CATION MIGRATION IN SMECTITE MINERALS: ELECTRON SPIN RESONANCE OF EXCHANGED Fe^{3+} PROBES

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Abstract—The migration of interlayer Fe^{3+} cations into the structure of heated montmorillonite and Laponite has been studied by electron spin resonance (ESR), Mössbauer spectroscopy, and magnetic susceptibility measurements. The intensity of the ESR signal corresponding to interlayer Fe^{3+} in air-dried montmorillonite and Laponite increased linearly as the amount of interlayer Fe^{3+} increased. Changes in the spectra after thermal treatment indicate that Fe^{3+} cations migrated into the pseudohexagonal cavities of dehydrated montmorillonite and Laponite. The electrostatic interaction between the Fe^{3+} and the oxygen atoms defining the entrance to these cavities and the proton of the structural OH groups at the bottom of the cavities differ for the two smectites. Ferric cations were apparently bound more strongly within the pseudohexagonal cavities of the dehydrated montmorillonite than within the cavities of Laponite, because the montmorillonite did not rehydrate after heating. The differences in the binding of Fe^{3+} cations within the pseudohexagonal cavities of montmorillonite and Laponite were probably due to variations in the ability of the protons of the structural OH groups to reorient. An additional electronic interaction occurred in the heated Laponite, in which small cations were able to promote the formation of structural defects, which gave rise to a sharp ESR signal at g = 2.00. No evidence for the penetration of Fe^{3+} cations into the vacant octahedral sites of montmorillonite was found.

Key Words—Electron spin resonance, Hofmann-Klemen effect, Ion migration, Iron, Laponite, Montmorillonite, Mössbauer spectroscopy.

INTRODUCTION

Irreversible migration of small cations (e.g., Li$^+$, ionic radius, r, = 0.7 Å) from the interlayer into the crystalline matrix of dioctahedral smectite occurs on mild heating with resultant collapse of the structure (Hofmann and Klemen, 1950). The observation that Mg^{2+}- and Al^{3+}-exchanged montmorillonite samples also exhibit a significant reduction in cation-exchange capacity on heating to temperatures sufficient to dehydrate the exchange cation led Glaeser and Méring (1967) to the conclusion that irreversible collapse was a general phenomenon. Cation migration in smectites affects physical properties, such as the ability to swell in water, and chemical properties, such as acidity. Aronowitz *et al.* (1982) suggested that electronic properties of the smectite lattice may also be modified.

The final location taken by the migrating interlayer cations in heated montmorillonite is uncertain. The original suggestion of Hofmann and Klemen (1950) was that Li$^+$ cations migrate into the vacant octahedral sites of montmorillonite and become fixed there. Although this hypothesis has found support, the results of infrared (IR) spectroscopic studies (Tettenhorst, 1962; Calvet and Prost, 1971) have suggested that the

bottom of the pseudohexagonal cavities is the more likely final site for Li$^+$ migration. Komarov *et al.* (1977) concluded the same for the migration of Cr^{3+} exchange cations in montmorillonite. Recently, Ben Hadj-Amara *et al.* (1987) examined cation migration in Ni^{2+}-exchanged beidellite using X-ray modeling techniques; their results support the migration of Ni^{2+} cations into the vacant octahedral sites.

The present study investigated cation migration of Fe^{3+} (r = 0.6 Å) exchange cations into the 2:1 layers of montmorillonite (vacant octahedral sites) and Laponite (no vacant octahedral sites). The paramagnetic Fe^{3+} exchange cations are subjected to *a priori* different local crystal fields as they migrate from the aqueous interlayers of the air-dried smectite into the 2:1 layers upon dehydration. The changing crystal field can be monitored by ESR spectroscopy. ESR studies to date have focused upon Cu^{2+} (McBride and Mortland, 1974; McBride *et al.*, 1975d) and Mn^{2+} (McBride *et al.*, 1975c) probe ions, but these cations have been able to define the site in which they come to rest on heating. The use of Fe^{3+} structural probes has the advantage that Fe^{3+} cations give distinct ESR signals, which allow assignment to specific types of sites and which may be confirmed by Mössbauer spectroscopy.

ESR OF Fe^{3+} IN CLAY MINERALS

Montmorillonite specifically, and other clay minerals in general, give powder ESR spectra containing a

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Table 1. Elemental analysis of ECCA/L montmorillonite and XLG Laponite.

