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Revisiting the nontronite Mössbauer spectra

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Abstract

The distribution of ferric iron (Fe^{3+}) between the octahedral and tetrahedral sheets of smectites is still an active problem due to the difficulty of identifying and quantifying the tetrahedral ferric iron ($^{[4]}Fe^{3+}$). Mössbauer spectroscopy has often been used to address this problem, with the spectra being fitted by a sum of doublets, but the empirical attribution of each doublet has failed to yield a uniform interpretation of the spectra of natural reference Fe^{3+}-rich smectites, especially with regard to $^{[4]}Fe^{3+}$, because little consensus exists as to the $^{[4]}Fe^{3+}$ content of natural samples. In an effort to resolve this problem, the current study was undertaken using a series of synthetic nontronites $[Si_{4-x}\ ^{[4]}Fe^{3+}_x]\ ^{[6]}Fe^{3+}_2O_{10}(OH)_2Na_x$ with x ranging from 0.51 to 1.3. Mössbauer spectra were obtained at 298, 77, and 4 K. Statistically acceptable deconvolutions of the Mössbauer spectra at 298 and 77 K were used to develop a model of the distribution of tetrahedral substitutions, taking into account: (1) the $^{[4]}Fe^{3+}$ content; (2) the three possible tetrahedral cationic environments around $^{[6]}Fe^{3+}$, i.e., [4Si]-(3$^{[6]}Fe^{3+}$), [3Si $^{[4]}Fe^{3+}$]-(3$^{[6]}Fe^{3+}$), and [2Si 2$^{[4]}Fe^{3+}$]-(3$^{[6]}Fe^{3+}$); and (3) the local environment around a $^{[4]}Fe^{3+}$, i.e., [3Si]-(2$^{[6]}Fe^{3+}$) respecting Lowenstein's Rule. This approach allowed the range of Mössbauer parameters for $^{[6]}Fe^{3+}$ and $^{[4]}Fe^{3+}$ to be determined and then applied to spectra of natural Fe^{3+}-rich smectites. Results revealed the necessity of taking into account the distribution of tetrahedral cations ($^{[4]}R^{3+}$) around $^{[6]}Fe^{3+}$ cations to deconvolute the Mössbauer spectra, and also highlighted the influence of sample crystallinity on Mössbauer parameters.

Keywords: Clay minerals, iron, Mössbauer spectroscopy, nontronite, smectites, tetrahedral iron