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SITE OCCUPANCY IN NONTRONITE STUDIED BY ACID DISSOLUTION AND MÖSSBAUER SPECTROSCOPY

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Abstract—The dissolution of two Ca^{2+}-exchanged nontronite samples has been studied in 10% HCl. Early acid-dissolution studies (Osthaus, 1954) have indicated that after two hours of dissolution most of the octahedral Fe^{3+} ($^{VI}Fe^{3+}$) would be removed leaving mainly tetrahedral Fe^{3+} ($^{IV}Fe^{3+}$) in the nontronite structure. In the present study, ^{57}Fe Mössbauer spectra of acid-treated samples were recorded and fitted with two octahedral Fe^{3+} ($2 \times {}^{VI}Fe^{3+}$) and two octahedral and one tetrahedral ($2 \times {}^{VI}Fe^{3+}$, $1 \times {}^{IV}Fe^{3+}$) doublet models. The Mössbauer spectra of acid-treated Garfield nontronite samples could be adequately fitted with two-doublet models but acid-treated Hohen Hagen nontronite samples could not. Isomer shift and quadrupole splitting values obtained from the two-doublet models corresponded to $^{VI}Fe^{3+}$ and not $^{IV}Fe^{3+}$, as was suggested by the Osthaus (1954) experiment. When an $^{IV}Fe^{3+}$ doublet was included in the model used to fit the Mössbauer spectra of acid-treated Garfield nontronite samples, a slight increase in the intensity of the $^{IV}Fe^{3+}$ doublet occurred with increasing dissolution, but this was much lower than indicated by Osthaus (1954). No trend in the intensity of the $^{IV}Fe^{3+}$ doublet was observed for acid-treated Hohen Hagen nontronite. Therefore, acid treatment appears to remove $^{VI}Fe^{3+}$ and $^{IV}Fe^{3+}$ from the nontronite structure at about the same rate. Mössbauer spectroscopy, infrared spectroscopy and X-ray powder diffraction data indicate that the nontronite that remains undissolved following acid treatment is structurally similar to the untreated nontronite.

Key Words—Acid dissolution, Mössbauer spectroscopy, Nontronite, Tetrahedral iron.

INTRODUCTION

The substitution of M^{3+} for Si^{4+} in the tetrahedral sheet of 2:1 phyllosilicates has an important effect on swelling, catalytic, and thermal properties (Glaeser and Mering, 1975; Poncelet and Schutz, 1986). For nontronites, a group of smectites with relatively high iron contents, Fe^{3+} may be present in the tetrahedral sheets, and it is not a simple matter to determine quantitatively or even *qualitatively* the amount of Fe^{3+} substituting in the tetrahedral sheet. This is especially true of nontronites having relatively low Fe contents. For these nontronites, the structural formula is usually written with all of the Fe^{3+} occupying the octahedral sites. In order to determine the amount of Fe^{3+} in the tetrahedral sheets it is necessary to use spectroscopic methods. Mössbauer spectroscopy has been the method of choice for many past investigations because, in principle, it allows both oxidation state and coordination number of Fe to be determined nondestructively. The Mössbauer spectrum of nontronite samples, however, consists of a broad envelope that must be computer-resolved into component subspectra.

Although the Mössbauer spectrum of nontronite should generally be fitted with two overlapping doublets, both having IS > 0.3 mm/s, some doubt exists over whether the fitting of a third doublet due to tetrahedrally coordinated Fe^{3+} ($^{IV}Fe^{3+}$) is warranted. Some workers, choosing to fit this third component to the spectrum of Garfield nontronite, have generally done so by using the results of an acid dissolution experiment (Osthaus, 1954) as the independent warrant necessary to establish the validity of a fitting model in Mössbauer spectroscopy (Law, 1973; Waychunas, 1986). Doubt is cast upon this independent warrant in the case of Garfield nontronite by the work of Bonnin *et al.* (1985). Using three spectroscopic methods, Mössbauer spectroscopy included, they came to the conclusion that the $^{IV}Fe^{3+}$ content of Garfield nontronite must be less than one percent. This amount is much smaller than that determined from Mössbauer experiments alone (Goodman *et al.*, 1976; Besson *et al.*, 1983; Johnston and Cardile, 1985). It seems desirable to examine further the acid dissolution technique used by Osthaus (1954).