Element (%)	Montmorillonite	Laponite
SiO_2	71.30	66.03
TiO_2	0.25	0.02
Al_2O_3	17.75	0.30
Fe_2O_3	0.79	0.06
MnO	0.01	0.01
MgO	3.59	29.03
CaO	2.58	0.34
NaO	1.81	3.19
K_2O	0.05	0.04
Li_2O	—	0.98
P_2O_5	1.94	0.02
Total	100.07	100.02

Table 2. X-ray powder diffraction parameters for montmorillonite samples containing no adsorbed Fe^{3+} and containing the maximum amount of adsorbed Fe^{3+}.

Condition	Untreated d(001) (Å)	Fe^{3+}-exchanged d(001) (Å)
Air-dried	14.1	14.8
100°C/24 hr	11.5	14.7
420°C/24 hr	9.6	9.8
420°C/24 hr/75% RH	13.6	9.8

multiplicity of lines, which essentially fall into three zones:

Zone 1—signals at or near g = 4.3. Two signals due to paramagnetic Fe^{3+} cations have been observed, a low-field strong resonance which is invariant and a higher-field weak resonance. Olivier et al. (1975a) attributed the g = 4.3 signals to *cis* and *trans* octahedral sites, having axial and rhombic symmetry, respectively, by measuring the angular dependence of the resonances of sedimented smectite samples. These assignments were in accord with work on mica minerals, which gave similar spectra (Kemp, 1972; Olivier et al., 1975b, 1977). Fine structure on the main g = 4.3 line has been assigned to Fe^{3+} in tetrahedral sites (Che et al., 1974; Olivier et al., 1975a).

Zone 2—very broad signals from g = 2.03–2.4. Most researchers agree that these signals of this type arise from exchange interactions between clusters of Fe^{3+} ions that may be present on the surfaces of the smectite as iron oxide-oxyhydroxide impurity phases (Goodman, 1978) or within interlayers (Gracium and Meghea, 1985; Che et al., 1974). For Fe^{3+}-exchanged montmorillonite, Coyne and Banin (1986) attributed a similar signal, which increased with percentage of Fe^{3+} exchange, to hydrated surface iron. Species of the type $[Fe(OH)(H_2O)_5]^{2+}$ are probably sufficiently distorted to give a very broad signal at g = 2 (Levanon et al., 1968) and are probably present within the interlayers of hydrated Fe^{3+}-exchanged smectites in which increased polarization of water molecules in the restricted environment causes the water molecules to dissociate (Mortland and Raman, 1968). Olivier et al. (1975a) attributed this signal at least in part to Fe^{3+} in the octahedral sheet.

Zone 3—sharp signals at g = 2.00. These signals have been assigned to structural defects (Wauchope and Haque, 1971).

EXPERIMENTAL

The two smectite samples used were selected because they both contain small amounts of iron, which was desirable to prevent ESR signals due to exchanged Fe^{3+} being obscured

by iron in structural sites. Montmorillonite, trade name ECCA/L, was obtained from English China Clays, and Laponite XLG was obtained from Baroid Division of NL Industries. These samples were used as received (Table 1). The montmorillonite contained Na^+ and Ca^{2+} interlayer cations and the Laponite only Na^+. No impurity phases were detected in the montmorillonite by X-ray powder diffraction (XRD), but the Laponite contained a minor amount of NaF which was removed by the exchange process.

Fe^{3+} exchange was accomplished by addition of an ethereal solution of the red $Fe(SCN)_n^{(3-n)+}$ complex to a stirred aqueous slurry of the smectite (Badran et al., 1977). Fe^{3+}-exchanged clays were produced ranging from the untreated montmorillonite [Fe^{3+}-mont(0)] and untreated Laponite [Fe^{3+}-Lap(0)] to a maximum exchanged Fe^{3+} content of 1.97% for montmorillonite [Fe^{3+}-mont(1.97)] and 1.49% for Laponite [Fe^{3+}-Lap(1.49)]. The Fe^{3+}-exchanged clay slurry was dried in air at 40°C, washed with ethanol until free of excess thiocyanate, and again air dried. The percentage of exchanged Fe^{3+} was determined using X-ray fluorescence spectroscopy.

X-band ESR spectra of air-dried and heated samples were obtained at room temperatures (RT) on a Varian E-112 spectrometer on which the first derivative of absorption was recorded. The microwave cavity was tuned to a klystron operation of 9.61 MHz with 10-mW power, this power rating having been checked to ensure that no saturation effects occurred for the highest Fe-containing samples. Spectra were recorded in the magnetic field range of 0–8000 Gauss unless otherwise stated, and the Varian Strong Pitch was used as a reference. Equal sample masses were packed in quartz tubes to the same height to ensure constant packing densities for samples of the same series, and the quartz tubes were placed in the same position in the cavity. Heated samples were allowed to cool in a desiccator before being packed into stoppered sample tubes. Spectra were recorded immediately to minimize readsorption of water.

