

## IRON SITES IN NONTRONITE AND THE EFFECT OF INTERLAYER CATIONS FROM MÖSSBAUER SPECTRA

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**Abstract**—The  $^{57}\text{Fe}$  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  $\text{Fe}^{3+}$ -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  $2.8 \times 10^5$  to  $9.2 \times 10^6$ . 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  $\chi^2$  value is used as a measure of the goodness of the fit, the spectra should be recorded to a background count greater than  $3 \times 10^6$ . The resulting  $\chi^2$  value then reflects both the validity of the model used and the extent of disorder within the structure. The  $\chi^2$  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  $\text{Fe}^{3+}$  and the interlayer cations give rise to two distinct electric field gradients within neighboring *cis*- $[\text{FeO}_4(\text{OH})_2]$  sites, and hence two octahedral  $\text{Fe}^{3+}$  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.

### INTRODUCTION

End-member nontronite has the idealized composition  $(\text{Ca}_{0.05}\text{Na})_{0.66}\text{Fe}_4^{3+}(\text{Si}_{7.34}\text{Al}_{0.66})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ . Some  $\text{Al}^{3+}$ , however, usually substitutes for  $\text{Fe}^{3+}$  in the octahedral sites. Montmorillonite has the same basic structure as nontronite with  $\text{Al}^{3+}$ , some  $\text{Mg}^{2+}$ , and minor  $\text{Fe}^{3+/2+}$  occupying the octahedral sites. In these smectite structures the  $\text{AlO}_4(\text{OH})_2$  octahedra are arranged in sheets with  $\frac{2}{3}$  of the sites (M2) having a *cis* arrangement of the OH ions and  $\frac{1}{3}$ , a *trans* arrangement (M1). The  $^{57}\text{Fe}$  Mössbauer spectrum of nontronite generally shows a broadened ferric resonance with a small quadrupole splitting. Goodman *et al.* (1976), Rozenon and Heller-Kallai (1977), and Heller-Kallai and Rozenon (1981) computer-fitted this resonance to two  $\text{Fe}^{3+}$  doublets with approximately the same isomer-shift ( $\delta$ ) values, but with quadrupole-interaction ( $\Delta$ ) values differing by a factor of 2. Inasmuch as a simple point-charge model shows that the quadrupole splitting of  $\text{Fe}^{3+}$  in octahedral coordination of the type  $\text{FeX}_4\text{Y}_2$  with the Y ligands in the *trans* positions is twice that when the Y ligands are *cis* (Goodman, 1976), the outer doublet has been assigned to  $\text{Fe}^{3+}$  in the  $\text{FeO}_4(\text{OH})_2$  site with the *trans* arrangement of the OH groups. Similarly, the inner doublet has been assigned to that with the *cis* arrangement of OH groups. Also, the *cis* doublet is usually about twice as intense as the *trans* doublet which corresponds to the actual ratio of these different types of sites in the smectite structure, suggesting that Fe substitutes to approximately an equal extent, in each site.

The experimental Mössbauer spectrum of montmorillonite is a similarly broadened  $\text{Fe}^{3+}$  resonance but with a larger quadrupole interaction. Again, this resonance can be computer-fitted to two overlapping doublets which have been assigned likewise to Fe in the *cis* and *trans* sites. Goodman *et al.* (1976) also managed to fit a further less intense  $\text{Fe}^{3+}$  doublet with a smaller value of  $\delta$  (Table 1) to the nontronite spectrum and attributed the doublet to  $\text{Fe}^{3+}$  substituting for (Si,Al) in the tetrahedral layer. From electron diffraction data, however, Mering and Oberlin (1967), and more recently Besson *et al.* (1983), showed that nontronite has a centrosymmetric space group, whereas montmorillonite has a non-centrosymmetric one. Hence, these two clay minerals are structurally different. An important consequence of this structural difference is that for a smectite structure to be centrosymmetric, the *trans* octahedral sites must be vacant (Goodman, 1978). Hence, in nontronite the only octahedral sites which can be occupied by  $\text{Fe}^{3+}$  ions are those with the *cis* arrangement (M2) of octahedral OH groups, whereas in montmorillonite both the *cis* (M2) and *trans* (M1) sites can be occupied. Therefore, for montmorillonite the assignment of the outer and inner  $\text{Fe}^{3+}$  doublets in the Mössbauer spectrum to the presence of  $\text{Fe}^{3+}$  in the *trans* and *cis* octahedral sites appears to be valid, but for nontronite such an assignment cannot be correct.

The question which now arises is that if the  $\text{Fe}^{3+}$  in nontronite is present in *cis* sites only, what gives rise to the two overlapping  $\text{Fe}^{3+}$  doublets in the Mössbauer

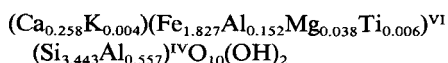
spectrum which have quadrupole interactions differing by a factor of  $\sim 2$ . To explain these doublets, Goodman (1978) showed that the magnitude of  $\Delta$  for the outer octahedral  $\text{Fe}^{3+}$  doublet is related to the extent of substitution in the  $(\text{Si,Al})\text{O}_4$  tetrahedra by  $\text{Fe}^{3+}$ . He also suggested that if  $\sim 15\%$  of the tetrahedral sites are randomly occupied by trivalent ions, about 60% of the octahedral sites should have a trivalent ion in a neighboring tetrahedral site. The octahedral (M2) sites are thus not equivalent, because the trivalent ion may be coordinated to an oxygen atom which is adjacent to both the hydroxyl groups, or to an oxygen atom which is adjacent to one hydroxyl but opposite the other. On the basis of a point-charge model, the former arrangement would increase the electric field gradient, whereas the latter would probably decrease it, thus, giving rise to the two octahedral  $\text{Fe}^{3+}$  doublets, consistent with the experimental data for nontronite.

It therefore seems that in such smectite structures not only next nearest neighbor atoms but also those slightly more distant have a significant effect on the electric field gradient of  $\text{Fe}^{3+}$  in the octahedral sites. If these long-range interactions are significant, the interlayer cations should similarly influence the Mössbauer spectrum. Also, if the tetrahedral and octahedral substitution by Fe is not random or there is a degree of disorder in the structure, perhaps arising from the extent of interlayer substitution, the Mössbauer spectrum should be influenced accordingly.

