Clays and Clay Minerals, Vol. 35, No. 3, 170–176, 1987.

IRON SUBSTITUTION IN MONTMORILLONITE, ILLITE, AND GLAUCONITE BY ^{57}Fe MÖSSBAUER SPECTROSCOPY

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Abstract—The ^{57}Fe Mössbauer spectra of an iron-rich montmorillonite, an illite, and two glauconites were measured and computer-fitted with appropriate Fe^{3+} and Fe^{2+} doublet resonances. The broad experimental Fe^{3+} resonance of montmorillonite probably arises from Fe^{3+} in the octahedral sites and a trans-arrangement of OH groups; however, a large variation in the neighboring environment of these sites exists. In illite this Fe^{3+} resonance is similar but shows less broadening; it arises from Fe^{3+} located predominantly in trans-OH octahedral sites, with some Fe^{3+} being located in cis-OH octahedral sites. Because of the increased iron content less variation exists, compared with montmorillonite, in the neighboring octahedral sites. The Fe^{3+} resonance is narrower still for the glauconites and represents Fe^{3+} substituting primarily into cis-OH octahedral sites, similar to that previously reported for nontronite.

The tetrahedral Fe^{3+} content is very low for montmorillonite and increases progressively for illite and glauconite, suggesting that a higher tetrahedral Fe^{3+} content directs Fe^{3+} in the octahedral layer into cis-OH sites. In montmorillonite, the Fe^{2+} is located only in trans-OH sites; in illite Fe^{2+} is largely in trans-OH sites and only slightly in cis-OH sites; and in glauconite, Fe^{2+} is located largely in cis-OH sites and only slightly in trans-OH sites. These assignments suggest that for Fe^{2-}, the doublet with the larger quadrupole interaction arises from Fe^{2+} in trans-OH sites and the doublet with the smaller quadrupole interaction, from Fe^{2+} in cis-OH sites.

Key Words—Glauconite, Illite, Iron, Montmorillonite, Mössbauer spectra.

INTRODUCTION

Montmorillonite, illite, glauconite, and nontronite are 2:1 phyllosilicates. Montmorillonite and nontronite are members of the smectite sub-group, but no definitive nomenclature exists for illites and glauconites. Illites and glauconites, however, usually contain potassium as their interlayer cation and are therefore often classified as micas (Fanning and Keramidas, 1977). On the basis of their iron content, illites and glauconites are intermediate between montmorillonite, which generally has a low iron content, and nontronite, which has a higher iron content. Recently, Johnston and Cardile (1985) and Cardile and Johnston (1985) carried out a systematic Mössbauer spectroscopic study of nontronites having different iron contents and interlayer cations and a number of montmorillonites (Cardile and Johnston, 1986). As a continuation of this work the results of a similar Mössbauer study of an iron-rich montmorillonite, an illite, and a glauconite are presented here, and the patterns of iron substitution in these phyllosilicates are discussed.

BACKGROUND

Early Mössbauer spectroscopic studies (see, e.g., review by Heller-Kallai and Rozenson, 1981) suggested that the ferric doublet spectrum of montmorillonite and nontronite, which could be computer-resolved into an outer and an inner overlapping doublet, represented iron in $MO_4(OH)_2$ octahedral sites having both cis- (inner doublet) and trans-(outer doublet) arrangements of the OH groups. Although these two nominal end members of the smectite group are considered to be structurally similar, the previous studies failed to address the fact that the quadrupole splitting of the nontronite ferric doublet is significantly narrower than that of montmorillonite. Also, occupancy of cis- and trans-octahedral sites by Fe^{3+} is at variance with the electron diffraction evidence of Méring and Oberlin (1967), Besson *et al.* (1983), Tsipursky and Drits (1984), and Drits *et al.* (1984) which shows that within the octahedral layer, the Fe in nontronites is located only in cis-OH octahedral sites, whereas in montmorillonites, the Fe is possibly present in both cis-OH and trans-OH sites.

Recent Mössbauer studies by Johnston and Cardile (1985) and Cardile and Johnston (1985) showed, however, that for nontronites the iron is indeed located in the two cis-OH octahedral sites, which are rendered inequivalent by interactions from the neighboring tetrahedral and interlayer cations and, hence, produce the two overlapping Fe^{3+} doublets. Fe^{3+} was also identified to a significant extent in the tetrahedral sites and to a minor extent in the interlayer. Cardile and Johnston (1986) showed that in montmorillonite Fe^{3+} is present largely in trans-OH octahedral sites. Some montmorillonites show considerable structural disorder which arises from their low iron content and the variety of

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Table 1. Location and compositions of samples.

Sample[1]	Location	Fe (wt. %)	Composition per $O_{10}(OH)_2$[1]
Montmorillonite	Drayton, Queensland, Australia	7.41	$(Ca_{0.27})(Si_{3.49}Al_{0.51})(Fe_{0.49}Al_{0.94}Mg_{0.82}Ti_{0.01})$
Illite	Lake Eyre, Muloorina, South Australia	8.41	$(Ca_{0.059}K_{0.655})(Si_{3.597}Al_{0.403})(Fe_{0.628}Al_{0.969}Mg_{0.420})$
Glauconite	Point Jackson, Francosia, Wisconsin	15.07	$(Ca_{0.096}K_{0.725})(Si_{3.611}Al_{0.389})(Fe_{1.097}Al_{0.849}Mg_{0.442}Ti_{0.003}Mn_{0.001})$
Glauconite	Fiji	18.86	$(Ca_{0.076}K_{0.779})(Si_{3.836}Al_{0.112}Fe_{0.051})(Fe_{1.345}Mg_{0.595}Mn_{0.004})$

[1] Sample supplied with analyses by K. Norrish, Division of Soils, C.S.I.R.O., Adelaide, Australia. Analyses are for Ca-saturated samples.

types and locations of octahedral cations. This disorder produces a broad experimental doublet spectrum that can be computer-resolved into two overlapping doublets which actually represent the mean extremes of a continuum of doublets arising from the disorder, rather than distinct cis-OH and trans-OH sites, as interpreted by previous workers (e.g., Rozenson and Heller-Kallai, 1977). In addition, Cardile and Johnston (1986) found Fe^{3+} to be present to a small extent in tetrahedral sites.

To stabilize the overall charge in the smectite structure, significant tetrahedral Fe^{3+} must direct the Fe^{3+} in the octahedral layer to cis-OH sites, as in nontronite. Conversely a low tetrahedral Fe^{3+} content must direct largely trans-OH occupancy, as in montmorillonite (Tsipursky and Drits, 1984).

The Mössbauer spectra of illite and glauconite have also been reported by a number of workers (Rolf *et al.*, 1977; Rozenson and Heller-Kallai, 1978; McConchie *et al.*, 1979; Ross and Longworth, 1980; Kotlicki *et al.*, 1981; De Grave *et al.*, 1985). In general, these spectra show the presence of both Fe^{2+} and Fe^{3+} in the structure, and most spectra have been resolved into two Fe^{3+} and two Fe^{2+} doublets (e.g., De Grave *et al.*, 1985). The two Fe^{3+} doublets have been assigned in the traditional manner, wherein the doublet having the smaller quadrupole interaction is considered to arise from Fe^{3+} in cis-OH octahedral sites and the doublet having the larger interaction, from trans-OH sites. A controversy exists, however, in assigning the Fe^{2+} doublets. Rolf *et al.* (1977), Rozenson and Heller-Kallai (1978), Kotlicki *et al.* (1981), and De Grave *et al.* (1985) considered that the Fe^{2+} doublet having the larger quadrupole interaction arises from Fe^{2+} in cis-OH sites, whereas McConchie *et al.* (1979) and Ross and Longworth (1980) assigned this doublet to Fe^{2+} in trans-OH sites.

To help resolve this discrepancy and to see if a relationship exists between the Mössbauer spectra and, hence, the pattern of the iron substitution in illites and glauconites with respect to end-member montmorillonites and nontronites, we have measured and computer-fitted the Mössbauer spectra of a montmorillonite, an illite, and two glauconites having a range of iron contents intermediate between the montmorillonites studied by Cardile and Johnston (1986) and the nontronites studied by Cardile and Johnston (1985).

EXPERIMENTAL

The locations of the samples, their iron contents, and their structural formulae (calculated in a conventional manner) are presented in Table 1. No impurity components could be detected by X-ray powder diffraction in any of the samples. The glauconites were supplied in a Ca-saturated form, and the Drayton montmorillonite sample was Mg saturated in a manner similar to that described by Cardile and Johnston (1985) before its Mössbauer spectrum was recorded.

The ^{57}Fe Mössbauer spectra were recorded at room temperature (298 K) using an ELSCINT AME40C spectrometer and a $^{57}Co/Rh$ source. The velocity scale was calibrated with reference to natural iron, with the midpoint of the iron hyperfine spectrum defining zero velocity. The spectra were recorded with the plane of the particular sample oriented at both 90° and 45° to the gamma ray direction, to check for any preferred orientation effects (Cardile and Johnston, 1986). No such effects were observed. To eliminate the effects of absorber thickness, all the absorber samples contained 7–10 mg Fe/cm^2.

The spectra were computer-fitted with a number of overlapping Lorentzian peak lineshapes using a non-linear regression χ^2 minimization procedure. To achieve convergence in all the fits, the widths and dips of the component peaks in a particular doublet were constrained to be equal. The 1% and 99% confidence limits for the χ^2 value (used as a measure of the goodness of the computer-fit) are 566 and 420 for an 8-peak fit and 562 and 416 for a 10-peak fit, respectively. In order for the χ^2 value to measure the goodness of fit and validity of the computer-fitted model and the degree of disorder within the structure, the spectra were recorded to a suitably high background count of 4–5 × 10^6 counts per channel (Johnston and Cardile, 1985).

RESULTS AND DISCUSSION

Drayton montmorillonite

The experimental Mössbauer spectrum for the Drayton montmorillonite showed the typical broad Fe^{3+}

