DETECTION OF TETRAHEDRAL Fe³⁺ SITES IN NONTRONITE AND VERMICULITE BY MÖSSBAUER SPECTROSCOPY

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Abstract—Mössbauer spectra were obtained for five Ca-exchanged nontronites and one Ca-exchanged vermiculite as the 2-layer hydrates following dehydration at 200°C. Exchange of the samples with Ca^{2+} and subsequent dehydration resulted in the appearance of a shoulder at about -0.50 mm/s in the Mössbauer spectra of some of the samples. The appearance of these shoulders necessitated the inclusion of doublets with Mössbauer parameters corresponding to tetrahedrally-coordinated Fe^{3+} ($^{IV}Fe^{3+}$) in the model used to fit the Mössbauer spectra. That the $^{IV}Fe^{3+}$ sites detected in these samples were those in the nontronite structure was confirmed using samples whose $^{IV}Fe^{3+}$ contents have been previously determined from chemical analysis. It appears that this sample preparation method allowed $^{IV}Fe^{3+}$ contents to be determined to within 40%. On this basis, the $^{IV}Fe^{3+}$ content appeared to be unrelated to the total Fe content for the samples studied.

Key Words—Dehydration, Isomorphic substitution, Mössbauer spectroscopy, Nontronite, Tetrahedral iron, Vermiculite.

INTRODUCTION

The ability to determine the nature of cation substitution in smectite minerals is paramount to understanding the relationship between structure and physical and chemical properties (Bleam, 1990; Fripiat, 1990). In Fe-rich smectites such as nontronite, substitution of Fe^{3+} can occur in either the tetrahedral or octahedral sheet in varying proportions. The proportion of substitution of Fe^{3+} in tetrahedral and octahedral sheets is not easily determined.

For nontronite samples that contain large quantities of Fe, chemical analysis can give an indication of the tetrahedral Fe^{3+} ($^{IV}Fe^{3+}$) content. For instance, on the basis of chemical analysis, the Koegas nontronite sample examined by Goodman *et al.* (1976) may be formulated as: $(Si_{6.61}Al_{0.08}Fe_{1.31})(Fe_{4.06}Mg_{0.10})0_{20}(OH)_4$. In this instance some Fe^{3+} must be assigned to the tetrahedral sheet. For nontronites with lower Fe contents however, chemical analysis may be of little use in determining site populations because the Fe^{3+} can be assigned equally to tetrahedral or octahedral sheets. Moreover, Mössbauer spectra of nontronites are broad and can be computer resolved using models for the site populations that are not unique. For this reason, effort has been made to corroborate models used to fit Mössbauer spectra using other spectroscopic methods (Bonnin *et al.,* 1985; Sherman and Vergo, 1988).

Luca and Cardile (1989) showed that when Washington nontronite (SWa-1) was Ca-exchanged and dehydrated, a previously unobserved resonance with large

quadrupole splitting (QS) and isomer shift (IS) of about 0.15 mm/s could be partially resolved in the Mössbauer spectrum of the dehydrated sample. This additional resonance had Mössbauer parameters corresponding to $^{IV}Fe^{3+}$, and its appearance was attributed to the movement of exchangeable Ca^{2+} cations toward Fe^{3+} sites in the tetrahedral sheet of the nontronite causing distortion of the $^{IV}Fe^{3+}$ sites. The improved resolution of the $^{IV}Fe^{3+}$ sites was apparently due to this change in Mössbauer parameters. These authors suggested that this effect might represent a useful general method for testing for the presence of $^{IV}Fe^{3+}$ in nontronites, and possibly other Fe-rich phyllosilicates.

The hypothesis needs to be tested that exchangeable cations such as Ca^{2+} move toward $^{IV}Fe^{3+}$ sites of nontronite during dehydration and cause them to be better resolved in the Mössbauer spectrum. One way to test this is to demonstrate a similar effect to that observed in the Mössbauer spectrum of SWa-1 by Luca and Cardile (1989) on samples which indisputably contain $^{IV}Fe^{3+}$. The Koegas nontronite examined by Goodman *et al.* (1976) and the Phalaborwa vermiculite examined by Cardile and Slade (1987) are good candidates because they have been shown by chemical analysis to contain about 16% Fe^{3+} substitution in the tetrahedral sheet. This $^{IV}Fe^{3+}$ content was corroborated by Mössbauer spectroscopy.

In the present study the effect of Ca-exchange and dehydration on the Mössbauer spectrum has also been studied for a range of other nontronites for which chemical analysis alone cannot furnish the $^{IV}Fe^{3+}$ content and for which Mössbauer spectroscopy of the hydrated samples has been inconclusive. The two clay mineral standard nontronite samples from Hohen Ha-

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Table 1. Iron contents and chemical formulae of nontronites and vermiculite samples.

Sample	Origin	Fe (%)	Formula	Reference
NG-1	Hohen Hagen, Federal Republic of Germany	25	$(Si_{7.40}Al_{0.60})(Fe_{3.60}Al_{0.26}Mg_{0.20})O_{20}(OH)_4$	(1)
Gar	Garfield, Washington, U.S.A.	25	$(Si_{6.84}Al_{1.05}Fe_{0.11})(Fe_{3.96}Mg_{0.04})O_{20}(OH)_4$	(2)
			$(SI_{6.93}Al_{1.07})(Fe_{3.97}Al_{0.01}Ti_{0.02})O_{20}(OH)_4$	(3)
Spo	Spokane County, Washington, U.S.A.	29	$(Si_{7.40}Al_{0.07}Fe_{0.53})(Fe_{3.85}Mg_{0.06}Mn_{0.008})O_{20}(OH)_4$	(4)
Koe	Koegas, Cape Province, Republic of South Africa	33	$(Si_{6.61}Al_{0.08}Fe_{1.31})(Fe_{4.06}Mg_{0.10})O_{20}(OH)_4$	(5)
Bing	Bingham Canyon, Utah, U.S.A.	20	$(Si_{6.98}Al_{1.02})(Fe_{2.92}Al_{0.86}Mg_{0.28}Ti_{0.042})O_{20}(OH)_4$	(4)
Phal	Phalaborwa, Republic of South Africa	12	$(Si_{5.83}Al_{0.93}Fe_{1.24})(Fe^{3+}_{0.39}Fe^{2+}_{0.08}Mg_{5.36}Ti_{0.14})O_{20}(OH)_4$	(6)

(1) Supplied by the Source Clays Repository of The Clay Minerals Society as Special Clay NG-1. Analysis from Schneiderhöhn (1965).

(2) Supplied by Ward's Scientific Establishment, Rochester, New York (API 33A). Analysis from Rozenson and Heller-Kallai (1976).

(3) Analysis from Goodman *et al.* (1976).