The Osthaus (1954) experiment was based on previous work with aluminum chlorites by Brindley and Youell (1951). He deduced that the dissolution rate curve obtained represented the summation of the rates of dissolution for octahedral and tetrahedral Fe^{3+}. The curve was made up of a steep portion and a straight, gradually decreasing portion. This latter part of the curve was interpreted to represent the dissolution of Fe^{3+} in tetrahedral coordination only; Fe^{3+} in octahedral coordination already having been dissolved. By extrapolating this latter linear portion back to zero time

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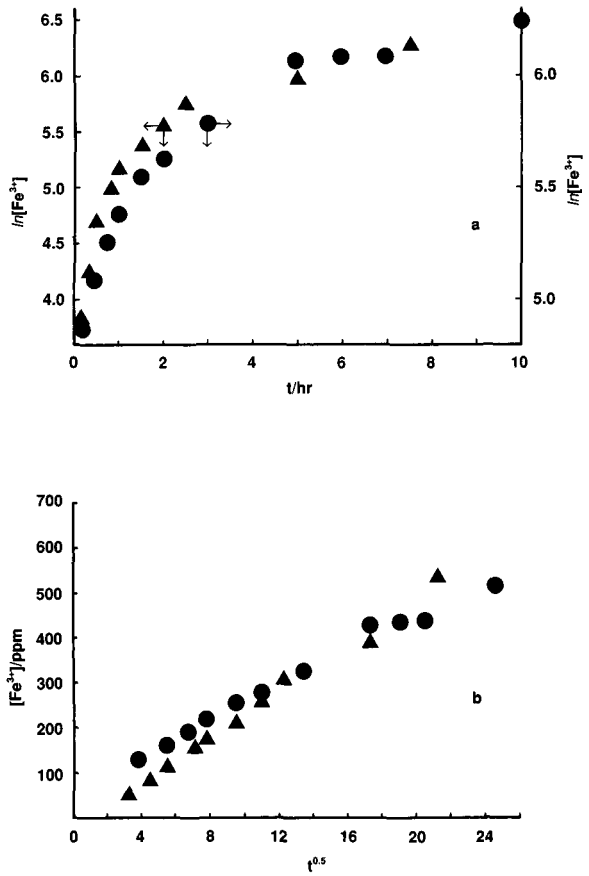


Figure 1. Plots of (a) ln[Fe] versus time and (b) [Fe] versus $t^{1/2}$ for the acid dissolution of Garfield (▲) and Hohen Hagen (●) nontronite samples in 10% HCl at 60°C.

a value for the $^{IV}Fe^{3+}$ content could be calculated. This technique has also been used by others to estimate the $^{IV}Fe^{3+}$ and $^{IV}Al^{3+}$ contents of smectite clays (Karšulin and Stubičan, 1954; Gastuche and Fripiat, 1962; Novák and Číčel, 1978).

The interpretation of the kinetic results is further complicated by the findings of Ross (1969) that the dissolution of a series of chlorites, including the one studied earlier by Brindley and Youell (1951), was congruous and that the rate of dissolution of the tetrahedral and octahedral aluminum sites was the same. He interpreted the kinetics in terms of a two-dimensional diffusion process.

The nontronite samples under investigation in the present work are clay mineral standards, and therefore determination of their chemical properties and information bearing upon their site occupancies are particularly important. The acid dissolution of the samples was followed with time to test the existence of two dissolution rates. Mössbauer spectra were recorded of samples treated with acid for various times. If the deductions of Osthaus (1954) are correct, the samples treated with acid should have become enriched with respect to tetrahedral Fe^{3+} as the dissolution proceeded, and after more than two hours of dissolution the samples should contain only $^{IV}Fe^{3+}$. This apparent total removal of $^{VI}Fe^{3+}$ from the nontronite structure to leave only $^{IV}Fe^{3+}$ should have been easily detected by Mössbauer spectroscopy.