In this paper a detailed study and computer-fitting of the Mössbauer spectra of Garfield, Washington, nontronite in its untreated and Ca- and K-saturated forms are presented to elucidate the site occupancy of Fe in the structure and to determine what effect the interlayer cation has on the spectrum. Inasmuch as the  $\chi^2$  test is usually used as a statistical measure of the goodness of fit, the way in which the  $\chi^2$  value varies with the total number of counts recorded for each spectrum and with the different structural models for cation substitution is also presented.

## EXPERIMENTAL

Samples of untreated and Ca- and K-saturated nontronite, A.P.I. H33a, from Garfield, Washington, were supplied by K. Norrish, Division of Soils, C.S.I.R.O., Adelaide, Australia. The analysis of the Ca-saturated sample gives the composition:



when calculated in the conventional manner, filling the tetrahedral sites only with Si and Al.

$^{57}\text{Fe}$  Mössbauer spectra were recorded over the range  $\pm 2.7$  mm/sec for all samples at room temperature using an ELSCINT AME40C Spectrometer and a  $^{57}\text{Co}$  source in a rhodium matrix. The velocity scale was calibrated with reference to natural iron, with the mid-

point of the hyperfine Fe spectrum defining zero velocity. The spectra were computer-fitted to a number of Lorentzian peak line-shapes using a  $\chi^2$  minimization procedure. To achieve convergence it was generally necessary to constrain the widths and dips of corresponding pairs of peaks in a particular doublet to be equal. Using the  $\chi^2$  value as a criterion for the goodness of fit, the 1% and 99% confidence limits are 574 and 427 for 4-peak fits, 570 and 424 for 6-peak fits, and 566 and 420 for 8-peak fits.

To determine how the value of  $\chi^2$  obtained for a particular model and computer-fit depended on the total number of recorded counts, the spectrum for the untreated sample was output at 10 different intervals with the background counts incremented from about  $2.8 \times 10^5$  to  $9.2 \times 10^6$ . The spectrum with a background count of  $7.6 \times 10^6$  was initially computer-fitted to a 4-peak model (2 octahedral  $\text{Fe}^{3+}$  sites), a 6-peak model (2 octahedral plus 1 tetrahedral or interlayer  $\text{Fe}^{3+}$  sites), and an 8-peak model (2 octahedral, 1 tetrahedral, and an interlayer  $\text{Fe}^{3+}$  sites). Convergence could only be achieved with the 4- and 8-peak models, hence, these models were fitted to the other spectra in this suite. For a few spectra, however, 6-peak fits were attempted but were unsuccessful. A similar set of 4-, 6-, and then 8-peak fits were also attempted for the Ca- and K-saturated samples. Only 6 peaks could be fitted satisfactorily to these spectra.

The X-ray powder diffraction patterns were recorded for all samples using a Philips PW 1730 Diffractometer equipped with a Co tube and a post-diffraction graphite monochromator.

## RESULTS AND DISCUSSION

A selection of the experimental Mössbauer spectra, together with their associated 4-, 6-, and 8-peak fits, for the untreated nontronite collected to various increasing total background counts are presented in Figures 1 and 3. As expected, the experimental spectra show a considerable scatter in the data points defining the experimental envelope for the low background count of  $2.8 \times 10^5$ . As the total count increased, this scatter was proportionally decreased, and the peak/background ratio increased, thereby producing a more clearly defined experimental spectrum (e.g., see Figures 1a to 1c).

When four peaks consistent with the two, octahedral- $\text{Fe}^{3+}$  doublet model used by previous workers were computer-fitted to the spectrum with  $2.8 \times 10^5$  background counts (Figure 1a), an acceptable  $\chi^2 = 542$  was obtained (Table 1). As this 4-peak model was successively fitted to each spectrum with an increased background count, however, the  $\chi^2$  value increased progressively to 1625 for the spectrum with  $9.2 \times 10^6$  counts (Table 1). A close inspection showed that for the spectra recorded with the increased counts (Figure 1c), the summed computer-fitted envelope deviated

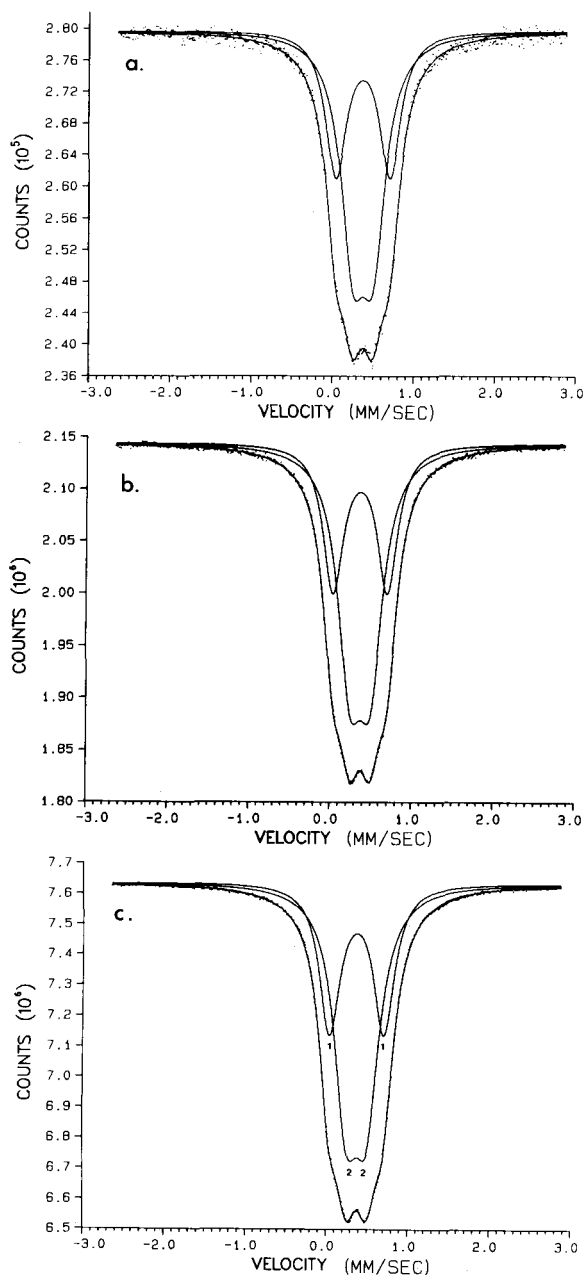


Figure 1. Experimental and computer-fitted Mössbauer spectra for the four-peak model defining two octahedral  $\text{Fe}^{3+}$  doublets for untreated Garfield, Washington, nontronite recorded to background counts of: (a)  $2.80 \times 10^5$ , (b)  $2.14 \times 10^6$ , (c)  $7.63 \times 10^6$  (doublets 1 = outer octahedral, 2 = inner octahedral).