(4) Supplied by C. M. Cardile. Analysis from Cardile (1985).

(5) Supplied by B. A. Goodman. Analysis from Goodman *et al.* (1976).

(6) Supplied by CSIRO, Division of Soils, Australia. Analysis from Cardile and Slade (1987).

gen, F.R.G. (NG-1) and from Garfield Washington, U.S.A., are in this group. Therefore, another aim of the present work is to attempt to determine the Fe^{3+} distribution in the structure of these and other nontronite samples.

EXPERIMENTAL

Table 1 lists the samples used, together with their total Fe contents and chemical formulae. Bingham nontronite was obtained in the Ca-exchanged form from C. M. Cardile, and has been described in greater detail by Cardile (1985) and Cardile *et al.* (1986). The Phalaborwa vermiculite was the same sample used in Cardile and Slade (1987), and was also in the Ca-exchanged form. Neither the Bingham nontronite nor the Phalaborwa vermiculite samples were given any further treatment. Koegas and Spokane nontronites were received after purification by the method of Goodman *et al.* (1976). They were Ca-exchanged by stirring the samples with 1 M $CaCl_2$ solution for 12 hr and repeating this process three times with separate portions of $CaCl_2$ solution. Excess ions were removed by washing and centrifugation until the washings gave a negative $AgNO_3$ test for Cl^-.

The Washington and Garfield nontronite samples were received as the crude materials. These clays were mechanically dispersed in water (1 g clay/100 ml water) and the <2-μm size fraction was separated by gravity sedimentation. This fraction was treated several times with 1 M LiCl solution and then dialyzed. The Li-exchanged clay was completely delaminated and formed a stable sol. This sol was allowed to stand until nonclay particles had settled out. The clay suspension was then converted to the Ca-exchange form as described above.

As noted by Lear *et al.* (1988), the crude Hohen Hagen nontronite contains large amounts of admixed Fe-oxide impurities. This nontronite was therefore purified by a slight variation of the above procedure. The crude nontronite was mechanically dispersed in distilled water and allowed to settle. Within 5 min, bright-green particles settled out leaving a brown-colored suspension, which was discarded. This procedure was repeated several times until only the green particles remained. This material was exchanged with Li^+ and treated in the same manner as the Washington and Garfield nontronite samples. No impurity phases were detected in the powder X-ray diffraction (XRD) pattern of the purified Ca-exchanged Hohen Hagen nontronite. Lear *et al.* (1988) reported goethite in their samples of Hohen Hagen nontronite, but it should be noted that the present samples have been purified differently.

Room-temperature Mössbauer spectra were recorded in 512 channels of a Cryophysics MS-102 spectrometer using a $^{57}Co/Rh$ source. The velocity scale was calibrated with elemental Fe. To optimize resolution, Mössbauer spectra were recorded in the velocity range -2.0–2.0 mm/s. Powdered nontronite samples (5–10 mg/cm²) in various states of hydration were immediately placed into piston-design Perspex sample holders. These were sealed with high-vacuum grease to prevent a change in water content.

To ensure that samples which had been dehydrated at 200°C had not rehydrated after the Mössbauer spectra had been recorded, the samples were removed from the Mössbauer sample holders as quickly as possible and their basal spacings measured by XRD. For all the samples, spacings between 9.6 and 10 Å were obtained, showing that the nontronites had remained essentially dehydrated during Mössbauer data collection.

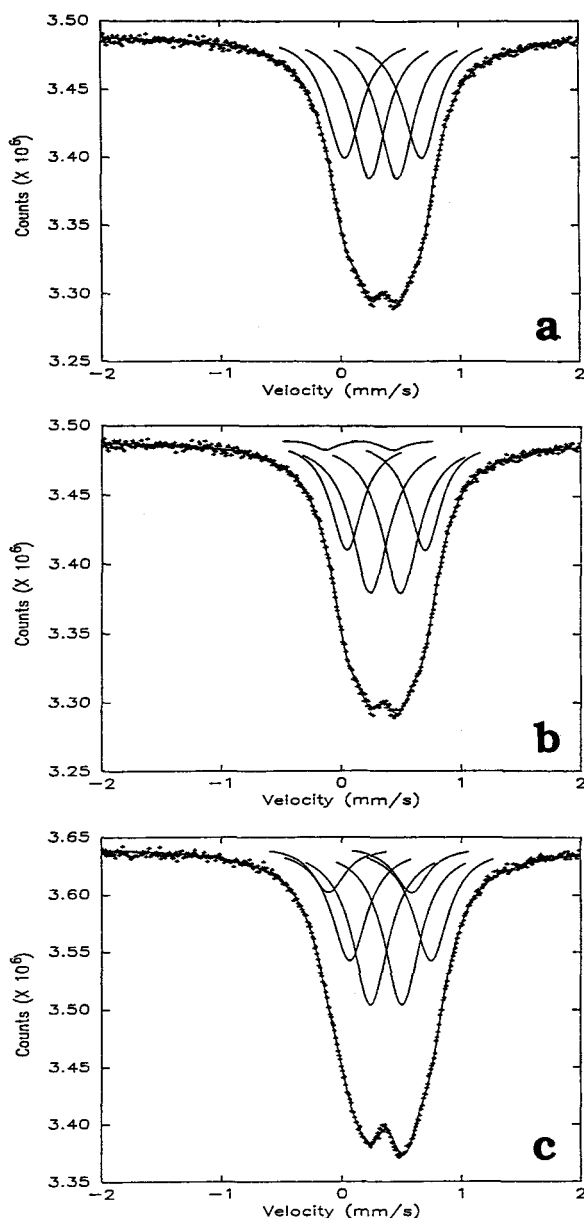To achieve a one-layer hydrate for the Koegas non-

Figure 1. Room-temperature computer-fitted Mössbauer spectra of Ca²⁺-Garfield nontronite: (a) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ doublets, (b) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ and one $^{IV}Fe^{3+}$ doublet, and (c) dehydrated at 200°C and fitted as for (b).

tronite, the sample was stored for one week at a relative humidity (RH) of 20%. After recording the Mössbauer spectrum of this sample, a basal spacing of 12.5 Å was obtained, confirming that it contained one layer of interlayer water.

X-ray diffraction patterns were recorded on a Philips diffractometer using Ni-filtered CuKα radiation and a graphite monochromater.

