Al, Mg, Si and Na Ka Peak Shifts in Common Silicate and Oxide Minerals

A presentation for the Advanced Instrumental Techniques
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John Fournelle

Eugene Cameron Electron Microprobe Lab
Department of Geology & Geophysics
University of Wisconsin
Madison, Wisconsin

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

- **How <u>wide</u> are the peak tops?**

- **Is there a problem with our peaking procedure?**

- **Are there chemical peak shifts?**
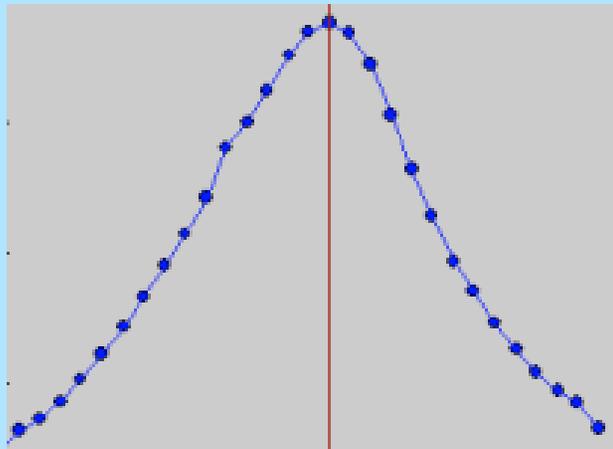
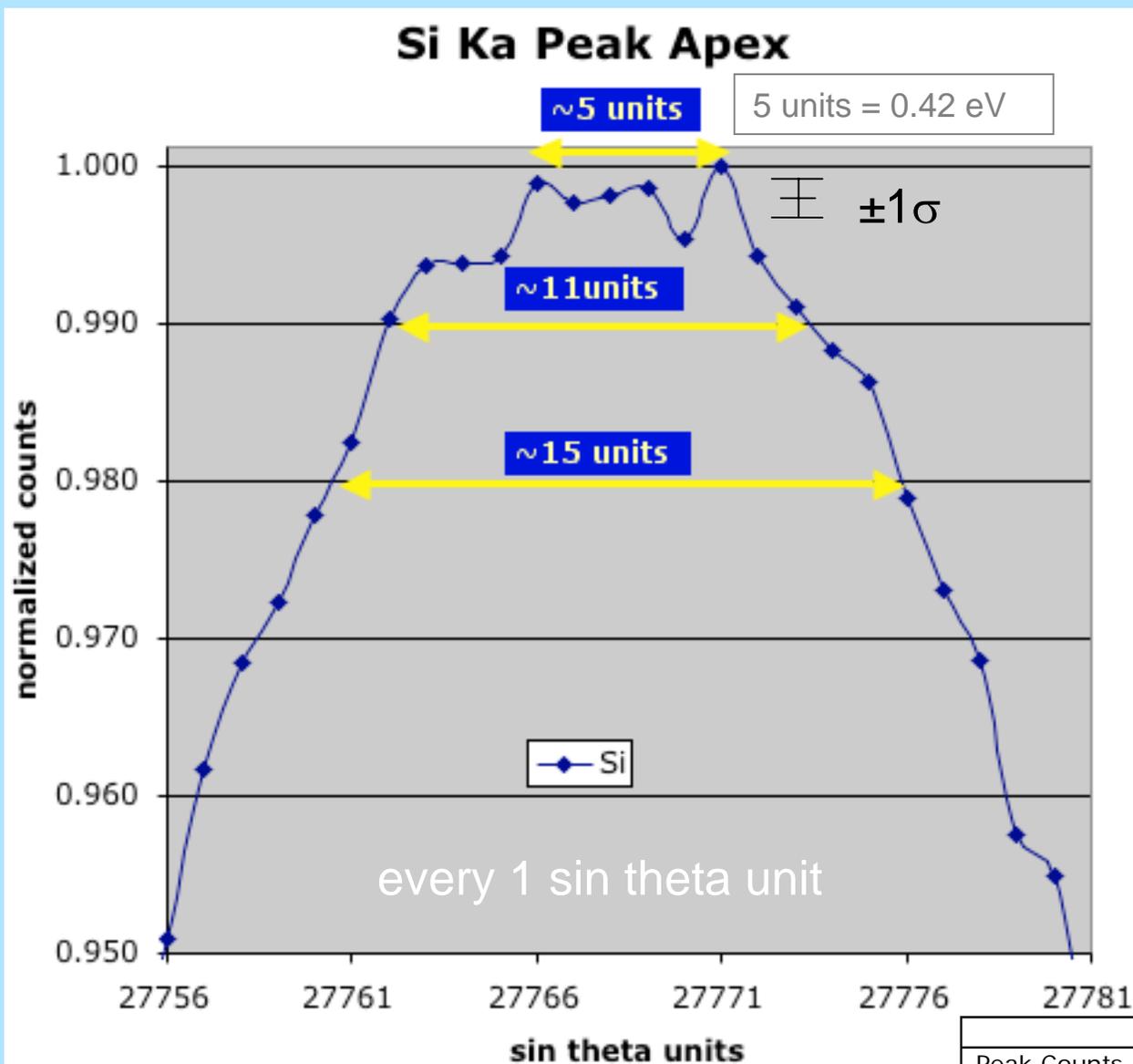We started with Si and Al Kα ... and worked up to Mg and Na Kα

