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STRUCTURAL STUDY OF A BENZIDINE-VERMICULITE INTERCALATE HAVING A HIGH TETRAHEDRAL-IRON CONTENT BY ^{57}Fe MÖSSBAUER SPECTROSCOPY

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Abstract—^{57}Fe Mössbauer spectra obtained at room temperature and 78 K for natural Mg-saturated, Ca-saturated, and benzidinium-intercalated vermiculite having a high tetrahedral iron content are presented. For all samples the spectra were computer-fitted with five overlapping doublets, representing Fe in both tetrahedral and octahedral sites. One doublet has parameters consistent with the weathered ilmenite known to be present as inclusions. For the intercalated vermiculite, the δ value of the doublet assigned to the tetrahedral Fe^{3+} increased with respect to the untreated sample, suggesting that the electron densities about the Fe sites had decreased following intercalation. A charge movement from the silicate layers towards the interlayer monovalent benzidinium ions is also implied. The direction of this charge movement is opposite to that found when blue monopositive radical cations form on montmorillonite surfaces. The Mössbauer evidence suggests the absence of an interlayer-Fe^{3+} complex.

Key Words—Benzidinium ion, Intercalate, Iron, Mössbauer spectra, Vermiculite.

INTRODUCTION

Vermiculite is a common trioctahedral member of the smectite group of phyllosilicates. Typically it has the composition $Mg_{0.35}(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2 \cdot 4.5H_2O$. Substitution of as much as ⅓ of the Si^{4+} in tetrahedral sites by Al^{3+} is common. Although possible, substitution of appreciable amounts of Si^{4+} by Fe^{3+} is less common. The vermiculite from Phalaborwa, Transvaal, having an unusually high level (15.5%) of Fe^{3+} substitution in tetrahedral sites (Norrish, 1973) makes this material ideal for Mössbauer spectroscopic studies. Fe^{3+} may also substitute for Mg^{2+} in the octahedral sites where it exists in $FeO_4(OH)_2$ octahedra having both cis- and trans-arrangements of OH groups. The Phalaborwa vermiculite also has Fe in octahedral sites.

Slade and Raupach (1982) reported that the intercalation of vermiculite by benzidinium ions at pH 1.6 produces a well-ordered intercalate having a basal spacing of 19.25 Å. More recently unpublished work by one of us (P.G.S.) has shown that for the Phalaborwa vermiculite, the same conditions of intercalation only produce intercalates having spacings of 15.2 or 16.9 Å. Apparently, the unusually high Fe content of the tetrahedral sites in this material prevents the intercalated benzidinium ions from adopting the steep inclination to the silicate layers found in vermiculites containing much less tetrahedral Fe.

In recent years few detailed ^{57}Fe Mössbauer spectroscopic studies have been carried out on chemically analyzed vermiculites. Various workers (Taylor *et al.*, 1968; Goodman and Wilson, 1973; Ericsson *et al.*, 1977; Heller-Kallai and Rozenson, 1981; Ericsson *et al.*, 1984) have reported Mössbauer spectra of vermiculites but have differed over the structural implications. Taylor *et al.* (1968) assigned two Fe^{3+} resonances to tetrahedral and octahedral sites, whereas Goodman and Wilson (1973) and Heller-Kallai and Rozenson (1981) resolved cis- and trans-OH Fe^{3+} octahedral sites and a cis-OH Fe^{2+} octahedral site. The other workers resolved Fe^{2+} and Fe^{3+} resonances but did not assign them to structural sites.

This paper details a Mössbauer study of the Phalaborwa vermiculite and considers whether benzidinium ions intercalated into it form an interlayer benzidinium-iron complex.