RESULTS

Mössbauer spectra of nontronite and vermiculite samples at ambient humidity

Room-temperature (RT) Mössbauer spectra of the five air-dried nontronite samples containing two layers of interlayer water are shown in Figures 1a–5a. Mössbauer parameters are listed in Table 2. Where appropriate, several fitting models are given. For the Bingham and Garfield nontronites, statistically acceptable χ^2 values of 626 and 598 were obtained if the fitting model included only two $^{VI}Fe^{3+}$ doublets (B1, G1; Table 2). The addition of a third doublet (B2, G2) resulted in a decrease in χ^2 of about 50 (i.e., an 8% reduction) for both these samples. The misfit parameter, however, responded differently to the incorporation of another doublet. For the Bingham sample, misfit increased slightly, whereas for the Garfield nontronite it decreased by about 45%. In contrast, the Spokane, Hohen Hagen, and Koegas nontronite samples gave χ^2 reductions of 45%, 25%, and 50%, respectively, on addition of an $^{IV}Fe_A^{3+}$ doublet (S2, H2, and K2).

The RT Mössbauer spectrum of the 2-layer hydrate Phalaborwa vermiculite is shown in Figure 6a. This vermiculite contains about 70% of its Fe in tetrahedral coordination as indicated by chemical analysis and Mössbauer spectroscopy (Cardile and Slade 1987). Cardile and Slade (1987) satisfactorily fit the Mössbauer spectrum of this vermiculite using a model that included: one $^{IV}Fe^{3+}$ doublet; one *trans* $^{VI}Fe^{3+}$ doublet; one *cis* $^{VI}Fe^{3+}$ doublet; and one doublet having IS = 0.6 mm/s and QS = 1.65 mm/s, attributed to ilmenite growths. A similar model was used in the present work (Table 3), and the two sets of Mössbauer parameters are in good agreement for the 2-layer hydrate. The doublet that was assigned to ilmentite by Cardile and Slade (1987) has been labeled $^{IV}Fe_?^{3+}$ to indicate uncertainty in this assignment.

Mössbauer spectra of dehydrated samples

For samples dehydrated at 200°C, XRD indicated that the interlayers had remained essentially dehydrated over the period required to record the Mössbauer spectra. Broad 001 reflections and d(001) values slightly greater than those expected for complete dehydration may indicate that some interlayers contained small amounts of water.

After dehydration at 200°C, the Mössbauer spectra of the Spokane, Hohen Hagen, and Koegas nontronite samples (Figures 3b, 4b, and 5c respectively) contained shoulders at about −0.5 mm/s, but the spectra of the Garfield and Bingham samples (Figures 1c, 2c) did not.

The Mössbauer spectrum of the Koegas nontronite dehydrated at 0% RH is shown in Figure 5b. After removing this sample from the Mössbauer holder, a basal spacing of 12.2 Å was found, which corresponds to a 1-layer hydrate. Even with one layer of water re-
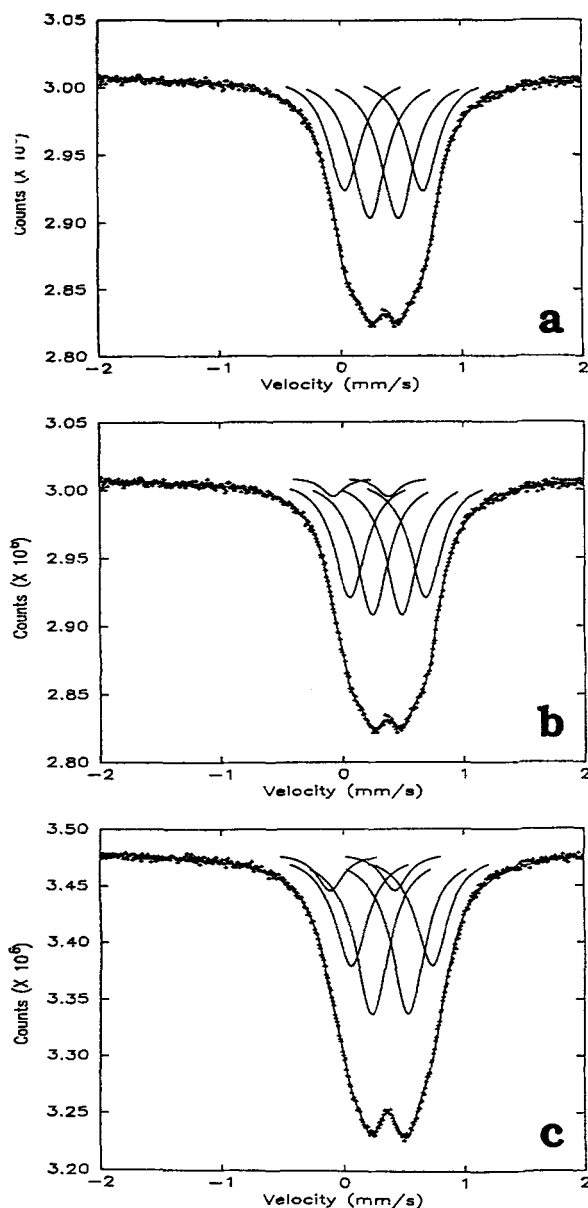
Figure 2. Room-temperature computer-fitted Mössbauer spectra of Ca^{2+}-Bingham nontronite: (a) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ doublets, (b) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ and one $^{IV}Fe^{3+}$ doublet, and (c) dehydrated at 200°C and fitted as for (b).

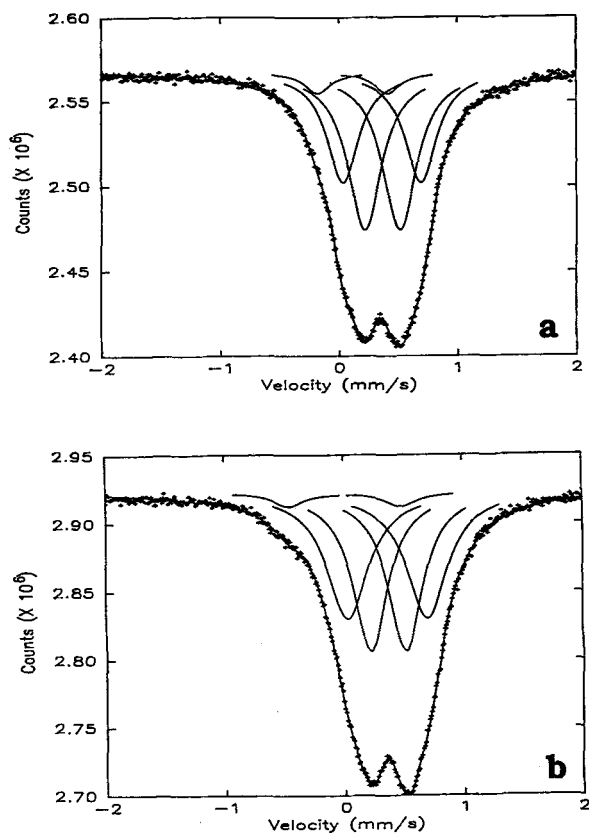
Figure 3. Room-temperature computer-fitted Mössbauer spectra of Ca^{2+}-Spokane nontronite: (a) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ and one $^{IV}Fe^{3+}$ doublet, and (b) dehydrated at 200°C and fitted as for (a).

maining in the nontronite interlayers, a shoulder was visible on the low-velocity side of the main absorption. This behavior is similar to that of the Washington nontronite (SWa-1) after dehydration at 0% RH (Luca and Cardile, 1989).

