-Duncumb-Reed ZAF

Mac30

cilzmu

Philibert-Duncumb-Reed ZAF

Frequency

Kexp / Kcorr

Calculated Compositions of TaSi2
Relative to PAP—FFAST Nominal K-ratios

PAPF with MAC	Wt% Si	Wt% Ta	Total
CM	14.74	73.74	88.48
M30	15.64	74.02	89.66
(FFAST)	23.69	76.31	100
LM	24.87	76.52	101.39
MM	25.96	76.85	102.81

EPMA Standards

The Good, the Bad and the Ugly

- **_The Good, the Bad and the Ugly_**
  (Italian: _Il buono, il brutto, il cattivo_)
  1966 Italian spaghetti western directed by Sergio Leone
  Clint Eastwood as Blondie, the Good (confident bounty hunter)
  Lee Van Cleef as Angel Eyes, the Bad (ruthless sociopathic killer)
  Eli Wallach as Tuco, the Ugly (oafish bandit and liar)
- Third film in the Dollars trilogy
  A Fistful of Dollars (1964), For a Few Dollars More (1965)
- Plot: three gunslingers compete to find a fortune in buried
  Confederate gold amid the violent chaos of gunfights, hangings,
  Civil War battles, and prison camps
- There are (similar?) challenges of using microanalysis standards that are
  Good, Bad, and just plain Ugly

EPMA Standards: Desirable Attributes

- EPMA standards should be well characterized
  Bulk and microchemical analysis of distribution material
  XRF, ICP-MS, INAA, Classical wet chemistry, etc.
  Supplemental to EPMA analysis
  Traceable
- Homogeneous on micron scale
  Minimal variation intra-grain and grain-to-grain
  Quantitative representation of homogeneity
- Stable under electron beam bombardment and non-reactive with air
- Similar in composition to samples being analyzed
- Amenable to mounting and polishing
- Relatively large grains for use (several hundred microns minimum)
- Widely available and in sufficient quantity to international community
- Inexpensive for purchase

EPMA Standards: Emphasis on Mineral and Glass Multielement Standards

- Pure element metal standards
  Minimal uncertainty in composition, typically assumed pure
  Useful for wide range of samples, EDS calibration
  Caution: Segregations at grain boundaries, oxidation
- End-member oxides, compounds, and minerals
  Assumed composition
  Al_2SiO_5, Mg_2SiO_4, etc., need WDS scans for minor elements
  Caution: $Mg(OH)_2$ on MgO, SiO_2 beam damage, etc.
  Stoichiometry is powerful constraint on composition
- Intermediate Composition Minerals, Glasses
  Kakanui Hornblende, K-411 glass, Corning 95-series trace glasses
  Minerals have stoichiometric constraint, glasses do not
  Minerals may have homogeneity issues, glasses may not

EPMA Standards: Il buono, the Good

- Eugene Jarosewich – Smithsonian microbeam standards:
  - Natural and synthetic minerals and glasses
  - Classical wet chemistry for primary analytical data (published values)
  - EPMA used for intra-grain and grain-to-grain variation
  - Sigma ratio: (actual sd / counting sd) data for quantitative homogeneity
    - Sigma of all grains, measure of homogeneity
    - Sigma of worst grain, indication of other material in separate?
  - Significant amount of available material
  - Widely distributed and routinely used
  - Free for the asking
- NIST Standard Reference Materials
  - Synthetic glasses (K-411, K-412, 61X-series, others)
  - CuAu and AgAu alloys
  - Certified values from extensive chemical and homogeneity analysis

EPMA Standards: Il brutto, the Bad

- Multielement standards we use fit into this category, in my opinion
- Widely distributed Taylor standards uncertain pedigree
  - Presumably EPMA analyses
  - Zircon contains inclusions, undocumented homogeneity
- Many mineral standards characterized by EPMA only
  - Few analytical details (standards, kV, instrument, correction algorithm)
  - Chemistry only reported, no k-ratios
- Informally distributed material is assumed to be that of analysis
  - Madagascar orthoclase (Fe, Ba differ)
- Material contains other elements and/or inclusions
  - Boatner REE phosphates, must use portion with lowest Pb from flux
- The upside:
  - Most of these standards could be analyzed to better their characterization

EPMA Standards: Il cattivo, the Ugly

- Worst offenders are oxidized metals in commercial mounts
  - If used as sole standard serious analytical errors may result
  - Only check is total on an unknown
- Homemade mounts that have a single decrepit grain
  - Poorly polished and not even perpendicular to the beam
  - Used exclusively as the primary standard
- Mounts that have never been repolished and recoated since purchase
  - A real need exists for refurbishing services
    - …that cost less than a new standard mount
- Again, a situation that is avoidable but is the responsibility of the analyst

Taylor Commercial Mount
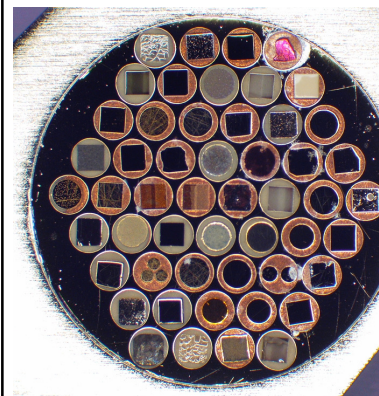
No. 203 Multi-Element Standard : T bar Left JEOL 8200
< 200 angstoms of evaporated carbon.