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

Consider the Si K$_\alpha$ Peak

Precise Peak: 4 minutes of scanning

Si Ka Peak Apex

~5 units

5 units = 0.42 eV

±1σ

~11units

~15 units

every 1 sin theta unit

— Si

normalized counts

sin theta units

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

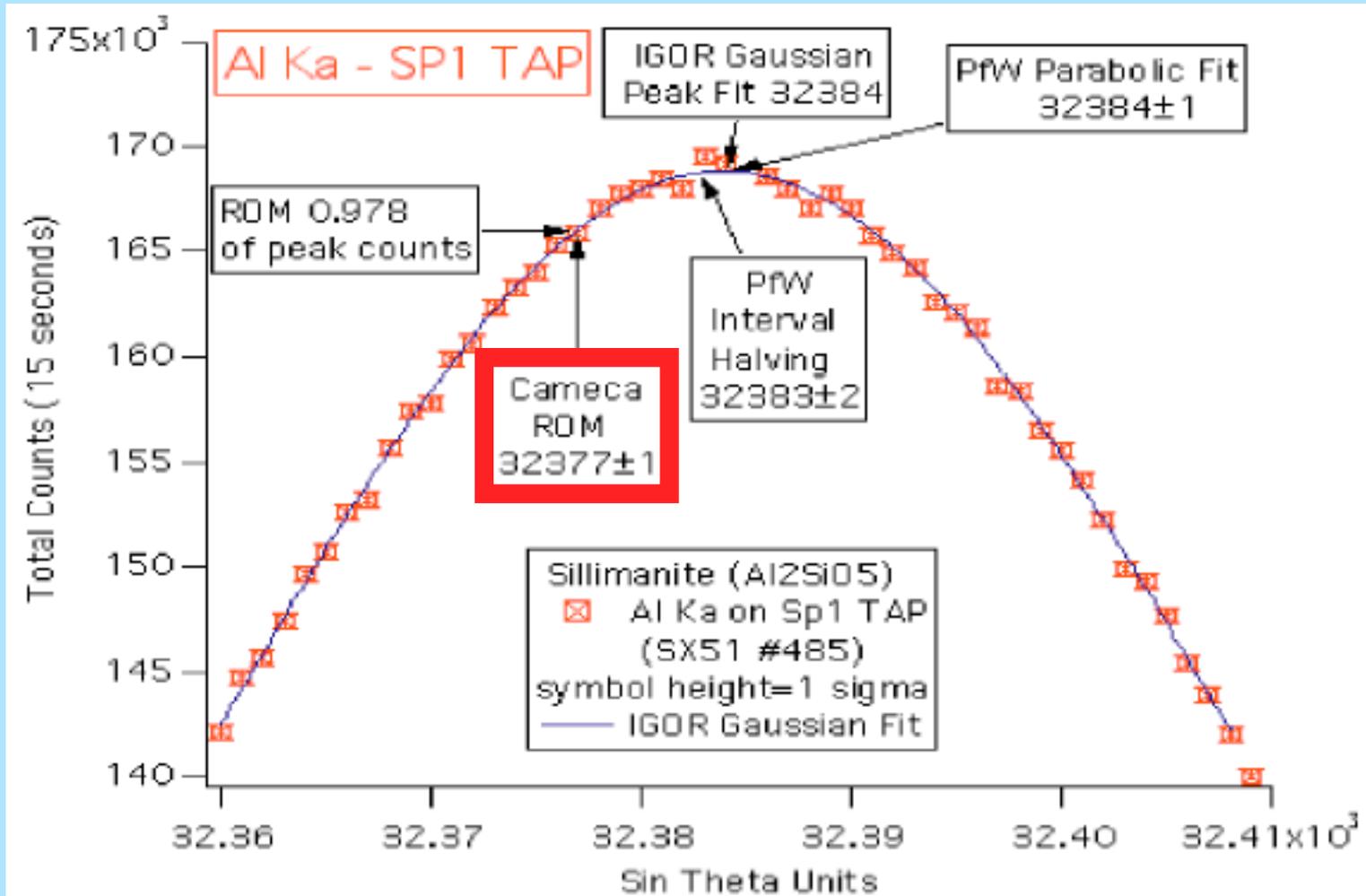|		Normalized
Peak Counts	493882	1.0000
1 sigma	703	0.0014
2 sigma	1406	0.0028
3 sigma	2108	0.0043

Conclusion 1

<u>Si and Al K$_\alpha$ Peak Widths on TAP:</u>

- Many peaks ~ 5 sin theta units wide

- For <u>correctly centered</u> 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 <u>doubled</u> for oxide values (oxygen by stoichometry)

Results of Automated Al K$_\alpha$ 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 …

Here is a post-scan on Al Kα, 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 Kβ peaks
(M-L transitions: M shell electrons =
valence electrons)

Al K$_\alpha$ Chemical Shifts

… have been recognized for ~50 years

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

Al Ka Shift vs coordination relative to Al metal:

Feldspar (IV): -0.07;
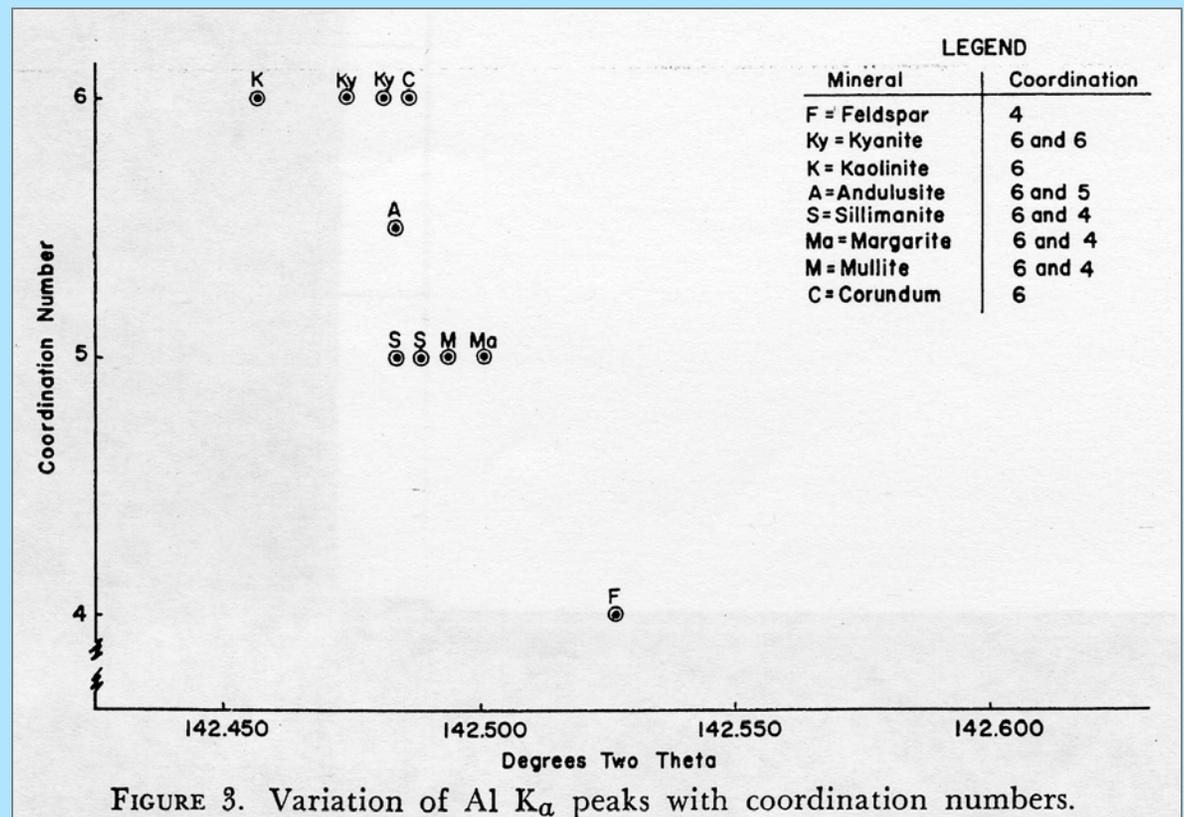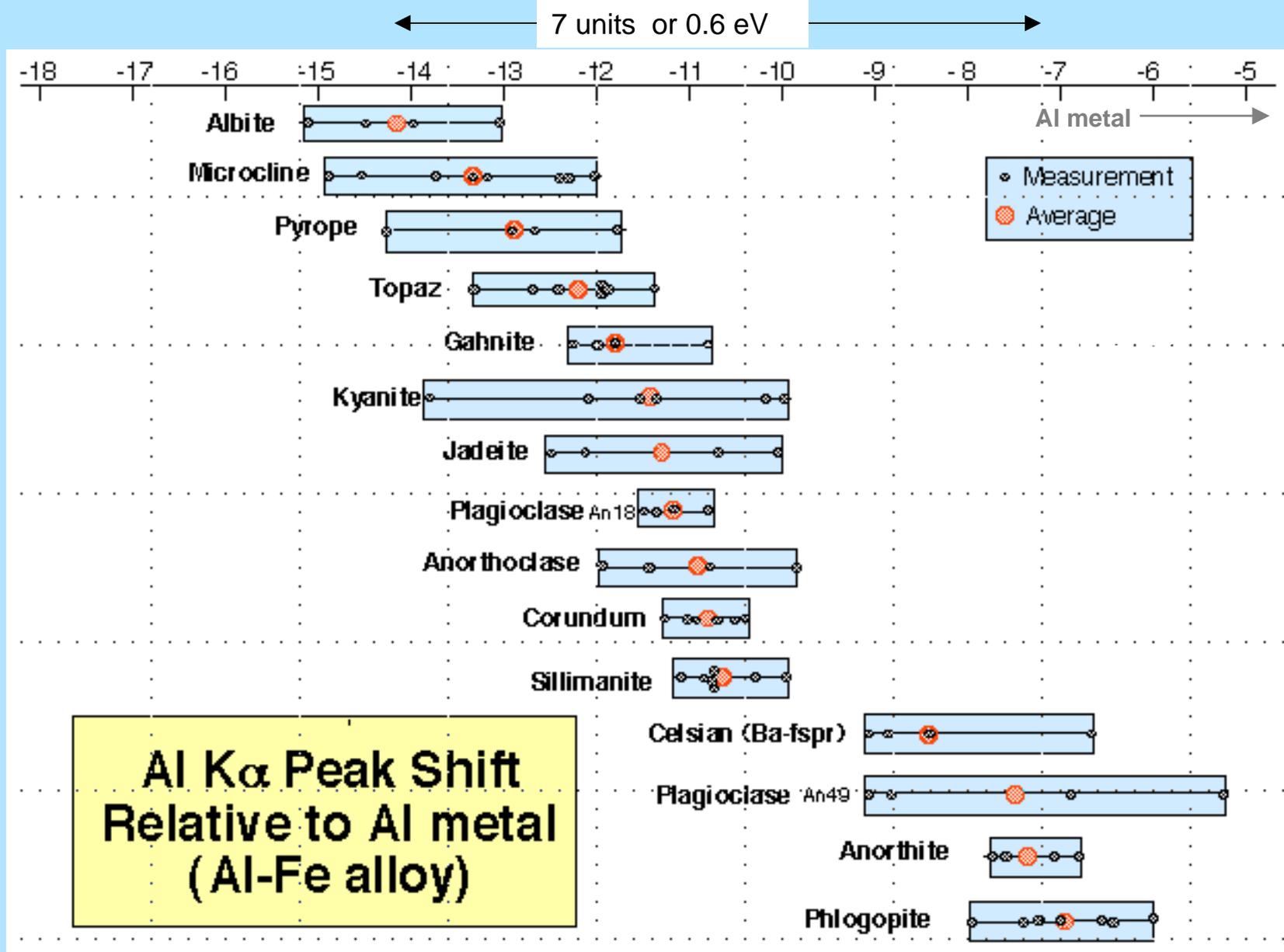**Sillimanite (IV+VI): -0.11;**
Kyanite (VI): -0.12

