Quantitative WDS Compositional Mapping Using the Electron Microprobe

John J. Donovan¹, Julie Chouinard¹, Julien M. Allaz², Anette von der Handt³, Gareth G. E. Seward⁴, Owen Neill⁵, Karsten Goemann⁶, and Paul Carpenter⁷

¹. CAMCOR, University of Oregon, Eugene, Oregon, USA.
². Institute of Geochemistry and Petrology, ETH Zürich, Zürich, Switzerland.
³. Department of Earth Sciences, University of Minnesota, Minneapolis, MN, USA.
⁴. Department of Earth Science, University of California Santa Barbara, Santa Barbara, CA, USA.
⁵. Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI, USA.
⁶. Central Science Laboratory, University of Tasmania, Hobart, Tasmania, Australia.
⁷. Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, Missouri, USA.

Quantification of pixels in X-ray intensity maps requires the same level of rigor applied in traditional point analysis. Accordingly, X-ray map quantification should include pixel-level corrections for WDS detector deadtime, corrections for changes in beam current (beam drift), changes in standard intensities (standard drift), high accuracy removal of background intensities (off-peak or mean atomic number), quantitative matrix corrections, quantitative correction of spectral interferences, and, if required, time dependent intensity corrections (for beam and/or contamination sensitive materials) as shown schematically in Figure 1. The purpose of quantification at the pixel level is to eliminate misinterpretation of intensity artifacts, inherent in raw X-ray intensity signals, which distort the apparent abundance of an element as demonstrated in Figure 2. Major and minor element X-ray signals can contain significant artifacts due to absorption and fluorescence effects [1]. Trace element X-ray signals can contain significant artifacts where phases with different average atomic number produce different X-ray continuum (bremsstrahlung) intensities, or where a spectral interference, even an apparently minor one, can produce a false-positive intensity signal [2, 3]. The methods we propose for rigorous pixel quantification requires calibration of X-ray intensities on the instrument using standard reference materials, as we already do for point analysis, which are then used to quantify multiple X-ray maps, and thus the relative time overhead associated with such pixel-by-pixel quantification is small [4].

Quantification of X-ray maps is critically important for accurate interpretation of element distributions, not only for minor and trace elements, but also elements whose emission lines suffer significant absorption or fluorescence. Raw X-ray maps remain an essential tool to reveal two-dimensional variation that cannot be fully ascertained by discrete point analysis, but because the same raw intensity can represent quite different concentrations in different phases, without quantification at the pixel level it would be significantly more risky to draw robust conclusions from merely qualitative X-ray maps.
Figure 1 (left). Flow chart of the proposed method for rigorously quantifying a series of raw intensity X-ray maps. These steps include normalization for pixel integration time, detector dead time, beam drift and standard drift (and optional off-peak map background corrections, TDI corrections and duplicate element aggregations), followed by iterative corrections for (MAN) background, matrix, and spectral interferences on each pixel individually.

Figure 2 (below). Element maps of a Fe-Ti mineral from the mafic-ultramafic Viravira Complex, Colombia. Conditions were 8 keV, 35 nA, and 100 ms per pixel. Oxygen Kα measured on LDE1 monochromator, and PROZA91 matrix correction was applied with MAC values from FFAST database. Field of view is 414 x 274 µm. (a,b) The raw intensity X-ray map of O Kα (a) in the Fe-Ti-oxide mixture shows significant differences when compared to the fully quantified X-ray map (b). (c,d) While the map of the calculated background intensities (d) correlates with Fe-rich core areas, the net intensities (c) are not affected due to the high peak-to-background ratios.
References: