



Al, Mg, Si and Na Ka Peak Shifts in Common Silicate and Oxide Minerals: Relevance to Achieving the Goal of 1% Accuracy in EPMA

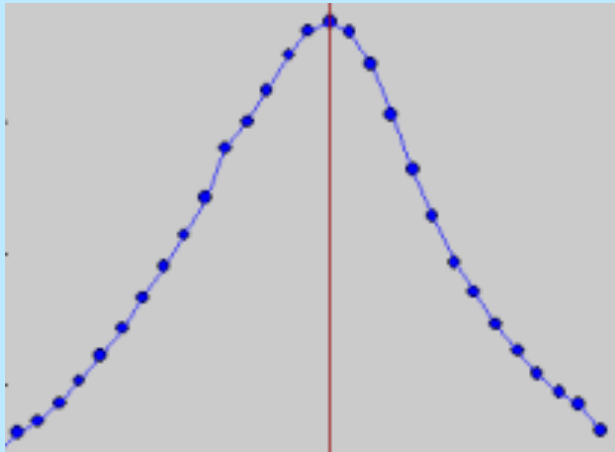
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A veteran prober had problems with silicates ... we narrowed down the problem to issues related to peaks of standards and unknowns:

- 1) How wide are the peak tops?**
- 2) Are there chemical peak shifts?**
- 3) Is there a problem with our peaking procedure?**



We started with Si and Al $K\alpha$... and worked up to Mg and Na $K\alpha$

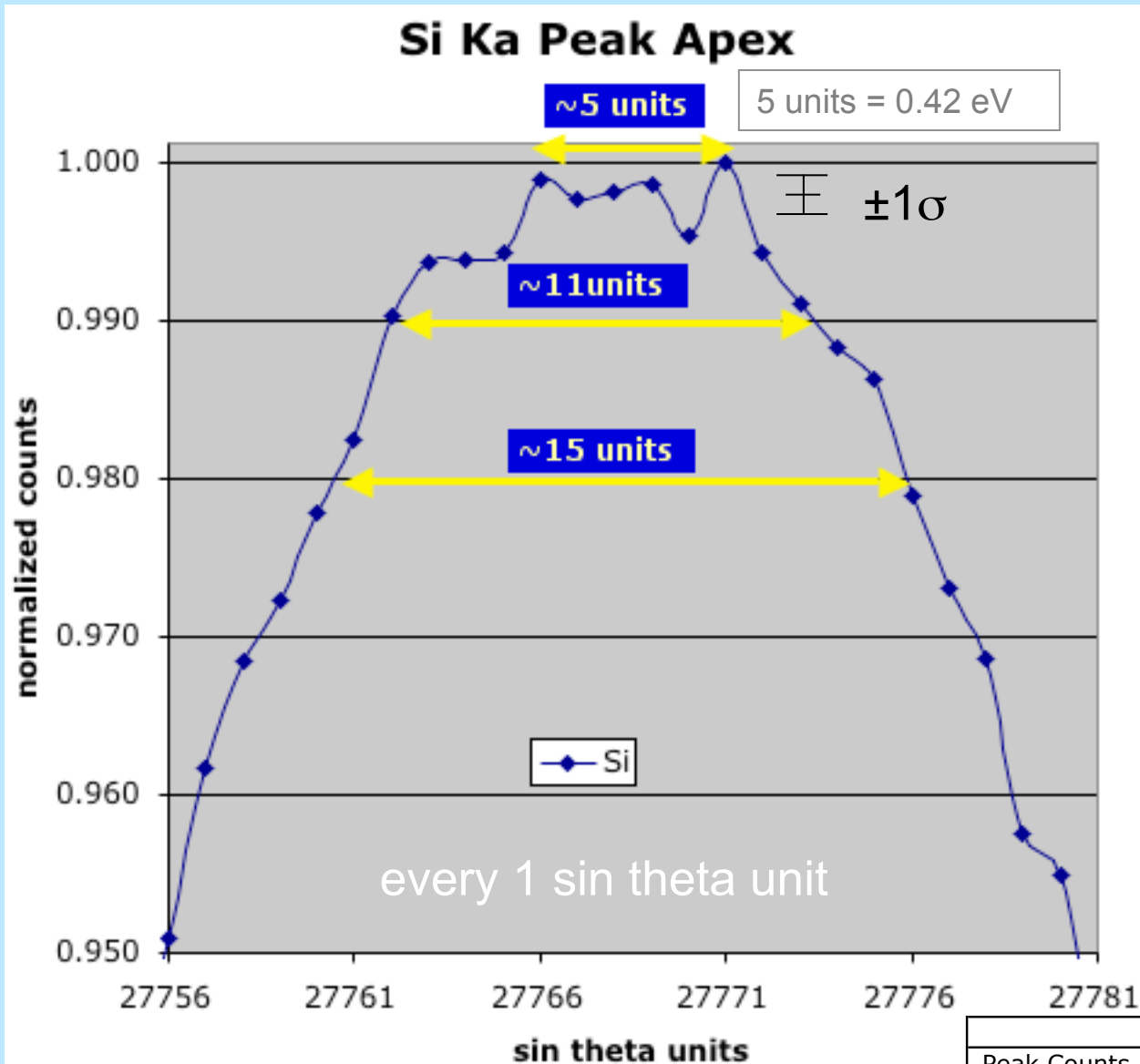
Answers 1. 5-10 sin theta units 2. Yes 3. Yes