EPMA Standards: Effect of Oxide Layer Formation
Oxidized Surface = Layered Structure

Substrate reduction, oxide layer increase: k-ratio ~0.001-.003 per nm
High Z oxides: Layer effect greater per unit thickness vs. low Z oxides
Crossover point: UO_2/U ~ 200nm, Fe_2O_3/Fe ~320nm Al_2O_3/Al ~520nm
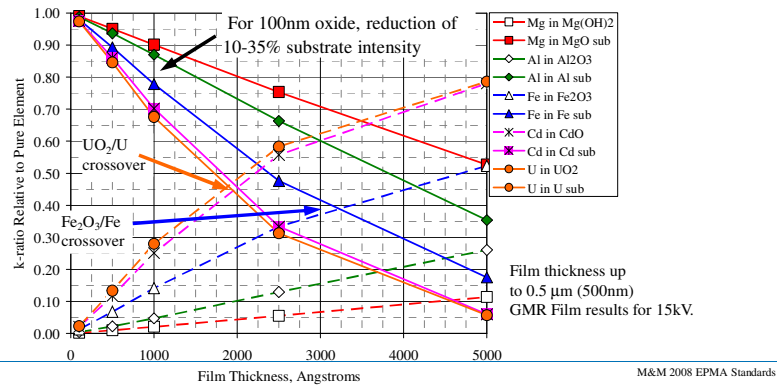**At thickness > crossover, oxide layer dominates k-ratio measurement**

For 100nm oxide, reduction of 10-35% substrate intensity

UO_2/U crossover

Fe_2O_3/Fe crossover

Film thickness up to 0.5 µm (500nm)
GMR Film results for 15kV.

Legend:
- Mg in Mg(OH)2
- Mg in MgO sub
- Al in Al2O3
- Al in Al sub
- Fe in Fe2O3
- Fe in Fe sub
- Cd in CdO
- Cd in Cd sub
- U in UO2
- U in U sub

y-axis: k-ratio Relative to Pure Element
x-axis: Film Thickness, Angstroms

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Advances in EPMA:
Geological Materials -- Standards

- EPMA standards requirements: Homogeneous on micron scale, grain to grain, well characterized on both scales, and available in large enough quantity to be used by microanalysis communities.

- Most materials fail one or more of these requirements.

- Natural and synthetic minerals, oxides, and glasses.
Minerals impose stoichiometry but may be inhomogeneous
Glasses lack stoichiometric control but can be homogeneous

- Glasses: targeted compositions that can be made in bulk and utilized by the microanalysis community.
(Corning 95-series trace element glasses)

- Internal consistency of EPMA standards used by the community is poorly known. Few comparison reports, generally anecdotal.

- Solution: calculate expected x-ray intensity for element of interest in suite of standards, compare measured intensities relative to end-member standard (oxide), i.e., k = ZAF / C. This highlights errors in composition as well as systematic errors in algorithm.

Basalt Glass Indian Ocean USNM 113716:
EPMA vs. Wet Chemistry Data

Plag

Glass

Devitrification
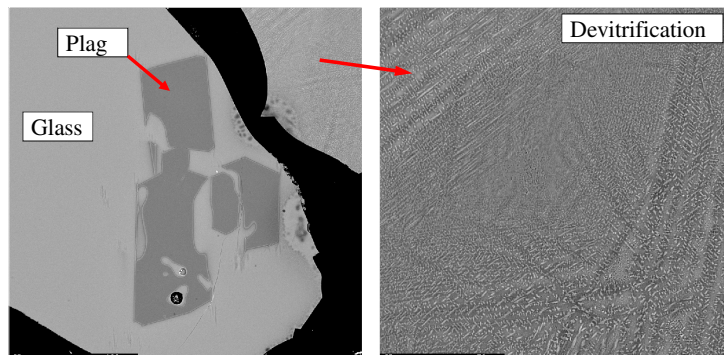
Of the 3-5 mounts of UNSM 113716, this is the first observation of mineral inclusions or crystallites in the glass. This is otherwise a homogeneous standard, consistent with EPMA of other glasses, but based on wet chemistry comparison.
How representative is this of the wet chemical analysis?