notably from the experimental envelope in the region of the peak apices and also slightly at the base of the envelope at about 1.4 mm/sec. With the lower total counts the experimental spectrum was less well defined; such deviations were not observed (Figure 1a),

and the  $\chi^2$  value was statistically acceptable. These results clearly indicate that the 4-peak model is inadequate and total counts of about  $2.3 \times 10^6$  or greater are required in order for  $\chi^2$  to measure acceptability. It is interesting to note that a plot of  $\chi^2$  vs. background counts was linear (Figure 2), and that a regression analysis gave  $r = 0.999$ . Although the  $\chi^2$  value became less statistically acceptable with increased counts, the respective widths, relative peak areas,  $\Delta$ , and  $\delta$  values did not change, indicating that the accuracy of the parameters in this 4-peak model was not improved with the increased counts. Up to about  $2 \times 10^6$  counts, the precision was, however, improved.

Because Goodman *et al.* (1976) were able to fit a further tetrahedral  $\text{Fe}^{3+}$  doublet to their spectrum for a Garfield nontronite (A.P.I. H33b), which is similar to the one used here, the next approach was to do likewise using first the spectrum of  $7.6 \times 10^6$  background counts. Even with width and dip constraints on the appropriate doublets, however, it was not possible to achieve convergence for such a 6-peak fit. Similar results were obtained for the 6-peak fits to a selection of the other spectra. As the small shoulder at about 1.4 mm/sec suggests, additional Fe must be present in interlayer sites (Diamant *et al.*, 1982), the next step was to fit 6 peaks defining the two octahedral and an interlayer  $\text{Fe}^{3+}$  doublet rather than a tetrahedral one. A converged fit was obtained for the  $7.6 \times 10^6$  count spectrum (Figure 3a), but the high  $\chi^2 = 1708$  suggested that the model was still incomplete. Eight peaks defining the two octahedral, an interlayer, and a tetrahedral  $\text{Fe}^{3+}$  doublet were successfully computer-fitted to this spectrum (Figure 3d). The summed fitted envelope coincided with the experimental envelope much more closely, and  $\chi^2 = 982$ , although greater than the 1% confidence limit, was significantly improved over that for the 4- and 6-peak models. A similar set of 8 peaks was fitted to the other spectra in this suite. The parameters of these fits are presented in Table 2, and the experimental and computer-fitted spectra with background counts of  $2.8 \times 10^5$ ,  $2.1 \times 10^6$ , and  $7.6 \times 10^6$  are shown in Figures 3b to 3d. As with the 4-peak model, only the  $\chi^2$  values for the spectra recorded to about  $5.3 \times 10^5$  counts were statistically acceptable. With increasing counts,  $\chi^2$  increased to 1032 for the spectrum with  $9.3 \times 10^6$  counts. In all spectra, however, these values were less than those for the corresponding 4-peak models (Tables 1 and 2).

The plot of the  $\chi^2$  value vs. counts in Figure 2 is linear, with  $r = 0.995$ . The increasing values of  $\chi^2$  with increasing counts again suggested that this 8-peak Lorentzian model was not completely consistent with the experimental spectrum and that the inconsistency was more pronounced when the experimental spectrum was more clearly resolved at higher counts. It is not possible for Fe to substitute in any other sites within the nontronite structure, and hence, the above inconsistency

Table 1. Computer-fitted Mössbauer spectral data for the four-peak model for untreated nontronite from Garfield, Washington.

Background counts	$\chi^2$	Inner octahedral Fe <sup>3+</sup> doublet				Outer octahedral Fe <sup>3+</sup> doublet			
		$\delta$ (mm/sec)	$\Delta$ (mm/sec)	Width (mm/sec)	Relative area	$\delta$ (mm/sec)	$\Delta$ (mm/sec)	Width (mm/sec)	Relative area
$2.80 \times 10^5$	542	0.362 (9)	0.244 (9)	0.36 (2)	0.62 (3)	0.361 (9)	0.662 (9)	0.31 (1)	0.38 (3)
$5.28 \times 10^5$	572	0.362 (7)	0.246 (7)	0.36 (1)	0.62 (1)	0.362 (7)	0.663 (7)	0.31 (1)	0.38 (2)
$1.65 \times 10^6$	711	0.364 (6)	0.245 (6)	0.36 (1)	0.62 (1)	0.363 (6)	0.662 (6)	0.31 (1)	0.38 (1)
$2.14 \times 10^6$	806	0.363 (4)	0.248 (4)	0.37 (1)	0.63 (1)	0.363 (4)	0.665 (4)	0.31 (1)	0.37 (1)
$3.38 \times 10^6$	932	0.364 (4)	0.247 (4)	0.37 (1)	0.62 (1)	0.363 (4)	0.665 (4)	0.31 (1)	0.38 (1)
$7.63 \times 10^6$	1465	0.364 (4)	0.248 (4)	0.371 (5)	0.620 (7)	0.363 (4)	0.668 (4)	0.310 (4)	0.380 (6)
$9.23 \times 10^6$	1625	0.364 (4)	0.248 (4)	0.371 (5)	0.618 (6)	0.363 (4)	0.667 (4)	0.311 (4)	0.382 (6)

must have arisen from other factors, such as disorder within the structure. It is likely that some disorder existed and that the variable local geometry around a particular type of crystallographic site within the structure produced on average a broadening of the Mössbauer resonance for that site. Such broadening could have led to lineshapes which could not be satisfactorily modeled by Lorentzians, as discussed next.

If a particular broadened peak is truly a single peak rather than a composite of two or more peaks, then the additional width and different shape may be due to the smearing out of the absorption maxima along the velocity (energy) axis, such that the absorption maximum for each resonant atom of the same crystallographic sites do not exactly coincide (Whipple, 1981). This slight energy shift arises from local disorder around the resonant atom sites caused by either structural imperfections or differing types and arrangements of the next nearest or even more distant neighboring atoms, even though the particular sites in question are crystallographically equivalent. This resulting line broadening is often termed "environmental broadening." The observed asymmetry and tailing of the peaks on the high-angle side in the XRD pattern, particularly

for the hk0 reflections, are evidence of structural disorder. Line broadening may also result from using a thick sample absorber, but this effect can be eliminated if the absorbers contain less than 10 mg/cm<sup>2</sup> of natural Fe (Bancroft, 1973), as was used here.