Peak Widths

Consider the Si K_{α} Peak

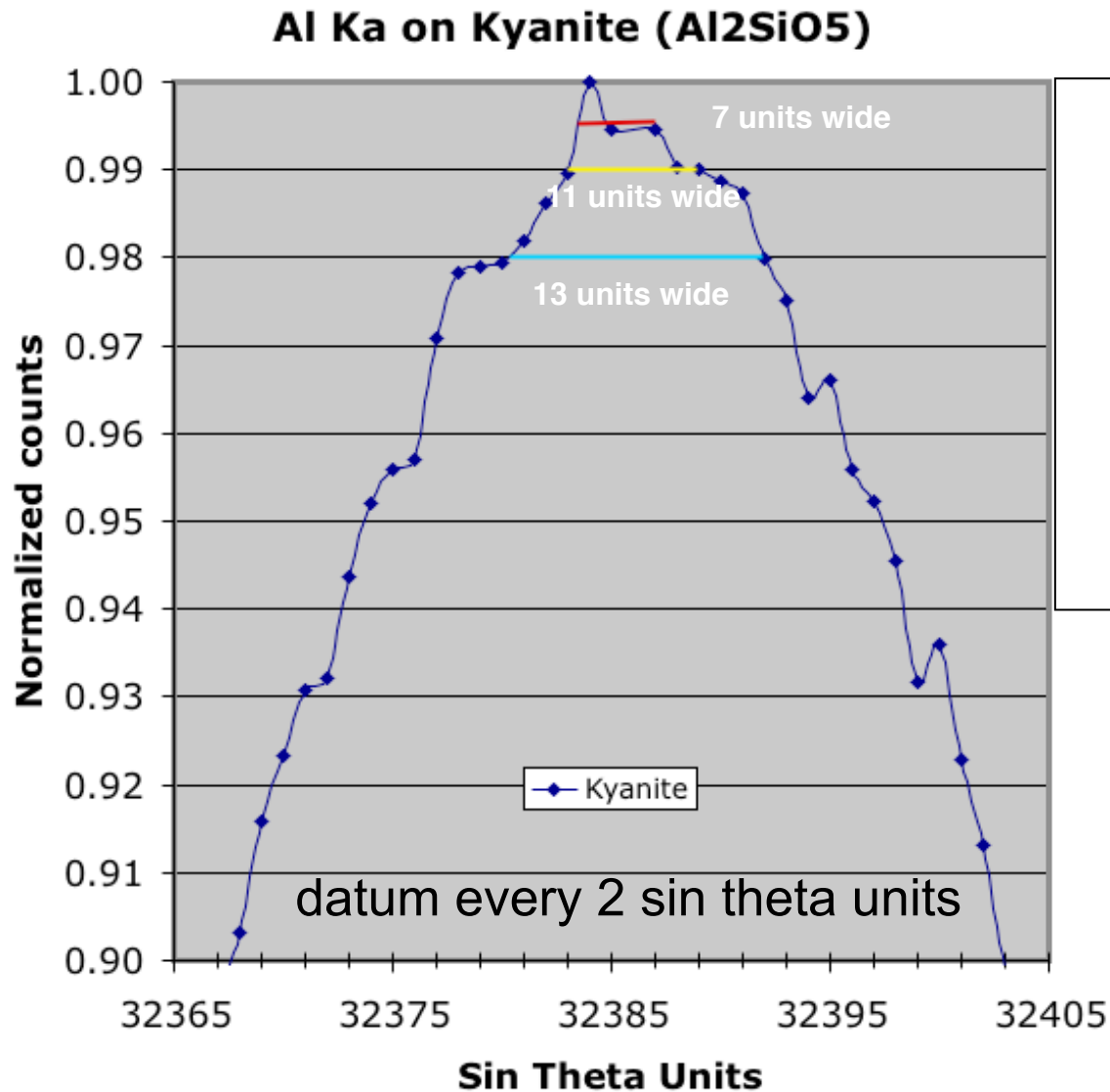
Precise Peak:
4 minutes of scanning



TAP, 15 keV, 20 nA, 10 sec/channel, Si metal

	Peak Counts	Normalized
	493882	1.0000
1 sigma	703	0.0014
2 sigma	1406	0.0028
3 sigma	2108	0.0043

Al K_{α} Peak Top Width: similar to Si — except some wider at top



Conclusion 1

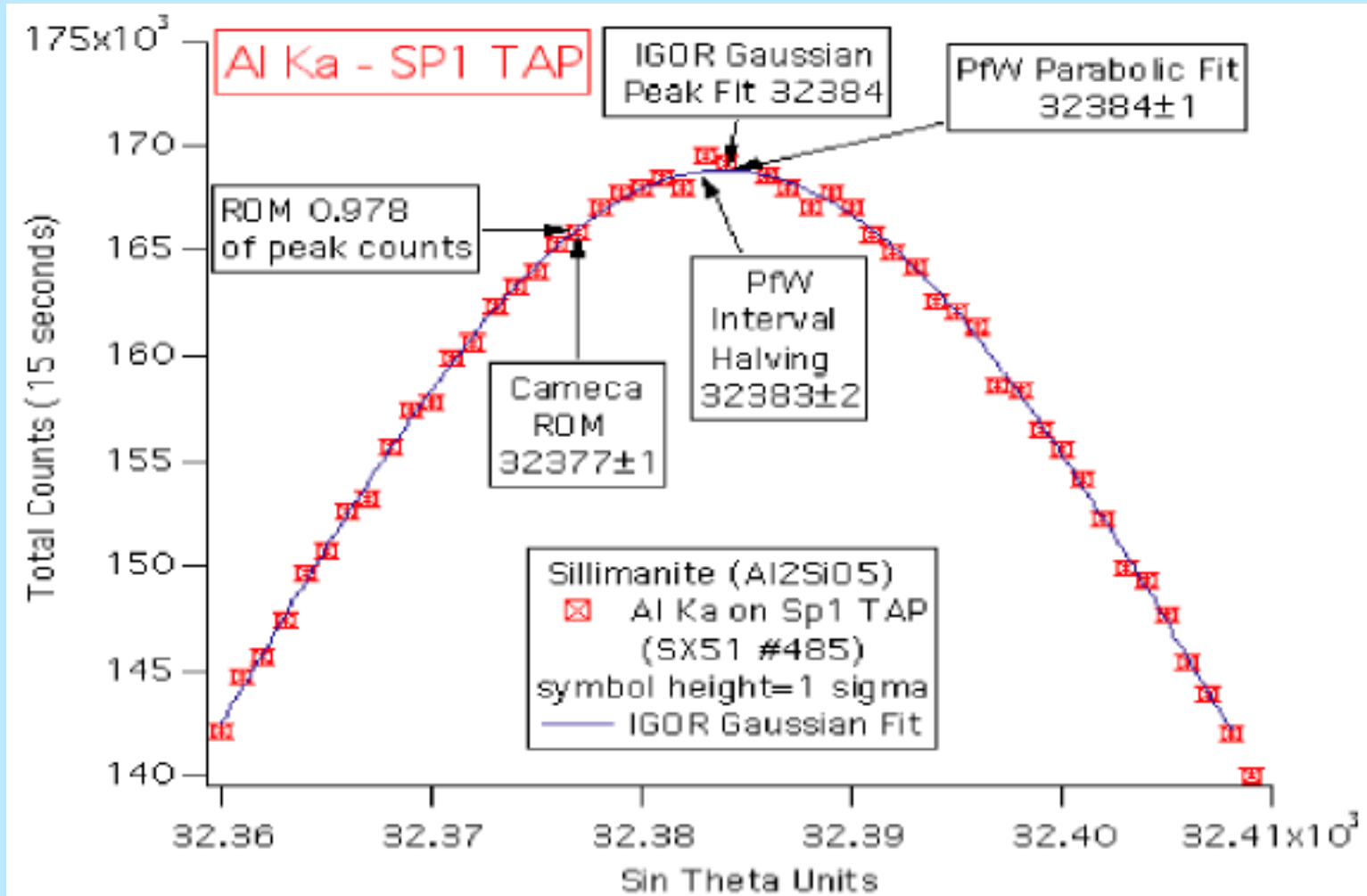
Si and Al K_{α} Peak Widths on TAP:

- Many peaks ~ 5 sin theta units wide
- For correctly centered peak position, $> 2-3$ sin theta unit shift will lose counts, and
 - For 5-6 units shift, at least 1% error
 - For 7-8 units shift, at least 2% error
 - And these errors would be doubled for oxide values (oxygen by stoichiometry)

Results of Automated Al K_{α} Peaking Options

ROM very reproducible: 10 measurements, s.d. of 1.2, range 32374-8

...and sometimes very wrong



We requested a modification of the peaking procedure in Probe for Windows ...

Peak Center

Elements to Peak (multi-select)

- Mg ka Spectro 1 TAP
- Si ka Spectro 4 TAP
- Mn ka Spectro 5 LIF
- Fe ka Spectro 5 LIF
- Ca ka Spectro 3 PET
- Ni ka Spectro 5 LIF

Peak Center Method

- Interval Halving
- Parabolic Fit
- ROM Based
- Manual (Pre/Post Scan Only)

Skip P/B Check

Peak Center Options

- Display Spectrometer Pre-Scan for Confirmation
- Display Spectrometer Post-Scan for Confirmation
- Move To On Peaks If Selected

Double-click element to move to spectrometer peak position

Plot Selected Peak Center

OK

Cancel

Al ka TAP

Position: 42843.8

Angstrom: 3.74853

Counts: 510.622

Peak Center Start Position Selection

Select Start Peaking Position for Al ka on spectro 1 TAP

Use the scroll bar to select the starting peak center position. Click OK when ready or click Cancel to skip this element.

32755.6

Here is a post-scan on Al $K\alpha$, showing that the peak center returned by ROM was several units off the true peak center.