FIGURE 3. Variation of Al K$_\alpha$ peaks with coordination numbers.

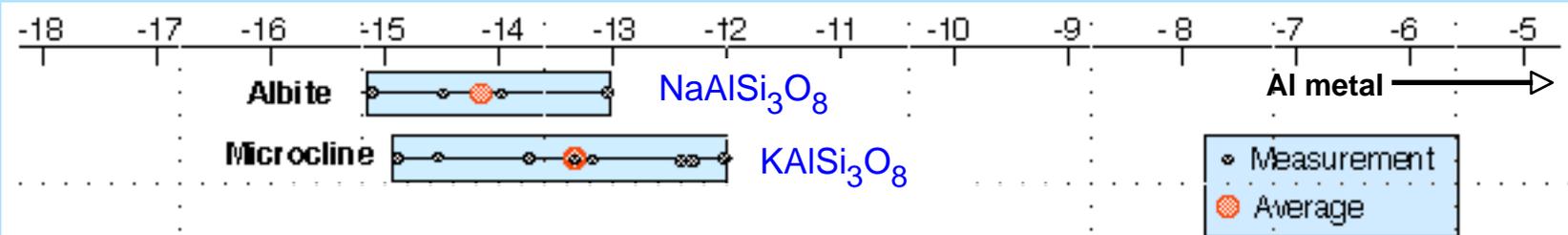**Also   Day, 1963, *Nature*;   Wardle and Brindley, 1971, *American Mineralogist***
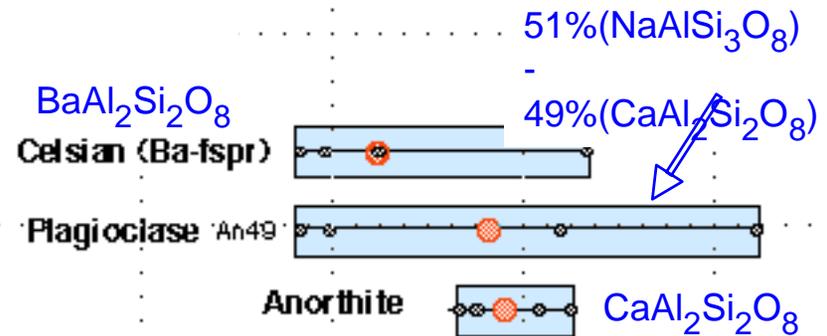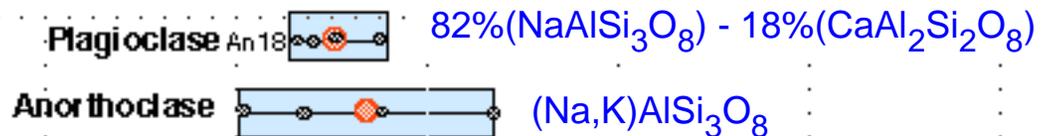
But apparently never
to this extent…

Al K$_\alpha$ Peak Shifts on UW SX51

7 units or 0.6 eV

Al Kα Peak Shifts - Feldspars Only

Al K$_\alpha$ Peak Shifts

Coord	Al Ka Peak Shift Relative to Al-Fe Alloy								Coord
	Mineral	Sp1 Ave	Std Dev	n	Mineral	Sp4 Ave	Std Dev		
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$_\alpha$ Peak Shifts in Garnets Also

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

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Si K_β, K_α Chemical Shifts: Historical

