

Iron and Aluminium Site Occupancies in Hydrus 2:1 Layer Silicates: I. Iron

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For all but the last 12 hours of our week-long session at the NSRRC, the ASRP end-station was unavailable for user use. Thus, we were unable to collect fluorescence data. Instead total electron yield (measured as drain current) data were collected on smectites at the Fe K edge on NSRRC beamline BL 24A1 (BM-WR-SGM) using the Taiwanese end-station. Sufficient resolution for the Fe L edge was observed (see Figures 1 and 2). We have confidence that we can better study structural relationships between Al and Fe in hydrus smectites, as was the original intent of the proposal.

Fe L edge NEXAFS

The Fe L-edge NEXAFS spectra were as drain current and in Partial Electron Yield (PEY). Fe L edge NEXAFS spectra, normalized to the total Fe content of the samples, are presented in Figure 1. The energy was calibrated against ferrihexacyanide.

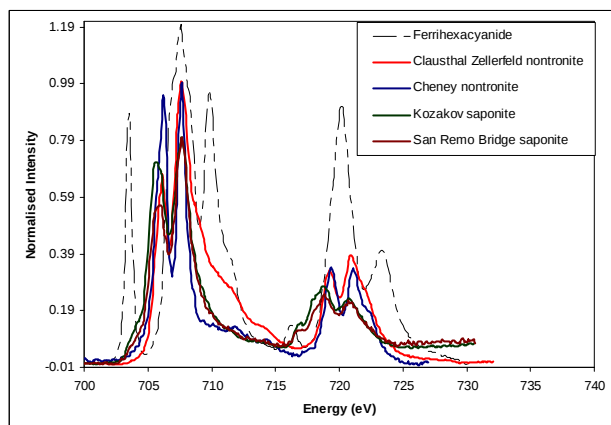


Figure 1. Normalized Fe L edge X-ray spectra of smectites.

The four smectite samples displayed above were two dioctahedral nontronites (Clausthal Zellerfeld, 44.23% Fe_2O_3 ; Cheney, 29.39 % Fe_2O_3) and two trioctahedral saponites (Kozakov, 4.2% Fe_2O_3 ; San Remo Bridge, 3.97% Fe_2O_3). The L3 resonances for octahedral Fe^{3+} are at 708.2 and 709.7 eV, but there appears to be little affect of tetrahedral Fe^{3+} for the two nontronites (Figure 2). Our preliminary results indicate that the first of these two peaks (708.2 eV) has lower relative intensity relative to the second (709.7 eV) with increasing tetrahedral Fe^{3+} content. Gates et al., (2002. *Clays and Clay Minerals*, 50:223-239) showed, using a variety of techniques, that Clausthal Zellerfeldt had considerably more tetrahedral Fe^{3+} than Cheney. Thus the ability of L-edge NEXAFS spectroscopy to enable differentiation of tetrahedral coordination in smectites might be limited compared to Fe K edges XANES and XAFS spectroscopy. The two saponites also have a significant amount (~30%) of

ferrous iron as FeO (Figure 2). Octahedral Fe^{2+} is evidenced in the L3 spectra as peaks with chemical shifts of about near 706 and 707.8 eV, or shifted by about 2 eV, as expected. Assignments in the L2 region of the X-ray spectra are tentative.

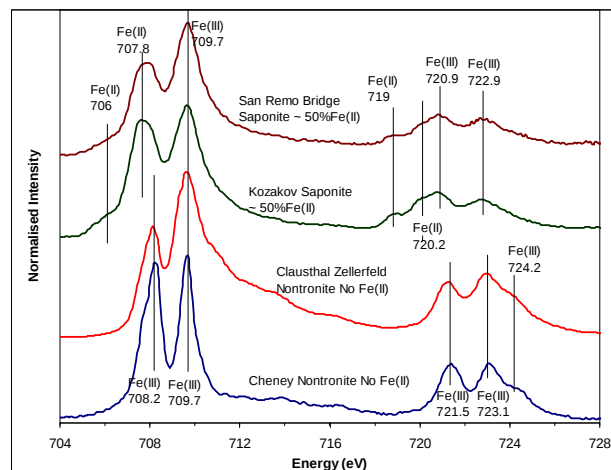


Figure 2. Details of the Fe L edge X-ray absorption spectra of dioctahedral and trioctahedral smectites.

These preliminary results indicate that the Fe L edge NEXAFS spectrum of nontronite is rich in information regarding valence state and possibly also coordination. However there is strong overlap between ferrous iron (707.8 eV) in the saponites and ferric Fe (708.2 eV) in the nontronites. Thus caution needs to be emphasized when using Fe L edge NEXAFS to study mixed valence states of iron in smectites. The lower Fe content of the saponite samples, together with probably greater disorder in the actual octahedral sites occupied by both ferric and ferrous Fe in these clays, result in significant broadening and loss of resolution. However, it appears that the energy resolution is sufficient to distinguish between not only ferrous and ferric Fe, but also tetrahedral and octahedral Fe.

Conclusions

The Fe L edge NEXAFS is potentially rich in detail and such study can add to the crystal-chemical information of iron rich smectites.