Owing to overlap between the g = 4.3 signals and signals near g = 2.0 in the region 1600–2300 Gauss, only the area of the left-hand side of the g = 4.3 peak and the right hand side of the g = 2.0 peak could be measured. Thus, the approximate peak areas were obtained by multiplying the width at half height squared by the peak-to-background peak height (Levanon and Luz, 1968; Wertz and Bolton, 1972).

The Mössbauer spectra were recorded using a Cryophysics MS-102 microprocessor-controlled spectrometer equipped with a $^{57}Co/Rh$ source. The 4-K and 77-K temperatures at which some spectra were recorded were achieved using liquid helium or nitrogen, respectively, in a bath cryostat. The samples were contained in sealed air-tight Perspex piston-type sample holders. The velocity scale was calibrated with reference to natural iron, with the midpoint of the iron hyperfine spectrum defining zero velocity. The spectra were computer-fitted to a number of Lorentzian peak lineshapes using a non-linear regression χ^2 minimization procedure, with only the widths and dips of components constrained to be equal.

Magnetic susceptibilties (χ) were measured by the Faraday method using a Varian electromagnet with a Hall-effect, field-dial controller. $Hg[Co(SCN)_4]$ with $\chi_{std} = 16.44 \times 10^{-6}$ cgs/g
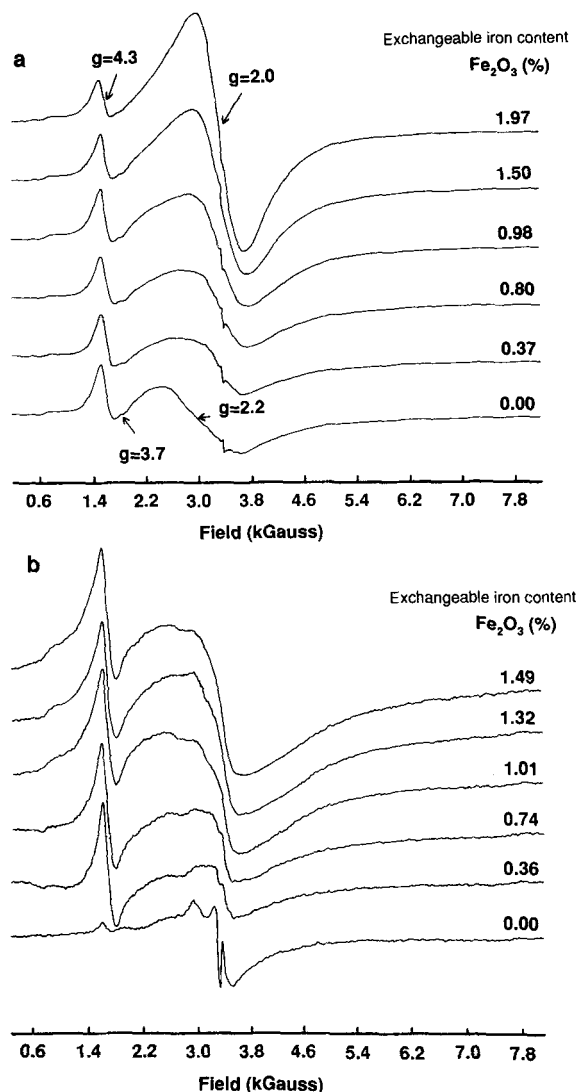
Figure 1. Electron spin resonance spectra of air-dried samples containing varying amounts of exchanged Fe^{3+} (a) montmorillonite (b) Laponite.

was used as the standard. Air-dried samples were corrected for adsorbed water content by subtracting the weight loss at 420°C.

