Techniques for Improving Quantitative Analysis of Mineral Glasses

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Points of Discussion

Standards for Si (silicate vs. glass)
- •Coordination Peak shifts?
- •Beam damage?
- •Charging Effects

Volatilization effects
- •Na, K
- •Si, Al

Water by difference
- •Matrix correction effects
- •Volatile Correction effects

Instrument drift
- •Beam drift corrections
- •Intensity drift corrections
- •Spectrometer drift

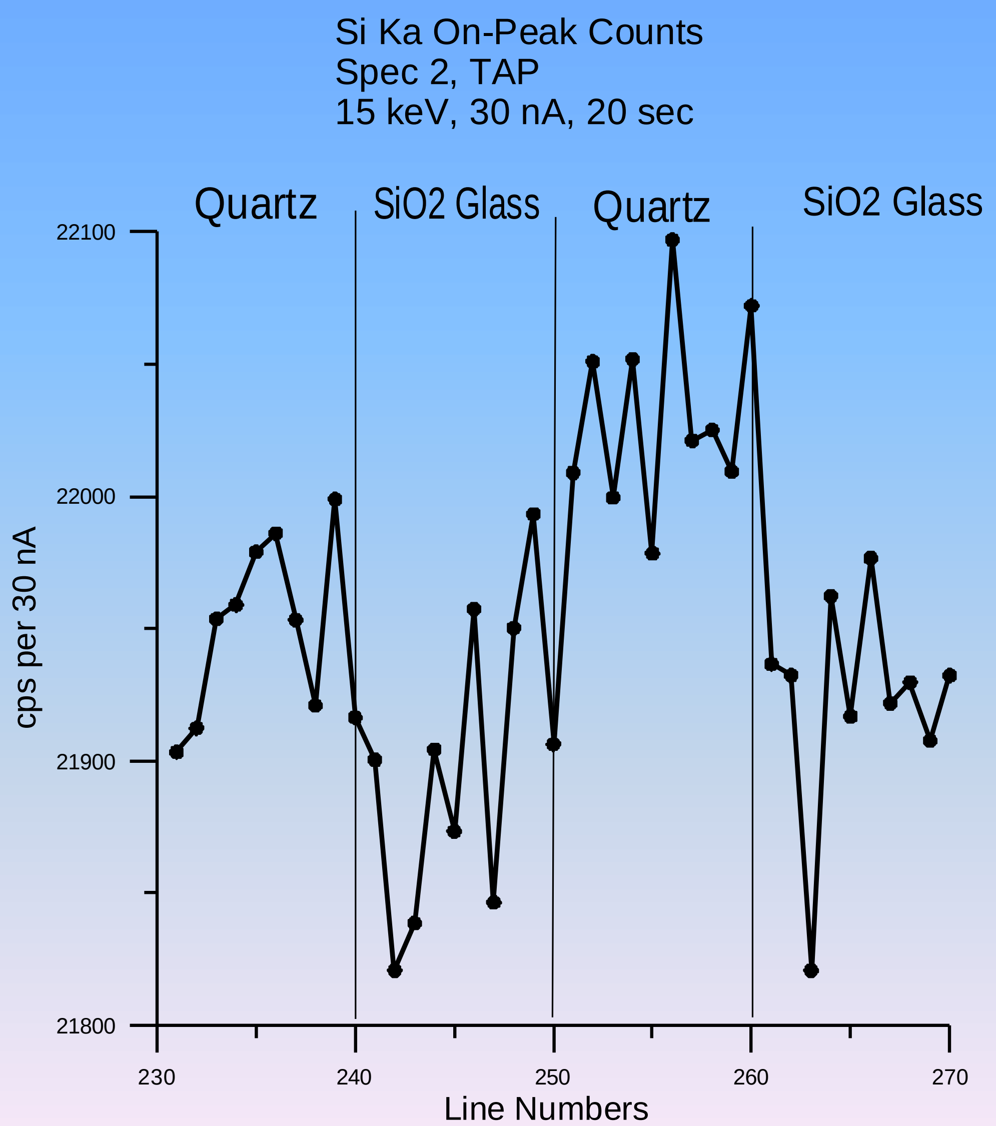
Sulfur Peak Shift Mechanisms
- •Peak Shape Changes?
- •Peak Position Changes?
- •Variables (time, current)

Standards for Glass Analysis

"Use Glass for Glass"

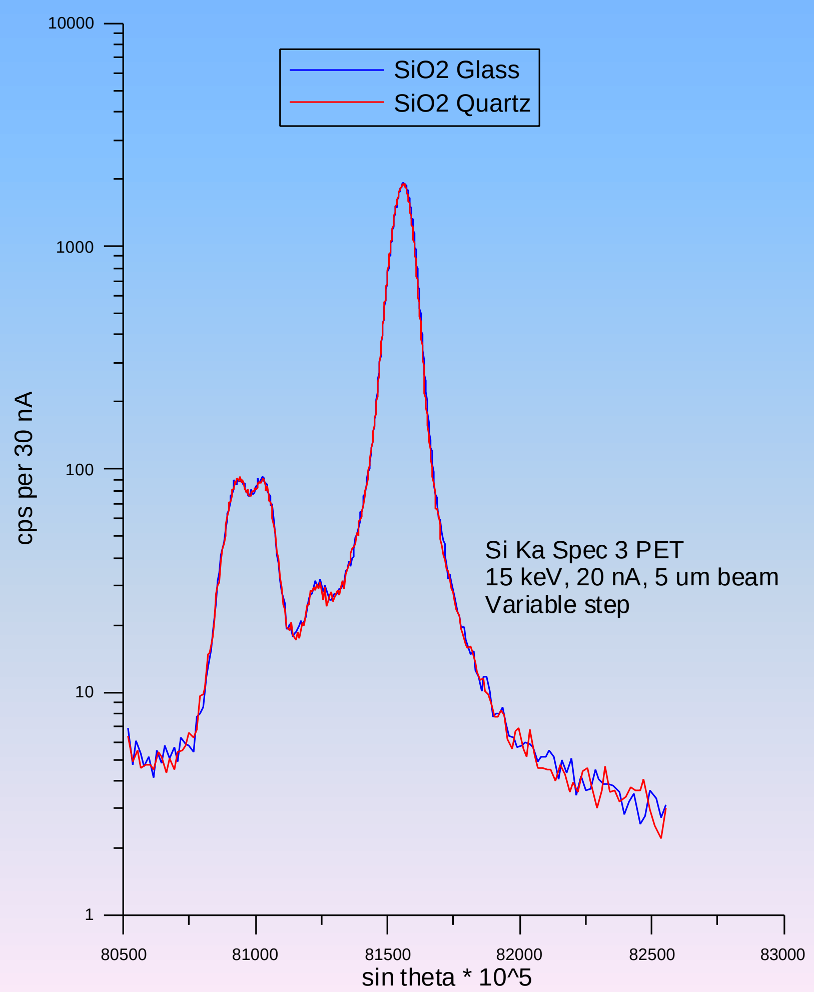
-but why?

What Is Going On Here?

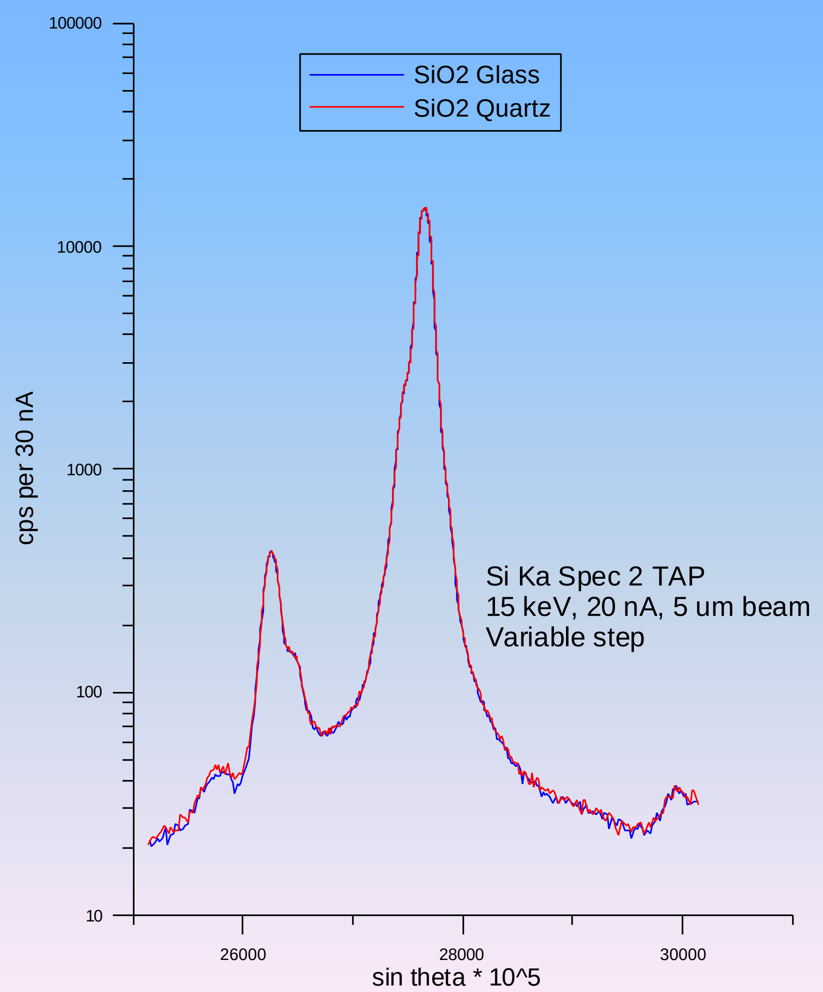


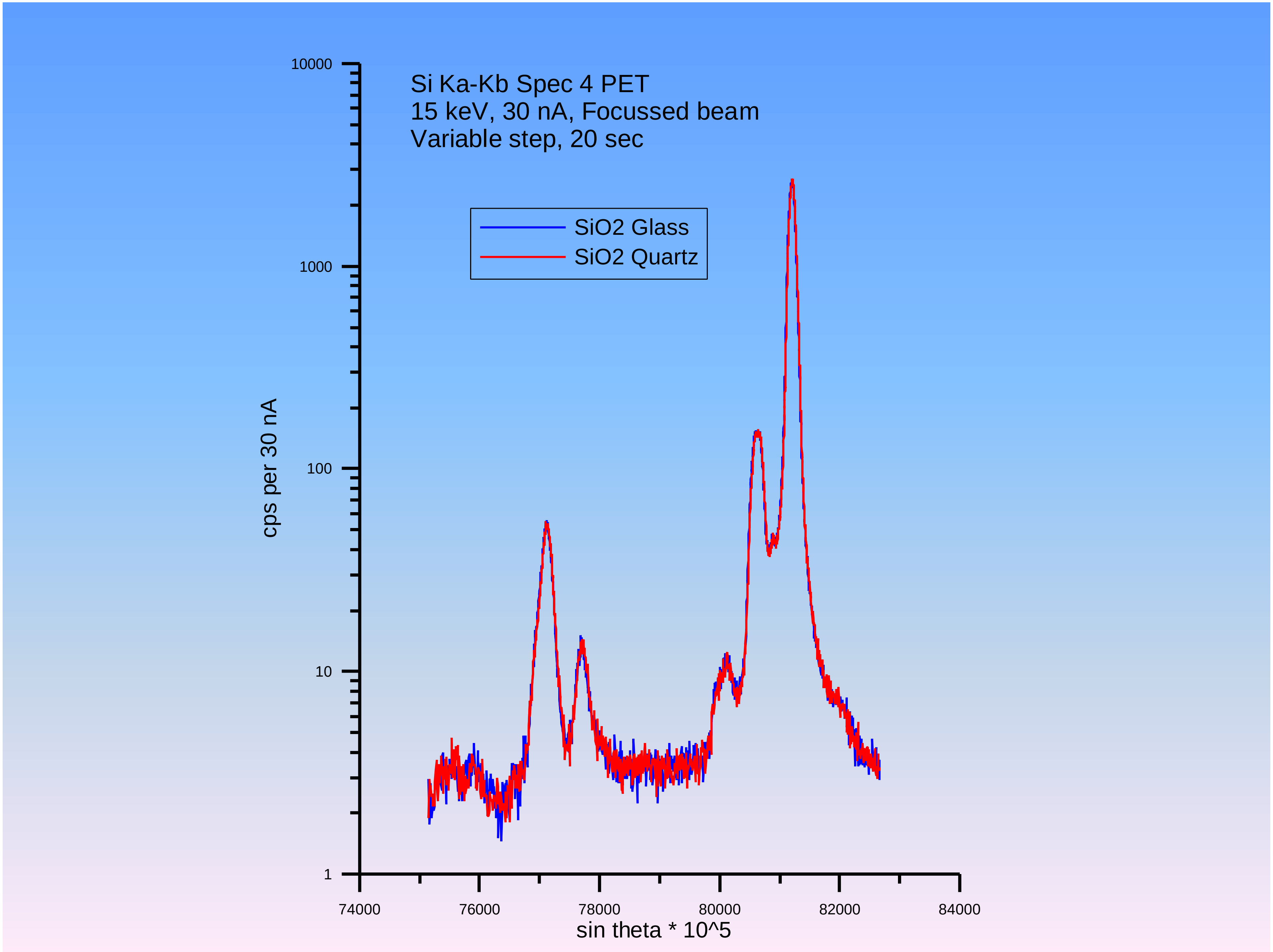
Standards for Glass Analysis

Satellite Lines?



