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Fe K-edge XANES and pre-edge polarization dependance for the determination of the oxidation state of iron in antigorite and other phyllosilicates

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Iron oxidation state in minerals is often a crucial indicator for the understanding of mineralogical reactions related to hydrothermalism, or various natural processes. We investigated here the influence of the linear polarization of the synchrotron X-ray beam on the determination of the iron oxidation state in phyllosilicates. Fe K-edge XANES spectra and pre-peaks of biotite (Bt), chlorite (Chl), talc (Tlc) and antigorite (Atg) crystals have been recorded at different crystal orientations. As a function of the crystal orientation, the experimental results show, 1) important changes both for XANES and pre-peaks, 2) typical changes of spectral signatures for all mineral species, 3) uncorrelated changes between XANES and pre-peaks, 4) important changes of the pre-peak energies, but no significant change of the integrated areas. Ab initio XANES calculations, performed for 6 orientations of the Bt structure are consistent with the experimental measurements. The energy position of the pre-peak centroids changes with crystal orientation by 0.4 eV for Bt and Tlc crystals, and by 0.2 eV for Chl and Atg, which correspond to $\mathrm{XFe}^{3+}_{(apparent)}$ variations (2δ) of 0.22 and 0.15, respectively. Measurements on powdered crystals show that – $(2/3)2\delta < \mathrm{XFe}^{3+}_{(powder)} < + (1/3)2\delta$. Therefore, the analysis of a randomly oriented crystal drives to an error of $(2/3)2\delta = 0.15$ at maximum for Bt and Tlc, and 0.10 for Chl and Atg. In agreement with the so-called "magic angle" theory, we propose an ideal positioning of the crystals relative to the incident X-ray beam to measure pre-edge peaks similar to powdered samples. Measurements performed perpendicular to the (100) or (010) planes should be done with an angle of $\sim 35^\circ$ between the electric-field vector of the X-ray beam and the [001] crystal direction. Measurements performed perpendicular to the (001) plane will systematically drive to an overestimation of the XFe^{3+} of ~ 0.07. The influence of the averaged redox of iron for the different minerals investigated will also be discussed. In conclusion, an appropriate positioning of the single crystals may reduce the XFe^{3+} uncertainty to the intrinsic error of pre-peak measurements (i.e., about ± 5 %), opening possibilities for in situ thin section analyses at the micrometric scale, potentially relevant for scientific fields such as hydrothermalism (serpentinization processes), as well as metamorphic, metallogenic or meteoritic petrology.