EXPERIMENTAL

The two nontronite samples used in this study were obtained from The Clay Minerals Repository of The Clay Minerals Society and approximate chemical formulae are: Hohen Hagen $(Si_{7.40}Al_{0.60})(Fe_{3.60}Al_{0.73}Mg_{0.20})O_{20}(OH)_4$ (Analysis from Schneiderhöhn, 1965); Garfield, Washington, nontronite $(Si_{6.89}Al_{1.11})(Fe_{3.65}Al_{0.30}Mg_{0.08})O_{20}(OH)_4$ (Analysis from Bonnin *et al.*, 1985).

The Garfield nontronite was purified by treating the crude material with 1 M LiCl solution and then dialyzing this suspension to remove excess ions. The <2-μm fraction was collected by gravity sedimentation, and the nontronite was converted to the Ca^{2+}-exchange form.

The Hohen Hagen nontronite was given an initial purification step because the crude clay contained considerable admixed iron oxides. In the first few minutes after allowing the dispersed particles to settle, large bright-green particles settled on top of a brown sediment layer, and fine, brown particles remained in suspension. It was the bright-green fraction that was converted to the Li form and further purified as for the Garfield nontronite.

Identical masses (0.25 g) of the air-dried Ca^{2+}-nontronite samples were placed in Teflon beakers. The experiment was commenced by simultaneously adding 100 ml of 10% HCl (at 60°C) to each of the beakers, which were then stirred in a thermostatically-controlled bath at 60°C. The beakers were removed from the water bath at various times, and the nontronite was separated immediately from solution by rapid vacuum filtration. The filtrate was collected and the Fe content analyzed. The solid was washed with distilled water and air-dried.

Analysis of Fe in the filtrates was carried out by atomic absorption. The air-dried solids were used to obtain X-ray diffraction (XRD) traces and infrared (IR) spectra. The infrared spectra were recorded as 1% samples in KBr disks (12 mm diameter).

Room-temperature Mössbauer spectra were recorded in 512 channels of a Cryophysics MS-102 spectrometer using a Co/Rh source. Velocity calibration was made with reference to natural iron. Powdered nontronite samples (5–10 mg/cm) at ambient humidity were placed in Perspex sample holders. Care was taken to avoid unnecessary compaction of the samples.

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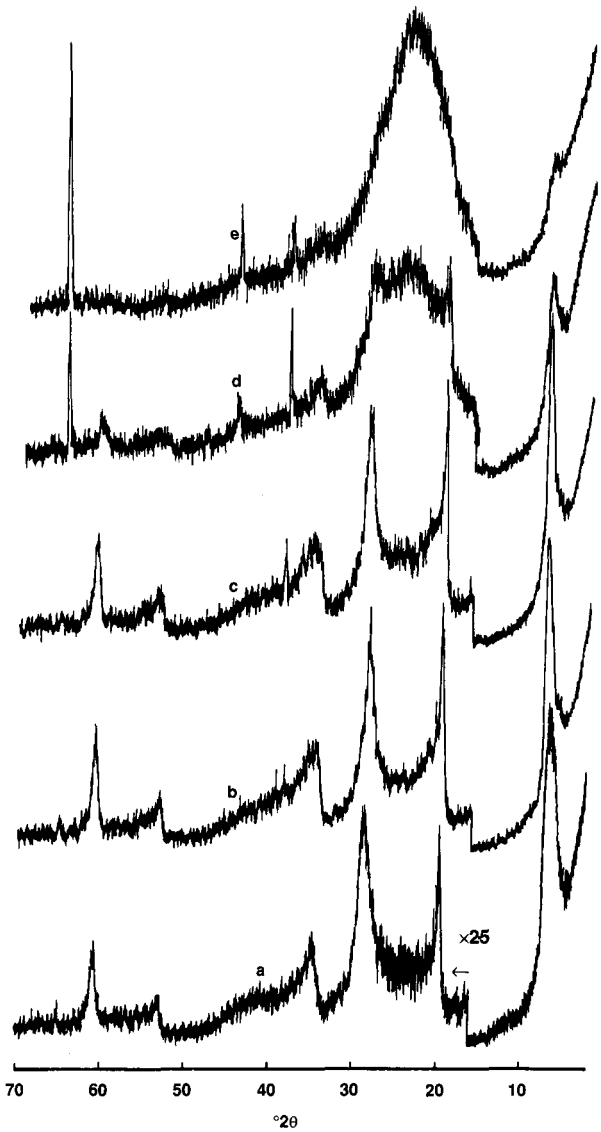


