

Revisiting the nontronite Mössbauer spectra

FABIEN BARON^{1,*}, SABINE PETIT¹, MARTIN PENTRÁK², ALAIN DECARREAU¹, AND JOSEPH W. STUCKI²

¹Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), UMR CNRS 7285 Université de Poitiers, Poitiers, France
²Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana–Champaign, Urbana, Illinois, U.S.A.

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 ($^{44}\text{Fe}^{3+}$). 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 $^{44}\text{Fe}^{3+}$, because little consensus exists as to the $^{44}\text{Fe}^{3+}$ content of natural samples. In an effort to resolve this problem, the current study was undertaken using a series of synthetic nontronites $[\text{Si}_{4-x}^{44}\text{Fe}_x^{3+}]^{6+}\text{Fe}_2^{3+}\text{O}_{10}(\text{OH})_2\text{Na}_x$ 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 $^{44}\text{Fe}^{3+}$ content; (2) the three possible tetrahedral cationic environments around $^{66}\text{Fe}^{3+}$, i.e., $[\text{4Si}]-(\text{3}^{66}\text{Fe}^{3+})$, $[\text{3Si}^{44}\text{Fe}^{3+}]-(\text{3}^{66}\text{Fe}^{3+})$, and $[\text{2Si}^{2^{44}\text{Fe}^{3+}}]-(\text{3}^{66}\text{Fe}^{3+})$; and (3) the local environment around a $^{44}\text{Fe}^{3+}$, i.e., $[\text{3Si}]-(\text{2}^{66}\text{Fe}^{3+})$ respecting Lowenstein's Rule. This approach allowed the range of Mössbauer parameters for $^{66}\text{Fe}^{3+}$ and $^{44}\text{Fe}^{3+}$ 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 ($^{44}\text{R}^{3+}$) around $^{66}\text{Fe}^{3+}$ 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