American Mineralogist, Volume 85, pages 89–102, 2000

An investigation of matrix effects in the analysis of fluorine in humite-group minerals by EMPA, SIMS, and SREF

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ABSTRACT

Accurate determination of F in minerals is a difficult task even when high F concentrations are present. Fluorine usually is determined by means of electron micro-probe analysis (EMPA) standardized on non-silicate-matrix compounds (e.g., fluorite), and some previous work has revealed the difficulties in determining F at high concentrations such as found in the humite-group minerals. Moreover, when both single-crystal structure refinement (SREF) and EMPA are available for the same crystal, the two estimates do not always agree. On the other hand, the secondary ion mass spectrometry (SIMS) technique is not easily applied at high F concentrations due to the existence of matrix effects related to the chemical composition and structure of the sample as well as to the concentration of the element itself. We tested the agreement among these analytical techniques in the estimation of high F contents and propose an analytical procedure for the analysis of fluorine. Our results indicate that careful selection of working conditions for EMPA of F together with appropriate correction, can yield accurate fluorine concentrations in minerals. Fluorine data extracted from refined site occupancies are systematically overestimated. New accurate working curves have been worked out for SIMS analysis of F taking Si and Mg, in turn, as the reference element for the matrix. Humite-group minerals show SIMS matrix effects on the order of ~10%. In analyzing fluoborite in the most unfavorable cases, the difference in Ion Yield (F/Mg) between "disoriented" humite-group minerals and "oriented" fluoborite samples can reach ~27%. Finally, a lower than expected IY(F/Si) from the F/Si working curve (made with humite minerals) is shown by topaz, which can be ascribed to chemical matrix effects, as well as to the covalent-type bonding between F and the major element in the matrix (Al).