Figure 2. X-ray powder diffraction patterns (CuKα radiation) for Ca^{2+}-Garfield nontronite samples reacted with 10% HCl at 60°C for various times: (a) 0 hr, (b) 0.66 hr, (c) 2 hr, (d) 10 hr, and (e) 15 hr.

RESULTS

Kinetic results

A plot of ln[Fe] vs time is given in Figure 1a for the Garfield and Hohen Hagen nontronite samples. These curves are similar to the one obtained by Osthaus and interpreted in terms of linear kinetics (Osthaus, 1954). The curves shown, however, are not adequately described by linear kinetics.

The data were also found to approximate a parabolic function for the rate of acid dissolution as shown by the linearity of [Fe] vs $t^{1/2}$ plots in Figure 1b ($r = .99$ for Garfield sample and $r = .98$ for Hohen Hagen).

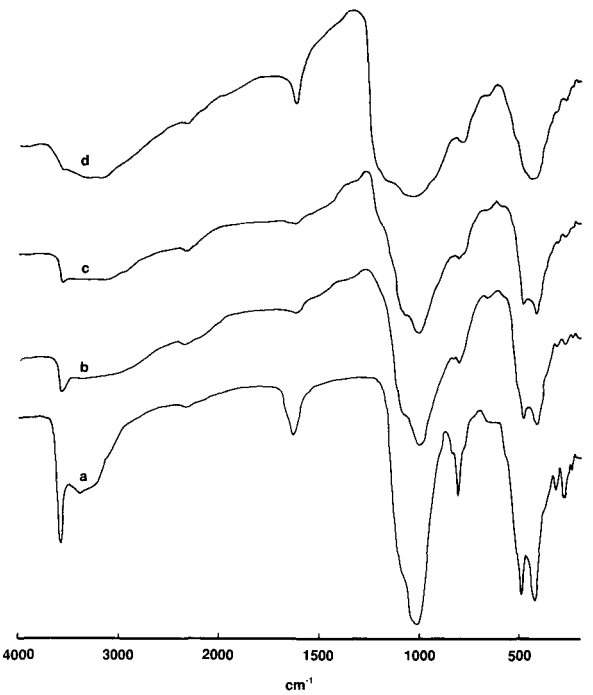


Figure 3. Infrared spectra of Ca^{2+}-Garfield nontronite reacted with 10% HCl at 60° for various times: (a) 0 hr, (b) 0.66 hr, (c) 2 hr, and (d) 7.5 hr.

X-ray powder diffraction

XRD patterns were recorded for each of the air-dried, acid-treated nontronite samples. Selected patterns for the dissolution of Garfield nontronite only, are shown in Figure 2. Both nontronite samples gave rise to similar changes in the XRD patterns. As the duration of acid treatment increased, intensity in the 20–28°2θ region increased. By contrast with the Hohen Hagen nontronite that had been treated for 10 hours (not shown), the XRD pattern of the corresponding Garfield nontronite also contained sharp peaks at 38.3 and 64.4°2θ after dissolution times greater than two hours. Even for samples treated for as long as 10 hours, reflections from smectite were still apparent, although considerable reduction in the intensity of the (001) peak occurred. Clearly from the very broad nature of the peaks generated in the 20–28°2θ region, a phase of poor crystallinity formed as the nontronite dissolved.