RESULTS

Basal spacing measurements

The basal spacings [d(001)] of Fe^{3+}-mont(0) and Fe^{3+}-mont(1.97) under various conditions are presented in Table 2. In the air-dried state both samples gave similar basal spacings, but at 100°C the basal spacing of Fe^{3+}-mont(0) collapsed to a value corresponding to one water layer (12.2–12.7 Å), whereas the Fe^{3+}-mont(1.97) remained expanded with two water layers (14.7–15.2 Å). These results indicated that Na^+ and Ca^{2+} in the untreated clay were replaced by Fe^{3+}, which has a higher hydration energy. Heating to 400°C totally collapsed the interlayer space in both samples, but Fe^{3+}-mont(0)
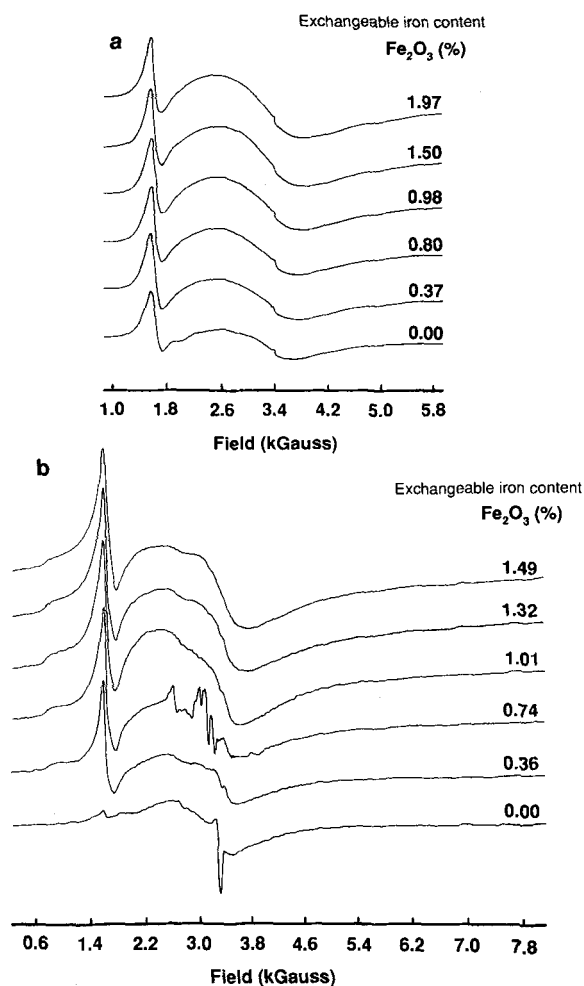

Figure 2. Electron spin resonance spectra of Fe^{3+}-exchanged samples heated to 420°C for 24 hr (a) montmorillonite (b) Laponite.

rehydrated after equilibration in a 75% RH atmosphere, whereas Fe^{3+}-mont(1.97) remained collapsed. Laponite samples treated in the same manner as the montmorillonites gave rise to diffuse basal reflections characteristic of almost complete disorder in layer stacking, which is typical of this smectite.

ESR spectra of air-dried samples

ESR spectra of air-dried montmorillonite and Laponite exchanged with different amounts of Fe^{3+} are shown in Figure 1. The spectrum of Fe^{3+}-mont(0) shows the features discussed in the Introduction. As the Fe^{3+} content of both the montmorillonite and the Laponite increased, the intensity of the broad g = 2.0 signal increased. The spectra of the montmorillonite samples are qualitatively similar to those obtained by Coyne and Banin (1986), who used a natural montmorillonite and the ion-exchange method of Banin (1973). Our spectra are also similar to those obtained by Evmiridis (1986) for Fe^{3+}-exchanged zeolites and show promi-

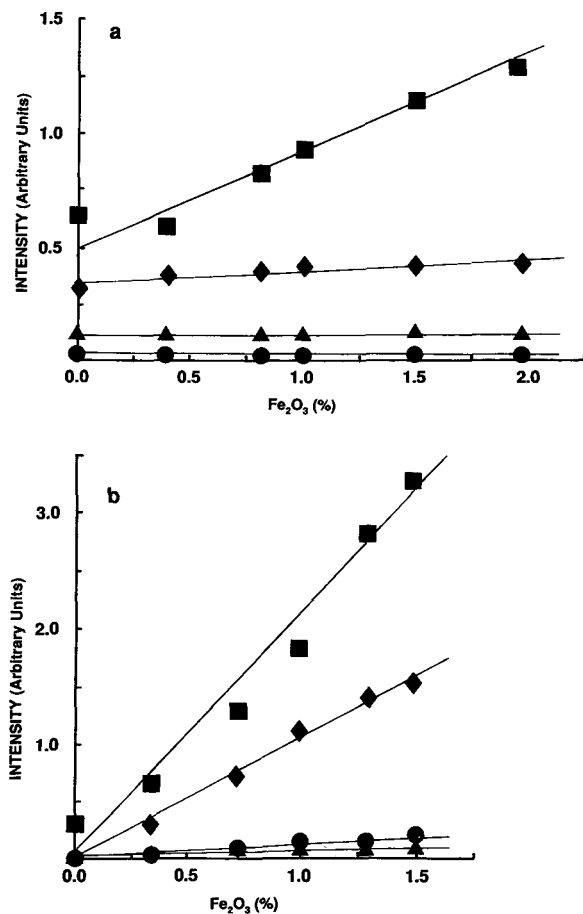Figure 3. Variation in intensity of g = 2.0 and g = 4.3 electron spin resonance signals for samples having varying Fe^{3+} contents (a) montmorillonite (b) Laponites. (■) g = 2.0 air dry (◆) g = 2.0 420°C (●) g = 4.3 air dry (▲) g = 4.3 420°C.