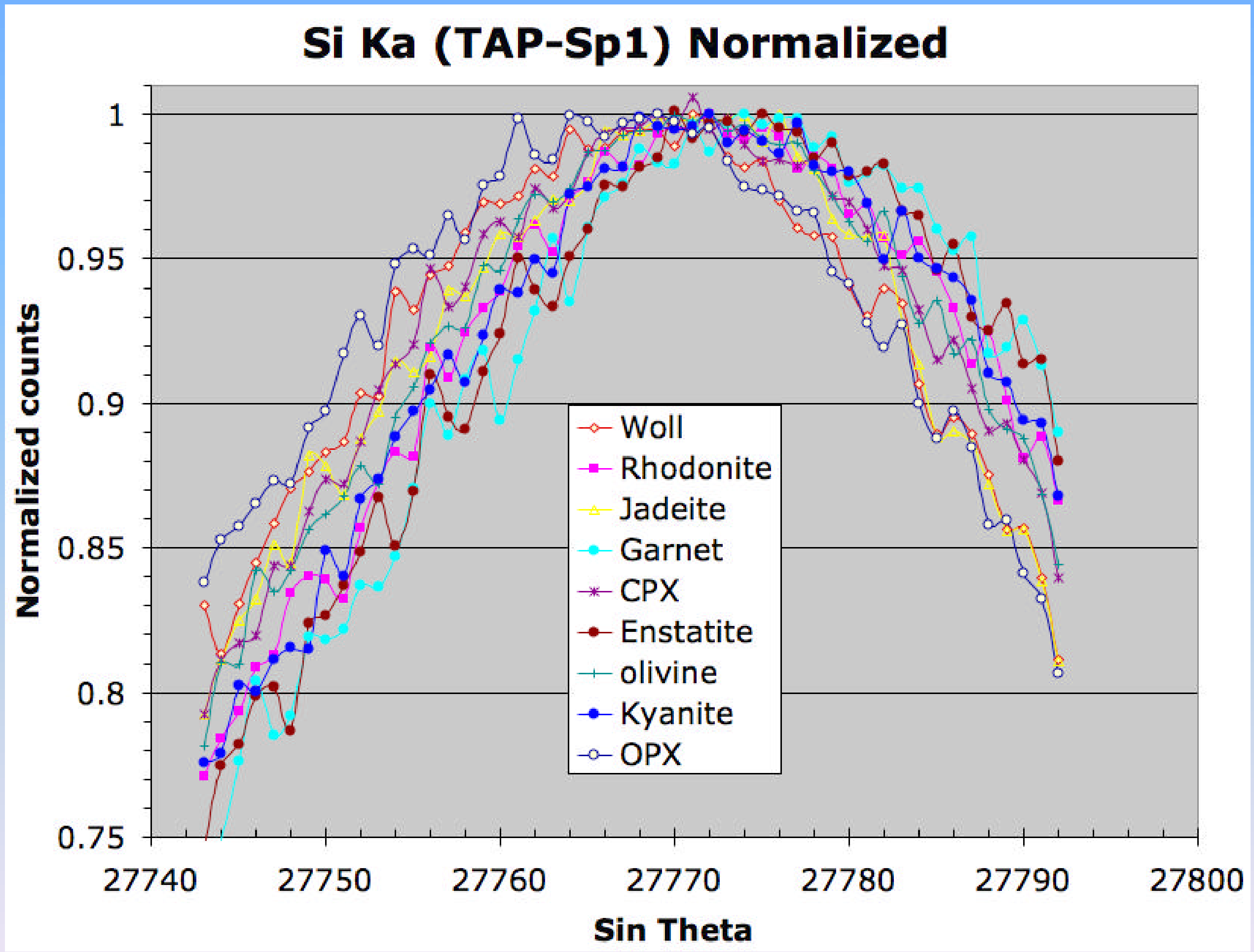
Beta Lines?




Si Ka-Kb Spec 4 PET
15 keV, 30 nA, Focussed beam
Variable step, 20 sec
SiO2 Glass
SiO2 Quartz
cps per 30 nA
10000
1000
100
10
1
74000
76000
78000
80000
82000
84000
sin theta * 10^5

Peak Shifts?

Subtle peak shift effects demonstrated for different silicate minerals



Fournelle, 2004, 2005

Al K_α Peak Shifts

Al Ka Peak Shift Relative to Al-Fe Alloy

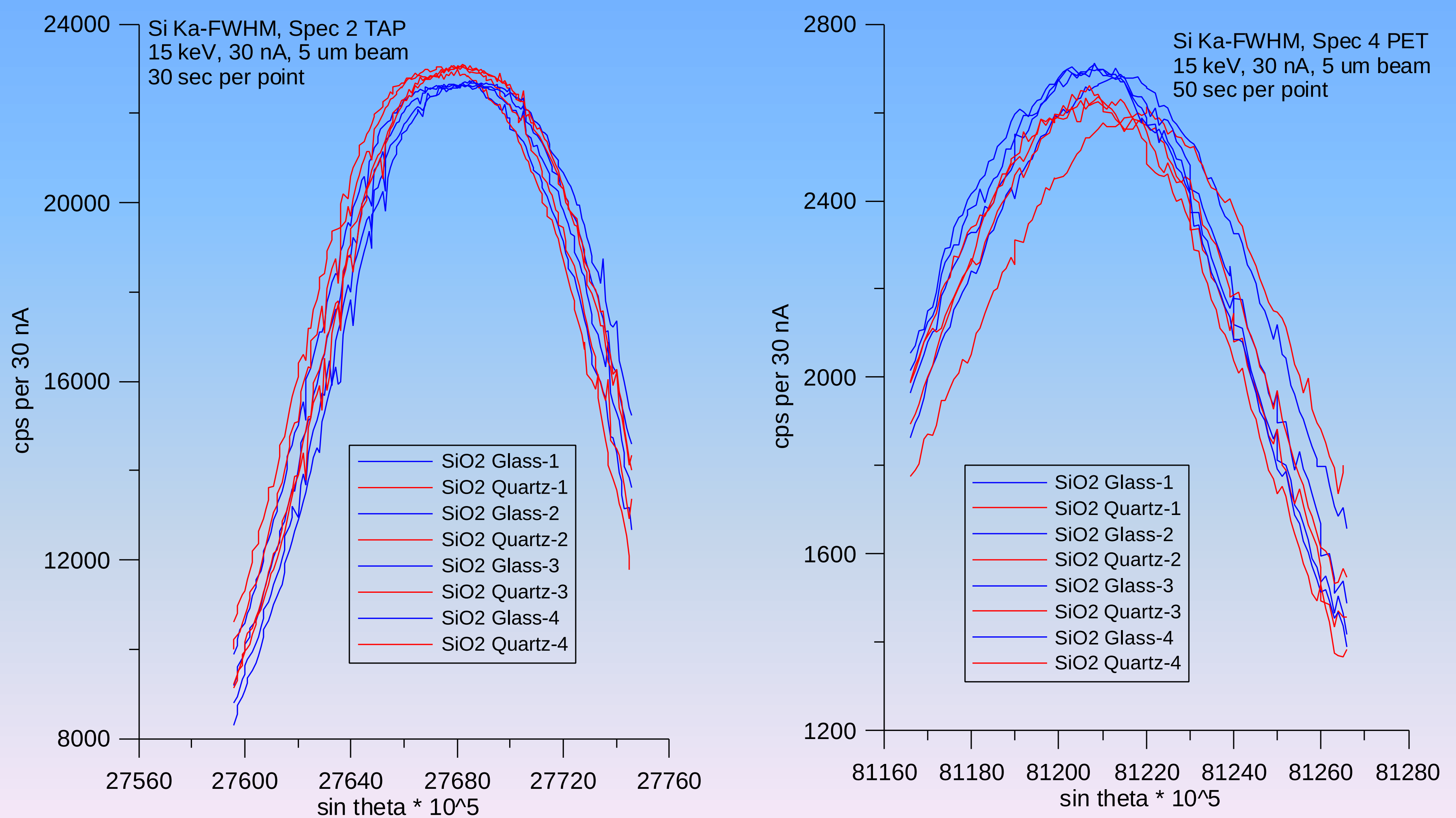
Coord	Mineral	Sp1 Ave	Std Dev	n
4	Albite	-14.2	0.7	4
4	Microcline	-13.3	1.0	8
6	Pyrope	-12.9	0.9	4
6	Topaz	-12.3	0.7	7
6	Gahnite	-11.8	0.5	4
	Alunite	-11.6	1.1	4
6	Kyanite	-11.5	1.2	7
6	Jadeite	-11.3	1.0	4
4	Plag - An18	-11.2	0.3	4
4	Anorthoclase	-11.0	0.8	4
6	Corundum	-10.8	0.3	7
6+4	Sillimanite	-10.7	0.3	7
4	Celsian	-8.5	1.0	4
4	Plag - An49	-7.5	1.6	4
4	Anorthite	-7.4	0.4	4
4	F Phlogopite	-7.0	0.7	7

Mineral	Sp4 Ave	Std Dev	Coord
Albite	-18.0	0.7	4
Pyrope	-16.5	1.0	6
Anorthoclase	-16.2	0.9	4
Alunite	-16.2	2.0	
Microcline	-15.8	0.8	4
Topaz	-15.1	0.5	6
Plag - An18	-14.9	0.4	4
Gahnite	-14.4	0.7	6
Jadeite	-13.9	0.5	6
Kyanite	-13.8	0.7	6
Corundum	-13.4	0.5	6
Sillimanite	-12.8	1.0	6+4
Celsian	-11.7	1.1	4
An49	-10.3	1.2	4
Anorthite	-9.9	1.0	4
F Phlogopite	-9.8	1.4	4