Infrared spectra

The IR spectra of samples of Garfield nontronite reacted with acid for various times are shown in Figure 3. The spectra are characterized by a hydroxyl band at about 3570 cm^{-1} from FeFeOH associations, a band at 811 cm^{-1} due to FeFeOH, and a band at 485 cm^{-1} due to the substitution of M^{3+} cations in the tetrahedral sheet (Gastuche and Fripiat, 1962). The stretching modes of the silicate anions in the tetrahedral sheet are centered at about 1000 cm^{-1}. On acid dissolution, the

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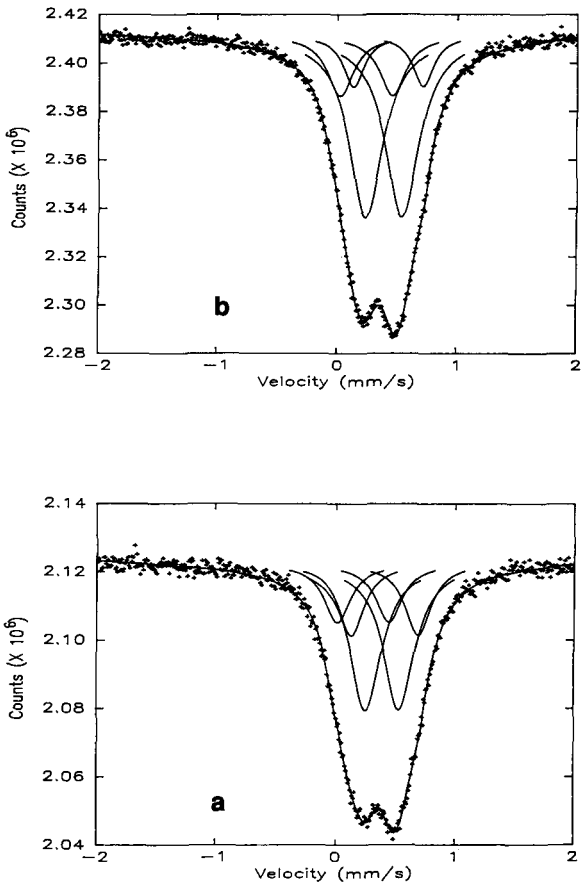


Figure 4. Room-temperature Mössbauer spectra of nontronite samples treated with 10% HCl at 60°C for various times: (a) Garfield nontronite, 7.5 hr, (b) Hohen Hagen nontronite, 5 hr.

bands due to the hydroxyl stretches were reduced considerably in intensity, whereas the bands due to the tetrahedral silicate anions were broadened and resolved into several components.

The persistence of bands in the IR spectra that were due to the clay structure indicates that, even after 7.5 hours of acid treatment, some particles of clay remain. These "clay bands" were no longer apparent after acid treatment times exceeding 7.5 hours.

Mössbauer spectra

Mössbauer spectra were recorded of Ca^{2+}-exchanged nontronite samples after the acid treatment times indicated in Table 1. The spectra have been fitted with two-doublet ($2 \times {}^{VI}Fe^{3+}$) and three-doublet ($2 \times {}^{VI}Fe^{3+}$ and $1 \times {}^{IV}Fe^{3+}$) models. Only spectra taken after about 5 hours of dissolution are shown for each nontronite (Figure 4) because the other spectra in each series were qualitatively similar.

The parameters of the two doublets in the two-doublet models of the acid-treated samples are distinctly those of Fe^{3+} in distorted octahedral coordination. The χ^2 and MISFIT values for these spectra are generally statistically acceptable, although for both samples the introduction of a third doublet resulted in a small reduction in χ^2 and MISFIT. The reduction in χ^2 was between 7.5 and 9.0% for the addition of the tetrahedral doublet to the spectra of acid-treated Garfield nontronite samples while for acid-treated Hohen Hagen nontronite samples the reduction in χ^2 was between 8 and 15%. The reduction in χ^2 and MISFIT after fitting an ${}^{IV}Fe^{3+}$ doublet to the Mössbauer spectrum of the untreated Ca^{2+}-exchanged sample of Garfield nontronite was comparable to that of the acid-treated samples. In contrast, χ^2 and MISFIT were reduced considerably when the ${}^{IV}Fe^{3+}$ doublet was included in the model used to fit the Mössbauer spectrum of the untreated Ca^{2+}-exchanged Hohen Hagen nontronite sample.