Figure 4. Electron spin resonance spectra of some Fe^{3+}-Laponite samples after heating for 24 hr at 350°C.

nent signals at g = 4.3. Two distinct signals are apparent in the 2–4-kGauss region of the air-dried montmorillonite spectra (Figure 1). Fe^{3+}-mont(0) produced a signal at g = 2.2, which was not observed as the Fe^{3+} content increased and the g = 2.0 signal became dominant. A small feature was visible at g = 3.7 in the spectra of the montmorillonite samples, but disappeared after heating the samples, consistent with the observations of McBride *et al.* (1975a, 1975b).

The intensity of the g = 4.3 signal in the spectra of the air-dried Laponite samples was not the same for all percentages of Fe^{3+} exchange. The Fe^{3+}-Lap(0) signal was very weak and increased at the lowest level of Fe^{3+} exchange, thereafter remaining constant as the Fe^{3+} content increased further. This effect could have been due to the formation of iron oxide or paramagnetic Fe^{3+} phases. Iron oxides deposited during Fe^{3+} exchange of synthetic zeolite X are apparently capable of giving a g = 4.3 signal (Evmiridis, 1986). Such a chemisorbed phase which formed initially in the pres-
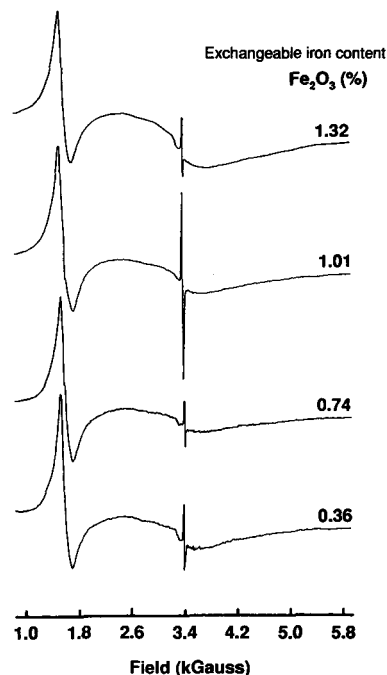
ent study probably did not increase in quantity on further addition of Fe^{3+}, because the intensity of the g = 4.3 signal remained constant. Mössbauer spectra recorded at 4 K did not clarify the situation.

ESR spectra of heated samples

For the montmorillonite samples heated to 420°C (Figure 2a), the intensities of all signals were almost equal for all degrees of Fe^{3+} exchange. A plot of the intensity data (Figure 3a) shows that the rate of increase in the intensity of the broad g = 2.0 signal lessened as the temperature increased. The intensity of the g = 4.3 signal was constant within experimental error over the entire range of Fe^{3+} exchange. Loss of spectral intensity in the 2–5-kGauss region after heating produced no proportional change in any parameter of the Fe^{3+} ESR spectrum. The signals which remained at fields of 2 kGauss for the heated Fe^{3+}-montmorillonite samples had the same g value as the signal produced by the untreated sample. It should be noted that the intensity of the g = 4.3 signal for all levels of exchange after the samples were heated to 420°C was approximately that of the untreated sample.

The Laponite samples also behaved differently after heating to 420°C (Figure 2b) in that the g = 2.0 signal did not completely disappear, as was noted for the montmorillonite. Figure 3b shows that the intensity of the g = 2.0 signal continued to increase after the sample had been heated to 420°C as the Fe^{3+} content increased, although at a slower rate than for the air-dried samples. The Fe^{3+}-Lap(0.74) sample, but no other, showed a
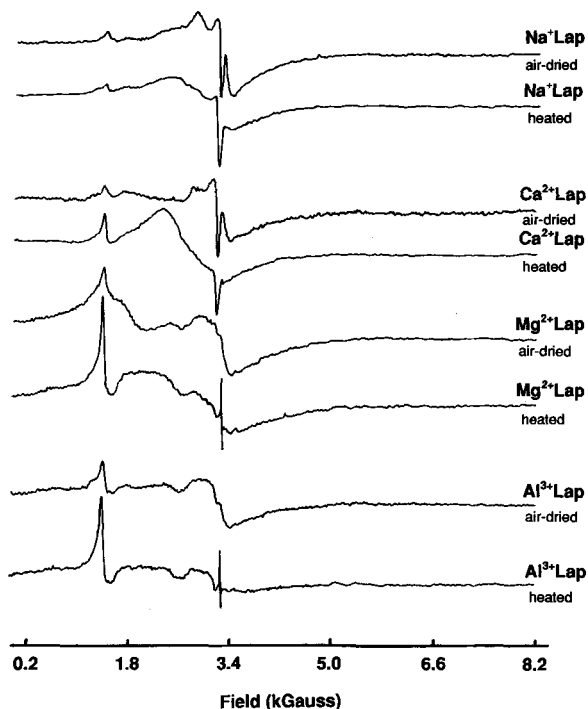
Figure 5. Electron spin resonance spectra of cation-exchanged Laponite samples heated at 350°C for 12 hr.