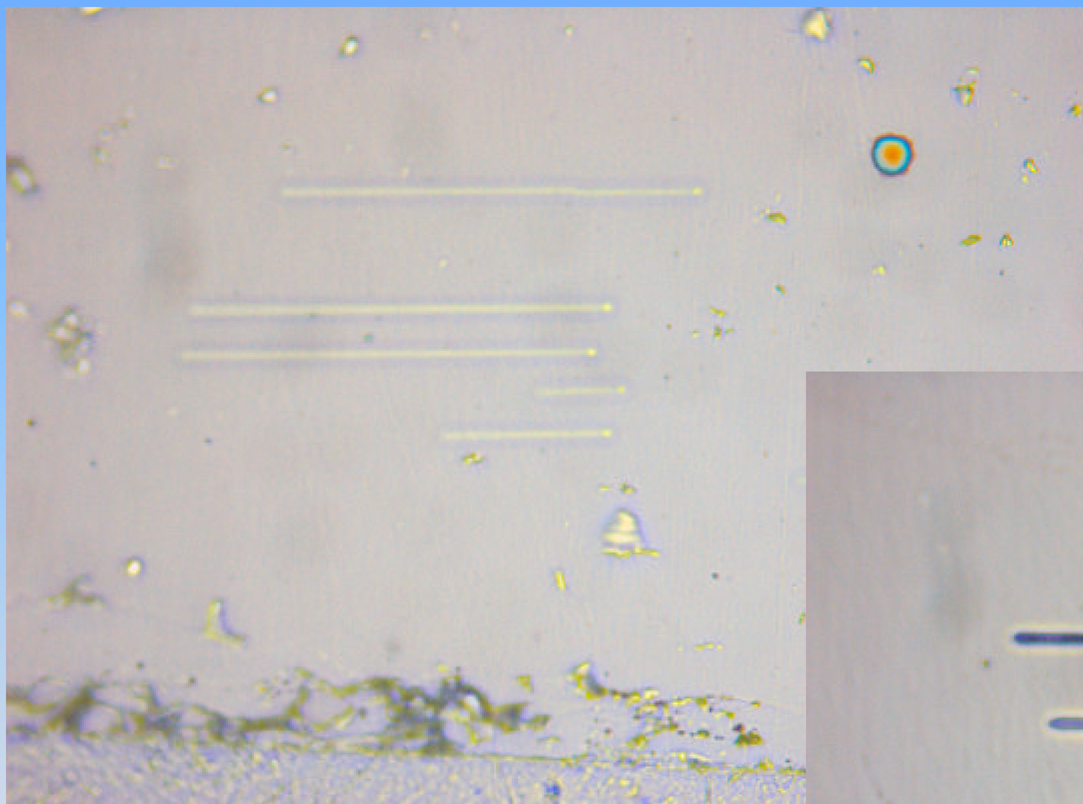
Two independent measurements, very similar trends

From: Fournelle, Al and Si quantitation in routine silicate epma: Maybe not so routine: 2005 Goldschmidt

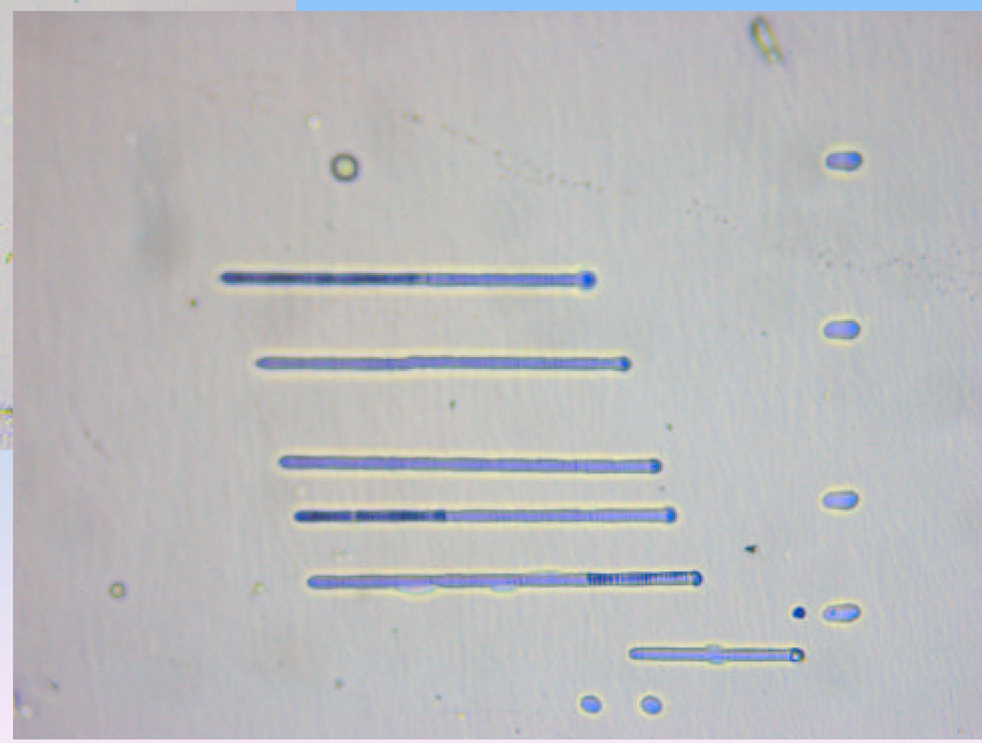
Between glass and crystal SiO2?



Sample Damage?