For Garfield nontronite subjected to 7.5 hours of acid treatment the Mössbauer parameters for the two-doublet model were similar to those obtained from non acid-treated Ca^{2+}-Garfield nontronite at ambient humidities. This was also the case for the Mössbauer parameters of the two-doublet models used to fit the spectra of Hohen Hagen nontronite samples.

The main feature of the ^{57}Fe-Mössbauer spectra of the acid-treated Garfield and Hohen Hagen nontronite samples fitted with three-doublet models is that in no sample did the area of the ${}^{IV}Fe^{3+}$ doublet ever exceed 19%. This result does not agree with the prediction made by Osthaus (1954) (assuming linear kinetics and the presence of differential rates for the dissolution of Fe), that Fe remaining in the acid-treated samples for greater than five hours should be almost entirely in the tetrahedral sites. Even after two hours of acid treatment, the Osthaus (1954) results indicated that ${}^{IV}Fe^{3+}$ sites should be 30 times more abundant than ${}^{VI}Fe^{3+}$ sites.

In the case of the three-doublet models fitted to the spectra of Garfield nontronite samples the area of the ${}^{IV}Fe^{3+}$ doublet seemed to increase with increasing dissolution time. This was not so for the Hohen Hagen nontronite where there was no trend in the area of the ${}^{IV}Fe^{3+}$ doublet with increasing dissolution time.

DISCUSSION

Acid-dissolution techniques have been used in the study of clay minerals to measure the concentration of cations in different structural sites (Brindley and Youell, 1951; Osthaus, 1954; Karšulin and Stubičan, 1954; Gastuche and Fripiat, 1962; Novák and Čičel, 1978). In these studies, differential dissolution and linear kinetics were observed for the dissolution of the clay minerals investigated. The differential dissolution and linear kinetics were interpreted as arising from a dif-

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Table 1. Room-temperature computer-fitted Mössbauer parameters of nontronite samples after various acid dissolution times (IS = isomer shift, QS = quadrupole splitting, W = full linewidth at half height, A = peak area).

