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

John Fournelle

Department of Geology and Geophysics, University of Wisconsin, Madison WI 53706

During the early years (1920s) of x-ray spectroscopy, Lindh and Lunquist [1] demonstrated the existence of shifts in P, S and Cl Kβ peaks. These were characterized as resulting from differences in the electronic bonding, i.e., differences in the valence state. Since 1959, systematic shifts in both Al Kα and Kβ positions resulting from different bonding environments in Al-bearing phases have been recognized [2,3,4]. There is a clear Si Kα peak shift between Si metal and silicates and Kβ peak shifts between most phases [5]. There is little published on Mg Kα, whereas Mg Kβ shifts are more obvious [6]. Many of these studies from 3-4 decades ago utilized the electron microprobe as an explicit tool for studying bonding of various silicates and oxides.

In 2003, during the course of troubleshooting some issues with accuracy of EPMA analyses of common alumino-silicate minerals in our lab [7], four facts emerged: 1) ROM automated peaking routines could return faulty peak center positions a significant number of times (not at the center of the peak, defined by fitting a curve to the upper ~90% of the peak and bisecting it), 2) the Al and Si Kα peak centers on TAP (99.5% of max counts) are ~5 sin theta units wide for feldspars, whereas wider (~12 units) on garnet, 3) there are systematic shifts in Al Kα peak positions for many common minerals, and 4) proper stage height (Z) is critical (i.e. Rowland circle focus), as a >2 micron error will act like a peak shift. The combination of subtle to not-so-subtle peak shifts between standard and unknown, exacerbated by ROM peak choices that were slightly off peak, lead to errors. One result was a modification of the software to include explicit operator controlled precise apex peaking during calibration [8].

Mg Kα peak shifts: eight silicate and oxide minerals were evaluated for peak shifts relative to an Mg-Al alloy (later MgO was used as the reference, and the determined offset from Mg metal added). See Table 1. The maximum relative shift was on the order of 10 sin theta units, with spinels (Cr-spinel and $MgAl_2O_4$) shifted 4-5 units below Mg metal, and the pyrope garnet ($Mg_3Al_2Si_3O_{12}$) shifted over 13 units below Mg metal. Forsteritic olivine, enstatite and diopside were intermediate, shifted 8-9 units below Mg metal. These peaks are not very narrow, ~8-12 sin theta units wide, and one might first think that peak shifts would not be critical. Figure 1 shows the relative offset between pyrope and chromite peaks, and demonstrates that there is ~8 unit shift between the Cr-spinel and the pyrope peaks. When counts from both standards are acquired at the two different peak positions, there are 3-4% errors. Incorrect ROM peaking has been found to yield this range of error. (Table 2).

Al Kα peak shifts: 14 silicate and oxide minerals were evaluated, relative to an Al-Fe alloy. Results are similar to those reported in 2004 [7] and to a recently discovered earlier study by Lauger cited by Weich [9], and we expanded our list to include 5 garnets (4 natural plus synthetic YAG) (Table 3). As before there is a ~4 unit shift with K and Na feldspars relative to Ca feldspar. Most surprising was the shift, both absolute and relative, in the garnets, with pyrope the most extreme relative to YAG and even almandine.

More attention needs to be paid to these issues as hardware improves: e.g., stage and spectrometer precision together with good optics yield more reproducible measurements, This also emphasizes the need for operator training, with some healthy skepticism of automation and computer outputs (e.g., "black box" features such as ROM focusing) -- and perhaps of the use of simple oxides as standards "with a robust matrix correction compensating for differences with the unknown". A matrix correction cannot correct for a peak shift, and so the philosophy of using similar standards to the unknowns makes good sense.

References

[1] M. Siegbahn, The Spectroscopy of X-Rays, Oxford (1925).
[2] E. White et al., Advan. X-ray Anal. 2 (1959) 239.
[3] D. Day, Nature 200 (1963) 649.
[4] R. Wardle and G. Brindly, Amer. Min. 56 (1971) 2123.
[5] D. Kaufman and S. Moll, Advan. X-ray Anal. 9 (1966) 393
[6] C. Dodd and G. Glen, J. Appl. Phys. 39 (1968) 5377.
[7] J. Fournelle, Microsc. & Microan. 10 (2004) 908CD.
[8] Probe for Windows-Enterprise, Probe Software Inc., www.probesoftware.com
[9] G. Weich in P. Day (ed) Emission and Scattering Techniques, NATO ASI (1980), Reidel 103.

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

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 3: Shift in Al Kα

Mineral	Type	Shift	Std Dev
Plag An95	Feldspar	-5.5	0.3
Plag An49	Feldspar	-7.3	0.4
YAG	Garnet	-7.3	0.2
MgAl2O4	Spinel	-7.4	0.1
Albite	Feldspar	-9.2	0.5
Sillimanite	Al2SiO5	-9.6	0.2
Microcline	Feldspar	-9.8	0.2
Chromite	Spinel	-10.5	0.4
Jadeite	Pyroxene	-10.5	0.2
Almandine	Garnet	-10.9	0.2
Al2O3	Oxide	-11.2	
Spessartine	Garnet	-11.5	0.2
Grossular	Garnet	-12.2	0.1
Pyrope	Garnet	-15.7	0.5

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