Figure 6. Computer-fitted Mössbauer spectra for Fe^{3+}-montmorillonite. (a) in the air-dried state; and (b) after heating at 420°C.

complex hyperfine splitting spectrum in the 2.3–3.4-kGauss region, which could have been due to a defect center.

ESR spectra of heated Laponites containing other exchange cations

Some of the Fe^{3+}-exchanged Laponite samples gave intense, sharp signals at g = 2.0 after heating to 350°C (Figure 4), which is characteristic of the presence of lattice defects (Wauchope and Haque, 1971). These signals disappeared after the samples were heated to 420°C. To determine if the signals were related to the nature of the exchange cations, ESR spectra of air-dried and heated samples exchanged with a variety of cations were recorded (Figure 5). The qualitative features of the ESR spectra were profoundly influenced by the exchange cations. First, only the Na^+- and Ca^{2+}-exchanged Laponite samples give an intense asymmetric signal at g = 2 superimposed upon the broad g = 2.0 signal. Second, for the Na^+- and Ca^{2+}-exchanged samples the g = 4.3 signal was the weakest signal in the spectrum, whereas for the Mg^{2+}-, Al^{3+}-, and Fe^{3+}-exchanged samples the g = 4.3 signal was more intense than the other signals. This result suggests that certain exchange cations were able to reduce the symmetry of the Fe^{3+} centers and to produce the asymmetric g = 2 signal, which caused these centers to resonate at lower fields (i.e., g = 4.3).
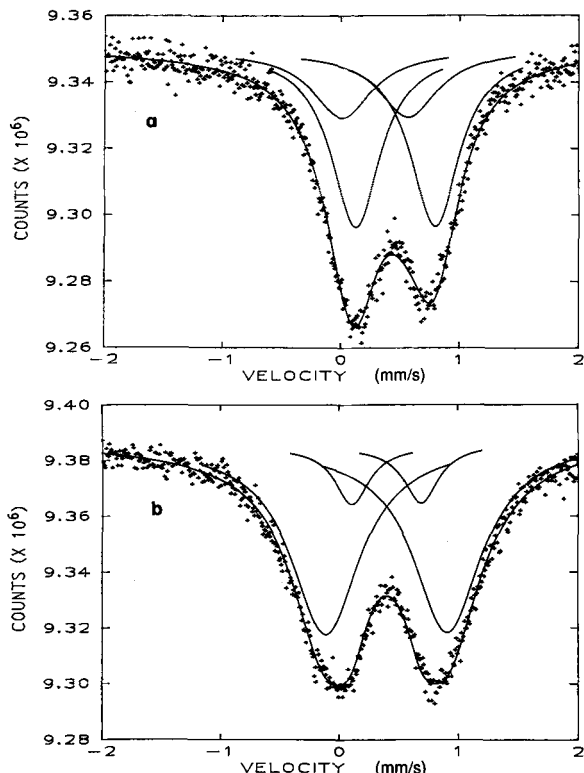
Mössbauer spectra of montmorillonites

The room-temperature Mössbauer spectrum of the air-dried Fe^{3+}-mont(1.97) sample was fitted with a two-doublet model (Figure 6); the fitted spectral parameters are presented in Table 3. The smaller inner doublet represents the Fe^{3+} originally present in the octahedral sites, and the outer doublet represents the exchanged Fe^{3+}. Significant absorption at RT indicates that the exchanged Fe^{3+} was not present as the free hydrated ion, because such an ion would have given no absorption because of its very low recoil-free fraction (R_f). The outer doublet was probably due to Fe^{3+} coordi-

Table 3. Computer-fitted Mössbauer spectral parameters for air-dried and heated montmorillonite samples.[1]

	δ	Δ	Γ	A	x^2
Air-dried Fe^{3+}-montmorillonite					
$^{VI}Fe^{3+}$(outer)	0.46(0.02)	0.67(0.02)	0.50(0.03)	69	574
$^{VI}Fe^{3+}$(inner)	0.29(0.08)	0.56(0.08)	0.61(0.10)	31	
Fe^{3+}-montmorillonite heated to 420°C/24 hr					
$^{VI}Fe^{3+}$(outer)	0.40(0.03)	1.02(0.03)	0.70(0.03)	87	581
$^{VI}Fe^{3+}$(inner)	0.40(0.02)	0.58(0.02)	0.35(0.09)	13	

[1] Isomer shift (δ) quadrupole splitting (Δ) and peak width (Γ) are given in mm/s with δ relative to iron metal; relative doublet areas (A) are given in %.