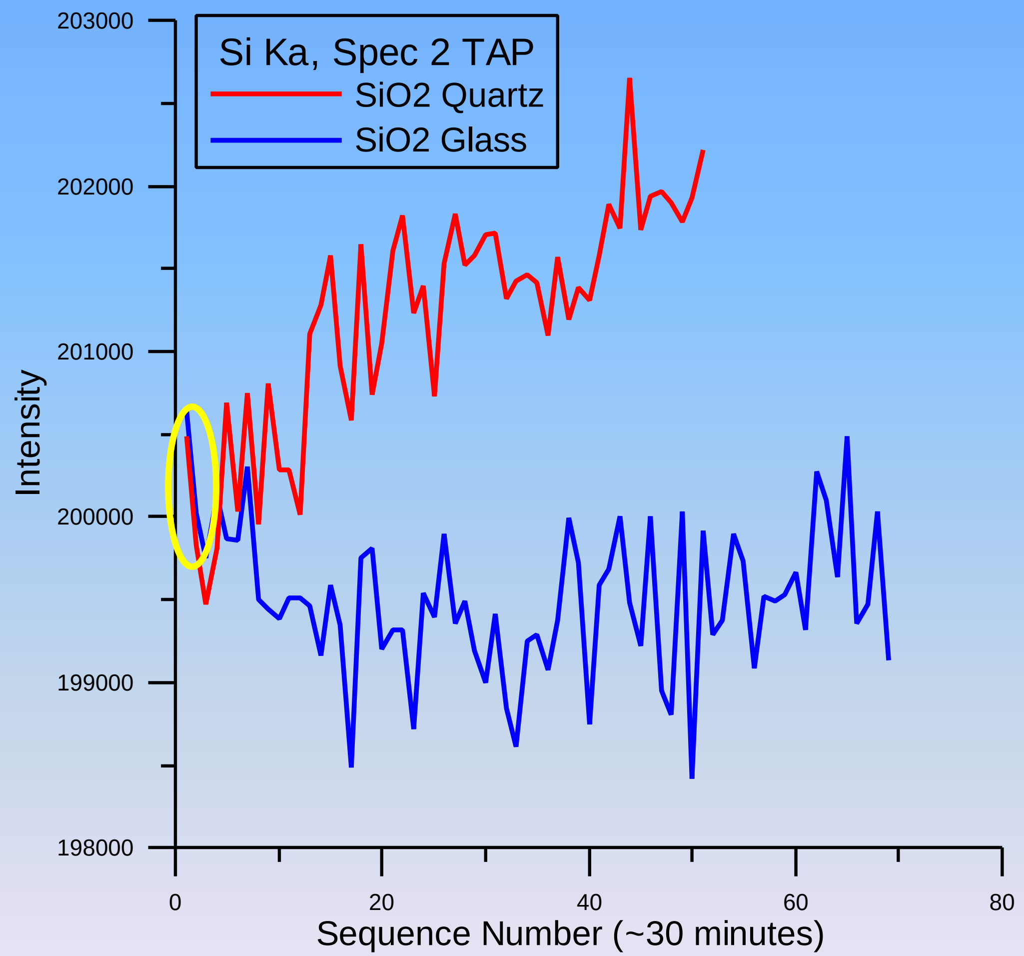


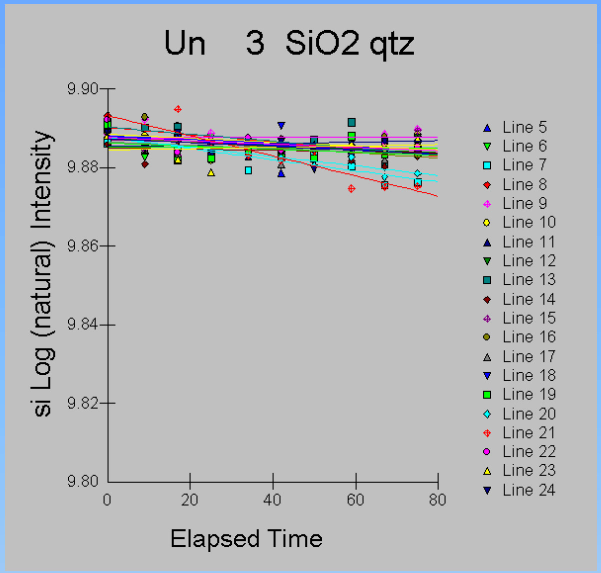
SiO2 Glass

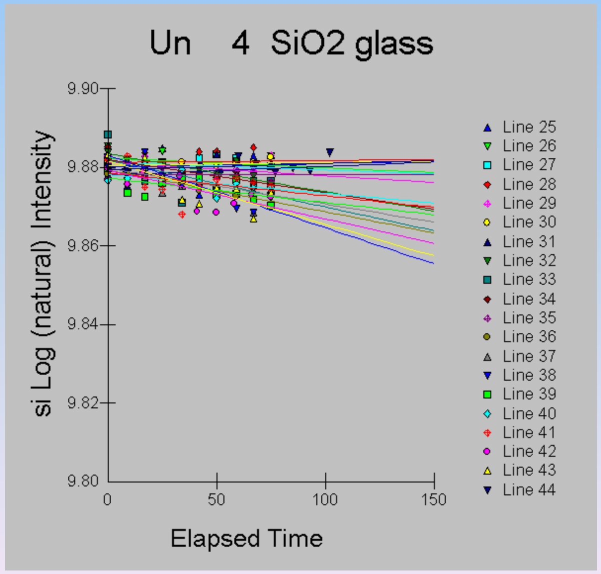


SiO2 Quartz

Beam Damage? Si Ka

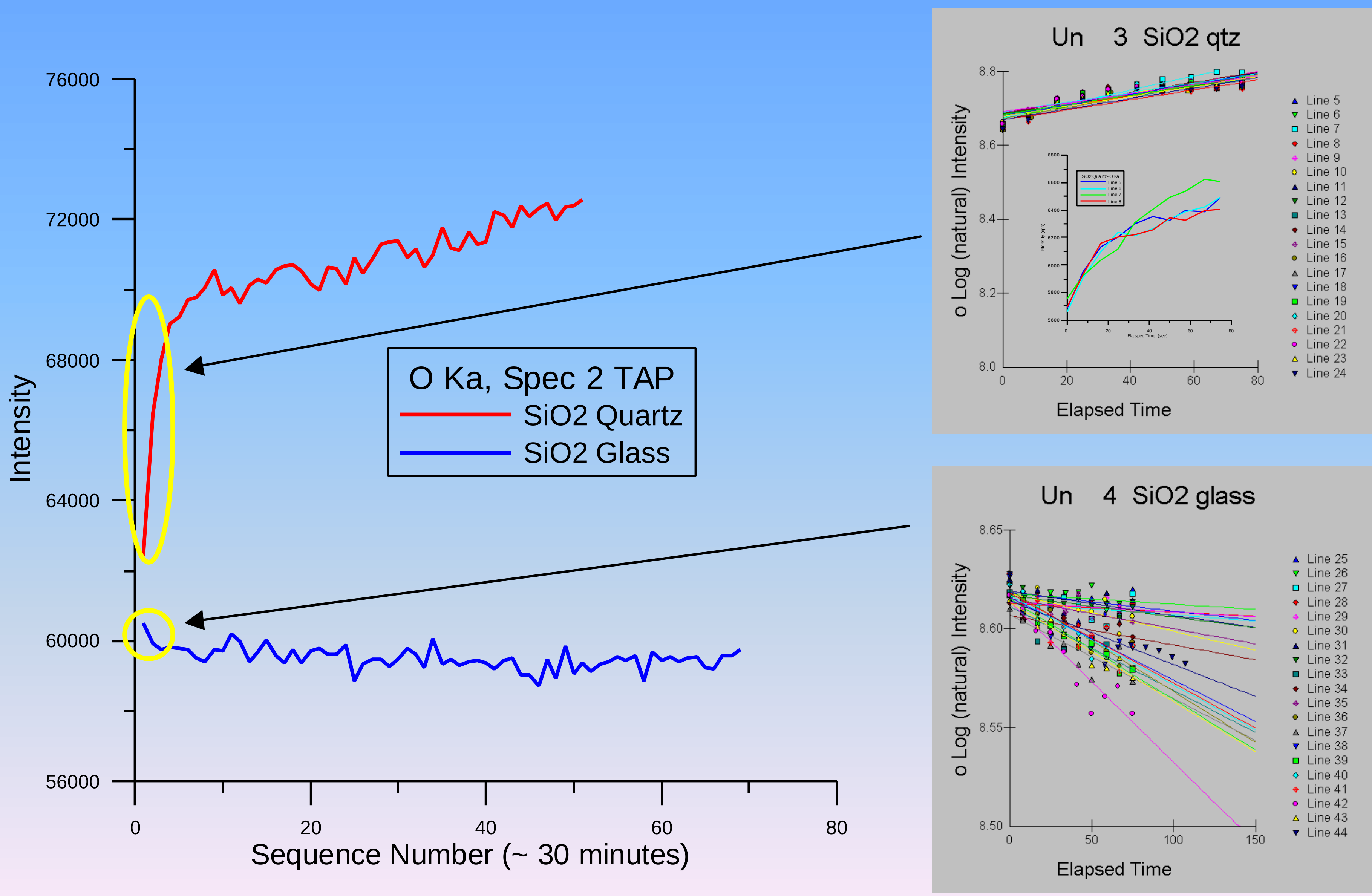




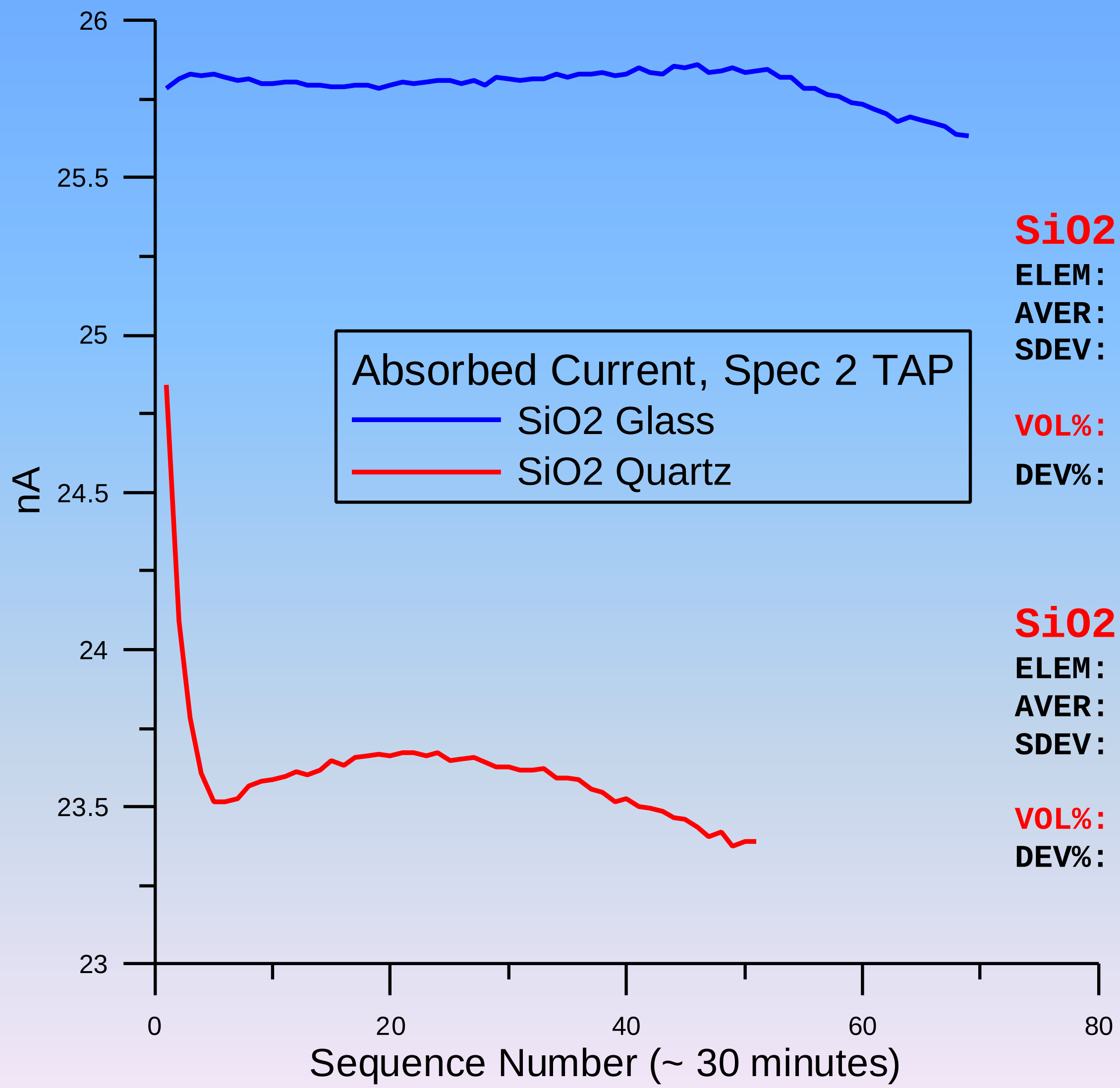


15 keV, 30 nA, focussed

Beam Damage? O Ka



Or Sub Surface Charging?



SiO2 Glass (80 sec elapsed time)

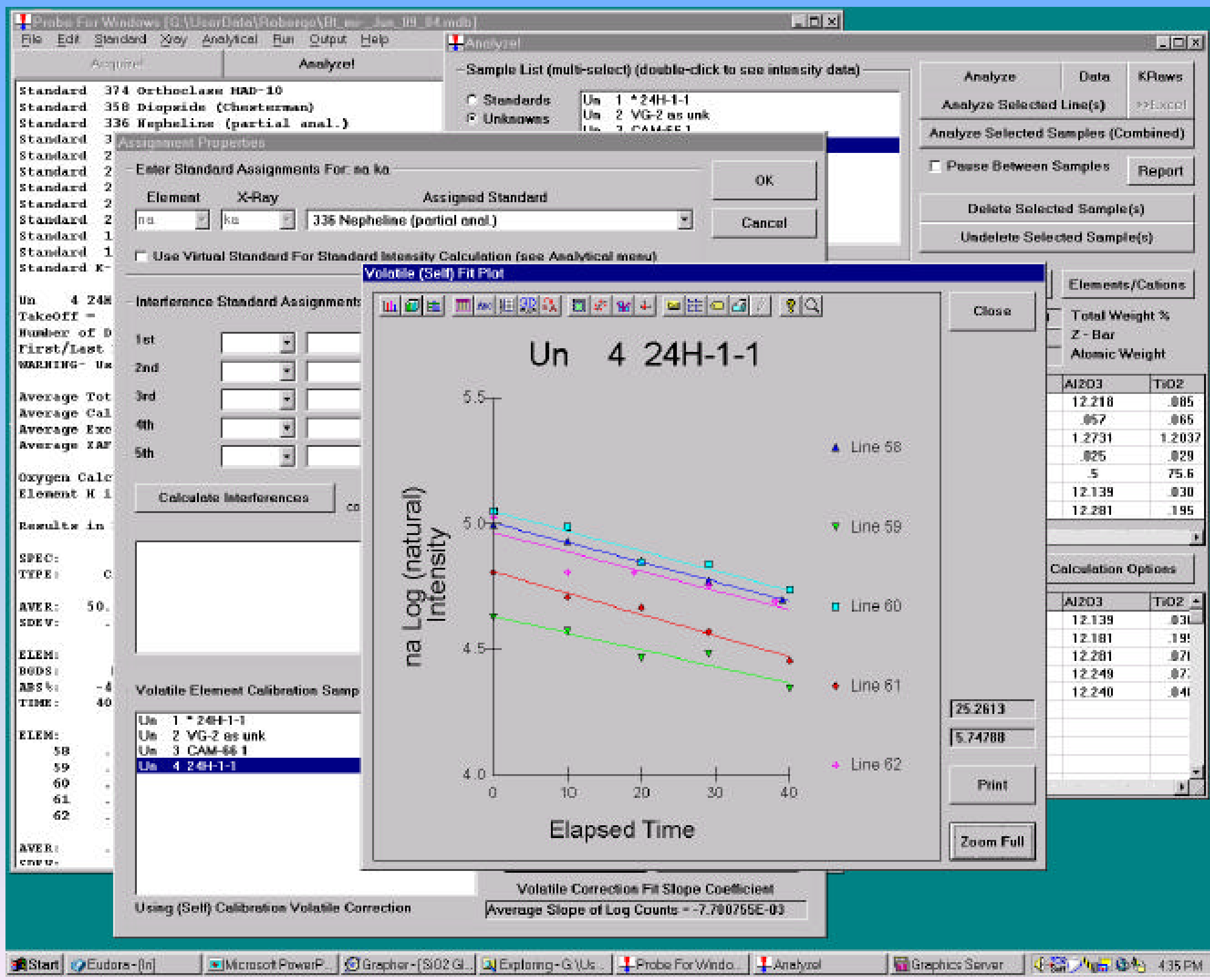
ELEM:	Si	Si	Si	O
AVER:	46.257	46.325	46.106	48.915
SDEV:	.120	.304	.299	.269
VOL%:	.348	.426	.478	1.786
DEV%:	.0	.1	.1	.1

SiO2 Quartz (80 sec elapsed time)

ELEM:	Si	Si	Si	O
AVER:	46.672	46.614	46.459	50.260
SDEV:	.145	.383	.327	.371
VOL%:	.346	.038	.290	-8.022
DEV%:	.0	.1	.1	.2