Olivine Standards: Mg-rich $(Mg,Fe)_2SiO_4$

Standard	Nat./Syn.	Minor/Trace Els.
Shankland forsterite Fo$_{100}$	Synthetic	Fe?
Boyd olivine Fo$_{93}$	Natural	Mn, Co, Ni, Zn?
LLNL "Fo85" (Fo$_{93}$)	Synthetic	<none>
San Carlos olivine Fo$_{90}$	Natural	Na?, Mg, Al, Ca, Ti?, Cr, Mn, Co, Ni
Fujisawa sintered Fo$_{90}$	Synthetic	Al, Ca, Mn, Zn
LLNL "Fo80" (Fo$_{85}$)	Synthetic	Al, Ca, Cr, Mn, Co?, Ni?
Springwater olivine Fo$_{82}$	Natural	Ca, Cr, Mn
LLNL "Fo67" (Fo$_{70}$)	Synthetic	<none>

Shankland from ORNL
LLNL olivines from George Rossman, Boyd and Fujisawa from Caltech
San Carlos and Springwater olivine from Smithsonian

Olivine Standards: Mn, Fe, Ni

Standard	Nat./Syn.	Minor/Trace Els.
Mn-olivine GRR-392	Synthetic	Fe
Mn-olivine RDS P-1087	Synthetic	Mg, Ca, Fe
Fayalite GRR-391	Synthetic	Mn
Fayalite RDS P-1086	Synthetic	Mg, Cr, Mn
Rockport Fayalite	Natural	Mg, Ca, Cr, Mn, Zn
Fayalite ORNL	Synthetic	Al?, Ca?, Cr
Ni-olivine P-877	Synthetic	Cr?, Fe, Co

GRR and RDS from George Rossman, P numbers Caltech probe standards
Rockport Fayalite from Smithsonian

Rockport Fayalite

- RF is widely used as primary Fe standard
  But Mg and Zn present, not in wet chemistry analysis
  [Low level oxides suspected to be variable not reported in wc analysis]
- Is ferric iron present? – apparently not:
  Wet Chemistry: Fe_2O_3 1.32, FeO 66.36 %, Tot: 99.18
  Dyar XANES: RF iron is completely reduced.
- Grunerite in separate: $Fe_7^{2+}Si_8O_{22}(OH)_2$
- Magnetite at locality, in separate $(Fe_2^{3+}Fe^{2+}O_4)$??
- Analysts should use EPMA analysis when using RF as primary standard.

Rockport Fayalite
Complete analysis needed for quantitative correction

Wet chem missing elements

```
ELEMENT  K-VALUE  ELEMWT%  OXIDWT%  ATOMIC%  FORMULA  KILOVOL
Si ka    .10211   13.659   29.221   14.299   1.001    15.0
Fe ka    .47949   52.508   67.551   27.644   1.935    15.0
Ti ka    .00024     .024     .040     .015     .001    15.0
Mn ka    .01487    1.657    2.140     .887     .062    15.0
O                           31.104     .000  57.156    4.000
TOTAL:                      98.952   98.952 100.000    6.998
```

Wet chem plus EPMA data

```
ELEMENT  K-VALUE  ELEMWT%  OXIDWT%  ATOMIC%  FORMULA  KILOVOL
Si ka    .10195   13.659   29.221   14.214    .995    15.0
Fe ka    .47983   52.508   67.551   27.480   1.924    15.0
Ti ka    .00024     .024     .040     .015     .001    15.0
Mn ka    .01488    1.657    2.140     .882     .062    15.0
Mg ka    .00014     .028     .046     .033     .002    15.0
Ca ka    .00032     .032     .045     .023     .002    15.0
Cr ka    .00045     .040     .059     .023     .002    15.0
Ni ka    .00005     .006     .007     .003     .000    15.0
Zn ka    .00394     .462     .575     .207     .014    15.0
O                           31.269     .000  57.120    4.000
TOTAL:                      99.684   99.684 100.000    7.003
```

Fayalite Standards

Oxide	Rockport Wet Chemistry	Rockport EPMA	RDS P-1086 EPMA	GRR391 EPMA**
MgO	Not reported	0.046	0.385	0
SiO_2	29.22	29.99	30.04	(29.49)
CaO		0.045	0	0.004
Cr_2O_3		0.059	0	0.010
MnO	2.14	2.13	0.092	0.212
FeO*	67.55	67.62	69.61	(70.34)
NiO		0.007	0.012	0.011
ZnO	Not reported	0.575	0.006	0.007
Total	99.18	100.48	100.16	(100.04)
$\Sigma\ M^{2+}$	1.999	1.982	1.979	1.999
Si	1.001	1.009	1.010	1.000