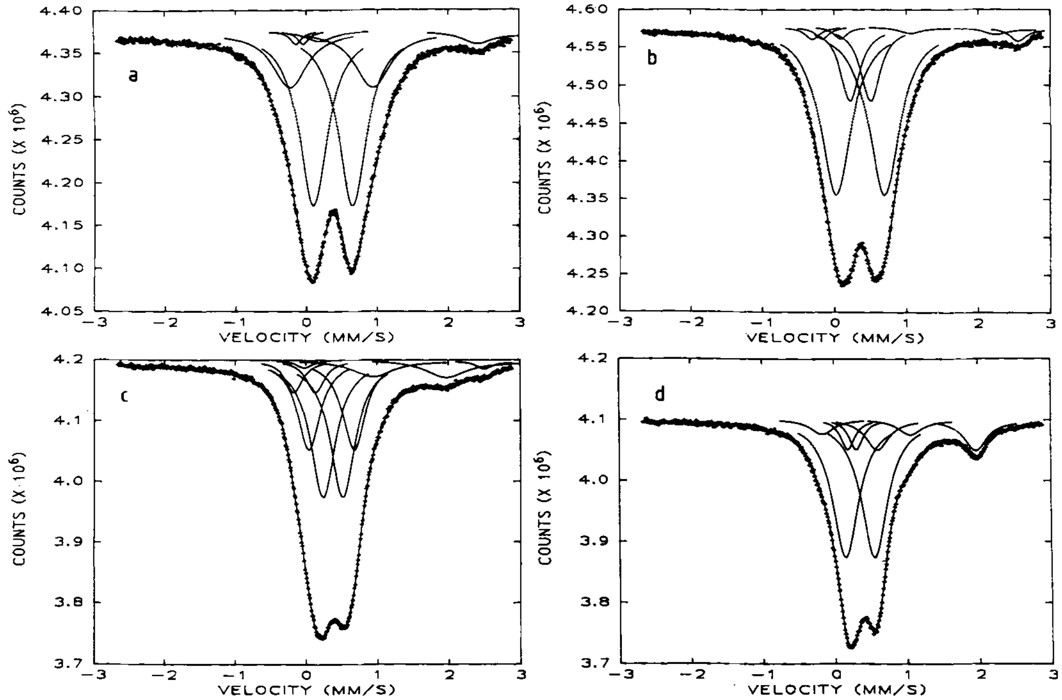

Figure 1. Experimental and computer-fitted ^{57}Fe Mössbauer spectra for: (a) Drayton montmorillonite, (b) Muloorina illite, (c) Francosia glauconite, (d) Fiji glauconite.

resonance observed for most montmorillonites (e.g., Cardile and Johnston, 1986); the intensities of the component peaks of this resonance are definitely asymmetric (Figure 1a). In addition, a resonance exists at about 2.45 mm/s consistent with the high velocity peak of Fe^{2+} ions in the octahedral layer (Figure 1a). The spectrum has been computer-fitted with three overlapping Fe^{3+} doublets and one Fe^{2+} doublet giving a χ^2 = 677 (Table 2). Because this sample was Mg saturated, it probably does not contain interlayer Fe^{3+}.

The broad ferric resonance was computer-fitted essentially with two overlapping Fe^{3+} doublets. The inner doublet having the narrower quadrupole interaction (Δ) was much more intense than the outer doublet; however, the component peaks of the outer doublet had much larger linewidths (Table 2). The average quadrupole interaction for these two doublets (0.86 mm/s) is significantly larger than a similar average value for the two cis-OH doublets of nontronite (0.44 mm/s) (Cardile and Johnston, 1985). Hence, the broad experimental resonance for Drayton montmorillonite may be considered to arise from Fe^{3+} located largely in trans-OH octahedral sites. The two computer-fitted overlapping Fe^{3+} doublets probably represent the mean extremes of a continuum of slightly different Fe^{3+} resonances arising from the variable nature of the environment surrounding these trans-OH sites, rather than from distinct trans-OH and cis-OH sites. The variable environment results from the substitution of Al^{3+}, Mg^{2+}, and Fe^{2+} in neighboring octahedral sites, from Fe^{3+} and Al^{3+} substituting to a small extent in the tetrahedral sites (*vide infra*), and from the interlayer cations (Cardile and Johnston, 1986). Ideally, a distribution of Fe^{3+} doublets having about the same isomer shift, but varying quadrupole interactions, should be computer-fitted to this broad montmorillonite resonance, rather than only the two discrete doublets; however, the computing resources available at the time of this study did not allow such an approach.

The linewidths for both the inner octahedral doublet (0.48 mm/s) and outer Fe^{3+} octahedral doublet (0.61 mm/s) (Table 2) were much larger than those observed for the nontronite octahedral doublets, which arise from the two inequivalent cis-OH sites (0.32 mm/s) (Johnston and Cardile, 1985; Cardile and Johnston, 1985), suggesting a greater variation in the types and arrangements of nearest neighbor ions about the octahedral sites in montmorillonite, compared with nontronite. Because of the low Fe content of montmorillonite, the slightly larger Fe^{3+} and Mg^{2+} may preferentially occupy trans-OH sites and the slightly smaller Al^{3+} may prefer cis-OH sites. Such a preference could not be readily detected by X-ray diffraction (see, e.g., Tsipursky and Drits, 1984), but it can be detected by Mössbauer spectroscopy, as is suggested here.