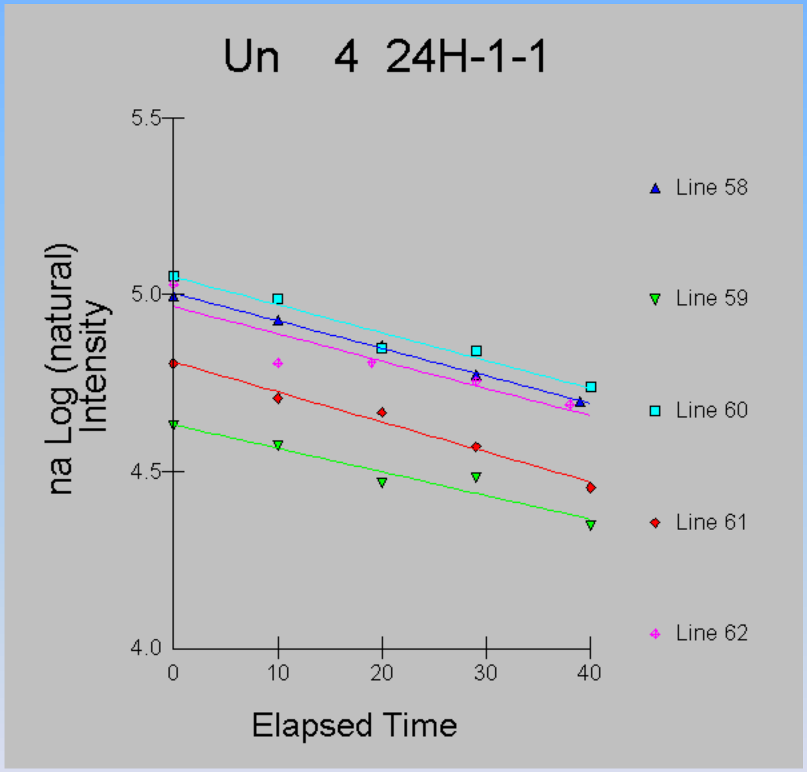
For more information see:
Cazaux, 2004

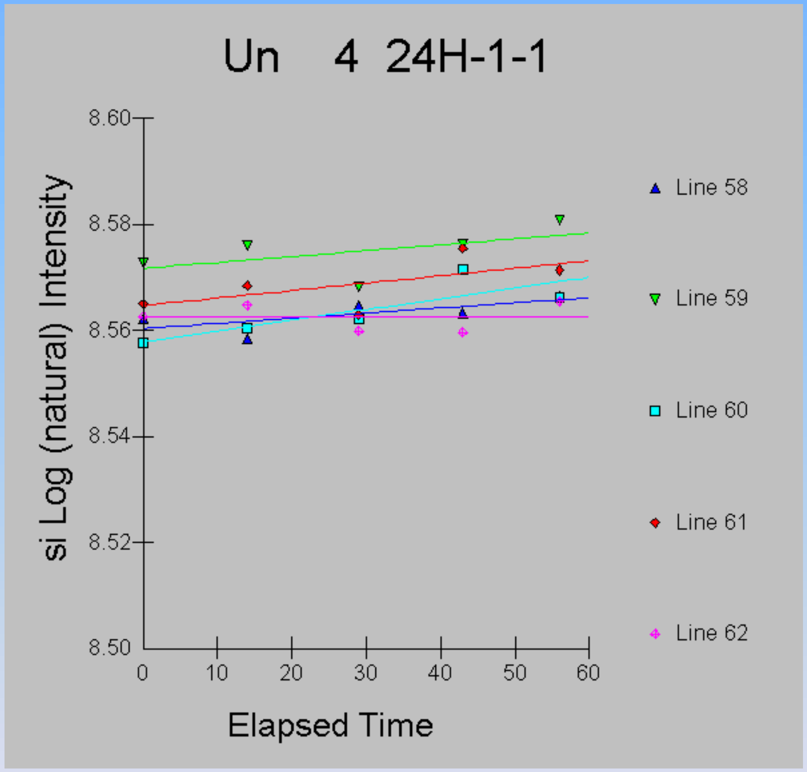
“Volatile” or Migrating Elements in Mineral Glasses



Correct for Na, K loss and Si and Al gain

Change in Intensity Over Time



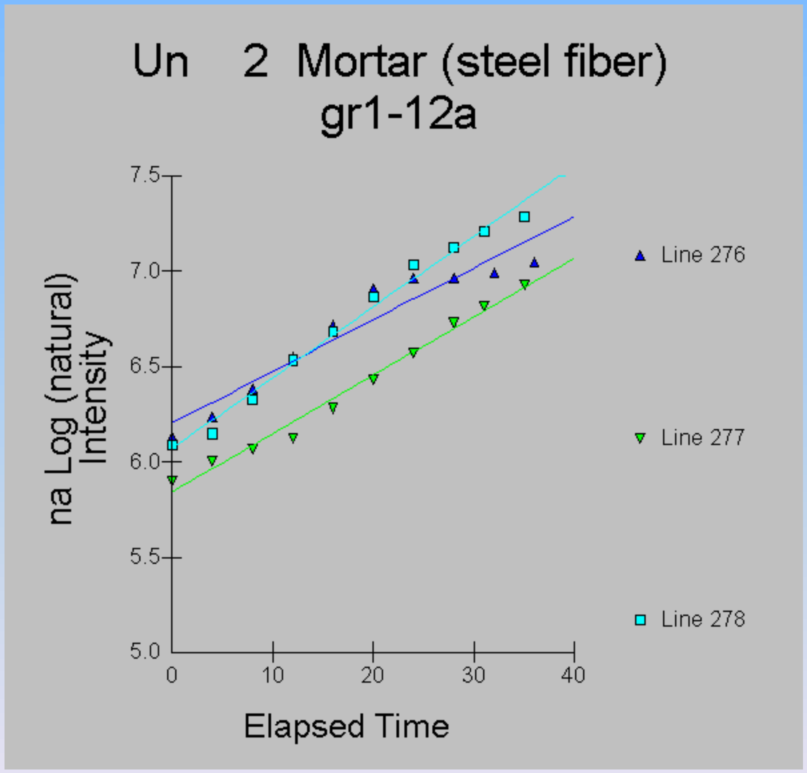


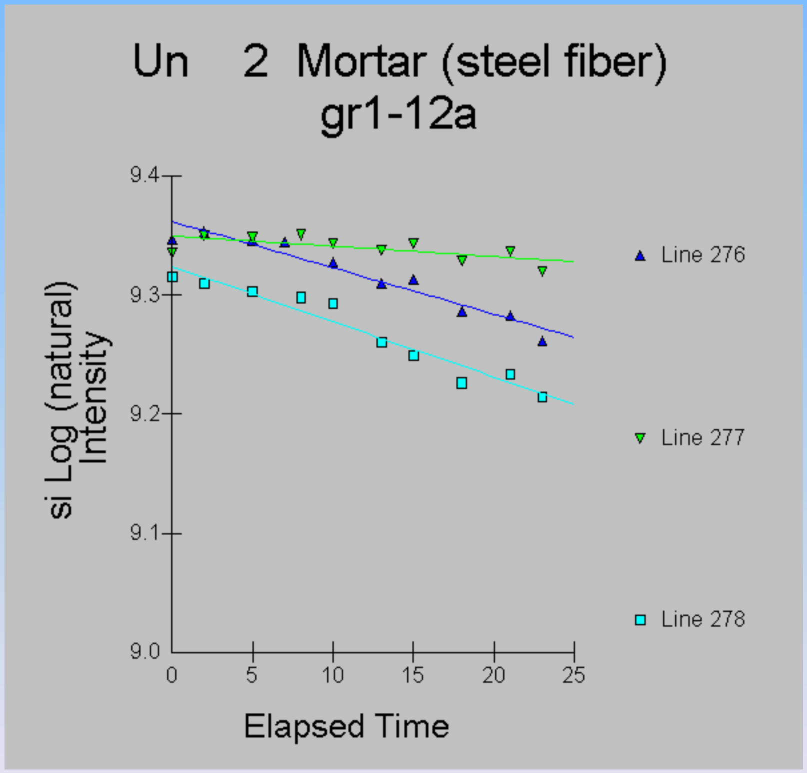
36% loss

0.6% gain

15 keV, 10 nA, 10 um (linear change regime)

But Not Always What You Expect!





Matrix Effects?

- Effects from Water By Difference
- Effects from Na, Si, etc “migration”

Matrix Effects

24H-1-1

No Volatile Correction, No Water By Difference

Results in Oxide Weight Percents

ELEM:	CaO	K2O	FeO	SiO2	MgO	Na2O	Al2O3	TiO2	P2O5	O	H2O	SUM
58	.411	4.900	.537	74.603	.036	2.644	11.975	.073	.000	.000	.000	95.180
59	.437	4.624	.612	75.386	.033	1.841	12.024	.113	.000	.000	.000	95.070
60	.423	4.998	.526	74.715	.023	2.765	12.113	.065	.000	.000	.000	95.628
61	.423	4.853	.637	75.000	.047	2.137	12.089	.055	.000	.000	.000	95.240
62	.435	4.847	.677	74.613	.048	2.561	12.089	.036	.011	.000	.000	95.317
AVER:	*.426*	*4.844*	*.598*	*74.863*	*.037*	*2.390*	*12.058*	*.068*	*.002*	*.000*	*.000*	*95.287*
SDEV:	.011	.137	.065	.333	.010	.387	.057	.028	.005	.000	.000	
%RSD:	2.5	2.8	10.8	.4	27.9	16.2	.5	41.5	223.6	418.3	.0	
ZCOR:	1.1202	1.1536	1.1987	1.2061	1.4303	1.8227	1.2568	1.1983	1.4641	.0000	.0000	
KRAW:	.0161	.3080	.0057	1.0344	.0003	.1323	.7242	.0006	-.0004	.0000	.0000	
PKBG:	4.96	59.36	4.84	370.59	1.42	30.93	77.40	1.46	.87	.00	.00	

Excel Spreadsheet Subtraction Gives ~ 4.7% H_2O

Volatile Correction Matrix Effects

24H-1-1 With Volatile Correction, No Water By Difference

Results in Oxide Weight Percents

ELEM:	CaO	K2O	FeO	SiO2	MgO	Na2O	Al2O3	TiO2	P2O5	O	H2O	SUM
58	.411	4.867	.537	74.378	.037	3.626	12.035	.030	.000	.000	.000	95.921
59	.437	4.740	.612	75.016	.034	2.426	12.063	.194	.000	.000	.000	95.521
60	.423	4.933	.526	74.057	.024	3.805	12.178	.076	.000	.000	.000	96.022
61	.423	5.220	.636	74.552	.048	3.025	12.147	.077	.000	.000	.000	96.128
62	.435	4.715	.677	74.794	.049	3.503	12.146	.048	.011	.000	.000	96.378
AVER:	*.426*	*4.895*	*.598*	*74.559*	*.038*	*3.277*	*12.114*	*.085*	*.002*	*.000*	*.000*	*95.994*
SDEV:	.011	.203	.065	.370	.010	.557	.062	.064	.005	.000	.000	
%RSD:	2.5	4.1	10.8	.5	27.3	17.0	.5	75.6	223.6	.0	.0	
ZCOR:	1.1198	1.1530	1.1983	1.2092	1.4391	1.8180	1.2625	1.1979	1.4627	.0000	.0000	
KRAW:	.0161	.3114	.0057	1.0276	.0003	.1819	.7242	.0008	-.0004	.0000	.0000	
PKBG:	4.97	60.00	4.84	369.28	1.43	42.09	77.77	1.58	.87	.00	.00	
VOL%:	*.000*	*1.135*	*.000*	*-.658*	*.000*	*36.111*	*.000*	*20.283*	*.000*	*.000*	*.000*	
DEV%:	.0	.2	.0	.0	.0	.4	.0	20.3	.0	.0	.0	