Rockport WC: FeO 66.36, Fe_2O_3 1.32, FeO* 67.55. TiO_2 0.04, H_2O 0.1
EPMA: PAPF, olivine stds, Heinrich 1986 macs, 20KV, n=4 **GRR391 std Si, Fe
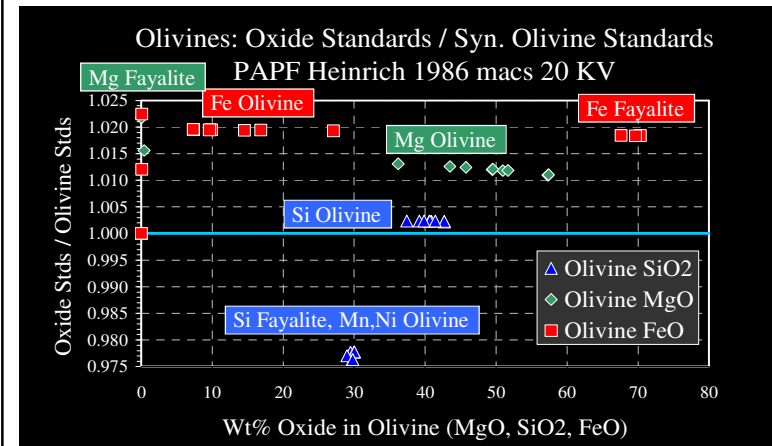
Systematic Errors in Olivine $M^{2+}_2SiO_4$
PAPF, Heinrich 1986 macs @ 20 KV, 40 TOA

Olivine Group	Standard Type	Analysis Total	σ, wt%	Si cations 1 ideal	σ	Σ M^{2+} 2 ideal	σ
Olivines	Oxide	101.14	0.42	0.989	0.004	2.023	0.007
	Syn. Olivine	100.22	0.37	0.994	0.003	2.012	0.006
Fayalites	Oxide	100.93	0.20	0.990	0.001	2.022	0.001
	Syn. Olivine	100.34	0.23	1.010	0.001	1.981	0.003
Mn,Ni Olivines	Oxide	99.32	0.33	0.991	0.003	2.018	0.006
	Syn. Olivine	100.07	0.30	1.002	0.003	1.995	0.005

Averages of total and cation stoichiometry for all olivines from test data set.
For olivines, Mg/(Mg+Fe) = 0.860 ± 0.080 (ox) vs. 0.861 ± 0.079 (oliv).
Identical k-ratios corrected using PAP full $\Phi(\rho z)$ and Heinrich 1986 macs, relative to oxide vs. synthetic olivine standards.
Olivine Formula: $M^{2+}_2SiO_4$

Systematic Error Using Oxide Standards

Olivines: Oxide Standards / Syn. Olivine Standards
PAPF Heinrich 1986 macs 20 KV

Mg Fayalite — Fe Olivine — Mg Olivine — Fe Fayalite — Si Olivine — Si Fayalite, Mn,Ni Olivine

Y-axis: Oxide Stds / Olivine Stds (0.975 to 1.025)
X-axis: Wt% Oxide in Olivine (MgO, SiO2, FeO) (0 to 80)

Legend:
△ Olivine SiO2
◇ Olivine MgO
□ Olivine FeO

Status Report: EPMA of Olivine

- EPMA using synthetic olivine standards better than oxide standards:
  Superior analysis total, Si cation ~1.0, and ΣM^{2+} ~ 2.0
- Improvement in EPMA accuracy for olivine using
  Armstrong $\Phi(\rho z)$ coupled with FFAST mac data set.
- Using oxide standards we observe:
  Overcorrection of Mg and Fe in olivine across Fo-Fa binary
  Undercorrection of Si in low-Mg olivine (Fayalite, Mn-ol, and Ni-ol)
  Marginal underestimation of Mg/(Mg+Fe).
- These relationships extend to all MgFe silicates relative to composition.
- Alpha-factor analysis of systematic errors in Fo-Fa system:
  EPMA and wet chemistry of natural olivines are not internally consistent.
  Worst: Boyd Forsterite Mg and Fe not consistent (Caltech standard)
  Best: Springwater Mg,Fe, and Mg in San Carlos (Fe in SC less so)

Conclusions

- Quantitative EPMA emphasizes
  Measurement issues and instrumental calibration
  Use of good microanalysis standards
  Attention to details of correction algorithms and data sets
- Experimental approach which confirms all is well:
  Use of K_{meas}/K_{calc} plot used for data analysis, WDS and EDS
  CMASTF standards provide instrument calibration data set
  Identification of inconsistent compositions
- Accuracy of analysis in CMASTF system better than 2%, precision limited
  SDD quantitative analysis data highly competitive with WDS
- Always think:
  Calibration, measurement, quantitation, evaluation, report and discuss