EXPERIMENTAL

The sample of Phalaborwa vermiculite used came from the mineral collection of the CSIRO Division of Soils. For the present study it was saturated with Ca^{2+} ions and intercalated with benzidinium ions. Norrish (1973) reported that the Ca-saturated material has the following structural formula:

$$(Ca_{0.78}K_{0.02})(Mg_{5.36}Ti_{0.14}Mn_{0.01}Fe^{2+}_{0.08}Fe^{3+}_{0.39})(Si_{5.83}Al_{0.93}Fe^{3+}_{1.24})O_{20}(OH)_4.$$

This formula corresponds to an Fe content of 12 wt. %. The benzidinium intercalation reaction was pre-

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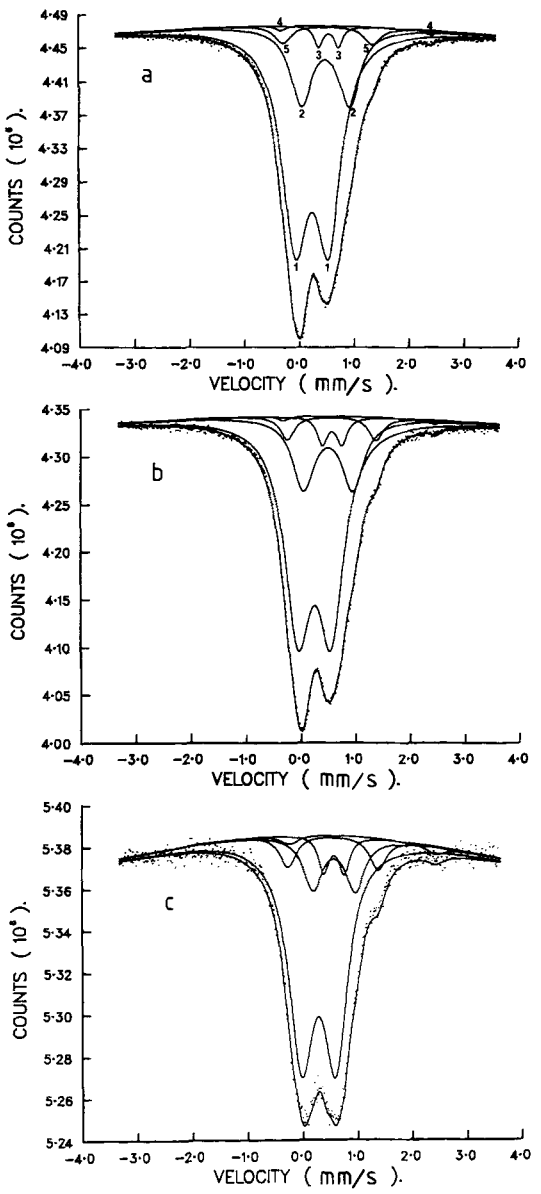


Figure 1. Experimental and computer-fitted Mössbauer spectra for (a) untreated, (b) Ca-saturated, and (c) benzidine-intercalated Phalaborwa vermiculite.

viously discussed by Slade and Raupach (1982). The untreated sample contains Mg as the interlayer cation.

^{57}Fe Mössbauer spectra for the various samples were recorded at room temperature over a range of ±3.5 mm/s using a 512-channel Cryophysics microprocessor-based spectrometer. This apparatus used a constant-acceleration drive system, a sawtooth waveform, and a ^{57}Co/Rh source. The 78-K spectra were recorded over a range of ±10 mm/s and were obtained with an Oxford Instruments DN700 liquid nitrogen cryostat. The velocity scales were calibrated by reference to natural Fe, and the mid-point of the room temperature magnetic hyperfine-iron spectrum defined zero velocity. The spectra were computer-fitted to a number of Lorentzian peak lineshapes by using a non-linear χ^2 minimization procedure. To achieve convergence in all the fits the widths and dips of component peaks in a particular doublet were constrained to be equal. The 1% and 99% confidence limits for χ^2 are 562 and 416, respectively, for a 10-peak fit. In order for this χ^2 value to be an indicator of both the validity of the model used and the extent of disorder within the structure, all spectra were recorded to a suitably high background count of $>4 \times 10^6$ (Johnston and Cardile, 1985).

RESULTS AND DISCUSSION

The computer-fitted ^{57}Fe Mössbauer spectra for the untreated, the Ca-saturated, and the benzidinium-intercalated Phalaborwa vermiculite are shown in Figure 1; the spectral data shown in Table 1 are for the computer-fitted individual components.