Whipple (1981) showed that for such environmentally broadened spectra, the lineshape is better modeled by a Lorentzian-squared distribution rather than a Lorentzian distribution. When using the Lorentzian-squared shape, the resulting  $\chi^2$  value was 25–28% less than for the corresponding Lorentzian shape, as was demonstrated by Whipple (1981) for a clinopyroxene, for which the spectrum was recorded to a background count of about  $3.2 \times 10^6$ . On this basis, if a Lorentzian-squared model were used for the Garfield nontronite, a similar 25% reduction in the  $\chi^2$  value would yield  $\chi^2 = 529$  and 699 for the 8- and 4-peak fits, respectively, to the spectrum with a background count of  $3.4 \times 10^6$ . This makes the 8-peak model statistically acceptable, but not the 4-peak one. These results add weight to the conclusion that the 8-peak model for this nontronite is correct and that the increased  $\chi^2$  values at increased counts were due to local disorder within the structure.

The computer-fitted parameters presented in Table 2 for these 8-peak fits show that the appropriate width, relative areas,  $\delta$ , and  $\Delta$  values for the respective octahedral and tetrahedral doublets were essentially the same for each of the spectra. Because the interlayer component was only about 1% of the total resonance and must have been close to the lower limit of detectability of the method, these parameters did not assume consistent values until a background count of  $3.4 \times 10^6$  was reached. The  $\delta$  and  $\Delta$  values for the two octahedral doublets (Table 2) are consistent with those of Goodman *et al.* (1976) when account is taken of the temperature dependence of  $\delta$  (Goodman *et al.* (1976) recorded their spectra at 78°K). The present results show that the inner of these doublets is slightly more intense than the outer, whereas they reported the reverse. It is interesting to note that if only two octahedral doublets are considered, the width of the outer one is greater than that of the inner (Table 1), which is also

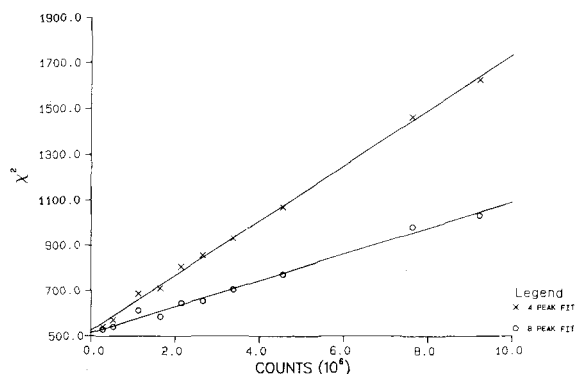


Figure 2. Dependence of the  $\chi^2$  value on the background counts for the four- and eight-peak models computer-fitted to the experimental Mössbauer spectra of untreated Garfield, Washington, nontronite.

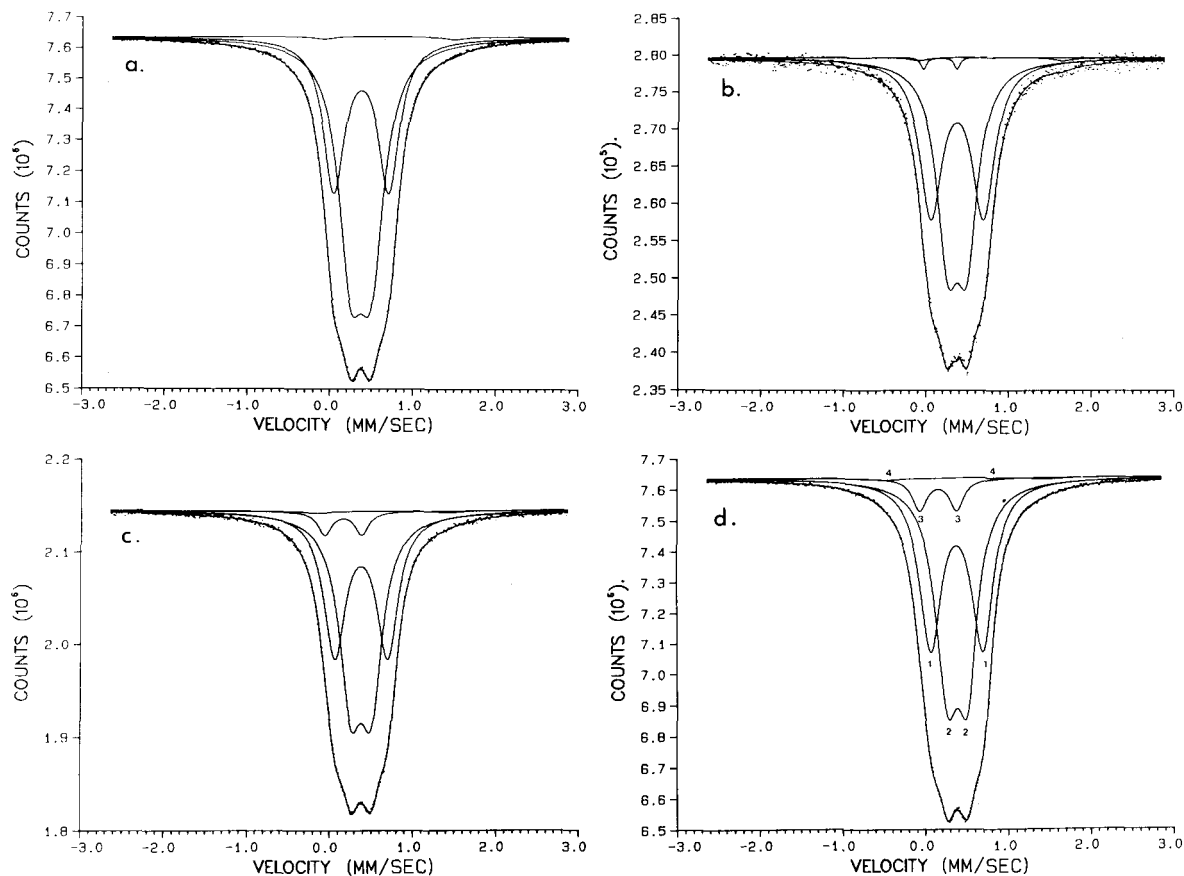


Figure 3. Experimental and computer-fitted Mössbauer spectra of untreated Garfield, Washington, nontronite for the six-peak model defining two octahedral and an interlayer  $\text{Fe}^{3+}$  doublet for the spectrum with  $7.63 \times 10^6$  counts (a); the eight-peak model defining two octahedral, a tetrahedral and an interlayer  $\text{Fe}^{3+}$  doublets for (b)  $2.80 \times 10^5$ , (c)  $2.14 \times 10^6$ , and (d)  $7.63 \times 10^6$  background counts (doublets: 1 = outer octahedral, 2 = inner octahedral, 3 = tetrahedral, 4 = interlayer).

