

## **Iron oxidation state in phyllosilicate single crystals using Fe-*K* pre-edge and XANES spectroscopy: Effects of the linear polarization of the synchrotron X-ray beam**

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### **ABSTRACT**

We investigated the influence of linear polarization of the synchrotron X-ray beam on the determination of iron oxidation state in phyllosilicates. Fe *K*-edge XANES spectra and pre-edge peaks have been recorded for various orientations of single crystals of biotite (Bt), clinocllore (chlorite group; Cli), talc (Tc), and antigorite (serpentine group; Ant). Ab initio XANES calculations, performed for 6 orientations of the biotite structure, support the experimental results. Depending on crystal orientation, the experimental results show, (1) important changes both for XANES and pre-edge peaks, (2) characteristic changes of spectral signatures regardless of the mineral species, (3) uncorrelated changes between XANES and pre-edge peaks, and (4) important changes of the energy position of pre-edge peaks, but with no significant change for their integrated areas. Regarding the crystal orientation, the pre-edge peak centroid varies in energy by ~0.4 eV in the case of Bt and Tc, and by ~0.2 eV for Cli and Ant. Such variations correspond to  $X\text{Fe}^{3+}$  (i.e.,  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ) of 0.22 and 0.15, respectively. Comparison with the analysis of powdered samples show that Fe-redox can be generally framed as follows:  $-(2/3)X\text{Fe}^{3+} < X\text{Fe}_{\text{(powder)}}^{3+} < +(1/3)X\text{Fe}^{3+}$ . In good agreement with the so-called “magic angle” theorem for powdered samples, we propose an ideal orientation of the single crystals that provide similar pre-edge peaks as for powdered samples. With the wavevector (i.e., beam direction) perpendicular to (100) or (010), measurements should be done with an angle of 35° between the electric-field vector and the [001] crystal direction. Moreover, measurements performed with the wavevector perpendicular to (001) systematically result in an overestimation of  $X\text{Fe}^{3+}$  up to 0.07. Finally, we show that the appropriate positioning of single crystals reduces the  $X\text{Fe}^{3+}$  uncertainty to the intrinsic error of pre-peak measurements. This approach opens possibilities for in situ analyses of Fe-bearing phyllosilicates in thin sections that are potentially relevant for scientific fields such as hydrothermal/metallogenic, metamorphic, meteoritic or environmental mineralogy.

**Keywords:** Iron, redox, polarization, XANES, phyllosilicates