White, McKinstry and Roy, 1962, GSA Abstract

<u>Measured major</u> Si K_β shifts in SiO_2 relative to Si metal: Stishovite (IV): -0.010 Å; Quartz, cristobalite (VI): -0.015Å

. though no Si K_α Shift between IV and VI seen

Kaufman and Moll, 1966, Advances X-ray Analysis

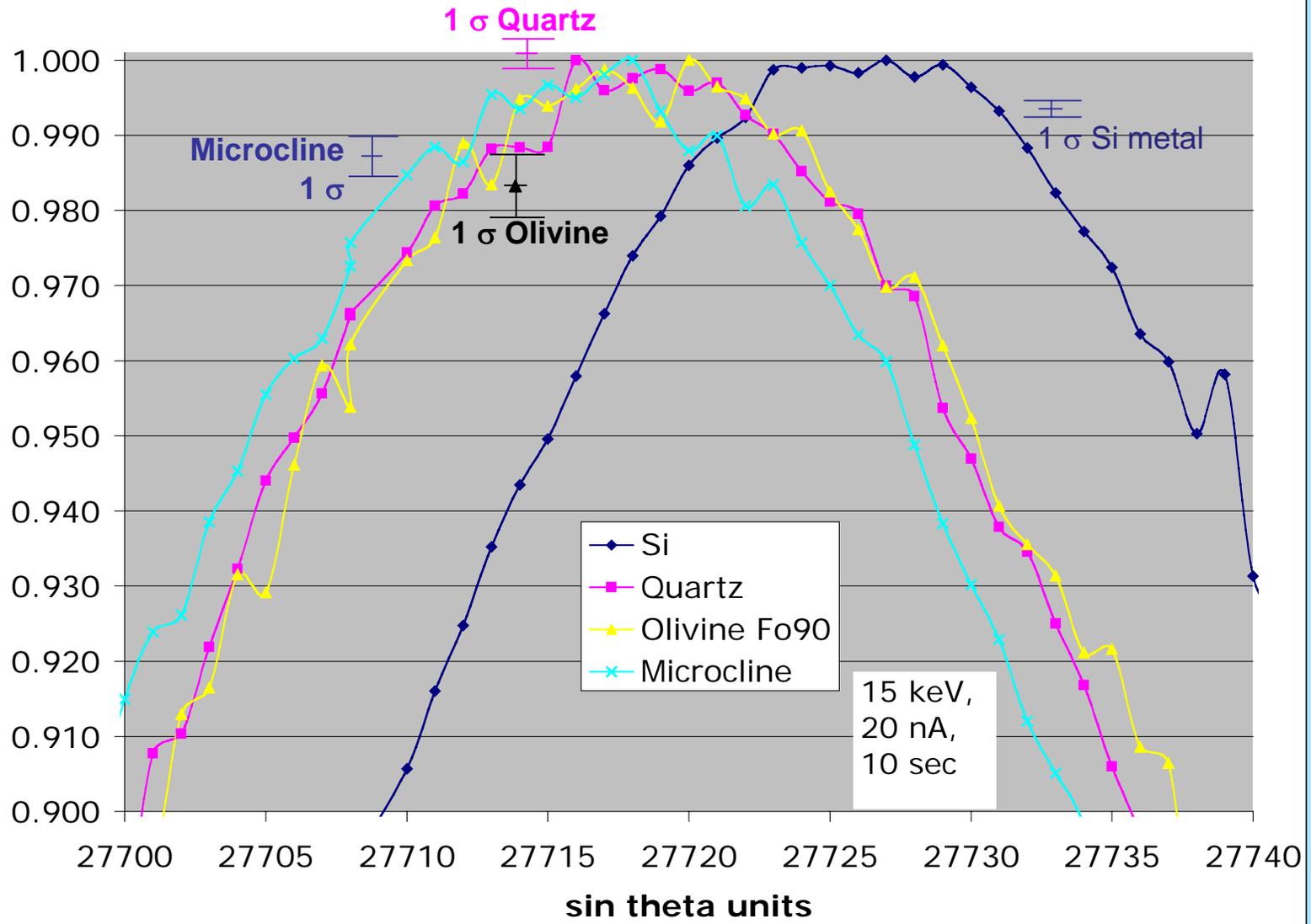Examined Si K_{α_1}, K_{α_3}, K_{α_4} and K_β for Si metal and 10 common silicate minerals; found differences between silicates <u>for all K lines but NOT for K_{α_1}</u>

Table II. Si K Lines from Silicon Metal and Silicates

Material	K_{α_1} λ	K_{α_1} I	K_{α_3} λ	K_{α_3} I	K_{α_4} λ	K_{α_4} I	K_β λ	K_β 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
$Mg_2Si_2O_6$	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
$CaMgSi_2O_6$	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
$NaAlSi_3O_8$	7.1244	1000	7.0766	51	7.0677	53	6.7640	24
$CaAl_2Si_2O_8$	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
$(Na, K) (Al, Si)_2O_4$	7.1244	1000	7.0763	52	7.0675	56	6.7627	25