consistent with the data of Goodman *et al.* (1976). When 8 peaks are considered these widths are similar. Rozenson and Heller-Kallai (1977) noted that in a Washington nontronite, although the parameters for the two octahedral doublet fit resembled those of Goodman *et al.* (1976), no improvement in  $\chi^2$  was achieved by the addition of a further tetrahedral doublet. The present results show that tetrahedral Fe is present and the  $\delta$ ,  $\Delta$ , and width values essentially agree with those of Goodman *et al.* (1976); however, the tetrahedral linewidth values of 0.08 (4) mm/sec for the spectrum with only  $2.8 \times 10^5$  counts are below those of natural linewidth (Table 2), and hence these peaks (Figure 2b) could not be resolved at the low count level. For all the spectra recorded to higher counts, these linewidths assumed acceptable values. Because Rozenson and Heller-Kallai (1977) recorded their spectra to  $2.4 \times 10^6$  counts, their inability to resolve this doublet was probably due to their using only 255 channels

to record the spectrum and constraining of the linewidths for all the  $\text{Fe}^{3+}$  peaks to be equal in their computer-fitting procedure.

Russell and Clark (1978) showed that for dioctahedral smectites the  $b$ -axis dimension is linearly dependent on the extent of  $\text{Fe}^{3+}$  in the tetrahedral sites. On this basis, the Garfield nontronite contains  $0.06 \text{ Fe}^{3+}/\text{O}_{10}(\text{OH})_2$  in the tetrahedral sites. If the Mössbauer peak areas are taken as a direct measure of the Fe content of that site, the results presented here give  $0.10 \text{ Fe}^{3+}/\text{O}_{20}(\text{OH})_4$ . However, as mentioned below, because of the difference in the recoilless fractions for each site, such an approach is not strictly valid. Even so, it may be concluded that  $\text{Fe}^{3+}$  is present in the tetrahedral sites of this mineral. The  $\delta$  value of 0.48 (4) mm/sec obtained for the interlayer Fe (Table 2) shows that this Fe is in the ferric state. The high value of  $\Delta = 1.94$  (4) mm/sec suggests that this interlayer site is rather distorted and is probably either considerably compressed

Table 2. Computer-fitted Mössbauer spectral data for the eight-peak model for untreated and the six-peak model for Ca- and K-saturated nontronite, Garfield, Washington.

Sample	Background counts	$\chi^2$	Inner octahedral Fe <sup>3+</sup> doublet				Outer octahedral Fe <sup>3+</sup> doublet			
			$\delta$ (mm/sec)	$\Delta$ (mm/sec)	Width (mm/sec)	Relative area	$\delta$ (mm/sec)	$\Delta$ (mm/sec)	Width (mm/sec)	Relative area
Untreated <sup>1</sup>	$2.80 \times 10^5$	530	0.366 (8)	0.230 (8)	0.32 (2)	0.51 (4)	0.366 (11)	0.634 (11)	0.33 (1)	0.47 (3)
	$5.28 \times 10^5$	542	0.374 (8)	0.239 (8)	0.31 (1)	0.49 (2)	0.376 (9)	0.628 (9)	0.32 (1)	0.45 (2)
	$1.65 \times 10^6$	586	0.376 (6)	0.243 (6)	0.32 (1)	0.50 (1)	0.379 (6)	0.629 (6)	0.32 (1)	0.44 (1)
	$2.14 \times 10^6$	647	0.374 (6)	0.246 (6)	0.32 (1)	0.52 (1)	0.377 (7)	0.634 (7)	0.31 (1)	0.43 (1)
	$3.38 \times 10^6$	705	0.376 (5)	0.245 (5)	0.322 (6)	0.501 (10)	0.378 (5)	0.633 (5)	0.318 (4)	0.440 (9)
	$7.63 \times 10^6$	982	0.377 (4)	0.245 (4)	0.318 (5)	0.492 (7)	0.379 (5)	0.632 (5)	0.321 (4)	0.445 (6)
Ca-sat. <sup>2</sup>	$9.23 \times 10^6$	1032	0.377 (4)	0.245 (4)	0.319 (5)	0.490 (6)	0.380 (4)	0.631 (4)	0.322 (4)	0.445 (5)
	$9.42 \times 10^6$	633	0.385 (7)	0.254 (7)	0.302 (9)	0.44 (1)	0.388 (7)	0.617 (7)	0.323 (6)	0.47 (1)
K-sat. <sup>3</sup>	$8.17 \times 10^6$	831	0.369 (6)	0.226 (6)	0.306 (11)	0.33 (1)	0.369 (6)	0.619 (6)	0.413 (5)	0.66 (1)
	—	437	0.50 (1)	0.27 (1)	0.32 (1)	0.54 (4)	0.50 (1)	0.62 (1)	0.29 (1)	0.37 (3)