Na, Si, K Intensity Over Time Iteration Gives ~ 4% H2O

Water By Difference Matrix Effects

24H-1-1

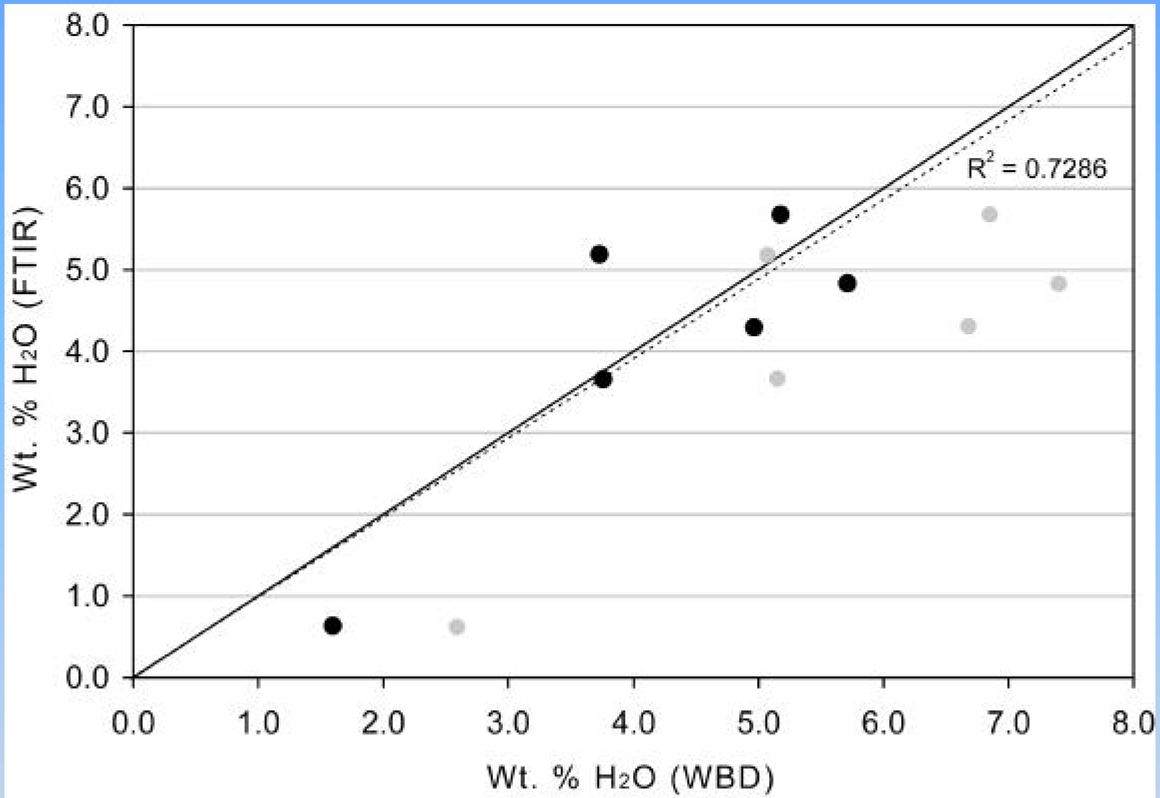
With Volatile Correction, Water By Difference

Results in Oxide Weight Percents

ELEM:	CaO	K2O	FeO	SiO2	MgO	Na2O	Al2O3	TiO2	P2O5	O	H2O	SUM
58	.414	4.885	.542	74.776	.039	3.668	12.139	.030	.000	.000	3.506	100.000
59	.441	4.759	.618	75.464	.036	2.457	12.181	.195	.000	.000	3.849	100.000
60	.426	4.951	.531	74.441	.026	3.848	12.281	.076	.000	.000	3.420	100.000
61	.426	5.239	.641	74.934	.050	3.058	12.249	.077	.000	.000	3.327	100.000
62	.438	4.730	.682	75.149	.051	3.539	12.240	.048	.011	.000	3.112	100.000
AVER:	*.429*	*4.913*	*.603*	*74.953*	*.041*	*3.314*	*12.218*	*.085*	*.002*	*.000*	*3.443*	*100.000*
SDEV:	.011	.203	.065	.385	.010	.562	.057	.065	.005	.000	.270	
%RSD:	2.5	4.1	10.8	.5	25.7	16.9	.5	75.6	223.6	-104.6	7.9	
ZCOR:	1.1241	1.1571	1.2053	1.2156	1.4515	1.8372	1.2731	1.2037	1.4591	.0000	.0000	
KRAW:	.0161	.3114	.0057	1.0276	.0004	.1821	.7244	.0008	-.0004	.0000	.0000	
PKBG:	5.03	60.00	4.89	372.20	1.46	43.35	78.99	1.58	.87	.00	.00	
VOL%:	.000	1.135	.000	-.658	.000	36.111	.000	20.283	.000	.000	.000	
DEV%:	.0	.2	.0	.0	.0	.4	.0	20.3	.0	.0	.0	

Both Na, Si, K Change and Water By Difference Gives 3.4% H_2O

Water By Difference vs. FTIR

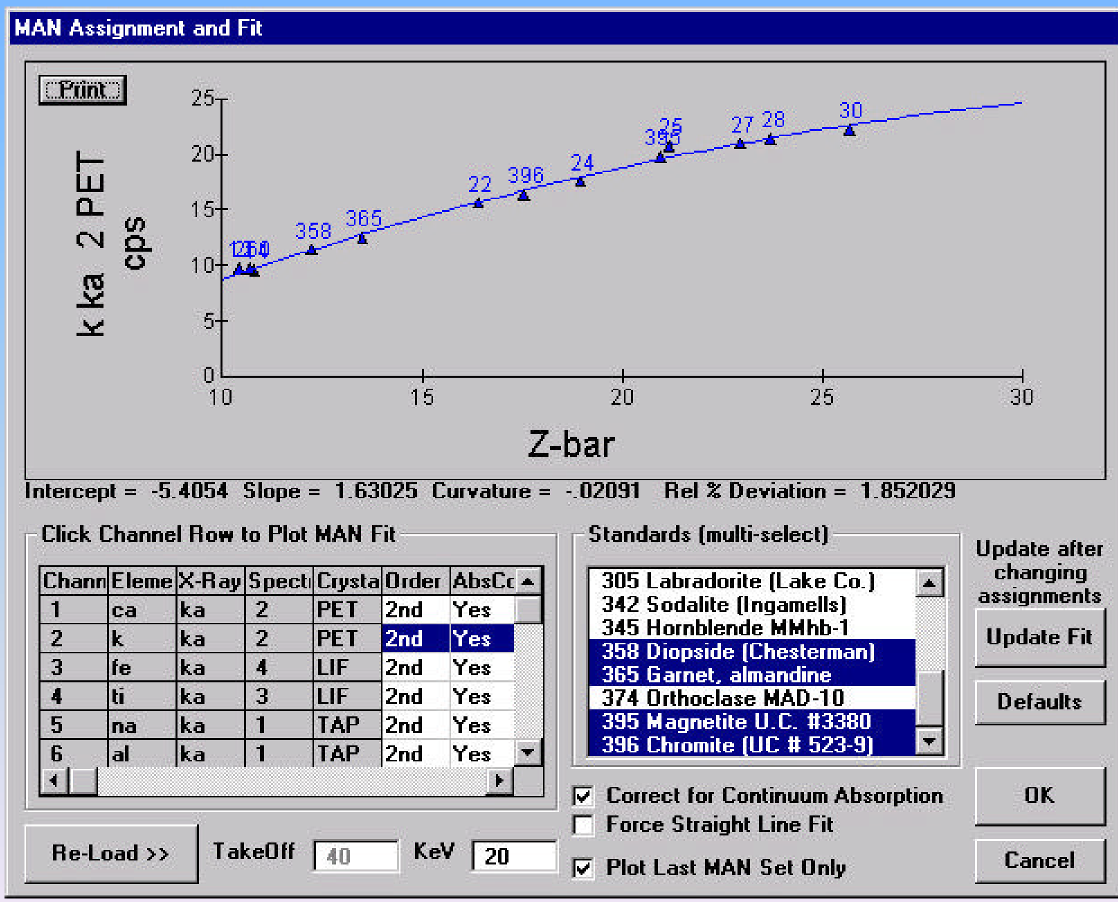


Comparison of melt inclusion water contents measured by FTIR in sub-micron melt inclusion water contents estimated as the difference between 100% and microprobe analysis totals or “water by difference” (WBD).

Solid diagonal line indicates 1:1 correspondence, dashed line is a linear regression fixed at the origin. Gray symbols show WBD water content before matrix correction of the analysis and black symbols show matrix-corrected WBD estimates.

From Roman, 2003

Minimize Analysis Time Using MAN Background Corrections

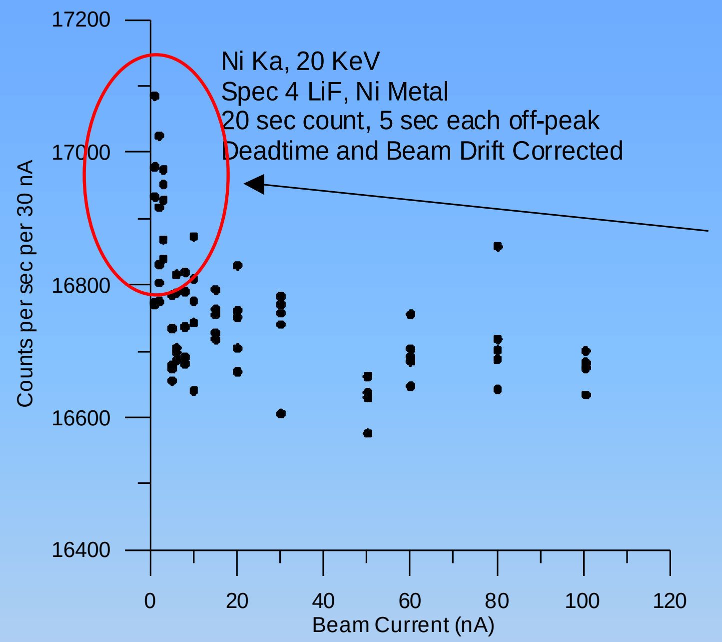


- Save Time! (t = $)
- Avoid Off-Peak Interferences
- Spectrometer Reproducibility
- Beam Sensitive Samples
- Quantitative Imaging

Instrument Effects

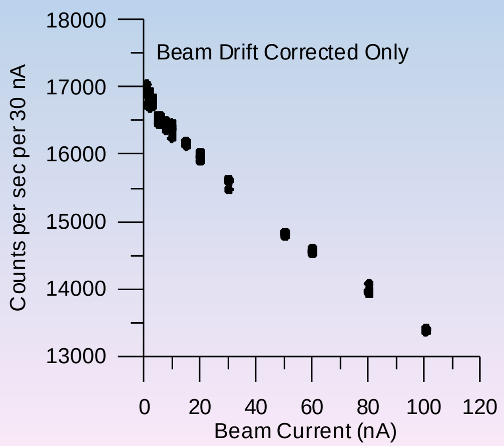
- Beam Drift/Deadtime Corrections
- Standard Drift Corrections
- Spectrometer Reproducibility

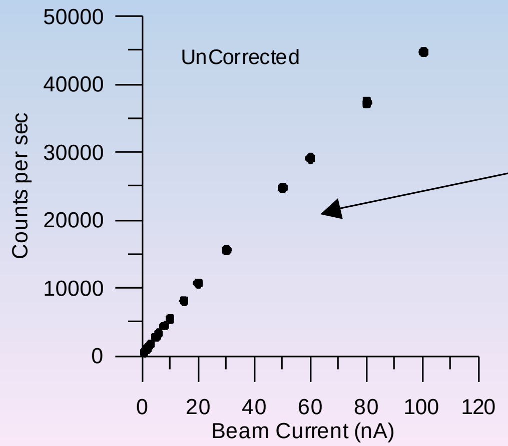
Beam and Deadtime Corrections



What is this?