Si Ka on TAP sp1

1 σ Quartz

Microcline 1 σ

1 σ Olivine

1 σ Si metal

Legend:
- Si
- Quartz
- Olivine Fo90
- Microcline

15 keV, 20 nA, 10 sec

sin theta units

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 <u>quartz</u>:
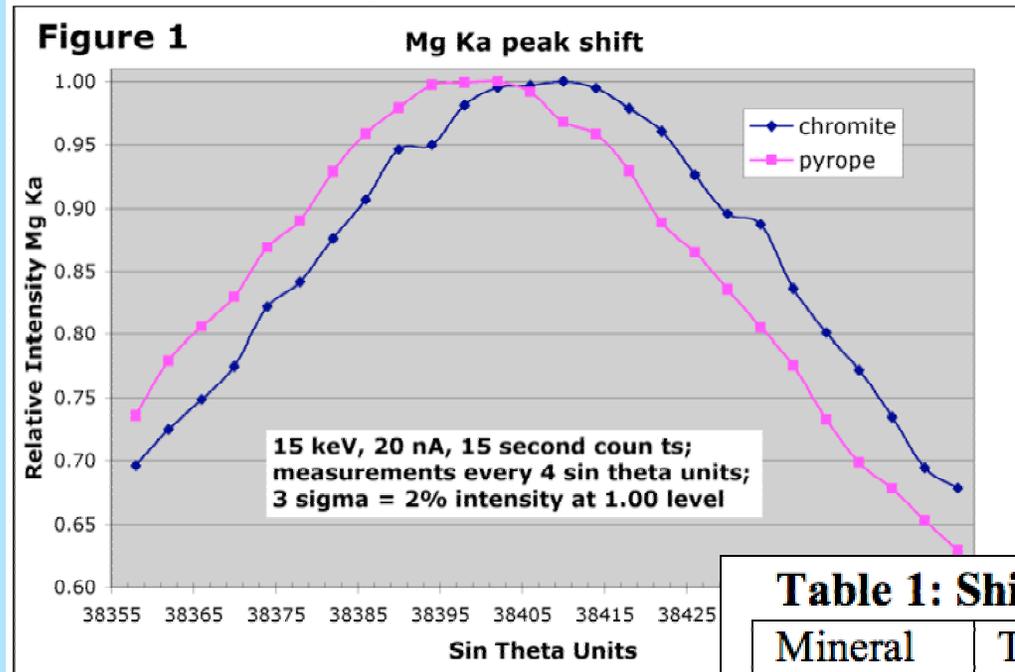**Spectro1 = 0.5 ±0.1 eV; Spectro4 =0.6±0.1 eV**
<u>Compare Above With</u>:

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) "SiO$_2$" 0.62 eV**

Implication: there is a 0.7 - 0.9 eV shift for <u>microcline</u> Si Ka relative to Si metal,
-- And one should NOT peak Si on K-feldspar for plagioclase.
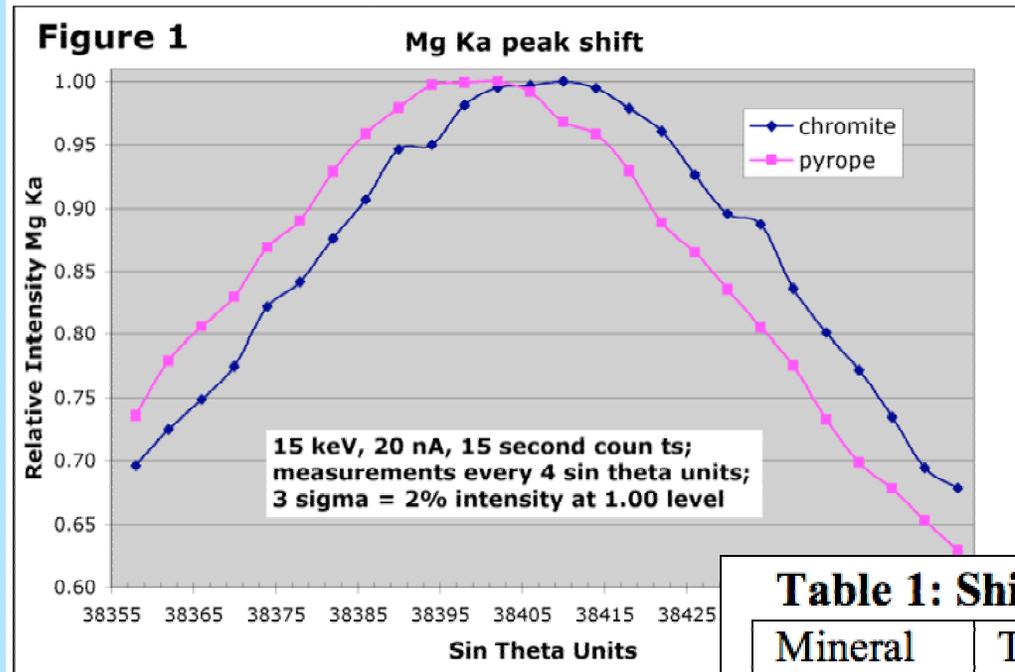
Mg K$_\alpha$ Peak Shifts:

Figure 1 — Mg Ka peak shift

15 keV, 20 nA, 15 second counts; measurements every 4 sin theta units; 3 sigma = 2% intensity at 1.00 level

Table 2: Mg Kα 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 Kα

Mineral	Type	Shift	Std Dev
Chromite	Spinel	-3.6	0.6
MgAl2O4	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
Fo90	Olivine	-8.9	0.6
Pyrope	Garnet	-13.3	0.7

Mg Kα Peak Shifts:

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Enstatite	Pyroxene	-8.4	0.8
Diopside	Pyroxene	-8.7	0.7
Fo90	Olivine	-8.9	0.6
Pyrope	Garnet	-13.3	0.7

# Na K$_\alpha$ 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)

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 (<u>feldspars especially</u>!)