Room-temperature Mössbauer spectra of dehydrated Hohen Hagen and Koegas nontronite samples fitted with a three-doublet model comprising two $^{VI}Fe^{3+}$ and one $^{IV}Fe_{B}^{3+}$ doublet (H3, K6) gave poor fitting statistics

(e.g., $\chi^2 = 951$ for the Koegas nontronite at 200°C). Improved fits were achieved for these dehydrated nontronites, if another $^{IV}Fe^{3+}$ doublet with QS close to that of the samples at ambient RH ($^{IV}Fe_{A}^{3+}$) was included in the fitting model (Figure 4b, 5c). For both the Hohen Hagen ($\chi^2 = 720$) and Koegas ($\chi^2 = 846$) nontronite samples, χ^2 was still high, even for these four-doublet models. The total area of the two $^{IV}Fe^{3+}$ doublets in the spectra of the dehydrated samples (H4, K7) was 12.7% and 13.3% for Hohen Hagen and Koegas samples respectively, compared with areas of 16 and 23% for the air-dried samples. The agreement between the two sets of $^{IV}Fe^{3+}$ contents derived from hydrated and dehydrated samples was particularly poor for the Koegas nontronite. Chemical analysis of the Koegas nontronite (Goodman *et al.,* 1976) indicates that 32% of the Fe is $^{IV}Fe^{3+}$, in reasonable agreement with the value obtained from the Mössbauer spectrum of the hydrated sample in this work. Because of the lower total Fe content of the Hohen Hagen nontronite, the $^{IV}Fe^{3+}$ content derived from chemical analysis could not be used to corroborate the Mössbauer data, although for this sample greater consistency between the area of the $^{IV}Fe^{3+}$

Table 2. Room-temperature, computer-fitted Mössbauer parameters for the various models fitted to nontronite samples in different states of hydration.

Sample[1]	$^{VI}Fe^{3+}_{OUTER}$ IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	$^{VI}Fe^{3+}_{INNER}$ IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	$^{IV}Fe^{3+}_A$ IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	$^{IV}Fe^{3+}_B$ IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	χ^2	MISFIT
B1 Amb[2]	0.36 (0.001)	0.65 (0.006)	0.32 (0.007)	43 (3)	0.36 (0.001)	0.24 (0.006)	0.35 (0.01)	57 (3)									626	$(1.2 \pm 0.2) \times 10^{-4}$
B2 Amb	0.38 (0.003)	0.63 (0.008)	0.32 (0.007)	44 (3)	0.37 (0.003)	0.25 (0.006)	0.32 (0.01)	51 (3)	0.15 (0.008)	0.46 (0.008)	0.22 (0.02)	5 (1)					577	$(1.4 \pm 0.2) \times 10^{-4}$
B3 200°C	0.36 (0.001)	0.71 (0.006)	0.36 (0.01)	60 (2)	0.36 (0.001)	0.29 (0.004)	0.36 (0.007)	41 (2)									1166	$(4.0 \pm 0.3) \times 10^{-4}$
B4 200°C	0.40 (0.003)	0.67 (0.008)	0.33 (0.006)	37 (2)	0.38 (0.002)	0.30 (0.005)	0.34 (0.006)	54 (2)	0.16 (0.005)	0.53 (0.005)	0.27 (0.01)	10 (1)					846	$(2.1 \pm 0.2) \times 10^{-4}$
G1 Amb	0.36 (0.001)	0.64 (0.008)	0.35 (0.03)	46 (7)	0.37 (0.001)	0.26 (0.009)	0.33 (0.01)	54 (5)									598	$(9 \pm 2) \times 10^{-5}$
G2 Amb	0.37 (0.002)	0.65 (0.009)	0.32 (0.01)	37 (4)	0.37 (0.002)	0.25 (0.009)	0.38 (0.02)	61 (4)	0.15 (0.01)	0.57 (0.03)	0.23 (0.05)	2 (1)					557	$(5 \pm 1) \times 10^{-5}$
G3 200°C	0.35 (0.001)	0.67 (0.009)	0.35 (0.008)	41 (3)	0.35 (0.001)	0.28 (0.007)	0.35 (0.01)	59 (3)									828	$(3.7 \pm 0.4) \times 10^{-4}$
G4 200°C	0.40 (0.004)	0.68 (0.009)	0.36 (0.007)	36 (2)	0.37 (0.001)	0.26 (0.005)	0.37 (0.009)	54 (2)	0.24 (0.008)	0.60 (0.01)	0.33 (0.02)	13 (2)					837	$(1.8 \pm 0.2) \times 10^{-4}$
S1 Amb	0.36 (0.001)	0.61 (0.009)	0.47 (0.004)	63 (2)	0.37 (0.001)	0.27 (0.005)	0.33 (0.009)	37 (2)									1261	$5.0 \pm 0.4) \times 10^{-4}$
S2 Amb	0.37 (0.002)	0.66 (0.01)	0.33 (0.01)	38 (4)	0.37 (0.001)	0.29 (0.009)	0.35 (0.01)	57 (4)	0.12 (0.009)	0.59 (0.009)	0.26 (0.02)	5.6 (0.9)					698	$(2.1 \pm 0.3) \times 10^{-4}$
S3 200°C	0.37 (0.002)	0.67 (0.01)	0.42 (0.007)	47 (3)	0.37 (0.002)	0.29 (0.007)	0.35 (0.01)	49 (3)					0.01 (0.02)	0.95 (0.04)	0.30 (0.03)	3.5 (0.3)	774	$(1.8 \pm 0.2) \times 10^{-4}$
H1 Amb	0.32 (0.001)	0.74 (0.006)	0.35 (0.008)	31 (2)	0.35 (0.001)	0.31 (0.005)	0.40 (0.007)	69 (2)									804	$(3.3 \pm 0.4) \times 10^{-4}$
H2 Amb	0.38 (0.004)	0.63 (0.01)	0.35 (0.01)	40 (5)	0.38 (0.002)	0.29 (0.01)	0.33 (0.01)	45 (4)	0.16 (0.006)	0.55 (0.005)	0.30 (0.01)	16 (2)					607	$(1.1 \pm 0.2) \times 10^{-4}$
H3 200°C	0.39 (0.002)	0.77 (0.02)	0.45 (0.03)	39 (5)	0.38 (0.001)	0.35 (0.01)	0.39 (0.02)	51 (5)					0.0 (0.005)	0.94 (0.007)	0.34 (0.01)	9.4 (0.4)	807	$(2.5 \pm 0.3) \times 10^{-4}$
H4 200°C	0.40 (0.005)	0.76 (0.01)	0.43 (0.02)	37 (3)	0.39 (0.002)	0.36 (0.006)	0.3 (0.009)	51 (3)	0.12 (0.008)	0.64 (0.02)	0.29 (0.06)	4 (2)	−0.02 (0.005)	0.94 (0.01)	0.31 (0.31)	8.7 (0.7)	720	$(1.8 \pm 0.3) \times 10^{-4}$
K1 Amb	0.33 (0.001)	0.67 (0.004)	0.32 (0.004)	44 (1)	0.35 (0.001)	0.27 (0.003)	0.32 (0.005)	56 (1)									1178	$(1.2 \pm 0.2) \times 10^{-4}$
K2 Amb	0.39 (0.001)	0.63 (0.03)	0.26 (0.02)	27 (6)	0.39 (0.002)	0.30 (0.01)	0.32 (0.03)	50 (5)	0.19 (0.003)	0.51 (0.003)	0.27 (0.006)	23 (1)					628	$(1.2 \pm 0.2) \times 10^{-4}$
K3 0% RH[3]	0.32 (0.002)	0.73 (0.007)	0.43 (0.007)	34 (2)	0.37 (0.001)	0.34 (0.003)	0.40 (0.005)	66 (2)									2041	$(1.00 \pm 0.05) \times 10^{-4}$