Deadtime Effects After Beam Drift Correction

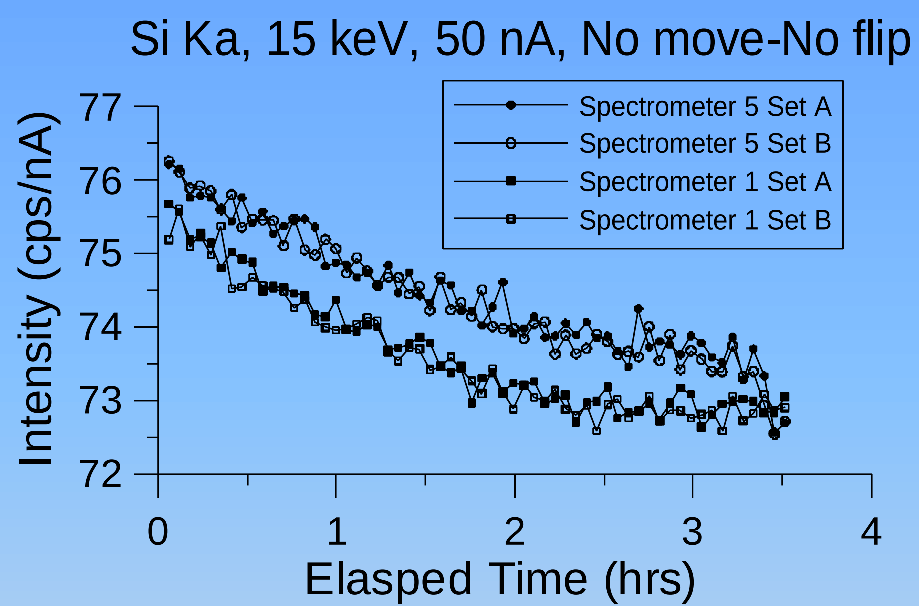


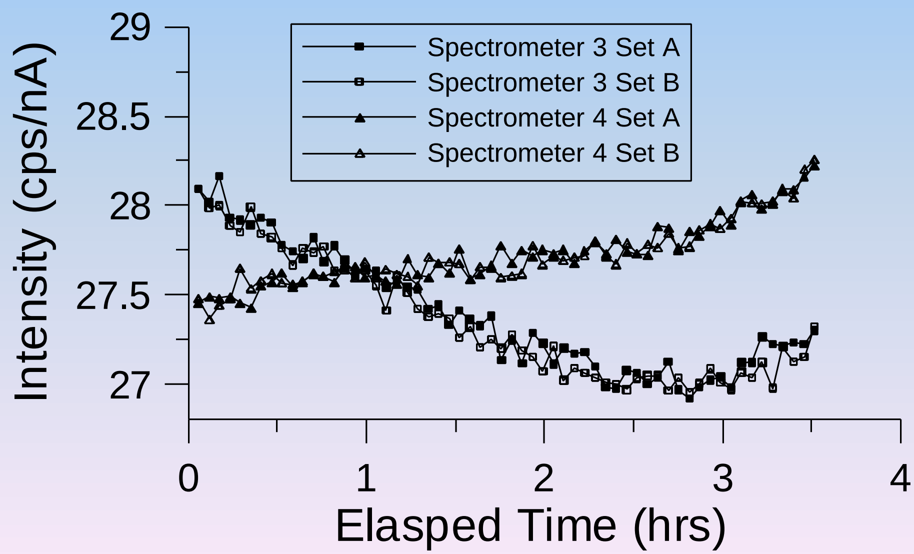


Raw data

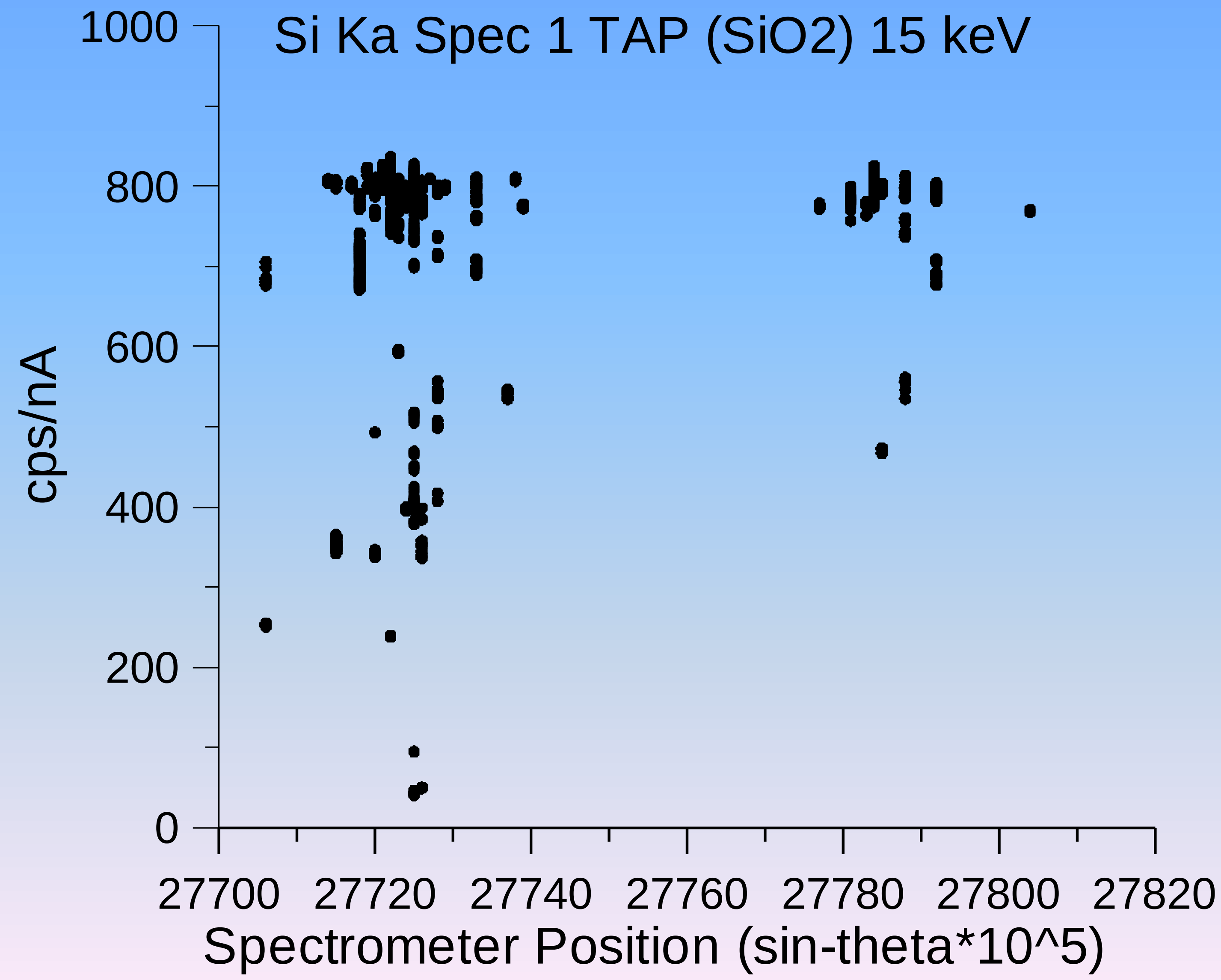
(Start Here)

Standard Drift

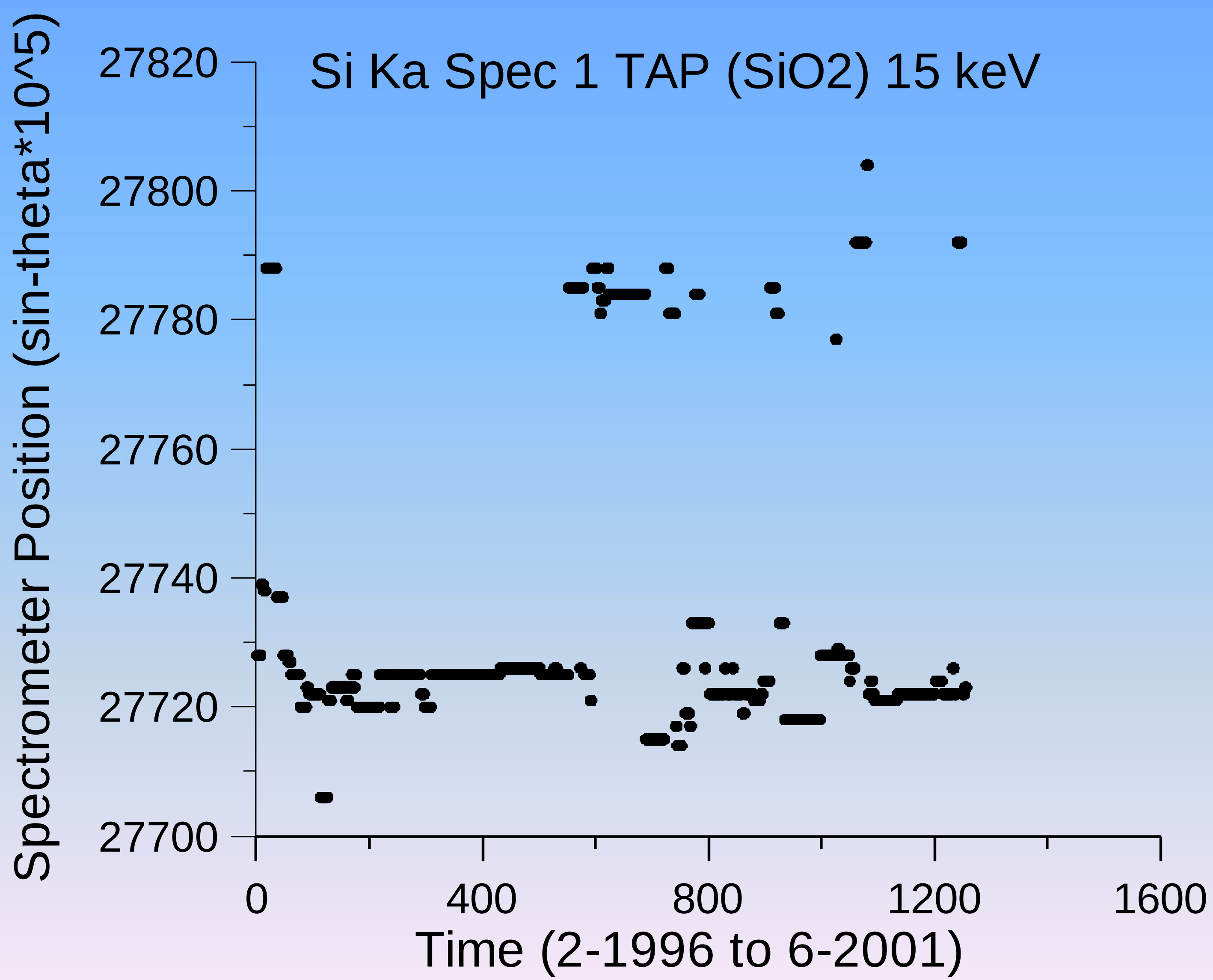




Spectrometer Reproducibility, UCB SX-51



Versus Time


Si Ka Spec 1 TAP (SiO2) 15 keV
Spectrometer Position (sin-theta*10^5)
27820
27800
27780
27760
27740
27720
27700
0
400
800
1200
1600
Time (2-1996 to 6-2001)

