Comparison of experimental and calculated spatial resolution in X-ray microanalysis of oxide and silicate minerals

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The spatial resolution in electron probe x-ray microanalysis is a detectable expression of the fundamental concept of interaction volume [1]. The knowledge of the later is critical on one hand for developing adequate theoretical basis for quantification of the concentrations of the measured elements and on the other for optimization of the experimental conditions during spectroscopic chemical analysis in the scanning electron microscope (SEM) [2]. The interaction volume is not readily accessible to simple direct measurements except in special circumstance, thus the major sources for experimental data about the interaction volume have been either analyses of layered structures with known composition and thickness or measurements of x-ray intensity variations of specific elements across a sharp interface boundary. With advancement of the theory of electron specimen interaction and the development of Monte Carlo methods for simulation it has become relatively straightforward to compare experimental measurements and theoretical calculations of the spatial resolution in x-ray microanalysis. Surprisingly there is very limited data in the literature reporting such measurements [3, 4, 5].

In this study attempt has been made to compare experimentally determined and theoretically calculated spatial resolution values for the characteristic x-ray signal obtained by energy dispersive spectrometry (EDS) for a set of chemical elements abundant in geological type materials. For the above purpose spinel and pyroxene crystals were selected with the following compositions: spinel – $Zn_{0.5}Mg_{0.4}Fe_{0.1}Al_2O_4$ and pyroxene - $Na_{0.2}Ca_{0.4}Fe_{0.1}Al_{0.5}MgSi_{1.8}O_6$. Spectral and linescan data across a sharp vertical interface boundary between the spinel and pyroxene crystals was acquired using EDAX® EDS equipped with Si(Li) detector at 5, 10, 15, 20, and 25 kV accelerating voltages in an FEI XL30-FEG SEM.

The experimental spatial resolution for each element in both spinel and pyroxene matrixes was determined by the change in slope of the x-ray intensity variation profile as determined from linescan data across the interface between the two mineral phases. The theoretical linescan data was calculated using the CASINO software package [6]. Different physical models were tested for the conditions of the experiment. Since absolute x-ray intensity measurements were not directly compared or determined it is assumed that the relative change in x-ray intensity as a function of position and matrix in both experiment and simulation represents an adequate measure of the spatial resolution as function of interaction volume and absorption.

The obtained data at accelerating voltages below 20 kV suggest that within the precision of the measurements the best match between experimental and simulated data for all elements is observed by utilizing tabulated values for Mott elastic and ionization cross sections [7] and stopping power values based on the approach by Joy and Luo (1989) [8]. At 25 kV significant departure is apparent between predicted and observed data for most of the measured elements [fig. 1]. At 20 kV the discrepancy is smaller but still significant. A notable exception is the behavior of SiK and O K signal for which the match is good at all tested voltages.

The fact that the discrepancy is affecting variably different elements with different absolute concentrations suggests that the observed differences reflect fundamental discrepancy between observation and model as opposed to effects of precision of measurement, which would have affected similarly elements with either similar concentrations or similar ionization energy. The discrepancy at and above 20 kV could be attributed to inadequate physical models for all studied elements except Si and oxygen in complex oxide and silicate phases. Most of the parameters incorporated in the physical models describing electron-specimen interactions and x-ray generation have been historically determined based on experimental measurements of pure elements or simple binary compounds [1, 2, 3, 4], where metal bonding dominates and density is related to composition by the rules of simple close packing and atomic weight. It is plausible that chemical bonding and density effects in complex oxide and silicate phases can cause deviation from the established physical models for the generated and emitted x-ray signal for many elements at specific accelerating voltages.

References
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Figure 1. Simulated (sim.) and measured values for the radius of CaK x-ray emitting area in pyroxene and spinel matrix as function of accelerating voltage.