

Polarized Fe Pre-Edge XANES Spectroscopy of Oriented Fe-Rich Micas

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Beamline(s): X26A

Introduction: The mica mineral group includes many rock-forming mineral species, all having perfect one-directional cleavage and considerable optical anisotropy. Because the intensity and energy of the Fe pre-edge peaks of micas reflect the oxidation state and coordination of Fe in single crystal XANES studies, understanding the magnitude and nature of their orientation dependence is critically important. In this study we have exploited the polarization of the X-ray beam to examine the effects of orientation on pre-edges of mica Fe K edge spectra.

Methods and Materials: Samples were prepared by orienting "books" of mica end-on, and embedding them in epoxy. Two polished faces perpendicular to the cleavage plane were made, creating a mounts approximately 30-100 μm thick. Spectra were run at beamline X26A at the NSLS using the X-ray microprobe and a beam size of <20 μm diameter. Pre-edges were extracted by fitting backgrounds to the pre-edge with a spline function.

Results: These spectra show the magnitude of effects of orientation on pre-edge features. Figures 1, 2, and 3 show mineral spectra taken with the polarization direction of the synchrotron beam at angles between perpendicular to and parallel to the cleavage direction. These spectra were run on samples that were previously studied using Mössbauer spectroscopy, and subsequently analyzed with optical and FTIR spectroscopy.

These data show variable amounts of energy shift with orientation when only singlet fits are used. The clintonite spectrum (Figure 1) is composed of a singlet peak corresponding to $^{54}\text{Fe}^{3+}$, the center of which does not move within errors. Its position varies from 7113.45 eV when the beam is polarized perpendicular to cleavage, to 7113.39 eV, 7113.27 eV, and 7113.33 eV at angles of 30° , 60° , and 90° from that cleavage. Although Mössbauer spectroscopy suggests that this sample does contain some 24% of the total Fe as Fe^{2+} , the weak peak corresponding to $^{56}\text{Fe}^{2+}$ simply is not visible because the tetrahedral peak is so intense.

Figures 2 (RS-MR-8) and 3 (Cape Ann) show great variation in the intensity of their pre-edge spectra with orientation. In both of these samples, almost all the Fe (100% for RS-MR-8 and 97% for Cape Ann) is in the octahedral sites. The orientation at which maximum intensity occurs is not necessarily parallel to or perpendicular to cleavage, and it is different for the two samples. This implies that the orientation of these two samples within the *a-b* plane is variable, such that different bonds are being sampled, and bonds around the octahedral site are noncentrosymmetric. Ironically, when singlet peaks are fit to these pre-edges, the results yield remarkably consistent centroids in eV space for all but the 60° orientation in RS-MR-8. The resultant % Fe^{3+} contents from 0- 90° are 72%, 74%, 89%, and 80% of the total Fe as Fe^{3+} for Cape Ann, and 54%, 61%, 31%, and 56% of the total Fe as Fe^{3+} for RS-MR-8. Mössbauer results on these samples were 55% Fe^{3+} and 31% Fe^{3+} , respectively.

Conclusions: Ultimately, in order to obtain the most precise quantitative results on $\text{Fe}^{3+}/\Sigma\text{Fe}$ in micas, it will probably be necessary to know the orientation of every grain. Clearly, the issue of identifying grain orientations in thin sections and properly interpreting the resultant XANES spectra will continue to remain a major problem in quantification of $\text{Fe}^{3+}/\Sigma\text{Fe}$ using this technique until further carefully-constrained measurements are made and the effects of orientation on pre-edge intensity are better understood.

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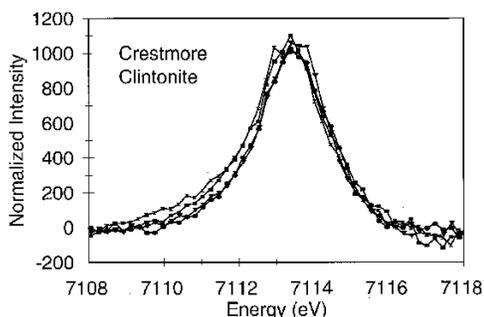


Figure 1. Pre-edge spectrum of clintonite, which is dominated by intense absorption by 4-fold Fe^{3+} .

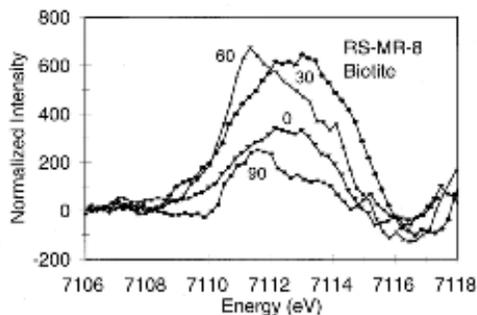


Figure 2. Octahedral Fe^{2+} and Fe^{3+} in biotite.

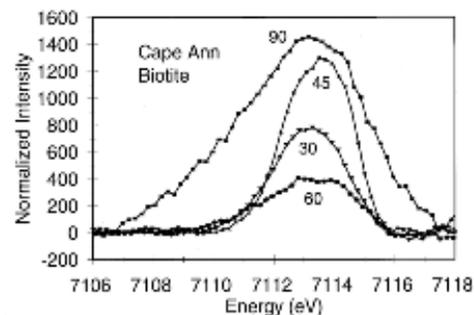


Figure 3. Oxidized biotite from Cape Ann, Mass.