Operator now has final say over peaking

Chemical Peak Shifts

Have been recognized since the origins of x-ray spectroscopy in the 1920s,

e.g., Cl and S $K\beta$ peaks

(M-L transitions: M shell electrons =
valence electrons)

Al K_{α} Chemical Shifts

... have been recognized for ~50 years

White, McKinstry & Bates, 1959, *Advan. X-ray Analysis*

Al K_{α} Shift vs coordination relative to Al metal:

Feldspar (IV): -0.07;

Sillimanite (IV+VI): -0.11;

Kyanite (VI): -0.12

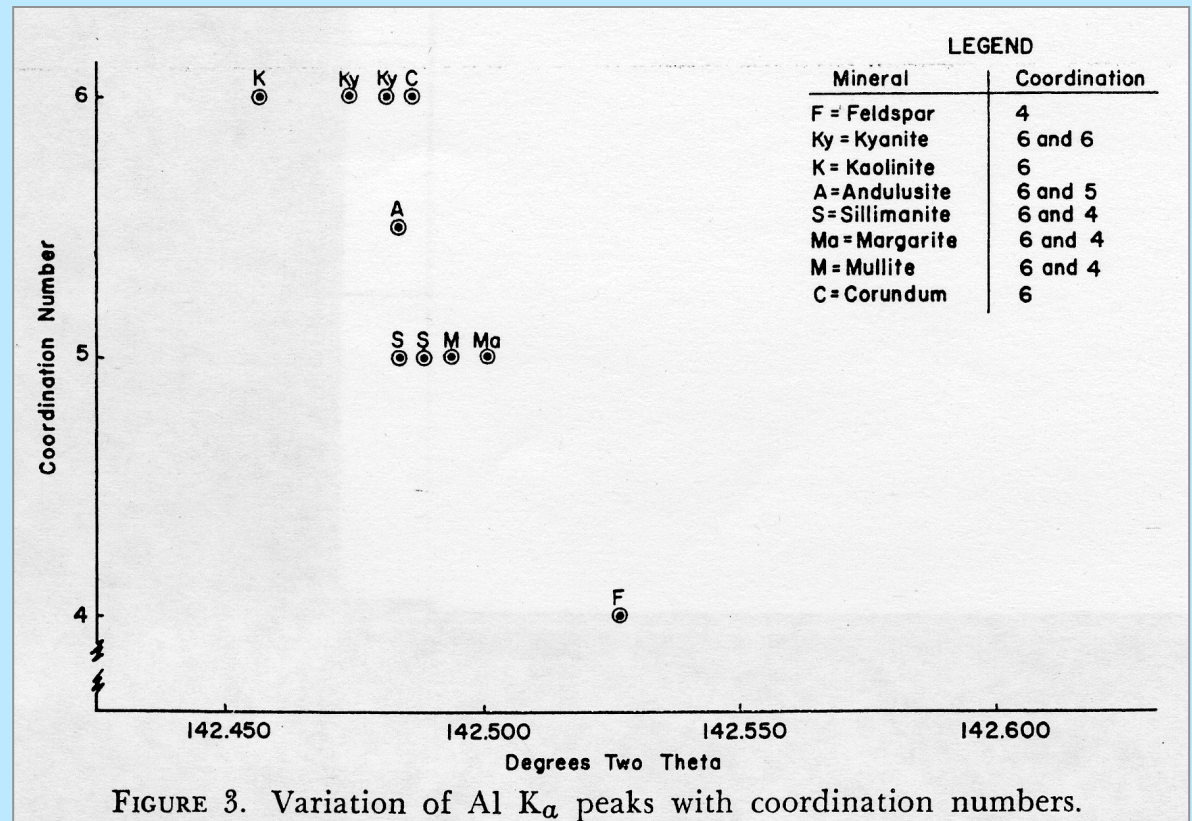
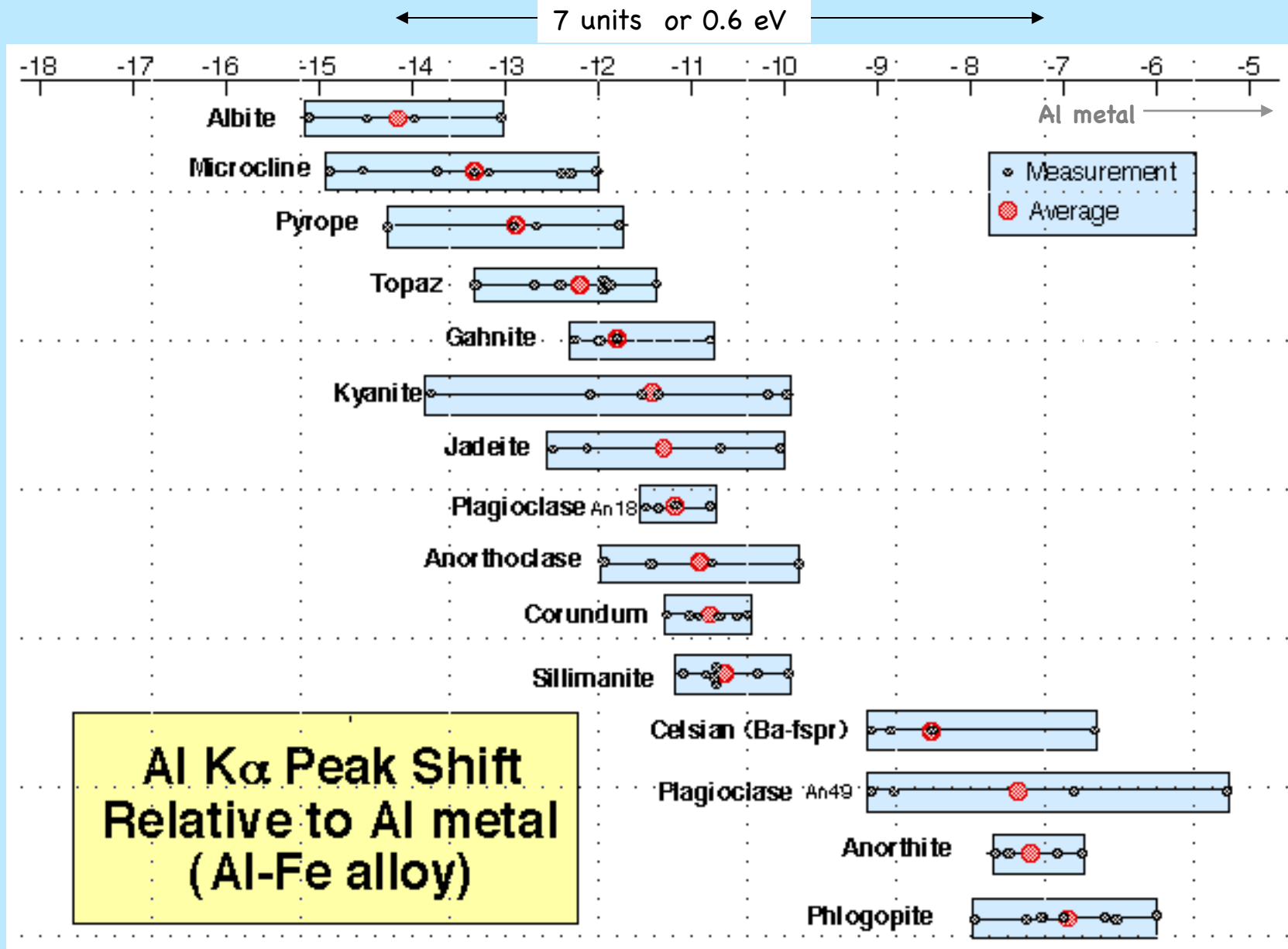


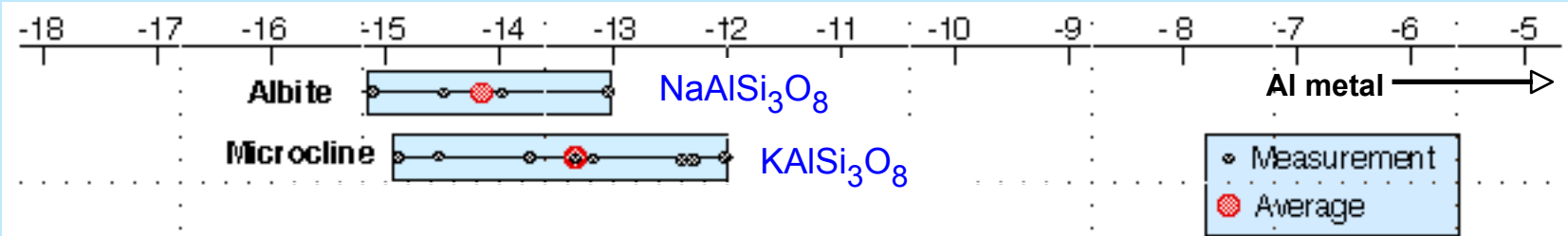
FIGURE 3. Variation of Al K_{α} peaks with coordination numbers.