Table 2. Continued.

Sample[1]	$^{VI}Fe^{3+}_{OUTER}$				$^{VI}Fe^{3+}_{INNER}$				$^{IV}Fe^{3+}_A$				$^{IV}Fe^{3+}_B$				χ^2	MISFIT
	IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)	IS (mm/s)	QS (mm/s)	W (mm/s)	A (%)		
K4 0% RH	0.36 (0.001)	0.71 (0.008)	0.36 (0.009)	33 (2)	0.36 (0.002)	0.31 (0.006)	0.36 (0.007)	58 (2)					0.11 (0.01)	0.91 (0.03)	0.39 (0.02)	8.3 (0.6)	1009	$(3.4 \pm 0.3) \times 10^{-4}$
K5 0% RH	0.38 (0.004)	0.68 (0.01)	0.34 (0.01)	33 (4)	0.37 (0.002)	0.31 (0.007)	0.35 (0.01)	53 (3)	0.15 (0.01)	0.59 (0.02)	0.30 (0.03)	9 (2)	0.09 (0.02)	1.03 (0.04)	0.29 (0.02)	5.2 (0.6)	796	$(1.9 \pm 0.2) \times 10^{-4}$
K6 200°C	0.38 (0.001)	0.79 (0.01)	0.39 (0.01)	31 (3)	0.38 (0.001)	0.38 (0.007)	0.38 (0.009)	60 (3)					0.00 (0.004)	0.96 (0.007)	0.27 (0.01)	8.8 (0.3)	951	$(5.0 \pm 0.4) \times 10^{-4}$
K7 200°C	0.41 (0.004)	0.76 (0.01)	0.37 (0.01)	29 (3)	0.39 (0.002)	0.38 (0.008)	0.37 (0.009)	58 (3)	0.15 (0.03)	0.64 (0.05)	0.23 (0.04)	4 (1)	0.00 (0.05)	0.97 (0.03)	0.28 (0.01)	9.3 (0.5)	846	$(3.9 \pm 0.4) \times 10^{-4}$

[1] Sample is indicated by letter: B = Bingham; G = Garfield; S = Spokane; H = Hohen Hagen; K = Koegas. The number refers to the model used for the fit. Hydration state or the temperature used for dehydration is indicated below.
[2] amb = ambient humidity.
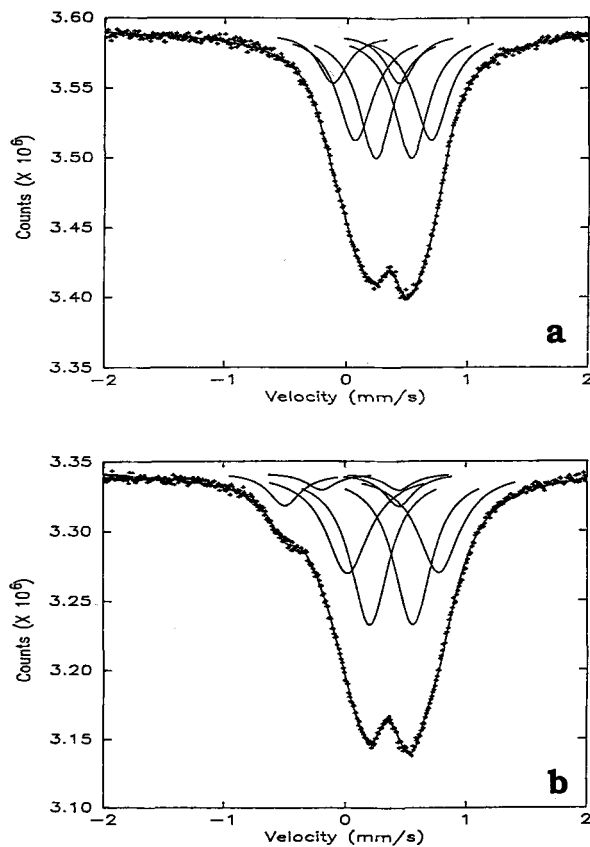[3] 0% RH = 0% relative humidity.

Figure 4. Room-temperature computer-fitted Mössbauer spectra of Ca^{2+}-Hohen Hagen nontronite: (a) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ and one $^{IV}Fe^{3+}$ doublet, and (b) dehydrated at 200°C and fitted with two $^{VI}Fe^{3+}$, one $^{IV}Fe^{3+}_A$, and one $^{IV}Fe^{3+}_B$ doublet.

doublet in the spectra of the hydrated and dehydrated material was obtained.

It was possible to achieve superior fits for the spectra of the dehydrated Bingham and Garfield samples if models that included no $^{IV}Fe^{3+}$ doublets were used. For example, the fitting of a model containing three $^{VI}Fe^{3+}$ doublets to the spectrum of dehydrated Bingham nontronite gave a χ^2 of 712 compared with a χ^2 of 846 for the standard model (two $^{VI}Fe^{3+}$ and one $^{IV}Fe^{3+}$ doublet).

