

THE EFFECT OF "MISSING" (UNANALYZED) OXYGEN ON QUANTITATIVE ELECTRON PROBE MICROANALYSIS OF HYDROUS SILICATE AND OXIDE MINERALS

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It is common practice in quantitative electron probe microanalysis of geological materials to calculate the oxygen content based on the stoichiometric metal-oxygen ratio. For hydrous silicate and oxide minerals, such as zeolites, micas, amphiboles and transition metal oxyhydroxides, this practice gives analytical totals that may be much less than 100% due to the "missing" oxygen associated with structural water and hydroxyl groups. By calculating k-ratios for mineral compositions reported in Deer et. al. (1966), it is shown that the error introduced into the ZAF or Phi-Rho-Z matrix correction increases with increasing structural water or hydroxyl; absolute errors up to 1-3 wt% for Na, Mg, Al and Si and relative errors up to 5% have been observed.

The discrepancies are readily attributed to the large mass absorption coefficients for oxygen. For certain zeolites and other minerals, the errors compensate so that the mineral formula calculation minimizes the relative errors. For Mg-rich chlorites, the errors are not compensated, and the formula calculation exaggerates the errors. Alternative methods of accounting for the missing oxygen include (1) calculating the missing oxygen by difference, (2) calculating the hydrogen (and hence the oxygen associated with either hydroxyl or water) based on the nominal hydrogen/total oxygen derived from the mineral formula or (3) calculating the hydrogen based on its ratio to another conservative element.

In all cases, these alternative formulations are performed iteratively in conjunction with the matrix correction procedure. Calculating the "missing" oxygen in this manner is not considered to be a quantitative result. However, including it in the matrix correction produces a more accurate analytical result. Comparative analyses of zeolites from Iceland and Fe-Mn oxyhydroxides from various ore deposits demonstrate the validity of the approach.

Note by John Donovan: Sadly, Tracy died several years ago, therefore all correspondence should be directed to one of the secondary authors. Thanks.

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