The smallest intensity doublet having an isomer shift of $\delta = -0.10$ mm/s (Table 2) is assigned to Fe^{3+} in tetrahedral coordination. The Fe^{2+} doublet having a

Table 2. Computer-fitted Mössbauer spectra data.[1]

Sample	χ^2	Fe^{3+} trans-OH[2]				Fe^{3+} cis-OH				Fe^{3+} tetrahedral			
		δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)
Drayton montmorillonite	667	0.37 (1) 0.35 (2)	0.55 (1) 1.17 (2)	0.48 (1) 0.61 (2)	67 27	—	—	—	—	−0.10 (1)	0.10 (2)	0.20 (3)	2
Muloorina illite	532	0.36 (1)	0.67 (1)	0.52 (3)	72	0.37 (1)	0.28 (1)	0.34 (2)	21	−0.04 (2)	0.26 (2)	0.24 (2)	2
Francosia glauconite	686	0.36 (2)	0.63 (2)	0.39 (3)	30	0.38 (1)	0.28 (1)	0.43 (3)	50	−0.01 (2)	0.30 (2)	0.31 (2)	8
Fiji glauconite	742	0.44 (1)	1.22 (1)	0.40 (2)	7	0.35 (1)	0.40 (1)	0.44 (1)	71	0.25 (1)	0.11 (1)	0.24 (2)	8

Sample	Fe^{2+} trans-OH				Fe^{2+} cis-OH			
	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)
Drayton montmorillonite	1.29 (3)	2.23 (5)	0.47 (6)	4	—	—	—	—
Muloorina illite	1.13 (1)	2.85 (1)	0.26 (2)	3	1.65 (2)	1.18 (3)	0.38 (6)	2
Francosia glauconite	1.24 (2)	2.52 (3)	0.27 (4)	2	1.46 (1)	1.02 (2)	0.69 (2)	10
Fiji glauconite	—	—	—	—	1.28 (1)	1.36 (1)	0.39 (1)	14

[1] All area values have an uncertainty of ±0.5.

[2] For Drayton montmorillonite, these two doublets are considered to represent a distribution over the sites (see text).

large value of $\Delta = 2.23$ mm/s (Table 2) is considered to arise from Fe^{2+} in trans-OH octahedral sites. Rozenson and Heller-Kallai (1977) reported a similar Fe^{2+} doublet having comparable quadrupole interaction and isomer shift values, but assigned it to Fe^{2+} in cis-OH octahedral sites. The illite and glauconite spectra discussed below, however, show an additional Fe^{2+} doublet having a narrower quadrupole interaction than that of the Fe^{2+} in the Drayton montmorillonite. Therefore, the Fe^{2+} in montmorillonite, like Fe^{3+}, is probably located largely in trans-OH sites.

Muloorina illite

The experimental Mössbauer spectrum of the Muloorina illite was computer-fitted with three overlapping Fe^{3+} and two overlapping Fe^{2+} doublets (Figure 1b). The prominent central doublet having values of $\delta = 0.36$ mm/s and $\Delta = 0.67$ mm/s (Table 2) is probably due to Fe^{3+} in trans-OH octahedral sites. The overall experimental Fe^{3+} envelope is notably narrower, particularly at the base of the resonance, than that found for Drayton montmorillonite (Figures 1a and 1b); hence, compared with montmorillonite, this illite shows substantially less variation in the neighboring environment surrounding the Fe-containing octahedral sites. A less intense Fe^{3+} doublet having values of $\delta = 0.37$ mm/s and $\Delta = 0.28$ mm/s was also fitted to the spectrum which, by comparison with the inner doublet of nontronite (Johnston and Cardile, 1985), is consistent with Fe^{3+} in cis-OH sites. Hence, the greater portion of the Fe^{3+} is located in trans-OH sites, but some Fe^{3+} is apparently located in cis-OH sites.

