Iron Sites in Nontronite and the Effect of Interlayer Cations From Mössbauer Spectra

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Abstract: The ^{57}Fe Mössbauer spectra of untreated, Ca- and K-saturated nontronite from Garfield, Washington, were measured. The spectrum of the untreated sample was computer-fitted to 8 peaks defining two octahedral, a tetrahedral, and an interlayer Fe^{3+}-quadrupole-split doublets. In the Ca- and K-saturated samples interlayer Fe was absent. Spectra of the untreated sample were recorded at increasing increments of background counts from 2.8×10^5 to 9.2×10^6. An evaluation of the initial 4- and 6-peak models and the acceptable 8-peak model, computer-fitted to each spectrum, shows that if the X^2 value is used as a measure of the goodness of the fit, the spectra should be recorded to a background count greater than 3×10^6. The resulting χ^2 value then reflects both the validity of the model used and the extent of disorder within the structure. The χ^2 value depends linearly on the background counts obtained.

A comparison of the spectra of the Ca- and K-saturated samples with that of the untreated sample shows that the interlayer cations exert a considerable influence on the individual component resonances, particularly the outer octahedral doublet. Hence, it is likely that electrostatic interactions of the nearby tetrahedral Fe^{3+} and the interlayer cations give rise to two distinct electric field gradients within neighboring *cis*-$[FeO_4(OH)_2]$ sites, and hence two octahedral Fe^{3+} doublets in the Mössbauer spectrum. These results are consistent with earlier electron diffraction data in the literature.

Key Words: Interlayer cation • Iron • Mössbauer spectroscopy • Nontronite • Octahedral site

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