Techniques for Improving Quantitative Analysis of Mineral Glasses

JOHN J. DONOVAN[1] AND MICHAEL ROWE[2]

[1]Dept. of Chemistry, University of Oregon, donovan@uoregon.edu
[2]Dept. of Geosciences, Oregon State University, 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 volatizing 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 consistantly 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 valences shifts due to it's 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.