▪ 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$_\alpha$ Peak Positions (on TAP) are very sensitive to stage Z position

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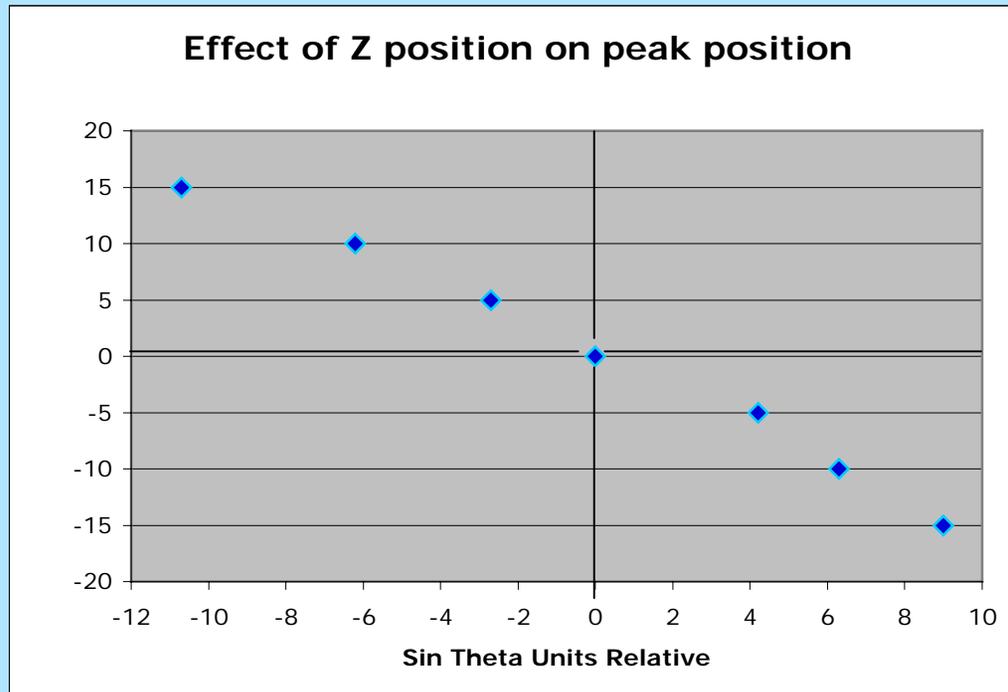
A misfocus of 5 microns in Z equals a peak shift of 3-4 sin theta units, not a trivial difference.

Conclusion 3

Effect of Z position on peak position
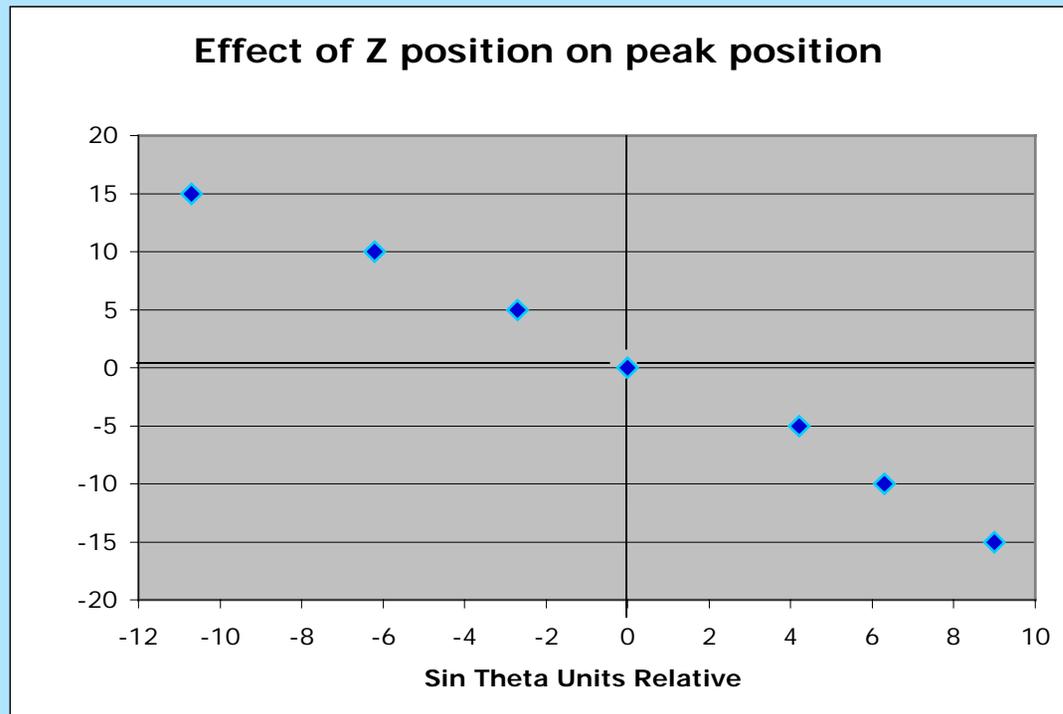
Well adjusted autofocus **critical** for multiple automated repeated measurements