Also Day, 1963, *Nature*; Wardle and Brindley, 1971, *American Mineralogist*

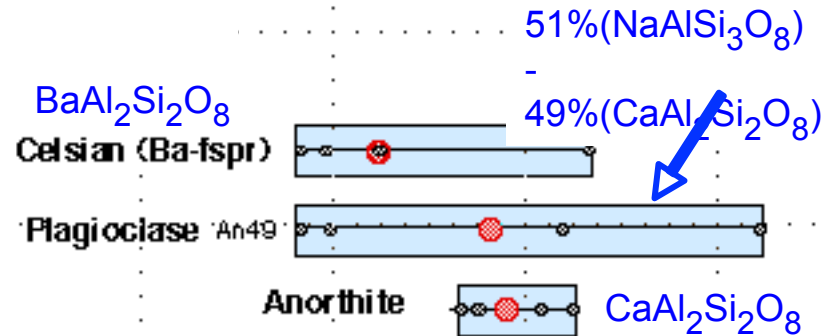
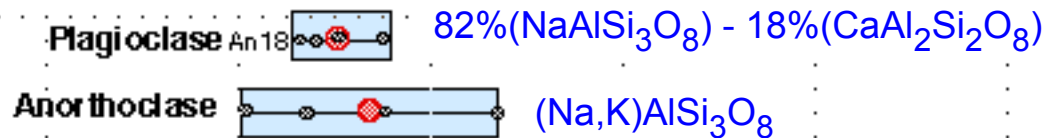
Al K_{α} Peak Shifts on UW SX51



Al K_{α} Peak Shifts - Feldspars Only



White and Gibbs, 1969, Am. Min., noted that K-feldspar had the greatest Al K_{α} peak shift relative to Al metal (and sanidine more than microcline).



**Al K_{α} Peak Shift
Relative to Al metal
(Al-Fe alloy)**

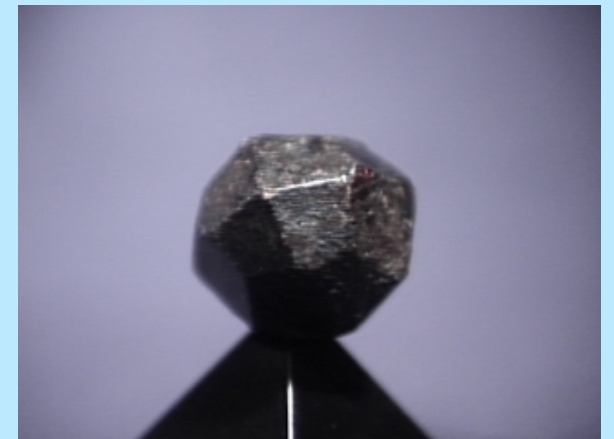
Al K_{α} Peak Shifts

		Al Ka Peak Shift Relative to Al-Fe Alloy							
Coord	Mineral	Sp1 Ave	Std Dev	n	Mineral	Sp4 Ave	Std Dev		Coord
4	Albite	-14.2	0.7	4	Albite	-18.0	0.7		4
4	Microcline	-13.3	1.0	8	Pyrope	-16.5	1.0		6
6	Pyrope	-12.9	0.9	4	Anorthoclase	-16.2	0.9		4
6	Topaz	-12.3	0.7	7	Alunite	-16.2	2.0		
6	Gahnite	-11.8	0.5	4	Microcline	-15.8	0.8		4
	Alunite	-11.6	1.1	4	Topaz	-15.1	0.5		6
6	Kyanite	-11.5	1.2	7	Plag - An18	-14.9	0.4		4
6	Jadeite	-11.3	1.0	4	Gahnite	-14.4	0.7		6
4	Plag - An18	-11.2	0.3	4	Jadeite	-13.9	0.5		6
4	Anorthoclase	-11.0	0.8	4	Kyanite	-13.8	0.7		6
6	Corundum	-10.8	0.3	7	Corundum	-13.4	0.5		6
6+4	Sillimanite	-10.7	0.3	7	Sillimanite	-12.8	1.0		6+4
4	Celsian	-8.5	1.0	4	Celsian	-11.7	1.1		4
4	Plag - An49	-7.5	1.6	4	An49	-10.3	1.2		4
4	Anorthite	-7.4	0.4	4	Anorthite	-9.9	1.0		4
4	F Phlogopite	-7.0	0.7	7	F Phlogopite	-9.8	1.4		4

Two independent measurements, very similar trends ...
 and not a simple function of Al coordination
 (e.g., consider the range in feldspars)

Al K_{α} Peak Shifts in Garnet

Garnet Type	Shift	Std Dev
YAG	-7.3	0.2
Almandine	-10.9	0.2
Spessartine	-11.5	0.2
Grossular	-12.2	0.1
Pyrope	-15.7	0.5



Si K_{β} , K_{α} Chemical Shifts: Historical

White, McKinstry and Roy, 1962, GSA Abstract

Measured major Si K_{β} shifts in SiO_2 relative to Si metal:
Stishovite (IV): -0.010 \AA ; Quartz, cristobalite (VI): -0.015 \AA