	$^{VI}Fe^{3+}_{outer}$				$^{VI}Fe^{3+}_{inner}$				$^{IV}Fe^{3+}$					
Sample[1]	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 (%)	χ^2	MISFIT
G(0)	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	$(9 \pm 2) \times 10^{-5}$
	0.40 (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	$(5 \pm 1) \times 10^{-5}$
G(0.66)	0.36 (0.001)	0.64 (0.01)	0.33 (0.01)	35 (4)	0.36 (0.001)	0.26 (0.009)	0.35 (0.01)	65 (4)					610	$(1.7 \pm 0.3) \times 10^{-4}$
	0.40 (0.009)	0.60 (0.02)	0.30 (0.02)	28 (5)	0.38 (0.005)	0.28 (0.01)	0.35 (0.01)	60 (7)	0.20 (0.01)	0.47 (0.01)	0.27 (0.02)	12 (4)	557	$(7.8 \pm 0.2) \times 10^{-4}$
G(2.5)	0.36 (0.002)	0.63 (0.02)	0.31 (0.02)	31 (6)	0.37 (0.001)	0.27 (0.01)	0.35 (0.02)	69 (6)					619	$(3.5 \pm 0.7) \times 10^{-4}$
	0.42 (0.009)	0.62 (0.02)	0.23 (0.02)	15 (3)	0.39 (0.006)	0.31 (0.01)	0.34 (0.01)	66 (7)	0.22 (0.01)	0.44 (0.01)	0.30 (0.02)	19 (5)	563	$(1.7 \pm 0.5) \times 10^{-4}$
G(7.5)	0.36 (0.002)	0.58 (0.02)	0.32 (0.01)	41 (6)	0.37 (0.001)	0.24 (0.01)	0.31 (0.02)	59 (6)					556	$(2.2 \pm 0.7) \times 10^{-4}$
	0.37 (0.001)	0.24 (0.01)	0.31 (0.02)	59 (6)	0.40 (0.008)	0.28 (0.02)	0.32 (0.02)	57 (11)	0.23 (0.02)	0.43 (0.01)	0.27 (0.02)	19 (7)	514	$(1.9 \pm 0.3) \times 10^{-4}$
H(0)	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	$(3.3 \pm 0.4) \times 10^{-4}$
	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	$(1.1 \pm 0.2) \times 10^{-4}$
H(0.75)	0.36 (0.001)	0.60 (0.02)	0.34 (0.01)	36 (6)	0.37 (0.001)	0.26 (0.01)	0.34 (0.01)	64 (6)					650	$(2.4 \pm 0.4) \times 10^{-4}$
	0.38 (0.002)	0.63 (0.009)	0.27 (0.007)	18 (4)	0.37 (0.006)	0.30 (0.02)	0.37 (0.02)	78 (4)	0.18 (0.009)	0.51 (0.01)	0.20 (0.03)	4 (1)	596	$(1.5 \pm 0.3) \times 10^{-4}$
H(1.5)	0.36 (0.001)	0.59 (0.02)	0.33 (0.01)	35 (6)	0.37 (0.001)	0.26 (0.01)	0.33 (0.01)	65 (6)					640	$(2.6 \pm 0.5) \times 10^{-4}$
	0.39 (0.008)	0.61 (0.02)	0.26 (0.02)	18 (4)	0.38 (0.003)	0.30 (0.01)	0.35 (0.009)	74 (5)	0.19 (0.01)	0.48 (0.02)	0.25 (0.03)	8 (3)	587	$(1.5 \pm 0.4) \times 10^{-4}$
H(5)	0.36 (0.001)	0.56 (0.01)	0.33 (0.01)	41 (5)	0.37 (0.001)	0.24 (0.009)	0.31 (0.01)	59 (5)					796	$(6.3 \pm 0.8) \times 10^{-4}$
	0.43 (0.008)	0.58 (0.02)	0.21 (0.02)	12 (2)	0.39 (0.005)	0.30 (0.009)	0.35 (0.007)	70 (5)	0.24 (0.01)	0.44 (0.01)	0.27 (0.02)	18 (4)	676	$(3.7 \pm 0.6) \times 10^{-4}$

[1] G = Ca^{2+}-Garfield; H = Ca^{2+}-Hohen Hagen; numbers in parentheses refer to the reaction times in hours.

ferent dissolution rate for cations in different structural sites.

In the present study the dissolution rate fits a parabolic function better than a linear function. Parabolic kinetics have been observed for the dissolution of a wide variety of silicate minerals including 2:1 phyllosilicates (Newman and Brown, 1969; Huang and Keller, 1973; Cabrera and Talibudeen, 1978) and can be interpreted in terms of diffusion mechanisms (Luce *et al.,* 1972; Grandstaff, 1977). Parabolic kinetics can also be explained in terms of the precipitation of reaction products (Holdren and Adams, 1982), or changing surface areas (Holdren and Berner, 1979; Schott *et al.,* 1981).

Using transition state theory and irreversible thermodynamics, which perhaps most successfully describe silicate dissolution (Murphy and Helgeson, 1987; Wieland *et al.,* 1988), overall dissolution processes can be envisaged as a sequence of adsorption, exchange, and detachment reactions at the mineral surfaces. Each ion in the mineral structure would form its own activated complex, the most stable of these decomposing at the slowest rate and therefore corresponding to the rate-limiting step for dissolution. A differential rate of dissolution may be observed if the relative energies of the sites involved are sufficiently different and factors such as rate-limiting diffusion do not intervene. Thus, there is no need to invoke differential dissolution of the octahedral and tetrahedral layers of clays to account for the observation of two separate linear dissolution rates observed by Osthaus (1954).