Untreated vermiculite

The spectrum for the untreated sample was computer-fitted with five overlapping doublets (Figure 1a). Four doublets represent Fe^{3+} resonances; the fifth represents an Fe^{2+} resonance. The prominent central doublet (1) with δ = 0.24(1) mm/s and Δ = 0.61(1) mm/s is significantly different from the experimental Fe^{3+} resonances observed for other smectites (Cardile and Johnston, 1985, 1986; Johnston and Cardile, 1987), where the δ values are ~0.37 mm/s. The lower δ value for the Phalaborwa vermiculite reflects a greater degree of covalency for the Fe^{3+} atoms involved in this resonance. Doublet (1) therefore is assigned to Fe^{3+} in those tetrahedrally coordinated sites, where it replaces Si. A resonance with these spectral parameters has not been reported in the literature for vermiculites to date, although such a δ value was reported for tetrahedral Fe^{3+} in clintonite (Annersten and Olesch, 1978). The spectral peak area, measured experimentally for the tetrahedral Fe^{3+} component, is 70.8(1.1)% (Table 1) and, hence, is close to the 72.5% value calculated from the structural formula. Taylor *et al.* (1968) assigned a component (δ = 0.41, Δ = 1.00 mm/s) to tetrahedral Fe^{3+}; however, this is very unlikely to be the correct assignment. Both δ and Δ values are too high for Fe^{3+} in such a covalent bonding environment. It is more likely that these workers resolved the octahedral Fe^{3+} resonance into two doublets (Coey, 1980).

The second most intense doublet (2) has a smaller peak area (Table 1) and δ and Δ values of 0.50(1) and 0.88(1) mm/s, respectively. This δ value is significantly larger than those observed for Fe^{3+} in nontronites and montmorillonites (Cardile and Johnston, 1985, 1986) and, thus, is in accord with the values obtained by other workers (e.g., Ericsson *et al.*, 1984), who associated

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their results with Fe^{3+} in octahedral O,OH coordination. The present δ value, however, is slightly larger than those reported by Goodman and Wilson (1973) and Heller-Kallai and Rozenson (1981). The difference probably arises because of the interaction between the large amount of Fe^{3+} present in the tetrahedral sites in the Phalaborwa vermiculite and the Fe^{3+} in its octahedral sites, causing the octahedral Fe^{3+} to appear more ionic. To some extent a difference may also arise because the previous authors did not recognize tetrahedral Fe^{3+} components in their vermiculites and took different approaches to the computer fitting of their Mössbauer spectra to the one used here. More details of the method used in this study are given in Cardile and Johnston (1986).

A smaller doublet (3) (δ = 0.57, Δ = 0.37 mm/s) is also assigned to Fe^{3+} in octahedral O,OH coordination. The linewidth for the inner octahedral Fe^{3+} doublet (0.18 mm/s) is rather narrow and is considered to be an artifact of computer-fitting a minor component to the experimental resonance of a disordered structure (Johnston and Cardile, 1985). The linewidth for the outer octahedral Fe^{3+} doublet (0.48 mm/s) is broader than those observed by Cardile and Johnston (1985) for nontronites (0.32 mm/s), but similar in magnitude to those for montmorillonites (Cardile and Johnston, 1986). The broader linewidth serves to indicate that vermiculite and montmorillonite have a similar degree of structural disorder resulting from the presence of other octahedral cations (e.g., Al^{3+}, Mg^{2+}). These nearest and next-nearest neighbor cations give variety to the type and arrangement of ions about each octahedral Fe^{3+} site and so broaden the octahedral Fe^{3+} doublets.

For the Mössbauer spectra of smectites, the inner Fe^{3+} doublet has been assigned to the cis-octahedral sites and the outer Fe^{3+} doublet to the trans-octahedral sites (e.g., see Rozenson and Heller-Kallai, 1977). Johnston and Cardile (1985) and Cardile and Johnston (1985), however, showed that nontronite has two nonequivalent cis-octahedral sites. Furthermore, for low-Fe montmorillonites, Cardile and Johnston (1986) showed that, in accord with electron diffraction evidence (Tsipursky and Drits, 1984), the Fe^{3+} is located essentially in the trans-octahedral sites for some samples. As a result of the relatively low iron levels in montmorillonites considerable variation exists in the arrangements of nearest and more distant neighboring cations. The resulting two-doublet computer-fits represent the mean extremes of a continuum of slightly different Fe^{3+} resonances. As mentioned above, these resonances arise from the variable environments about the trans-octahedral sites.