The RT Mössbauer parameters of the model used to fit the spectrum of the Phalaborwa vermiculite changed dramatically after the sample was dehydrated at 300°C. The overall width of the spectrum increased only slightly, but the shape of the resonance changed markedly (Figures 6a, 6b). The largest component of the fitted spectrum of the dehydrated sample was a doublet having parameters characteristic of *trans* $^{VI}Fe^{3+}$. The area of this doublet, however, increased by a factor of two compared with that found for the sample containing two water layers. The area of the doublet with IS corresponding to $^{IV}Fe^{3+}$ was halved after dehydration, and QS increased to 1.31 mm/s. The area of the
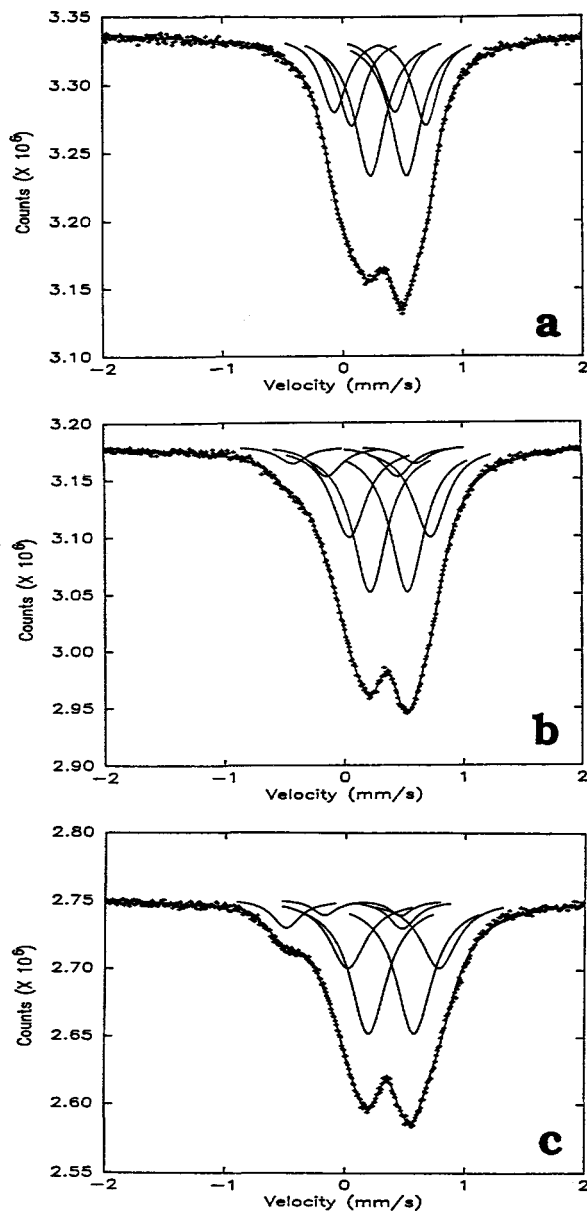
Figure 5. Room-temperature computer-fitted Mössbauer spectra of Ca²⁺-Koegas nontronite: (a) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$ and one $^{IV}Fe^{3+}$ doublet, (b) dehydrated at 0% RH and fitted with two $^{VI}Fe^{3+}$, one $^{IV}Fe_A^{3+}$, and one $^{IV}Fe_B^{3+}$ doublet, (c) dehydrated at 200°C and fitted as for (b).

Table 3. Room-temperature Mössbauer spectroscopic parameters of hydrated and dehydrated Phalaborwa vermiculite.

Sample	$^{VI}Fe_{trans}^{3+}$				$^{VI}Fe_{cis}^{3+}$				$^{IV}Fe^{3+}$				$^{VI}Fe_?^{3+}$				χ^2	MISFIT
	QS (mm/s)	IS (mm/s)	W (mm/s)	A (%)	QS (mm/s)	IS (mm/s)	W (mm/s)	A (%)	QS (mm/s)	IS (mm/s)	W (mm/s)	A (%)	QS (mm/s)	IS (mm/s)	W (mm/s)	A (%)		
V1 amb	0.47 (0.006)	0.83 (0.009)	0.45 (0.02)	26 (2)	0.54 (0.005)	0.33 (0.01)	0.17 (0.01)	2.6 (0.2)	0.23 (0.002)	0.57 (0.004)	0.52 (0.008)	67 (1)	0.54 (0.005)	1.58 (0.01)	0.28 (0.02)	4.7 (0.5)	661	$(1.7 \pm 0.3) \times 10^{-4}$
V2 300°C	0.32 (0.001)	0.67 (0.008)	0.51 (0.008)	63 (2)	0.62 (0.006)	0.32 (0.01)	0.21 (0.01)	2.9 (0.2)	0.29 (0.002)	1.31 (0.01)	0.47 (0.01)	31 (2)	0.58 (0.007)	1.53 (0.01)	0.19 (0.02)	2.5 (0.2)	639	$(1.6 \pm 0.3) \times 10^{-4}$

cis $^{VI}Fe^{3+}$ doublet and the doublet possibly due to ilmenite ($^{IV}Fe_?^{3+}$) were not significantly affected by dehydration. The reduction in the area of the $^{IV}Fe^{3+}$ doublet after the sample had been heated may have been due to partial rehydration of the sample, so that some of the tetrahedral sites continued to resonate with the parameters characteristic of the 2-layer hydrate and overlapped strongly the resonance from the *trans* $^{VI}Fe^{3+}$ doublet. Thus, the area of the $^{VI}Fe_{Trans}^{3+}$ doublet in-

creased at the expense of the area of the $^{IV}Fe^{3+}$ doublet. In other words, 50% of the interlayers may have rehydrated prior to recording the Mössbauer spectrum. However, the increase in the QS of the $^{IV}Fe^{3+}$ doublet paralleled directly the behavior of these sites in the nontronite samples examined.

The basal reflection of the dehydrated vermiculite sample taken immediately after removal of the sample from the sealed Mössbauer holder confirmed that some of the interlayers had rehydrated. By repeatedly scanning the XRD pattern over a small 2θ range it was deduced that rehydration was extremely rapid. Rapid rehydration made it very difficult to establish with certainty the hydration state of the mineral during the time required to record the Mössbauer spectrum. It seems likely that at least some of the interlayers had probably rehydrated prior to packing the sample and recording the Mössbauer spectrum.

DISCUSSION

The sample of Koegas nontronite has a composition which necessitates that 16% of the tetrahedral sites are occupied by Fe^{3+}. Of the nontronite samples studied, the shoulder that develops at about -0.5 mm/s is best resolved in the Mössbauer spectrum of the dehydrated Ca^{2+}-Koegas sample. Such a shoulder could only be observed for samples exchanged with Ca^{2+}, but not for samples exchanged with Na^+ or K^+, and only when the number of layers of interlayer water was less than two. Moreover, this effect was found to be reversible. To account for the shoulder in the Mössbauer spectrum of the dehydrated Ca-exchanged Koegas nontronite it was necessary to use a model that included at least one doublet with parameters corresponding to $^{IV}Fe^{3+}$ sites in micas and clay minerals. Such $^{IV}Fe^{3+}$ sites have IS = 0–0.30 mm/s and more variable QS (Annersten and Olesch, 1978; Pavlishin *et al.*, 1978; Sanz *et al.*, 1978; Coey *et al.*, 1984; Dyar and Burns, 1986; Cardile and Slade, 1987; Dyar, 1987; Ferrow, 1987).

It should be emphasized that the shoulder in the Mössbauer spectrum of the Koegas nontronite sample depends on the hydration state of the nontronite and the type of exchangeable cation present in the nontronite interlayers. Since cation exchangeability and the ability to form discrete hydration states are specific properties of smectites, it may be concluded that the $^{IV}Fe^{3+}$ sites detected by Mössbauer spectroscopy are probably those known to exist in the tetrahedral sheets of the Koegas nontronite.

Another possible explanation for the appearance of $^{IV}Fe^{3+}$ sites in the spectrum of the dehydrated Ca^{2+}-Koegas sample could be that these sites somehow arise from Fe-oxide impurities present in the Koegas nontronite sample. Though certain Fe-oxides could contain some $^{IV}Fe^{3+}$ sites, this explanation does not seem likely as there is no easy way to explain the present results on the basis of an Fe-oxide phase.
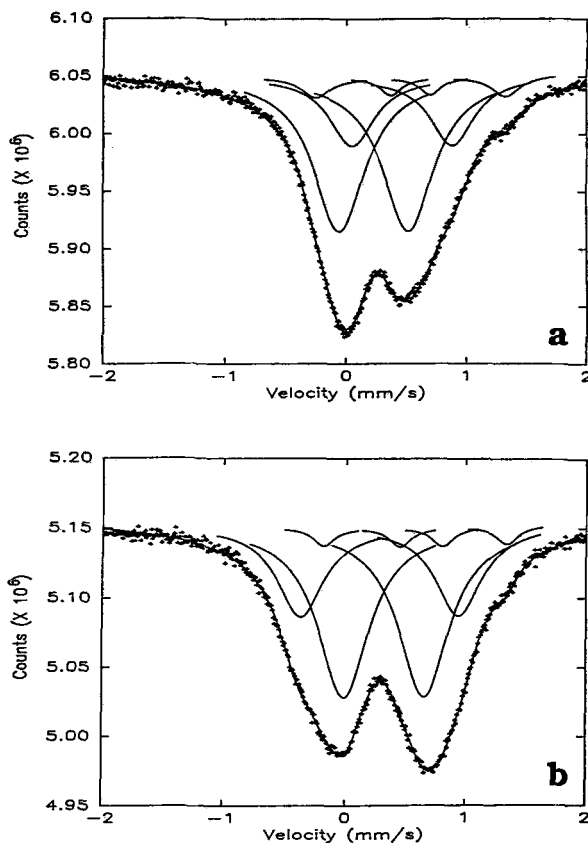

Figure 6. Room-temperature computer-fitted Mössbauer spectra of Ca^{2+}-Phalaborwa vermiculite: (a) 2-layer hydrate fitted with two $^{VI}Fe^{3+}$, one $^{IV}Fe^{3+}$ doublet and one doublet due to putative ilmenite ($^{IV}Fe_2^{3+}$), and (b) dehydrated at 300°C and fitted as for (a).

Iron oxide minerals are commonly present as impurity phases in nontronite samples and are difficult to detect and remove selectively. The conventional method for removal of crystalline and noncrystalline Fe-oxide phases associated with clay minerals involves treatment with dithionite/citrate/bicarbonate (DCB) buffer solutions. This treatment reduces Fe^{3+} to Fe^{2+} in the Fe-oxide, and the Fe^{2+} is removed by complexation. Unfortunately, DCB treatment also causes reduction of some of the Fe^{3+} in the clay structure itself (Ericsson *et al.*, 1984), and also induces other structural changes in smectites (Cardile *et al.*, 1987). Reduction of the structural Fe^{3+} in the nontronites would have been undesirable in the present experiment because the resonance from Fe^{2+} would interfere with that of Fe^{3+}. Additionally, the possibility of structural damage to the nontronite structure could not be risked as this also could bias the experimental results in an undesirable way. Therefore, treatment for the removal of possible Fe-oxide impurities was avoided, and in the present study the smectites were purified by completely delaminating the clays and then separating impurity phases by gravity sedimentation as described by Goodman *et*

al. (1976). There is, however, no guarantee that this procedure would remove Fe-oxide phases intimately bound to clay particles. The absence of peaks due to impurity phases in the XRD pattern of the Ca^{2+}-Koegas nontronite suggests, at least, that there were no significant quantities of crystalline Fe-oxides in this sample.

If the $^{IV}Fe^{3+}$ sites detected in the Mössbauer spectrum of the dehydrated Ca^{2+}-Koegas nontronite sample are due to Fe-oxides, then the concentration of this hypothetical Fe-oxide would be at the very least 13%; the relative area of doublets $^{IV}Fe_A^{3+}$ and $^{IV}Fe_B^{3+}$. This, of course, assumes that all the Fe in a hypothetical Fe-oxide is tetrahedrally coordinated. Goodman *et al.* (1976) recorded the 77 K Mössbauer spectrum of the same Koegas nontronite used in this work and found no evidence for the presence of crystalline Fe-oxides. If present, these Fe-oxides would be expected to give a six-line, magnetically-split spectrum at 77 K. The inner two lines of a magnetically-split Fe-oxide spectrum (which are of lower intensity than the outer lines) would almost certainly have been observed in the velocity range studied by Goodman *et al.* (1976) if greater than 13% Fe-oxide were present. Further evidence to suggest that little or no Fe-oxides are present in the Koegas nontronite samples derives from the fact that it was possible for Goodman *et al.* (1976) to write a chemical formula.

From the preceding discussion it is clear that the Koegas nontronite sample consists essentially of one phase, and that the changes observed after dehydration of the sample are of a magnitude such that they must indeed be attributable to this phase.