Sample	Tetrahedral Fe <sup>3+</sup> doublet				Interlayer Fe <sup>3+</sup> doublet			
	$\delta$ (mm/sec)	$\Delta$ (mm/sec)	Width (mm/sec)	Relative area	$\delta$ (mm/sec)	$\Delta$ (mm/sec)	Width (mm/sec)	Relative area
Untreated <sup>1</sup>	0.157 (14)	0.403 (14)	0.08 (4)	0.01 (1)	0.77 (9)	1.75 (9)	0.29 (16)	0.01 (1)
	0.159 (13)	0.439 (13)	0.20 (2)	0.05 (1)	0.57 (17)	1.69 (17)	0.53 (34)	0.01 (1)
	0.160 (8)	0.445 (8)	0.21 (1)	0.05 (1)	0.54 (12)	1.87 (12)	0.65 (28)	0.01 (1)
	0.160 (8)	0.445 (8)	0.20 (1)	0.05 (1)	0.64 (8)	1.58 (8)	0.32 (11)	0.01 (1)
	0.158 (7)	0.447 (7)	0.207 (10)	0.051 (5)	0.48 (6)	1.93 (6)	0.45 (12)	0.008 (3)
	0.160 (5)	0.448 (5)	0.211 (7)	0.056 (3)	0.50 (4)	1.91 (4)	0.43 (9)	0.007 (2)
Ca-sat. <sup>2</sup>	0.160 (5)	0.450 (5)	0.214 (7)	0.057 (3)	0.48 (4)	1.94 (4)	0.42 (8)	0.007 (1)
	0.174 (9)	0.452 (9)	0.25 (1)	0.09 (1)	—	—	—	—
K-sat. <sup>3</sup>	0.07 (2)	0.52 (2)	0.17 (4)	0.01 (1)	—	—	—	—
	0.30 (1)	0.47 (1)	0.22 (1)	0.09 (2)	—	—	—	—

Table 2. Continued.

<sup>1</sup> d(001) = 15.31 Å, d(060) = 1.52 Å.<sup>2</sup> d(001) = 15.54 Å, d(060) = 1.52 Å.<sup>3</sup> d(001) = 12.22 Å, d(060) = 1.52 Å.<sup>4</sup> Goodman *et al.* (1976). Spectrum measured at 77°K.

or expanded along one of the electric field gradient axes, as has been observed for  $\text{Fe}^{3+}$  in epidote (Bancroft *et al.*, 1967).

These results show, therefore, that for such materials, if the  $\chi^2$  value is used as a measure of the goodness of the fit, the spectrum must be collected to a background count of preferably greater than  $3 \times 10^6$ , particularly if components amounting to only a few percent of the total resonance are to be resolved. A resulting value of  $\chi^2$  lying above the upper confidence level suggests that either further resonances are present that contribute to the experimental envelope which have not been considered, or disorder within the structure has resulted in Mössbauer absorption lineshapes which deviate from Lorentzian lineshape and are perhaps better modeled by a Lorentzian-squared lineshape. The existence of tetrahedral  $\text{Fe}^{3+}$  from the Mössbauer spectra shows that the usual practice in calculating the structural formulae of nontronites from their elemental composition, by compensating any deficiency in tetrahedral Si by Al, and only when this is exhausted inferring tetrahedral  $\text{Fe}^{3+}$ , is not justified. Tetrahedral  $\text{Fe}^{3+}$  may occur *in preference* to  $\text{Al}^{3+}$  (Heller-Kallai and Rozenson, 1981), and, hence, from the results presented here, the structural formula expressed earlier for this Garfield nontronite is not completely correct.

The Mössbauer spectrum for the Ca- and K-saturated Garfield nontronite samples recorded to  $9.4 \times 10^6$  and  $8.2 \times 10^6$  counts, respectively, are presented in Figure 4. It was only possible to fit 6 peaks defining the two octahedral and one tetrahedral doublets to each spectrum (Table 2). For each sample, when an interlayer component was introduced, the computer-fitting procedure reduced the widths and dips of these peaks to zero. The  $\chi^2 = 633$  for the Ca-saturated sample (Table 2) was significantly improved over that of  $\chi^2 = 1032$  for the corresponding untreated sample (Table 2), whilst that of  $\chi^2 = 831$  for the K-saturated sample also showed some improvement. These decreased  $\chi^2$  values suggest that, particularly for Ca, the saturation replaced the interlayer  $\text{Fe}^{3+}$  and probably any other alkali/alkaline earth ions as well. The net result of this replacement was to increase the structural order within the interlayer and, hence, to allow the  $\text{Fe}^{3+}$  substituting in the octahedral sites to experience a more uniform electric field gradient. The Mössbauer resonances for these sites can therefore be better modeled by Lorentzian lineshapes. Hence, it seems that such disorder present in the nontronite structure was primarily a result of the influence of the interlayer cations.

It is of considerable significance to note the differences that were present particularly in the widths and intensities of the respective two octahedral and tetrahedral doublets, between the unsaturated, Ca-, and K-saturated samples of this nontronite (Table 2; Figures 3 and 4). The Fe content in these sites was not altered, and it is unlikely that any diffusion of ions

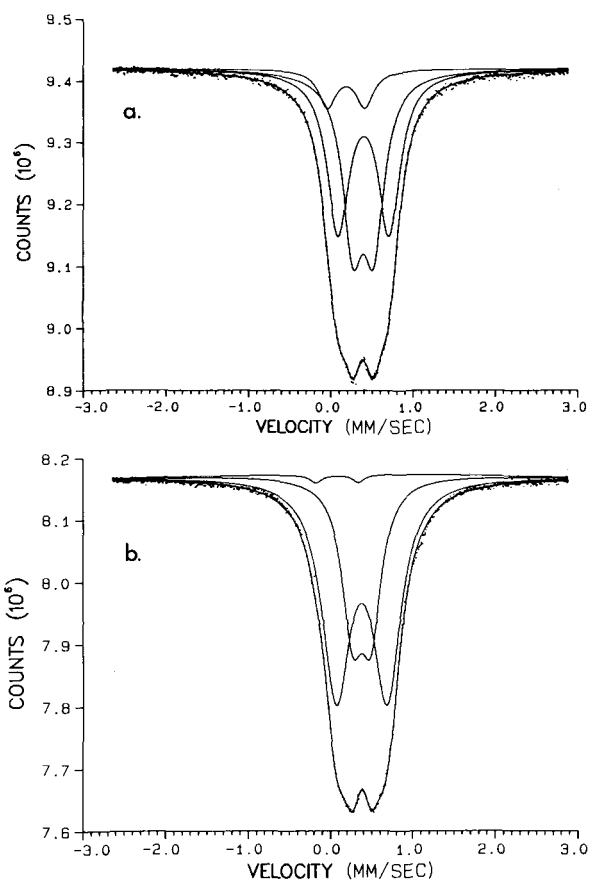


Figure 4. Experimental and computer-fitted Mössbauer spectra for the six-peak model defining two octahedral and a tetrahedral  $\text{Fe}^{3+}$  doublets to (a) Ca-saturated, (b) K-saturated Garfield, Washington, nontronite.

within the octahedral or tetrahedral layer took place, because the saturation process involved only shaking the clay in the appropriate Ca- or K-containing solution at room temperature. Only the interlayer ions were affected, and the saturation process displaced the interlayer Fe.