The third less-intense Fe^{3+} doublet ($\delta = -0.04$, $\Delta = 0.26$ mm/s) arises from iron substituting into tetrahedral sites (Table 2). Two Fe^{2+} doublets were also fitted to this illite spectrum. The Fe^{2+} having the larger quadrupole interaction ($\Delta = 2.85$ mm/s) (Table 2) is the more intense of the two Fe^{2+} doublets and is assigned to Fe^{2+} in trans-OH octahedral sites (Table 2). The less intense Fe^{2+} doublet having $\Delta = 1.18$ mm/s is therefore assigned to Fe^{2+} in cis-OH sites. These assignments for montmorillonite and illite are consistent with the electron diffraction evidence (Tsipursky and Drits, 1984) and Goodman's (1976) theoretical model which suggests that the trans-OH site has the larger quadrupole interaction and the cis-OH site the smaller.

From these data, this illite sample has about 72% of the Fe^{3+}, as well as a slightly greater percentage of the Fe^{2+} within the octahedral layer located in trans-OH sites, and about 21% of the Fe^{3+} and the remaining Fe^{2+} in cis-OH sites. Hence, this sample probably represents the region, with respect to increasing iron content, where the iron begins to fill cis-OH sites rather than trans-OH sites. The relative tetrahedral occupancy of Fe^{3+} in the Muloorina illite (2.4%) is slightly greater than that for the Drayton montmorillonite (2.1%), consistent with the suggestion of Tsipursky and Drits (1984) that an increasing tetrahedral substitution by Fe^{3+} directs Fe^{3+} substitution within the octahedral layer preferentially into cis-OH sites.

Francosia and Fiji glauconites

The Mössbauer spectra of the Francosia and Fiji glauconites are presented in Figures 1c and 1d, respectively. The overall shape of the experimental envelope for the Francosia glauconite is generally similar to that of Muloorina illite (Figures 1b–1c). The prominent Fe^{3+} resonance of the Francosia glauconite is, however, significantly narrower, particularly towards the apex of the peaks. In addition, the relative intensities of the two Fe^{2+} resonances are reversed compared with those of illite. The experimental envelope for Francosia glauconite was computer-fitted with three Fe^{3+} and two Fe^{2+} resonances (Figure 1c).

The δ and Δ values for the octahedral Fe^{3+} doublets for Francosia glauconite are comparable with those of the Muloorina illite (Table 2); however, the inner Fe^{3+} doublet having the narrower quadrupole interaction ($\Delta = 0.28$ mm/s) assigned to Fe^{3+} in cis-OH octahedral sites is more intense (50%) than the outer Fe^{3+} doublet arising from Fe^{3+} in trans-OH sites (30%). Hence, in the Francosia glauconite, Fe^{3+} is preferentially located in cis-OH octahedral sites.

The least intense Fe^{3+} doublet ($\delta = -0.01$ mm/s, $\Delta = 0.30$ mm/s) is assigned to tetrahedral Fe^{3+}. This is the first time that tetrahedral Fe^{3+} has been identified in the Mössbauer spectrum of a glauconite, probably because previous workers failed to record their spectra to a suitably high background count and thus were unable to test their computer-fitted model completely or to identify the relatively low-intensity tetrahedral Fe^{3+} component (Johnston and Cardile, 1985).

The respective isomer shift and quadrupole interaction parameters for the two Fe^{2+} doublets suggests that the doublet having the larger value of $\Delta = 2.52$ mm/s can be assigned to Fe^{2+} in trans-OH sites and the doublet with $\Delta = 1.02$ mm/s to Fe^{2+} in cis-OH sites (Table 2). In contrast to the illite, the inner Fe^{2+} doublet for this glauconite is more intense than the outer doublet, suggesting that the Fe^{2+} substitutes preferentially into cis-OH sites, consistent with the pattern for Fe^{3+}. This glauconite has a higher iron content and also a large tetrahedral Fe^{3+} component, which also confirms the hypothesis that an increasing extent of Fe^{3+} tetrahedral substitution progressively directs iron substitution within the octahedral layer towards cis-OH sites. This assignment of the Fe^{2+} resonances confirms those of McConchie *et al.* (1979) and Ross and Longworth (1980) and negates those of Rolf *et al.* (1977), Rozenson and Heller-Kallai (1979), Kotlicki *et al.* (1981), and De Grave *et al.* (1985).

