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Nanometer-scale measurements of $Fe^{3+}/\Sigma Fe$ by electron energy-loss spectroscopy: A cautionary note

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ABSTRACT

The effects of electron-beam damage on the $Fe^{3+}/\Sigma Fe$ (total iron) ratio were measured by electron energy-loss spectroscopy (EELS) with a transmission electron microscope (TEM). Spectra were acquired from crushed and ion-beam-thinned cronstedtite. For fluences below 1×10^4 e/Å^2, the $Fe^{3+}/\Sigma Fe$ values from crushed grains range between 0.43 and 0.49, consistent with undamaged material. These measurements were acquired from flakes 180 to 1000 Å thick. With increase in fluence, samples <400 Å thick become damaged and exhibit $Fe^{3+}/\Sigma Fe$ values >0.5. The critical fluence for radiation damage by 100 kV electrons as defined by $Fe^{3+}/\Sigma Fe$ <0.5 for cronstedtite at 300 K, is 1×10^4 e/Å^2. The absorbed dose to the speciman during acquisition of a typical EELS spectrum is large, with values around 2.2×10^{10} Gy (J/kg), equivalent to the deposition of 620 eV/Å^3. Cooling to liquid N_2 temperature did not significantly slow the damage process. Ion-beam thinning produces an amorphous layer on crystal surfaces. Spectra from the thinnest regions, which are amorphous, exhibit $Fe^{3+}/\Sigma Fe$ >0.7. With increase in sample thickness, the $Fe^{3+}/\Sigma Fe$ values decrease to a minimum, consistent with data from the undamaged material. The increase of $Fe^{3+}/\Sigma Fe$ with respect to electron-beam irradiation is likely caused by loss of H. At low fluences, the loss of H is negligible, thus allowing consistent $Fe^{3+}/\Sigma Fe$ values to be measured. The cronstedtite study illustrates the care required when using EELS to measure $Fe^{3+}/\Sigma Fe$ values. Similar damage effects occur for a range of high-valence and mixed-oxidation state metals in minerals. EELS is the only spectroscopic method that can be used routinely to determine mixed-valence ratios at the nanometer scale, but care is required when measuring these data. Consideration needs to be given to the incident beam current, fluence, fluence rate, and sample thickness.