Little difference was noted between the spectrum of the Ca-saturated samples and that of the untreated nontronite insofar as the  $\delta$ ,  $\Delta$ , and width values of the respective octahedral and tetrahedral doublets are concerned (Table 2, Figure 4). The area of the outer octahedral doublet for the Ca-saturated sample, however, assumed a slightly greater value than for the inner one, whereas in the untreated sample the reverse was true. This trend was even more marked between the Ca- and K-saturated samples where the outer octahedral doublet assumed a much greater area and linewidth (Table 2) for the latter. Also, the tetrahedral doublet for the K-saturated sample was reduced in both width and area relative to the Ca-saturated and untreated samples (Figures 3d and 4).

The d(001) basal spacing in the XRD pattern expanded slightly from 15.31 Å for the untreated sample to 15.54 Å for the Ca-saturated sample (Table 2). This expansion was expected as  $\text{Ca}^{2+}$  has a larger radius than  $\text{Fe}^{3+}$ , although the expansion will be buffered to some extent by its surrounding hydration sphere. With K-saturation, the d(001) spacing decreased to 12.22 Å (Table 1), suggesting a more mica-like structure with some interlayer water. Because the d(060) spacing (1.52 Å) was the same for all three samples (Table 2), the octahedral and tetrahedral layers within the structure were probably largely unaffected by the change in interlayer substitution (Russell and Clark, 1978).

The Mössbauer spectra were, however, certainly affected to a significant extent by the interlayer cations, confirming that atoms/ions, other than nearest neighbor ones, yet in close proximity to the particular iron atom in question, influenced the Mössbauer resonance for that site. In the nontronite structure the presence and bonding of the interlayer cation to the tetrahedral layer was transmitted through this tetrahedral layer to the octahedral layer. In the mica structure interlayer  $\text{K}^+$  ions are about 5.1 Å away from the octahedral ( $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) ions (Radoslovich, 1960). For the K-saturated nontronite, this distance should have been similar and was apparently close enough to influence the bonding of octahedral  $\text{Fe}^{3+}$ . As these electrostatic interactions were transmitted through the tetrahedral layer, they necessarily influenced the Mössbauer resonance of  $\text{Fe}^{3+}$  substituting for (Si,Al) in this layer, as exemplified by the changes in the computer-fitted tetrahedral  $\text{Fe}^{3+}$  doublet in the three appropriate spectra (Figures 3d and 4). The value of  $\delta = 0.07(2)$  mm/sec for the tetrahedral doublet in the K-saturated sample was significantly smaller than the 0.16–0.17 mm/sec value of the Ca-saturated and untreated nontronites, showing that K increased the electronegativity of the bonds to this tetrahedral  $\text{Fe}^{3+}$ . The changes in  $\Delta$  for the two octahedral and tetrahedral sites for these three samples show that the interaction arising from the respective interlayer cations influenced the electric field gradient which the Fe experienced in these sites. In a Mössbauer study of phlogopite, Krishnamurthy *et al.* (1981) showed that the electric field gradient experienced by  $\text{Fe}^{3+}$  in an octahedral site was influenced by ions as distant as 30 Å. Because the peak areas changed markedly, the recoilless free fraction of the sites was also influenced significantly, especially with the K-saturation. The significant effect the interlayer cation has on the outer octahedral doublet confirms the model of two distinct octahedral sites rather than simply a continuum of similar sites of slightly differing geometry, such as for the poorly ordered hydrous iron oxide, ferrihydrite (Johnston and Lewis, 1983).

It is now possible to see how two octahedral doublets with approximately the same  $\delta$  but different  $\Delta$  values can arise from the presence of  $\text{Fe}^{3+}$  in only the *cis*-

[ $\text{FeO}_4(\text{OH})_2$ ] sites. As mentioned above, Goodman (1978) suggested that these doublets could arise from the substitution of  $\text{Fe}^{3+}$  in the tetrahedral sites. The present work shows that the interlayer cation also affects these resonances. Because the interlayer cations exert an influence on the tetrahedral cations, the subsequent effect that tetrahedral  $\text{Fe}^{3+}$  has on generating two electrostatically different octahedral sites, as suggested by the Goodman (1978) model, would be even more pronounced by the interlayer cations. The larger linewidth of the outer octahedral doublet, particularly for the K-saturated sample (Table 2), indicates that the geometry of the cations influencing this site is more varied than for the inner octahedral doublet. Alternatively, or in addition, the cation-site positions within the interlayer could be arranged such that a proportion of them are closer to one set of the two octahedral *cis*-OH sites and the remaining proportion closer to the other. Such a model, however, is difficult to verify or to dispute, because the actual positions of the interlayer cations in smectite are not precisely known. Nevertheless, it is likely that the two overlapping octahedral doublets can be attributed to  $\text{Fe}^{3+}$  in only the *cis*-OH sites and that the differing quadrupole interactions arise from the different electric field gradients originating from the substitution and arrangements of ions in the tetrahedral and interlayer sites.

Because the nature of the interlayer cation significantly affects the recoilless fraction and hence the intensity of the Mössbauer absorption, estimates of the relative proportion of Fe in octahedral and tetrahedral sites based upon Mössbauer spectral peak areas must be in doubt. The effect on the recoilless fraction is particularly noticeable for the outer doublet in the K-saturated sample (Table 2), which suggests that the increased electrostatic interactions, arising from the K-substitution, influence the bonding within the layers and significantly increase the recoilless fraction for this site. Notwithstanding this proviso, if the recoilless fractions are assumed to be the same for the different sites, this untreated Garfield nontronite has 49.0(6)% of its  $\text{Fe}^{3+}$  in the *cis*-octahedral site with the smaller quadrupole interaction, 44.5(5)% in the other *cis*-octahedral site, 5.7(3)% in the tetrahedral site, and 0.7(1)% in the interlayer. These percentages correspond to 0.895, 0.813, 0.104, and 0.012 units of  $\text{Fe}^{3+}/\text{O}_{10}(\text{OH})_2$ , respectively.

#### ACKNOWLEDGMENT

We thank K. Norrish, Soils Division, C.S.I.R.O., Adelaide, South Australia, for supplying the samples used in this study.