Sulfur in Silicate Glasses

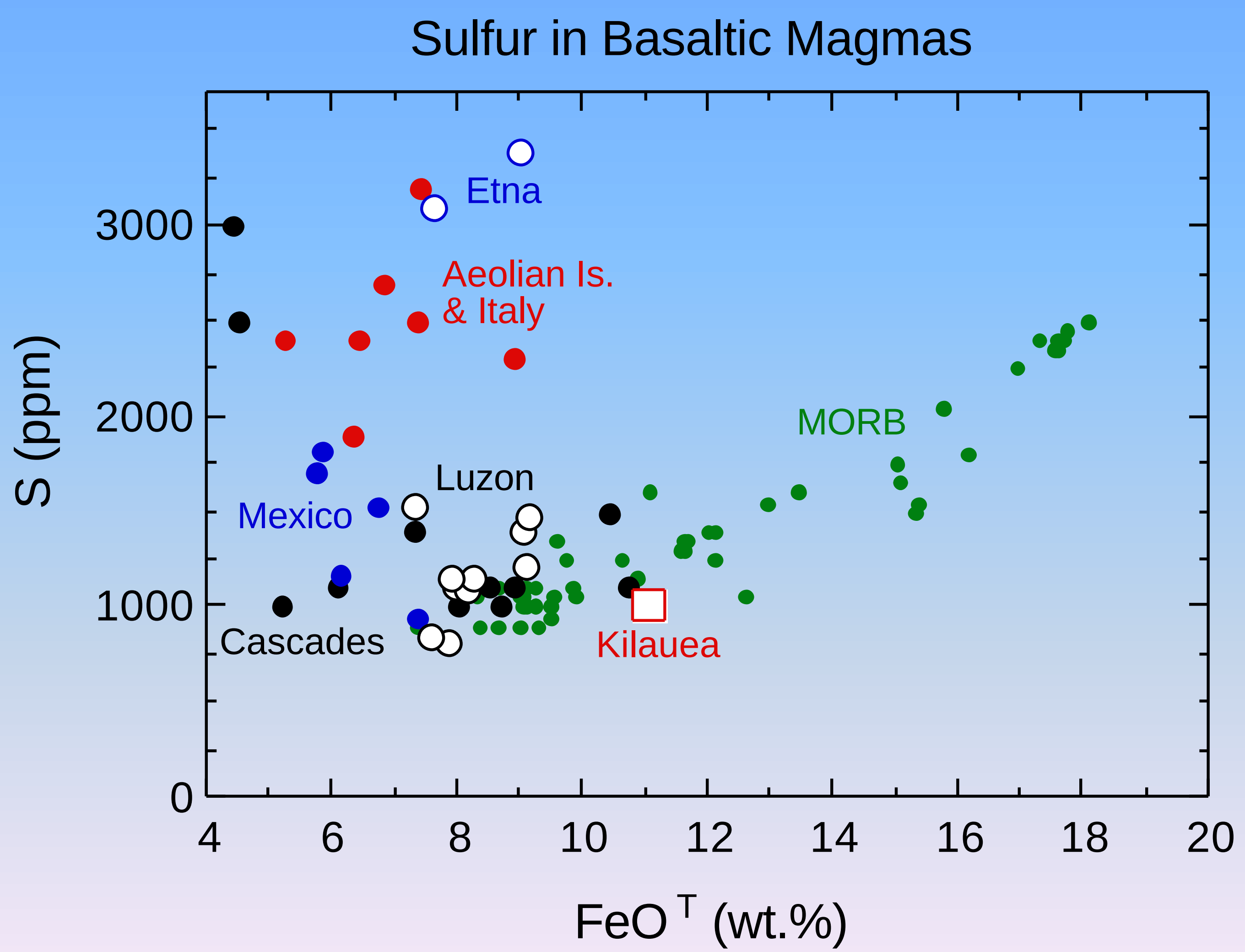
- Sulfur occurs in both oxidized (sulfate - S^{6+}) and reduced (sulfide - S^{2-}) forms in natural silicate glasses

- Spectroscopic (μXANES) evidence suggests that sulfite (S^{4+}) may also be present, but only about 15% of total sulfur

- The wavelength of S*K*α radiation in glass changes as a function of the mean oxidation state of sulfur

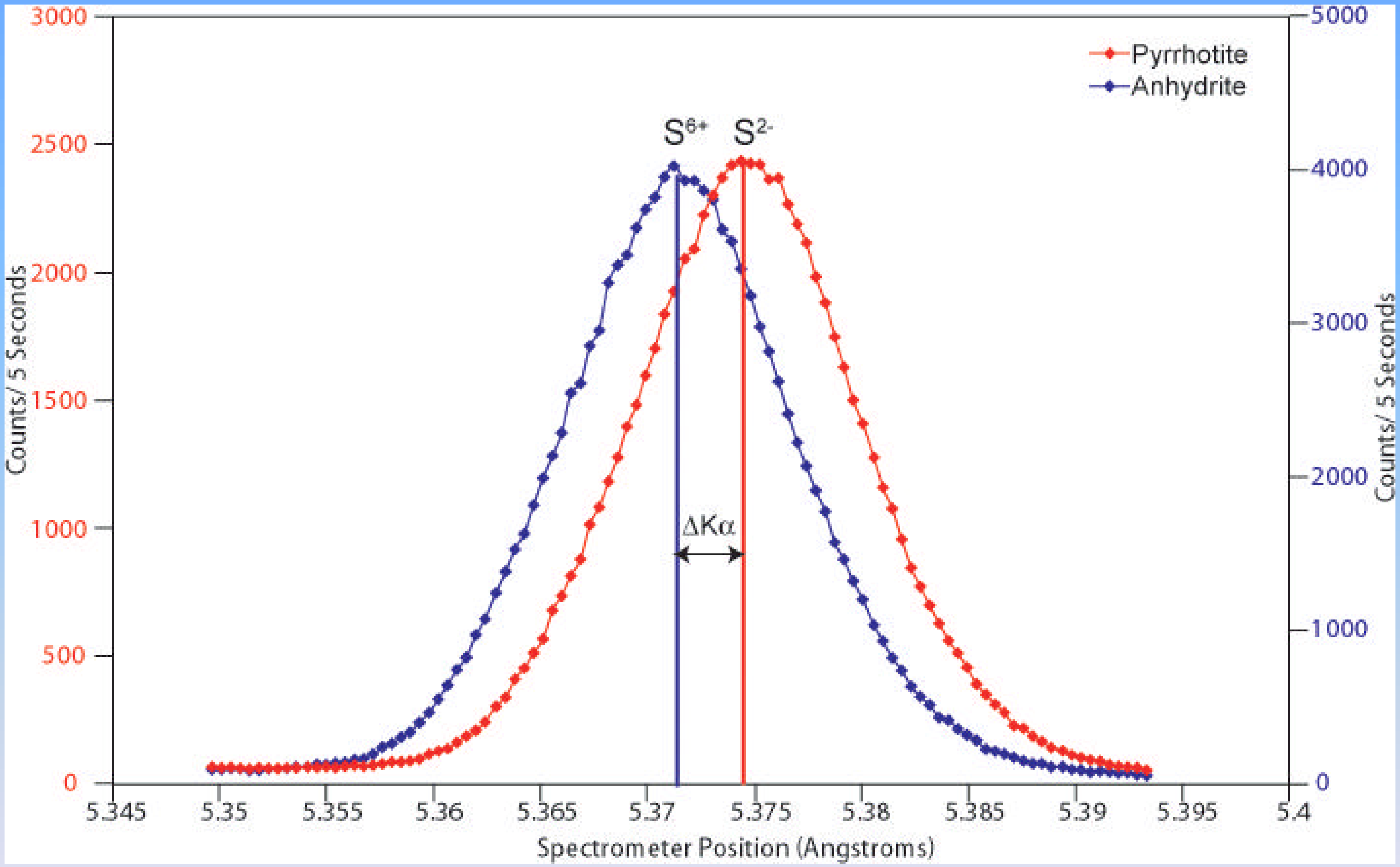
Kucha, 1989
Wallace, 1994
Brown, 1999

Trace Sulfur in Glasses



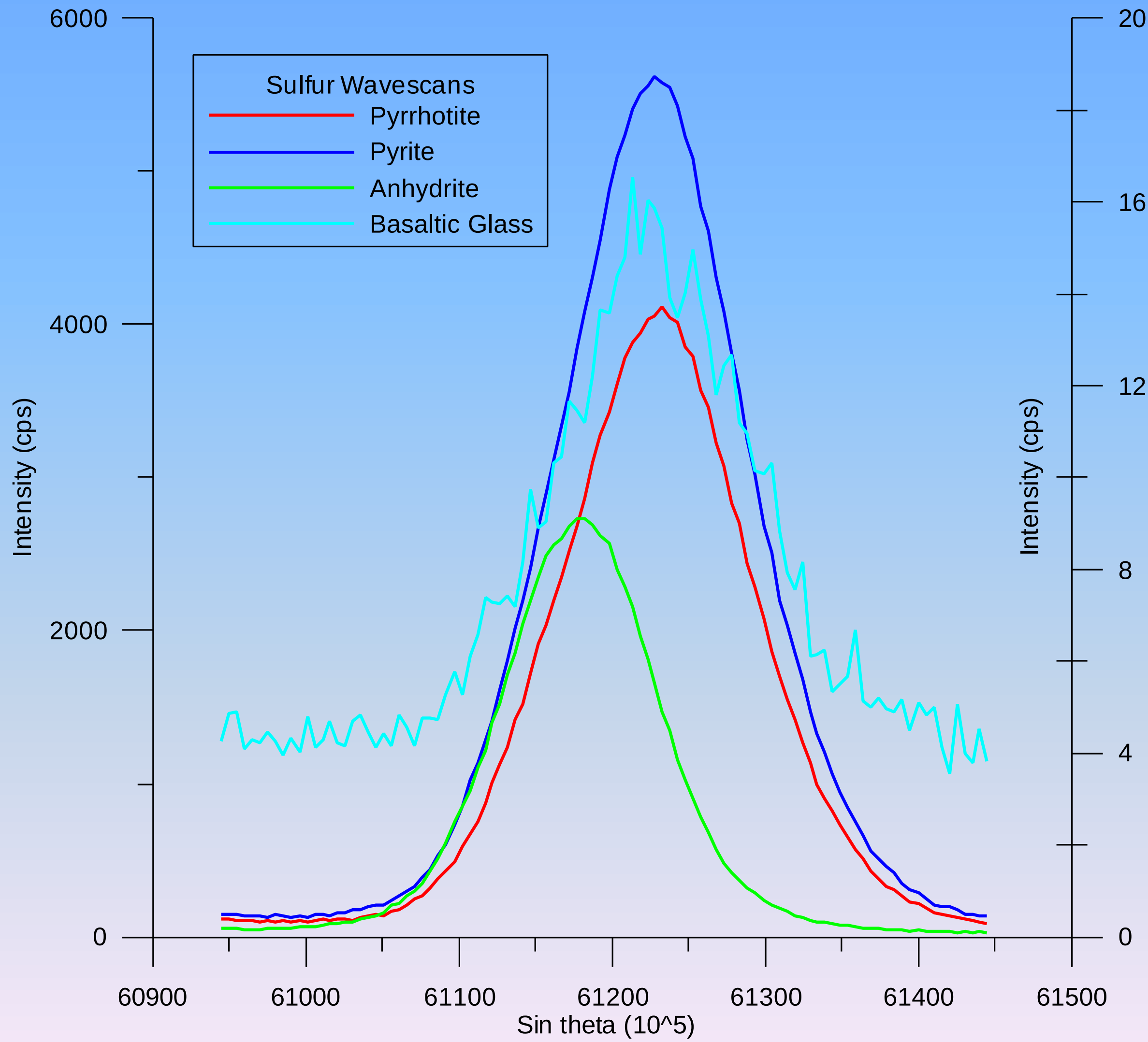
From Wallace

Sulfur Wavelength Shift



From Wallace

Peak Shifts for Sulfur Phases



Does the peak shape change also?

VG-2 glass S analysis (spectrometer re-peaked on each standard)

Primary Std	S weight percent (15 kev, 10 sec)
Anhydrite:	**.14452**
Pyrite:	**.14470**
Pyrrhotite:	**.13285 (assumed 50/50)**
Pyrrhotite:	**.14968 (Fe(1-x)S, where x=0.17) (from web database)**
Pyrrhotite:	**.14472 (Fe(1-x)S, where x=0.13) (from EPMA analysis of actual standard)**

Analysis Conditions

- Operating conditions: 15 kV accelerating voltage, 25-30 nA beam current, 10 μm beam diameter
- PET crystal
- Spectrometers: moved through a total range of 0.005 sin θ units in 100 steps of 0.00005 sin θ units per step
- Counting time: 20-40 s per step for glass samples; 5-10 s for standards

Pitfalls

- Leaving the electron beam in a single spot longer than about 15 minutes causes an 'apparent' increase in $\Delta\lambda(SK\alpha)$, i.e., oxidation
- Therefore the electron beam must be moved to a new spot after each step in the scan

Suggestions for Improved Accuracy

•Standards (use glass for glass)

•Matrix effects of H2O (iterated re-calculation)

•Re-peaking vs re-standardizing (drift corrections and reproducibility)

•MAN backgrounds for speed (minimize damage)

•Intensity changes over time ("volatile" corrections, matrix effects)

•Acquisition parameters (keV, beam focus, current: linear regime)