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

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**ABSTRACT**

The effects of electron-beam damage on the Fe$^{3+}$/ΣFe (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 $1 \times 10^4$ e/Å$^2$, the Fe$^{3+}$/ΣFe 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$^{3+}$/ΣFe values >0.5. The critical fluence for radiation damage by 100 kV electrons as defined by Fe$^{3+}$/ΣFe <0.5 for cronstedtite at 300 K, is $1 \times 10^4$ e/Å$^2$. The absorbed dose to the specimen during acquisition of a typical EELS spectrum is large, with values around 2.2 to 10$^4$ 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$^{3+}$/ΣFe >0.7. With increase in sample thickness, the Fe$^{3+}$/ΣFe values decrease to a minimum, consistent with data from the undamaged material. The increase of Fe$^{3+}$/ΣFe 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$^{3+}$/ΣFe values to be measured. The cronstedtite study illustrates the care required when using EELS to measure Fe$^{3+}$/ΣFe 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.

**INTRODUCTION**

Electron energy-loss spectroscopy (EELS) with a transmission electron microscope (TEM) is a powerful method for determining oxidation state at the nanometer scale (Sauer et al. 1993; Garvie et al. 1994; Garvie and Craven 1994; Garvie and Buseck 1998, 1999; van Aken and Liebscher 2002). EELS spectra of different monovalent Fe-bearing minerals exhibit distinct L$_3$, edge shapes and chemical shifts, whereas minerals containing Fe$^{3+}$ and Fe$^{2+}$ exhibit L$_2$, edges that are intermediate in shape between the two single-valence end-members (Garvie and Buseck 1998; van Aken and Liebscher 2002). The changes in relative heights of the L$_2$ edge maxima reflect changes in Fe$^{3+}$/ΣFe (Garvie and Buseck 1998; van Aken and Liebscher 2002; Zega et al. 2003).

Accurate determination of Fe$^{3+}$/ΣFe requires spectra free of damage induced by the electron beam. Damage effects observed in inorganic materials in the TEM include hole drilling (Duscher et al. 1998), element loss (Champness and Devenish 1992), sample decomposition and formation of new materials (Rez et al. 1995; Zenser and Gruehn 2001), change in coordination of elements (van Aken et al. 1998), and change in oxidation state (Garvie and Craven 1994; Garvie and Buseck 1999). Beam damage is usually accompanied by amorphization of the sample (e.g., van Aken et al. 1998), although new materials can form under the beam. For example, electron irradiation under high electron fluences causes thorianite (ThO$_2$) to react with the C grid of the TEM to form a Th carbide. Also, Be(OH)$_2$, LiF, and FeCl$_2$·nH$_2$O can decompose to the metal (Garvie, unpublished data).

The effect of the electron beam on inorganic materials depends on factors that include incident electron energy, probe current density, dimensions of the irradiated volume, and sample temperature (Egerton et al. 1987; Inui et al. 1990; Champness and Devenish 1992). In addition, the structure of the material and presence of water and OH will affect the rate and type of damage caused by the beam. Studies of ionic inorganic solids have shown that the primary damage effect is decomposition, for example, transformation of CaCO$_3$ to CaO. This damage results from the effects of ionization within the irradiated area by the incident electron beam (Hobbs 1979). At high fluence rates it is also possible to remove cations such as Al$^{3+}$ in minerals (Champness and Devenish 1992).

Certain metals are susceptible to reduction in the TEM by the...