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(Received 12 October 1983; accepted 26 June 1984)

**Резюме**—Измерялись  $^{57}\text{Fe}$  мессбауеровские спектры необработанного насыщенного Са и К нонtronита из Гарфелда, Вашингтон. Спектр необработанного образца был приспособлен с помощью компьютера к 8 пикам, определяющим два октаэдрические, тетраэдрический и межслойный  $\text{Fe}^{3+}$ -квадруполь-разделенные дублеты. Межслойный Fe отсутствовал в образцах, насыщенных Са и К. Спектры необработанных образцов регистрировались при увеличении фонового счета от  $2,8 \times 10^5$  до  $9,2 \times 10^6$ . Оценка предварительных 4 и 6 пиковых моделей и приемлемой 8 пиковой модели, приспособленной компьютерно к каждому спектру, показывает, что если величина  $\chi^2$  используется как мера качества приспособления, спектры должны регистрироваться до фонового счета большего, чем  $3 \times 10^6$ . В этом случае результирующая величина  $\chi^2$  отражает и обоснованность используемой модели и степень неупорядочения внутри структуры. Величина  $\chi^2$  линейно зависит от получаемого фонового счета.

Сравнение спектра образцов, насыщенных Са и К, с необработанными образцами показывает, что межслойные катионы оказывают значительное влияние на резонансы индивидуальных компонентов, в особенности на внешний октаэдрический дублет. Следовательно, это вероятно, что электростатические взаимодействия соседних тетраэдрических  $\text{Fe}^{3+}$  и межслойных катионов приводят к двум различным градиентам электрических полей внутри соседних местоположений *cis*- $[\text{FeO}_4(\text{OH})_2]$  и, следовательно, к двум октаэдрическим  $\text{Fe}^{3+}$  дублетам в мессбауеровском спектре. Эти результаты согласуются с более ранними опубликованными данными по дифракции электронов. [E.G.]

**Resümee**—Es wurden die  $^{57}\text{Fe}$ -Mössbauerspektren von unbehandeltem sowie von Ca- und K-gesättigtem Nontronit von Garfield, Washington, untersucht. Das Spektrum der unbehandelten Probe wurde mittels Computer auf 8 Peaks normiert, die zwei oktaedrische, eine tetraedrische und eine Zwischenschicht-Fe-Dublette aufgrund von Quadrupol-Aufspaltung beschreiben. In den Ca- und K-gesättigten Proben war kein Zwischenschicht-Fe vorhanden. Die Spektren der unbehandelten Probe wurden bei zunehmenden Inkrementen der Untergrund-counts von  $2,8 \times 10^5$  bis  $9,2 \times 10^6$  ausgezeichnet. Eine Auswertung der ursprünglichen 4- und 6-Peakmodelle und des angenommenen 8-Peakmodells, die mittels Computer jedem Spektrum angepaßt wurde, zeigt, daß, wenn der  $\chi^2$ -Wert als Maß für die Genauigkeit verwendet wird, die Spektren gegen einen Untergrundcount größer  $3 \times 10^6$  gemessen werden sollten. Die resultierenden  $\chi^2$ -Werte geben dann die Güte des verwendeten Modells und das Ausmaß der Unordnung innerhalb der Struktur wieder. Der  $\chi^2$ -Wert zeigt eine lineare Abhängigkeit von den erhaltenen Untergrundcounts.

Ein Vergleich der Spektren von Ca- und K-gesättigten Proben mit dem der unbehandelten Probe zeigt, daß die Zwischenschichtkationen einen beachtlichen Einfluß auf einzelne Komponentenresonanzen ausüben, vor allem auf die äußeren Oktaederdubletten. Es ist daher wahrscheinlich, daß elektrostatische Wechselwirkungen zwischen nahegelegenen tetraedrischen  $\text{Fe}^{3+}$ -Ionen und den Zwischenschichtkationen zwei verschiedene elektrostatische Feldgradienten innerhalb benachbarter *cis*- $[\text{FeO}_4(\text{OH})_2]$ -Plätze verursachen und daher zu zwei oktaedrischen  $\text{Fe}^{3+}$ -Dubletten im Mössbauer Spektrum führen. Diese Ergebnisse stimmen mit Elektronenbeugungsdaten aus der Literatur überein. [U.W.]

**Résumé**—Les spectres de Mössbauer de  $^{57}\text{Fe}$  de nontronite non traitée, saturée de Ca, et de K, de Garfield, Washington, ont été mesurés. Le spectre de l'échantillon non traité a été associé par ordinateur à 8 sommets définissant deux doublets  $\text{Fe}^{3+}$ -quadrupole-fendus octaédriques, un doublet  $\text{Fe}^{3+}$ -quadrupole-

fendu tétraédral et un doublet  $\text{Fe}^{3+}$ -quadrupole-fendu intercouche. Dans les échantillons saturés de Ca et de K, le Fe intercouche était absent. Les spectres de l'échantillon non traité ont été enregistrés à des étapes accroissantes de comptes d'arrière-plan de  $2,8 \times 10^5$  à  $9,2 \times 10^6$ . Une évaluation des modèles initiaux à 4 et 6 sommets et le modèle acceptable à 8 sommets, associés à chaque spectre, montre que si la valeur  $\chi^2$  est employée comme mesure de la précision de l'association, les spectres devraient être enregistrés à un compte d'arrière-plan plus élevé que  $3 \times 10^6$ . La valeur  $\chi^2$  résultante reflète alors à la fois la validité du modèle employé et l'étendue du désordre endéans la structure. La valeur  $\chi^2$  dépend de manière linéaire des comptes d'arrière-plan obtenus.

Une comparaison des spectres des échantillons saturés de Ca et de K, et de ceux de l'échantillon non traité montre que les cations intercouche exercent une influence considérable sur les résonances des comptes individuels, particulièrement du doublet octaédral extérieur. Ainsi, il est probable que les interactions électrostatiques des cations  $\text{Fe}^{3+}$  tétraédraux proches et des cations intercouche produisent deux gradients de champ électrique distincts endéans les sites *cis*- $[\text{FeO}_4(\text{OH})_2]$  voisins, et ainsi deux doublets octaédraux  $\text{Fe}^{3+}$  dans le spectre de Mössbauer. Ces résultats sont consistants avec les données précédentes de diffraction d'électrons dans la littérature. [D.J.]