Table 4. Magnetic susceptibilities of air-dried and heated montmorillonite and Laponite samples having maximum Fe^{3+} content.

Sample	χ (cgs/g $\times 10^6$)
Air-dried untreated montmorillonite	1.3 ± 0.1
Untreated montmorillonite heated 420°C	1.2
Air-dried Fe^{3+}-montmorillonite	3.5
Fe^{3+}-montmorillonite heated 420°C	2.7
Air-dried untreated Laponite	0.3
Untreated Laponite heated 420°C	0.2
Air-dried Fe^{3+}-Laponite	2.3
Fe^{3+}-Laponite heated 420°C	2.2

nated to basal oxygens and water molecules in accord with Helsen and Goodman (1983). The 77-K spectrum of the air-dried Fe^{3+}-mont(1.97) showed no indication of a resonance having an isomer shift (δ) = 0.6 and a quadrupole splitting (Δ) = 1.6 mm/s, which was assigned to the free hydrated Fe^{3+} ion by Helsen and Goodman (1983) and Berry *et al.* (1986). More recently, this resonance has been attributed to an oxo-bridged dimer (Meagher, 1988).

Heating the samples to 420°C increased the Δ value from 0.56 to 1.02 mm/s (Table 3), whereas the Δ value for the structural Fe^{3+} inner doublet remained constant. The increase in Δ for the exchanged Fe^{3+} indicates that Fe^{3+} ions moved into octahedrally coordinated sites more distorted than those in the air-dried sample. For the heated sample, the inner doublet contributed less to the total absorption, indicating an increase in the R_f value of the exchanged Fe^{3+} as it moved into the clay matrix.

Magnetic susceptibility measurements

The χ value of the Fe^{3+}-mont(1.97) sample significantly decreased on heat treatment (Table 4); however, the χ values of the Laponite sample remained the same. The χ values of the untreated samples were unchanged by heat treatment.

DISCUSSION

The broad signal at g = 2.0 that increased linearly with Fe^{3+} content for both air-dried smectite samples (Figure 3) is assigned to surface hydrated Fe^{3+} species, as discussed in the Introduction. Evmiridis (1986) assigned a signal having comparable position and line-width to hydrated Fe^{3+} ions associated with the framework of synthetic zeolites A and X. In synthetic Y zeolites, broad signals having a line-width of 500 Gauss and g = 2.0–2.1 were also assigned to Fe^{3+} ions coordinated to oxygens of the aluminosilicate framework and water molecules (Derouane *et al.*, 1974; Wichterlova, 1981; Wichterlova *et al.*, 1985; Ratnasamy *et al.*, 1985; Kustov *et al.*, 1987). Therefore, the g = 2.0 signal in montmorillonite and Laponite having a large line-width and intensity greater than that for the unexchanged samples was probably due to Fe^{3+} coordinated

to basal surface oxygens and water molecules. The Mössbauer spectroscopic results support this coordination environment for interlayer Fe^{3+}. The very broad signal at g = 2.2 in the ESR spectrum of the unexchanged montmorillonite was possibly due to Fe^{3+} in octahedral sites (Olivier *et al.*, 1975a) or ferric polymers (Goodman, 1978).

If Fe^{3+} cations moved into vacant octahedral sites in montmorillonite, the intensity of the g = 4.3 signal should have increased as the Fe^{3+} content increased. If the vacant sites being occupied were *trans* sites, these additional Fe^{3+} cations should also have produced an increase in spectral intensity in the 2–4-kGauss region beyond that of the untreated sample. The intensities of the g = 4.3 and 2.2 signals for all the heated Fe^{3+}-montmorillonite samples were similar to those for the untreated sample, both at 350° and 420°C, indicating that interlayer Fe^{3+} cations did not penetrate into vacant octahedral sites. The loss in intensity of the g = 2.0 signal for interlayer Fe^{3+}, which occurred on heating, must still be explained, inasmuch as it was not accompanied by a corresponding increase in the intensity of any other signal in the ESR spectra of the heated samples.