Johnston and Cardile (1987) also showed that illites and glauconites have Fe^{2+} and Fe^{3+} distributed throughout cis- and trans-OH octahedral sites and, as such, represent intermediate phases between the high-

Table 1. Computer-fitted Mössbauer spectral data for Phalaborwa vermiculite samples.

Sample	χ^2	Cis-OH octahedral Fe^{3+} doublet (3)				Trans-OH octahedral Fe^{3+} doublet (2)			
		δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)	δ (mm/s)	Δ (mm/s)	Width (mm/s)	Area (%)
Untreated	732	0.57(1)	0.37(1)	0.18(2)	2.4(0.3)	0.50(1)	0.88(1)	0.48(2)	22.4(0.3)
Ca-saturated	661	0.58(1)	0.36(1)	0.23(2)	3.8(0.4)	0.51(2)	0.90(2)	0.49(3)	20.9(1.6)
Benzidine-intercalate	665	0.59(3)	0.38(3)	0.24(6)	5.3(2.1)	0.59(5)	0.77(5)	0.42(8)	13.7(3.6)

Sample	Tetrahedral Fe^{3+} doublet (1)				Octahedral Fe^{2+} doublet (4)				Ilmenite (5)			
	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 (%)
Untreated	0.24(1)	0.61(1)	0.58(1)	70.8(1.1)	1.06(4)	2.75(4)	0.21(5)	0.6(0.2)	0.55(2)	1.65(2)	0.35(3)	3.8(0.4)
Ca-saturated	0.25(1)	0.61(1)	0.58(1)	70.3(1.5)	1.07(4)	2.78(4)	0.21(6)	0.6(0.2)	0.57(2)	1.62(2)	0.31(3)	4.4(0.4)
Benzidine-intercalate	0.29(1)	0.63(1)	0.55(2)	71.9(3.6)	1.11(28)	2.66(28)	0.41(13)	2.2(0.8)	0.57(6)	1.65(6)	0.35(5)	6.9(1.2)

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Fe nontronites and the low-Fe montmorillonites. The question arises, therefore, where does vermiculite fall within the smectite series? The 12% Fe content of the Phalaborwa material suggests that its Mössbauer spectra should show characteristics somewhere between those of high-Fe illites and low-Fe glauconites (Johnston and Cardile, 1987). The different δ values for the two Fe^{3+} octahedral sites for the vermiculite probably indicate that both its cis- and trans-OH octahedral sites are occupied, thus showing the vermiculite is indeed intermediate between montmorillonite and nontronite on the basis of its Fe content. In accord with Goodman and Wilson (1973) and Heller-Kallai and Rozenson (1981) the doublet (3) having the smaller Δ value is assigned to Fe^{3+} in those octahedral sites associated with a cis-arrangement of OH groups. Doublet (2), having the larger Δ value, is consequently assigned to Fe^{3+} in the octahedral sites which have a trans-arrangement of OH groups. As noted by Goodman and Wilson (1973), there is a preference for Fe^{3+} to occupy the trans-OH octahedral site, rather than the cis-OH site.

A small Fe^{2+} component, doublet (4), has been computer-fitted with δ and Δ values of 1.06(4) and 2.75(4) mm/s, respectively. These values are consistent with those for Fe^{2+} in octahedral O,OH coordination where the OH groups are in a trans-orientation (Johnston and Cardile, 1987).

