

## Techniques for improving quantitative analysis of mineral glasses

JOHN J. DONOVAN<sup>1</sup> AND MICHAEL ROWE<sup>2</sup>

<sup>1</sup>Dept. of Chemistry, University of Oregon, USA  
(donovan@uoregon.edu)

<sup>2</sup>Dept. of Geosciences, Oregon State University, USA  
(rowem@geo.oregonstate.edu)

In the effort to achieve the highest possible accuracy in the analyses of mineral glasses using electron microprobe analysis (EPMA), especially when attempting certain sensitive procedures such as “water by difference”, attention must be paid to several subtle, yet systematic sources of error.

In addition to the usual considerations of beam drift, spectrometer reproducibility and standard drift, the analyst must also consider x-ray intensity changes as a function of beam exposure and time due to element volatilization and/or migration. These occur both for migrating elements such as Na and K, but also for elements such as Si and Al whose intensity changes as a function of the change in the absorption correction from the volatilizing or migrating elements. Brute force methods (cryo-stage) for minimizing this loss or migration are possible, but are usually time-consuming and cumbersome in practice. However, accurate corrections in software can be applied if the degree of loss can be characterized as consistently exponential during the acquisition phase.

Trace element analysis can also be problematic due to certain subtle problems with x-ray intensity measurements such as peak shift due to valence and coordination. Typically sulfur exhibits the largest of these valence shifts due to its wide range of oxidation state (+6 to -2) and must be carefully compensated, for the most accurate analyses. In addition, the possibility for in situ oxidation of the sulfur in the glass means that the analyst must sometimes take additional precautions in these determinations when long acquisition times for wavelength scans are required due to low concentrations of the element in the mineral glass.

When all these procedures are handled correctly the microprobe is capable of the high accuracy required for “water by difference” calculations, which can be seen by comparison with other more specialized techniques such as FTIR. One additional consequence of these improved techniques is that comparison of glass analyses to those obtained with older methods is a little like comparing apples to oranges.

## Al and Si quantitation in routine silicate EPMA: Maybe not so routine

JOHN H. FOURNELLE

Department of Geology and Geophysics, UW-Madison,  
Madison, WI 53706, USA (johnf@geology.wisc.edu)

Most geological electron microprobers assume EPMA is a “turnkey” microanalytical technique, and that “any” grad student can easily master getting good analyses from common silicate minerals. As hardware (spectrometer, stage) reliability increases, this assumption may fail.

*History:* A veteran prober refused to accept slightly low totals and values of SiO<sub>2</sub> in “simple” silicate analyses from our modern electron probe (SX51). I narrowed the problem to 3 issues related to analytical peak positions: 1) peak width (how many units in peak shift require recalibration?); 2) how we had been determining the peak position; and 3) chemical peak shifts in common silicates. I started with Si Ka and expanded to Al Ka.

*Peak Widths:* I define peak apex width as the small plateau where 99.5-100% of max counts occur. Si Ka on TAP and PET have similar widths. On TAP, it is ~5 sin theta (Cameca) units. Al Ka is similar for some, but some peaks up to double that. For a 5 unit peak width, a centered peak that suffered a shift of more than 3 units would result in count degradation, with a 5-6 unit shift yielding at least 1 wt% elemental error, and if oxygen is calculated by stoichiometry, the SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> would be low by >2 wt%.

*Peaking Procedures:* I found the ROM peaking (SX51) that we had uncritically used for years was very precise, but could be critically off peak at times. Modifications in software (Probe for Windows) to permit the operator to manually locate the optimal peak position improved results drastically, particularly for SiO<sub>2</sub>.

*Chemical Peak Shifts:* From 1959-71, workers reported on a few shifts within silicates for Al Ka, but none for Si Ka (though for Si Kb). *Si Ka shift:* I found, of 11 minerals studied, microcline was shifted 4-6 units relative to others (which generally were at the same position). Measurement of the quartz shift relative to Si metal (8-9 units, .5-.6 eV) agrees well with HRXFS. (TAP data are from 2 spectros.) *Al Ka shift:* This study of 15 minerals revealed a range spanning 7 sin theta units, from phlogopite, to albite.. Seven feldspars included showed the same large range, from albite and microcline, to anorthite and plag (An49).

These measurements require precise Z-focus—a misfocus of 5 Z units = a peak shift of 3-4 spectro units; operator control of peaking (to verify it); and reproducible spectrometers. Everett Glover studied this here in 1971 (ARL EMX) but epma technology was not ready. It is now.