The Koegas nontronite sample exemplifies the influence that the proximity of exchangeable cations has on the QS of the tetrahedral Fe^{3+} sites. The computer-fitted 77 K spectrum of the Na-exchanged form of this nontronite obtained by Goodman *et al.* (1976) yielded an $^{IV}Fe^{3+}$ content of 28%, in close agreement with the value indicated by chemical analysis. In reasonable agreement with Goodman *et al.* (1976), the RT Mössbauer spectrum of the 2-layer hydrate of Ca-exchanged Koegas nontronite in the present work gave an $^{IV}Fe^{3+}$ content of 23%. If the sample was dehydrated at 200°C and two $^{IV}Fe^{3+}$ doublets fitted, a total of 14% tetrahedral Fe^{3+} was obtained. This suggests that the method of dehydrating nontronite samples containing exchangeable Ca^{2+} may enable the $^{IV}Fe^{3+}$ sites to become partially resolved but is incapable of providing good estimates of $^{IV}Fe^{3+}$ contents. The need to incorporate an $^{IV}Fe_A^{3+}$ doublet in the fitting model (K5, K7) of the dehydrated Ca^{2+}-Koegas nontronite sample suggests that either some $^{IV}Fe^{3+}$ sites do not have exchangeable Ca^{2+} cations in close proximity, or that the Ca^{2+}-Koegas nontronite was not totally dehydrated. That is, some Ca^{2+} cations remain solvated and are separated from $^{IV}Fe^{3+}$ sites by at least one water molecule. The $^{IV}Fe^{3+}$

sites compensated by solvated Ca^{2+} cations would continue to give Mössbauer parameters typical of fully hydrated nontronite ($^{IV}Fe_A^{3+}$). Indeed, XRD patterns of the Ca^{2+}-Koegas nontronite after recording the Mössbauer spectrum gave broad 001 reflections that indicated slight rehydration of the sample. The presence of more than one type of $^{IV}Fe^{3+}$ site in the dehydrated samples introduces uncertainty in the fitting that could, in principle, be removed if: 1. the cation-exchange sites were completely saturated with compensating cations, 2. the sample was uniformly dehydrated, and 3. the recoil-free fractions of the tetrahedral and octahedral sites were similar (Coey, 1980). If these criteria are met, a method could be envisaged for estimating $^{IV}Fe^{3+}$ contents in nontronite samples. In this regard, the Koegas nontronite is a potential calibration standard, inasmuch as the $^{IV}Fe^{3+}$ content can be estimated from the chemical composition alone.

The doublets responsible for the shoulders at low-velocity in the spectra of the dehydrated Ca-exchanged Spokane and Hohen Hagen nontronite samples all have IS values for the $^{IV}Fe^{3+}$ doublet similar to that of the Ca^{2+}-Koegas nontronite. Therefore, in these nontronites the $^{IV}Fe^{3+}$ sites detected are also probably due to Fe^{3+} in the tetrahedral sheets of these nontronites.

The shoulder at about -0.50 mm/s was not evident in the spectra of the Bingham and Garfield samples. This suggests that there is little or no Fe^{3+} in the tetrahedral sheets of these minerals. The spectrum of the Garfield nontronite sample at ambient humidity can be adequately computer-fitted without recourse to the introduction of an $^{IV}Fe^{3+}$ doublet. If this doublet is introduced, the improvement in χ^2 of about 50 does not justify the acceptance of the three-doublet model as the correct model. The present results corroborate the work of Bonnin *et al.* (1985) and, more recently, Sherman and Vergo (1988), who concluded that the Garfield nontronite contained <2% tetrahedral Fe^{3+}. Goodman *et al.* (1976), Rozenson and Heller-Kallai (1977), Besson *et al.* (1983), Johnston and Cardile (1985), and Cardile (1988), however, suggested that the Garfield nontronite contains >5% tetrahedral Fe^{3+}.

The χ^2 values obtained by Johnston and Cardile (1985), Goodman *et al.* (1976), and Besson *et al.* (1981) for a three-doublet fit (two $^{VI}Fe^{3+}$ doublets and one $^{IV}Fe^{3+}$ doublet) to the Mössbauer spectrum of the Garfield nontronite are lower than those obtained in the present study. However, χ^2 depends on background counts (Ruby, 1973; Dyar, 1984; Johnston and Cardile, 1985), and these are different for the various data. Moreover, a lower χ^2 does not necessarily imply the correctness of one theoretical model over another giving a slightly higher χ^2 value (Law, 1973). The acceptance of a model depends on corroborating evidence (Waychunas, 1986).

The present results also suggest that the effect of exchangeable cations such as Ca^{2+} on the QS of the

tetrahedral Fe^{3+} sites can be generalized to vermiculites with high tetrahedral Fe^{3+} contents. Also, the fact that this effect is observed in nontronites which differ appreciably in composition (compare Hohen Hagen and Koegas nontronites) suggest that it may be a general property of smectites in which the layer charge originates in the tetrahedral sheet. The extent to which FeO_4 tetrahedra are distorted seems to depend on the proximity of the exchangeable cations that can form inner-sphere associations with the basal oxygen atoms of these tetrahedra as the mineral is dehydrated. However, the formation of inner-sphere associations is expected only if the particular tetrahedral substitution results in the localization of charge on the basal oxygen atoms. Suquet *et al.* (1987) suggested that such a localization is likely for FeO_4 tetrahedra. Therefore, tetrahedral distortion should be a general property of Fe-containing tetrahedra.

The definite presence of $^{IV}Fe^{3+}$ in the Hohen Hagen nontronite sample studied herein and the Washington nontronite sample studied by Luca and Cardile (1989), but its apparent absence in Garfield and Bingham nontronite samples indicates that there is no relationship between Fe-content and tetrahedral Fe-content, as suggested by Goodman *et al.* (1976). This raises the question of what governs the distribution of cation substitutions in 2:1 phyllosilicates. Clearly, it is not a simple site-preference problem, but depends on the Eh, pH, and the concentration of ions in the solutions from which the minerals crystallize.

SUMMARY AND CONCLUSIONS

The room-temperature Mössbauer spectrum of dehydrated Ca^{2+}-Koegas nontronite possesses a distinct shoulder at about -0.5 mm/s that was not present in the hydrated sample. To account for this shoulder a doublet with Mössbauer parameters of $^{IV}Fe^{3+}$ must necessarily be included in the fitting model. Since the Koegas nontronite sample contains sufficient Fe to fill almost all the octhedral sites and 16% of the tetrahedral sites, this nontronite sample must contain tetrahedral Fe^{3+}. This result supports the hypothesis of Luca and Cardile (1989) that $^{IV}Fe^{3+}$ responsible for the shoulder are due to $^{IV}Fe^{3+}$ sites in tetrahedral sheets of the nontronite. Similar changes in the Mössbauer parameters of $^{IV}Fe^{3+}$ sites known to exist in the Phalaborwa vermiculite suggest that this effect is a general one.

The broader implication of this work is that the amount of Fe^{3+} in the tetrahedral sheet of Fe-rich 2:1 dioctahedral clay minerals may be conveniently estimated by recording Mössbauer spectra of dehydrated Ca-exchanged samples. Inasmuch as a reasonable estimate of $^{IV}Fe^{3+}$ may be made if the samples can be maintained in the totally dehydrated state while the Mössbauer spectrum is recorded, the present study could represent a solution to a difficult problem.

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