A fifth doublet (5) (Figure 1a) resolved in the present spectrum has parameters δ = 0.55, Δ = 1.65 mm/s (Table 1). Although unusual, these parameters are associated with a titanium-rich, ilmenitic phase which appears as microscopic growths on the basal cleavages. The spectral parameters obtained here are inconsistent with those normally associated with ilmenite (e.g., δ = 1.07, Δ = 0.70 mm/s; Gibb *et al.*, 1969); however, the present δ value is intermediate between that of pure ilmenite and "weathered" ilmenite (δ = 0.36 mm/s; Gibb *et al.*, 1969), probably indicative of the extent to which the present ilmenite has altered. As the Fe^{2+} in the ilmenite oxidized to Fe^{3+}, some Fe polymerized and was adsorbed onto the vermiculite. Hence, the large Δ value is a result of the interaction within the interlayer causing considerable site distortion, either compression or expansion along one of the electric field-gradient axes (Goodman and Wilson, 1973; Johnston and Cardile, 1985). The ilmenite Fe^{2+} component contributes about 4% to the total Fe content of the vermiculite.

Ca-saturated vermiculite

The computer-fitted Mössbauer spectral data (Table 1) for the Ca-saturated vermiculite (Figure 1b) are similar to those for the untreated material. Apparently Ca^{2+} and Mg^{2+} have similar electronic interactions with respect to the Fe species.

Benzidinium-intercalated vermiculite

The Mössbauer spectrum for the benzidinium-intercalated vermiculite was also resolved into five, closely overlapping doublets (Figure 1c); the assignments for these doublets are similar to those discussed for the untreated sample. A notable difference between the intercalated and the untreated sample is their different resonance absorption, ~3% and ~9%, respectively. This difference suggests that the organic interlayer species has 'elasticized' the vermiculite structure and thereby reduced the recoilless fraction for the Fe sites. As a result, larger than normal experimental errors are associated with the computer-fitted spectral parameters. The δ value for the doublet assigned to the tetrahedral Fe^{3+} resonance, however, is larger than that of the untreated sample, indicating that the electron densities about this site have changed. Annersten and Olesch (1978) suggested that an increased δ value indicates a decrease in electron density for the Fe site in question. A similar effect was also observed for the octahedral Fe^{3+} resonances, associated principally with the outer octahedral doublet. Apparently, a transfer of charge away from the Fe^{3+} within the vermiculite structure takes place towards the organic intercalate. This charge movement is opposite of that which occurs when blue monopositive radical cations form at montmorillonite surfaces. In the latter reaction, Tennakoon *et al.* (1974) found that structural Fe^{3+} acted as an electron acceptor; however, the intercalate discussed in the present paper was produced by the uptake of monovalent benzidinium ions from an acidic aqueous solution. Upon intercalation, these monovalent, cationic species caused a charge movement from the silicate layers.

The Mössbauer spectra for all vermiculite samples were also recorded at 78 K, but over a wider velocity scale. The spectra for the untreated and Ca-saturated samples were not significantly different from those recorded at room temperature; however, the spectrum for the benzidinium-intercalate showed a very small six-line component having a magnetic hyperfine field strength of ~486(1) kOe. Whereas such a field strength at 78 K is likely to indicate a polymeric goethite-type Fe^{3+} complex (Johnston and Lewis, 1986), it probably does not indicate an organic-Fe^{3+} complex. This complex would not magnetically order well, and therefore the six-line component more likely resulted from the polymeric Fe^{3+} associated with the weathering of the interlayer ilmenite.

The intercalation reaction was carried out in an acid medium with benzidine monohydrochloride but D. L. Pisaniello (Chemistry Department, University of Adelaide, Adelaide, South Australia, personal communication) showed that cations were released from the vermiculite structure at pH 1.6. During the benzidin-

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ium intercalation some of the Fe may have been released, and from the Mössbauer evidence, this Fe appears to have become incorporated into a polymeric Fe^{3+} complex rather than into an interlayer organic-Fe^{3+} complex as initially postulated. A small amount of organic-Fe^{3+} complex, however, was not likely to have been detected by the Mössbauer spectroscopy discussed here, as the fraction of recoilless nuclei was probably very low.

At present, no explanation can be given as to how the high levels of tetrahedrally coordinated iron found in Phalaborwa vermiculite, for example, induce intercalated benzidinium ions to orient differently from those intercalated into low-Fe vermiculites. A charge-transfer mechanism between the organic species and the silicate structure may be involved, and relatively "flat" long axes of the benzidinium ions may facilitate it.

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