The experimental and computer-fitted spectra for the Fiji glauconite are shown in Figure 1d. The prominent Fe^{3+} doublet is slightly narrower than that from the Francosia glauconite and significantly narrower than the corresponding illite and montmorillonite resonances. This doublet was computer-fitted with a Fe^{3+} doublet resonance (δ = 0.35 mm/s, Δ = 0.40 mm/s), consistent with Fe^{3+} in cis-OH octahedral sites (Table 2). In this region, the spectrum therefore resembles that of nontronite rather than montmorillonite. Only one Fe^{2+} doublet is present, and the values of δ = 1.28 mm/s suggest that it arises from Fe^{2+} in cis-OH sites (Table 2). The very much less-intense Fe^{3+} doublet (δ = 0.44 mm/s, Δ = 1.22 mm/s), which is largely responsible for the marked shoulders at the base of the experimental Fe^{3+} resonance, arises from Fe^{3+} in trans-OH sites. The resonance (δ = 0.25 mm/s, Δ = 0.11 mm/s) was assigned to Fe^{3+} in tetrahedral sites. The relative intensity of this doublet (8%) is comparable with that of the Francosia glauconite.

The χ^2 values for the computer-fits to the Drayton montmorillonite, Muloorina illite, and Francosia and Fiji glauconite spectra are comparable (Table 2) and generally slightly above the upper statistical confidence limits (see experimental section), indicating that some slight degree of disorder exists within the structures of these materials (Johnston and Cardile, 1985). This finding is consistent with the general nature of these layer type materials and, on the basis of the χ^2 value discussed above, the Fiji glauconite shows the greatest disorder and the Muloorina illite shows the least.

SUMMARY

The Mössbauer spectra of illite and glauconite are "intermediate" between those of montmorillonite and nontronite. The spectrum of illite more closely resembles that of montmorillonite, whereas the spectrum for glauconite resembles that of nontronite. In montmorillonite, the Fe^{3+} and Fe^{2+} in the octahedral layer are located largely in trans-OH sites, with a relatively small amount of Fe^{3+} being located in tetrahedral sites. The prominent experimental Fe^{3+} resonance of montmorillonite is broad and represents a range of slightly differing environments surrounding the Fe^{3+} in trans-OH octahedral sites. This resonance is slightly narrower for illite, which has a higher total iron content. In illite, most of the octahedral Fe^{3+} is probably in trans-OH sites, as is most of the Fe^{2+}; however, some Fe^{3+} and Fe^{2+} is present in cis-OH sites. The tetrahedral Fe^{3+} content of the illite is slightly higher than that of the montmorillonite. The prominent experimental Fe^{3+} resonance of glauconite is much narrower than those of illite and montmorillonite, suggesting that most of the Fe^{3+} in glauconite is in cis-OH octahedral sites. A similar pattern was observed for Fe^{2+} iron. Also, the tetrahedral Fe^{3+} content of glauconite is higher than that of illite or montmorillonite. The glauconite spectra, therefore, more closely resemble those of nontronite. From the 2:1 phyllosilicates studied here, an increasing amount of Fe^{3+} in the tetrahedral layer, progressively directs substitution of the Fe^{3+} (and Fe^{2+}) in the octahedral layer into cis-OH sites.

ACKNOWLEDGMENTS

We thank K. Norrish, Soils Division, C.S.I.R.O., Adelaide, for supplying the samples studied here.

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(Received 29 November 1985; accepted 7 October 1986; Ms. 1540)