though no Si K_{α} Shift between IV and VI seen

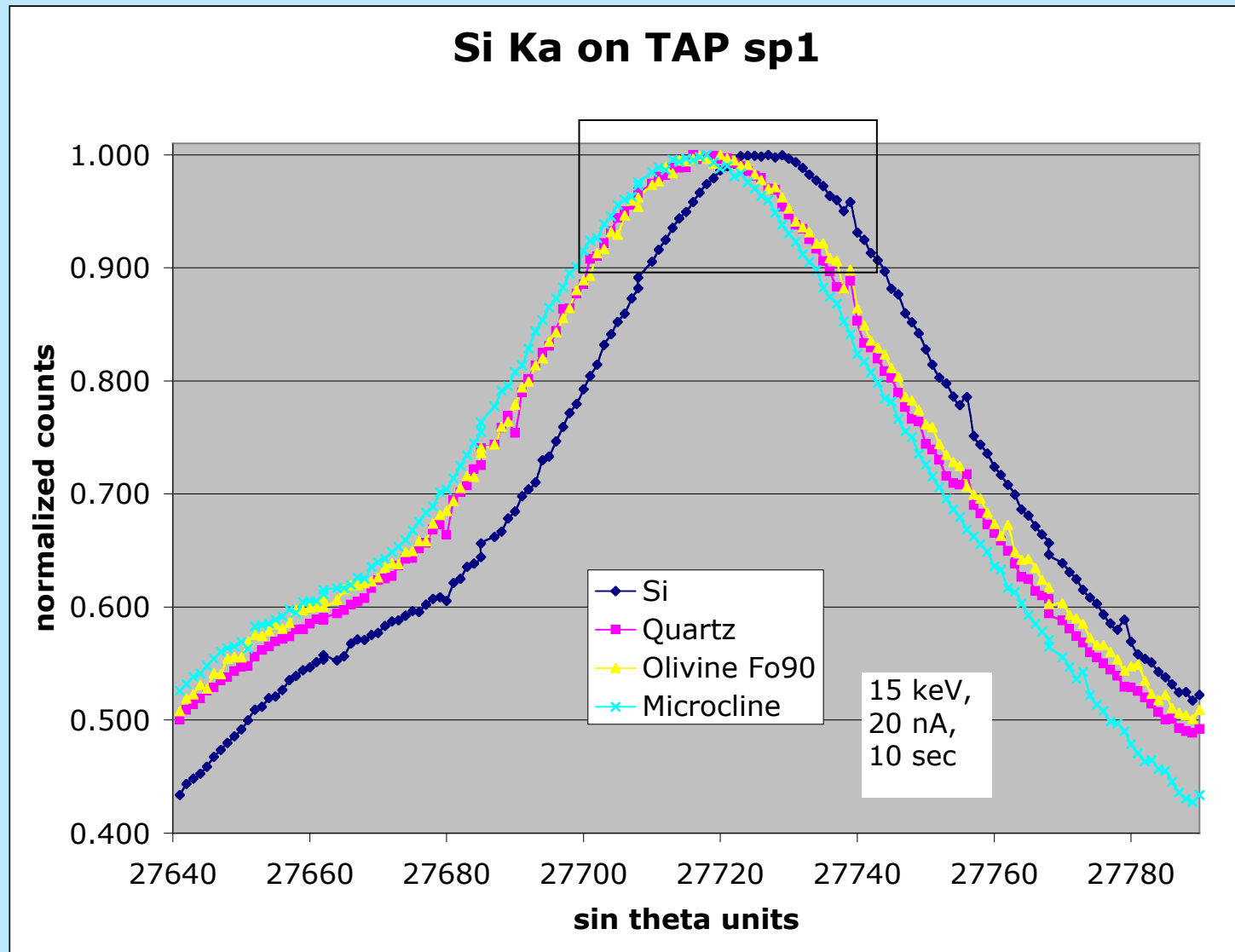
Kaufman and Moll, 1966, Advances X-ray Analysis

Examined Si K_{α_1} , K_{α_3} , K_{α_4} and K_{β} for Si metal and 10 common silicate minerals; found differences between silicates for all K lines but NOT K_{α_1}

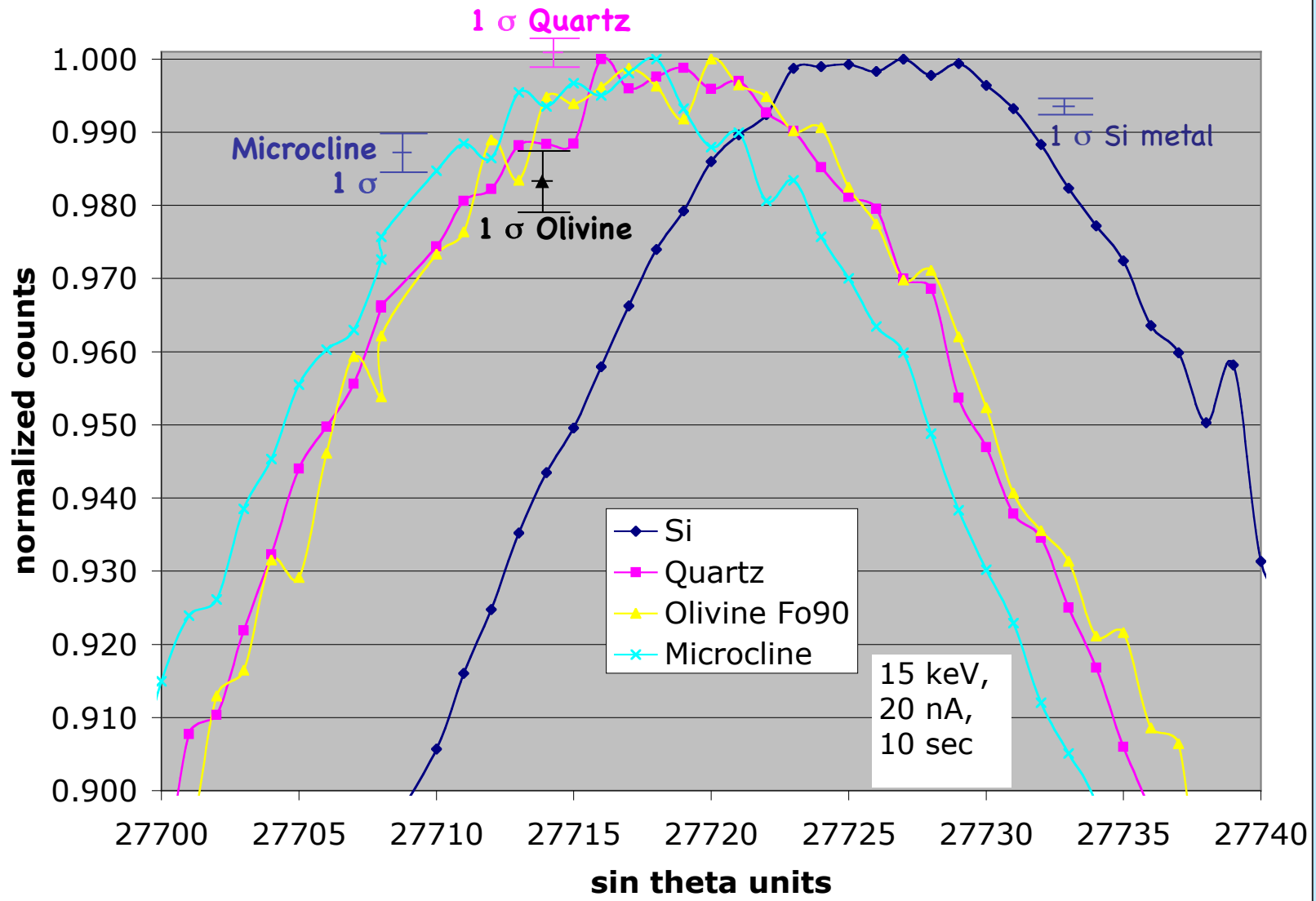
Table II. Si K Lines from Silicon Metal and Silicates

Material	Line							
	K_{α_1}		K_{α_3}		K_{α_4}		K_{β}	
	λ	I	λ	I	λ	I	λ	I
Si	7.1262	1000	7.0803	66	7.0713	41	6.7506	28
SiO_2	7.1244	1000	7.0765	52	7.0673	54	6.7666	30
$\text{Mg}_2\text{Si}_2\text{O}_6$	7.1244	1000	7.0768	50	7.0680	53	6.7617	25
CaSiO_3	7.1244	1000	7.0770	51	7.0680	53	6.7594	23
KAlSi_2O_6	7.1244	1000	7.0772	52	7.0680	56	6.7649	20
$\text{CaMgSi}_2\text{O}_6$	7.1244	1000	7.0770	50	7.0682	53	6.7611	25
KAlSi_3O_8	7.1244	1000	7.0765	50	7.0678	54	6.7644	22
$\text{NaAlSi}_3\text{O}_8$	7.1244	1000	7.0766	51	7.0677	53	6.7640	24
$\text{CaAl}_2\text{Si}_2\text{O}_8$	7.1244	1000	7.0763	49	7.0677	51	6.7614	25
Fe_2SiO_4	7.1244	1000	7.0773	50	7.0680	53	6.7630	23
$(\text{Na, K})(\text{Al, Si})_2\text{O}_4$	7.1244	1000	7.0763	52	7.0675	56	6.7627	25