The most likely explanation for the above observation is that the Fe^{3+} cations that migrated into the montmorillonite structure gave an ESR signal which was so broad that it was smeared over the background. Such a signal could have been produced by a shortening of the spin lattice relaxation (Adrian, 1968) and/or the presence of spin pairing. Clearly Fe^{3+} cations in the octahedral sheet of montmorillonite and Laponite did not have such a short relaxation time, because they give distinct signals at g = 4.3 and were in the high-spin state. Thus, on heating, dehydrated interlayer cations probably moved into the pseudohexagonal cavities and, thus, did not penetrate through to the vacant octahedral sites.

The decrease in the χ value of the dehydrated Fe^{3+}-mont(1.97) sample may have taken place because the Fe^{3+} cations interacted with structural hydroxyls and/or oxygens of the pseudohexagonal ring, possibly resulting in a change in spin state. The Mössbauer spectrum of the heated Fe^{3+}-mont(1.97) showed that the Fe^{3+} cations had migrated into a highly distorted six-fold site.

Comparison of montmorillonite and Laponite

The small reduction, with respect to the montmorillonite, for the Fe^{3+}-Laponite samples in the intensity of the g = 2.0 signal from interlayer Fe^{3+} after heating (Figure 3b) and the reduction in the χ value were probably due to the inability of Fe^{3+} cations to become fixed within the pseudohexagonal cavities. The protons of the structural OH groups of Laponite, a trioctahedral mineral, are oriented perpendicular to the *a,b* plane (Giese, 1979).

Fe^{3+} cations moving into the pseudohexagonal cavities probably repelled the proton, which was deflected toward the octahedral sheet, but remained above the a,b plane, because the octahedral sites were completely occupied. For montmorillonite, however, in which the proton may have been deflected down into octahedral vacancies, this reaction did not occur. In celadonite, in which the layer charge originates in the octahedral sheet and all tetrahedra are occupied by Si, Bookin and Drits (1982) showed that the OH bonds project into the center of the octaheral sheet. If this orientation exists in celadonite in which the interlayer K^+ cations are too large to penetrate far into the pseudohexagonal cavities, it was probably also present in the collapsed montmorillonite, in which the repulsive interaction of the OH proton should have provided greater impetus for relocation of the proton within the octahedral sheet. Moore and Hower (1986) used this mechanism to explain the ordered interstratification of Na^+-montmorillonite. Movement of structural protons into the octahedral sheet under the influence of migrating interlayer cations also may have provided a way of locally neutralizing the octahedral sheet charge deficit. Moreover, if the octahedral layer charge resided on these OH groups in montmorillonite, the Fe^{3+} cations may have coordinated to the oxygen or OH group, once the protons reoriented.

Influence of exchange cations on ESR spectra of Laponite

The ESR spectrum of Laponite was dependent on the exchange cations. In particular, sharp signals at g = 2.00 appeared only in the spectra of heated Mg^{2+}-, Fe^{3+}-, and Al^{3+}-Laponite samples. Similar signals have usually been ascribed to lattice defects (Wauchope and Haque, 1971; Angel and Hall, 1972; Coyne *et al.,* 1988). McBride *et al.* (1975c) noted that sharp intense signals at g = 2.0 appeared in the ESR spectra of Cu^{2+}- and Mg^{2+}-hectorite and Mn^{2+}-doped Na^+-hectorite after heating to 210°C, but not in similarly treated montmorillonite. They tentatively attributed these signals to a defect in the silicate structure.

In the Laponite samples examined here, the sharp g = 2.00 signal appeared only in the spectra of heated Mg^{2+}-, Fe^{3+}-, and Al^{3+}-Laponite samples, but not in those of Na^+- and Ca^{2+}-Laponite samples. With the exception of Fe^{3+}, the exchange cations used are diamagnetic and, thereby unlikely to have contributed to the g = 2.00 signal. Furthermore, the two groups of cations differ in the extent to which they are able to recess within the pseudohexagonal cavities. Cations having r <0.7 Å (Mg^{2+}, Fe^{3+}, and Al^{3+}) are able to recess completely, whereas those having r >0.7 Å can only partially recess. It is this property of the exchange cations that may have influenced the defect structure of Laponite. Lemons and McAtee (1983) showed that, in general, smectite clays containing fixed Li^+ cations

exhibit greater thermoluminescent activity than smectites containing Na^+ and K^+ exchange actions. They ascribed this increase in thermoluminescent behavior to the greater ability of the fixed Li^+ cations to act as electron traps. The present results show that small cations that were fully recessed within the pseudohexagonal cavities of heated Laponite may have stimulated the formation of electrons or hole centers and that the released electrons gave rise to the sharp g = 2.00 ESR signals.

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