Though the data obtained in this study suggest that the dissolution kinetics are parabolic, it is not possible to distinguish which of the models mentioned above for the dissolution mechanism is the correct one. It is possible that a combination of several models might be required in order to obtain an adequate description.

As dissolution proceeds the intensities of the IR bands from nontronite decrease but their frequencies are not altered. The reflections characteristic of smectite persist in the XRD patterns of samples treated for up to 10 hours. This indicates that the amount of nontronite decreases as dissolution proceeds and that this nontronite is structurally similar to the untreated nontronite. The XRD data further demonstrate that at least one other phase that is structurally very different from smectite forms as dissolution proceeds. The structural similarity of the acid-treated nontronite to the untreated nontronite is also suggested by the Mössbauer data. For instance, after acid treating the Hohen Hagen nontronite sample for five hours the Mössbauer spectrum is virtually identical to that of the untreated sample. Acid treatment of the Garfield nontronite sample for up to 7.5 hours results only in changes to the areas of the $^{IV}Fe^{3+}$ and outer $^{VI}Fe^{3+}$ doublets. The relative invariance of the Mössbauer spectra of the acid-treated samples also suggests that the phases that are shown by XRD to precipitate as dissolution proceeds contain little or no Fe. If the dissolution products contained significant proportions of Fe, considerable changes in the characteristics of the Mössbauer spectra would have been expected. Thus, the present data seem to support a diffusion-controlled mechanism in which acid attack occurs at particle edges leaving intact the nontronite structure beyond the dissolution front while the phases which form behind the dissolution front are depleted in Fe. That is, as dissolution proceeds the amount of essentially intact nontronite decreases while the amount of dissolution product containing little if any Fe increases.

As regards the determination of the $^{IV}Fe^{3+}$ content of Garfield nontronite, the acid dissolution study of Osthaus (1954) indicated that after more than two hours of dissolution the clay layers contain $^{IV}Fe^{3+}$ sites almost exclusively. If this were so, the Mössbauer spectra of acid-treated samples should possess only doublets with parameters corresponding to $^{IV}Fe^{3+}$. This clearly is not what is observed in the present study when either a two-doublet or three-doublet model is used to fit the spectra of acid-treated samples. For Garfield nontronite, the intensity of the $^{IV}Fe^{3+}$ doublet in the three-doublet model did seem to increase with increasing acid-dissolution time, but to nowhere near the extent indicated by Osthaus (1954). Moreover, an increase in acid-dissolution time from 2.5 to 7.5 hours had no effect on the Mössbauer spectrum. Given that the χ^2 values obtained for the two-doublet fits to the Mössbauer spectra of the series of Garfield nontronites are already statistically acceptable, the three-doublet model may not even be valid. The intensity of the $^{IV}Fe^{3+}$ doublet showed no trend with increasing acid-dissolution time for the Hohen Hagen nontronite sample. Reductions in χ^2, however, were far greater after the addition of $^{IV}Fe^{3+}$ doublets to the spectra of the Hohen Hagen nontronite samples than the Garfield nontronite samples.

The most important conclusion of the present work is that it is not possible to determine $^{IV}Fe^{3+}$ concentrations in nontronite clays using the acid-dissolution technique. Consequently, previous Mössbauer studies assigning more than approximately 2% $^{IV}Fe^{3+}$ sites to Garfield nontronite, and using the findings of Osthaus (1954) to support this result (Besson *et al.,* 1983; Cardile, 1988), must be considered uncorroborated and based on statistical arguments only. In other studies of Garfield nontronite by Bonnin *et al.* (1985), and Sherman and Vergo (1988), a range of techniques have been used in conjunction with Mössbauer spectroscopy and the conclusion has been that Garfield nontronite probably contains less than 3% $^{IV}Fe^{3+}$. Only in these studies has independent evidence been provided to properly test the hypothetical model used to fit the Mössbauer spectra.

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