On the basis for chemical shift in Al and Si Kα

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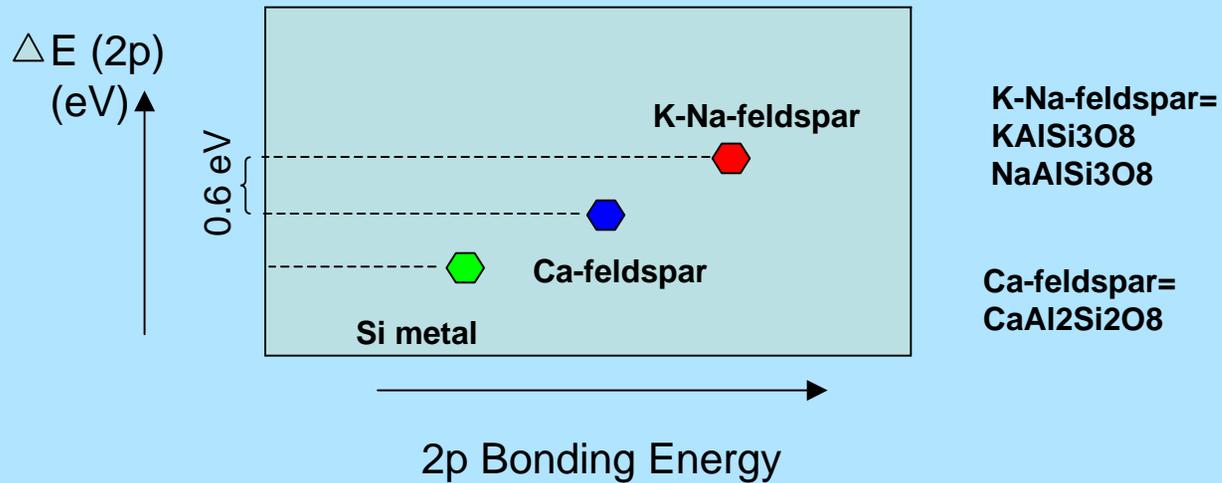
$\Delta E(Ka) = \Delta E(1s) - \Delta E(2p)$

**Ka peak shift =
Difference (vs Si metal) in K binding energy
minus
Difference in L binding energy**
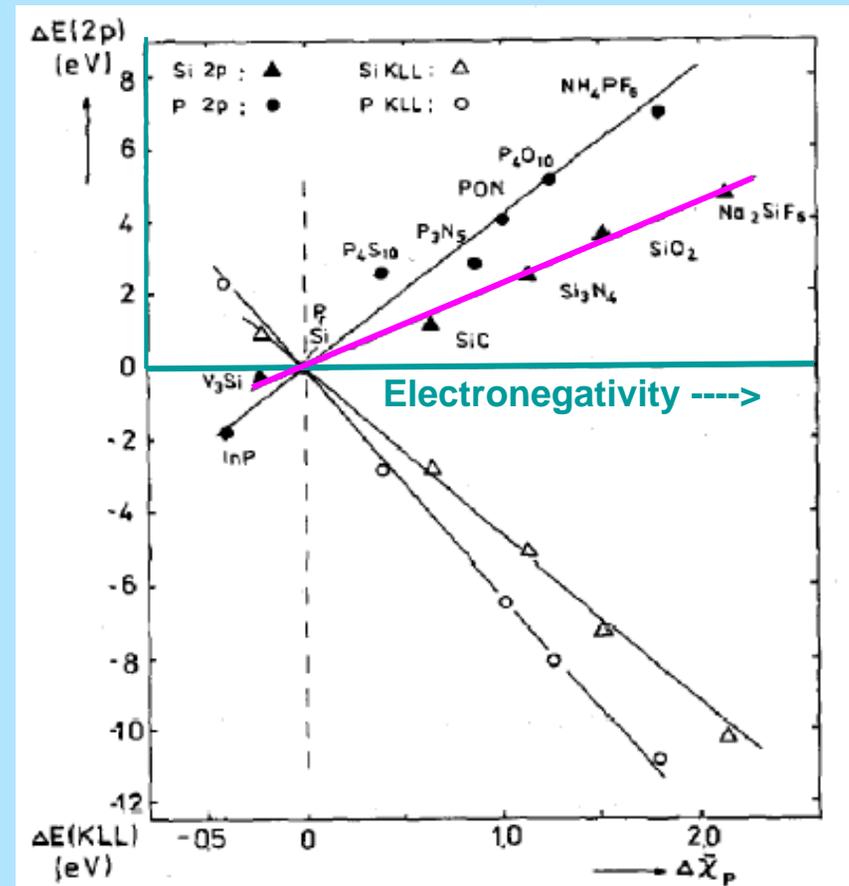
Suggested reason for Al Kα shifts in Ca vs K-Na feldspars

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

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

$\triangle E\ (2p)$
(eV)

0.6 eV

K-Na-feldspar

Ca-feldspar

Si metal

2p Bonding Energy

K-Na-feldspar=
KAlSi3O8
NaAlSi3O8

Ca-feldspar=
CaAl2Si2O8

Summary

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

- **There are Al, Mg and Si Kα 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.**