Si K_{α} Peak Shifts - UW SX51 - 2004



Si Ka on TAP sp1



TAP: Si Ka Peak Shift Relative to Si Metal									
mineral	Sp1	Ave	Std Dev	n		mineral	Sp4	Ave	Std Dev
Microcline	-10.6		0.7	4		Microcline	-14.0		0.6
Quartz	-8.0		0.2	4		Quartz	-9.1		0.8
Enstatite	-6.8		0.8	4		Topaz	-8.0		1.3
Anorthite	-6.8		0.5	4		Plagioclase An49	-8.0		1.4
Andradite	-6.8		0.6	4		Wollastonite	-7.9		0.8
Diopside	-6.8		0.8	4		Anorthite	-7.8		0.7
Topaz	-6.7		1.3	4		Hornblende	-7.7		0.6
Wollastonite	-6.5		0.5	4		Enstatite	-7.6		0.6
Hornblende	-6.3		0.2	4		Andradite	-7.6		1.0
Olivine-Fo90	-5.8		0.9	4		Diopside	-7.2		0.9
Plagioclase An49	-5.6		1.2	4		Olivine-Fo90	-6.8		0.7

A check

Translating the above data as Ka shifts for quartz:

Spectro1 = 0.5 ± 0.1 eV; Spectro4 = 0.6 ± 0.1 eV

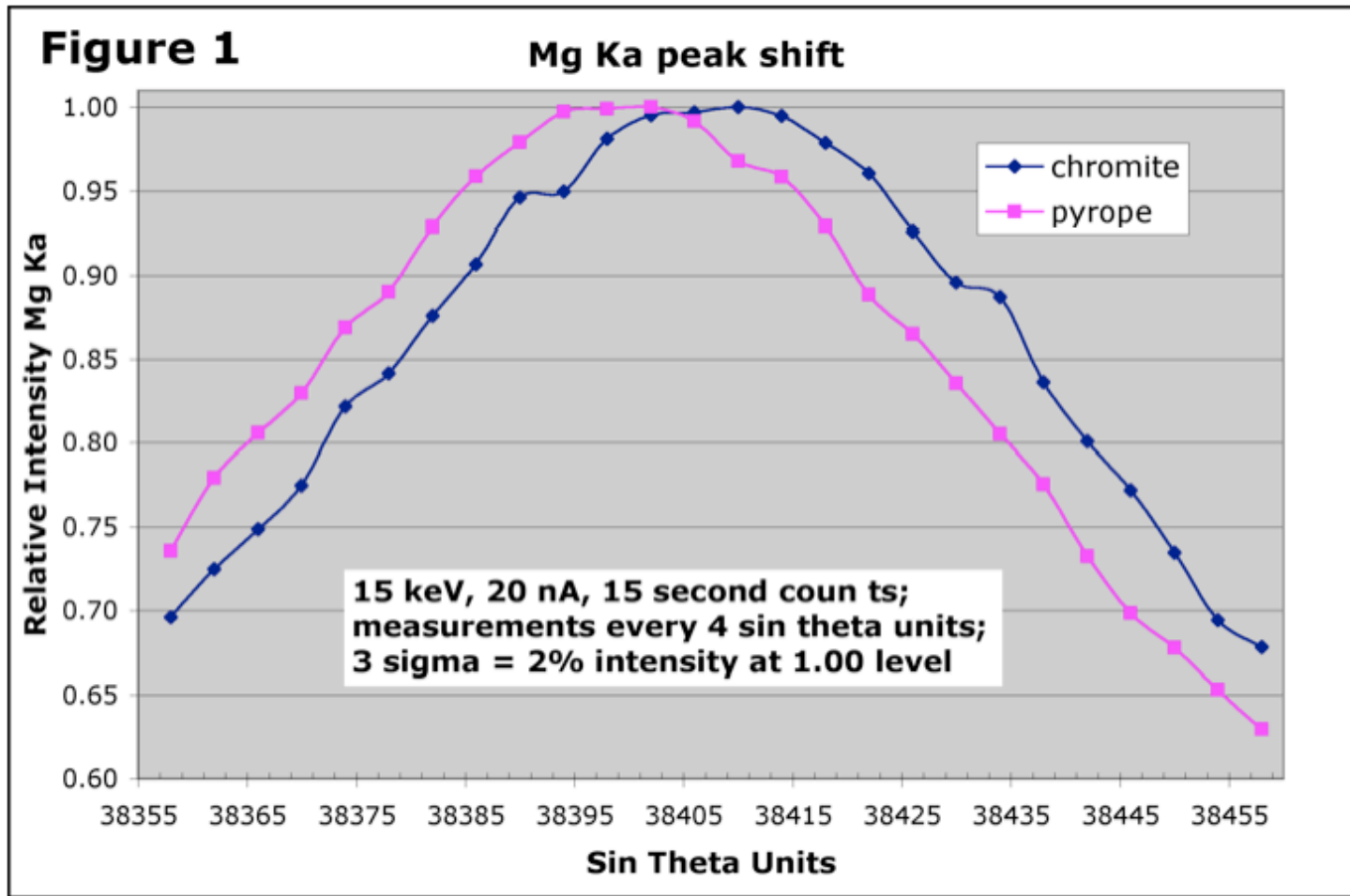
Compare Above With:

Si Ka shifts of Quartz by HRXFS (high resolution x-ray fluorescence spectroscopy)

- Okura et al (1990 Spectrochimica Acta) α -quartz 0.655 eV
- Liu et al (2004 Physical Review B) "SiO₂" 0.62 eV

**Implication: there is a 0.7 - 0.9 eV shift for microcline Si Ka relative to Si metal,
-- And one should NOT peak Si on K-feldspar for plagioclase.**

Mg K_{α} Peak Shifts:



Mg K α Peak Shifts:

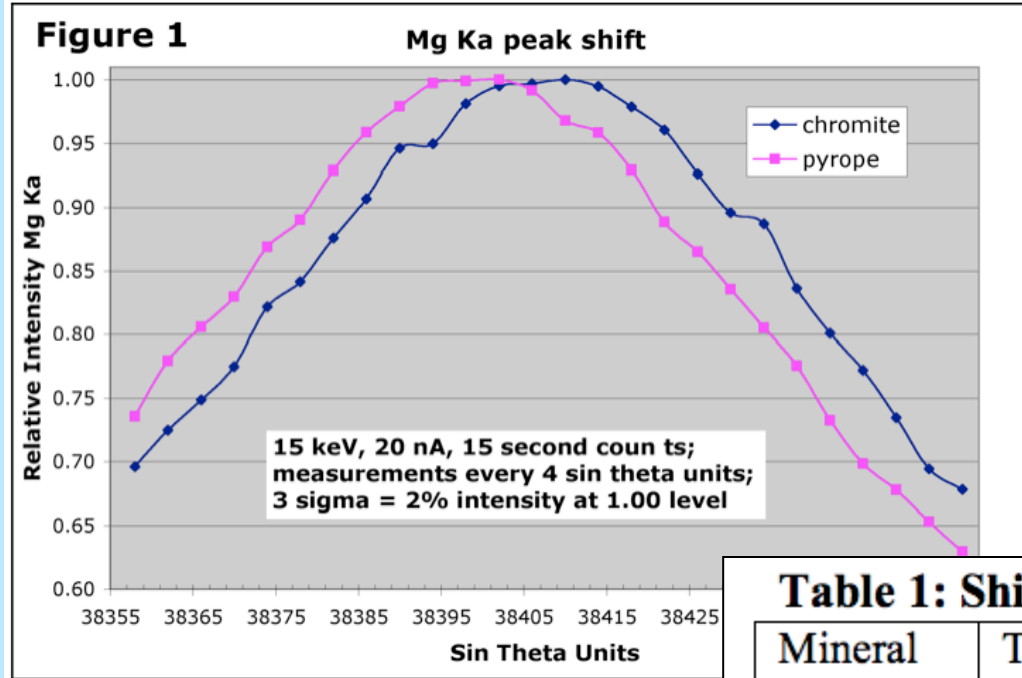


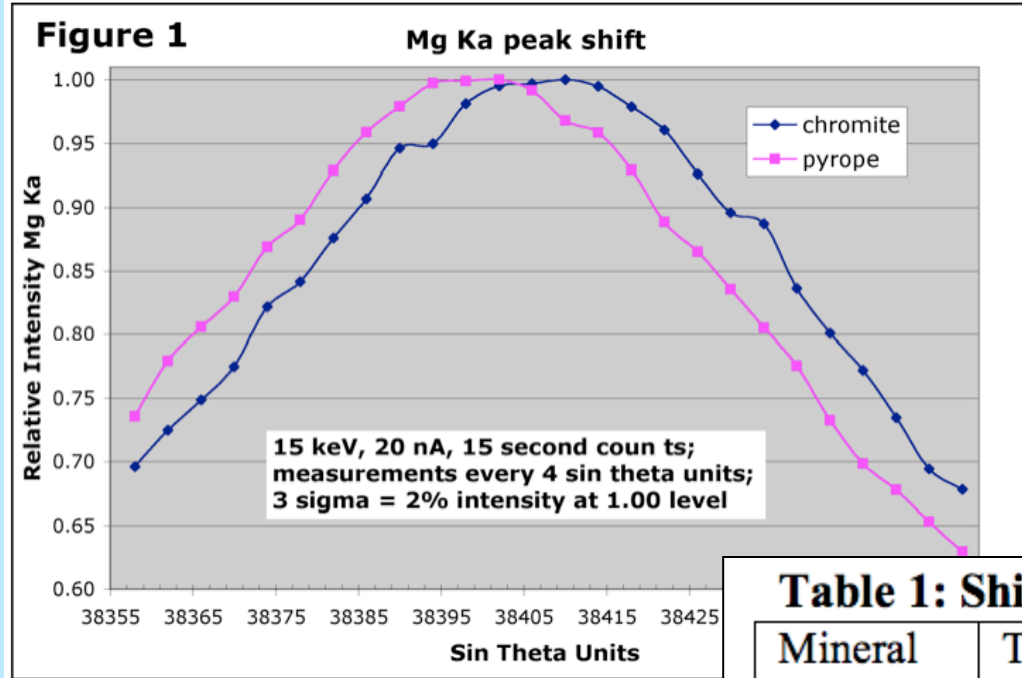
Table 2:

Mg K α Peak	Relative Counts on Pyrope	Relative Counts on Chromite
Pyrope Peak	1.000	0.968
Chromite Peak	0.956	1.000

Table 1: Shift in Mg K α

Mineral	Type	Shift	Std Dev
Chromite	Spinel	-3.6	0.6
MgAl ₂ O ₄	Spinel	-5.1	0.5
Kaersutite	Amphibole	-5.8	0.8
MgO	Oxide	-6.0	0.5
Enstatite	Pyroxene	-8.4	0.8
Diopside	Pyroxene	-8.7	0.7
Fo ₉₀	Olivine	-8.9	0.6
Pyrope	Garnet	-13.3	0.7

Mg K α Peak Shifts:



Mg Kα Peak	Relative Counts on Pyrope	Relative Counts on Chromite
<u>Pyrope Peak</u>	1.000	0.968
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Mineral	Type	Shift	Std Dev
<u>Chromite</u>	<u>Spinel</u>	-3.6	0.6
<u>MgAl₂O₄</u>	<u>Spinel</u>	-5.1	0.5
<u>Kaersutite</u>	<u>Amphibole</u>	-5.8	0.8
<u>MgO</u>	<u>Oxide</u>	-6.0	0.5
<u>Enstatite</u>	<u>Pyroxene</u>	-8.4	0.8
<u>Diopside</u>	<u>Pyroxene</u>	-8.7	0.7
<u>Fo₉₀</u>	<u>Olivine</u>	-8.9	0.6
<u>Pyrope</u>	<u>Garnet</u>	-13.3	0.7

Na K_{α} Peak Shifts in Silicates:

Preliminary results:

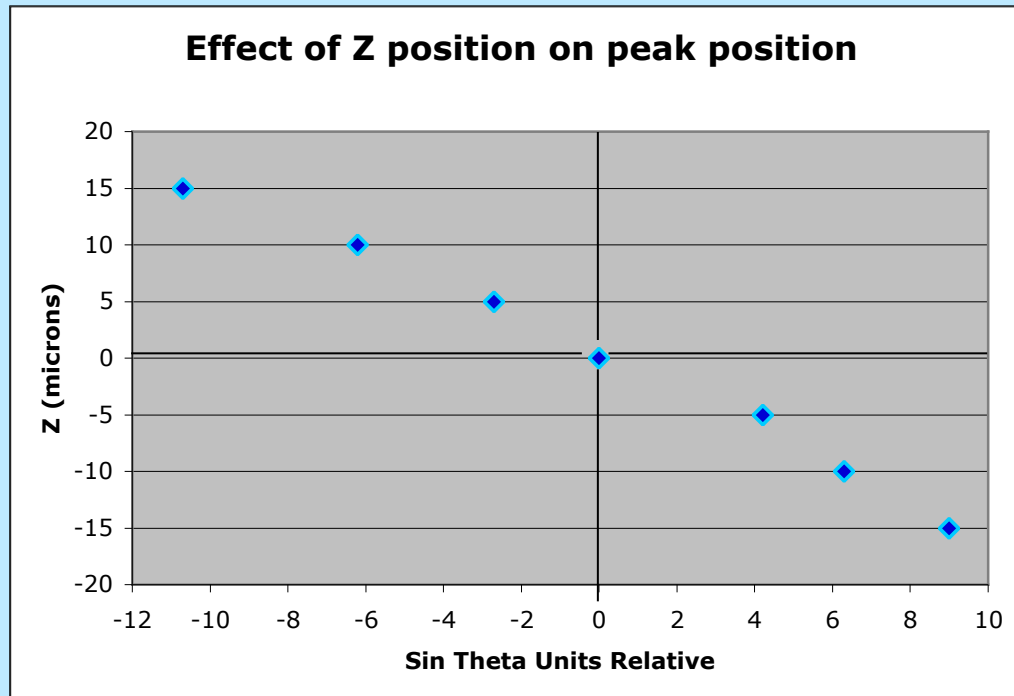
- There are chemical peak shifts (albite vs jadeite, ~10 unit peak shift)
- Peaks are very wide (albite ~18 units wide)
- Other issues muddy the waters (element migration, lower counts -> poor statistics)

Conclusion 2

Si, Al and Mg K_{α} Peak Shifts:

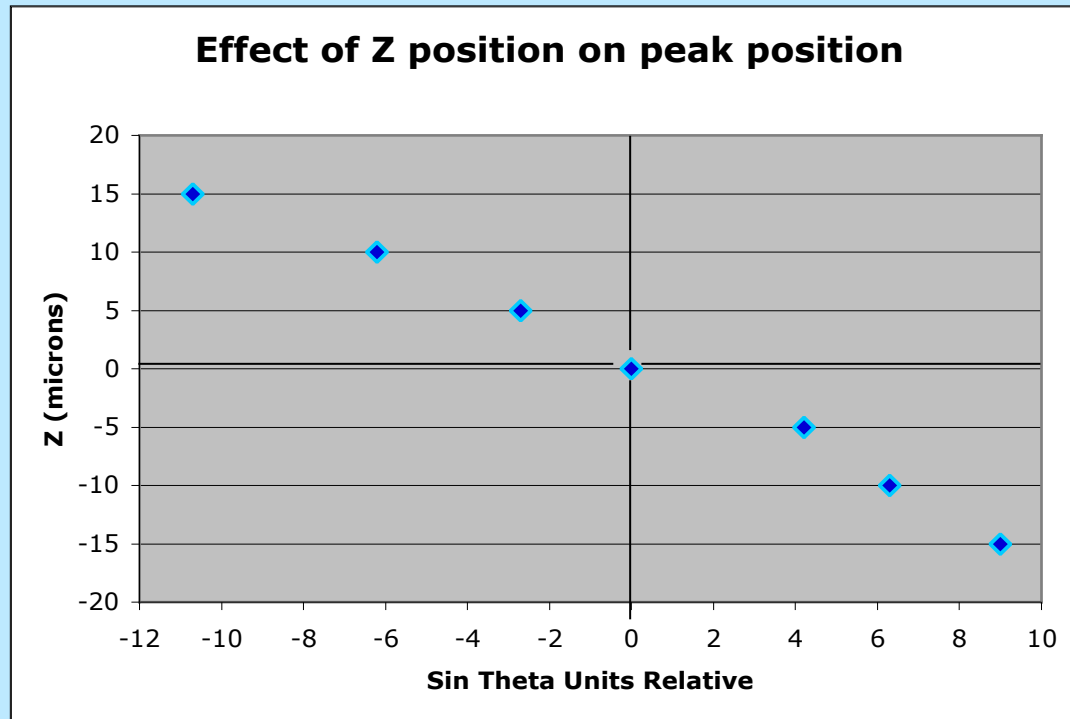
- Al: need pay special attention to which specific minerals are being analyzed, and use appropriate standard for peaking/counting (feldspars especially!)
- Si: special attention to K, Na feldspars
- Mg: MgO is not necessarily a good standard for all silicates; use like phases for standards

Al K_{α} Peak Positions (on TAP) are very sensitive to stage Z position



A misfocus of 5 microns in Z equals a peak shift of 3-4 sin theta units, not a trivial difference.

Conclusion 3



Well adjusted autofocus **critical** for multiple automated repeated measurements

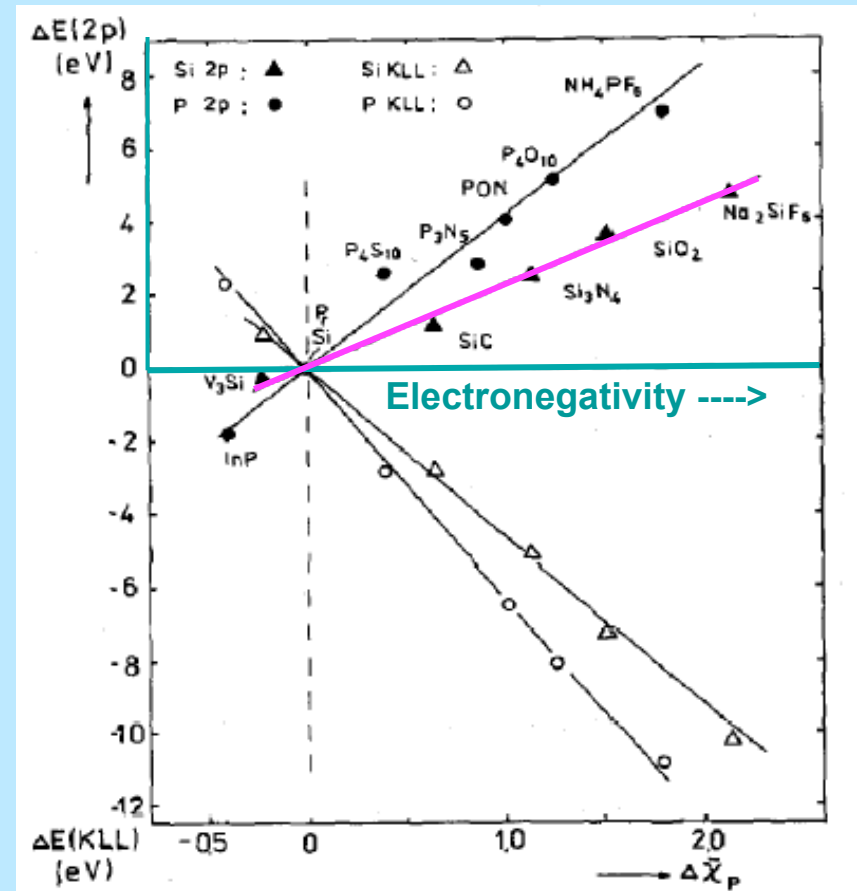
On the basis for chemical shift in Al and Si $K\alpha$

Precision of EPMA peak measurements is much less than that possible using XPS and AES, and those fields' literature provide a basis for understanding the EPMA observations.

Streubel et al (1991 J. Electron Spectro & Related Phenom): Data on Si and P chemical shifts using XPS and AES

Figure 2 (top) plots relative Pauling Electronegativity vs relative binding energy of L shell (2p)

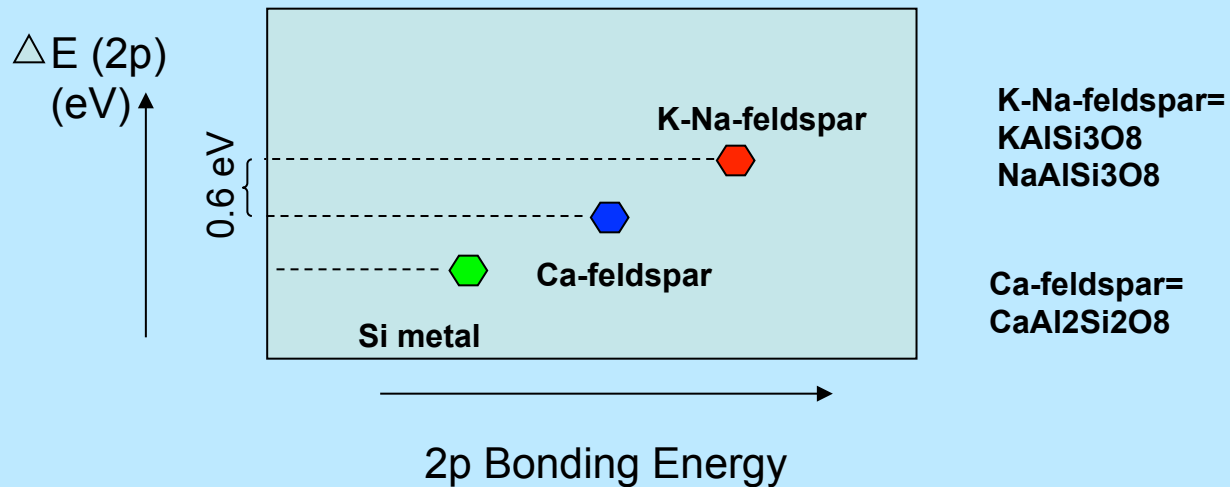
$\Delta E(K\alpha) = \Delta E(1s) - \Delta E(2p)$
 Ka peak shift =
 Difference (vs Si metal) in K binding energy
 minus
 Difference in L binding energy



Suggested reason for Al $K\alpha$ shifts in Ca vs K-Na feldspars

$$\Delta E(K\alpha) = \Delta E(1s) - \Delta E(2p)$$

K α peak shift =
Difference (vs Si metal) in K binding energy
minus
Difference in L binding energy



Summary

Accuracy in EPMA of Al, Mg and Si in silicate minerals requires attention to one of the first steps in calibration, defining the peak positions, because

- **There are Al, Mg and Si $K\alpha$ chemical peak shifts between some “common” silicate minerals and oxides.**
- **Vertical stage drift can yield peak shifts.**
- **Automated peak search routines should be used with a critical eye.**

